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ON THE THEORY OF COLLISIONS OF ATOMS IN RYDBERG STATES WITH NEUTRAL PARTICLES

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Résumé. — On rediscute de façon unifiée la théorie des transitions par collisions entre états de Rydberg et de l'élargissement et du déplacement des raies optiques impliquant un de ces états. On montre que le potentiel de Fermi peut être généralisé en utilisant la matrice de réaction de la collision d'un électron libre avec le perturbateur, de façon à obtenir les courbes de potentiel adiabatiques de la quasi-molécule sous une forme analogue à celle de la théorie du défaut quantique. Un critère d'adiabaticité est proposé pour distinguer entre les collisions nettement inélastiques et les collisions quasi élastiques. L'approximation de la longueur de diffusion et des fonctions d'onde JWKB sont utilisées pour obtenir une expression approchée des sections efficaces des collisions quasi élastiques ($\Delta n = 0$), pour des valeurs de *n* intermédiaires ($n \sim 15$ -20). On montre aussi qu'il est possible d'expliquer le comportement observé de l'élargissement et du déplacement des raies optiques pour les gaz rares et les alcalins pour des valeurs de *n* intermédiaires ou élevées.

Abstract. — The theory of transitions between Rydberg states induced by thermal collisions, and of the broadening and shift of optical lines involving such states, is reconsidered. It is shown that the Fermi potential can be generalized in terms of the reaction matrix of the collision between a free electron and the neutral perturber. Adiabatic potential curves of the quasi-molecule are thus obtained in analogy with quantum defect theory. An adiabaticity criterion is proposed to distinguish between inelastic and quasi-elastic collisions. The scattering length approximation and JWKB wave-functions are used to obtain an approximate expression for cross-sections of quasi-elastic collisions ($\Delta n = 0$) for intermediate *n* values ($n \sim 15-20$). It is also shown that it is possible to explain the observed behaviour of the broadening and the shift of optical lines by noble gases and alkalis for intermediate or high *n* values.

1. Introduction. — In Rydberg states the valence electron is very loosely bound to the remaining atomic core. Accordingly, the interaction of an atom in a Rydberg state with a particle B is dominated by the properties of the interaction of e^- with B. As a result, charged particles, and especially electrons, are generally much more efficient than neutral ones in perturbing Rydberg states, as in ionization, transitions between adjacent energy levels, line broadening, etc. The theory of collisions of atoms in Rydberg states with charged particles has been studied in great detail, using in particular the semi-classical methods developed by Percival and his collaborators (see e.g. [1]).

On the contrary, when B is *neutral*, the range of the interaction e^- -B is very short. Consequently, the perturbation induced by B in the electron wave function is relatively weak when the effective principal quantum number n^* is very large. Accordingly, when $n^* > 10$ cross-sections for collisions with neu-

tral particles are generally much smaller than the geometrical cross-section $n^{*4} \pi a_0^2$ even for quasielastic processes. On the other hand, because of their low velocity, thermal neutral particles are very inefficient in inducing transitions with a change of n^* for $n^* < 10$. Thus, although some cross-sections can reach very large values — almost of the order of $n^{*4} \pi a_0^2$ for $n^* < 10$ — for quasi-elastic processes such as line broadening and resonant *l*-mixing, Rydberg states as a whole are not so sensitive to collisions with neutrals as may be expected.

The theory of collisions of Rydberg states with neutrals has been periodically revisited during the last forty years, following the development of experimental studies. Measures of shift and broadening of optical lines have been performed continually during this period [2-6]; reviews of early work can be found in different places (see e.g. [7-9]). The development of tunable lasers will certainly produce a strong revival of these line broadening studies. The corresponding theory, first formulated by Fermi [10] and slightly refined by following workers [11-16], is very successful in directly relating the shift of very high Rydberg

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levels $(n^* > 20)$ to the scattering length of e^- -B collisions, especially when B is a noble gas atom (see also [17-18]). The corresponding line broadening is also rather well explained. However, the situation is much less satisfactory in the case where the perturber B is an alkali, despite a certain amount of effort [19]. Furthermore, there does not yet exist a satisfactory theory for any perturbers in the case of intermediate n^* values ($5 < n^* < 15$).

Transitions between different Rydberg levels induced by collisions with neutrals have to be considered in the determination of the statistical equilibrium in plasmas. They can play an important role in the case of low-lying states in a weakly-ionized medium, but they are generally negligible compared to collisions with charged particles. This is particularly true for the very high Rydberg states studied in astrophysics through observation of recombination lines. The corresponding theory has been developed for rather large n^* values mainly using semi-classical methods, in particular by Flannery (see [20] and references therein). The problem is more difficult [21] for small n^* values, where only certain special cases have been treated for which the interatomic potential has been determined [22]. Here we shall not consider at all the related problem of ionization by neutrals and the accompanying processes (association, attachment, etc. (see e.g. [23, 24] and references therein))

The use of tunable lasers now allows more selective experiments to be performed and direct measurements of well-defined transition rates to be made. The magnitude of the cross-sections depends strongly on the energy of the transition : they are several orders of magnitude larger for *l*-mixing transitions between nearly-degenerated levels [25] than for transitions involving s or p levels [26, 27]. Simple theories of nearly-degenerated *l*-mixing transitions have appeared recently [28, 29]. They describe the qualitative behaviour of the cross-sections well, but they need to be refined and extended to inelastic collisions.

The purpose of the present work is first to try to relate the different previous studies, and then to discuss their limits of validity and a number of possible improvements :

i) extensions of the Fermi potential to derive an interatomic potential in a close and explicit form, using the exact behaviour of e^- scattering by B, and directly relating the position of the adiabatic energy levels to the electronic scattering phase shifts, in analogy with quantum defect theory [30] (section 2).

ii) Discussion of collision-induced transition probabilities in terms of the adiabaticity criterion, and a rough derivation of the qualitative behaviour of *l*-mixing transitions (section 3).

iii) Discussion of some aspects of line broadening and shift in the case of perturbation by alkalis, and for intermediate values of n in the case of perturbation by noble gases (section 4). 2. The pseudo-potential. — 2.1 INTRODUCTION. — As already stated, all the treatments of the interaction of a very excited atom A* with a neutral perturber B are based on the fact that the dimensions of A* are much larger than those of B. The problem is thus reduced to the highly-localized interaction of B with the excited electron, which is very loosely bound to A⁺, and finally to the properties of e^- -B collisions (¹).

The situation is particularly simple when B is located in the region of classical motion of the electron, and when the wave function $\Psi(\mathbf{r})$ of the electron is well represented by the semi-classical (JWKB) approximation. In the neighbourhood of B, $\Psi(\mathbf{r})$ is then a superposition of plane waves of the same energy (see eqs. (2.25), (2.35) and (2.38)), and one has essentially to project the corresponding scattered wave onto the wave functions of the different eigen-states of A.

In the case of very large values of n, one need consider only the region of classical motion and assume that the interaction is zero outside. However it is possible, using a certain method, to extend the same treatment to the external region where $\Psi(\mathbf{r})$ exponentially decreases, or even to any position of B if one describes the e^- -B scattering by the approximation of the scattering length L. In this case, as discussed again below (eq. (2.43)), the potential of a non-degenerate level is just [12, 31-33] (²)

$$V(\mathbf{R}) = 2 \pi L | \Psi(\mathbf{R}) |^2. \qquad (2.1)$$

As the wave function $\Psi(\mathbf{r})$ is distributed over a very large volume, the very localized interaction with B does not perturb it very much. In the present section, we intend to show that eq. (2.1) may be very simply generalized in terms of the reaction *R*-matrix of e^{-} B scattering. We thus obtain an expression for the pseudo-potential $V(\mathbf{R})$ describing the modification of the eigen-states and eigen-energies of A due to the presence of B at the point **R**.

2.2 PSEUDO POTENTIAL AND R MATRIX. — Let us denote by $V_{\rm A}(\mathbf{r})$ the (essentially coulombic) interaction potential of the electron with the core A⁺. Assuming the perturber B is at rest at point **R**, we will suppose, in order to simplify the discussion, that the e⁻-B interaction can be represented by a potential $V_{\rm B}(\mathbf{r} - \mathbf{R})$ (the effects of the interaction of A⁺ with B will be discussed in section 2.6).

$$t_0 = a_0/v_0 = 2.419 \times 10^{-17} \,\mathrm{s}$$

transition rate $K_0 = a_0^2 v_0 = 6.126 \times 10^{-9} \text{ cm}^3/\text{s}.$

 $^(^{1})$ This treatment presents some analogies with the impulse approximation (see e.g. [35] p. 683). However, we do not suppose that the kinetic energy of B is much larger than the electron binding energy.

^{(&}lt;sup>2</sup>) Atomic units will be used throughout : $e = m = \hbar = a_0 = 1$. The values of some other units are : energy (hartree) $E_0 = 27.21$ eV, velocity $v_0 = \alpha c = 2.188 \times 10^8$ cm/s, time

Let \mathcal{K} be the hamiltonian of the electron and G its resolvent [35]

$$\mathcal{K} = T_{e} + V_{A} + V_{B} = \mathcal{H}_{A} + V_{B} \qquad (2.2)$$

$$G = \frac{1}{E - \mathcal{K}}.$$
 (2.3)

One looks for an approximate expression of G in terms of the resolvent of \mathcal{K}_A :

$$G_{\mathbf{A}} = \frac{1}{E - \mathcal{K}_{\mathbf{A}}}.$$
 (2.4)

One has formally :

$$G = G_{A} + G_{A} V_{B} G_{A} + G_{A} V_{B} G_{A} V_{B} G_{A} + \cdots$$
(2.5)

However, although its resultant effect on $\Psi(\mathbf{r})$ is relatively small, the localized interaction of B with the electron, represented by $V_{\rm B}$, is generally strong and cannot be represented by a perturbation expansion (Born approximation). Therefore we will look for an expansion of G not in terms of the powers of $V_{\rm B}$, but in terms of the reaction matrix R (³) defined for the collision of an electron of (kinetic) energy

$$E_{\mathbf{R}} = E - V_{\mathbf{A}}(\mathbf{R})$$

R satisfies the equation (see e.g. ref. [35] eq. (362b)).

$$R(E_{\mathbf{R}}) = V_{\mathbf{B}} + V_{\mathbf{B}} G_{\mathbf{A}\mathbf{R}}^{0} R(E_{\mathbf{R}}) \qquad (2.6)$$

where

$$G_{AR}^{0} = \frac{\Im}{E - \mathscr{H}_{AR}} = \frac{\Im}{E_{R} - T_{e}} \qquad (2.7)$$

and f denotes the Cauchy principal value.

It is shown in appendix A that G satisfies the expansion

$$G = G_{\mathbf{A}} + G_{\mathbf{A}} R \sum_{n=0}^{\infty} \{ (G_{\mathbf{A}} - G_{\mathbf{AR}}^{0}) R \}^{n} G_{\mathbf{A}}.$$
 (2.8)

We are interested in determining the perturbation of a set α of degenerate or quasi-degenerate states corresponding to n_{α} ($n_{\alpha} \ge 1$). In the products of eq. (2.8) the closure relation introduces intermediate states n_i . For n_i values far enough from, n_{α} ($|n_i - n_{\alpha}| \ge 1$), one may replace the distribution of discrete levels *i* by a distribution continuous in E_i and symmetric with respect to E_{α} . In this energy range, there is consequently cancellation between G_A and G_{AR}^0 in the different terms of the r.h.s. of eq. (2.8). This is particularly clear for the continuum states of A ($E_i > 0$). For very small energies ($E_i \ll E_{\alpha}$), it is seen that the compensation holds only if $n_i \ge 1$, which implies $n_{\alpha} \ge 1$.

In these conditions, one may replace R in eq. (2.8) by \overline{R} restricted to states *i* of energy relatively close to E_{α} (typically $|n_i - n_{\alpha}| \leq n_{\alpha}$). Assuming further that the matrix elements of R are approximately constant in this energy range, one may neglect the terms containing G_{AR}^0 , so that

$$G = G_{\mathbf{A}} + G_{\mathbf{A}} \,\overline{R} \sum_{n=0}^{\infty} \, (G_{\mathbf{A}} \,\overline{R})^n \, G_{\mathbf{A}} \qquad (2.9)$$

which is just the expansion of

$$G = \frac{1}{E - \mathscr{K}_{\mathsf{A}} - \overline{R}}.$$
 (2.10)

Accordingly, we will adopt as a pseudo-potential

$$V(\mathbf{R}) = \overline{R}(E_{\mathbf{R}}) . \qquad (2.11)$$

This is essentially the result recently proposed by Ivanov [16]. We will see in the following subsections how one can use the expression of $R(E_{\mathbb{R}})$ in terms of scattering phase shifts to find the position of the adiabatic energy curves of A-B either by perturbation theory or by a direct diagonalization of $\mathcal{H}_A + \overline{R}$ leading very naturally to results comparable with those of the quantum defect theory [30].

2.3 EXPRESSION OF $V(\mathbf{R})$ IN TERMS OF PHASE SHIFTS. — In the case of atomic diamagnetic perturbers $(J_p = 0)$, such as noble gases, V_B is a central potential independent of the electron spin. The matrix elements of R between two plane waves \mathbf{k}_a and $\mathbf{k}_b (k_a = k_b = k)$ have simple expressions in terms of phase shifts η'_l (see e.g. Ref. [34], eqs. (XIX-51) and (XIX-52)) :

$$\langle \mathbf{k}_{a} | R | \mathbf{k}_{b} \rangle = 4 \pi \sum (2 l + 1) R_{l} P_{l}(\hat{k}_{a} \cdot \hat{k}_{b})$$
 (2.14)

where

$$R_l = - \operatorname{tg} \eta'_l / (2 k) . \qquad (2.15)$$

In order to compute the matrix elements of $R(E_{\mathbf{R}})$ between two eigenstates *i* and *j* of atom A, it is always possible to expand their wavefunctions in terms of plane waves by mean of the Fourier transformation :

$$\Psi_i(\mathbf{r}) = \frac{1}{(2 \pi)^{3/2}} \int e^{i \mathbf{p} \cdot (\mathbf{r} - \mathbf{R})} \Phi_i(\mathbf{p}) d\mathbf{p} \quad (2.16)$$

so that

$$\langle j | R | i \rangle = \frac{1}{(2 \pi)^3} \int d\mathbf{p} \, d\mathbf{p}' \, d\mathbf{r} \, d\mathbf{r}' \langle \mathbf{p}' | R | \mathbf{p} \rangle \times e^{i\mathbf{p}'.(\mathbf{r}'-\mathbf{R})-i\mathbf{p}.(\mathbf{r}-\mathbf{R})} \Psi_j^*(\mathbf{r}') \Psi_i(\mathbf{r}) . \quad (2.17)$$

However, only values of **r** and **r'** close to **R** make an important contribution to this integral. Accordingly, in eqs. (2.16) and (2.17), p and p' remain close to $k_{\mathbf{R}} = \sqrt{2(E - V_{\mathbf{A}}(\mathbf{R}))}$ since the wavelength

 $^(^{3})$ Note that the reaction matrix is very often denoted by K.

of the electron is well-defined and nearly constant in the neighbourhood of **R**. One may therefore use eq. (2.14) for $\langle \mathbf{p}' | R | \mathbf{p} \rangle$. It is then easy to show that eq. (2.17) may be written

$$\langle j | R(E_{\mathbf{R}}) | i \rangle = 4 \pi \sum_{l} (2 l + 1) \times R_{l} \{ P_{l}(\nabla' \cdot \nabla/k_{R}^{2}) \Psi_{j}^{*}(\mathbf{r}') \Psi_{i}(\mathbf{r}) \}_{\mathbf{r}=\mathbf{r}'=R}.$$
 (2.18)

Thus, the first two terms are

$$\langle j | V_0(\mathbf{R}) | i \rangle = 4 \pi R_0 \Psi_j^*(\mathbf{R}) \Psi_i(\mathbf{R})$$
 (2.19)

$$\langle j | V_1(\mathbf{R}) | i \rangle = \frac{12 \pi}{k_R^2} R_1 \nabla \Psi_j^*(\mathbf{R}) \cdot \nabla \Psi_i(\mathbf{R}) .$$
 (2.20)

In the limit of very small energies $k_R^2/2$, all R_l are zero except R_0 which becomes independent of k_R and is equal to half the scattering length,

$$R_0 = L/2 , \qquad (2.21)$$

which is the well-known result of the Fermi approximation [10] (see eq. (2.1)).

If the long-range part of $V_{\rm B}$, $-\frac{1}{2}\alpha |\mathbf{r} - \mathbf{R}|^{-4}$, where α is the polarizability of B, is not negligible, one can use the expressions for the phase shifts η'_l given by Spruch *et al.* (see e.g. [37]), so that

$$R_0 = \frac{L}{2} \left\{ 1 + \frac{\pi}{3} \frac{\alpha k}{L} + \frac{4}{3} \alpha k^2 \ln(2 \, dk) \right\}$$
(2.22)

$$R_{l} = -\frac{\pi}{2} \frac{\alpha k}{(2l+3)(2l+1)(2l-1)} \quad l \ge 1 \quad (2.23)$$

where d is of the order of the dimension of atom B.

In fact, as pointed out for instance by Ivanov [16], the terms of first order in αk in R_0 and R_i do not contribute to forward scattering.

For eq. (2.22) to be valid,

and

$$kL \ll 1$$
 (2.24*a*)
 $\alpha k^2 \ll 1$. (2.24*b*)

With these conditions, the terms corresponding to the effective range r_0 are always negligible. One also sees that in such a case $kR_l \ll 1$ and $\eta'_l \ll 1$.

Values of L and α for the different noble gases are given in table I. As $k \sim n^{-1}$, it is seen that for He and Ne, conditions (2.24) are satisfied for *n* values as small as 5. For Ar, and *a fortiori* for Kr and Xe, larger *n* values are needed (n > 10). In such conditions the logarithmic term of eq. (2.22) is always very small, except for $n \sim 10$ for heavy noble gases. The second term of eq. (2.22) is often significant, especially for Ne. However, as already stated, it does not contribute to line shifts, but only to transition probabilities implying rather large changes in the momentum **k** of the electron.

TABLE I

Values of the scattering lengths of electrons by noble gases, and of polarizabilities of noble gases and alkalis, in atomic units.

	He	Ne	Ar	Kr	Xe
7					
$L^{(17)}$	1.19	0.24	- 1.70	- 3.7	- 6.5
α ⁽³⁸⁾	1.384	2.663	11.08	16.73	27.79
	Li	Na	K	Rb	Cs
α ⁽³⁹⁾	165	166	281	296	363
a ⁽⁴⁰⁾	161	155	277	297	358

Note that the JWKB wave function of a Σ state in the neighbourhood of **R** (see eqs. (2.35) (2.38)) is :

$$\Psi_{\Sigma} = F(R) \sin(k_R r + \varphi_0)$$
. (2.25)

Accordingly,

$$\langle \Sigma \mid V(\mathbf{R}) \mid \Sigma \rangle = 2 \pi F^2(\mathbf{R}) \sum_{l=0}^{\infty} (2 l + 1) \times R_l \{ 1 - (-)^l \cos(2 k_R R + 2 \varphi_0) \}.$$
(2.26)

Smirnov [32] and Roueff [33] have given a very similar expression for a wave function of the form $e^{-\beta r}$ in the neighbourhood of **R**. Note that the cross term cos $(2 k_R R + 2 \varphi_0)$ is zero when averaged with respect to **R**.

In the same way, for a Π state :

$$\Psi_{\Pi}(\mathbf{r}) = \sin \theta \, e^{i\varphi} \, G(R) \sin \left(k_R \, r + \varphi_1\right) \quad (2.27)$$

and one finds, neglecting the cross term,

$$\langle \Pi | V(\mathbf{R}) | \Pi \rangle =$$

= $2 \pi \frac{G(R)^2}{k_R^2 R^2} \sum_{l=1}^{\infty} (2 l + 1) l(l + 1) R_l$ (2.28)

again similar to Smirnov's result [32] which lacks the factor l(l + 1). However, as $k_R R \sim n$, this term is generally negligible compared to $\langle \Sigma | V(\mathbf{R}) | \Sigma \rangle$.

These results may obviously be generalized to the case where the ground state of B is a $S_{1/2}$ state (hydrogen, alkalis, etc.) by defining the matrices $R_{\rm S}$ and $R_{\rm T}$ of singlet and triplet states, respectively.

For very small k values, R_{Sl} and R_{Tl} satisfy eq. (2.22). However, typical values of polarizabilities and scattering lengths of alkalis [41, 42] are much larger than in the case of noble gases (see table I). Accordingly, eq. (2.24) require much larger values of k^{-1} , and hence of n, to be valid; typically $n \approx 30$.

When conditions (2.24) are not fulfilled, exact values of $R_l(E_{\mathbf{R}})$ are needed [41-43]. However, R_l can be rather large, and even diverge in the case of resonances. Typical resonances appear in particular in

the ³P phase shifts of alkalis in the vicinity of $k \sim 0.1$ [41, 42, 43]. In such cases it is obviously not possible to use a perturbation expansion in terms of \overline{R} , and a complete diagonalization of $\mathcal{K}_A + \overline{R}$ is required (section 2.5). Furthermore, when $\alpha k^2 > 1$, one has to take into account the interaction between B and the electron at distances larger than k^{-1} . One should then consider whether this interaction is still sufficiently localized to be well-represented by the *R* matrix.

2.4 DIFFERENT REPRESENTATIONS OF $V(\mathbf{R})$. — As in any collision problem, one has to make a choice between different basis states which determines the matrix elements of $V(\mathbf{R})$. In many cases the potential may be approximated by the Fermi potential

$$V_{ij}(\mathbf{R}) = 2 \pi L \Psi_i(\mathbf{R})^* \Psi_i(\mathbf{R}) . \qquad (2.29)$$

Accordingly, one should choose a basis which contains as many wave functions as possible equal to zero at the point \mathbf{R} .

In the case of very large *n* values, the Rydberg states are essentially hydrogenic. However, the degeneracy of the n^2 states pertaining to the same value of *n* is not perfect for small values of *l*, where the energies are well-approximated by a quantum defect δ_l :

$$E_{nl} = -1/\{2(n-\delta_l)\}^2. \qquad (2.30)$$

Some values of quantum defects δ_l are given in table II. The energy shifts are thus equal to $-\delta_l/n^3$. In a similar way, the fine structure splittings, for instance between $J = L \pm 1/2$ levels of alkalis, can be approximated in many cases by $\Delta E = d/n^3$. Some values of d are also given in table II.

TABLE II

Approximate mean values of quantum defects δ_l for $n \sim 10$ [50, 51]. The numbers in brackets give the order of magnitude of the variation of δ_l due to fine structure (doublet) splitting.

	s	р	d	f
Na	1.3	$0.85(10^{-3})$	$1.4 \times 10^{-2} (10^{-5})$	1.3×10^{-3}
Κ	2.2	1.7 (3×10^{-3})	$6 \times 10^{-2} (10^{-4})$	10 ⁻²
Rb	3.15	2.7 (1.3×10^{-2})	1.35 (10 ⁻³)	2×10^{-2}
Cs	4	3.6 (3×10^{-2})	$2.5(10^{-2})$	3×10^{-2}

Assuming nevertheless an ideal hydrogenic situation of n^2 completely degenerate states, it is straightforward using the n^2 wave functions $\Psi_i(\mathbf{r})$, to build $n^2 - 1$ functions equal to zero at point **R**. They correspond to $n^2 - 1$ states which remained degenerate and non-perturbed. The only shifted state is then given by

$$|\varphi_n\rangle = A^{-1} \sum_{i=1}^{n^2} \Psi_i^*(\mathbf{R}) |i\rangle \qquad (2.31)$$

where

$$A^{2} = \sum_{i=1}^{n^{2}} | \Psi_{i}(\mathbf{R}) |^{2} . \qquad (2.32)$$

It is shifted by the amount [19, 44]

$$\Delta_n^{\{1\}}(R) = 2 \pi L \sum_{i=1}^{n^2} | \Psi_i(\mathbf{R}) |^2 . \qquad (2.33)$$

We will use these expressions to find the exact values of the eigen-energies of $\mathcal{K}_A + V(\mathbf{R})$. However, we will see that they are not always very useful in the treatment of the collision (see section 3). Furthermore they do not account for the non-degeneracy of small *l* levels. Therefore, we will also use other atomic representations, with the usual *n*, *l*, *m* quantum numbers.

In the first one (see e.g. [29]), the internuclear axis AB is taken as the quantization axis. Only atomic states with m = 0 have a wave function different from zero at the point **R** (they essentially correspond to Σ molecular states) :

$$\Psi_{nl\sigma}(\mathbf{R}) = \sqrt{\frac{2l+1}{4\pi}} R_{nl}(R) \qquad (2.34)$$

where $R_{nl}(r)$ is the radial part of the wave function $\Psi_{nl\sigma}$ of the Σ state corresponding to nl.

A fixed axis system is often preferable for a classical path treatment of the collision. We will choose the z-axis perpendicular to the collision plane and the x- and y-axes parallel to the impact parameter **b** and to the relative velocity **v** respectively (Fig. 1). Accordingly, $\theta = \pi/2$ and φ is the angle between AB and **b**:

$$\Psi_{nlm}(\mathbf{R}) = R_{nl}(R) Y_l^m \left(\frac{\pi}{2}, \varphi\right) \qquad (2.35)$$

 (π)

where

$$Y_{l}^{m}(\pi/2, 0) = (-)^{p+m} \frac{\sqrt{(l+m)!(l-m)!4\pi}}{2^{l}p!(p+m)!\sqrt{2l+1}}$$

if $l-m=2p$ (2.36)
$$Y_{l}^{m}(\pi/2, 0) = 0$$
 if $l-m=2p+1$ (2.37)



As regards the explicit expression of $R_{nl}(R)$, in the case of not too large *n* values one may use the exact hydrogenic functions. However, their JWKB approximations are simpler to use and well suited to the discussions of both the potential and the collision. One may recall their form [45] :

$$R_{nl}(r) = \sqrt{\frac{2}{\pi n^3}} \frac{1}{r\sqrt{p_r}} \sin\left\{\int_{r_1}^r p_r \, \mathrm{d}r + \frac{\pi}{4}\right\} \quad (2.38)$$

where p_r is the radial impulsion :

$$p_r = \sqrt{2/r - 1/n^2 - (l + 1/2)^2/r^2}$$
 (2.39)

and r_1 and r_2 are the roots of p_r which delimit the region of classical motion.

From this expression, it is easy to rederive the result of Presnyakov [19] for the value of $\Delta_n^{(1)}(R)$ (eq. (2.33)), by using for instance eq. (2.34) :

$$\sum_{i} |\Psi_{i}(\mathbf{R})|^{2} = \sum_{l=0}^{n-1} \frac{2l+1}{4\pi} R_{nl}(R)^{2}.$$
 (2.40)

The JWKB approximation for $R_n(R)^2$ is used, and the summation over *l* is replaced by an integral limited to *l* values such that p_r is real (eq. (2.39)).

Replacing the sine squared by 1/2, one then obtains :

$$A^{2} = \sum_{i} |\Psi_{i}(R)|^{2} = \sqrt{2/R - 1/n^{2}}/(2 \pi^{2} n^{3})$$
(2.41)

hence

$$\begin{aligned} \Delta_n^{(1)}(R) &= L \sqrt{2/R - 1/n^2} / (\pi n^3) \\ &= k_R L / (\pi n^3) \text{ if } R < 2 n^2 \\ \Delta_n^{(1)}(R) &= 0 \qquad \text{if } R > 2 n^2 \end{aligned}$$
(2.42)

which is the result of Presnyakov (ref. [19] eq. (29)).

In the case of non-degenerate levels (small l), their first-order shift is obviously given by Fermi's result :

$$\Delta_{nl\sigma}^{(1)} = \langle nl\sigma \mid V(\mathbf{R}) \mid nl\sigma \rangle = 2 \pi L \mid \Psi_{nl\sigma}(\mathbf{R}) \mid^2.$$
(2.43)

2.5 COMPLETE DIAGONALIZATION OF $\mathcal{K}_A + V(\mathbf{R})$. — The validity of first-order perturbation theory is obviously limited to the cases where the energy shift $\Delta_n^{(1)}$ is much smaller than the energy splitting $1/n^3$, i.e.

$$|L| \sqrt{2/R - 1/n^2/\pi} = |L| k_R/\pi = |\lg \eta'_0|/\pi \ll 1.$$

(2.44)

In order to find the eigen-energies for any value of the phase-shift, we first assume that all the η'_l are equal to zero, with the exception of η'_0 which can take any value. The matrix elements of V are still given by eq. (2.19). Accordingly, we will consider only its matrix elements between the different φ_n (eq. (2.31)). $\Delta_n^{(1)}$ as given by eq. (2.42) is a slowly varying function of *n*. Therefore we may assume that all matrix elements $\langle \varphi_n | V | \varphi_n \rangle$ are equal to $\Delta_n^{(1)}$, if $|n - n'| \leq n$.

We show in appendix B how to diagonalize the resulting matrix. The result is very simple in the case of pure hydrogenic levels. To each value of n there corresponds a level shifted by the amount

$$\Delta_{n0} = -\eta_0'/(\pi n^3) . \qquad (2.45)$$

One immediately sees the complete analogy with the quantum defect theory [30]. The short range interaction e⁻-B produces a shift of the *s*-wave *relative to B* in the same way as the short range interaction e⁻-A⁺ produces a shift $-\delta_l/n^3$ of the *l*-wave relative to A⁺; and in the limit of vanishing energy [30], $\delta_l = n_l/\pi$, where n_l is the phase-shift for e⁻-A⁺ scattering.

Eq. (2.45) may obviously be extended to the other phase shifts $\eta'_{l'}$, so that to every pair of values of *n* and *l'* there corresponds a level (2 *l'* + 1)-times degenerate and shifted by the amount

$$\Delta_{nl'} = - \eta_{l'}^{\prime} / (\pi n^3) . \qquad (2.46)$$

Of course, this result implies that, from the n^2 hydrogenic wave functions relative to n, it is possible to build as many approximately independent l' m'-wave functions as necessary relative to B. Accordingly, the highest value of l' to be considered must be such that $l'^2_{max} \ll n^2$.

Where this last condition holds, one may also consider that the s, p, d waves (relative to A^+) are nearly independent of these l' m'-waves relative to B. It is then shown in appendix B, that in the case when $\eta'_{l'} = 0$ $(l' \neq 0)$, the shift of the level $nl\sigma$ is

$$\Delta_{n\sigma} = -\zeta/n^3 \tag{2.47}$$

where the additional quantum defect ζ satisfies

$$\zeta \left\{ 1 - \operatorname{cotg} \left\{ \pi(\zeta + \delta_l) \right\} \operatorname{tg} \eta'_0 \right\} = -\Delta_{nl\sigma}^{(1)} n^3.$$
(2.48)

In particular, when the scattering length approximation holds (eqs. (2.15) (2.21))

$$\Delta_{nl\sigma} \simeq \Delta_{nl\sigma}^{(1)} \{ 1 - Lk_R \cot g \pi \delta_l \} \qquad (2.49)$$

where $|Lk_R \cot \pi \delta_l| \ll 1$.

In the case of large *n*, this last condition is generally well satisfied except when $\delta_l \ll 1$. The correction to $\Delta_{nl\sigma}^{(1)}$ is therefore more important in the case of small δ_l , as for the d states of Na. However, it can be seen that the line shifts are then no longer directly related to the adiabatic level shift $\Delta_{n\sigma}$.

2.6 TERMS OF THE POTENTIAL RELATED TO THE INTER-ACTION A^+ -B, AND CONCLUSION. — As the probability of finding B very close to the core A^+ is very small, the interaction A^+ -B is dominated by the long-range electrostatic interaction. One may distinguish two types of interactions : those which result from the direct interaction of B and A^+ as if they were alone, and those which introduce a modification in the interaction of A^+ with the electron through the polarization of B. These effects have been known for a very long time (see e.g. Fermi [10] and Firsov [12]). Therefore we shall just recall the conclusions of these authors.

When B has neither a permanent dipole nor a quadrupole moment, the leading term in the long-range A^+ -B electrostatic interaction is

$$V(\mathbf{R}) = - \alpha / (2 R^4)$$
 (2.50)

where α is the polarizability of **B**.

We will assume that, for very highly-excited levels, this potential may simply be added to the generalized Fermi potential $V(\mathbf{R})$ previously discussed. For low-lying states, and in particular for the ground state, one should of course use a complete exact potential $V_{AB}(\mathbf{R})$. However its effect is generally negligible compared to the perturbation of Rydberg states by $V(\mathbf{R})$ or U(R).

U(R) is obviously completely negligible in evaluating collision induced transition probabilities between Rydberg states, as long as it does not perturb the trajectory of B. However, it can affect optical line shifts appreciably, and even dominate line broadening as discussed for instance by Reinsberg [11] and Alekseev and Sobelman [13] (see section 4).

As concerns the second type of effect, i.e. the interaction of e^- (or A^+) with the dipole induced in B by A^+ (or e^-), the essential result is very simple. The presence of gas B inside the electronic orbit modifies the dielectric constant and hence the position of the energy levels. However the effect is always small and negligible in practice.

In conclusion, for very large values of n, the interaction of A and B should be well-represented by $U(R) + V(\mathbf{R})$. General methods of diagonalization and perturbation can be applied to $V(\mathbf{R})$, with the express condition of excluding distant levels such as the continuum. The positions of adiabatic energy levels are very simply expressed in terms of e^- -B scattering phase shifts by an extension of the quantum defect theory. However several problems remain, for instance :

— a precise discussion of the values of n for which this potential is valid would require a complete study of the A-B potential. The result obviously depends on the value of the scattering length L of B, and also on its polarizability α . However, one might think that, in most cases, this potential is a good approximation for n > 10. In many cases, it seems that it might be used in the range 5 < n < 10. However, the region forbidden to classical motion may then be important in the derivation of transition probabilities and of line broadening. Moreover,

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it is known that the same type of approximation provides an order of magnitude estimate of the potential, even for still smaller n values and for distances into the region forbidden to classical motion where the wave function decays exponentially;

— in the case where B is an alkali, the very large values of α and of e⁻-B scattering cross sections make the validity conditions more restrictive. Furthermore, the scattering phase shifts are still rather uncertain for most of the alkalis at the very low energies implied. As a result there remains a large uncertainty in the potential of interaction of Rydberg states with alkali atoms in their ground states;

- even when the adiabatic energy levels are known exactly, the computation of the effect of the collision on transition probabilities, line shifts and broadenings may be difficult. In particular, because of the very large number of states involved, great care should be exercised in the use of perturbation theory. In the limit of rapid motion, as discussed in sections 3 and 4, the determination of adiabatic levels is often useless. On the contrary one should then express transition probabilities, line shifts and broadenings directly in terms of the transition T matrix of $e^{-}-B$ scattering, as is done by Alekseev and Sobelman [13]. However, this limit of rapid motion is valid only for rather large n (typically n > 30, see section 3-1). Accordingly, detailed knowledge of the matrix elements and of the eigen-energies of $V(\mathbf{R})$ is necessary for the intermediate values of n.

3. Collision matrix and transition probabilities. — 3.1. PERTURBATION TREATMENT IN FIXED AXES AND CORRELATION TIME. — We shall here assume that it is justified to represent the interaction of atoms A in a Rydberg state with the gas B in terms of independent binary collisions. One may consider a quantum treatment of the collision (see e.g. [13, 29]). However because of the very long range of the potential, the classical-path method seems appropriate. Furthermore, it is clear that the trajectory of B is rectilinear to a very good approximation, except in the effective range of the R^{-4} potential (⁴). In the present section, we are interested in computing the probabilities of transitions between Rydberg states, postponing the discussion of optical line broadening and shift to section 4. Accordingly, assuming first a straight line path, we neglect the R^{-4} potential and we consider only the Fermi

$$\sigma_L = \frac{2 \pi}{v} \sqrt{\frac{\alpha}{M^*}} \sim 2 \pi \sqrt{\frac{\alpha}{3 kT}} \sim 80 \sqrt{\alpha}$$

^{(&}lt;sup>4</sup>) The cross-section for orbiting by the R^{-4} potential is given by the Langevin relation (see e.g. [46]) :

which is equal to 95, 130 and 270 for collisions with He, Ne and Ar respectively. These cross-sections are much smaller than the cross-sections measured for quasi-elastic transitions [25], but of the same order of magnitude as the cross-sections for inelastic transitions [26, 27].

potential $V(\mathbf{R})$, and especially its simplified form in terms of the scattering length (eq. (2.29)).

Schroedinger's equation during the collision is then

$$\frac{\mathrm{d} \mid \Psi \rangle}{\mathrm{d}t} = -i \left\{ \mathcal{K}_{\mathrm{A}} + V(\mathbf{R}) \right\} \mid \Psi \rangle \quad (3.1)$$

where $V(\mathbf{R})$ depends on t through \mathbf{R} :

$$\mathbf{R} = \mathbf{b} + \mathbf{v}t \,. \tag{3.2}$$

First-order time-dependent perturbation theory yields the collision matrix :

$$S^{(1)} = -i \int_{-\infty}^{\infty} e^{i\mathcal{R}_{\Lambda}t} V(t) e^{-i\mathcal{R}_{\Lambda}t} dt \qquad (3.3)$$

and the transitions probabilities

$$P_{ij} = \left| \left\langle i \mid S^{(1)} \mid j \right\rangle \right|^2 = 4 \pi^2 L^2 \times \left| \int_{-\infty}^{\infty} e^{i \omega_{ij} t} \Psi_i^*(t) \Psi_j(t) \, \mathrm{d}t \right|^2 \quad (3.4)$$

where $\omega_{ij} = E_i - E_j$.

We will discuss the validity of perturbation theory in subsection 3. When eq. (3.4) is valid, the transition probabilities are proportional to the square of the Fourier component of $V_{ij}(t)$ at the frequency, ω_{ij} . Accordingly, they are directly related to the correlation time τ_c of V(t); they are very small if

$$\omega_{ij} \tau_{c} \ge 1 . \tag{3.5}$$

Usually, in collision theory, τ_c is of the order of magnitude of the duration, T_c , of the collision. Such is not the case here, because $V_{ij}(t)$ oscillates strongly during the collision. In order to explain this point, let us consider the shape of $\Psi_i(t)$ in the vicinity of the point $\mathbf{R}(t)$. One may write (see eqs. (2.35) 2.38)):

$$\psi_i(t) \simeq \sum_{\alpha} F_{i\alpha}(\mathbf{R}) e^{i\mathbf{k}_{i\alpha} \cdot (\mathbf{v}t + \mathbf{b})}$$
(3.6)

where $F_{i\alpha}(\mathbf{R})$ is a slowly-varying function of **R** and hence of t, and $k_{i\alpha} = k_R$. In the vicinity of **R**, $V_{ij}(t)$ is thus the sum of terms oscillating at frequencies $(\mathbf{k}_{i\beta} - \mathbf{k}_{i\alpha})$.v. The transition probability is therefore very small, if during the whole collision

$$\left| \left(\mathbf{k}_{i\beta} - \mathbf{k}_{i\alpha} \right) \cdot \mathbf{v} \right| \leqslant \omega_{ij} \tag{3.7}$$

and in particular if

$$k_{\mathbf{R}} v \sim n^{-1} v \ll \omega_{ij} \tag{3.8}$$

or, with

$$\omega_{ij} = \Delta n/n^3 , \qquad (3.9)$$

$$n^2 v \ll \Delta n \tag{3.10}$$

which implies, in the case of $\Delta n = 1$, *n* values larger than 30 or 100 for v equal to 10^{-3} or 10^{-4} (2.2 × 10^{4} or 2.2×10^5 cm/s).

One may also say that the correlation time is

$$\mathbf{t}_{\mathbf{c}} \sim \{ (\mathbf{k}_{j\beta} - \mathbf{k}_{i\alpha}) \cdot \mathbf{v} \}^{-1} \sim n/v \qquad (3.11)$$

while the duration of a collision is

$$T_{\rm c} \sim n^2 / v \,. \tag{3.12}$$

When $\omega_{ij} T_c \sim \Delta n / (nv) \ll 1$, one may certainly neglect the factor $\exp(i\omega_{ij} t)$ in the computation of P_{ij} (eq. (3.4)). The question is much less clear when

$$T_{\rm c}^{-1} < \omega_{ij} < \tau_{\rm c}^{-1}$$
 (3.13)

 P_{ij} may then be large and can differ appreciably from the result obtained on neglecting the term $\exp(i\omega_{ii} t)$, as was done for instance by Gersten [28].

When the condition

$$\left| \left(\mathbf{k}_{j\beta} - \mathbf{k}_{i\alpha} \right) \cdot \mathbf{v} \right| T_{c} \ge 1$$
 (3.14)

is satisfied almost everywhere during the collision, the transition probability may be assumed to be concentrated in the vicinity of stationary phase points, such as :

$$\omega_{ij} + (\mathbf{k}_{j\beta} - \mathbf{k}_{i\alpha}) \cdot \mathbf{v} = 0 \qquad (3.15)$$

which is just the expression of momentum conservation in the direction of v. One could then use the usual stationary phase method to derive S_{ij} and hence P_{ii} . However, it should require numerical computations, and its conditions of validity are not well satisfied for a given transition.

Using JWKB wave functions (eq. (2.38)) in a representation in which the z-axis is perpendicular to the collision plane, the transition probabilities may be explicitly written :

$$P_{nim,n'l'm'} = \frac{16 L^2}{n^6} Y_l^m \left(\frac{\pi}{2}, 0\right)^2 Y_{l'}^{m'} \left(\frac{\pi}{2}, 0\right)^2 \times \\ \times \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' e^{i\omega_{nn} (t-t')} e^{i(m'-m)(\varphi-\varphi')} \\ \times R^{-2} R'^{-2} (p_R p_{R'} p_R' p_{R'}')^{-1/2} \\ \times \sin P_R \sin P_{R'} \sin P_R' \sin P_{R'}' \quad (3.16)$$

where $p_{R'}$, etc., is given by eq. (2.39) and

$$P_R = \int_{r_1}^r p_r \, \mathrm{d}r \, + \, \pi/4 \, ... \qquad (3.17)$$

One thus sees that

$$\mathbf{k}_{ia} = m/R\hat{\varphi} \pm p_r(R)\,\hat{R}\,. \tag{3.18}$$

We shall use eq. (3.16) to estimate the values of 10) sums of $P_{nlm,n'l'm'}$ over m', m, l', l and n'.

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3.2 APPROXIMATE SUMMED CROSS-SECTIONS. — It is not generally possible to measure the individual transition probabilities $P_{nlm,n'l'm'}$, but only their sum over m' and m, and, in certain cases, l', l or n'. We shall obtain rough estimates of these discrete sums by replacing them by integrals. We shall distinguish between two cases, according to whether the energy levels with $n' \neq n$ are accessible or not (see inequality (3.10)).

3.2.1 Sum with respect to $n' (n^2 \ge v^{-1})$. — When condition (3.10) is not fulfilled for levels n' close to n, i.e. when

$$n^2 \gg v^{-1} \tag{3.19}$$

one may, in $\sum_{n'} P_{nlm,n'l'm'}$, replace n' by n in all terms of eq. (3.16) except in $\exp[i\omega_{nn'}(t-t')]$, and write

$$\sum_{n'} e^{i\omega_{nn'}(t-t')} \simeq \int_{-\infty}^{\infty} \exp\left[i\frac{\Delta n}{n^3}(t-t')\right] d(\Delta n) =$$
$$= 2 \pi n^3 \delta(t-t') . \quad (3.20)$$

We then obtain

$$P_{nl} = \frac{1}{2 l + 1} \sum_{n'l'm'm} P_{nlm,n'l'm'}$$
$$= \frac{L^2}{2 \pi n^3} \sum_{l'} (2 l' + 1) \int_{-\infty}^{\infty} \frac{dt}{R^4 p_R p_R'}$$
(3.21)

where $\sin^2 P_R$ and $\sin^2 P'_R$ have been replaced by 1/2, and use has been made of the relation :

$$\sum_{m} |Y_{l}^{m}(\pi/2, \varphi)|^{2} = (2 l + 1)/(4 \pi) . \quad (3.22)$$

Furthermore,

$$\sum_{l'} \frac{2 l' + 1}{R^2 p_R'} \simeq \int_0^{l \max} \frac{2 x \, dx}{\sqrt{2/R - 1/n^2 - x^2}} = 2 \sqrt{2/R - 1/n^2} . \quad (3.23)$$

The cross-sections,

$$\sigma_{nl} = 2 \pi \int_0^\infty P_{nl} b \, \mathrm{d}b \qquad (3.24)$$

are then easily derived :

$$\sigma_{nl} = 8 L^2/(nv) \quad \text{if} \quad l \ll n \qquad (3.25)$$

and

$$\sigma_n = n^{-2} \sum (2 \, l + 1) \, \sigma_n = 32 \, L^2 / (3 \, nv) \, . \quad (3.26)$$

One thus recovers the result of Alekseev and Sobelman [13]; the collision rate in state i is just the rate for a free electron :

$$v\sigma_i = 4 \pi L^2 \langle v_e \rangle_i \tag{3.27}$$

where $4 \pi L^2$ is the scattering cross-section of a free electron in the approximation of the scattering length, and $\langle v_e \rangle_i$ is the mean velocity of the electron in state *i*. Eqs. (3.25), (3.26) are easily derived by using the distribution $W_{n0}(v_e) = 4 n \pi^{-1} (1 + n^2 v_e^2)^{-2}$ (see e.g. ref. [13] eq. (23)) for states such that $l \ll n$, and the distribution $W_n(v_e) = 32 \pi^{-1} n^3 v_e^2 (1 + n^2 v_e^2)^{-4}$ (see e.g. ref. [20a] eq. (28b)) for the whole set of sublevels of *n*.

It is thus seen that the probability of leaving state i is the same as that of elastic scattering for free electrons with the same velocity distribution, *if* condition (3.19) is met, i.e. *if the distribution of accessible states may be considered as continuous*. This condition typically implies n values at least of the order of 50. Contrary to the assertion of Alekseev and Sobelman ([13] p. 885), eq. (3.27) is valid only in these conditions, where the Rydberg electron essentially undergoes inelastic collisions.

3.2.2 Transitions $\Delta n = 0$. — We now assume the factor exp { $i\omega_{ij}(t - t')$ } in eq. (3.16) is negligible, as in the case $\Delta n = 0$ for instance, and we first perform the summation with respect to l' and m' and then the average with respect to l and m in order to calculate the mean probability of leaving the initial state nlm

$$P_{nn} = n^{-2} \sum_{ll'mm'} P_{nlm,nl'm'} . \qquad (3.28)$$

This summation is equivalent to summing over all possible directions of the wave-vectors \mathbf{k} and \mathbf{k}' of the electron. It is shown in appendix C that the element of solid angle of \mathbf{k} at point \mathbf{R} is

$$\mathrm{d}\Omega_{k} = 2 \,\pi^{2} \, \overline{Y}_{l}^{m} (\pi/2, \, 0)^{2} \, R^{-2} \, p_{R}^{-1} \, k_{R}^{-1} \, \mathrm{d}l \, \mathrm{d}m \,. \quad (3.29)$$

It will be seen (eq. (3.31)) that the summation over Ω_k and $\Omega_{k'}$ again introduces the function $\delta(t - t')$. Accordingly, we replace R' by R in all terms of eq. (3.16) except in exp $\pm ip_R R'$. Eq. (3.1) may then be written

$$P_{nn} = \frac{L^2}{16 \pi^4 n^8} \int dt \, dt' \, d\Omega_k \, d\Omega_{k'} \, k_R^2 \times \\ \times \exp \left\{ i(\mathbf{k}_R' - \mathbf{k}_R) \cdot (\mathbf{R} - \mathbf{R}') \right\} \quad (3.30)$$

and, using the relation

$$\frac{\sin^2 k_R |\mathbf{R} - \mathbf{R}'|}{k_R^2 |\mathbf{R} - \mathbf{R}'|^2} = \frac{\pi}{k_R} \delta(|\mathbf{R} - \mathbf{R}'|) = \frac{\pi}{v k_R} \delta(t - t')$$
(3.31)

$$P_{nn} = \frac{L^2}{\pi n^8 v} \int_{-\infty}^{\infty} k_R \, \mathrm{d}t \;. \tag{3.32}$$

Finally, the cross-section is easily derived by using $2 \pi b \, db \, dt = v^{-1} 4 \pi R^2 \, dR$:

$$\sigma_{n,n} = 2 \pi L^2 / (n^3 v^2) . \qquad (3.33)$$

It is obvious that this expression can also be used for $\sigma_{n,n'}$ if $|n - n'|/(n^2 v) \ll 1$ (cf. eq. (3.10)), and if the assumption of classical motion of B is justified, which implies $|n' - n|/n^3 \ll k_B T$, i.e. $n \ge 10$ for $n' = n \pm 1$.

The average over a thermal distribution of the transition rate $v\sigma_{n,n}$ yields exactly eq. (68) of Flannery [20a] for transitions $n' = n \pm 1$:

$$\overline{K}_{n,n} = 2 \sqrt{2 \pi M^* / k_{\rm B} T} L^2 / n^3 . \qquad (3.34)$$

This shows that our method and the treatment of Flannery are equivalent; both are semi-classical and use a binary instantaneous interaction.

The probability of leaving a particular l state can be estimated in the same way :

$$P_{nl,n} = (2 l + 1)^{-1} \sum_{mlm'} P_{nlm,n}.$$
 (3.35)

Assuming that one may replace R' by R as before,

$$P_{nl,n} = \frac{L^2}{4 \pi^2 n^6 (2 l + 1)} \int dt \, dt' \, d\Omega_{k'} \sum_{\mathbf{k}_R} Y_l^m(\pi/2, 0) \times k_R \, p_R^{-1} \, R^{-2} \exp[i(\mathbf{k}_R' - \mathbf{k}_R) \cdot (\mathbf{R} - \mathbf{R}')] \quad (3.36)$$

where the summation over \mathbf{k}_R involves the summation over *m* and over the two possible orientations of the projection of \mathbf{k}_R onto **R** included in sin P_R . The integration over $\Omega_{k'}$ yields

$$P_{nl,n} = \frac{L^2}{\pi n^6 (2 \ l + 1)} \int dt \frac{dx}{k_R \ v} \times \frac{\sin x}{x} \sum_u \frac{\exp(-ixu) \ k_R \ Y_l^m(\pi/2,0)}{p_R \ R^2} \quad (3.37)$$

where u denotes the cosine of the angle of \mathbf{k}_R and $\mathbf{R} - \mathbf{R}'$. As positive and negative values of u are equally probable, the integral over x may be replaced by π . Consequently,

$$P_{nl,n} = \frac{L^2}{2 \pi n^6 v} \int \frac{\mathrm{d}t}{R^2 p_R}$$
(3.38)

and

$$\sigma_{nl.n} = 2 \pi L^2 / (n^3 v^2) \tag{3.39}$$

which is equal to $\sigma_{n,n}$ (eq. (3.33)). Accordingly, in this approximation, the probability of leaving the state l is independent of l.

The dependence of $\sigma_{n,n}$ on n and v is thus very different from that of σ_{nl} and σ_n (eqs. (3.25) (3.26)). One sees that $\sigma_{n,n} = \sigma_n$ when $n^2 v = 3 \pi/16$, of the order of magnitude of the limit of validity of eqs. (3.25) (3.26).

On the other hand, the validity of the perturbation treatment used to derive $\sigma_{n,n}$ implies weak collisions for all values of b, which is certainly not true for n < 10 as discussed in the following subsection.

It is interesting to compare the values predicted for $\overline{K}_{nl,n}$ by eq. (3.34) with the experimental results in the case of d levels of sodium [25]. For the largest *n* studied, n = 15, where the assumption of weak collision is approximately justified, the respective values in the case of collisions with He, Ne and Ar are as follows : measurements [25] : 3.7, 0.41 and 4.8; eq. (3.34) : 4.5, 0.32 and 19.

Besides the use of this semi-classical model (JWKB wave-functions, continuous summations, δ -functions, etc.), there are some other obvious sources of error :

— The scattering length approximation is not well justified for Ne and Ar; the introduction of the corrections of eqs. (2.22) (2.23) should make the j agreement better for Ne and Ar.

— Eq. (3.39) includes transitions to s, p and d levels which do not contribute to the experimental results; transitions to d levels for obvious reasons, transitions to s and p levels because of the large energy gap which makes them much less probable and negligible [26].

- Collisions are not completely weak (cf. subsection 3) especially in the case of Ar.

 The quantum defect of d levels of Na is perhaps not entirely negligible.

— Transitions with $\Delta n \neq 0$ are perhaps not completely negligible, especially in the case of He.

On the other hand, only the values for Ne exhibit approximately the predicted n^{-3} dependence. The slower decrease observed for He and Ar is probably due mostly to strong collisions.

3.3 STRONG COLLISIONS AND ADIABATIC REPRE-SENTATION. — An obvious limitation of the validity of the weak collision approximation is that the total probability $P_{nl,n}$ of leaving the state nl must remain smaller than unity. From eq. (3.38) it can be seen that, for $l \leq n$, $P_{nl,n}$ is approximately (to within about 10 %) equal to

$$P_{nl,n} \simeq 0.53 \ L^2 / (n^6 \ v^2 \ \sqrt{b})$$
. (3.40)

Accordingly, $P_{nl,n}$ remains smaller than unity for most of the collisions when

$$n > (L/v)^{2/7}$$
 (3.41)

which yields approximately 9, 7 and 12 for collisions of Na with He, Ne and Ar respectively.

However, this condition is not sufficient in itself to ensure the validity of first-order time-dependent perturbation theory (eq. (3.4)), or even the convergence of the perturbation expansion. For instance, this perturbation treatment is certainly not valid when the adiabaticity condition is satisfied :

$$\Delta E_{\rm ad} \, \tau_{\rm c} \gg 1 \tag{3.42}$$

$$n \ll [L/(\pi v)]^{1/3}$$
 (3.43)

which is roughly equivalent to the inverse of the inequality (3.41). It thus appears that eq. (3.40) certainly overestimates $P_{nl,n}$ in the region where $n \sim (L/\pi v)^{1/3}$. As proposed by Gersten [28], one can think of using the Anderson approximation [47] to represent strong collisions : $P_{nl,n} = A$ for $b < b_0$ such that $P_{nl,n}(b_0) = A$, with $A = 1 - 9 n^{-2}$ for l = 2. However, it is not surprising that this approximation used with eq. (3.40) gives cross-sections much larger than the experimental results [25], probably because $P_{nl,n}$ remains appreciably smaller than unity in strong collisions. It should be noted in particular that the measured cross-sections are at least one order of magnitude smaller than the geometrical cross-sections $4 \pi n^4 a_0^2$.

An exact treatment of strong collisions appears difficult because there are at least about $n^2/2$ coupled differential equations to be considered. It seems therefore preferable to look for approximate treatments. The two-level model used by Olson [29] is certainly much too crude; there is no obvious reason why one should consider only transitions between $D_{5/2}$ and $F_{5/2}$ levels and neglect rotational coupling.

It would seem preferable to use, as usual (see e.g. [48]), a fixed axis basis at long range, and an adiabatic basis at short range; and to try to reduce as much as possible the number of relevant coupled equations in both regions, with the use of perturbation methods, when these are justified.

3.4 INELASTIC COLLISIONS. — The measured crosssections [26, 27] for inelastic collisions ($\Delta n^* \sim 1$) with noble gases are generally smaller than 100 a_0^2 , i.e. much smaller than those of quasi-elastic collisions [25] ~ 10³-10⁴ a_0^2 . On the contrary, inelastic collisions are again of the order of 10⁴ a_0^2 for collisions with alkalis [26].

Thus, inelastic transitions with noble gases are probably the result of very short range interactions. The computation of such cross-sections should take into account the R^{-4} potential, abandoning the straight line path assumption (see footnote (⁴)), and using a more elaborate potential than the one proposed in section 2.

On the other hand, transitions induced by alkalis mainly occur at long range, where the trajectory is approximately linear. The very large inelastic rates observed are certainly due to the great strength of the interaction of the Rydberg electron with the alkali B, and probably to the existence of crossings between the adiabatic potential energy curves. Such avoided crossings occur when a phase shift $\eta'_{l'}$ of the scattering of e^- by B equals $\pi \delta_l$, where δ_l is the quantum defect of the initial level. Accordingly, a crossing is almost certain in the presence of a resonance of $\eta'_{l'}$ in the range of kinetic energy of the Rydberg electron. As a resonance seems to exist for every alkali in the vicinity of 0.1 eV [41, 42], at least for the ³P wave, one can expect crossings for very large values of $b : b \approx 100-300 a_0$ for n > 10.

One can then obtain a very rough order of magnitude of the transition probability in the following way, by the Landau-Zener formula (Ref. [45] p. 309) :

$$w = 4 \pi U^2 / (vF) \tag{3.44}$$

where U is the potential matrix element between the levels crossing. For instance in the case of an s'-wave, U is given by eqs. (2.19) and (2.31) (see also eq. (2.48)). Although it is actually an oscillating function of R, U is therefore, to an order of magnitude (see eq. (2.41))

$$U \sim n^{-4}$$
. (3.45)

On the other hand,

$$F = | dE_{\varphi_n} / dR | \sim n^{-5} \tag{3.46}$$

so that

$$w \sim 1/(n^3 v)$$
 (3.47)

which shows that one can expect non-negligible transition probabilities for $n \approx 20$. The order of magnitude of the observed cross-sections [26] is therefore not surprising.

4. Broadening and shift of optical lines. — 4.1 INTRODUCTION. — The broadening and shift of optical lines involving a Rydberg state are entirely dominated by the perturbation of the Rydberg state itself, so that one can completely ignore the perturbation of the lower level of the transition. In general, the shift is governed by the long-range part of the interaction and provides an estimate of the mean value of the potential. On the other hand, the major part of the broadening can come from shorter range interaction. In addition, it is essential to distinguish between the impact and quasi-static line broadening theories.

Up to now, most optical line measurements have been performed at rather high pressures (~ 1 atm) because of the large apparatus widths of conventional spectroscopy (~ 1 cm⁻¹). Such conditions, as discussed by Alekseev and Sobelman [13], correspond to the transition between impact and quasi-static regimes. However, in order to simplify, and in anticipation of new experiments using high-resolution spectroscopy, we will restrict ourselves to the discussion of the impact theory. Nearly all existing experimental results concern absorption in principal lines of alkalis perturbed either by a foreign gas (mainly noble gases) or by the alkali vapour itself. For very high members (n > 30) and noble gas perturbers, the agreement between experiment and theory is excellent (see e.g. [5a-b, 13, 16]).

The *shift* is dominated by the Fermi interaction (eq. (2.1)) with a small contribution of the polariza-

TABLE III

Broadening and shift rates in atomic units. K_{sc}^{δ} and K_{sc}^{γ} are deduced from the scattering lengths of table I (eqs. (4.1) and (4.4)); K_{sc}^{γ} is computed for n = 30. The polarization rates are calculated with the mean relative velocity corresponding to 760 K, and to Na* in the case of perturbation by noble gases. We recall that the atomic rate unit $K_0 = 6.126 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} = 0.874 \text{ cm}^{-1}/\text{amagat}$.

He	Ne	Ar	Kr	Xe	K	Rb	Cs
7.48	1.51	- 10.7	– 23.2 –	- 40.8			
0.77 -	0.98	- 2.4	- 3.1 -	- 4.3 —	20 –	18 –	19
0.19	0.01	0.39	1.83	5.63			
0.45	0.57	1.40	1.78	2.46	11.4	10.5	11.0
-	He 7.48 0.77 0.19 0.45	He Ne 7.48 1.51 0.77 - 0.19 0.01 0.45 0.57	HeNeAr $ 7.48$ 1.51 $ 0.77$ $ 0.98$ 0.19 0.01 0.39 0.45 0.57 1.40	HeNeArKr 7.48 1.51 -10.7 -23.2 0.77 -0.98 -2.4 -3.1 0.19 0.01 0.39 1.83 0.45 0.57 1.40 1.78	HeNeArKrXe $ 7.48$ 1.51 $ 10.7$ $ 23.2$ $ 0.77$ $ 0.98$ $ 2.4$ $ 3.1$ $ 0.19$ 0.01 0.39 1.83 5.63 0.45 0.57 1.40 1.78 2.46	HeNeArKrXeK 7.48 1.51 -10.7 -23.2 -40.8 0.77 -0.98 -2.4 -3.1 -4.3 -20 0.19 0.01 0.39 1.83 5.63 0.45 0.57 1.40 1.78 2.46 11.4	HeNeArKrXeKRb $ 7.48$ 1.51 $ 10.7$ $ 23.2$ $ 40.8$ 0.77 $ 0.98$ $ 2.4$ $ 3.1$ $ 4.3$ $ 20$ $ 18$ 0.19 0.01 0.39 1.83 5.63 5.63 0.45 0.57 1.40 1.78 2.46 11.4 10.5

tion (R^{-4}) potential. In the scattering length approximation, the Fermi shift is written

$$\delta_{\rm sc} = K_{\rm sc}^{\delta} N_{\rm p} = 2 \pi L N_{\rm p} . \qquad (4.1)$$

A more precise value, taking into account eq. (22), is given by Ivanov [16].

The polarization shift is (ref. [13] eq. (34)) :

$$\delta_{\rm p} = K_{\rm p}^{\delta} N_{\rm p} = - 6.22 (\alpha^2 v)^{1/3} N_{\rm p} . \qquad (4.2)$$

On the other hand, the broadening can come mainly from the polarization interaction [11, 13]. The corresponding half-width at half-height is (ref. [13] eq. (34)) (⁵) :

$$\gamma_{\rm p}/2 = K_{\rm p}^{\gamma} N_{\rm p} = 3.59 (\alpha^2 v)^{1/3} N_{\rm p} .$$
 (4.3)

As discussed in section 3 (eq. (3.25)), the expression given by Alekseev and Sobelman [13] of the broadening due to the scattering of e^- by B is

$$\gamma_{\rm sc}/2 = K_{\rm sc}^{\gamma} N_{\rm p} = (4 \ L^2/n) N_{\rm p} \qquad (4.4)$$

corresponding to inelastic collisions from the nl level considered, to adjacent levels n'. It is valid only for n values large enough to satisfy the non-adiabaticity criterion (eq. (3.10)) (n > 30-50).

The different broadening and shift rates are tabulated in table III. We note the large values of these rates and of the corresponding cross-sections :

$$\sigma = 3\ 700\ a_0^2 \simeq 1\ 000\ \text{\AA}^2$$

in the case of Na^{*}-Ar collisions for n = 30.

We will now discuss two cases where the preceding results do not apply : alkali-noble gas collisions for intermediate n values, and alkali-alkali collisions.

4.2 ALKALI-NOBLE GAS COLLISIONS. INTERMEDIATE n VALUES. — For very small values of n^* ($n^* < 6$) both the broadening and the shift of the principal lines of alkali perturbed by noble gases exhibit a sharp increase with n; these levels are not proper

Rydberg states, and we shall not discuss them here. For intermediate values of n^* , the width decreases strongly (factor ~ 3) between $n^* ~ 6$ and $n^* ~ 15$, and then rapidly reaches its asymptotic value for larger *n* (see e.g. Fig. 2). We now propose an approximate interpretation of this behavior.

The experiments of Mazing et al. [5b] on Cs perturbed by Ar were performed at $T \sim 570$ K, at relatively low pressure ($p \sim 0.2$ atm) so that one can consider that the conditions of application of the impact approximation were satisfied. However, for the values of *n* under consideration, one cannot consider independently the effects of the polarization potential and of the Fermi potential. Furthermore, the broadening is certainly not due to inelastic collisions, since the quenching rates of p levels, measured in similar conditions [26], are smaller than the broadening rates by nearly two orders of magnitude. The fine structure interval ΔE between ${}^{2}P_{1/2}$ and ${}^{2}P_{3/2}$ levels equals approximately $3 \times 10^{-2}/n^{*3}$. Accordingly, the adiabaticity criterion (3.10) is approximately satisfied for $n^* < 10$ ($\overline{v} = 2.9 \times 10^{-4}$), and we will neglect, in a first approximation, the transitions between the two levels of the doublet. The broadening is therefore essentially produced by elastic collisions, which are necessarily rather strong, since the broadening and the shift have the same order of magnitude.

In addition, we will assume that the interaction can be approximated by the isotropic part of the potential, avoiding a detailed calculation of transitions between Zeeman substates. This approximation together with the neglect of hyperfine transitions certainly modifies the broadening rates, but we believe only slightly. Accordingly, we take as a first-order potential

$$V^{(1)}(\mathbf{R}) = -\frac{\alpha}{2 R^4} + \frac{2 \pi L}{2 l + 1} \sum_m |\Psi_{nlm}^2|. \quad (4.5)$$

This potential will be used alone in order to obtain a first estimate of the broadening.

In the semi-classical approximation :

$$V^{(1)}(R) = -\frac{\alpha}{2 R^4} + \frac{1}{2 \pi n^3 R^2 \sqrt{2/R - 1/n^2}}.$$
(4.6)

 $^(^5)$ The broadening derived by Reinsberg [11] and quoted in references [6, 9] is too large by a factor of approximately 2.

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The perturbation expansion of the S-matrix is then

$$S = 1 - iW - W^2/2 + \cdots$$
 (4.7)

where

$$W = \int_{-\infty}^{\infty} V^{(1)}(R) \, \mathrm{d}t \,. \tag{4.8}$$

It can be shown that an approximate expression for W is (see eq. (3.40))

$$W \simeq -\frac{\pi}{4} \frac{\alpha}{vb^3} + \frac{0.53}{n^3} \frac{L}{v\sqrt{b}}.$$
 (4.9)

The two terms of the r.h.s. are equal for

$$b_0 = (1.48 \ \alpha n^3/L)^{2/5} \tag{4.10}$$

which varies from 23 to 41 for $6.4 < n^* < 10.4$, in the case of Cs*-Ar. For $b \ll b_0$ the Fermi potential can be neglected; the polarization potential is negligible for $b \gg b_0$. The cross-section for optical broadening is defined as usual from the half-width at halfheight $\gamma/2$, by the relation

$$\gamma/2 = \sigma \overline{v} N_{\rm p} = K^{\gamma} N_{\rm p} . \qquad (4.11)$$

In the Anderson approximation [47]

$$\sigma = \pi b_{\mathbf{w}}^2 + \pi \int_{b_{\mathbf{w}}}^{\infty} W^2 b \, \mathrm{d}b \qquad (4.12)$$

where the Weisskopf radius b_{w} is defined by

$$W^2/2 = 1$$
. (4.13)

An estimate of the cross-section σ is given by

$$\sigma = \sigma_{\rm p} + \sigma_{\rm F} \tag{4.14}$$

where σ_p would be the cross-section if the polarization potential were present alone :

$$\sigma_{\rm p} \simeq \frac{3}{2} \pi \left(\frac{\pi \alpha}{4\sqrt{2} \ \bar{v}} \right)^{2/3} = \pi b_1^2 \qquad (4.15)$$
$$b_1 \simeq (\alpha/\bar{v})^{1/3}$$

and $\sigma_{\rm F}$ is the cross-section corresponding to the action of the Fermi potential $V_{\rm F}$ alone in the range $b_1 < b < 2 n^2$. If one defines the Weisskopf radius corresponding to $V_{\rm F}$ alone :

$$b_2 = \frac{1}{2} \left(\frac{0.53 L}{n^3 \bar{v}} \right)^2 \tag{4.16}$$

it is straightforward to see that

$$\sigma_{\rm F} = 2 \pi b_2 (2 n^2 - b_1) \qquad \text{if} \quad b_2 < b_1 \quad (4.17a)$$

$$\sigma_{\rm F} = \pi (4 b_2 n^2 - b_2^2 - b_1^2) \quad \text{if} \quad b_2 > b_1 \,. \quad (4.17b)$$

The corresponding broadening rates K are plotted in figure 2, in the case of Cs lines broadened by Ar at 570 K (L=-1.7, $\alpha=11$, $v=2.9\times10^{-4}$, $b_1=34$).



FIG. 2. — Broadening rates K^{γ} of the caesium absorption lines in Ar. Experimental results $[5b] : \bigcirc 6 {}^{2}S_{1/2} \cdot n {}^{2}P_{1/2}$ components; • $6 {}^{2}S_{1/2} \cdot n {}^{2}P_{3/2}$ components. Theoretical estimates : (1) eqs (4.17) and (4.11); (2) same as (1) plus broadening by Cs [5c]; (3) same as (2) plus K_{sc}^{γ} (eq. (4.4)) for n > 30. (1 amagat = 2.69 × 10¹⁹ cm⁻³ (1 atmosphere at 0 °C), 1 cm⁻¹/amagat = 7.01 × 10⁻⁹ cm³ s⁻¹ = 1.14 atomic unit.)

All existing experimental results seem questionable : the old results of Fuchtbauer et al. [3] must probably be corrected as pointed out by Unsöld quoted by Alekseev and Sobelman (ref. [13] footnote (5)). The more recent results of Mazing et al. [5b] seem to have to be corrected for the broadening by Cs [5c], which for n > 20 can amount to 30% of the observed broadening; furthermore, it is not completely clear how the theoretical results presented in figure 2 of reference [5b] were derived; the value calculated in table 3 for $n \sim 30$, in agreement with the numerical value of $\gamma_{\rm p}$ in reference [13] p. 886, is about 20 % smaller than the value of reference [5b]. These experimental results are also plotted in figure 2. It is seen that the agreement with our theoretical estimates is quite reasonable if one takes into account the correction for broadening by Cs (curve 2) and a possible effect of K_{sc}^{γ} (eq. (4.4)) for large *n* (curve 3).

Accordingly, for small values of n^* , the broadening is mainly due to elastic scattering by the Fermi potential, and is dominated by the polarization potential for larger values of n^* . It should be noted that, as demonstrated by the results of Gounand *et al.* [26], the inelastic collisions can account for at most 2 % of the observed broadening for n < 20.

The difference observed by Mazing *et al.* [5*a-b*] between the shifts of the two components of the doublet of Cs perturbed by Ar for $n^* < 10.4$, seems harder to understand. Its sign is contrary to that expected from the second-order potential, which repels the levels of the doublet. Accordingly, a detailed study taking into account the exact potential and computing the exact collision matrix appears necessary.

4.3 BROADENING AND SHIFT BY ALKALIS. — The measurements performed mainly concern selfbroadening and shift : K*-K [5c, 6a], Rb*-Rb [6], Cs*-Cs [5]; and also K*-Cs [6a]. Earlier measurements by Kusch *et al.* [6a-b] must not be considered since, for Rb*-Rb, they differ from later results presented by the same group [6c] by as much as a factor 5. The other results are summarized in table IV. In all cases, the broadening and the shift appear nearly constant for 30 < n < 50. In the cases of K*-K and Rb*-Rb, the width decreases monotonically for 20 < n < 30, whereas the width and the shift of Cs*-Cs present well-behaved oscillations in the same range; the shift of K*-K exhibits a maximum at $n \sim 20$.

TABLE IV

Measured self-broadening and shift in atomic units $(6.126 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} = 0.874 \text{ cm}^{-1}/\text{amagat})$. Broadening cross-sections (eq. (4.11)) in atomic units (0.280 Å^2) .

It is seen from table IV that the results of Mazing and Serapinas [5] on K* and Cs appear hardly consistent with those of Wendt and Kusch [6c] on Rb, especially for large n. Accordingly, new experimental results are clearly needed. The theoretical situation is no clearer. As seen in tables III and IV, the polarization broadening is approximately four times smaller than the smallest experimental result [6c] (⁶). Accordingly, the main part of the broadening probably comes from the generalized Fermi potential, as pointed out by Presnyakov [19]. However, it seems hardly possible to attach a precise value to the expression for the broadening given by Presnyakov (ref. [19] eq. (33)). This result seems to have been deduced from the following model : the absorbing level p is taken as the superposition

$$|\psi_{0}\rangle = \frac{1}{\sqrt{2}}(|\varphi_{n}\rangle - |\varphi_{\rm NS}\rangle) \qquad (4.18)$$

where $|\varphi_n\rangle$ is the state defined by eq. (2.31) shifted by the amount $\Delta_n^{(1)}(R)$ (eq. (2.42)), and $|\varphi_{NS}\rangle$ is a non-shifted level. The elements of the S-matrix are respectively

$$\langle \varphi_{\rm NS} | S | \varphi_{\rm NS} \rangle = 1$$
 (4.19)

$$\langle \varphi_n | S | \varphi_n \rangle = \exp \left\{ -i \int_{-\infty}^{\infty} \Delta_n^{(1)}(R) dt \right\}$$

(4.20)

which yields eq. (33) of reference [19]. Accordingly, Presnyakov does not take into account the very large quantum defect of the p levels, and the presence of the n-2 other levels; nor does he allow for non-adiabatic effects.

Nevertheless the real situation can have a similarity with the Presnyakov model in the vicinity of the crossing of $|\varphi_n\rangle$ with the unshifted p level, which is then strongly mixed with $|\varphi_n\rangle$.

However, it is not impossible that the non-crossing region could account for the main part of the observed broadening. The corresponding cross-section is given approximately by

$$\sigma \simeq \int_{0}^{2n^2} b \, \mathrm{d}b \left| \int_{-\infty}^{\infty} \Delta_{nl\sigma} \, \mathrm{d}t \right|^2 \qquad (4.21)$$

where $\Delta_{nl\sigma}$ is given by eq. (B. 12), so that

$$\sigma \sim \int_0^{2n^2} b \ db/(n^6 \ v^2) \sim 2/(n^2 \ v^2) \ .$$
 (4.22)

This yields $\sigma = 3 \times 10^4$ for n = 32 and $\sigma = 1.2 \times 10^5$ for n = 16, which is smaller than but not incompatible with the experimental results of Wendt and Kusch for Rb [6c], when allowing for the roughness of this theoretical estimate. The measured shifts also appear compatible with the mean value of $\Delta_{nl\sigma}/3$ (eq. (B.12)), as discussed by Norcross [41].

Accordingly, it appears desirable to perform a careful calculation of the broadening and of the shift from the potential derived from the best estimates of the different scattering phase shifts. In this respect, for $n \leq 30$, it is probably well justified to restrict the calculation of the collision matrix to the three p sublevels, and to ignore the other channels. This calculation should thus be much simpler than the evaluation of transition probabilities and can hopefully provide a practical test of the theory of low energy electron scattering by alkalis.

5. Conclusion. — In the present work we have followed the usual procedure of the theory of thermal collisions and of line broadening; i.e. derivation of the adiabatic energy curves, and then of the collision *S*-matrix. It is obviously not the only one possible. In particular, the semi-classical methods developed by Percival *et al.* [1] for charged particles, and by Flannery [20] for neutral particles have proved very powerful. However, we think that the methods we have discussed are very well suited to the problems involving not too high *n* values, such as $n^2 v \leq 1$ (eq. (3.10)) i.e. $n \leq 30$.

In this domain, the expressions of section 2 (eqs.

^{(&}lt;sup>6</sup>) The agreement claimed by Wendt and Kusch [6c] between their results and the polarization broadening cannot be considered as relevant : the *Reinsberg* value drawn on figures 6 and 7 of reference [6c] does not correspond to the Reinsberg formula (eq. (8) of reference [6c] and numerical estimate p. 268 of reference [6b]), which itself overestimates the polarization broadening (see footnote (⁵)).

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(2.45-2.48)) should give reasonable estimates of adiabatic potential curves in terms of electronic scattering phase shifts, when the latter are accurately determined. However, it still remains to specify the exact limit of validity of such potentials for small n, and also for short ranges for any value of n. In these regions, it will probably be necessary to develop the method already used for lower levels, despite the difficulty due to the very large number of states involved. It is obvious that, in any case, the derivation of the potential is much more difficult for perturbation by alkalis than by noble gases.

As regards the calculation of transition probabilities by using these potentials, we believe that the distinction between quasi-elastic ($\Delta n^* \sim 0$) and inelastic $(\Delta n^* \gtrsim 1 \text{ for } n < 30)$ collisions is essential as attested by the order of magnitude of experimental results, and as predicted by the adiabatic criterion (3.10). The main difficulty is obviously the very large number of open channels which makes approximate methods absolutely necessary. For quasi-elastic collisions, the accuracy of the simple formula (3.39) is probably not much worse than other existing calculations [28, 29]. For weak collisions it should be carefully checked by comparison with numerical computations and improved as discussed in section 3.2b. The problem of strong collisions is certainly not so simple. Some efforts should be made to extend the usual approximate methods of collision theory in such a way as to solve it at a reasonable cost. Similar methods should also be applied to the calculations of inelastic collisions; however, a quantum treatment is then probably unavoidable, and a good knowledge of the shortrange potential is essential. Finally, inelastic transitions induced by alkalis require a special treatment because of the very long range of the interaction. It is possible that a semi-classical computation with a Landau-Zener approximation provides a reasonable accuracy.

The shift by noble gases of optical lines involving large n is very well described by the Fermi theory and its extensions. Their broadening is also well understood. For intermediate n, and also for large nin the case of perturbation by alkalis, a more elaborate theory is required. It is certainly easier than the computation of transition probabilities by collisions, because the levels studied are generally isolated. In most of the cases, inelastic collisions can therefore be neglected in the calculation of broadening, which is essentially determined by the quasi-elastic part of the S-matrix involving a very small number of states. Accordingly, when the potential is known, usual semi-classical methods can be directly used to compute the broadening and the shift, as well as the depolarization and the fine structure transfers. The rough estimates of section 4 show that most of the observed features can thus be explained, but not all of them, especially oscillations in the broadening of Cs by Cs.

Detailed numerical computations are obviously necessary.

It appears quite desirable to perform new experiments involving higher n values, other elements, other l values and other perturbers, in order to complete the experimental knowledge of transition probabilities and of broadening, and to extend them to the measure of depolarization and of fine structure transfers. It also seems necessary to confirm certain results already available, concerning in particular the broadening by alkalis. Finally, it should also be necessary to improve the theory of electron scattering by heavy alkalis, if one wants to derive a useful check of this theory from the study of Rydberg states.

Appendix A : Expansion of the resolvent in terms of the reaction matrix (eq. (2.8)). — We will show only that the r.h.s. of eq. (2.8) is formally equal to Gwhen all quantities appearing are numbers; and we will suppose that eq. (2.8) also holds when operators are involved. When G_A , G_{AR}^0 and R are numbers, the r.h.s. of eq. (2.8) may be written

$$X = G_{A} + G_{A} R \{ G_{A}^{-1} [1 - (G_{A} - G_{AR}^{0}) R] \}.$$
(A.1)

In the case of numbers, eq. (2.6) yields

$$1 + G_{AR}^0 R = V_B^{-1} R \tag{A.2}$$

so that

$$X = G_{\rm A} + G_{\rm A} R [G_{\rm A}^{-1} V_{\rm B}^{-1} R - R]^{-1}$$
(A.3)

and since

$$G_{\rm A}^{-1} = G^{-1} + V_{\rm B} \tag{A.4}$$

$$X = G_{\rm A} + G_{\rm A} V_{\rm B} G = G$$
. (A.5)

Appendix B : Diagonalization of the adiabatic potential. — 1. PURE HYDROGENIC LEVELS. — We assume that only s-wave scattering of e^- by B is important. Then, the only matrix elements of V to be considered relate two states $|\varphi_n\rangle$ and $|\varphi_n'\rangle$ defined by eq. (2.31), where n and n' are nearly equal. Accordingly, by an obvious generalization of eq. (2.42),

$$\langle \varphi_n | V | \varphi_n \rangle \simeq \Delta_n^{(1)}(R) = -\operatorname{tg} \eta_0'/(\pi n^3).$$
 (B.1)

Therefore, the secular determinant yielding the energies

$$E = -1/(2 n^2) + s$$
 (B.2)

of the adiabatic levels may be written

$$\begin{vmatrix} \Delta + p\alpha - s & \Delta & \Delta & \Delta \\ \Delta & \Delta + (p-1)\alpha - s & \Delta & \Delta \\ - & - & - & - \\ \Delta & \Delta & \Delta - s & \Delta \\ - & - & - & - \\ \Delta & \Delta & \Delta & \Delta - p\alpha - s \end{vmatrix} = 0$$
(B.3)

where Δ stands for $\Delta_n^{(1)}(R)$ and $\alpha = 1/n^3$.

Subtracting the middle column (p = 0) from each of the others yields

$$\Delta - s + 2\Delta s^2 \sum_{p=1}^{\infty} (s^2 - p^2 \alpha^2)^{-1} = 0 \quad (B.4)$$

or

$$\alpha \Delta^{-1} = \alpha/s - 2(s/\alpha) \sum (p^2 - s^2/\alpha^2)^{-1}$$
. (B.5)

The r.h.s. of eq. (B.5) just equals $\pi \cot (\pi s/\alpha)$ (see ref. [49] eq. (4.3.91)). One immediately deduces (see eq. (B.1))

$$s = -\eta'_0/(\pi n^3)$$
 (B.6)

2. INFLUENCE OF A NON-DEGENERATE LEVEL. — We consider the model where just one non-degenerate level *nl* is added to the hydrogenic levels. One has to add to the determinant (B.3) one line and one column, all terms of which equal $\sqrt{\Delta \varepsilon}$, where

$$\varepsilon = -2 \pi k \operatorname{tg} \eta_0' | \psi_{n i \sigma}(\mathbf{R}) |^2 = \Delta_{n i \sigma}^{(1)} (\mathbf{B}.7)$$

except the diagonal term equal to $\varepsilon - \alpha \delta - s$, where δ is the quantum defect of the *nl* level.

After subtraction of the middle column multiplied by $\sqrt{\epsilon/\Delta}$ from this additional column, eq. (B.4) becomes

$$- (\delta \alpha + s) \left[\Delta + 2 \Delta s^2 \sum_{p=1}^{\infty} (s^2 - p^2 \alpha^2)^{-1} - s \right] - s\varepsilon = 0 \quad (B.8)$$

or

$$- (\delta \alpha + s) \left[\alpha^{-1} \Delta \pi \cot g (\pi s / \alpha) - 1 \right] = \varepsilon \quad (B.9)$$

which yields eq. (2.48) on writing

$$s = -\alpha(\zeta + \delta) = -(\zeta + \delta)/n^3$$
. (B.10)

Eq. (2.48) may be written

$$\Delta_{nl\sigma} = -\zeta/n^3 = (2 \pi/k_R) |\psi_{nl\sigma}(\mathbf{R})|^2 / \\ /\{ \operatorname{cotg} [\pi(\zeta + \delta)] - \operatorname{cotg} \eta_0' \} \quad (B.11)$$

so that

$$\Delta_{nl\sigma} \simeq (2 \pi/k_R) |\psi_{nl\sigma}(\mathbf{R})|^2 / \{ \cot g \pi \delta - \cot g \eta'_0 \}$$
(B.12)

when η'_0 is very different from $\pi\delta$, which yields $\zeta \ll \delta$. And

$$\Delta_{nl\sigma} \simeq \pm \sin \eta'_0 \sqrt{2 |\psi_{nl\sigma}(\mathbf{R})|^2 / (n^3 k_R)} \quad (B.13)$$

in the vicinity of the level crossing $\eta'_0 = \pi \delta$.

Accordingly, there is an avoided crossing with a level distance of the order of $n^{-4} \sin \eta'_0$. The region of the crossing can be defined by a variation of η'_0 equal to

$$\Delta \eta'_0 = \pi |\zeta| = \pi n^3 \Delta_{nl\sigma} \sim n^{-1} \qquad (B.14)$$

where δ and η'_0 are assumed large.

It is difficult to estimate the corresponding ΔR , since it depends on $d\eta'_0/dR$. However, it seems that, in the case of large values of η'_0 , ΔR is more often $\lesssim n$ than of the order of n^2 .

Appendix C : Derivation of eq. (3.29). — At point **R**, the impulsion of the electron is (eq. (2.39))

$$k_R = \sqrt{2/R - 1/n^2} = \sqrt{p_R^2 + \overline{l}^2/R^2}$$
 (C.1)

where $\overline{l} = l + 1/2$. Its polar angles satisfy (see eq. (3.18))

$$\cos \theta_k = \pm \sqrt{\bar{l}^2 - m^2} / (Rk_R) \qquad (C.2)$$

$$\operatorname{tg} \varphi_k = \pm m/(Rp_R) \qquad (C.3)$$

it is thus straightforward to show that

$$\mathrm{d}\Omega_k = \sin \theta_k \,\mathrm{d}\theta_k \,\mathrm{d}\varphi_k = \frac{\bar{l}\,\mathrm{d}\bar{l}\,\mathrm{d}m}{\sqrt{\bar{l}^2 - m^2}\,R^2 p_R \,k_R} \,. \quad (\mathrm{C}.4)$$

By using the Stirling formula in eq. (2.36), it is easy to show that for large l, m and l - m:

$$Y_l^m(\pi/2, 0) \simeq \overline{l}/(\pi^2 \sqrt{\overline{l}^2 - m^2})$$
 (C.5)

) for l - m = 2 p. However, the mean value \overline{Y}_l^m of $Y_l^m(\pi/2, 0)$ is two times smaller since $Y_l^m(\pi/2, 0) = 0$ if l - m = 2 p + 1.

Combining eqs. (C.4) and (C.5) immediately yields eq. (3.29).

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