IONIZATION IN SLOW TWO-ATOM COLLISIONS

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The case is considered in which one energy level of a system AB crosses an infinite system of parallel levels adjacent to the ground state of the system AB^+. A general mathematical model is employed which yields the wave function, in the form of a contour integral, for the nonstationary problem of the interaction between a system of parallel states and a state that intersects this system. The probabilities of ionization and of the formation of highly excited states are derived, and the smooth transition from the discrete spectrum (excitation) to the continuous spectrum (ionization) is traced. The limits of applicability of the theory are considered.

1. INTRODUCTION

LET us consider a reaction of the type

$$A + B \to A + B^+ + e. \qquad (1)$$

Prior to the collision each atom can exist in its ground state or an excited state. We shall assume, however, that the excitation energy is then below the ionization potential, so that the ionization mechanism proposed by Penning (see [1], for example) is not operative in the present case. If we neglect the interaction between the initial state of the AB system and the states in which one electron is free or nearly free, we may find as a result that when the atoms are closer than some critical distance R_0 the energy of this state exceeds the ground-state energy of the system $A + B^+$, i.e., a bound electronic state will exist for $R < R_0$ against the background of the continuous energy spectrum of the AB system. We can then expect that under certain conditions the ionization cross section in even slow collisions will be of considerable magnitude and will be comparable with the geometric cross section πR_0^2. These considerations were applied to the simplest case of collision between a negative ion and an atom in [2,3]. Here the bound state can actually disappear by merging with the continuous spectrum. If we know the shapes of the AB^- and AB potential curves at the point of merging we can calculate the electron energy distribution, the detachment probability etc. In this case a weakly bound electron is in the field of the two atoms A and B, which falls off rapidly at large distances. The ionization problem is more complicated by the fact that at large distances the ejected electron is in the effective Coulomb field of the system AB^+. The continuous spectrum will then be accompanied by an infinite number of bound states with arbitrarily low binding energies. The corresponding energy levels of the system AB will lie almost parallel to the AB^+ ground state but will be crowded below the latter (Coulomb crowding). In describing the process we must obviously take all these levels into account; therefore we must consider both ionization and the probability that highly excited states of the atom B will be formed. According to the von Neumann—Wigner theorem, the initial state cannot intersect each state in an infinite set of Coulomb-crowded states; therefore after taking account of the interaction the general appearance of the levels in the vicinity of the point R_0 will be represented approximately by Fig. 1.

In our present problem we must therefore con-

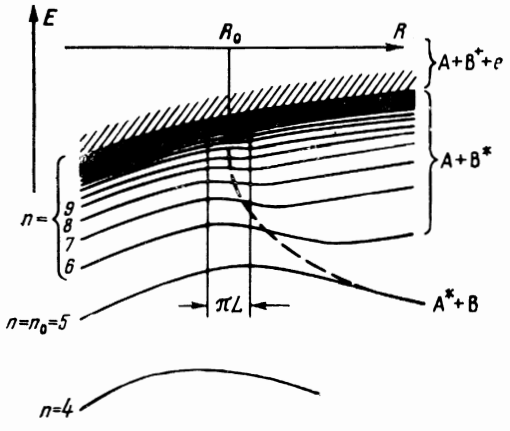

FIG. 1

sider the interaction of one state with an infinite number of parallel states and with a continuous spectrum. The mathematical apparatus enabling us to describe this interaction has been explained in [4], and the simplest examples of its application are given in [2,3]. We shall assume that the kinetic energy of the atoms is considerably above the ionization potential. We can then treat the motion of the nuclei classically and solve the corresponding nonstationary problem. In a quantum description of the nuclear motion, which is required when the nuclear energy is near the threshold, the given method can be used if the system of parallel levels is horizontal or only slightly inclined; this problem will not be considered here.

2. INITIAL APPROXIMATION

Our problem requires a time-independent operator H_0 describing the system of parallel levels and the continuous spectrum of the AB system. The simplest choice for H_0 will obviously be the energy operator of a particle in the Coulomb field of the system AB^+. The state corresponding to the initial level will be represented by a function φ. Assuming that during the entire process R varies very little, remaining close to R_0, we can take φ to be time-independent. If, finally, it is assumed that in the absence of an interaction the level corresponding to the initial state φ depends on time linearly, the wave function of the nonstationary problem can be represented by a contour integral:

$$|\psi\rangle = N\int_c (H_0-E)^{-1}|\varphi\rangle \exp\left(iA\int^E \langle\varphi|(H_0-E')^{-1}|\varphi\rangle\, dE' - iEt\right) dE, \qquad (2)$$

and the determination of transition probabilities reduces to an investigation of the properties of $\langle\varphi|(H_0-E)^{-1}|\varphi\rangle$. The residues at the poles for $E<0$ and the jump Δ of the imaginary part at the cut for $E>0$ must be determined; the energy of the system AB^+ is taken to be zero. The Green's function for the motion of a particle in a Coulomb field is [5]

$$G(\mathbf{r},\mathbf{r}',E) = \frac{\Gamma(1-n)}{\pi(x-y)}\left[W_{n,1/2}\left(\frac{x}{n}\right)M'_{n,1/2}\left(\frac{y}{n}\right) - W'_{n,1/2}\left(\frac{x}{n}\right)M_{n,1/2}\left(\frac{y}{n}\right)\right],$$

$$x = r + r' + |\mathbf{r}-\mathbf{r}'|, \quad y = r + r' - |\mathbf{r}-\mathbf{r}'|, \quad n = (-2E)^{-1/2}, \qquad (3)$$

where the functions $M_{\lambda_1\nu}$ and $W_{\lambda_1\nu}$ are related to confluent hypergeometric functions and are defined in [6]. For the case of a pure Coulomb field in H_0 the problem thus reduces finally to quadratures. However, this solution is not especially interesting, because a real field is of the Coulomb type only at large distances and the spectrum of our system coincides with that of a pure Coulomb field only for low energies, i.e., for large n. In order to make the accuracy of the solution consistent with the accuracy of the initial approximations we use the asymptotic form of the Green's function for large n, obtained by using the asymptotic representations of $M_{\lambda_1\nu}(x/\lambda)$ and $W_{\lambda_1\nu}(x/\lambda)$ with large first indices.[7] [1)] We thus obtain

$$G \sim \frac{1}{x-y}\left(\frac{\partial}{\partial x}-\frac{\partial}{\partial y}\right)(xy)^{1/2}J_1(2\sqrt{y})[\operatorname{ctg}\pi n\cdot J_1(2\sqrt{x}) + N_1(2\sqrt{x})], \qquad (4)^*$$

where J_1 and N_1 are Bessel and Neumann functions. The term containing N_1 is entirely independent of n, approaches infinity as $|\mathbf{r}-\mathbf{r}'|$ approaches zero, and is of no interest here. Equation (4) shows that the energy and coordinate variables are separated in the remaining, regularized, part of the Green's function, so that for large n (small E) we have the matrix element

$$\langle\varphi|G|\varphi\rangle \sim -D\operatorname{ctg}\pi n, \quad D>0, \qquad (5)$$

and the characteristics of the system are thus reduced to the single constant D. Equation (4) is valid for not too large values of r and r', when the points $\mathbf{r}$ and $\mathbf{r}'$ are located far from the boundary of the classically permissible region for a given value of E. The equation is inapplicable for negative n, since the true Green's function has no poles (but only a logarithmic branch cut) for negative n. However, the equation does hold true in the right-hand half-plane of n (the physical region of E), including the imaginary axis (positive E).

The asymptotic form (4) reflects the physical fact [8] that far from the turning point all wave functions of highly excited states differing in the value of n but identical in l and m are very similar, differing only in their normalizing factors. The factor by which cot πn is multiplied is proportional to the density matrix for the set of

[1)] We note that the formulas in [7] which we must use here contain errors.

*ctg ≡ cot.

Coulomb functions that are degenerate in l and m and have zero energy.[9]

3. TRANSITION PROBABILITIES

The wave function that reflects correctly the contributions of highly excited states will be

$$|\psi\rangle = N\int_c G|\varphi\rangle \exp\left(-iB\int^E \operatorname{ctg}\pi(-2E')^{-1/2}\,dE' - iEt\right)dE, \tag{6}$$

where the constant $B > 0$ includes both D and the constant A in (2) that characterizes the time rate of the level represented by φ.

The residues of cot πn are

$$R_n = \frac{1}{\pi}\frac{dE}{dn} = \frac{1}{\pi n^3}, \tag{7}$$

and the jump of the imaginary part at the branch cut is

$$\Delta = 2\operatorname{cth}\pi\nu, \quad \nu = (2E)^{-1/2}, \tag{8}*$$

or simply $\Delta \approx 2$ for the small values of E that are required to render this approximation valid.

With the aid of the general formulas in [4] we obtain the simplest result for the total probability W(E) of transitions of the system to all states having energies above E. For $E = E_n = -2/n^2 < 0$ we have

$$W(E_n) = W_0\exp\left(-2\pi B\sum_{k=n_0}^{n} R_k\right)$$

$$= W_0\exp\left(-2B\sum_{k=n_0}^{n} k^{-3}\right) \tag{9}$$

and for $E > 0$ (the continuous spectrum),

$$W(E) = W_0\exp\left(-2\pi B\sum_{k=n_0}^{\infty} R_k - B\int_0^E \Delta(E')\,dE'\right)$$

$$= W_0\exp\left[-2B\left(E + \sum_{k=n_0}^{\infty} k^{-3}\right)\right]. \tag{10}$$

The summations in these formulas begin at the value n_0 for which our approximation becomes valid. W_0 is the probability that the system reaches the level $E_0 = E(n_0)$ when the atoms come into proximity. This probability depends on the detailed behavior of the levels for small n and cannot be calculated generally.

When R_0 is sufficiently large, then for small n we are in the sub-barrier region, the residues R_n are exponentially small and can be neglected, and n_0 is given by $E_0 = (2n_0^2)^{-1} \approx R_0^{-1}$. This can also be done when the electron detachment energy prior to a collision is small (for example, if atom A or B is in an excited state). Then the initial level does not approach the levels for small n and the probability of transitions to the latter is small. The order of magnitude of E_0 then depends on this detachment energy. Thus, under conditions that are favorable for ionization W_0 can be at least a little smaller than unity and E_0 can be small, of the order of one electron volt or less ($n_0 \sim 4 - 5$).

Introducing the function

$$F(E) = \begin{cases} E & E > 0, \\ \sum\limits_{k \geqslant (-2E)^{-1/2}}^{\infty} -k^{-3}, & E < 0, \end{cases} \tag{11}$$

which is plotted in Fig. 2, we combine (9) and (10) to give

$$W = W_0\exp\left[-2B(E_0 + F(E))\right]. \tag{12}$$

The figure shows that the definition F(E) = E can be extended approximately to small negative values of E, where the stepped character of F(E) is almost unobservable. We then obtain

$$W(E) = W_0\exp\left\{-2B(E_0 + E)\right\}, \tag{13}$$

which is sufficiently accurate for our approximation in both the discrete and continuous spectra.

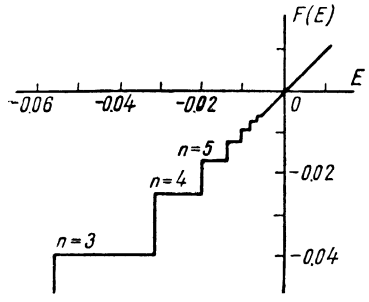

FIG. 2

We now investigate the constant B in (13), making use of the fact that the saddle points in (2) and (6) coincide with the instantaneous eigenvalues of the energy operator.[4] From (6) we obtain

$$B\operatorname{ctg}\pi n + t = 0,$$

$$n = -\frac{1}{\pi}\operatorname{Arcctg}\frac{t}{B} = -\frac{1}{\pi}\operatorname{Arcctg}\frac{R_0 - R}{vB}, \tag{14}*$$

where v is the velocity of internuclear approach at R_0.

We find that if the variable n is used instead of E, all n(R) curves for highly excited states

*cth ≡ coth.

*Arcctg ≡ $\cot^{-1}$.

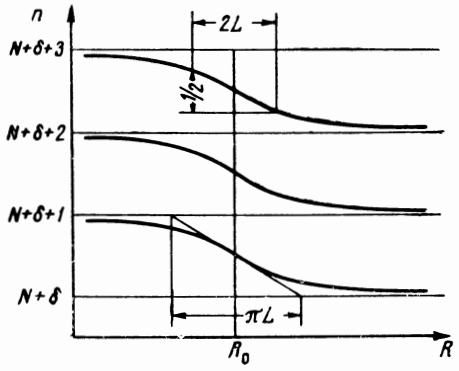

FIG. 3

behave in an identical manner around R_0 (Fig. 3). When a quantity L having the dimension of a length is introduced through the formula vB = L, its significance is shown by Fig. 3: 2L is the interval of R in the vicinity of R_0 within which the principal quantum number n of highly excited states changes by the amount 0.5. The constant L can also be expressed through the derivative with respect to R, at the point R_0, of the squared modulus of the projection of φ on the subspace of the eigenfunctions for zero energy. If this is too difficult to calculate, then L remains the only undetermined constant characterizing the relative distribution of the probabilities of excited states and ionization with different energies of the ejected electron.

We obtain finally, in arbitrary units,

$$W(E) = W_0 \exp\left[-\frac{2L}{\hbar v}(E_0 + E)\right], \qquad (15)$$

which is valid in the interval $-E_0 \lesssim E \lesssim E_0$. L is associated with the behavior of the system near E = 0 and $R = R_0$. The other parameters depend on its behavior far from the boundary of the continuous spectrum for $R > R_0$. The total ionization probability is obviously

$$W(0) = W_0 \exp\left(-\frac{2LE_0}{\hbar v}\right). \qquad (16)$$

4. DISCUSSION

The foregoing results hold true only if the values of $\exp(-2L/n^3v)$ for the probabilities of different transitions are all close to unity. In the opposite case, for sufficiently small n and v, we must also take into account the retrograde motion of the point R_0 when the two atoms move apart. This factor will be disregarded since it has little effect on the filling of levels in the discrete spectrum. For the continuous spectrum we must determine to what degree the wave packet formed at R_0 can spread in a time T during which the interatomic separation is $R < R_0$. This spreading destroys the coherence of the different wave-packet components. Proceeding as in [2], we obtain the probability of recapture

$$w = \left|\frac{2L}{v}\int_0^\infty \exp\left[-\left(\frac{2L}{v} + iT\right)E\right]dE\right|^2 = \left(1 + \frac{v^2T^2}{4L^2}\right)^{-1}. \qquad (17)$$

Since vT is comparable with R_0 in order of magnitude, the condition $w \ll 1$ for the applicability of the theory reduces to the single requirement $L \ll R_0$, i.e., n should change by one-half within an interval of R that is small compared with R_0. However, the results will evidently be qualitatively true also when R_0 exceeds L only slightly.

Equation (15) may appear almost obvious, since it agrees with the formulas obtained customarily for the probabilities of nonadiabatic transitions. However, the simplicity of this formula is based largely on the character of the Coulomb field; in other cases that appear simpler at first glance,[2,3] we obtain more complex formulas. For the collisions $A^- + B$ and $A^- + A$ the distributions of low-energy ejected electrons were proportional to $E^{1/2}$ and $E^{3/2}$, respectively. Here the distribution function differs from zero at the threshold (E = 0), after which it decreases monotonically with increasing energy. This results from the fact that the Coulomb crowding of energy levels around E = 0 increases the number of states in this region and leads to a smooth transition between the discrete and continuous spectra (which is reflected in the form of the function F in Fig. 2). Similar results are well known for other problems in which the Coulomb field has an essential role, e.g., for the ionization of an atom or ion by electron impact, for the excitation functions of ions etc.[10]

An additional merit of Eq. (15) lies in the fact that in the present case the characteristic length in the adiabatic criterion is identical for all highly excited states (E < 0) and for the continuous spectrum (E > 0), and is related in a very simple manner to the behavior of the energy levels in the vicinity of $R = R_0$ and E = 0.

The presence of a Coulomb field, although it introduces a formal complication, simplifies the problem considerably and leads to the simplest formula, Eq. (15). The simplification lies in the fact that extremely small modifications of the theory are required when the initial state possesses higher symmetry (t = 0 etc.). The character of the Coulomb crowding of levels does not change, and we obtain different expressions only for the coordinate part of the Green's function (4), i.e., only the method of determining B is modified.

The Coulomb field influences the entire system so strongly that the consideration of symmetry, leading only to the exclusion of a few values of the quantum numbers l and m, has little effect on the final result.

Among all states for different l and m accompanying a given value of the principal quantum number n, the only excited state is the projection of the state φ on the subspace of states at the given energy level E_n. All other states can be considered orthogonal to φ and are not excited in our approximation.

Any difference between the effective potential well for H_0 and a Coulomb well at small distances will affect mainly the form of the Green's function at large $|E|$ (small $|n|$). As we know, this effect can be taken into account for large n by introducing the so-called quantum defect $\delta(n)$ that approaches a constant value δ as $n \to \infty$ and that characterizes the deviation from integers for the principal quantum number n of highly excited levels. Then the matrix element for large n will be

$$\langle\varphi|G|\varphi\rangle \sim B \operatorname{ctg} \pi(n-\delta), \tag{18}$$

and all our results remain valid with n differing from integers by the amount δ.

The deviation from a Coulomb field and from spherical symmetry at short distances removes the degeneracy of the energy levels with respect to l and m. Our basic equations remain unchanged. The function F will have a larger number of steps for negative E, so that its replacement by a linear function will be all the more justified in this region. Of course, the size of the steps can vary greatly from level to level, leading to very different occupation probabilities for the different states (some of which can be nearly orthogonal to φ), but an averaged Eq. (15) remains valid.

5. THE SIMPLEST SPHERICALLY SYMMETRIC MODEL

The solution becomes especially simple when $R_0 = 0$ and φ is a δ function, i.e., when the Coulomb field is accompanied by a potential well of small radius and variable depth at the coordinate origin. Then the regular part of the Green's function is easily calculated from (3) for $r = r' = 0$, using expansions of M and W for small values of x and y:[7]

$$\begin{aligned} G_{reg}(0,0,E) &= \pi^{-1}\left[\ln n - \Psi(1-n) - (2n)^{-1}\right] \\ &= \pi^{-1}\left[\ln n - \Psi(n) - \pi \operatorname{ctg} \pi n - (2n)^{-1}\right], \end{aligned} \tag{19}$$

where Ψ is the logarithmic derivative of the Γ function. The residues of Greg in the E plane for integer n are exactly $R_n = (\pi n^3)^{-1}$ and the jump Δ of the imaginary part is

$$\Delta = 2/(1 - e^{-2\pi\nu}), \quad \nu = +(2E)^{-1/2}. \tag{20}$$

The same values can be derived directly from the expressions for normalized functions pertaining to both the discrete and continuous spectra:

$$R_n = |\psi_{n,0,0}(0)|^2, \quad \Delta = \frac{1}{\pi}|\psi_{E,0,0}(0)|^2.$$

For large n, Ψ can be represented asymptotically.[11] We then obtain

$$G_{reg} = -\operatorname{ctg} \pi n + O(1/n^2), \tag{21}$$

which is valid everywhere except in a narrow sector cutting out the negative real semiaxis. Therefore we obtain (9), as previously, for the discrete spectrum, except that now $n_0 = 1$ and the results hold for all, even small, n. For the continuous spectrum we obtain

$$W(E) = \exp\left\{-2B\left[\zeta(3) + \int_0^E \left(1 - \exp\frac{-2\pi}{\sqrt{2E'}}\right)^{-1} dE'\right]\right\}, \tag{22}$$

where

$$\zeta(3) = \sum_{n=1}^{\infty} n^{-3} \approx 1.202,$$

in agreement with our previous result at low energies. At high energies ($n \ll 1$) we obtain $\Delta \approx (2\pi)^{-1}(2E)^{1/2}$, which is the same as for a free particle. In other words, the Coulomb crowding of levels ceases to play a part at high energies, and the spectrum becomes the same as in the case of short-range forces when the single bound state disappears, having merged with the continuous spectrum.[2]

The foregoing result is of no practical interest because for $n \lesssim 1$ a real potential well cannot be considered to have a short range and the distribution function will differ in this region. It can be stated, however, that the distribution function for large n will fall off more rapidly than Eq. (15) indicates.

We note in conclusion that we have not considered the possibility that a quasistationary state of the AB system may be formed for $R < R_0$. This would greatly reduce the probability of wave packet breakdown for $R < R_0$ and would increase the probability of wave packet formation. This means that the constant L in the formula can be very small, so that, although our theory would be true, as previously, for small E, there would exist only a very low probability that following

the collision the electron would have a low energy in the interval $-E_0 < E < E_0$. A larger fraction of the electrons would be ejected with high energies and their distribution could be determined only by investigating the process in greater detail. In this case the low-energy electrons could be dominant only in very slow collisions. It is evident from the same considerations that the theory has little application to fast collisions. Our treatment is quasiadiabatic; it is based on the wave functions of the instantaneous energy operator in the nonstationary problem, and is obviously inapplicable when the velocity of the nuclei approaches the velocity of the electrons in the initial (but not in the final) state.

Our formulas could be improved easily by averaging over different impact parameters as was done in [3] for the problem of electron detachment from a negative ion. However, such averaging would affect the result only slightly and will not be presented here.

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