DEPOLARIZATION OF EXCITED ATOMS IN A MEDIUM

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It is shown that the probability for transition between two states with different magnetic quantum numbers depends on the interference of the states arising for various directions of the relative collision velocity **v**. The interference does not vanish on averaging, even over a spherically symmetric distribution of the particles with respect to velocity. The cross section for the depolarization of the P-state of an atom is calculated for collision of the atom with a charged particle moving along a classical trajectory. The cross section is inversely proportional to the absolute value of the collision velocity. A model solution of the problem is considered for interactions of the BR^{-n} or $Be^{-\gamma R}$ type. The resonance case of collision between an excited atom and a similar atom in the ground state is also considered.

INTRODUCTION

THE question of the change of the direction of the angular momentum of an atom in a medium is of interest from several points of view. The rate of random rotation of the momentum must be known in investigations of the interaction between polarized light and a gas. Collisions produced in a gas by an excited atom that absorbs a polarized quantum cause the re-radiated photon to have a variable polarization.

One of the basic applications of this process is the interpretation of experiments aimed at observing the polarization of excited atoms produced by electron impact. Secondary collisions of the excited atoms, both with unexcited gas atoms and with electrons of the exciting beam, can greatly distort the picture, in view of the fact (which will be demonstrated below) that the depolarization cross sections are very large.

It is also of interest to know the population of highly excited atomic states with different values of the magnetic quantum number in studies of ternary recombination of a dense plasma.

From the theoretical point of view, this problem is of interest because the probability of rotation of the angular momentum depends not only on the magnitude but also on the direction of the relative collision velocity **v**, since the atom has an angular momentum in both the initial and final states.

In order to compare the result of collisions with different directions of **v**, it is necessary to project the wave function (and not the square of its modulus) on a direction that is independent of **v**. Therefore the resultant transition probability will depend also on the difference between the phases of the states with different projections of the angular momentum, a difference which builds up as a result of the collisions.

We consider in this article the change in the projection of the angular momentum $l = 1$ (P-state) of a spinless atom as a result of collision with a charge or with other particles.

DEPOLARIZATION BY COLLISION WITH CHARGES

We consider transitions between three P-states

$$\psi_x = \sqrt{3/4\pi}\,Q(r)\sin\theta\sin\varphi, \quad \psi_y = \sqrt{3/4\pi}\,Q(r)\sin\theta\cos\varphi, \quad \psi_z = \sqrt{3/4\pi}\,Q(r)\cos\theta, \tag{1}$$

brought about by a moving charge, and neglect the connection between these transitions and all other states of the atom. Here θ and φ are the spherical angles of the bound electron, and Q(r) is its radial wave function. We use an atomic system of units: $e^2 = m = \hbar^2 = 1$. Assume that initially we have only the state ψ_z, which goes over under the influence of the perturbation into a combination of all three functions (1). Let the perturbing unit charge move on a straight-line classical trajectory with impact parameter ρ. Expanding the solution of the time-dependent Schrödinger equation with Hamiltonian

$$\mathcal{H} = H_0 + V(\mathbf{R}, \mathbf{r}), \quad V(\mathbf{R}, \mathbf{r}) = \frac{1}{|\mathbf{R}-\mathbf{r}|} - \frac{1}{R} \tag{2}$$

(**R**—radius vector of the incoming charge, H_0—Hamiltonian of the isolated atom), we get a system of three differential equations

$$i\frac{dA_n}{d\Phi} = \sum_m \frac{V_{mn}}{\dot{\Phi}} A_m \quad (m, n = 1, 2, 3), \tag{3}$$

under the assumption that the states (1) are degenerate. Here Φ is the trajectory angle between ρ and R, $\dot{\Phi} = \rho v/R^2$. The matrix element V_{mn} depends in a rather complicated manner on Φ and on the direction of **v**, so that in general it is impossible to solve the system (3).

The problem can be greatly simplified by using the symmetry of the complete Hamiltonian (2) with respect to reflections in the trajectory plane. If we introduce a Cartesian coordinate system with z axis parallel to **v** and with axis y parallel to ρ, then ψ_z and ψ_y do not change upon reflection, and ψ_x reverses sign. Consequently, an equation for ψ_x can be separated from the system of equations (3), and ψ_y and ψ_z remain coupled. The system of three equations (3) is transformed into a system of two equations for ψ_y and ψ_z and an independent equation for ψ_x.

The fact that for each direction of v it is necessary to introduce a separate system of coordinates will be accounted for in the following fashion. We introduce a new system of coordinates x′y′z′ with a z′ axis which is the same for the entire gas, i.e., independent of **v**. This is just the system in which the initial condition is specified. In order to be able to operate in a variable coordinate frame, it is necessary to project the initial condition in this system, solve (3) in this system with the obtained initial conditions, and to reproject the result in the system x′y′z′. The projection is with the aid of the well-known rotation operators that align the xyz system with x′y′z′. It is known[1] that the function $\psi_{jm}(x, y, z)$ is transformed in this case in terms of the functions $\psi_{jm'}(x', y', z')$ with different m′ and with the same angular momentum j. This makes it possible to draw the following general conclusion: The transition probabilities $W^{ll'}_{mm'}$ with specified m and m′ depend on the direction of v, but the sum $\sum_{mm'} W^{ll'}_{mm'}$ does not depend on the direction of v.

The alignment of x′y′z′ with xyz can be realized by three rotations through Euler angles[1]: rotation through the angle ζ_1 until the y′ axis coincides with the projection of **v** on the plane z′ = 0, rotation through the angle α until z′ coincides with the direction of **v**, and finally rotation through the angle ζ_2 around the new direction of the z′ axis until the y′ axis coincides with ρ. The transformation of functions with angular momentum $l = 1$ under such rotations is best determined as a result of these three successive planar rotations. Using the well-known formulas for coordinate transformation in planar rotations, we obtain, for example, for rotation through an angle ζ_1 around the z′ axis:

$$\psi_x = \psi_{x'}\cos\zeta_1 + \psi_{y'}\sin\zeta_1, \quad \psi_y = \psi_{y'}\cos\zeta_1 - \psi_{x'}\sin\zeta_1, \quad \psi_z = \psi_{z'}. \tag{4}$$

If, for example, we have a state $\psi_{z'}$ at first, then in the variable system of coordinates the initial condition is

$$\psi|_{t=-\infty} = \psi_{z'} = \psi_z\cos\alpha - \psi_y\cos\zeta_2\sin\alpha + \psi_x\sin\zeta_2\sin\alpha. \tag{5}$$

The solution obtained with such a combined initial condition is the same linear combination of solutions with unity initial conditions (linearity of the Schrödinger equation). Solving (3) and retransforming to the system x′y′z′, we get

$$\psi|_{t=+\infty} = A_z{}^z\psi_{z'} + A_y{}^z\psi_{y'} + A_x{}^z\psi_{x'},$$

$$A_z{}^z = c_z{}^z\cos^2\alpha + c_x{}^x\sin^2\alpha - (c_z{}^y + c_y{}^z)\sin\alpha\cos\alpha\cos\zeta_2 + (c_y{}^y - c_x{}^x)\sin^2\alpha\cos^2\zeta_2, \tag{6}$$

where c^{ν}_{μ} are the solutions of (3) for $t = +\infty$ (after the charge has passed by) in the coordinate system xyz, the upper index denoting solutions with definite initial condition $\psi_{t=-\infty} = \psi_{\nu}$. The remaining coefficients A^z_y and A^z_x, which have not been written out here to save space, do not enter in the result, since the depolarization probability is $1 - |A^z_z|^2$. This probability, as can be seen from (6), depends both on the moduli and on the phases of all three coefficients c, and this dependence does not vanish upon averaging over the angles α and ζ_2 (which will be effected below). Expression (6) does not depend on ζ_1 simply because $\psi_z \sim \cos\theta$ does not change upon rotation around the z axis.

Expanding the interaction $V(\mathbf{R}, \mathbf{r})$ in reciprocal powers of R, we find even in first approximation of perturbation theory that the principal role is assumed by the interaction between the charge and the quadrupole

$$V = \frac{r^2}{R^3}P_2(\cos\mathbf{r}\hat{\mathbf{R}}), \tag{7}$$

where $P_2(x) = (3x^2 - 1)/2$ is the second Legendre polynomial. The second approximation (polarization) and higher approximations are neglected, since the cross sections are very large.

It will be necessary in what follows to introduce a third coordinate system x″y″z″, with z″ axis directed along **R** and rotating together with R. The transformation from xyz to x″y″z″ is effected with the aid of formula (4). Expanding the wave function in terms of $\psi_{\nu''}$ in the x″y″z″ system, we obtain the following equation (a_ν are the expansion coefficients)

$$\frac{da_\nu}{d\Phi} + \sum_{\mu} a_\mu\left(\frac{d}{d\Phi}\right)_{\nu\mu}\exp\left\{-i\int_{\pi}^{\Phi}\frac{E_\nu - E_\mu}{\dot{\Phi}}d\Phi\right\} = 0. \tag{8}$$

The complete Hamiltonian (2) in this system of functions is diagonal, and therefore the energy levels are

$$E_x = E_y = E_0 + V_0, \quad E_z = E_0 + V_1,$$
$$V_0 = \frac{2}{5}\frac{\langle r^2\rangle}{R^3}, \quad V_1 = -\frac{1}{5}\frac{\langle r^2\rangle}{R^3}. \tag{9}$$

Let us write down now the system (3) in explicit form. It is most convenient to calculate the matrix elements in the x″y″z″ system. If the complete function is sought in the form

$$\Psi = c_x\psi_x + c_y\psi_y + c_z\psi_z, \tag{10}$$

then the system of equations becomes

$$i\frac{db_z}{dt} = \frac{V_0 - V_1}{2} b_z \cos 2\Phi + \frac{V_1 - V_0}{2} b_y \sin 2\Phi.$$
$$i\frac{db_y}{dt} = \frac{V_1 - V_0}{2} b_y \cos 2\Phi + \frac{V_1 - V_0}{2} b_z \sin 2\Phi, \tag{11}$$
$$c_{z,y} = b_{z,y}e^{-2iq/3}, \quad c_x = c_x^{(0)}e^{4iq/3}, \quad q = 3\langle r^2\rangle/10\rho^2 v.$$

For numerical calculations, it is convenient to go over in the system (11) to a new variable $\xi = \cos\Phi$, and then

$$idb_z/d\xi = q[(2\xi^2 - 1)b_z - 2\xi\sqrt{1-\xi^2}\, b_y],$$
$$idb_y/d\xi = q[-2\xi\sqrt{1-\xi^2}\, b_z - (2\xi^2 - 1)b_y]. \tag{12}$$

It is seen from (11) and (12) that $b_y^y = (b_z^z)^*$ and $b_z^y = -(b_y^z)^*$. With the aid of these relations and (6) we obtain, after averaging over the angles, the values of the cross section and probability of depolarization (assuming the distribution with respect to v to be spherically symmetrical),

$$\sigma = 2\pi\int_0^\infty W(\rho)\rho d\rho = \frac{3\pi\langle r^2\rangle}{10v}\int_0^\infty \frac{W(q)}{q^2}dq, \tag{13}$$

$$W = \frac{4}{15}\{2[1 - (\mathrm{Re}\, b_z^z)^2] - (\mathrm{Im}\, b_z^z)^2 - (\mathrm{Im}\, b_y^z)^2$$
$$+ 1 - (\mathrm{Re}\, b_z^z)\cos 2q\} \tag{13′}$$

In the limit as $q \to 0$ or $\rho \to \infty$ we obtain by perturbation theory from (12) that $W(q) \sim q^2$, so that the integrand in (13) is finite in this limit.

It is interesting to trace the second limit $q \to \infty$ or $\rho \to 0$. In this case, the ratio of the splitting of the levels (9) to angular velocity $\dot\Phi$ tends to infinity and, as follows from (8), there are no transitions between the quasimolecular states, i.e., states in the x″y″z″ system. It now follows from the transformation formulas (4) that there are likewise no transitions between the atomic states in this system. Indeed, after passage of the charge the z″ axis is rotated by π, i.e., ψ_z only reverses sign. The coefficients c_μ^ν can be obtained in this limit from the equation (8), and are equal to

$$c_z^z(\Phi = 0) = -\exp\{-i8q/3\}, \quad c_y^z(0) = c_x^z(0) = 0. \tag{14}$$

Substituting this in (13′) we find that W differs from zero as a result of the interference terms, and is equal to

$$W(q) = \frac{4}{15}\left[2 + \cos\frac{8q}{3}\left(\cos 2q - \cos\frac{8q}{3}\right)\right]. \tag{15}$$

We see that the probability (13′) is not equal to the probability of depolarization $1 - |b_z^z|^2$, which was determined directly in the xyz system.

Since in this problem the Schrödinger equation (3) and (12) depends only on one parameter q, the dependence of the cross section on the velocity can be established immediately[2]. If $V \sim R^{-n}$, then $\sigma \sim v^{2/(1-n)}$. To determine the constant in this dependence, the system (12) was solved with an electronic computer and it was found that

$$\int_0^\infty W(q)\frac{dq}{q^2} = 1{,}25. \tag{16}$$

The mean-squared radius $\langle r^2\rangle$ of, say, the 2^1P state of helium can be assumed equal to that of hydrogen[3], $\langle r^2\rangle = 30$. The cross section (13) thus turns out to be very large at small collision velocities v.

MODEL SOLUTION OF THE PROBLEM IN COLLISIONS OF OTHER PARTICLES

In calculating the cross section corresponding to the change in the direction of the angular momentum of the atom, it is convenient to rewrite (8) in a rotating coordinate system. We introduce new variables

$$c_z = a_z\cos\Phi + a_y\sin\Phi, \quad c_y = -a_z\sin\Phi + a_y\cos\Phi.$$

such that $a_z = c_z\cos\Phi - c_y\sin\Phi$ and $a_y = c_z\sin\Phi + c_y\cos\Phi$. We use these variables to rewrite (8) in the form

$$i\frac{dc_z}{dt} = \frac{V_0 - V_1}{2}c_z - i\dot\Phi c_y, \quad i\frac{dc_y}{dt} = \frac{V_1 - V_0}{2}c_y + i\dot\Phi c_z. \tag{17}$$

The employed change of variable corresponds to projecting the angular momentum of the atom in the rotating coordinate system on the axis joining the nuclei. As follows from the system (17), if the rotation of the axis of the quasimolecule is slow, $\dot\Phi \ll (V_0 - V_1)/2$, then the angular momentum of the atom precesses about the axis of the quasimolecule. In the opposite limiting case $\dot\Phi \gg (V_0 - V_1)/2$, the coupling between the axis of the quasimolecule and the angular momentum of the atom is weak, so that no change in the direction of the angular momentum of the atom takes place under these conditions.

Using the foregoing analysis, let us determine the cross section for the change in direction of the

angular momentum of the atom in the case when the atom collides with another atomic particle. We use the following model: We replace the system (17) by a model system such that when $|V_0 - V_1| \geq 2k\dot{\Phi}$ we neglect the terms Φ in this system of equations, and when $|V_0 - V_1| \leq 2k\dot{\Phi}$ we neglect the terms $(V_0 - V_1)/2$ (k is a constant of the order of unity). Then, solving this system of equations under the initial conditions $a_z = 1$ and $a_y = 0$ when $t = -\infty$, we get for $t = +\infty$

$$a_z = \cos\varphi\cos\eta' - i\sin\eta', \quad a_y = -\sin\varphi\cos\eta',$$

where

$$\eta' = \int \frac{V_0 - V_1}{2}\,dt, \quad \cos(\varphi/2) = \frac{\rho}{R_m},$$

R_m is determined by the relation

$$V_0(R_m) - V_1(R_m) = 2k\dot{\Phi}(R_m)$$

and the integral η' is calculated over the time interval during which $|V_0 - V_1| \geq 2k\dot{\Phi}$, in which time the axis of the quasimolecule rotates through an angle φ.

According to (13′), the change in the projection of the angular momentum in the employed model, averaged over the initial direction of the momentum, is

$$W = {}^4/_{15}\Big[({}^3/_2 + \sin^2\varphi - {}^1/_2\cos\varphi) - (3 - 4\cos^2(\varphi/2))\cos 2\eta'\cos^2(\varphi/2) - 2\cos\varphi\sin\frac{\eta - \eta'}{2}\sin\left(\frac{3\eta}{2} + \frac{\eta'}{2}\right)\sin\frac{5\eta' - \eta}{2}\Big]. \quad (18)$$

Let us consider the case when $(V_0 - V_1)/2 = B/R^n$ and the elastic scattering of the atoms does not influence the process under consideration, so that for the relative motion of the nuclei $R^2 = \rho^2 + v^2t^2$ and $\dot{\Phi} = \rho v/R^2$. In this case

$$\cos\frac{\varphi}{2} = \frac{\rho}{R_m}, \quad R_m = \left(\frac{B}{k\rho v}\right)^{1/(n-2)}$$

and the cross section for the projection of the angular momentum is

$$\sigma = 2\pi\left(\frac{B}{kv}\right)^{2/(n-1)}\int_0^1 z^{(n-3)/(n-1)}W(z)\,dz,$$

where

$$z = \cos(\varphi/2) = \left(\frac{k\rho^{n-1}v}{B}\right)^{1/(n-2)}.$$

The phases contained in (18) are equal to

$$\eta' = \frac{2k}{z^{n-2}}\sqrt{1 - z^2}, \quad \eta = \frac{2k}{z^{n-2}}.$$

Using these expressions, let us calculate the cross section. Inasmuch as in the region $1 > z > 0$ the phases η and η' change from zero to infinity, the last term in formula (18) should yield a small quantity when integrated with respect to dz. Neglecting this term, we obtain for the cross section

$$\sigma = \frac{8\pi}{15}\left(\frac{B}{kv}\right)^{2/(n-1)}\left\{\left[1 + \frac{n(n-2)}{2(2n-3)(3n-4)}\right] + \overline{\cos 2\eta'}\,\frac{n(n-2)}{2(2n-3)(3n-4)}\right\},$$

where

$$\overline{\cos 2\eta'} = \int (3 - 4\cos^2(\varphi/2))\cos 2\eta\cos^2\frac{\varphi}{2}\,d(\rho^2).$$

We see that the last term in the expression for the cross section makes a small contribution to the cross section, even if we assume that $|\overline{\cos 2\eta'}| \sim 1$. In fact, in the region of impact parameters that make the main contribution to the cross section, the quantity $\cos 2\eta'$ oscillates strongly (especially for large n), so that we also have $|\overline{\cos 2\eta'}| \ll 1$. Thus, this term of the cross section can be neglected, so that the cross section for the change in the direction of the angular momentum takes the form

$$\sigma = \frac{8\pi}{15}\left(\frac{B}{kv}\right)^{1/(n-2)}\left[1 + \frac{n(n-2)}{2(2n-3)(3n-4)}\right]. \quad (19)$$

The higher the value of n, the closer the employed model is to reality. This is connected with the fact that at large values of n the region where both terms play the same role in the system (17) turns out to be narrow compared with the transition region. Therefore, the proposed model yields an asymptotically exact result when $n \to \infty$. At large values of n, the cross section depends little on the constant k which enters in formula (19) and which is close to unity. At large values of n, the cross section can be determined by means of formula (19), introducing the constant k in such a manner that in the region of these values of n the cross section coincides with that calculated on the basis of the exact solution of the system (18). It follows here, from the very idea of the proposed model, that the constant k depends little on n. In our case the system (8) was solved for n = 3 and the cross section obtained in this manner yielded k = 0.5. Since the constant k expressed in terms of the exact cross section with the aid of (19) depends little on n, especially when n n is large, the cross section for the change in the direction of the angular momentum can be determined, with reliable accuracy from formula (19) by putting k = 0.5.

We have considered so far the case when the Σ-Π splitting of the terms was determined by the relation $V_0 - V_1 = 2B/R^n$. Let us investigate a case of practical interest, when $(V_0 - V_n)/2 =$

$= B \exp(-\gamma R)$, with $\gamma R \gg 1$ in the transition region. In this case R_m is determined from the condition $B \exp(-\gamma R_m) = k\rho v/R_m^2$ and is practically independent of ρ. Therefore, introducing the maximum impact parameter

$$\frac{V_0 - V_1}{2}\Big|_{\rho_{max}} = \frac{kv}{\rho_{max}},$$

for which the transition is still possible under the conditions of the given model, and confining ourselves in (18) to the first significant term, we get

$$\sigma = \int_0^{\rho_{max}} \frac{4}{15}[2 + (3 - 4\cos^2(\varphi/2))\cos^2(\varphi/2)]\pi d\rho^2 = \frac{26}{45}\pi\rho_{max}^2. \quad (20)$$

This formula is valid also for the relation $V_0 - V_1 \sim R^{-n}$ at large values of n.

Let us consider the case of a collision between a charged particle with a dipole molecule, when $(V_1 - V_0)/2 \simeq cR^{-2}$. In this case the system (8) can be solved[4], with

$$\mathrm{Re}\, b_z{}^z = \cos(\pi\sqrt{1+z^2}),\ \mathrm{Im}\, b_z{}^z = z(1+z^2)^{-1/2}\sin(\pi\sqrt{1+z^2}),$$
$$\mathrm{Re}\, b_y{}^z = (1+z^2)^{-1/2}\sin(\pi\sqrt{1+z^2}),\quad \eta = 2\pi z,$$

where $z = c/2\rho v$. Inasmuch, as follows from (13), the change in the projection of the angular momentum of the molecule as a result of collision is $W \sim \rho^{-2}$ at large impact parameters of the collision, the cross section for the change in the projection of the angular momentum diverges in this case.

RESONANCE DEPOLARIZATION

We now consider a case of practical importance, that of transitions between three P-states (1) of an excited atom. These transitions are produced by interaction with the same atom in the ground state. At low collision velocities, the cross sections are very large[4] ($\sigma \sim v^{-1}$), so that we can confine ourselves to the asymptotic expression for the interaction of the atoms, namely the interaction of two dipoles

$$V = \frac{2z_1z_2 - (x_1x_2 + y_1y_2)}{R^3}, \quad (21)$$

where $x_{1,2}$, $y_{1,2}$, and $z_{1,2}$ are the projections of the radius vectors of the electrons (relative to their nuclei) on the coordinate axes xyz, so chosen that the z axis is parallel to **R**, the vector of the relative placement of the nuclei of the atoms. For identical atoms, there is an additional symmetry with respect to permutation of the states[2], so that the quasimolecular states (the states with the nuclei fixed) should be symmetrical or antisymmetrical relative to rotations in a plane passing through the center of **R** and perpendicular to **R**

$$\Psi_\nu{}^\pm = [\psi_s(r_2)\psi_\nu(r_1) \mp \psi_s(r_1)\psi_\nu(r_2)]/\sqrt{2}, \quad (22)$$

where ψ_s is the ground state of the atom, ψ_ν is one of the states (1). Thus, there are six states between which the transitions take place. The states (22) have dipole moments, and therefore the diagonal matrix elements of (21) differ from zero and are equal to

$$V_x{}^\pm = \int \Psi_x{}^\pm V \Psi_x{}^\pm d\tau_1 d\tau_2 = V_y{}^\pm = \mp\frac{2}{3}\frac{\langle r\rangle^2}{R^3} \equiv V_1{}^\pm,$$
$$V_z{}^\pm = \pm\frac{4}{3}\frac{\langle r\rangle^2}{R^3} = V_0{}^\pm. \quad (23)$$

The dipole moments in the states Ψ_ν and $\Psi_{\nu'}$ with $\nu \neq \nu'$ are usually perpendicular, and therefore the nondiagonal elements of (21) are equal to zero. On the other hand, states with different symmetries, Ψ_ν^+ and Ψ_ν^-, are not connected, since the total Hamiltonian of the system (and in particular the interaction (21)) is symmetrical with respect to permutation of the nuclei. This means that the system of six states (22) breaks up into two systems, each with three interacting states, and the explicit form of each system is identical to (11). The latter statement follows from the fact that the function (22) transforms just like (1) under rotations of the coordinate system. The systems of equations for symmetrical and antisymmetrical states differ in the sign of the parameter q:

$$q = \pm\langle r\rangle^2/\rho^2 v.$$

If initially the excitation $\psi_Z(1)$ was applied to the atom 1, then the initial conditions written in the form

$$\Psi_{t=-\infty} = \psi_s(2)\psi_{z''}(1) = 2^{-1/2}[\Psi_z{}^+ + \Psi_z{}^-]. \quad (24)$$

Assume that after the collision we have the combination

$$\Psi_{t=+\infty} = \sum_\nu [{}^+A_\nu\Psi_\nu{}^+ + {}^-A_\nu\Psi_\nu{}^-], \quad (25)$$

where ${}^-A = ({}^+A)^*$. The probability for the excitation to remain at the atom 1 with the same projection $\psi_{Z''}$ is equal to

$$\omega_0 = \left|\int \psi_s(2)\psi_{s''}(1)\Psi_{t=+\infty}d\tau_1 d\tau_2\right| = \frac{1}{4}|{}^+A_z + {}^-A_z|^2, \quad (26)$$

and the probability that the excitation with the same projection $\psi_{Z''}$ will go over to the atom 2 is

$$\omega_1 = \frac{1}{4}|{}^+A_z - {}^-A_z|^2. \quad (27)$$

If it is immaterial on which atom the excitation is to remain, then the probability of the depolarization

$$W(\rho) = 1 - |{}^\pm A_z{}^z|^2 \quad (28)$$

is the same function of the parameter q as (13'). Consequently, the cross section for depolarization is equal to (after averaging over the angles)

$$\sigma_p = \pi \frac{\langle r \rangle^2}{v} \int_0 \frac{W(q)\,dq}{q^2} = \frac{1.25\pi \langle r \rangle^2}{v} = \frac{1.875\pi |d|^2}{v} \quad (29)$$

with the same constant

$$1.25 = \int_0^\infty W(q) \frac{dq}{q^2}.$$

We have also calculated the total excitation-transfer cross section averaged over the initial states (1). The probability of this process no longer depends on the direction of the collision velocity v, since the probability that the excitation will be located at any particular atom does not depend on the choice of the coordinate frame. We obtained

$$\sigma_p = \frac{3\pi}{2} \frac{|d|^2}{v} \gamma, \quad \gamma = 2{,}22 \pm 0.02, \quad (30)$$

which agrees with the result of Watanabe[5,6]: $\gamma = 2.26$, and does not agree with the result of Vaĭnshteĭn and Galitskiĭ[7].

It is of interest to note the following singularity of the resonant depolarization. The matrix element of the transition between the states $\psi_\nu(r_1)\psi_s(r_2)$ and $\psi_{\nu'}(r_1)\psi_s(r_2)$ is equal to zero, and therefore at the given atom 1 the projection of the angular momentum may change only by a double transition, whereby the excitation first goes from atom 1 to 2 and then returns with another projection. This means that in the case of a small interaction ($\rho \to \infty$) the probability of depolarization without excitation transfer is a quantity of higher order of smallness than the probability of depolarization with excitation transfer. On the other hand, the total cross sections are in this case of the same order, since the region of these impact parameters makes no decisive contribution.

Since the probability of depolarization depends on the direction of v, it is clear that $\overline{\sigma v}$ depends on the distribution of the depolarizing particles with respect to the direction of v. We have averaged above over the angles only for a spherically symmetrical distribution. On the other hand, uniform population of the sublevels occurs for any type of distribution, since detailed balancing calls for $\sigma_{mm'}(v) = \sigma_{m'm}(v)$.

The dipole moment d is connected with the resonant oscillator strength f by the relation

$$|d|^2 = \frac{1}{2} \frac{f}{\Delta E}.$$

The resonator oscillator strength of helium was calculated by Dalgarno[8] and is equal to f = 0.276. The cross sections for helium are then $\sigma_p = 1.28/v$ and $\sigma_d = 1.07/v$, which yields $\sim 6 \times 10^{-13}$ cm^2 at an energy of 300°K. The quantity $\overline{\sigma v}$ is constant and equal to 6×10^{-8} cm^3/sec.

The region of applicability of the theory is determined by the approximations made, namely the approximation of straight-line classical trajectories for the motion of the nuclei and the limitation connected with the consideration of three states (1) only. Introduction of classical trajectories is possible if the angular momentum of the nuclei is large. Inasmuch as in our problem the characteristic impact parameters are $\rho \sim v^{-1/2}$, we obtain the following limitation on the collision velocity

$$v \gg M^{-2}. \quad (31)$$

It is possible to disregard the curvature of the trajectories (and to introduce a single trajectory for a given energy) under the condition that the kinetic energy of the relative motion of the nuclei is much larger than their interaction and the level splitting, which vary like $\rho^{-3} \sim v^{3/2}$. This requirement likewise leads to (31).

The smallness of the level splitting of the states (1) compared with the distance to the neighboring levels $\Delta\epsilon$ leads to an upper bound on the velocity

$$v \ll (\Delta\varepsilon)^{2/3} \sim 1. \quad (32)$$

There is also the requirement that the characteristic quantities ρ be much larger than the atomic dimensions (only in such a case can the interaction be written in asymptotic form ((21)). This means $\rho \sim v^{-1/2} \gg E_0^{-1/2}$ or $v \ll E_0$ (E_0 is the energy of the three states (1)), which agrees quantitatively with (32). Apparently a much more important limitation than (32) results from neglecting the exchange contribution to the interaction. Since the ground state of the helium is a singlet state, its interaction will be resonant ($\sim \rho^3$) only with singlet P-excitations. In this case, allowance for the electron spin leads simply to an exchange addition to the levels (4) at distances which are larger than the atomic dimensions only by several times. Then it is necessary to substitute in the right side of the inequality (32) a quantity which is several times smaller than unity. The region of applicability of the theory is altered also by neglecting the radiation during the time of collision. The results are valid if the radiation probability is small during the time of collision or $\rho/v \ll \tau_{rad}$, which leads, in the case of $\tau_{rad} \sim 10^{-8}$ sec, to the condition $v \gg \tau_{rad}^{-2/3} \sim 10^{-6}$ at. un.

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