Effects of Configuration Interaction on Intensities and Phase Shifts

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The interference of a discrete autoionized state with a continuum gives rise to characteristically asymmetric peaks in excitation spectra. The earlier qualitative interpretation of this phenomenon is extended and revised. A theoretical formula is fitted to the shape of the 2s2p 1P resonance of He observed in the inelastic scattering of electrons. The fitting determines the parameters of the 2s2p 1P resonance as follows: \( E = 60.1 \text{ ev} \), \( P \approx 0.04 \text{ ev}, f \approx 2 \times 10^{-4} \). The theory is extended to the interaction of one discrete level with two or more continua and of a set of discrete levels with one continuum. The theory can also give the position and intensity shifts produced in a Rydberg series of discrete levels by interaction with a level of another configuration. The connection with the nuclear theory of resonance scattering is indicated.

I. INTRODUCTION

Electron states of atoms and molecules are usually classified as belonging to various configurations, according to the independent-particle approximation. The actual stationary states may be represented as superpositions of states of different configurations which are “mixed” by the “configuration interaction,” i.e., by terms of the Hamiltonian that are disregarded in the independent-particle approximation. The effects of configuration interaction are particularly conspicuous at energy levels above the lowest ionization threshold, where states of different configurations coincide in energy exactly since at least some of them belong to a continuous spectrum. The mixing of a configuration belonging to a discrete spectrum with continuous spectrum configurations gives rise to the phenomenon of autoionization. The exact coincidence of the energies of different configurations makes the ordinary perturbation theory inadequate, so that special procedures are required for the treatment of autoionization and of related phenomena.

A basic treatment of stationary states with configuration mixing under conditions of autoionization was developed long ago by Rice. It was also pointed out that autoionized levels manifest themselves in continuous absorption spectra as very asymmetric peaks because, in the mixing of configurations to form a stationary state of energy \( E \), the coefficients vary sharply when \( E \) passes through an autoionized level. This remark accounted qualitatively for the character of rare-gas spectra in the range between the two ionization thresholds corresponding to the doublet (\( P_1 \) and \( P_1 \)) ground states of rare-gas ions.

Interest returns to this phenomenon as more extensive exploration of high levels of excitation is undertaken by means of far-ultraviolet light, of electron bombardment, and also of energy transfer in molecular collisions. It may then be worthwhile to return to the theory of reference 2, which can be extended and improved in several respects. In particular, we propose to analyze an asymmetric peak of the He spectrum observed by Silverman and Lassettre to the point of obtaining parameters of the 2s2p autoionized level. The interpretation of the Beutler rare gas spectra will be modified to some extent. The objective is to present procedures that can be applied to the quantitative analysis of experimental data and to point out the significance of the parameters obtained from such analysis.

Section 2 presents a reformulation of the theory of reference 2, avoiding the bypass through quantization in a finite box which had also been utilized in reference 1. This reformulation brings out the connection with the theory of scattering in the proximity of a resonance. Indeed, the main results of this paper are implied by the scattering theory which deals, in essence, with processes inverse to those considered here. Breit-Wigner cross-section formulas will be rederived through the approach of this paper in Appendix C. Section 3 analyzes the experimental data on the 2s2p level of He. Section 4 extends the theory to continuous spectra of different configurations interacting with a single discrete autoionized level. This extension is relevant, for example, to the rare gases where a free electron in \( d_1, d_1 \), or \( g_1 \) states may couple with the lowest, \( P_{2 \circ} \), state of the ion to form three different \( P_{2 \circ} \) continua. Section 5 extends the theory to the interaction of a number of discrete levels with one continuous spectrum.

The effects of direct interaction of different continua (as distinguished from coupling through a discrete level) will not be considered in this paper.

The effects of configuration interaction upon the position and the intensity of the lines of a Rydberg spectrum are

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* Note added in proof. The most relevant material of this reference is to be published by E. N. Lassettre and S. M. Silverman. I thank Professor Lassettre for permitting me to publish his data and for having shown me his paper ahead of publication.

series in a discrete spectrum are equivalent to the effects on a continuum. This application will be outlined in Appendix B.

2. ONE DISCRETE STATE AND ONE CONTINUUM

Consider an atomic system with a number of zero-approximation states, and among these states one \( (\varphi) \) belonging to a discrete configuration and a continuum of states \( \psi_{E'} \). Each of these states is nondegenerate, all degeneracy having been removed by specification of an adequate set of quantum numbers (angular momentum, magnetic, etc.). We wish to diagonalize the portion of the energy matrix that belongs to the subset of states \( \varphi, \psi_{E'} \). The elements of this portion of the energy matrix constitute a square submatrix and will be indicated by

\[
(\varphi | H | \varphi) = E_{\varphi}, \tag{1a}
\]

\[
(\psi_{E'} | H | \varphi) = V_{E'}, \tag{1b}
\]

\[
(\psi_{E'} | H | \psi_{E'}) = E'\delta(E'-E'). \tag{1c}
\]

The Dirac \( \delta \) factor in Eq. (1c) implies that the submatrix belonging to the more limited subset of states \( \psi_{E'} \) had previously been diagonalized in the zero approximation. It is assumed that a pair of states of the same Rydberg series or continuum yields a vanishing off-diagonal element of the energy matrix. It is understood that the discrete energy level \( E_{\varphi} \) lies within the continuous range of values of \( E' \).

Each energy value \( E \) within the range of \( E' \) is an eigenvalue of the matrix (1). The corresponding eigenvector, which we wish to determine, has the form

\[
\psi_{E'} = a\varphi + \int dE' b_{E'} \psi_{E'}. \tag{2}
\]

It is understood that \( a \) and \( b_{E'} \) are functions of \( E \), but this dependence will be indicated explicitly only where necessary. These coefficients are determined as solutions of the system of equations pertaining to the matrix (1),

\[
E_{\varphi}a + \int dE' V_{E'}a b_{E'} = E_{\varphi}a, \tag{3a}
\]

\[
V_{E'}a + E'b_{E'} = Eb_{E'}. \tag{3b}
\]

The solution of this system can be carried out exactly, so that diagonalization of the matrix (1) is achieved.

System (3) has peculiarities arising from its continuous spectrum. To solve it, we shall express \( b_{E'} \) in terms of \( a \), utilizing (3b), and enter the result in (3a). This procedure involves a division of (3b) by \( E - E' \) which may be zero. This obstacle was circumvented in references 1 and 2 by quantization in a finite box, which replaces the continuous spectrum with a discrete one, and eventual transition to the limit of an infinite box. Here we follow Dirac’s procedure\(^9\) of introducing the formal solution of (3b),

\[
b_{E'} = \frac{1}{E - E'} + \frac{\sqrt{\pi} \delta(E - E')}{V_{E'} a}, \tag{4}
\]

with the understanding that, upon substitution in (3a), one shall take the principal part of the integral over \( (E - E')^{-1} \) and that \( z(E) \) is to be determined later. Scattering problems usually involve conditions implying that \( z = \text{constant} \). In our treatment \( z(E) \) will be real.\(^{10}\) Notice that if the states \( \psi_{E'} \) are represented by a wave function with asymptotic behavior \( \propto \sin[k(E')r + \delta] \), their superposition with the coefficients (4) yields the following result. The integral over the first term on the right side of (4) multiplied by \( \sin[k(E')r + \delta] \) yields, for large \( r \),

\[
-\frac{\pi}{2} \cos[k(E)r + \delta] V_{E'}, \tag{5}
\]

The sum of the two terms can then be cast in the form

\[
\int dE' b_{E'} \psi_{E'} \propto \sin[k(E)r + \delta + \Delta], \tag{6}
\]

in which

\[
\Delta = -\arctan\left(\frac{\pi}{2}\right) \tag{6}
\]

represents the phase shift due to configuration interaction of \( \psi_{E} \) with the state \( \varphi \).

The value of \( z \) is itself determined by substituting the expression (4) of \( b_{E'} \) into (3a). The coefficient \( a \) factors out so that (3a) reduced to

\[
E_{\varphi} + F(E) + z(E) | V_{E'} |^2 = E, \tag{7}
\]

where

\[
F(E) = P \int dE' \frac{|V_{E'}|^2}{E - E'}, \tag{8}
\]

and \( P \) indicates “principal part of.” We have, then,

\[
z(E) = \frac{E - E_{\varphi} - F(E)}{|V_{E'}|^2}. \tag{9}
\]

Notice that \( |V_{E'}|^2 \), an index of the strength of the configuration interaction, has the dimensions of an energy since \( \psi_{E'} \) is normalized “per unit energy” according to (1c). The phase shift varies swiftly by \( \sim \pi \) as \( E \) traverses an interval \( \sim |V_{E'}|^2 \) about the “resonance” at \( E = E_{\varphi} + F \). The quantity \( F \) represents thus a shift of the resonance position with respect to \( E_{\varphi} \). This shift did not appear in reference 2 because of the unrealistic assumption \( V_{E'} = \text{constant} \), which yields \( F = 0 \).

The coefficient \( a \), which factors out of (3a), is determined by normalization. The ortho-normalization condition for the continuous spectrum must be expressed in terms of the coefficients \( a \) and \( b_{E'} \), for a pair of values of \( E \), indicated by \( E \) and \( E' \), which need not

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coincide:

\[ (\Psi_E | \Psi_E) = a^*(\bar{E}) a(E) + \int dE' b_{E'}^*(\bar{E}) b_{E'}(E) = \delta(\bar{E} - E). \]  

(9')

Substitution of (4) yields

\[
 a^*(\bar{E}) \left[ 1 + \int dE' V_{E'} \left[ \frac{1}{E - E'} + z(\bar{E}) \delta(E - E') \right] \right] \times \left[ \frac{1}{E - E'} + z(E) \delta(E - E') \right] V_{E'} a(E) = \delta(\bar{E} - E). \tag{10}
\]

Attention must be paid here to the integration over \( E' \) at the point of double singularity \( \bar{E} = E \). Appendix A shows that the factor \( 1/(E - E') \) is properly resolved into partial fractions plus a singular term according to

\[
\frac{1}{(E - E')(E - E')} = \frac{1}{E - E'} \left[ \frac{1}{E - E'} - \frac{1}{E - E'} \right] + \pi \delta(\bar{E} - E) \delta(E - E') \right]. \tag{11}
\]

Substituting (11) into (10) and considering that

\[
\delta(\bar{E} - E') \delta(E - E') = \delta(\bar{E} - E) \delta(E - E') \right]
\]

and that \( \delta(E - E') f(E') = \delta(E - E') f(E) \), one finds

\[
|a(E)|^2 V_{E'} \left[ \frac{1}{E - E'} + z(E) \delta(E - E') \right] \Omega(\bar{E} - E) + a^*(\bar{E}) V_{E'} \left[ \frac{1}{E - E'} - \frac{1}{E - E'} \right] \times \left[ \frac{1}{E - E'} + z(\bar{E}) \delta(E - E') \right] \Omega(\bar{E} - E) = \delta(\bar{E} - E). \tag{12}
\]

The expression in braces vanishes, owing to (7), so that (12) is fulfilled by

\[
|a(E)|^2 \left[ \frac{1}{V_{E'}} \left[ \frac{1}{E - E'} + z(E) \delta(E - E') \right] \Omega(\bar{E} - E) \right] \Omega(\bar{E} - E) = \frac{|V_{E'}|^2}{[E - E_0 - F(E)]^2} \tag{13}
\]

This result shows that the configuration interaction "dilutes" the discrete state \( \varphi \) throughout a band of actual stationary states whose profile is represented by a resonance curve with half-width \( \pi |V_{E'}|^2 \). If the system under consideration were prepared in the state \( \varphi \) at a certain instant, it would autoionize with the mean life \( \hbar/2\pi |V_{E'}|^2 \).

With reference to (6) and (4) we can finally write

\[
a = \frac{\sin \Delta}{\pi V_{E'}}, \tag{14a}
\]

\[
b_{E'} = \frac{\sin \Delta}{\pi V_{E'}^2 E - E'} \cos \Delta \delta(E - E'), \tag{14b}
\]

where

\[
\Delta = -\arctan \frac{\pi |V_{E'}|^2}{E - E_0 - F(E)}, \tag{15}
\]

according to (6) and (9).

The purpose of this section was not so much to study the eigenvector \( \Psi_E \) as a function of \( E \) as to study the resulting variation of the probability of excitation of the stationary state \( \Psi_E \). Whatever the excitation mechanism is, this probability may be represented as the squared matrix element of a suitable transition operator \( T \) between an initial state \( i \) and the state \( \Psi_E \). In view of (2) and (14) this matrix element is expressed in terms of the phase parameter \( \Delta \) by

\[
(\Psi_E | T | i) = \frac{1}{\pi V_{E'}} \left( \frac{\Phi(T | i)}{E - E'} \right) \sin \Delta - \frac{1}{\pi V_{E'}} \left( \frac{\Phi(T | i)}{E - E'} \right) \cos \Delta \tag{16}
\]

where

\[
\Phi = \varphi + P \int dE' V_{E'} \Psi_{E'} \tag{17}
\]

indicates the state \( \varphi \) modified by an admixture of states of the continuum. [This modification did not appear in reference 2 where \( V_{E'} \) and the states \( \Psi_{E'} \) had been regarded as independent of \( E' \) so that the integral in (17) would vanish.]

The sharp variation of \( \Delta \) as \( E \) passes through the resonance at \( E = E_0 + F \) causes a sharp variation of \( (\Psi_E | T | i) \). More specifically, \( \sin \Delta \) is an even function of \( E - E_0 - F \), whereas \( \cos \Delta \) is an odd function of this variable. Therefore, as anticipated in Sec. 1, the contributions to \( (\Psi_E | T | i) \) represented in (16) by \( \Phi(T | i) \) and \( (\Psi_E | T | i) \) interfere with opposite phase on the two sides of the resonance. In particular the transition probability vanishes on one side of the resonance, at \( \Delta = \Delta_0 \) —that is, \( E = E_0 \), where

\[
\tan \Delta_0 = \frac{E_0 - E_0 - F(E_0)}{\pi |V_{R_0}|^2} = \frac{\pi V_{R_0}^2 (\Psi_{E_0} | T | i)}{(\Phi | T | i) \tag{18}
\]

Notice that experimental investigation of a transition probability in the vicinity of an autoionized level will determine directly the resonance energy \( E_0 + F \), rather than the position \( E_0 \) of the unperturbed level, and will similarly provide information on the matrix element \( (\Phi(T | i) \) of transition to the "modified" state \( \Phi \) rather than on \( (\Psi_E | T | i) \) itself.

The ratio of the transition probability \( (\Psi_E | T | i)^2 \) to
the probability \(|\langle \psi_{E}|T|i\rangle|^2\) of transition to the unperturbed continuum can be represented by a single family of curves. These curves are functions of the reduced energy variable

$$\epsilon = \frac{E - E_\omega - F(E)}{\pi |V_E|^2} = \frac{E - E_\omega - F}{\frac{1}{2} \Gamma},$$

in which \(\Gamma = 2\pi |V_E|^2\) indicates the spectral width of the autoionized state \(\varphi\), and of the parameter

$$q = \frac{(\Phi|T|i)}{\pi V_E^2 \langle \psi_{E}|T|i\rangle}$$

$$= \frac{(\varphi|T|i) + F \int dE' \langle \varphi|H|\psi_{E}\rangle \langle \psi_{E}|T|i\rangle/(E' - E)}{\pi (\varphi|H|\psi_{E}) \langle \psi_{E}|T|i\rangle},$$

which coincides with \(\cot \Delta_0\) at \(E = E_\omega\) and is independent of phase normalizations. These curves are represented by

$$\frac{|\langle \psi_{E}|T|i\rangle|^2}{|\langle \psi_{E}|T|i\rangle|^2} = \frac{(q + \epsilon)^2}{1 + \epsilon^2} = \frac{q^2 - 1 + 2q\epsilon}{1 + \epsilon^2}.$$  

This function is plotted in Fig. 1 for a number of values of \(q\), which is regarded as constant in the range of interest. Notice that

$$\frac{1}{2} \pi q^2 = |\langle \Phi|T|i\rangle|^2/|\langle \psi_{E}|T|i\rangle|^2$$

is the ratio of the transition probabilities to the "modified" discrete state \(\Phi\) and to a bandwidth \(\Gamma\) of unperturbed continuum states \(\psi_{E}\). Notice also that the curves of Fig. 1 are of the type shown in Fig. VIII.8.2 of Blatt and Weisskopf.\(^8\)

If the ratio \(q\) and the line's shift and width functions, \(F(E)\) and \(\Gamma = \pi |V_E|^2\), can be regarded as independent of \(E\) over a sufficient range, integration of (21) yields the excess transition probability due to the discrete state \(\varphi\), in the form

$$\int dE \frac{|\langle \psi_{E}|T|i\rangle|^2 - |\langle \psi_{E}|T|i\rangle|^2}{\pi (q^2 - 1) \Gamma} = \frac{|\langle \psi_{E}|T|i\rangle|^2}{\pi (\langle \psi_{E}|T|i\rangle)^2 \Gamma}.  

(23)$$

This integral should in fact equal \(|\langle \varphi|T|i\rangle|^2\), because the diagonalization of the energy matrix carried out in this section is a unitary transformation and therefore cannot affect the total transition probability. Any departure of the right-hand side of (23) from \(|\langle \varphi|T|i\rangle|^2\) should be attributed to inadequate constancy of \(q\) and \(\Gamma\). Notice that the term of (21) odd in \(E\), whose contribution to (23) was dropped, actually converges weakly to zero as \(|\epsilon| \to \infty\).

Often the probability of excitation of the state \(\psi_{E}\) is proportional not to the squared matrix element of a single transition operator \(T\), but to the sum of squared matrix elements of a vectorial or tensorial set of operators \(T_q\), such as the set of components \(\sum_i x_i, \sum_j y_j, \sum_j z_j\) of the dipole moment of an atom. In this event, the ratios among the matrix elements of the various \(T_q\) are fixed by geometrical considerations, known as the Wigner-Eckart theorem, i.e., we have

$$\frac{|\langle \Phi|T_q|i\rangle|^2}{|\langle \Phi|T_q|i\rangle|^2} = \frac{|\langle \psi_{E}|T_q|i\rangle|^2}{|\langle \psi_{E}|T_q|i\rangle|^2}.  

(24)$$

It follows that \(|\langle \psi_{E}|T_q|i\rangle|^2\) vanishes at the same energy value, determined by (18), for all values of \(q\). This circumstance was overlooked in reference 2, where it was suggested incorrectly that a transition probability proportional to \(\sum_q |\langle \psi_{E}|T_q|i\rangle|^2\) need not vanish for any value of \(E\), since the various terms of the sum might have different points of zero. Failure of the interference to yield a complete cancellation of the transition probability must rather be sought in the effect of degeneracies which have been excluded in this section but are treated in Sec. 4. Of course, a complete cancellation may escape observation owing to insufficient resolving power; this factor could hardly have been paramount in the Beutler experiment\(^4\) considered in reference 2, even though it has a dominant influence on the data discussed in the next section.

3. ANALYSIS OF THE 2s2p 1P LEVEL OF HELIUM

Silverman and Lassette\(^7\) have observed the cross section for forward inelastic scattering of 500-ev electrons by He. The results obtained by them in the region of 60-ev energy losses are shown in Fig. 2. There seems to be little doubt that the main peak in the experimental curve is associated with the 2s2p 1P autoionized level of double excitation. The discussion of the data in reference
be unfrquent by still another order of magnitude. The operator $T$ reduces to a dipole operator in the limit $k \to 0$, but this limit is not approached very closely for $k \approx 0.2 \text{ Å}^{-1}$. Therefore the data in Fig. 2 probably include a certain amount of quadrupole excitations of $1S$ and $1D$ states. However these excitations form a background unperturbed by the discrete level, owing to the difference in angular momentum, and will also be disregarded. (Additional peaks, corresponding to levels of double excitation such as $2s^22p^2 \, 1S$ and $2s2p^3 \, 1P$, would be detectable if there were a substantial amount of quadrupole or triplet excitation.)

The interpretation of the lower peak in Fig. 2 is doubtful. This peak might be associated with a $2s3p$ and or with a $3s2p$ excitation. Since the two peaks and their wings appear rather well separated, the lower peak will be ignored here and we shall endeavor to reproduce only the region between 58 and 62 ev.

In this region, the interpolated continuous background appears to slope down at the rate of 10% per ev. Accordingly we set

$$|\langle \psi_{\text{E}} | T | \psi \rangle|^2 = \left[ |\langle \psi_{\text{E}} | T | \psi \rangle|^2 \right]_{E=E_F} \times \left[ 1 - 0.1(E - E_{\text{F}} - F) \right], \quad (26)$$

with $E$ expressed in ev and $F$ constant. When this expression is substituted in (21), the product of the second term in the brackets of (26) and the second term in the brackets of (21) would yield a negligible contribution. Accordingly we shall try to fit the spectrum of Fig. 2 starting from the assumed natural shape

$$f(E) = 1 - 0.1(E - E_{\text{F}} - F) + \frac{q^2 - 1 + 4q(E - E_{\text{F}} - F)/\Gamma}{1 + 4(E - E_{\text{F}} - F)/\Gamma^2}, \quad (27)$$

This natural shape should be folded, for comparison with Fig. 2, into the line shape which is observed by the spectrometer when it receives monoenergetic electrons. We assume the folded shape of the spectrum to be

$$g(E) = \int_{-\infty}^{\infty} \exp \left[ - \frac{(E - E')^2}{(0.2)^2} \right] f(E') \frac{dE'}{0.2 \sqrt{\pi}}. \quad (28)$$

We have now two parameters at our disposal for the fitting of $g(E)$ to the shape of the main peak in Fig. 2, namely, $q$ and the natural linewidth $\Gamma$. In addition, sliding of the scale of abscissas to best fit determines the resonance position $E_{\text{E}} + F$. The excess transition probability, over the interpolated continuous background, has been determined by planimetry of the curve in Fig. 2 and comparison with (23). The result is

$$\frac{1}{2} \pi (q^2 - 1) \Gamma = 0.15 \text{ ev.} \quad (29)$$

This value is not modified by the folding in (28). The fact that the peak is steeper on the high than on the low-energy side shows that $q$ is negative. The remaining main step of fitting has been performed by trial and
error, assuming alternative values of \( \Gamma \) in (25) and (29) and calculating the integral in (28) numerically.\textsuperscript{15} Figure 3 shows the plots of \( g(E) \) obtained for \( \Gamma = 0.02 \), 0.04, and 0.06 ev, together with experimental points taken from Fig. 2 with their ordinates reduced in the scale of 1:7500 counts/10 sec. The intermediate value

\[
\Gamma = 0.04 \text{ ev},
\]

(30)
gives the best over-all fit. The appropriate value of the resonance energy is

\[
E_p + F(E_p) = 60.1 \text{ ev},
\]

(31)
with an uncertainty lower than 0.1 ev.

No single value of \( \Gamma \) appears to fit the peak equally well on both sides. The peak/trough ratios for the troughs on the two sides of the peak were taken as indices for this purpose and could not be fitted simultaneously. Our analysis of the data thus appears significantly too coarse, even though the instrumental line width is 10 times larger than the natural width.

Equations (29) and (30) yield the value

\[
\frac{1}{2} \pi q^2 = 5.3
\]

(32)
for the ratio of matrix elements (22). This result provides an estimate of the transition probability to the "modified" discrete state \( \phi \) in terms of the probability of transition to the unperturbed continuum \( \psi_R \). The relevant data for the continuum have to be obtained by interpolation from observations in the unperturbed range, far from the resonance on either side of it. Of particular interest are data on the optical oscillator strengths which are obtained from inelastic electron scattering data extrapolated to \( k = 0 \). This extrapolation adds considerable uncertainty and we can only gather, from the extensive data in reference 7, that the density of optical oscillator strength in the unperturbed continuum of He at 60 ev probably lies between 0.01 and 0.02 per ev. On this basis the oscillator strength of the (modified) 2s2p \( 1P \) level should be between 0.002 and 0.004.

The accuracy of these estimates could presumably be increased considerably if new experiments were performed, either by electron scattering or by optical absorption spectroscopy, for the specific purpose of providing input data for theoretical analysis.

Let us compare, anyhow, the estimates obtained here with evidence from other sources. The 2s2p state has often been discussed, but not very conclusively and in connection with transitions to states other than the ground state. Bransden and Dalgarno\textsuperscript{13} calculated the binding energy of the 2s2p \( 1P \) state to be 61.2 ev above the ground state. Considering the approximations involved, the experimental value of 60.1 ev appears to be well within the range of theoretical estimates.\textsuperscript{14} The dispersion shift \( F \) should be not much larger than the linewidth and therefore negligible at this stage.

The linewidth estimate \( \Gamma \sim 0.04 \text{ ev} \), corresponding to a decay rate of \( 6 \times 10^{13} \text{ sec}^{-1} \) for the autoionized state, coincides very nearly with Tai You Wu \textsuperscript{15} value of \( 5 \times 10^{13} \text{ sec}^{-1} \) for the triplet state. Bransden and Dalgarno,\textsuperscript{13} on the other hand, obtained \( 1 \times 10^{15} \text{ sec}^{-1} \) for the singlet itself. The reason of this discrepancy is not understood, but it may be noted that the experimental estimate from Fig. 3 could not be in error by one order of magnitude.

Our estimate of the oscillator strength of the \( 1s^2 \rightarrow 2s2p \) transition is one order of magnitude smaller than current estimates\textsuperscript{16} of the total strength of double excitations or ionizations starting from the ground state. This result is not surprising since the strength of the single excitation \( 1s^2 \rightarrow 1s2p \) is also a small fraction of the total strength of single excitations in He.

Finally, an attempt may be made at interpreting the sign of the parameter \( q \), which is certainly negative because the peak in Fig. 2 slopes sharply on the high-energy side. Two terms contribute to \( q \), as shown on the right-hand side of (20). The second term,

\[
P \frac{\int dE' V_R^* (|\psi_r| T |i\rangle / (E - E')}{\pi V_R^* (|\psi_r| T |i\rangle},
\]

(33)
is certainly positive since \( (|\psi_r| T |i\rangle \) grows larger than \( (|\psi_r| T |i\rangle \) at \( E' < E \), i.e., where \( E - E' > 0 \); it should also be of the order of 1. Therefore the first term must be larger than \( |q| \) in magnitude and negative. This term is

\textsuperscript{14} C. W. Scherr (private communication).
\textsuperscript{15} T. Y. Wu, Phys. Rev. 66, 291 (1944).
\textsuperscript{16} W. F. Miller, thesis, Purdue University, 1956 (unpublished), p. 36.

\textsuperscript{12} I am indebted to J. W. Cooper for this integration.
represented by
\[ \frac{(2s2p \mid T \mid 1s^2)}{\pi(2s2p \mid V \mid 1sEp)(1sEp \mid T \mid 1s^2)}. \] (34)

In attempting an interpretation of the sign of this ratio, it is convenient to make some normalization convention for purpose of analysis even though the ratio is independent of such conventions. We assume all single electron-wave functions to be positive near the nucleus. The matrix element of the Coulomb interaction \( V \) is the sum of a direct and of an exchange term. Because of angular momentum selection rules the two terms arise, respectively, from the scalar and the dipole term of the multipole expansion of \( V \). Presumably, the scalar term is small because of quasi-orthogonality of the 1s and 2s wave functions and negative because the ground state 1s should be more screened than 2s. The dipole term is then presumably dominant and it is positive, like all quasi-hydrogenic dipole moments with our convention. The transition matrix elements would also be positive, except for the projection factor \( (2s \mid 1s) \) in the numerator of (34), which should be negative, though small, as noted above. This last factor, or, more specifically, the ratio of \( (2s \mid 1s) \) to the projection \( (1s \mid 1s) \) in the denominator, would thus determine the sign of (34).

4. ONE DISCRETE STATE AND TWO OR MORE CONTINUA

The treatment of Sec. 2 can be readily applied to the configuration interaction of a discrete state \( \Psi \), with states of different continua \( \Psi_{E'}, \cdots \). These continua may be distinguished by suitable quantum numbers, e.g., by the coupling scheme that obtains when an electron is removed to infinite distance from the residual ion. We shall refer to two continua only, for the sake of simplicity, unless some purpose is served by explicit reference to the case of \( n \) continua.

The eigenvectors to be determined have the form
\[ \Psi_{E'} = a \varphi + \int dE' [b_{E'} \Psi_{E'} + c_{E'} \Psi_{E'}], \] (35)
where \( h \) indicates a set of \( n-1 \) parameters required to specify \( \Psi \), since each value of \( E \) is an \( n \)-fold degenerate eigenvalue. The coefficients \( a, b_{E'}, c_{E'} \), are functions of \( E \) and \( h \). The determination of their eigenvectors is almost trivial, because \( n-1 \) orthogonal continua are readily found, with \( b_{E'}, c_{E'} \), such as to cancel the interaction with \( \varphi \) and, therefore, with \( a = 0 \). The single remaining linearly independent eigenvector is then determined by the method of Sec. 2.

The elements of the energy submatrix to be diagonalized will be indicated, in analogy with (1), by
\[ (\varphi \mid E \mid \varphi) = E_\varphi, \quad (\Psi_{E'} \mid E \mid \Psi_{E'}) = E_{E'}. \] (36a)
\[ (\varphi \mid H \mid \varphi) = V_{E'}, \quad (\Psi_{E'} \mid H \mid \Psi_{E'}) = W_{E'}. \] (36b)

\[ (\Psi_{E'} \mid H \mid \Psi_{E'}) = (X_{E'} \mid H \mid X_{E'}) = E''(E'' - E'), \] (36c)
\[ (X_{E'} \mid H \mid X_{E'}) = 0. \] (36d)

The last of these formulas implies that the matrix has already been diagonalized with respect to the smaller set of states \( \Psi_{E'}, X_{E'} \). This assumption is made in order to focus on the interaction with the discrete state.

The system of equations analogous to (3) is then,
\[ E_\varphi a + \int dE' [V_{E'} b_{E'} + W_{E'} c_{E'}] = E_\varphi a, \] (37a)
\[ V_{E'} a + E' b_{E'} = E b_{E'}, \] (37b)
\[ W_{E'} a + E' c_{E'} = E c_{E'}. \] (37c)

Two orthogonal linear combinations of (37b) and (37c), with coefficients \( (V_{E'}^*, W_{E'}) \) and \( (W_{E'}, -V_{E'}) \), respectively, are
\[ (|V_{E'}|^2 + |W_{E'}|^2) a + E' |V_{E'}| b_{E'} + W_{E'} c_{E'} = 0, \] (38)
\[ E' |W_{E'}| b_{E'} - V_{E'} c_{E'} = 0. \] (39)

Equation (38) contains the same combination of \( b_{E'} \) and \( c_{E'} \) as (37a), and forms with (37a) a system equivalent to (3), whereas (39) is decoupled from a. In solving the system of Eqs. (37a) and (38), for the dependent variables \( a \) and \( [V_{E'}^* b_{E'} + W_{E'}^* c_{E'}] \), Eqs. (7) and ff. of Sec. 2 apply provided \( |V_{E'}|^2 \) is replaced by \( |V_{E'}|^2 + |W_{E'}|^2 \). The solution \( [W_{E'} b_{E'} - V_{E'} c_{E'}] \) is simply \( b(E' - E) \) to a normalization factor. From these solutions, two orthogonal solutions of the system (37) with the dependent variables \( a, b_{E'}, c_{E'} \) are obtained. These solutions are
\[ a_1 = \frac{\sin \Delta}{\pi(|V_{E'}|^2 + |W_{E'}|^2)} \] (40a)
\[ b_{1_{E'}} = \frac{V_{E'}}{(|V_{E'}|^2 + |W_{E'}|^2)^{1/2}} \] (40b)
\[ c_{1_{E'}} = \frac{W_{E'}}{(|V_{E'}|^2 + |W_{E'}|^2)^{1/2}} \] (40c)
where
\[ \Delta = -\arctan \frac{\pi(|V_{E'}|^2 + |W_{E'}|^2)}{E - E_a - G(E)} \] (41)
\[ G(E) = \int dE' \frac{|V_{E'}|^2 + |W_{E'}|^2}{E - E'E} \] (42)
and
\[ a_3 = 0, \]  
\[ b_{2E'} = \frac{W_E^*}{\left( |V_K|^2 + |W_E|^2 \right)^{1/2}} \delta(E - E'), \]  
\[ c_{2E'} = -\frac{V_{K}^*}{\left( |V_K|^2 + |W_E|^2 \right)^{1/2}} \delta(E - E'). \]  

(43a)

(43b)

(43c)

If there are \( n > 2 \) continua, the extension of solution 1 is straightforward. Additional terms being added to \( |V_K|^2 + |W_E|^2 \) wherever this expression appears in (40), (41), and (42), and additional dependent variables \( d_{1E'}, \ldots \), being given by formulas analogous to (40b) and (40c). Solution 2 is extended into a set of \( n - 1 \) orthogonal solutions of the \( n \)-variable homogeneous equation
\[ V_{E'}^* b_{E'} + W_{E'}^* c_{E'} + \cdots = 0. \]

The probability of transitions from an initial state \( i \) to all the stationary states of energy \( E \) is
\[ |\langle \Psi_{1E'} | T | i \rangle|^2 + |\langle \Psi_{2E'} | T | i \rangle|^2 + \cdots. \]  

(44)

The first term of this sum varies as a function of energy in the proximity of the resonance at \( E_\sigma + G \) according to the pattern discussed in Sec. 2. The remaining term or terms are wholly unaffected by the resonance. Therefore, in the presence of two or more continua, one should expect to observe an excitation spectrum of the type shown in Fig. 1 superposed on a smooth background. The spectral intensity should not be observed to drop to zero, even with ideal resolution, unless the states \( \Psi_{2E'}, \ldots \), cannot be excited.

This result accounts at least in part for the fact, noted in Sec. 1, that the intensity of the rare-gas optical absorption spectra never appear to vanish altogether in the range between the two series limits. The interaction of different discrete levels could not be responsible for this result, as will be seen in the next section. The experimental data also show some blurring, presumably due to limited resolving power and no attempt will be made here to account for them in detail. The treatment of the present section is equivalent to the theory of multichannel resonance scattering, as outlined in Appendix C.

5. A NUMBER OF DISCRETE STATES AND ONE CONTINUUM

Consider now the situation where a set of discrete states \( \varphi_1, \ldots, \varphi_n, \ldots \) experiences configuration interaction with a set of states \( \Psi_{E'} \) belonging to one continuous spectrum. The energy submatrix which we want to diagonalize is
\[ \left( \begin{array}{c} \varphi_n \mid H \mid \varphi_n \end{array} \right) = E_n \delta_{mn}, \]  
\[ \left( \begin{array}{c} \Psi_{E'} \mid H \mid \varphi_n \end{array} \right) = V_{E'n} \delta_{mn}, \]  
\[ \left( \begin{array}{c} \varphi_n \mid H \mid \Psi_{E'} \end{array} \right) = E' \delta(E'' - E'). \]  

(45a)

(45b)

(45c)

Equation (45a) implies that the smaller submatrix corresponding to the discrete states \( \varphi_n \) alone has been diagonalized in a previous operation.

The eigenvectors we seek have now the form
\[ \Psi_E = \sum_n a_n \varphi_n + \int dE' b_E \Psi_{E'}, \]  
and there must be one of them for each value of \( E \) in the energy range we are considering. The coefficients \( a_n \) and \( b_E \) are solutions of the system of equations
\[ E_n a_n + \int dE' V_{E'n} b_{E'} = E a_n, \]  
\[ \sum_n V_{E'n} a_n + E' b_{E'} = E b_{E'}. \]  

(47a)

(47b)

Equation (47b) is solved formally, as (3b), by
\[ b_{E'} = \left[ \frac{1}{E - E'} + z(E) \delta(E - E') \right] \sum_n V_{E'n} a_n. \]  

(48)

Substitution of (48) in (47a) yields the generalization of (7), namely,
\[ E_n a_n + \sum_m F_{nm} a_m + z(E) V_{E'n} \sum_m V_{E'm} a_m = E a_n. \]  

(49)

Here
\[ F_{nm}(E) = P \int dE' \frac{V_{E'n} V_{E'm}}{E - E'} \]  

(50)

is now a matrix which represents the second-order interaction among the discrete states arising from their coupling with intermediate continuum configurations. The diagonal elements of this matrix represent the first approximation line shifts caused by this interaction.

Equation (49) represents a system of homogeneous equations and therefore leads to an actual eigenvalue problem. This problem can be subdivided into two stages, the first of which concerns only the discrete states, whereas the second, which deals with the main discrete-continuum interaction, has a rather simple solution.

In the first stage we diagonalize the matrix \( E_n \delta_{mn} + F_{nm} \), that is, we consider the effect of the interaction matrix \( F_{mn} \) upon the discrete states. This effect perturbs the states \( \varphi_n \) and their energies \( E_n \) and replaces them with new states
\[ \varphi'_n = \sum_n a_n \varphi_{n'} \]  
and with energies \( E_n' \) which are obtained by solving the system
\[ E_n a_n' + \sum_m F_{nm} a_{m'} = A_{n'} E_{m'}. \]  

(51)

(52)

The replacement of the energies \( E_n \) with the \( E_n' \) corresponds to the replacement of \( E_n + P \) in Sec. 2. It may be anticipated that the matrix \( F_{nm} \) will often constitute a small perturbation, so that (52) is solved adequately by perturbation theory. Since the matrix \( F_{nm} \) depends on \( E_n \), even though slowly, the solutions of (52) will also be functions of \( E_n \).
Assuming that the coefficients \( A_n \), and energies \( E_n \) have been obtained, we replace the coefficients \( a_n \) in (45) by new coefficients \( a_n \), setting

\[
a_n = \sum_r A_{ns} \tilde{a}_r
\]  

(53)

The matrix \( F_{nm} \) can now be eliminated from (49) by means of (52), and (49) becomes

\[
\sum_r A_{ns} E_n \tilde{a}_r + \sum_r \sum_m V_{nR} A_{ns} \tilde{a}_r = E \sum_r A_{ns} \tilde{a}_r.
\]  

(54)

Multiplication by \((A^{-1})_{ns}\), summation over \( n \) and application of the orthonormality \( \sum_s (A^{-1})_{nm} A_{ns} = \delta_{mr} \) yields finally

\[
E \tilde{a}_r + \sum_r \sum_m V_{nR} \delta_{mr} \tilde{a}_r = E \tilde{a}_r,
\]  

(55)

where

\[
V_{nR} = \sum_n V_{nR} A_{ns}.
\]  

(56)

The second step of our problem consists of solving the system (55). This system has a matrix of the form \( M_{ns} = (\sum V_{nR}) (\sum V_{nR}^*) \) and thus belongs to the class whose solutions are expressed in terms of a polarizability function. Multiplication of (55) by \( V_{nR}^*/(E - E_n) \) and summation over \( n \) shows that (55) is subject to the consistency requirement

\[
\sum_r \left[ \frac{|V_{nR}|^2}{(E - E_n)^2} \right] = 1,
\]  

(57)

which plays the role of a secular equation and determines the eigenvalue \( z(E) \). Under this condition, (55) is solved by

\[
\tilde{a}_r = \frac{z(E)}{E - E_r} \sum_r V_{nR} \tilde{a}_r,
\]  

(58)

in terms of the expression

\[
\sum_r V_{nR} \tilde{a}_r = \sum_n V_{nR} a_n,
\]  

(59)

which plays the role of a normalization constant. We shall represent \( z \) in terms of a phase shift \( \Delta \), as in (6) and (15), and rewrite (57) in the form

\[
\pi z = - \tan \Delta = \sum_r \frac{\pi |V_{nR}|^2}{E - E_n} = - \sum_r \tan \Delta_r.
\]  

(60)

Here \( \Delta_r \) represents the phase shift that would be contributed by the state \( \varphi_r \), if alone.

The remaining determination of the normalization constant (59) is analogous to the determination of \( a \) in Sec. 2, Eqs. (9) ff. We write

\[
\langle \Psi_E | \varphi \rangle = \sum \tilde{a}_n^* \langle \tilde{E} | a_n \rangle
\]

+ \int dE' b_{nR}^* \langle \tilde{E} | b_{nR} \rangle = \delta (E - E'),
\]  

(61)

substitute \( b_{nR} \) from (48) and utilize (11). The equation analogous to (12) is then,

\[
\sum_n V_{nR} a_n(E) |\frac{\pi^2 + \pi^2(E)}{z(E)} \hat{a}(E - E) + \sum_m a_m^* \hat{a}(E) | \\
\times \{1 + (E - E)^{-1} |F_{nm}(E) - F_{nm}(E)\hat{a}(E) + \hat{a}(E) V_{nR} V_{mR} \hat{a}(E) \} a_m \hat{a}(E) = \delta (E - E).
\]  

(62)

The \( \sum_m \) vanishes owing to (49), so that the normalization is given by

\[
|\sum_n V_{nR} a_n(E) |^2 = \frac{1}{\pi^2 + \pi^2(E)} = - \sin^2 \Delta.
\]  

(63)

The final, normalized solution of our problem may then be given in the form

\[
\tilde{a}_r = \cos \Delta \tan \Delta_r / \pi V_{nR},
\]  

(64a)

\[
b_{nR} = \cos \Delta \left[ \sum \frac{V_{nR}}{E - E'} \tan \Delta_r \right] \delta (E - E'),
\]  

(64b)

which combines (48), (58), (60), and (63). Equation (64) reduces to (14) when there is a single state \( \varphi_r \).

The transition matrix element for excitation of the energy eigenstate \( \Psi_E \) is given in analogy with (16) by

\[
\langle \Psi_E | T | i \rangle = \cos \Delta \left[ \sum \frac{\tan \Delta_r}{\pi V_{nR}} \langle \varphi_r | T | i \rangle \right]
\]

+ \frac{\tan \Delta_r}{\pi V_{nR}} \int dE' \frac{V_{nR}^* (\Psi_E | T | i)}{E - E'}

= \cos \Delta \left[ \sum \frac{\tan \Delta_r}{\pi V_{nR}} \langle \Phi_r | T | i \rangle - \langle \Psi_E | T | i \rangle \right]

= \langle \Psi_E | T | i \rangle \cos \Delta \left[ \sum \tan \Delta_r - 1 \right],
\]  

(65)

where

\[
\Phi_r = \varphi_r + \int dE' \frac{\Psi_E^* V_{nR}^*}{E - E'},
\]  

(66)

\[
q_r = \frac{\langle \Phi_r | T | i \rangle}{\pi V_{nR} (\Psi_E | T | i)},
\]  

(67)

in analogy with (17) and (18). Notice that \( \cos \Delta \tan \Delta_r \) has the same role here as \( \sin \Delta \) has in Sec. 2, in that \( \cos \Delta \tan \Delta_r \) remains finite at the resonance point \( \Delta_r = \frac{\pi}{2} \) (i.e., \( E = E_r \)) because \( \cos \Delta \) vanishes there. Notice also that \( \sum \tan \Delta_r = \sum \tan \Delta_r \frac{|V_{nR}|^2}{(E - E_n)^2} \) swings all the way from \( - \infty \) to \( \infty \) in each interval between successive resonances and thus causes a rapid variation of \( \langle \Psi_E | T | i \rangle \). In particular \( \langle \Psi_E | T | i \rangle \) vanishes once in each of these successive intervals.

The behavior of the resonances corresponding to a Rydberg series of autoionized states is also of interest. The numerical parameter \( q_r \) should remain nearly constant throughout the upper part of the series even
though the numerator and the denominator of its expression (67) become rapidly smaller as the series limit is approached. This is because $\langle \Phi_s | T | i \rangle$ and $V_{s=1}$ decrease, in the main, in proportion to the same factor, namely, the normalization constant of the wave function $\varphi_s(r)$ near the surface of the atom. On the other hand the resonance width $2\pi V_{s=1}$ should decrease rapidly, in proportion to the spacing between resonances. Thus the intensity alternations of the excitation spectrum should remain uniformly sharp throughout the series, in proportion to the line spacings, as they do in ordinary optical spectra, except for the broadening influence of collisions or other external perturbations.

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**APPENDIX A**

The fraction $1/(\bar{E} - E)(E - E')$ in the integral (10) has simple poles at $E' = \bar{E}$ and $E' = E$ when $\bar{E} \neq E$, it being understood that the principal part is to be taken in integrations over these poles, but has a double pole when $\bar{E} = E$. The usual analysis of this fraction into partial fractions implies that $\bar{E} \neq E$ and leaves out the double-pole singularity.

This singularity may be taken into account by analysis of the Fourier representation of $1/(\bar{E} - E)(E - E')$:

$$
\begin{align*}
(\bar{E} - E)^{-1} &= -\pi i \int_{-\infty}^{\infty} dk \left( k / | k | \right) \exp[2\pi ik(\bar{E} - E')], \\
(\bar{E} - E')^{-1} &= \pi i \int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} dk' \left( k/k' \right) \\
& \quad \times \exp\{2\pi ik(\bar{E} - E') + k'(E - E')\}. 
\end{align*}
$$

(A1)

(A2)

We replace the variables $k$ and $k'$ by

$$
u = k + k', \quad v = \frac{1}{2}(k - k'),$$

and notice that

$$
\frac{kk'}{|kk'|} = \frac{u^2 - 4v^2}{|u^2 - 4v^2|} = -1 + 2St(u^2 - 4v^2),
$$

(A4)

where $St$ is the unit step function. Equation (A2) be-

Comparison with (A1) yields finally (11).

**APPENDIX B**

**Application to the Perturbation of a Rydberg Series**

The energy levels of a Rydberg series of an atom are represented by

$$
E_n = -I_H/(n - \sigma)^2,
$$

(B1)

where $I_H$ is the ionization potential of the H atom ($I_H = 1$ ry) and $\sigma$ is the quantum defect, a numerical constant or at most a very slowly varying function of $E_n$. This formula implies that the levels are determined by two quite separate factors: (a) the Coulomb field that acts on an optical electron well outside the rest of the atom (the "core") at distances, say, $\geq 20$ Bohr radii from the nucleus; (b) the mechanical factors within the core whose influence is entirely represented by the quantum defect $\sigma$. It is known\(^{18}\) that $\sigma$ is related to the relative phase of oscillation in the region outside the core of the actual wave function with energy $E_n$ and of a Coulomb function with same energy. Comparison of the radial logarithmic derivative of these two wave functions, at any radius outside the core, yields their phase difference $\delta$ which is equal to $\pi \sigma$. If the Coulomb field were altered outside the core, the level formula (B1) would be changed, but the influence of the core would still be represented in the new formula by the quantum defect $\sigma$, or by an equivalent parameter. Suppose, for example, that the potential ceased to rise according to the $-e^2/r$ law at $r = 20$ Bohr radii, and remained fixed at $-e^2/20r$ for $r \geq 20$. All discrete stationary states with


\( (n-\sigma)^2 > 20 \) would then be replaced by a continuum, but the core would influence the scattering of a free electron in this continuum just by a phase-shift contribution \( \delta = \pi \sigma \).

Configuration interaction may be regarded as a core effect, even though it takes place in the outer region of the core. Accordingly the perturbation exerts on the levels of a Rydberg series should be represented by an appropriate change of \( \sigma \) in (B1) to the same degree of approximation as is involved in the justification of (B1) itself. Moreover, since \( \sigma \) is determined, for each energy range of the optical electron, independently of the field outside the core, i.e., independently of whether the electron is bound or free, the results of Sec. 2 are directly applicable to the perturbation of a discrete spectrum. The effect on a continuum caused by interaction with a single discrete state \( \varphi \), with energy \( E_{\varphi} \), is represented according to (5) by adding to the phase shift \( \delta \) a further shift \( \Delta \) given by (6) and (15). Since \( \delta/\pi \)

\[
\Delta = \arccot \frac{E_n - E_{\varphi} - F(E_n)}{\pi |V_{en}|^2},
\]

(B2)

Notice that, when \( |E_n - E_{\varphi} - F| > \pi |V_{en}|^2 \), (B2) reduces to the perturbation formula of Langer,\(^9\) as was to be expected.

The bypass through the treatment of a continuum is not necessary. One may treat a Rydberg series of unperturbed states \( \varphi_n \) directly, along the lines of Sec. 2, replacing (1) by

\[
(\varphi|H|\varphi) = E_{\varphi}, \quad (\varphi_n|H|\varphi) = V_n,
\]

(2) by

\[
\varphi_n = a_n \varphi + \sum_{\nu} b_n \varphi_\nu, \quad V_n = E_n a_n
\]

and (3) by

\[
E_n a_n + \sum \nu V_n a_\nu a_n = E_n b_n
\]

(B5a)

\[
V_n a_n + E_n b_n = E_n b_n
\]

(B5b)

The solution of (B5b), which replaces (4), is

\[
b_n = \frac{[V_n/(E_n - E_n)]}{a}
\]

and one does not have to worry here about \( E_n \) coinciding with \( E_{\varphi} \). Substitution of (B6) into (B5a) yields the eigenvalue equation of reference 2

\[
E_\varphi + \sum \frac{|V_n|^2}{E_n - E_n} = E_n
\]

(B7)

The attention centers now on the sum in (B7). This sum varies from \( \infty \) to \( -\infty \) as \( E_n \) traverses each interval between two successive unperturbed levels \( E_n \) and \( E_{n+1} \). One root of (B7), i.e., one perturbed level, lies therefore in each such interval. In reference 2 it was assumed for simplicity that \( |V_n|^2 \) is independent of \( n \) and that the \( E_n \) are uniformly spaced. This assumption permits one to carry out the summation in closed form, but is probably needlessly restrictive. The essential point is that \( |V_n|^2 \) depends on \( n \) primarily through a normalization factor, proportional to the average \( \tau_n \) of the two level spacings, above and below \( E_n \). We can thus set

\[
|V_n|^2 = |V_{En}|^2 \tau_n
\]

(B8)

where \( |V_{En}|^2 \) is a slowly varying function of \( E_n \). This function is determined entirely by the configuration interaction within the core, whereas \( \tau_n \) is determined by details of the field at large distance from the core. Under these circumstances, the \( \sum_n |V_n|^2/(E_n - E_n) \) may be resolved into one contribution that depends only on the slow variation of \( |V_{En}|^2 \) and one that depends on the local value \( |V_{En}|^2 \). The former one can be evaluated by replacing the sum by an integration, the integral being just the quantity \( F(E_n) \) given by (8), so that we have

\[
\sum \frac{|V_n|^2}{E_n - E_n} = F(E_n) + |V_{En}|^2 \sum \frac{\tau_n}{E_n - E_n}
\]

(B9)

The residual sum on the right of (B9) receives a significant contribution only from terms with \( E_n - E_n \), since the contributions from other terms cancel out. Furthermore, if the \( E_n \) are given by (B1) and we deal with \( (n-\sigma) > 1 \), the spacings

\[
\tau_n = 2I_H(n-\sigma)[(n-\sigma)^2 - 1]^{1/2} = 2(E_n)^{1/2}/I_H^{1/2}
\]

vary slowly from level to level. The \( \sum \tau_n/(E_n - E_n) \) has therefore approximately the same value as though \( \tau_n \) had the constant value \( \tau_m \) pertaining to an unperturbed level \( E_m \) in the vicinity of \( E_n \), namely \( \pi \cot \pi (E_n - E_m)/\tau_m \).\(^1\) With this assumption the eigenvalue equation (B7), analogous to (7), becomes

\[
E_\varphi + F(E_n) + \pi |V_{En}|^2 \cot \left( \frac{E_n - E_m}{\tau_m} \right) = E_n
\]

that is

\[
\cot \left( \frac{E_n - E_m}{\tau_m} \right) = \frac{E_n - E_{\varphi} - F(E_n)}{\pi |V_{En}|^2}
\]

for \( E_n \sim E_m \),

(B11)

(B11')

or

\[
\frac{E_n - E_m}{\tau_m} = -\Delta(E_n) = \arccot \left( \frac{E_n - E_{\varphi} - F}{\pi |V_{En}|^2} \right)
\]

(B11'')

This equation is readily solved graphically or numerically. It states that, if \( \Delta \) be regarded as a function of \( E_n \) as in (B2) and (15), an eigenvalue lies at a fraction \( -\Delta/\pi \) of the interval between each unperturbed level \( E_n \) and the next unperturbed level.

The probability of excitation of the levels of a Rydberg series perturbed by configuration interaction is given, in substance, by the treatment of Sec. 2. The energies \( E'\)
and \( E \) have to be replaced by \( E_a \) and \( E_c \) in the various formulas, and the squared matrix elements \( | \langle \Psi \rangle |^2 \) and \( | \langle \Psi | T | i \rangle |^2 \), which represent probability distributions differential in the energy spectrum, have to be multiplied by the value of the line spacing \( \tau \) appropriate to \( E_a \) or \( E_c \) to yield the probability of transition to a discrete state.

**Appendix C**

**Connection with the Theory of Multichannel Resonance Scattering**

Suppose that the continuum states \( \psi_{1c}, \chi_{1c}, \cdots \) considered in Sec. 4 are states in which particles differing in any respect, indicated respectively by \( b, c, \cdots \), have sufficient energy to break away from the rest of the system. These alternative break-ups are often called "channels." We assume, for simplicity, that the particles are spinless and call their orbital quantum numbers \( l_b, l_c, \cdots \). For large values of the distance \( r \) between the separated particle and the rest of the system, the wave functions \( \psi_{1c}(r_b), \chi_{1c}(r_c), \cdots \) have the asymptotic form

\[
\psi_{1c}(r) \sim k_{1c}^{-1}(E) \sin[k_{1c}(E)r_b + \delta_b + \frac{1}{2} \pi l_b] \chi_{1c}(r) \sim k_{1c}^{-1}(E) \sin[k_{1c}(E)r_c + \delta_c - \frac{1}{2} \pi l_c]
\]

where the factors of \( k^{-1} \) correspond to normalization per unit energy and where all factors not relevant to our purpose have been omitted.

Consider now a scattering process, in which the system is formed by combining an incident particle \( b \) with the "rest" and then the system breaks up releasing alternatively either the same particle \( b \) or another particle \( c, \cdots \). This process is represented by an eigenvector \( \Psi_{bc}(b \rightarrow b, c \cdots) \), with the form (35). The wave function representation of \( \Psi_{bc}(b \rightarrow b, c \cdots) \) consists asymptotically, for large values of \( r_b, r_c, \cdots \), of the sum of one incoming wave, proportional to \( \exp(ik_sr_b) \), and of two, or more, outgoing waves, proportional to \( \exp(ik_sr_b) \), \( \exp(ik_sr_c) \), \cdots. To achieve this form, we may represent the eigenvector as a superposition of the eigenvectors \( \Psi_{kk} \) of Sec. 4,

\[
\Psi_{bc}(b \rightarrow b, c \cdots) = \sum_k A_k \Psi_{kk}
\]

and choose the coefficients \( A_k \) suitably.

Entering in (35) the coefficients (40) or (43) and the wave functions (C1) yields—as explained above Eq. (5)—the asymptotic representations

\[
\psi_{bc}(r) \sim \left[ \frac{1}{V_{bc}^* + |W_{bc}|^2} \right]^{1/2} \chi_{bc}(r) \sim \left[ \frac{1}{V_{bc}^* + |W_{bc}|^2} \right]^{1/2}
\]

The term \( \alpha \) of (35) does not contribute to the asymptotic representation because it corresponds to a bound state. We are limiting ourselves, here and in the following, to the explicit treatment of a two-channel system, with free particles \( b \) and \( c \), so that \( k = 1, 2 \) in (C2).

The asymptotic expression of \( \Psi_{bc}(b \rightarrow b, c) \), obtained by substituting (C3) in (C2) includes a term proportional to

\[
\text{[A}_1 \text{W}_b \exp(-i\Delta) + \text{A}_2 \text{W}_b^*]e^{-ik_sr},
\]

which represents an incoming wave in channel \( c \) contrary to our specifications. Since all other terms comply with the specifications for \( \Psi_{bc}(b \rightarrow b, c) \), this eigenvector is identified by choosing \( A_1 \) and \( A_2 \) so that (C4) vanishes, namely, by setting

\[
A_1 = \frac{V_{bc}^*}{|V_{bc}|^2 + |W_{bc}|^2}, \quad A_2 = -\frac{W_{bc}}{|V_{bc}|^2 + |W_{bc}|^2}
\]

This choice yields

\[
\Psi_{bc}(b \rightarrow b, c) = \frac{1}{2ik_b(E)} \left[ \exp(-i[k_b(E)\delta_b + \Delta - \frac{1}{2} \pi l_b]) \chi_{bc}(r) \right] Y_{l_b}(\theta_b, \phi_b)
\]

\[
- \frac{|V_b|^2 \exp(i\Delta) + |W_b|^2 \exp(-i\Delta)}{|V_b|^2 + |W_b|^2}
\]

\[
\frac{\sin\Delta}{k_b^j(E)} \frac{V_{bc}^* W_b}{|V_b|^2 + |W_b|^2} \chi_{bc}(r) Y_{l_b}(\theta_b, \phi_b)
\]

\[
- \frac{\exp(-i[k_b(E)\delta_b + \Delta - \frac{1}{2} \pi l_b])}{k_b^j(E)} \frac{1}{2i} \left[ \frac{|V_b|^2 \exp(2i\Delta) + |W_b|^2}{|V_b|^2 + |W_b|^2} - 1 \right] \left[ \exp(i[k_b(E)\delta_b + \frac{1}{2} \pi l_b]) \right] Y_{l_b}(\theta_b, \phi_b)
\]

\[
- \frac{1}{k_b^j(E)} \frac{V_{bc}^* W_b}{|V_b|^2 + |W_b|^2} \chi_{bc}(r) \left[ \frac{\sin\Delta}{|V_b|^2 + |W_b|^2} \exp[i(k_b(E)\delta_b + \frac{1}{2} \pi l_b)] Y_{l_b}(\theta_b, \phi_b) \right].
\]
The term \( \sin[k_s(E)r_b - \frac{1}{2}\pi I_s] \) represents a spherical-wave component of a plane, unscattered wave. The remaining terms of the last expression in (C6) represent outgoing scattered waves. Their coefficients are, therefore, elements of the scattering matrix to within suitable normalization coefficients. The cross section for the scattering or reaction of \( b \) particles (through their state of angular momentum \( I_b \)) are then obtained by a well-known procedure and are

\[
\sigma(b \rightarrow b) = \frac{\pi(2I_b+1)}{k^2(E)} \left| e^{i\Delta} \frac{|V_E|^2 \exp(2i\Delta) + |W_E|^2}{|V_E|^2 + |W_E|^2} - 1 \right|^2
\]

\[= \frac{\pi(2I_b+1)}{k^2(E)} \left| i\pi |V_E|^2 \frac{E - E_s - G(E) + i\pi(|V_E|^2 + |W_E|^2)}{E - E_s - G(E) + i\pi(|V_E|^2 + |W_E|^2)} + e^{-i\Delta} - 1 \right|^2 \tag{C7}
\]

\[
\sigma(b \rightarrow c) = -\frac{\pi(2I_b+1)}{k^2(E)} \left| \frac{2iV_E^*W_E}{|V_E|^2 + |W_E|^2} \sin \Delta \right|^2
\]

\[= \frac{\pi(2I_b+1)}{k^2(E)} \frac{2\pi |V_E|^2 2\pi |W_E|^2}{[E - E_s - G(E)]^2 + 2\pi^2 (|V_E|^2 + |W_E|^2)^2} \tag{C8}
\]

where \( \Delta \) has been taken from (37). The last form of (C7) represents the interference of resonance and potential scattering amplitudes and reduces to the Breit-Wigner formula in the absence of potential scattering, i.e., for \( \delta = 0 \). The reaction cross section (C8) has the Breit-Wigner form. Equations [\( \text{(C7)} \) and \( \text{(C8)} \)] are equivalent, respectively, to (VIII.7, 20 and 19) of Blatt and Weisskopf, except that the resonance shift \( G(E) \) is included explicitly in the present calculation.

The derivation of a multi-level scattering formula by the method of this Appendix would require the prior development of a multicontinuum multi-level treatment which combines the features of Sec. 4 and 5.