Line Profiles in the Far-uv Absorption Spectra of the Rare Gases

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The line profiles of a dozen series of widely different appearance, observed recently in the rare-gas optical absorption spectra between 20 and 100 eV, are analyzed by adapting and extending previously developed theory. Theory characterizes each profile by its linewidth, q index, and correlation coefficient ρ and relates these parameters to matrix elements of the energy and of the electric dipole moment. Because the profiles result from interference effects, the signs of these matrix elements are highly relevant. Crude estimates of such, hitherto hardly accessible, matrix elements are obtained from experimental evidence and from atomic theory, and are intercompared and found to be in general agreement. Similarities and differences among the line profiles are thereby tentatively explained. The connection of Rydberg series and absorption edges is discussed and the occurrence of downward jumps at some edges is explained. This exploratory investigation demonstrates how one can treat experimental data, and it surveys the kind and volume of information on the dynamics of highly and multiply excited atoms made accessible by recent experimental techniques.

1. INTRODUCTION

AN earlier paper,[1] referred to here as I, pointed out that the profiles of absorption lines in the ionization continuum of atomic (and molecular) spectra are represented by the formula

$$\sigma(\epsilon) = \sigma_a[(q+\epsilon)^2/(1+\epsilon^2)] + \sigma_b. \tag{1.1}$$

Here

$$\epsilon = (E - E_r)/\tfrac{1}{2}\Gamma \tag{1.2}$$

indicates the departure of the incident photon energy E from an idealized resonance energy E_r which pertains to a discrete auto-ionizing level of the atom; this departure is expressed in a scale whose unit is the half-width $\tfrac{1}{2}\Gamma$ of the line (h/Γ is the mean life of the discrete level with respect to auto-ionization). Also, $\sigma(\epsilon)$ represents the absorption cross section for photons of energy E whereas σ_a and σ_b represent two portions of the cross section corresponding, respectively, to transitions to states of the continuum that do and do not interact with the discrete auto-ionizing state (I, Sec. 4). Finally q is a numerical index which characterizes the line profile as shown in Fig. 1 of I. The values of q, Γ, σ_a, and σ_b are regarded as practically energy independent in the proximity of a line. The theory was applied in I only to then existing evidence[2] on the excitation of the $2s2p$ level of helium by electron bombardment. Arguments were presented indicating that q should be negative for that level.

In the course of 1963–1964 extensive observations of absorption spectra, particularly of the rare gases, have been carried out in the far ionization continuum up to photon energies of more than 100 eV ($\lambda \sim 100$ Å).[3-7]

These observations have revealed hundreds of new absorption lines whose profiles vary widely but are represented at least approximately by (1.1) with a wide range of values of q. Detailed quantitative analysis of the line positions and profiles will provide much information on the internal mechanics of highly excited atoms. This paper attempts an initial analysis and interpretation of the q values observed thus far, with particular reference to the study of the He absorption spectrum between 60 and 80 eV (160 to 210 Å) in Ref. 6. Some information on the linewidths Γ and on the ratio $\rho^2 = \sigma_a/(\sigma_a + \sigma_b)$ will also be discussed. Our purpose is to discuss a number of concrete examples, for the guidance of future experimental and theoretical work, rather than to maximize at this time the extraction of theoretical information from the experimental evidence or from calculations based on first principles.

From the analysis developed in this paper the following picture appears to emerge: (a) The numerous qualitative experimental results and the few quantitative data which are available on line shapes can be accounted for by qualitative arguments and by semi-quantitative theoretical estimates. (b) The building blocks of this interpretation are certain atomic parameters, namely, off-diagonal matrix elements of the dipole moment and of the energy, of which knowledge is scarce and of which preliminary estimates of magnitude *and sign* are obtained in several examples. (c) Continued experimental and theoretical investigation of the line-shape parameters should provide a great deal of new information on atomic mechanics and particularly on two-electron correlations and interactions. (d) A substantial theoretical effort on two-electron mechanics will be required to provide a firm quantitative account of experimental evidence; conversely the availability of detailed experimental information should provide guidance and incentive for further theoretical work.

The theory presented in I is limited by its assumption that each discrete auto-ionizing level lies in effect infinitely far from the others and thus can be treated individually. In fact, the levels of neutral atoms and

[1] U. Fano, Phys. Rev. **124**, 1866 (1961).

[2] E. N. Lassettre and S. Silverman, J. Chem. Phys. **40**, 1265 (1964).

[3] R. P. Madden and K. Codling, Phys. Rev. Letters **10**, 516 (1963).

[4] K. Codling and R. P. Madden, Phys. Rev. Letters **12**, 106 (1964).

[5] R. P. Madden and K. Codling, J. Opt. Soc. Am. **54**, 268 (1964).

[6] R. P. Madden and K. Codling (unpublished).

[7] J. A. R. Samson, Phys. Rev. **132**, 2122 (1963).

positive ions generally belong to Rydberg series and each series should be appropriately treated as a unit, together with the continuum adjoining the series limit. The extension of the theory in this direction, begun in Sec. 5 of I, will be treated elsewhere, as the limited purposes of the present paper can be achieved within the theoretical frame of Secs. 1–4 of I.
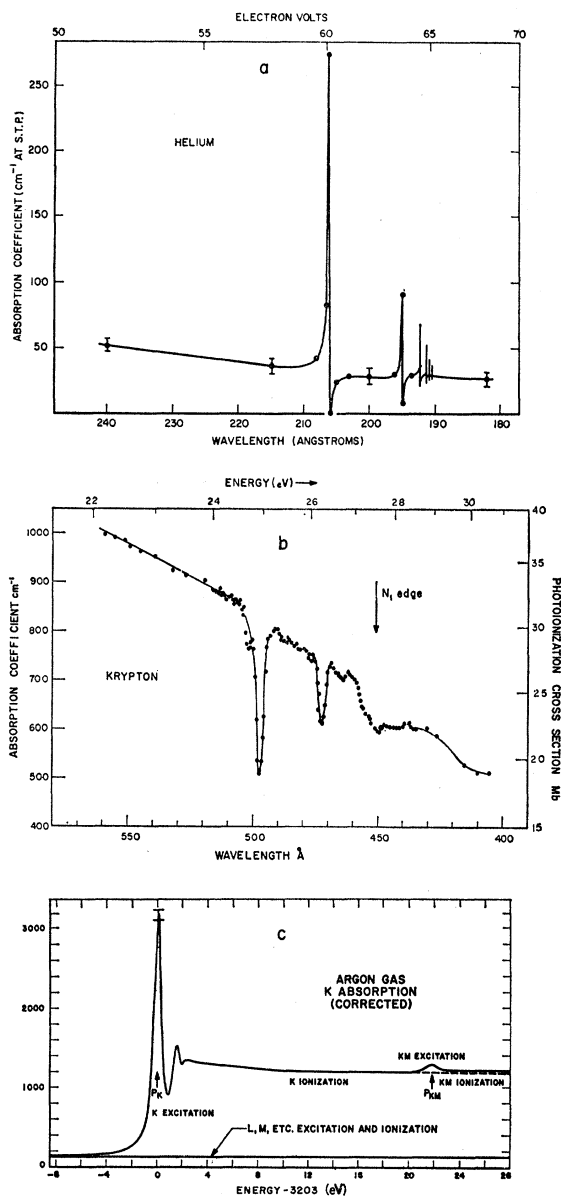

FIG. 1. Different types of absorption spectra. Each plot shows a partially resolved Rydberg series converging to the threshold for a new photoionization process: (a) He, near the $n=2$ level of He^+ (Ref. 6); (b) Kr near the N_I edge (Ref. 7); (c) Ar near the K edge (Ref. 8). See Refs. 3, 5, and 6, for spectrographic evidence for (a) and (b) with much higher resolution; Ref. 4 shows spectra of Kr and Xe near the $M_{IV, V}$ and $N_{IV, V}$ edges which are more similar to (c), especially when observed with lower resolution as in Ref. 34. Note the evidence of additional absorption jumps on the right of (c).

However, some qualitative features of the Rydberg level series and of the continua adjoining their limits in the far uv deserve comment at this point. The limit of each Rydberg series of levels in an absorption spectrum constitutes the energy threshold for a new mechanism of photo-ionization, which leaves the residual ion in an excited state that was not accessible at lower photon energies. Such thresholds are familiar major features of the plots of x-ray absorption coefficients versus photon energy, where they appear as "absorption jumps" associated with the onset of inner shell photoionizations. The Rydberg series of levels, which precede each threshold in the photon-energy scale, also provide an alternative indirect mechanism of ionizaton, by absorption into a short-lived state followed by auto-ionization. As the series approaches its limit and blends into the adjoining continuum, the two mechanisms are not readily distinguished and indeed the observed absorption jumps result from their joint contributions. This situation is intrinsically the same for all photo-ionization thresholds beyond the lowest one, but takes a quite *different appearance in different energy ranges*. For purposes of illustration, profiles of different series are shown in Fig. 1.

Since a Rydberg series extends over a few eV of the photon spectrum, it constitutes merely a fine structure of the absorption jump in the x-ray range; here observations with moderate resolution locate the jump at the position of the first Rydberg line. However, the spectral extension of Rydberg series becomes increasingly prominent at lower photon energies and their lines become narrower. Moreover the height of the absorption jumps is generally much lower at lower energies then it is for x rays and indeed can be negative as noted below. Altogether the Rydberg series associated with inner electron or multiple electron excitations become the dominant features of far uv absorption spectra whereas the thresholds themselves fade out.

In the lower energy range, large numbers of ionization thresholds have now been observed corresponding to different modes of excitation of the outer electrons of the residual ion. In the x-ray range one considers primarily thresholds corresponding to the onset of ejection of a single internal electron, but each of them should be followed at somewhat higher energy by additional thresholds corresponding to simultaneous excitation of outer electrons. Some evidence of such additional thresholds has been observed.[8,9]

The theory of I was worked out primarily for the case in which the discrete levels can auto-ionize into a single type of continuum states. The essence of the theory for the case of alternative continua were also worked out, but the results were not cast in a form suitable for

[8] K. Schnopper, Phys. Rev. **131**, 2558 (1963), and Report No. 39, Material Science Center, Cornell University, Ithaca, New York (1962) (unpublished).
[9] C. Bonnelle and F. Wuilleumier, Compt. Rend. **256**, 5106 (1963).

direct application to photoionization. Accordingly, Sec. 2 of this paper will present results drawn from I in a form suitable for the intended applications. It will emphasize the correlation between the continuum states generated by auto-ionization and by direct optical transition and represent it by a coefficient ρ. Section 3 will then present the results of numerical estimates of the values of q and Γ for the excitation of the $2s2p$ level of He; these results confirm the qualitative arguments presented in I and agree with the experimental measurements within the rather low accuracy of theory. Section 4 points out that the line profiles should be approximately equal for all lines of a Rydberg series and that the line widths should vary from line to line approximately as the inverse cube of the effective principal quantum number n^*. It also relates the values of q, Γ, and ρ to the height of absorption jumps and points out that *downward jumps* can occur [Fig. 1(b)] owing to the repulsion between different states. Section 5 points out a condition under which the q values of the He series classified[10] as $1s^2 \, ^1S \rightarrow sp2n+ \, ^1P$ and $1s^2 \, ^1S \rightarrow sp2n- \, ^1P$ would be equal, which is not inconsistent with preliminary experimental evidence. Section 6 considers the q values of the He series that begin with $1s^2 \, ^1S \rightarrow 3s3p \, ^1P$ and $1s^2 \, ^1S \rightarrow 4s4p \, ^1P$; extension of the arguments pertaining to the $2s2p$ level shows why these q values are positive, whereas that of $2s2p$ is negative, and gives crude estimates in agreement with visual inspection of the spectrograph plates. Section 7 considers the q values pertaining to the excitation of s-subshell electrons in Ne and in the heavier rare gases. Section 8 deals with the excitation of inner shell electrons in Kr and Xe and points out why the $|q|$ values for these and for deeper-shell excitations in the x-ray range are so high that the line profile no longer departs obviously from the traditional Lorentz shape.

2. GENERAL DEFINITIONS AND FORMULAS

Consider an atom, molecule, or ion, whose ground-state wave function is indicated by ψ_0.[11] At energies above the first ionization potential of this system one can identify discrete states φ_n, whose wave function vanishes at infinity, as well as continuum states ψ_{jE} orthogonal to them[12]; these are not exact eigenstates of the Hamiltonian. The index j serves to distinguish alternative continuum states mutually orthogonal but with the same mean value E of the energy. The following

[10] J. W. Cooper, U. Fano, and F. Prats, Phys. Rev. Letters **10**, 518, (1963).

[11] Thereby it is assumed implicitly that this state is nondegenerate. The extension to degenerate ground states, which does not introduce any difficulty, was touched upon at the end of Sec. 2 of I.

[12] This selection of base states, utilized in I, has been discussed in greater detail by U. Fano and F. Prats, in *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 600; equivalent treatments are given, e.g., by H. Feshbach, Rev. Mod. Phys. **36**, 1076 (1964), Ann. Phys. (N. Y.) **5**, 357 (1958), **19**, 287 (1962), and by L. Fonda and R. G. Newton, *ibid.* **10**, 490 (1960).

stipulations made in I [Eqs. (1) and (36)] about these wave functions shall be maintained here: (a) The ψ_{jE} result, in principle, from a procedure of previous partial diagonalization of the Hamiltonian H,[12] such that

$$(\psi_{j'E'}|H|\psi_{jE}) = E\delta(E-E')\delta_{jj'}. \qquad (2.1)$$

(b) The ψ_{jE} behave asymptotically at large distance from the atom as standing waves; hence they can and will be regarded as real. Equation (2.1) implies that the ψ_{jE} are normalized per unit energy range. Stipulation (b) has been made for the sake of simplicity and insures that *all quantities* considered in this paper will be *real* and, therefore, that all matrices of interest will be symmetric.

The cross section for absorption of photons with energy E far removed from any resonance ($\epsilon \sim \pm\infty$), is indicated by $\sigma_a + \sigma_b$ according to (1.1). Its expression in terms of dipole transition matrix elements is[13]

$$\sigma_a + \sigma_b = 4\pi^2(e^2/\hbar c)E\sum_j(\psi_{jE}|z|\psi_0)^2. \qquad (2.2)$$

Here z indicates the component of the dipole moment of the atom in the direction of photon polarization and is the sum of the coordinates of all electrons along this axis. Notice that, because of the normalization of ψ_{jE} per unit energy range, the squared matrix elements $(\psi_{jE}|z|\psi_0)^2$ have the dimensions of $(\text{length})^2/(\text{energy})$, and the $(\psi_{jE}|z|\psi_0)$ themselves of $(\text{length})/(\text{energy})^{1/2}$.

Section 4 of I points out that the interaction of one discrete state φ with the continuum is concentrated on a specific superposition of the states ψ_{jE} with various j and has no effect on superpositions orthogonal to it. Indeed, the interaction matrix element with an arbitrary superposition $\psi_E^{(\lambda)} = \sum_j c_j^{(\lambda)} \psi_{jE}$ is

$$(\psi_E^{(\lambda)}|H|\varphi) = \sum_j c_j^{(\lambda)} (\psi_{jE}|H|\varphi). \qquad (2.3)$$

The maximum value of $(\psi^{(\lambda)}E|H|\varphi)^2$ corresponds to the choice of a normalized set $c_j^{(a)}$ proportional to the matrix elements $(\psi_j|H|\varphi)$, that is, of a wave function

$$\psi_E^{(a)} = \frac{\sum_j(\varphi|H|\psi_{jE})\psi_{jE}}{[\sum_j(\varphi|H|\psi_{jE})^2]^{1/2}}. \qquad (2.4)$$

Any alternative $\psi_E^{(\lambda)}$ with coefficients $c_j^{(\lambda)}$ orthogonal to the $c_j^{(a)}$ clearly yields a zero value for (2.3). Therefore $(\psi_E^{(a)}|H|\varphi)$ embodies the whole interaction of φ with the continuum.

Having defined $\psi_E^{(a)}$ we partition the cross section (2.2) into two terms σ_a and σ_b, of which only the first one will be affected by the interaction whereas the second represents a steady background. We define

$$\sigma_a = 4\pi^2 \frac{e^2}{\hbar c} E(\psi_E^{(a)}|z|\psi_0)^2$$

$$= 4\pi^2 \frac{e^2}{\hbar c} E \frac{[\sum_j(\varphi|H|\psi_{jE})(\psi_{jE}|z|\psi_0)]^2}{\sum_j(\varphi|H|\psi_{jE})^2}, \qquad (2.5)$$

[13] See, e.g., H. A. Bethe and E. E. Salpeter, *Quantum mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), p. 296.

and consequently

$$\sigma_b = 4\pi^2 \frac{e^2}{\hbar c} E \sum_j (\psi_{jE}|z|\psi_0)^2 - \sigma_a. \qquad (2.6)$$

Following this partition, the procedure of Sec. 2 of I can be applied to the treatment of the interaction between the continuum states $\psi_E{}^{(a)}$ and the discrete state φ, ignoring continuum states orthogonal to $\psi_E{}^{(a)}$. The interaction causes the term σ_a of the total cross section to be multiplied by the energy-dependent factor (21) of I, thus yielding (1.1) of this paper. [The same result can be obtained by following through the results of Sec. 4 of 1, particularly of Eq. (40).] Equation (1.2) above and the definition of Γ follow from Eqs. (19) and (1b) of I, with $\psi_E{}^{(a)}$ from (2.4) substituted for ψ_E of I. Specifically one finds

$$\Gamma = 2\pi \sum_j (\psi_{jE}|H|\varphi)^2 = 2\pi \ (\psi_E{}^{(a)}|H|\varphi)^2. \qquad (2.7)$$

(Notice that, because of the normalization of ψ_{jE} per unit energy range, the squared matrix elements $(\psi_{jE}|H|\varphi)^2$ have the dimensions of energy^2/energy $=$ energy.) Substitution of $\psi_E{}^{(a)}$ for ψ_E in (20) of I yields similarly

$$q = \frac{(\Phi|z|\psi_0)}{\pi \sum_j (\varphi|H|\psi_{jE})(\psi_{jE}|z|\psi_0)} \qquad (2.8)$$

$$= \frac{(\varphi|z|\psi_0) + P \int_0^\infty dE' \sum_j (\varphi|H|\psi_{jE'})(\psi_{jE'}|z|\psi_0)/(E-E')}{\pi \sum_j (\varphi|H|\psi_{jE})(\psi_{jE}|z|\psi_0)}, \qquad (2.9)$$

where ψ_0 and z have replaced the symbols i and T of I and P, indicates, as in I, the principal part of the integral at the singularity $E'=E$. Both the numerator and the denominator of (2.8) have the dimensions of a length owing to the normalization of ψ_{jE}.

The symbol Φ indicates here, as in (17) of I, the wave function φ of the discrete state modified by an admixture of states of the continuum. A few words may be added regarding the contribution to q of this admixture, a contribution that we shall often disregard in crude estimates of q. The second term of (2.9) has the analytical form

$$\frac{1}{\pi} P \int_0^\infty \frac{dE'}{E-E'} \frac{f(E')}{f(E)} \qquad (2.10)$$

with $f(E) = \sum_j (\varphi|H|\psi_{jE})(\psi_{jE}|z|\psi_0)$. Cancellation of the contributions from positive and negative values of $E-E'$ tends to make (2.10) smaller than 1, *unless* the ratio $f(E')/f(E)$ varies very rapidly. One should therefore bear in mind the possibility that (2.10) is not small and try to study at least some concrete examples in detail. Notice that the range of integration that contributes effectively to (2.10) bears no relation to the, generally small, linewidth Γ.

The cross section (1.1) has a minimum at $\epsilon = -q$, where the first term on the right-hand side vanishes so that the cross section reduces to σ_b. This minimum appears in the spectra as a "transmission window." At the point of minimum, the absorption is reduced in a ratio

$$\sigma_a/(\sigma_a+\sigma_b) = 1 - \sigma_b/(\sigma_a+\sigma_b) \qquad (2.11)$$

with respect to its value away from the resonance ($\epsilon \sim \pm \infty$). This ratio, which is an important measurable index, is represented theoretically, according to (2.5) and (2.2), by

$$\frac{\sigma_a}{\sigma_a+\sigma_b} = \frac{[\sum_j (\varphi|H|\psi_{jE})(\psi_{jE}|z|\psi_0)]^2}{[\sum_j (\varphi|H|\psi_{jE})^2][\sum_j (\psi_{jE}|z|\psi_0)^2]} = \rho^2. \qquad (2.12)$$

We have introduced here the symbol ρ^2 to represent this reduction ratio because its theoretical expression has the structure of a squared *correlation coefficient* between the sets of matrix elements $(\psi_{jE}|z|\psi_0)$ and $(\varphi|H|\psi_{jE})$. Clearly $\rho^2 = 1$ when there is only one state ψ_{jE}.

This concept of correlation coefficient is illustrated by considering the continuum wave function analogous to (2.4) which is defined by

$$\psi_E{}^{(d)} = \frac{\sum_j (\psi_0|z|\psi_{jE})\psi_{jE}}{[\sum_j (\psi_0|z|\psi_{jE})^2]^{1/2}}. \qquad (2.13)$$

The wave function $\psi_E{}^{(d)}$ represents what may be called the direct dipole state of the continuum at energy E, that is, the state which is excited by dipole transitions directly from the ground state. [The squared dipole matrix element $(\psi_E{}^{(\lambda)}|z|\psi_0)^2$ for an arbitrary superposition of continuum states is maximum for $\psi_E{}^{(\lambda)} = \psi_E{}^{(d)}$ and vanishes for all $\psi_E{}^{(\lambda)}$ orthogonal to $\psi_E{}^{(d)}$.] Thus we are led to define

$$\rho = \frac{\sum_j (\varphi|H|\psi_{jE})(\psi_{jE}|z|\psi_0)}{[\sum_j (\varphi|H|\psi_{jE})^2]^{1/2}[\sum_j (\psi_{jE}|z|\psi_0)^2]^{1/2}}$$

$$= (\psi_E{}^{(a)}|\psi_E{}^{(d)}) \qquad (2.14)$$

as the auto-ionization-to-dipole correlation coefficient. This coefficient is known in wave mechanics as the *overlap integral* of the continuum states $\psi_E{}^{(a)}$ and $\psi_E{}^{(d)}$

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which arise, respectively, by auto-ionization of φ and by direct dipole transition from the ground state.

Useful formulas involving combinations of the profile indices q, Γ, and ρ can be obtained from the preceding equations. Among these are

$$q = \frac{(\Phi | z | \psi_0)}{(\frac{1}{2}\pi\Gamma)^{1/2}\rho(\psi_E^{(d)} | z | \psi_0)} \quad (2.15)$$

$$(\tfrac{1}{2}\pi\Gamma)^{1/2}\rho = \pi \frac{\sum_j (\varphi | H | \psi_{jE})(\psi_{jE} | z | \psi_0)}{|(\psi_E^{(d)} | z | \psi_0)|}. \quad (2.16)$$

3. $1s^2 \to 2s2p$ LINE OF He

The absorption continuum in the proximity of this line pertains to the single type of state $1sEp\,^1P°$.[14] No summation over the index j is, therefore, required in (2.8) and (2.9). The contribution of the second term in the numerator of (2.9) will be disregarded in this section [see the discussion following (2.10)]. The wave function symbols ψ_0, φ, and ψ_{jE} will be replaced here by the symbols that represent specifically the corresponding spectroscopic configurations, namely, $1s^2$, $2s2p$, and $1sEp$, respectively. The expression (2.9) of the profile index then takes the form

$$q_{2s2p} = \frac{(2s2p | z | 1s^2)}{\pi(2s2p | H | 1sEp)(1sEp | z | 1s^2)}, \quad (3.1)$$

analogous to (20) of I.

From the values of q_{2s2p} and Γ_{2s2p} measured by Madden and Codling and from other experimental evidence,[15] we can determine the three matrix elements in (3.1) to within certain ambiguities of sign. The relevant experimental data are[6,15]

$$q_{2s2p} = -2.80 \pm 0.25 \quad (3.2)$$

$$\Gamma_{2s2p} = 0.038 \pm 0.004 \text{ eV} \quad (3.3)$$

$$\sigma_{1s^2 \to 1sEp}(60.1 \text{ eV}) = 1.4 \pm 0.2 \times 10^{-18} \text{ cm}^2. \quad (3.4)$$

The value of Γ gives us the square of the energy matrix element in (3.1), owing to its definition (2.7); hence we have

$$(2s2p | H | 1sEp) = \pm(0.078 \pm 0.004) \text{ (eV)}^{1/2}. \quad (3.5)$$

The cross section (3.4) for photon absorption in the proximity of the $2s2p$ line gives us, according to (2.2), the squared matrix element $(1sEp | z | 1s^2)^2$ or, equivalently, the spectral density of oscillator strength df_{1sEp}/dE,

$$(1sEp | z | 1s^2) = \pm(2.9 \pm 0.2)10^{-10} \text{ cm}/(\text{eV})^{1/2} \quad (3.6)$$

$$df_{1sEp}/dE = 0.013 \pm 0.002 \text{ (eV)}^{-1}. \quad (3.6')$$

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[14] Here, as throughout this paper, E indicates the total energy of the system above that of the ground state.

[15] J. F. Lowry and D. H. Tomboulian, Tech. Rept. No. 3, ARO(D) Project 2810P Cornell University, Ithaca, New York, 1963 (unpublished).

Finally, the q value (3.2), together with (3.1), (3.5), and (3.6), yields

$$(2s2p | z | 1s^2) = \pm(1.9 \pm 0.4)10^{-10} \text{ cm} \quad (3.7)$$

$$f_{2s2p} = 0.0057 \pm 0.0024. \quad (3.7')$$

The sign of (3.2), implies that among the $\pm$ signs in (3.5), (3.6), and (3.7) an *odd number* must be negative. Clearly, the $\pm$ signs of these equations depend on normalization conventions for the wave functions, but they are not independent of one another.

The discussion of (3.1), at the beginning of p. 1872 of I, assumed a standard normalization that all radial wave functions are positive when both electrons are in the proximity of the nucleus. With this normalization, it was conjectured that the matrix element $(2s2p | H | 1sEp)$ is positive, which is plausible since the electron-electron repulsion contributes mostly to it. Similarly, the dipole matrix element corresponding to direct photo-ionization, $(1sEp | z | 1s^2)$, should also be positive, like all dipole elements of optical excitations in hydrogenic systems. On the other hand, the dipole matrix element $(2s2p | z | 1s^2)$ should be *negative* for the following reason. Use of approximate wave functions which are symmetrized products of one-electron wave functions yields

$$(2s2p | z | 1s^2) \sim \sqrt{2}(2s | 1s)(2p | z | 1s). \quad (3.8)$$

According to this formula, the matrix element for two-electron excitation is the product of a one-electron dipole matrix element, which is certainly positive with our convention, and of the "overlap integral" $(2s | 1s)$; this integral will be negative if the $2s$ electron of the $2s2p$ state is less screened from the nuclear charge than the $1s$ electron of $1s^2$. Indeed the $2p$ electron is kept away from the nucleus by the centrifugal force and can hardly provide any screening in the inner region which is relevant to the overlap integral. In essence, it is this negative overlap integral which appears to be responsible for the negative sign of q_{2s2p}.

To corroborate these conjectures, consider first the calculation of $(1sEp | z | 1s^2)$. One of us[16] has shown that alternative calculations agree with the experimental measurement (3.4), within their (comparable) limits of error. Reference 15 includes a more recent summary of available data. Most of the theoretical literature provides only information on $(1sEp | z | 1s^2)^2$, but Ref. 16 states that the dipole matrix itself, Eq. (8.6), has *positive sign* with the normalization convention described above.

The calculation of $(2s2p | H | 1sEp)$ meets greater difficulties, primarily because values of the wave functions for positions of both electrons rather close to the nucleus are of critical importance, as discussed below, whereas current methods of determining wave functions aim at some average accuracy over the whole volume occupied by the electrons. A recent discussion

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[16] J. W. Cooper, Phys. Rev. 128, 681 (1962).

of various results[17] has shown that any of the reasonable methods of calculation utilized heretofore should yield estimates of $|(2s2p|H|1sEp)|$ within approximately a factor of two of one another and of the experimental value (3.5). Also, the sign of the *matrix element is indeed positive*, with the normalization described above.

More specifically, the calculations[17] were carried out with symmetrized products of wave functions of the separate electrons. The contributions of the kinetic energy and central field portions of H was then disregarded because it is small owing to the quasi-orthogonality of one-electron wave functions. The residual contribution, due to the electron-electron interaction, consists of two terms which correspond, respectively, to the transfer of zero and one unit of angular momentum between the electrons,

$$(2s2p\,{}^1P|H|1sEp\,{}^1P)$$
$$= e^2\{R^0(2s2p,1sEp)+\tfrac{1}{3}\,R^1(2s2p,Ep1s)\}\,, \quad (3.9)$$

where the R^k are Slater integrals.[18] Both terms are positive, contrary to a further conjecture of I, as shown in Table I.

Table I. Calculated values of energy matrix elements under various assumptions for the wave functions. (a) Discrete state: Hartree-Fock, continuum state: unscreened $1s$ and Ep moving in the field of $1s$. (b) Discrete state: unscreened hydrogenic orbitals, continuum state: same as (a). (c) Hydrogenic approximation, all orbitals taken as unscreened hydrogenic.

	e^2R_0 (eV)$^{1/2}$	e^2R_1 (eV)$^{1/2}$	$(2s2p|H|1sEp)$ (eV)$^{1/2}$	Γ (eV)
(a)	0.061	0.050	0.078	0.037
(b)	0.102	0.057	0.121	0.092
(c)	0.092	0.162	0.146	0.13

The dipole matrix element $(2s2p|z|1s^2)$ was calculated by Vinti[19] who found $f_{2s2p}=0.0114$, to be compared with the experimental value 0.0055 in (3.7'). This discrepancy had been anticipated[19] owing to a specific inaccuracy of the $1s^2$ wave function; a similar calculation by Salpeter and Zaidi[20] with a Hylleraas $1s^2$ wave function gave $f_{2s2p}=0.0050$. Neither of these references considers the sign of $(2s2p|z|1s^2)$, but the relevance of the conjecture based on (3.8) is readily apparent from Ref. 19.

To appreciate the limitations of these results, consider first that the overlap integral $(2s|1s)$ would vanish, owing to orthogonality, if the $2s$ and $1s$ orbitals were subject to the same nuclear attraction and hence depends critically on screening assumptions. Since the screening effect on the $1s$ orbital is represented approxi-

mately by replacing the $Z=2$ charge of the nucleus by $Z_{\text{eff}}\sim1.7$, the choice of $1.7\leqslant Z_{\text{eff}}\leqslant 2$ for the $2s$ orbital affects q greatly. Moreover the whole matrix element $(2s2p|z|1s^2)$ depends on the values of the wave function for positions of *both electrons* at which the $1s^2$ wave function differs appreciably from zero. One needs then a $2s2p$ wave function reasonably accurate within $1/4000$ of the configuration space of both electrons. (Since the radii of the $n=2$ and $n=1$ shells are in a ratio of ≈ 4, their volumes are in a ratio of ≈ 64, for each electron.) This limitation is not relevant to the calculation of $(1sEp|z|1s^2)$.

The value of $(2s2p|H|1sEp)$ also depends mostly on integration over the inner region of the atom, even though only the $1s$ orbital, among the four orbitals involved, is confined to that region and even though the electric interactions have a long range. Physically, this fact stems from the large momentum transfer between the electrons in the transition $2s2p\to 1sEp$. Such a momentum transfer occurs with substantial probability only in a region where the electrons are close to one another and to the nucleus so as to interact strongly. Mathematically, the $1sEp$ wave function oscillates rapidly throughout the $n=2$ shell and the integral over the oscillations tends to vanish. Also, the quasi-orthogonality of the $1s$ and $2s$ orbitals curtails sharply any contribution to R^0 in (3.9) from the region external to the $1s$ orbital.

The observation that contributions to $(2s2p|H|1sEp)$ stem mostly from the small volume occupied by $1s^2$ has important physical implications. Specifically, it shows that this matrix element is small and, consequently, the spectral line is narrow because the transition between $2s2p$ and $1sEp$ depends on a geometrically unlikely close encounter of the electrons. [Otherwise, since the electron-electron potential energy in the $2s2p$ state is of the order of 5–10 eV, the matrix element might have approached $1(\text{eV})^{1/2}$.] Quite generally, the interaction significant for auto-ionization is seen to be confined to the interior of the atom; this circumstance permits important simplifications which will be exploited in the following sections, but implies that $(2s2p|H|1sEp)$ and analogous matrix elements depend on approximations applicable in a small region atypical for the whole auto-ionizing state.

4. LINES OF RYDBERG SERIES

An electron that is almost detached from an atom, molecule or ion, lies predominantly in a region of space, outside the rest of the system, where it is subject to hydrogenic attraction. Atomic systems have series of stationary states with an almost detached electron, whose energies are represented by the Rydberg formula

$$E_n=E_{\text{lim}}-I_H/n^{*2}=E_{\text{lim}}-I_H/(n-\sigma)^2. \quad (4.1)$$

Here E_{lim} is the energy of the series limit, at which the outer electron becomes fully detached; $I_H=13.6$ eV

[17] J. W. Cooper, *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 607.

[18] See, e. g., E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1963), p. 175.

[19] J. P. Vinti, Phys. Rev. **42**, 632 (1932).

[20] E. E. Salpeter and M. H. Zaidi, Phys. Rev. **125**, 248 (1962).

is the ionization energy of a H atom; n is the principal quantum number of the state; $n^* = n - \sigma$ is the effective quantum number; and σ is the quantum defect. For application to positive ions with charge ze, I_H should be multiplied by $(z+1)^2$.

Equation (4.1) may be regarded as an approximation implying that the details of the interaction between the outer electron and the rest of the system influence the energy levels through the single parameter σ which is the same for all levels of the series. Alternatively, when the approximation proves inadequate, (4.1) may be used to define a separate value of the quantum defect, $\sigma(E_n)$, from the experimental value E_n of each level, and hence to construct by interpolation a smooth function $\sigma(E)$. In the following we shall assume σ to be constant or at least slowly varying.

Physically, the approximation rests on the circumstance that energy differences $E_n - E_{n'}$ are negligible, at least for $n, n' \gg 1$, as compared to the kinetic energies of electrons within the interior of an atom. The corresponding wave functions φ_n, $\varphi_{n'}$ obey Schrödinger equations that practically coincide *in the interior of the system;* in fact replacement of the eigenvalue term $E_n \varphi_n$ by $E_{n'} \varphi_n$ or even by $E_{\lim} \varphi_n$ would represent a perturbation small as compared to the magnitude of the other terms of the Schrödinger equation. The following can be said about the dependence of the wave functions on the coordinates (r, ϑ, φ) of a single electron: (a) for values of r pertaining to the outer portion of the system, φ_n and $\varphi_{n'}$ differ from one another but are hydrogenic; (b) for values of r in the interior they are not hydrogenic but are equal except for a *normalization factor* N_n.

A theoretical approximation treatment valid for $n \gg 1$, determines the dependence of N_n on the quantum number n to lowest order in $1/n$; this dependence is $N_n = \text{const}/n^3$.[21] For the purpose of extending a semi-empirical analysis down to low values for n, we utilize a more specific, somewhat arbitrary, definition of N_n in terms of the mean separation of the energy levels adjacent to E_n, namely,

$$N_n^2 = \tfrac{1}{2}(E_{n+1} - E_{n-1})$$

$$= I_H \frac{2n^*}{(n^{*2} - 1)^2} = I_H \frac{2(n-\sigma)}{[(n-\sigma)^2 - 1]^2}. \quad (4.2)$$

21 See, e.g., H. A. Bethe, *Intermediate Quantum Mechanics* (W. Benjamin, Inc., New York, 1964), p. 29 ff. and pp. 151–152. Numerous treatments of atomic properties have been based on the same approximation as the Rydberg formula; for dipole matrix elements in the optical range see M. J. Seaton, Mon. Not. Roy. Astron. Soc. 118, 504 (1958), and for the x-ray range see M. A. Blokhin, *Fizika rentgenovskikh luchei*, Gosudarstvennoe Izdatel'stvo Tekhniko-teoreticheskī Literatury, Moskva (1957) [English transl.: *The Physics of X Rays*, U. S. Atomic Energy Commission, tr 4502, p. 315 ff (unpublished)]. The definitions (4.2) and (4.3) enable one to represent, e.g., squared dipole matrix elements in the form $(\varphi_n|z|\psi_0)^2 = N_n^2 (\bar{\varphi}|z|\psi_0)^2$ and to represent them graphically, for successive values of n, by adjacent rectangular areas of base N_n^2 and height $(\bar{\varphi}|z|\psi_0)^2$; thus one obtains a histogram showing a smoothed out distribution of dipole strength along the spectrum.

The ratio

$$\bar{\varphi} = \varphi_n / N_n, \quad (4.3)$$

which may be called a reduced wave function, is then nearly independent of n for electron positions in the interior of an atom. For these electron positions, $\bar{\varphi}$ also represents approximately the wave function of a state with energy just a little larger than $E_{\lim}$, that is, with a detached electron normalized *per unit energy range.*

The reduced wave functions $\bar{\varphi}$ are of interest for the theory of absorption spectra because, as discussed in Sec. 3 for the $2s2p$ level of He, both processes of excitation and auto-ionization take place in the interior of the atom. A transition from the ground state to a state with an almost detached electron necessarily involves this electron directly, but this electron may or may not participate directly in the subsequent auto-ionization process. These alternatives will be called 1 and 2, respectively, of which 1 is relevant to most of the applications treated in this paper.

By expressing the line shape indices q, ρ, and Γ in terms of reduced wave functions $\bar{\varphi}$, we shall show that some of these indices have approximately the same value for all lines of a Rydberg series while others vary from line to line in predictable fashion. We still regard each line of a series as infinitely distant from the next line as noted in Sec. 1.

4.1 Full Participation of the Outer Electron

Consider now the definition of the profile index q_n, Eq. (2.8), pertaining to the various levels n of a Rydberg series, namely

$$q_n = \frac{(\Phi_n|z|\psi_0)}{\pi \sum_j (\varphi_n|H|\psi_{jE})(\psi_{jE}|z|\psi_0)}. \quad (4.4)$$

To the extent that the Rydberg approximation holds *and* the contributions to the matrix elements arise only from integration over the *interior of the atom* as discussed at the end of Sec. 3, we have

$$q_n = \frac{N_n(\bar{\Phi}|z|\psi_0)}{\pi \sum_j N_n(\bar{\varphi}|H|\psi_{jE})(\psi_{jE}|z|\psi_0)}$$

$$= \frac{(\bar{\Phi}|z|\psi_0)}{\pi \sum_j (\bar{\varphi}|H|\psi_{jE})(\psi_{jE}|z|\psi_0)} = \bar{q}, \quad (4.5)$$

that is, a single value $q_n = \bar{q}$ for the whole series. Similarly we have, for the correlation coefficient (2.14),

$$\rho_n = \bar{\rho}. \quad (4.6)$$

The same procedure yields a relationship among the widths of successive lines of a Rydberg series, namely,

$$\Gamma_n = 2\pi \sum_j (\varphi_n|H|\psi_{jE})^2 = 2\pi N_n^2 \sum_j (\bar{\varphi}|H|\psi_{jE})^2$$

$$= I_H \frac{2n^*}{(n^{*2} - 1)^2} \bar{\Gamma}. \quad (4.7)$$

In view of the definition (4.2) of N_n, $\bar{\Gamma}$ represents the ratio of each line width to the average separation of the adjacent lines; this *ratio is constant* for the whole series and may be called the reduced linewidth.

The indices $\bar{q}$, $\bar{\rho}$, and $\bar{\Gamma}$ should, of course, be constant for all lines of a series insofar as their energies fit (4.1) with a single constant σ; this fit is often very good for nearly all lines of a series. Otherwise $\bar{q}$, $\bar{\rho}$, and $\bar{\Gamma}$ should be regarded as suitable reduced indices that vary slowly from one line to the next.

We can now relate the ratios $\bar{\Gamma}$, $\bar{q}$, and $\bar{\rho}$ to the magnitude of the photoelectric absorption jump associated with the Rydberg series and with the ionization threshold at its limit. Equation (23) of I gives the excess absorption cross section due to a discrete state φ_n, integrated over a spectral range that includes the whole line. In the notation of (1.1), this formula is

$$\int dE[\sigma(\epsilon)-\sigma_a-\sigma_b]=\sigma_a\tfrac{1}{2}\pi\Gamma_n(q_n{}^2-1)$$
$$=(\sigma_a+\sigma_b)\tfrac{1}{2}\pi\Gamma_n\rho_n{}^2(q_n{}^2-1). \quad (4.8)$$

When dealing with a Rydberg series one is interested in the total excess cross section for the whole series, or rather with the average excess over a spectral range that includes many lines.[22] Since the linewidth Γ_n in (4.8) is actually proportional to the distance of successive lines, according to (4.7) and (4.2), the average excess cross section is

$$\langle\sigma(\epsilon)-\sigma_a-\sigma_b\rangle=\sigma_a\tfrac{1}{2}\pi\bar{\Gamma}(\bar{q}^2-1)$$
$$=(\sigma_a+\sigma_b)\tfrac{1}{2}\pi\bar{\Gamma}\bar{\rho}^2(\bar{q}^2-1). \quad (4.9)$$

To interpret this formula, and particularly the fact that the "excess" it represents is in fact negative when $\bar{q}^2<1$, one may substitute in it the expressions of σ_a, σ_b, $\bar{\Gamma}$, and $\bar{q}$ from (2.5), (2.6), (4.5), and (4.7). The cross section averaged over the whole line profile becomes

$$\langle\sigma(\epsilon)\rangle=4\pi^2(e^2/\hbar c)E\ \Big\{\sum_j(\psi_{jE}|z|\psi_0)^2$$

$$-\pi^2[\sum_j(\bar{\varphi}|H|\psi_{jE})(\psi_{jE}|z|\psi_0)]^2$$

$$+\Big[(\bar{\varphi}|z|\psi_0)+P\int dE'\sum_j(\bar{\varphi}|H|\psi_{jE'})$$

$$\times(\psi_{jE'}|z|\psi_0)/(E-E')\Big]^2\Big\}. \quad (4.10)$$

The first term in the braces corresponds to $\sigma_a+\sigma_b$ and

represents the total photoionization cross section in the absence of the Rydberg series, that is, apart from the occurrence of the absorption jump. The contribution of the term $(\bar{\varphi}|z|\psi_0)$ represents the average photoabsorption that would be brought about by the Rydberg series in the absence of the continuum states ψ_{jE}; this is exactly the *same photoabsorption* that would pertain, beyond the threshold at $E_{\lim}$, to the new continuum whose wave function is just $\bar{\varphi}$ as noted above. The remaining terms in the braces stem from the interaction of the series with the continuum states ψ_{jE}. The last term brings about the effective replacement of $\bar{\varphi}$ with the modified wave function Φ that contains an admixture of the continuum states ψ_{jE}; the possibility that $(\Phi|z|\psi_0)^2<(\bar{\varphi}|z|\psi_0)^2$ represents a possible reduction of the intensity of the series by destructive interference. The second term in the braces, which is inherently negative, represents the effect of *repulsion of the continuum states* ψ_{jE}[23] by the discrete states φ_n and indeed by the very onset of the Rydberg series *and* the adjoining continuum. That is, the occurrence of an absorption jump has the effect of *reducing the intensity* of the preexisting continuum.

This reduction, which has not been emphasized previously, appears strikingly in certain series of Ar, Kr and Xe, as shown in Fig. 1(b) and discussed in Sec. 7. Comparison of (4.10) with (2.12) shows the reduction to be proportional to the squared correlation coefficient $\bar{\rho}^2$. Physically, one can say that a discrete level actually repels the states $\psi_E{}^{(a)}$, represented by (2.4), with which it interacts; thereby it digs a hole in the spectral distribution of optical absorption by direct transition to the continuum, but only to the extent of the overlap of $\psi_E{}^{(a)}$ and $\psi_E{}^{(d)}$. The present treatment, within the frame of I which considers each line as infinitely apart from the others and thus implies $\bar{\Gamma}\ll1$, represents this effect only to lowest order in the interaction parameter $\bar{\Gamma}$. The reduction is presumably compensated by a weaker but widespread increase at lower photon energies, which again is not covered by the present treatment. The structure of (4.10) makes it plausible that this formula remain valid by extrapolation above the threshold at $E_{\lim}$; this continuity has indeed been established theoretically[24] and will be discussed again in a forthcoming more complete treatment of the problem. This continuity enables one to state that the eventual height of the absorption jump is the same as implied by (4.9), namely,

$$\langle\sigma(\epsilon)\rangle/(\sigma_a+\sigma_b)=1+\tfrac{1}{2}\pi\bar{\Gamma}\bar{\rho}^2(\bar{q}^2-1). \quad (4.11)$$

[22] Only the average cross section is measurable near the limit, because only a finite number of lines can be resolved. In this connection, it is of the essence that the average response of a spectrometer will measure directly the average cross section *only* if this response is accurately proportional to the cross section over a *very broad* range of values of this quantity. Discontinuities of absorption that have been observed at limits should generally be regarded as instrumental artifacts.

[23] One may think of the continuum as the aggregate of a set of closely spaced discrete levels that are singled out by boundary conditions at the walls of a large box surrounding the atom. The concept of repulsion between levels of different configurations, which is familiar in atomic physics, is then seen to be directly applicable.

[24] A. I. Baz, Zh. Eksperim. i Teoret. Fiz. **36**, 1762 (1959) [English transl.: Soviet Phys.—JETP **9**, 1256 (1959)]; L. Fonda, Nuovo Cimento Suppl. **20**, 116 (1961).

4.2 Auto-Ionization of the Inner Core

When one atomic electron is almost detached and the "inner core"—consisting of the other electrons—is sufficiently excited, auto-ionization can result from the interaction of two core electrons through an Auger-type process. The outer electron is then left undisturbed, or at most it may be disturbed as a by-product of the inner core's further ionization. The probability of auto-ionization is no longer limited by the low probability that the outer electron penetrates the core to interact closely with its electrons. Therefore we must reconsider the formulas derived in the preceding subsection.

To this end one may conveniently represent the continuum states ψ_{jE} in terms of the set of one-electron states utilized for the representation of the discrete state φ_n. In this representation, the continuum states can be classified into two groups. One group of states, labeled j_2, has one electron ionized and another still left in the excited orbital of φ_n. The remaining group, labeled j_1, consists of the states with no electron in the excited orbital of φ_n. The matrix elements $(\varphi_n|H|\psi_{j_1E})$ can be factored in the form $N_n(\bar{\varphi}|H|\psi_{j_1E})$ as in Sec. 4.1, but the matrix elements $(\varphi_n|H|\psi_{j_2E})$ cannot be so factored because integration over the whole space occupied by the outer electron contributes to it. In other words, $(\varphi_n|H|\psi_{j_2E})$ does not get smaller and smaller with increasing n, and is in fact independent of

n, because the outer orbital of φ_n overlaps exactly an outer orbital of ψ_{j_2E}.

Therefore, Eq. (4.7) is now appropriately written in the form

$$\Gamma_n = 2\pi \sum_{j_1}(\varphi_n|H|\psi_{j_1E})^2 + 2\pi \sum_{j_2}(\varphi|H|\psi_{j_2E})^2 = N_n{}^2\bar{\Gamma}_1 + \Gamma_2. \tag{4.12}$$

Fitting this formula to experimental linewidths of a Rydberg series should afford an opportunity to estimate the separate contributions of the two groups of terms j_1 and j_2, i.e., of the two auto-ionization mechanisms. The Γ_2 term is generally understood to predominate in the x-ray range. The ratio of linewidth to line separation, $\Gamma_n/N_n{}^2 = \bar{\Gamma}_1 + \Gamma_2/N_n{}^2$, increases indefinitely with increasing n, as $N_n{}^2$ decreases, so that the lines eventually merge with one another, unless Γ_2 vanishes.

Consider now the denominator of the expression (4.4) of q_n. The $\sum_j$ can be separated here too into $\sum_{j_1}$ and $\sum_{j_2}$. The j_1 terms contain the matrix elements $(\varphi_n|H|\psi_{j_1E}) = N_n(\bar{\varphi}|H|\psi_{j_1E})$. The j_2 terms contain $(\varphi_n|H|\psi_{j_2E})$ which cannot be so factored, but here we can factor the dipole matrix element $(\psi_{j_2E}|z|\psi_0) = N_n(\bar{\psi}_{j_2E}|z|\psi_0)$, because the excitation from ψ_0 to ψ_{j_2E} involves a *double jump*, with one electron landing in the *same outer orbital* as is occupied in φ_n. Therefore the final result is equivalent to (4.5),

$$q_n = \frac{(\Phi|z|\psi_0)}{\pi \sum_{j_1}(\bar{\varphi}|H|\psi_{j_1E})(\psi_{j_1E}|z|\psi_0) + \pi \sum_{j_2}(\varphi|H|\psi_{j_2E})(\bar{\psi}_{j_2E}|z|\psi_0)} = \bar{q}. \tag{4.13}$$

The dependence of ρ_n on n is now complicated, because the denominator of (2.14) contains both n-dependent and n-independent contributions. Therefore no simple extension of (4.6) exists. However, the combined expression (2.16) is easily seen to be proportional to N_n and we can write

$$(\tfrac{1}{2}\pi\Gamma_n)^{1/2}\rho_n = \pi N_n \frac{\sum_{j_1}(\bar{\varphi}|H|\psi_{j_1E})(\psi_{j_1E}|z|\psi_0) + \sum_{j_2}(\varphi|H|\psi_{j_2E})(\bar{\psi}_{j_2E}|z|\psi_0)}{|(\psi_E^{(d)}|z|\psi_0)|} = N_n[\tfrac{1}{2}\pi\langle\Gamma\rho^2\rangle_{\rm red}]^{1/2}. \tag{4.14}$$

Equation (4.11) is accordingly extended by the simple replacement of $\bar{\Gamma}\bar{\rho}^2$ with $\langle\Gamma\rho^2\rangle_{\rm red}$ defined by (4.14):

$$\frac{\langle\sigma(\epsilon)\rangle}{\sigma_a + \sigma_b} = 1 + \tfrac{1}{2}\pi\langle\Gamma\rho^2\rangle_{\rm red}(\bar{q}^2 - 1). \tag{4.15}$$

Notice finally that, since Γ_n may be written in the form $2\pi \sum_j(\varphi_n|H|\psi_{jE})(\psi_{jE}|H|\varphi_n)$ and since q_n contains $\sum_j(\varphi_n|H|\psi_{jE})(\psi_{jE}|z|\psi_0)$, these two expressions are independent of the representation chosen for the states ψ_{jE}. Therefore the validity of the results (4.12), (4.13), and (4.14) is not restricted by our choice of a representation which distinguishes the two groups of states ψ_{j_1E} and ψ_{j_2E}.

5. THE $mn\alpha \, {}^1P^\circ$ SERIES OF He

The application of the results of Sec. 3 to the series of doubly excited levels of He requires preliminary con-

sideration of certain special circumstances. Since the ion He^+ is hydrogenic, its excited levels which constitute the limits of our series are degenerate, in the sense that the $2s$ and $2p$ levels of He^+ coincide (in a nonrelativistic approximation) and so do $3s$, $3p$, and $3d$, etc. This degeneracy amplifies the effects of interaction between the two electrons of doubly excited He, to such an extent that this interaction must be treated by a close coupling procedure rather than as a perturbation. Therefore, as pointed out previously,[10] the line series which begins with $1s^2 \to 2s2p$ should not be classified as either as $1s^2 \to 2snp$ or as $1s^2 \to ns2p$ but as $1s^2 \to sp2n+$, where $sp2n+$ indicates a superposition of $2snp$ and $ns2p$ with approximately equal coefficients. The same degeneracy has also a major effect on the scattering of electrons by an excited hydrogenic system, which

involves states of the continuum adjoining the discrete levels under consideration.[25]

Levels that were designated as $sp2n-$ in Ref. 10 have since been observed by Madden and Codling[6] with weak but not altogether negligible intensity. This observation confirms the theoretical prediction of a destructive interference arising from the superposition of $2snp$ and $ns2p$ in these levels, but this destructive effect is not as complete as might be implied by the notation of Ref. 10. Reference 25 brings out a further circumstance, namely that configurations $2pnd$ also contribute to $^1P^\circ$ series converging to the $n=2$ level of He$^+$. Accordingly, there should exist a third series, which has not yet been identified experimentally.

To provide a more comprehensive notation, which shall include this additional series and apply equally to still higher excitations, we designate the wave functions of doubly excited states of He, which combine optically with the ground state, by

$$\varphi_{mn\alpha}(^1P^\circ).\qquad(5.1)$$

Here n indicates, as before, a specific level of a series and m indicates the principal quantum number of the He$^+$ level to which the series converges $(m \leqslant n)$. The quantum number α is a generalization of the $\pm$ quantum number of Ref. 10 and identifies one among the series converging to the limit m. The symbol $^1P^\circ$ may be omitted from (5.1) as we deal here only with states of this spectral class. (Transitions to other classes of states are strongly forbidden in He.)

In the approximation where (5.1) can be regarded as a superposition of states with a definite assignment of orbital angular momentum to each electron, we write

$$\varphi_{mn\alpha}=\sum_{l=0}^{m-1}\sum_{l'=l\pm1}c_{ml,nl'}{}^{(mn\alpha)}\varphi_{ml,nl'}.\qquad(5.2)$$

The orbital momenta l and l' are understood to be coupled to $^1P^\circ$; this limits l' to $l\pm1$. The sets of coefficients for given (m,n) and different α are understood to constitute an orthonormal set of vectors; their determination as eigenvectors of a relevant matrix will not be discussed in this paper.[26]

[25] M. Gailitis and R. Damburg, Zh. Eksperim. i Teoret. Fiz. 44, 1644 (1963) [English translation: Soviet Phys.—JETP 17, 1107 (1963)]; M. J. Seaton, Proc. Phys. Soc. (London) A77, 174 (1961). The eigenvalue λ in these references corresponds to the quantum number α in (5.1).
[26] When the present work was completed, Dr. P. G. Burke kindly informed us of a forthcoming paper, by P. G. Burke, D. D. McVicar and K. Smith [Phys. Letters, 12, 215 (1964)], which reports the results of calculations on the states $\varphi_{2n\alpha}$ for $n=5,6$. While the positions and widths of the levels thus obtained agree rather well with the experimental data of Ref. 6 (pairs of theoretical levels are so close as to remain unresolved), the asymptotic form of $\varphi_{2n\alpha}$ at large distances departs from the surmises presented here on (5.2). However, our treatment centers on the properties of (5.2) inside the atom, so that the two sets of results need not be inconsistent. *Note added in proof.* The consistency of the results of Burke *et al.* with those of this work and of Ref. 10 has now been supported by a comparison of maps of wave functions inside the atom.

Reference 10 dealt with $m=2$ and only with two values of α, namely $+$ and $-$, and assumed the coefficients to be, for all $n>2$,

$$c_{20,n1}{}^{(2n\pm)}=\sqrt{\tfrac{1}{2}},\quad c_{21,n0}{}^{(2n\pm)}=\pm\sqrt{\tfrac{1}{2}}.\qquad(5.3)$$

The assumption of c independent of n, which is implied by the existence of a well-defined Rydberg series for each α will be preserved in the present paper and we shall also disregard values of l or $l'>1$, even though this approximation might fail for $m>2$. Thus we shall consider only $(l,l')=(0,1)$ or $(1,0)$ and only two values of α, but the c's need not otherwise have the particular values (5.3).

We introduce next a further approximation from which follow relationships between the $\bar{q}$ and $\bar{\Gamma}$ values for the series with different α, namely, the assumption that states $\varphi(m0,n1)$ and $\varphi(m1,n0)$ interact equally with other states:

$$(\varphi_{m0,n1}|z|\psi_0)\sim(\varphi_{m1,n0}|z|\psi_0),\qquad(5.4)$$

$$(\varphi_{m0,n1}|H|\psi_{jE})\sim(\varphi_{m1,n0}|H|\psi_{jE}).\qquad(5.5)$$

These equations rest again on the importance of the values of the wave functions φ in the interior of the atom and thus extend our earlier treatment of the states of Rydberg series. The two states $\varphi_{m0,n1}$ and $\varphi_{m1,n0}$ differ in the allotment of radial excitation energy between electrons with different orbital angular momenta. However, this difference is far smaller than the kinetic energy of electrons in the interior of the atom and should therefore have little effect on the wave functions in this region.

For the same reason, one would then say that each of the matrix elements (5.4) and (5.5) should depend on the quantum number n at most through a normalization coefficient N_n, to be factored out as in (4.3) and (4.5). Accordingly we set tentatively

$$(\varphi_{mn\alpha}|z|\psi_0)\sim N_n(\sigma_\alpha)[c_{0,1}{}^{(m\alpha)}+c_{1,0}{}^{(m\alpha)}]$$
$$\times(\bar{\varphi}_m|z|\psi_0),\qquad(5.6)$$

$$(\varphi_{mn\alpha}|H|\psi_{jE})\sim N_n(\sigma_\alpha)[c_{0,1}{}^{(m\alpha)}+c_{1,0}{}^{(m\alpha)}]$$
$$\times(\bar{\varphi}_m|H|\psi_{jE}),\qquad(5.7)$$

where the bar over $\bar{\varphi}_m$ denotes again a wave function normalized to unit energy range. Upon substitution of (5.6) and (5.7) in the expression (2.9) of the profile index q, all factors that depend on n and $m\alpha$ cancel out to yield

$$q_{mn\alpha}\approx\frac{(\bar{\Phi}_m|z|\psi_0)}{\pi\sum_j(\bar{\varphi}_m|H|\psi_{jE})(\psi_{jE}|z|\psi_0)}=\bar{q}_m,\qquad(5.8)$$

namely a unique value of $\bar{q}_m$ for all lines of all Rydberg series that converge to the mth level of He. While this result is consistent with visual observation of the He series with $m=2$,[6] it remains tentative at this time.

Substitution of (5.7) into (4.7) yields a value of $\bar{\Gamma}$

that depends on m and on α,

$$\bar{\Gamma}_{m\alpha}=\frac{\Gamma_{mn\alpha}}{N_n^2(\sigma_\alpha)}\approx[c_{01}{}^{(m\alpha)}+c_{10}{}^{(m\alpha)}]^2$$
$$\times 2\pi \sum_j(\bar{\varphi}_m|H|\psi_{jE})^2. \quad (5.9)$$

Visual inspection of spectrograph plates indicates that the lines 2,9+ (or 2,10+) and 2,3− of He have similar appearance[6] and therefore, presumably, the same excess absorption (4.9), so that $\Gamma_{2,9+}\bar{\rho}_+{}^2(\bar{q}_+{}^2-1)$ $\sim\Gamma_{2,3-}\bar{\rho}_-{}^2(\bar{q}_-{}^2-1)$. If we assume $\bar{q}_+\sim\bar{q}_-$ and utilize (5.9) and $\bar{\rho}_+=\bar{\rho}_-=1$, this yields the preliminary estimate

$$\frac{\bar{\Gamma}_{2+}}{\bar{\Gamma}_{2-}}\sim\frac{[c_{01}{}^{(2+)}+c_{10}{}^{(2+)}]^2}{[c_{01}{}^{(2-)}+c_{10}{}^{(2-)}]^2}\sim 100. \quad (5.10)$$

We have applied to He the formulas of Sec. 4.1, rather than those of Sec. 4.2, because its "core" consists of a single electron and could not auto-ionize by itself.

From the normalization condition

$$[c_{01}{}^{(m\alpha)}]^2+[c_{10}{}^{(m\alpha)}]^2=1,$$

it follows that

$$[c_{01}{}^{(m\alpha)}+c_{10}{}^{(m\alpha)}]^2\leqslant 2. \quad (5.11)$$

Further, if α is restricted to two eigenvalues, the orthonormality of the c yields

$$\sum_\alpha[c_{01}{}^{(m\alpha)}+c_{10}{}^{(m\alpha)}]^2=2 \quad (5.12)$$

so that

$$\sum_\alpha\bar{\Gamma}_{m\alpha}=4\pi\sum_j(\bar{\varphi}_m|H|\psi_{jE})^2$$
$$=4\pi(\bar{\varphi}_m|H|\psi_E{}^{(a)})^2. \quad (5.13)$$

The estimate (5.10) yields then, in agreement with the qualitative prediction of Ref. 10,

$$[c_{01}{}^{(2+)}+c_{10}{}^{(2+)}]^2\approx 1.98,$$
$$[c_{01}{}^{(2-)}+c_{10}{}^{(2-)}]^2\approx 0.02. \quad (5.14)$$

For $n=m=2$ there are of course no two distinct states $\varphi_{m0,n1}$ and $\varphi_{m1,n0}$ and no two distinct values of α arise. If the Rydberg-type approximation (5.6)–(5.7) is stretched further to apply to $n=m$ one finds

$$\Gamma_{22}\approx N_n^2 2\pi \sum_j(\bar{\varphi}_2|H|\psi_{jE})^2$$
$$\approx\frac{2(1.61)I_H}{(1.61^2-1)^2}\tfrac{1}{2}\sum_\alpha\bar{\Gamma}_{2\alpha}. \quad (5.15)$$

On the other hand, we have, for the second most prominent line

$$\Gamma_{23+}\approx\frac{2(2.79)I_H}{(2.79^2-1)^2}\bar{\Gamma}_{2+}=\frac{2(2.79)I_H}{(2.79^2-1)^2}1.98\tfrac{1}{2}\sum_\alpha\bar{\Gamma}_{2\alpha}, \quad (5.16)$$

so that

$$\frac{\Gamma_{23+}}{\Gamma_{22}}\approx 1.98\frac{2.79(1.61^2-1)^2}{1.61(2.79^2-1)^2}=0.2 \quad (5.17)$$

in good agreement with the experimental estimate.[6]

6. THE $\bar{q}_m$ VALUES OF He LINES WITH $m>2$

Madden and Codling have recently observed doubly excited levels of He with $m=3$ and $m=4$.[6] The q values of these levels are clearly seen to be positive and not very small. Thus $\bar{q}_2$ is negative (Sec. 3) but $\bar{q}_3$ and $\bar{q}_4$ are positive.

In the discussion of these results we disregard again the difference between Φ and φ in (2.8), (2.9), and consider, instead of $\bar{q}_m$ as given by (5.8), its reciprocal

$$\bar{q}_m{}^{-1}=\pi\sum_j\frac{(\bar{\varphi}_m|H|\psi_{jE})(\psi_{jE}|z|\psi_0)}{(\bar{\varphi}_m|z|\psi_0)}. \quad (6.1)$$

For $m=2$, in Sec. 3, only one continuum state ψ_{jE} is relevant namely, the state $1sEp$ ^1P which is reached from the ground state by excitation of a single electron. For $m>2$ additional continua occur, with the ion He$^+$ in an excited state with quantum number $m'<m$. The wave functions ψ_{jE} of these states can be obtained by extrapolation from the discrete-state wave function $\varphi_{m'n\alpha}$ considered in Sec. 5, and can accordingly be identified as $\bar{\varphi}_{m'E\alpha}$. We then replace (6.1) by

$$\bar{q}_m{}^{-1}=\pi\frac{(\bar{\varphi}_m|H|\psi_{1sEp})(\psi_{1sEp}|z|\psi_0)}{(\bar{\varphi}_m|z|\psi_0)}$$
$$+\pi\sum_{m'=2}^{m-1}\sum_\alpha\frac{(\bar{\varphi}_m|H|\bar{\varphi}_{m'E\alpha})(\bar{\varphi}_{m'E\alpha}|z|\psi_0)}{(\bar{\varphi}_m|z|\psi_0)}. \quad (6.2)$$

In this expression the quantum number m appears as an index of $\bar{\varphi}_m$ and in the limit on the summation over m'. The $\bar{\varphi}_m$ are involved only in matrix elements to which the main contribution accrues from the interior of the atom. The reasoning followed in Secs. 4 and 5 suggests that these matrix elements depend on m primarily through a normalization coefficient which cancels out from the numerator and denominator of each term on the right of (6.2). Accordingly we disregard the dependence of $\bar{q}_m$ on m through $\bar{\varphi}_m$.

Consider now successive terms on the right of (6.2). For $m=2$ we have a single term, which is simply the reciprocal of q_{2s2p} and is therefore negative and approximately equal to -0.4 as seen in Sec. 3. For higher m, the first term on the right of (6.2) is then simply -0.4 if its dependence on m is disregarded, so that the observation of positive values of $\bar{q}_m$ for $m>2$ implies that the additional terms on the right of (6.2) are positive and larger than 0.4.

The first term of (6.2) is negative because the double-excitation dipole element $(\bar{\varphi}_2|z|\psi_0)$ is negative (see Sec. 3), whereas for a one-electron transition $(\psi_{1sEp}|z|\psi_0)$ is positive. Each of the other terms of (6.2) has also one dipole element in its numerator and one in its denominator, but *both* of them pertain to *two-electron transitions;* therefore both of these matrix elements are presumably negative and their *ratio is positive*, as is required to account for the experimental

observation on $\bar{q}_3$ and $\bar{q}_4$. This argument implies that all interaction matrix elements $(\bar{\varphi}_m|H|\bar{\varphi}_{m'E\alpha})$ are positive, as will be verified below.

Finally, we consider the magnitudes of the various terms of (6.2) to determine whether the negative contribution of the first term is likely to be smaller than the positive contributions of following terms with increasing m'. The energy transfer from an electron dropping from the mth to the m'th shell to the ejected electron decreases as m' approaches m. Since the probability of auto-ionization is limited by the slowness of large energy transfers between electrons (see Sec. 3), the auto-ionization channel with $m'=m-1$, requiring the least energy transfer, is most likely. [Equivalently, the volume of space that contributes substantially to $(\bar{\varphi}_m|H|\bar{\varphi}_{m'E\alpha})$, with $m'<m$, extends roughly over the whole m'th shell, so that the term of (6.2) with largest m' dominates. Also, in the Auger effect electron vacancies tend to move outward through the atom one shell at a time.] Before proceeding to quantitative estimates, we simplify (6.2) further by disregarding the dependence of $(\bar{\varphi}_m|H|\bar{\varphi}_{m'E\alpha})$ and $(\bar{\varphi}_{m'E\alpha}|z|\psi_0)$ on the variations of E within the 13.6 eV interval which includes all He$^+$ levels with $m'>2$. The dependence on α can then be factored out as in (5.6) and (5.7), to yield

$$\sum_\alpha (\bar{\varphi}_m|H|\bar{\varphi}_{m'E\alpha})(\bar{\varphi}_{m'E\alpha}|z|\psi_0)$$
$$\approx \sum_\alpha (\bar{\varphi}_m|H|\bar{\varphi}_{m'})[c_{01}^{(m'\alpha)}+c_{10}^{(m'\alpha)}]^2(\bar{\varphi}_{m'}|z|\psi_0)$$
$$=2(\bar{\varphi}_m|H|\bar{\varphi}_{m'})(\bar{\varphi}_{m'}|z|\psi_0), \quad (6.3)$$

where (5.12) has been utilized. Thereby (6.2) reduces to

$$\bar{q}_m^{-1}=\pi\frac{(\bar{\varphi}_m|H|\psi_{1sEp})(\psi_{1sEp}|z|\psi_0)}{(\bar{\varphi}_m|Z|\psi_0)}$$
$$+2\pi\sum_{m'=2}^{m-1}\frac{(\bar{\varphi}_m|H|\bar{\varphi}_{m'})(\bar{\varphi}_{m'}|z|\psi_0)}{(\bar{\varphi}_m|z|\psi_0)}. \quad (6.4)$$

Since this equation applies equally to all levels with a given m, according to Secs. 4 and 5, we carry out the evaluation of $\bar{q}_3$ by replacing $\bar{\varphi}_3$ by φ_{3s3p}, which yields

$$q_{3s3p}^{-1}=\pi\frac{(\varphi_{3s3p}|H|\psi_{1sEp})(\psi_{1sEp}|z|\psi_0)}{(\varphi_{3s3p}|z|\psi_0)}$$
$$+2\pi\frac{(\varphi_{3s3p}|H|\bar{\varphi}_2)(\bar{\varphi}_2|z|\psi_0)}{(\varphi_{3s3p}|z|\psi_0)}. \quad (6.5)$$

The first term on the right we take as ~-0.4, as discussed above. In the second term, consider first the matrix element $(\varphi_{3s3p}|z|\psi_0)$. Salpeter and Zaidi[20] estimate the oscillator strength of the transition $1s^2\rightarrow 2s3p$ to be 3.9×10^{-4}. We assume that the wave functions φ_{3s3p} and φ_{2s3p} differ, in the region of $1s^2$, merely by the normalization factor $2^3/3^3$ pertaining to unscreened hydrogenic wave functions. Thereby we find

$$f_{3s3p}\approx(2^3/3^3)f_{2s3p}=1.2\times10^{-4}, \quad (6.6)$$

and hence, taking into account that the energy of this transition is 70 eV,

$$(\varphi_{3s3p}|z|\psi_0)\approx-2.6\times10^{-11}\text{ cm.} \quad (6.7)$$

The negative sign has been introduced following Sec. 3.

To evaluate $(\bar{\varphi}_2|z|\psi_0)$ we can take Salpeter and Zaidi's[20] value $df_{2sEp}/dE=6.4\times10^{-4}$ (eV)$^{-1}$, for E at 4.6 eV above the $m=2$ threshold. Following (5.4) we take $df_{2sEp}/dE\sim df_{2pEs}/dE$ and obtain

$$(\bar{\varphi}_2|z|\psi_0)=-5.9\times10^{-11}\text{ cm/(eV)}^{1/2}, \quad (6.8)$$

with the negative sign in accordance with Sec. 3. Alternatively, we can divide the experimental value (3.7) of $(2s2p|z|1s^2)$ by N_2 according to (4.3), a procedure previously applied in (5.15), and obtain

$$(\bar{\varphi}_2|z|\psi_0)=-4.6\times10^{-11}\text{ cm/(eV)}^{1/2}. \quad (6.9)$$

Information on $(\varphi_{3s3p}|H|\bar{\varphi}_2)$ is obtained by a calculation closely related to Pincherle's work on Auger transitions.[27] The matrix elements $(\varphi_{3s3p}|H|\psi_{1sEp})$, $(\varphi_{3s3p}|H|\psi_{2sEp})$ and $(\varphi_{3s3p}|H|\psi_{2pEs})$ were calculated with unscreened hydrogenic wave functions. As shown in Table I, the estimate of $(\varphi_{2s2p}|H|\psi_{1sEp})$ obtained in this manner differs from the experimental value by a factor of 2. To improve our approximation, only the ratios among the hydrogenic values of the energy matrix elements were utilized and the experimental value of the matrix element for the $2s2p$ level served as a normalization constant. Thus we calculate

$$\frac{(\varphi_{3s3p}|H|\bar{\varphi}_2)^2}{(\varphi_{2s2p}|H|\psi_{1sEp})^2}$$
$$\approx\frac{1}{2}\frac{(\varphi_{3s3p}|H|\psi_{2sEp})^2+(\varphi_{3s3p}|H|\psi_{2pEs})^2}{(\varphi_{2s2p}|H|\psi_{1sEp})^2}$$
$$=\frac{1}{2}\frac{(0.142)^2+(0.138)^2}{(0.145)^2}=0.94, \quad (6.10)$$

and note that all relevant energy matrix elements are positive. The ratio

$$(\varphi_{3s3p}|H|\psi_{1sEp})^2/(\varphi_{2s2p}|H|\psi_{1sEp})^2=0.063 \quad (6.11)$$

was also obtained. The experimental value (3.5) combined with (6.10) yields now

$$(\varphi_{3s3p}|H|\bar{\varphi}_2)\approx0.073\text{ (eV)}^{1/2}. \quad (6.12)$$

Finally we substitute into (6.5) the value -0.4 for the first term and the values (6.7), (6.8), and (6.12)

[27] L. Pincherle, Nuovo Cimento 12, 81 (1935). Hydrogenic calculations of Slater integrals are equally applicable to all atoms; therefore their results serve as a ready source of preliminary answers to a large number of questions.

of the matrix elements, and find

$$q_{3s3p}^{-1} \sim -0.4 + 2\pi \frac{0.073 \times (-5.9) \times 10^{-11}}{-2.6 \times 10^{-11}}$$

$$= -0.4 + 1.0 = 0.6, \quad (6.13)$$

$$q_{3s3p} \approx 1.7. \quad (6.14)$$

This estimate is obviously crude and appears lower than one would surmise by inspection of the spectrograph plates (Fig. 3 of Ref. 6). It does, however, indicate the relative magnitude of the various relevant quantities and it confirms the surmise that the term of (6.5) with $m' = m - 1$ has a controlling influence.

It appears from (6.11), (6.12), and (3.5) that auto-ionization to ψ_{1sEp} is negligible. Accordingly (4.7) reduces to

$$\Gamma_{3s3p} \sim 2\pi(\varphi_{3s3p}|H|\psi_{2sEp})^2 + 2\pi(\varphi_{3s3p}|H|\psi_{2pEs})^2$$
$$= 4\pi(\varphi_{3s3p}|H|\bar{\varphi}_2)^2 = 4\pi \times 0.94 \times (0.078)^2$$
$$= 0.072 \text{ eV}. \quad (6.15)$$

(Here again the formula from Sec. 4.1 is relevant because we deal with He.) This value agrees with the appearance of the $3s3p$ line in Fig. 3 of Ref. 6.

The correlation coefficient ρ is certainly low for the $3s3p$ line, because auto-ionization leads almost entirely to the $\bar{\varphi}_2$ continuum, as noted above, whereas direct dipole transitions from the ground state lead primarily to ψ_{1sEp}, as shown by the ratio of (3.6) and (6.8). The direct calculation of ρ, by substituting estimates of the matrix elements in (2.14), has very low accuracy, owing to inaccuracies of the individual matrix elements and to partial cancellations. Its result,

$$\rho \sim -0.1, \quad (6.16)$$

serves only as an indication of order of magnitude. The spectrograph plate shows a transmission window clearly, though faintly, thus indicating a value of ρ somewhat larger than (6.16), lying between the limits $0.01 \ll \rho^2 \ll 1$.

7. INNER s SUBSHELL EXCITATIONS IN Ne, Ar, Kr, AND Xe

In the extensive far-uv absorption spectra of Ne and of the heavier rare gases, one Rydberg series of lines of each element stands out for the breadth, brilliance, and number of its observed lines. This series was classified promptly[3] because its limit of convergence is determined accurately and coincides with a known level of the residual ion, namely the level in which the inner s subshell is ionized while the outermost p^6 subshell remains unaffected. In x-ray language this limit is called the L_I edge for Ne, M_I for Ar etc. Accordingly, these line series have the classification

$$ms^2mp^6 \, {}^1S \rightarrow ms \, mp^6np \, {}^1P^\circ, \quad (7.1)$$

with $m = 2, 3, 4, 5$ for Ne, Ar, Kr, Xe, and with $n > m$. The present discussion will be limited to these series,

because other line systems in the same spectral regions are far more complex and their analysis is still in an early stage. The LS coupling classification ${}^1P$ is probably not quite appropriate to the upper levels of Kr and Xe, but we shall disregard this matter here.

The series (7.1) of Ne differs greatly in appearance from the corresponding series of the other rare gases, in that its q value is rather large and negative (~ -3) whereas for the other gases q is very small. (A preliminary analysis of Samson's data[7] for Ar gives $q \sim -0.4$.) Neon is already known to differ greatly from the heavier rare gases in the gross intensity distribution of its far-uv absorption spectrum; this behavior relates to the circumstance that the $2p$ wave functions of Ne have no radial nodes, whereas the corresponding mp wave functions of the other rare gases have one or more nodes.[16] Therefore, the analysis of Ne on the one hand and of the heavier gases on the other presents us with quite separate tasks. Here we deal mainly with Ne and can make only tentative remarks for the other gases.

The discrete excited levels indicated in (7.1) can auto-ionize only into states of the continuum whose configuration is indicated by ms^2mp^5Ed or ms^2mp^5Es. (The energy is too low for auto-ionization to other channels; therefore the treatment of Sec. 4.1 is appropriate.) For the present purposes we can enumerate and classify these continuum states simultaneously for Ne and for the other gases. The mp^5 group has a doublet of states ${}^2P_{3/2,1/2}$ each of which interacts separately with the continuum electron. Thus one can identify five different states ψ_{jE}, based on the two levels of the doublet, whose coupling is not even approximately LS. Here we single out a set of states ψ_{jE} whose interaction with the discrete excited states $msmp^6np$ and with the ground state is particularly simple, rather than the usual set of states whose mutual interaction via spin-orbit coupling has been minimized.[28] This is the set of 5 states ψ_{jE} constructed by LS coupling, namely,

$$ms^2mp^5Es \, {}^1P_1{}^\circ, \, {}^3P_1{}^\circ$$
$$\text{and} \quad ms^2mp^5Ed \, {}^1P_1{}^\circ, \, {}^3P_1{}^\circ, \, {}^3D_1{}^\circ. \quad (7.2)$$

Among these states *only the two* ${}^1P^\circ$ are related to the ground state or to the discrete ${}^1P^\circ$'s, respectively, by nonvanishing matrix elements of the dipole z or of the nonmagnetic Hamiltonian H.[29] The other continuum states can be disregarded for our limited purpose.

a. The q_{3p} Value for Ne

With these understandings and with suitable adaptations of the notation of (2.8), the q index of the first Ne

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[28] This temporary departure from the stipulation (2.1) is merely a device for simplifying formulas, without any substantive effect. It takes advantage of the fact that both $\psi_E{}^{(a)}$ and $\psi_E{}^{(d)}$, defined by (2.4) and (2.13), are ${}^1P^\circ$ states.

[29] The magnetic spin-orbit terms of the Hamiltonian are disregarded in the present analysis, even though they can bring about precession rates far from negligible as compared to the auto-ionization rates. These terms cannot contribute to auto-ionization as shown in the text following (7.4).

line (7.1) can be written as

$$q_{3p} = \frac{(\varphi_{3p}|z|\psi_0)}{\pi[(\varphi_{3p}|H|\psi_{Es})(\psi_{Es}|z|\psi_0)+(\varphi_{3p}|H|\psi_{Ed})(\psi_{Ed}|z|\psi_0)]} . \qquad (7.3)$$

Here, as in Secs. 3–6, Φ_{3p} has been replaced by φ_{3p}, thus disregarding the second term in the numerator of (2.9). (This simplification is presumably acceptable for Ne but not for the heavier gases whose q values are small so that minor additive terms acquire importance.)

Dipole matrix elements for rare-gas dipole transitions to the continuum states Es and Ed have been calculated by one of us (JWC) in Ref. 16. Comparison with subsequent experiments[30] on photon absorption in Ne shows the calculated absorption to be 10–20% too large at the energies of interest. Therefore, for Ne we take the sign and the ratio of the dipole matrix elements from calculation, with the sign convention of Sec. 3, and adjust their magnitude to fit the experimental data. The values shown in Table II are thereby obtained. The dipole matrix element for excitation of the $3p$ discrete level calculated by the method of Ref. 16 is also shown in Table II. Since the sign of all these dipole matrix elements is positive,[31] the negative value of q observed experimentally for Ne implies negative values of the energy matrix elements.

For the energy matrix elements in (7.3) a more explicit notation is desirable, namely, for the $3p$ level of Ne

$$(2s2p^63p\ ^1P|H|2s^22p^5Es\ ^1P),$$
$$(2s2p^63p\ ^1P|H|2s^22p^5Ed\ ^1P). \qquad (7.4)$$

We deal here with auto-ionizing transitions in which a $2p$ and a $3p$ electron gain or lose one unit of angular momentum. Therefore, *only* the electron-electron interaction energy terms of H yield a nonvanishing contribution. This contribution reduces, for the "Es" matrix element, to a linear combination of the two Slater integrals[18]

$$R^1(2pnp,2sEs) \quad \text{and} \quad R^1(np2p,2sEs) \qquad (7.5)$$

and to similar integrals for the "Ed" element.

The first of these integrals corresponds to the one-electron transitions $(2p \rightarrow 2s, 3p \rightarrow Es)$, the second to $(3p \rightarrow 2s, 2p \rightarrow Es)$. The second of these processes may be regarded as a transition *via* the ground state, the first one as an Auger process in which the "hole" left in the $2s$ subshell by the initial excitation migrates

[30] D. L. Ederer and D. H. Tomboulian, Phys. Rev. **133**, 1525 (1964).

[31] Notice that the dipole matrix element for the unrealistic transition $2s \rightarrow 2p$ is *negative* in Ne, for the reasons discussed in Ref. 16. Negative values of dipole matrix elements are shown there to change into positive values as the excitation energy increases. For the $2s \rightarrow np$ series the sign reversal is known to lie between $n=2$ and $n=3$ in Li; the same situation is now shown to obtain for Ne. By comparison the matrix elements for all discrete transitions $3s \rightarrow np$ are negative in Na, the sign reversal occurring in the continuum (see Ref. 16).

to the $2p$ subshell and releases the energy for auto-ionization of the $3p$ electron. Since the hole represents a positive charge, its interaction with the excited electron has sign opposite to the interaction that operates in the transition *via* the ground state.

This qualitative conjecture is borne out by actual calculation of the matrix elements (7.4). The calculation, which has some unusual aspects from the standpoint of spectroscopy theory, will be reported elsewhere. Its results are

$$(2s2p^63p\ ^1P|H|2s^22p^5Es\ ^1P)$$
$$= \tfrac{1}{3}\{-R^1(2p3p,2sEs)+2R^1(3p2p,2sEs)\},$$
$$(2s2p^63p\ ^1P|H|2s^22p^5Ed\ ^1P) \qquad (7.6)$$
$$= \tfrac{1}{3}\sqrt{2}\{-R^1(2p3p,2sEd)+2R^1(3p2p,2sEd)\}$$

The negative sign in the first term within the braces of each equation derives from an antisymmetry property of the wave functions for shells with a single vacancy, and thus bears out our conjecture regarding the migration of a hole. The ratio of 2 between the coefficients of the two terms in braces means that in one process all electrons $2p^6$ can be ionized to Es or Ed but in the other only half of them have a spin orientation that matches the hole in $2s$.

Calculations of the Slater integrals in (7.6) have been performed using the numerical central-field wave functions described in Ref. 16. Unfortunately the larger integrals depend sensitively on the energy E; this implies a low accuracy, especially in view of an inconsistency in the zero point of the scale of electron kinetic energies for the continua. The excitation to $3p$ involves the absorption of a 45.4 eV photon, which exceeds by 24.2 eV the 21.2 eV experimental threshold for ionization of $2p^6$; however, the model utilized for the calculation yields an unduly high threshold of 23.9 eV, so that a 45.4 eV photon would release electrons of only 21.5 eV. For purposes of orientation the calculation was performed using both of the above values of the kinetic energy. Its results are shown in Table II. Notice that the "hole migration" process with ejection of a d electron, whose contribution is represented by the Slater integral $R^1(2p3p,2sEd)$, has a dominant influence on q, Γ, and ρ, and in particular determines the sign of q. Destructive interference between the contributions of the two processes to the ejection of s electrons minimizes their net contribution.

The theoretical estimates shown in Table II are consistent with evidence obtained from the spectrograph plates (Ref. 3 and private communication). Notice in particular that $|\rho|$ approaches 1, in agreement with the brightness of the transmission window in the line.

TABLE II. Calculated values of theoretical parameters for the $n=3$ line of the series (7.1) of Ne. Calculations were made for two values of photoelectron kinetic energy (see text): (a) "theoretical model" value, 21.5 eV, (b) "experimental" value, 24.2 eV.

		(a)	(b)
$(\psi_{Es}|z|\psi_0)$	cm/(eV)$^{1/2}$	1.9×10^{-10}	1.9×10^{-10}
$(\psi_{Ed}|z|\psi_0)$	cm/(eV)$^{1/2}$	7.5×10^{-10}	7.5×10^{-10}
$(\varphi_{3p}|z|\psi_0)$	cm	1.5×10^{-10}	
$R^1(2p3p,2sEs)$	atomic units	0.012	0.005
$R^1(2p3p,Es2s)$	atomic units	0.007_6	0.007
$R^1(2p3p,2sEd)$	atomic units	0.015	0.009
$R^1(2p3p,Ed2s)$	atomic units	-0.0004	-0.0001_5
$(\varphi_{3p}|H|\psi_{Es})$	(eV)$^{1/2}$	0.005	0.007
$(\varphi_{3p}|H|\psi_{Ed})$	(eV)$^{1/2}$	-0.042	-0.030
q		-1.4	-2.2
Γ	eV	0.011	0.006
ρ		-0.9_4	-0.8_4

This result follows from the low probability of transitions to the Es state, whether by direct transition or by auto-ionization, which causes both $\psi_E^{(a)}$ and $\psi_E^{(d)}$ to differ but little from Ed.

b. Ar, Kr, and Xe

As noted earlier, the main series of lines (7.1) for these three gases is singled out by its "window" appearance, that is, by the presence of brilliant maxima of transmission (minima of photon absorption) which are not accompanied by comparable transmission minima [see Refs. 3, 7, and Fig. 1(b)]. This appearance corresponds to $|q|$ values substantially smaller than 1, and to values of ρ^2 not too much smaller than 1. As explained at the end of Sec. 4, $q^2<1$ implies that the absorption through the discrete state fails to compensate the effect of repulsion of the continuum states away from a discrete level.

To account for this behavior in Ar, Kr, and Xe and for its absence in Ne one should see whether and why the matrix elements in the denominator of q, as given, e.g., by (7.3), are substantially larger for Ar than for Ne as compared to the matrix element in the numerator. Evidence in this direction is provided by the basic difference between the continuum oscillator strengths of Ne on the one hand and of the heavier gases on the other.[16] Recent observations, displayed conveniently by Samson and Kelly,[32] show that the continuum cross sections of Ar, Kr, and Xe are over three times larger than that of Ne at the respectively relevant energies. Note, however, that: (a) q depends on the dipole elements $(\psi_{Ed}|z|\psi_0)$ and $(\psi_{Es}|z|\psi_0)$ whereas the cross sections depend on their squares, and (b) these two dipole elements have opposite sign, according to Ref. 16, and therefore could conceivably interfere destruc-

[32] J. A. R. Samson and F. L. Kelly, Tech. Rept. 64-3-N, Geophysical Corporation of America, Bedford, Massachusetts, 1964 (unpublished) Fig. 15.

tively and thereby enhance rather than reduce the value of $|q|$ in Ar, Kr, and Xe. One should also consider the second term of q, in the numerator of (2.9), which we have disregarded thus far but which is probably large in the present circumstance. Since the spectral region of interest coincides with a rapid, rather localized drop of the spectral distribution of the dipole matrix elements $(\psi_{El}|z|\psi_0)$,[32] the ratio $f(E')/f(E)$ in (2.10) is likely to be substantially larger at $E'<E$ that at $E'>E$, so as to make the integral (2.10) not too small and positive. If, then, the first term of q, as given by (7.3), is ~-1—a likely value—the addition of the second term may reduce $|q|$ substantially and bring q to its approximate experimental value for Ar obtained from Ref. 7, namely, ~-0.4.

The first of the Ar lines $(3s\to4p)$ appears rather wide on the spectra.[3,7] Its estimated width is

$$\Gamma\sim0.05-0.07\text{ eV}, \qquad (7.7)$$

that is, appreciably greater than for Ne. The corresponding values of the matrix elements, $(\varphi_{4p}|H|\psi_{Ed})$ and $(\varphi_{4p}|H|\psi_{Es})$, should contribute to reduce the value of $|q|$, again with the proviso that no major effect of destructive interference arise between the two terms of $\sum_l(\varphi_{4p}|H|\psi_{El})(\psi_{El}|z|\psi_0)$.

The theoretical determination of the sign of q_{4p} for Ar is difficult. Among the three important matrix elements, $(\varphi_{4p}|z|\psi_0)$, $(\varphi_{4p}|H|\psi_{Ed})$ and $(\psi_{Ed}|z|\psi_0)$, the $(\psi_{Ed}|z|\psi_0)$ has been calculated in Ref. 16 and found to be *negative* at the energy of interest; experiments[7] have shown the results of this calculation to be poor in the relevant energy range, but nevertheless indicate that the negative sign should be correct.[33] Agreement with the experiment would then require $(\varphi_{4p}|H|\psi_{Ed})$ and $(\varphi_{4p}|z|\psi_0)$ to be of the same sign. Attempts at calculating these matrix elements have given results critically dependent on the theoretical model, even with regard to their sign. The dipole elements $(\varphi_{np}|z|\psi_0)$ in Ar, Kr, Xe, might be expected[31] to be negative and decreasing in magnitude towards a point of zero in the Ep continuum. However, the position of this zero has been found to depend on the model; for Ar, $(\varphi_{4p}|z|\psi_0)$ is found to be negative by use of a Hartree-Fock $3s$ orbital, but already positive with an orbital of the fixed central field of Ref. 16.

8. INNER SHELL EXCITATIONS IN Kr AND Xe TRANSITION TO THE X-RAY RANGE

The absorption spectra of Kr and Xe observed with synchrotron light exhibit, between 120 and 195 Å

[33] Reference 16 predicts negative values of $(\psi_{Ed}|z|\psi_0)$ which are very large at the ionization threshold and then decrease smoothly to a zero about 25 eV above his threshold; the energy of interest to us lies in the middle of this range. The experimental absorption cross section, instead, is much lower at threshold than predicted and remains flat for about 12 eV, crossing the theoretical curve, up to a knee at which it drops rapidly toward the low minimum predicted by theory. It seems likely that $(\psi_{Ed}|z|\psi_0)$ is indeed negative but that its plot as a function of E is flat up to a knee like the plot of the total cross section.

(65–100 eV), line series corresponding to transitions

$$(m-1)d^{10}ms^2mp^6 \rightarrow (m-1)d^9(^2D_{5/2,3/2})ms^2mp^6np, \quad (8.1)$$

where $m=4$ and 5 for Kr and Xe, respectively, and $n>m$.[4] This classification rests on the identification of the series limits as the $M_{\mathrm{IV,V}}$ and $N_{\mathrm{IV,V}}$ edges of the x-ray spectra of Kr and Xe and on the knowledge of quantum defects of their np levels. The lines of these series appear as rather sharp, symmetric peaks of absorption without any trace of the asymmetry or "window" character discussed in previous sections. The lines become rapidly faint along each series and only 3 or 4 per series have been observed; however, the linewidths decrease rather slowly and remain larger than the instrumental resolution. Complementary observations of the spectra (8.1) have been made with a bremsstrahlung source[34]; use of a spectrometer provided measurements of absorption coefficients but resolved only one line of each series. A spectrum pertaining to the $N_{\mathrm{II,III}}$ edges of Xe has also been observed.[34]

In the final state of (8.1), the core $(m-1)d^9ms^2mp^6$ can auto-ionize, e.g., to $(m-1)d^{10}ms^2mp^5Ed$, without participation of the excited electron np. Therefore the formulas of Sec. 4.2 apply instead of those of Sec. 4.1; in particular the variations of the linewidth Γ_n versus n should follow the two-term formula (4.12). Inspection of the spectrograph plates of Ref. 4 shows Γ_{n+1}/Γ_n to be 0.7 for $n=m+1$ and not appreciably <1 for higher n. Thus auto-ionization appears to proceed at comparable rates with or without participation of the np electron for $n=m+1$ and predominantly without such participation for higher n; this situation is intermediate between those found at lower photon energies and in the usual x-ray spectra. Since the integrated intensity of the lines should decrease with increasing n in proportion to the normalization factor N_n^2 (Sec. 4), the asymptotic approach of Γ_n to a constant Γ_2 implies that the lines fade out rapidly as observed[4]; indeed only 3–4 lines are seen in contrast to nearly ten lines for the main series of He, Ne, and Ar. The plates of Ref. 4 appear consistent with estimates $\bar{\Gamma}_1 \sim 0.01$ or 0.02 and $\Gamma_2 \sim 0.1$ eV of the parameters of (4.12).

[34] A. P. Lukirskii, T. M. Zimkina and I. A. Britov, Izv. Akad. Nauk U.S.S.R. Ser. Fiz. 28, 772 (1964).

The height (4.15) of the absorption jump over the spectra (8.1) has been estimated in Ref. 34 to be for the combined doublet

$$[1+\tfrac{1}{2}\pi\langle\Gamma\rho^2\rangle_{\mathrm{red}}(\bar{q}^2-1)]_{5/2}[1+\tfrac{1}{2}\pi\langle\Gamma\rho^2\rangle_{\mathrm{red}}(\bar{q}^2-1)]_{3/2}$$
$$=1.6\pm0.15; \quad (8.2)$$

in the spectrographs of Ref. 4 the jump is not even clearly discernible. The approximate symmetry of the lines and the absence of any transmission imply then

$$|\bar{q}| \gg 1, \quad \langle\Gamma\rho^2\rangle_{\mathrm{red}} \ll 1, \quad (8.3)$$

that is, characteristics such as are generally found in x-ray spectra. On the other hand, the magnitude (8.2) of the jump is decidedly lower than the values (~ 5 to 10) that are typical for x-ray spectra. This low value relates to the failure to detect transitions analogous to (8.1) but with the outer electron landing in a nf rather than np orbital.[4,34] The transitions to f orbitals, which involve most of the oscillator strength of the $(m-1)d$ electrons, have recently been found to occur almost entirely at energies well above the absorption edges[35]; therefore they do not contribute to the absorption jump at and near the edges themselves. This intensity shift upward from the edges has been attributed[36] to failure of hydrogenlike approximations in the outer region of the atoms where the $(m-1)d \rightarrow f$ transition takes place; therefore it cannot occur in the absorption of harder x rays which stems from transitions in the hydrogenlike interior of atoms.

ACKNOWLEDGMENT

[35] D. L. Ederer and D. H. Tomboulian, Bull. Am. Phys. Soc. 9, 405 (1964); A. P. Lukirskii, I. A. Britov, and T. M. Zimkina, Opt. i Spektroscopiya 17, 438 (1964) [English transl.: Opt. Spectr. 17, 234 (1964)]; D. L. Ederer, Phys. Rev. Letters 13, 760 (1964).
[36] J. W. Cooper, Phys. Rev. Letters 13, 762 (1964).