Transitions between the degenerate states of an excited hydrogenlike ion during distant collisions with a charged particle

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The transitions between the $n^2$ ($n$ is the principal quantum number) degenerate states of an excited hydrogenlike ion during distant collisions with a heavy charged particle are considered. It is assumed that the nuclei move along classical trajectories, the interaction between them at large distances being close to the Coulomb interaction. The four-dimensional symmetry group of the nonrelativistic hydrogenlike atom is used in the dipole approximation for the interaction between an atomic electron and a charged particle to solve exactly the nonstationary Schrödinger equation for the electron in the basis of the $n^2$ degenerate states. The dynamical terms between which no transitions occur in the course of a collision and the dynamical wave functions of the quasimolecule that correspond to these terms are found. Interference between these states leads to oscillations in the angular dependences of the probabilities of transition between states with spherical quantum numbers. The limits of applicability of the theory are discussed. As an example, the reaction $\text{He}^+ + \text{He}^+(2s) \rightarrow \text{He}^+ + \text{He}^+(2p)$ is considered in detail.

1. INTRODUCTION

We shall consider the collision between a hydrogen atom or a hydrogen-like ion in an excited state with the principal quantum number $n$ and a charged particle—a positive or negative ion whose structure will not be taken into consideration. We shall describe the relative motion of the two particles classically, assuming the trajectory of the motion to be given. As a result of the collision, a mixing of the $n^2$ degenerate states of the hydrogen-like system will occur; under certain conditions all the other transitions in the colliding particles can be neglected.

Transitions between degenerate states have the peculiarity that the adiabatic approximation is not a good approximation even for the colliding-particle velocities, and the system of $n^2$ first-order differential equations must be solved exactly, which significantly complicates the problem. Owing to the additional degeneracy with respect to the quantum number $l$ and the presence of the linear Stark effect, a hydrogen-like system possesses a unique characteristic: there arises in a transition-inducing interaction with a charged particle a long-range term proportional to $R^{-2}$ ($R$ is the inter-nuclear distance), i.e., a charge-dipole interaction arises. It is clear that this interaction plays the dominant role in sufficiently distant collisions, and the terms that fall off more rapidly with increasing $R$ can be neglected. In its turn, for a purely dipole interaction the system of equations describing the mixing can be solved exactly, and we can construct from the degenerate hydrogen wave functions linear combinations which are closely related to the four-dimensional rotation group, which explains the additional degeneracy.

The total cross section for transition between degenerate states turns out to be infinite in the approximation under consideration here. A finite cross section is obtainable only in the more exact calculation which takes into account the relativistic level splitting that decreases the transition probability for very distant collisions.

The differential cross section for these transitions is obtained as a result of the interference between the dynamical eigenstates, but to compute the cross section we must know the trajectory of the relative motion of the particles. This trajectory is known with sufficient accuracy if the two colliding particles are charged, so that only their Coulomb interaction need be considered, the additional forces inducing the transitions being neglected. Such a calculation is carried out in Sec. 3 for the reaction $\text{He}^+ + \text{He}^+(2s) \rightarrow \text{He}^+ + \text{He}^+(2p)$, for which the characteristic interference oscillations of a cross section are obtained. For the collision between an ion and a hydrogen atom, the computation of the differential cross section is complicated by the fact that the dipole interaction, which in this case not only induces the transitions, but is the main cause of the particle deflection, is different for different dynamical states, and we cannot restrict ourselves to the consideration of one trajectory when computing the scattering in a given direction.

Measurements of both the total and the differential cross sections for the process in question have not as yet been performed. Among the measurements within our reach, the easiest is the measurement of the cross section for the decay of metastable atoms or ions in the $2s$ state during collisions with ions, i.e., the experiment with crossed beams and the registration of $L_\alpha$ photons. The measurement of the differential cross section will require, in addition, the use of the coincidence technique to simultaneously register the $L_\alpha$ photons and the ions scattered in a given direction, a procedure which is now apparently on the verge of the possibilities of modern experimental techniques (allowing for the fact that the cross sections here are very high). We note also that the reaction under consideration may be important for astrophysics.
The n = 2 case has been theoretically investigated in a number of papers[8-10], the most complete of which is the paper[10] by Chibisov. In all these papers only the total scattering cross section (which can in principle be estimated without solving the system of equations) is determined, and the case of rectilinear flight is considered. Thus, the greater part of the information which is obtained upon the solution of the system of equations, and which allows the determination of the angular dependences, is not used. The method applied in these papers does not make use of the symmetry of the hydrogen atom, and does not allow a generalization to an arbitrary n.

Furthermore, the results of[11] were used in[19] to compute the collision-induced broadening of hydrogen spectral lines with arbitrary n, a broadening which is directly related to the process under consideration here. However, the authors did not determine the transition cross sections and the angular dependences, nor did they investigate the interference phenomena.

It should be noted that the use of the four-dimensional symmetry of the hydrogen atom in the theory of atomic collisions is of fundamental interest in itself, and it is remarkable that the present problem is practically insoluble in the general form without the use of this symmetry.

2. THE ELECTRON PROBLEM

The wave function of the electron of a hydrogen-like system A with a nuclear charge Z_A satisfies the non-stationary Schrödinger equation

$$\frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar} H \Psi \equiv \mathbf{H} \Psi = \mathbf{H}' \Psi,$$

(1)

We locate the origin at the center of the system A, set the charge of the incoming ion B equal to Z_B, and assume that the vector R(t) of the relative disposition of the particles is a given function of the time and that it is at all times large compared to the dimensions of the wave function of the system A, so that we can restrict ourselves to the consideration of the dipole term in the interaction. Here and below we use atomic units. Let us direct the x axis in opposition to the incoming-particle flux, i.e., along the vector R(-\infty). Further, let the trajectory R(t) lie in the xy plane, and let us measure \( \chi(t) \)--the azimuthal angle of R(t) in this plane—from the x axis.

Let us introduce a rotating coordinate system with the z' axis coinciding with the z axis of the fixed system and the x' axis directed along the vector R(t); we shall distinguish the quantities pertaining to this system by a prime. Then the Schrödinger equation assumes the form

$$\frac{\partial \Psi'}{\partial t} = \mathbf{H}' \Psi' = 0,$$

(2)

where

$$\mathbf{H}'(t) = \mathbf{H}' = \mathbf{H} - \frac{Z_A}{2} \frac{\mathbf{R}(t)}{R(t)}, \quad \mathbf{H} = -\frac{\hbar^2}{2m} \nabla^2 + \frac{\mathbf{L} \cdot \mathbf{L}}{2}, \quad m = \frac{M A + M_B}{M_A + M_B}.\tag{3}$$

Here \( L \) is the angular momentum operator of the electron of the system A and L is the angular momentum of the relative motion of the heavy particles. The vector L is directed along the z axis and is equal to

$$L = L_{\parallel} = M R^2 d\Omega/dt.$$  

(5)

The operator \( \mathbf{H}' \) coincides with the energy operator of a hydrogen atom located in crossed electric and magnetic fields if the diamagnetic term is neglected:

$$\mathbf{H}' = \mathbf{H} = \mathbf{H}' + \frac{1}{2c} \mathbf{H}.'$$  

(6)

(c is the velocity of light). The electric field \( \mathbf{E} \) is directed parallel to the x' axis, and is equal in magnitude to \( E = -Z_B R^{-2} \). The effective magnetic field \( \mathbf{H} \) is directed parallel to the z axis, and is equal to \( H = 2cL_B / MR^2 \). Its appearance in the rotating coordinate system is a consequence of the well-known Larmor theorem[6].

Finally, let us assume that the transitions occur only between states with a given n, i.e., we shall consider Eq. (2) in the n subspace of the n' eigenfunctions corresponding to the eigenvalue \( \mathbf{H}'_n = -Z_A(2n')^2 \) of \( H' \). Then the problem can be solved exactly in the general form if the results of[13] are used. The diagonalization of the energy operator (6) in the n subspace turns out to be possible owing to the operational equation in this subspace:

$$\mathbf{R} = -3nA/2Z_A,$$  

(7)

where \( A \--a \) subsidiary integral of the motion—is the Runge-Lenz operator

$$A = -2\mathbf{H}' \left( \frac{1}{2} [\mathbf{p} \mathbf{X} \mathbf{I}] - [\mathbf{I} \mathbf{X} \mathbf{p}] \right) \mathbf{R} \cdot \mathbf{R} \mathbf{R}.$$

(8)

connected with the O(4) symmetry group of the hydrogen atom. In the n subspace the eigenvalues of \( \mathbf{H}' \) have, according to[1], the form

$$\mathbf{H}'_{n,n'} = \mathbf{H}'_n + \frac{\gamma}{2} R^2(n' + n'), \quad n, n' = j, j + 1, \ldots, j = \frac{n-1}{2}.$$

(9)

The quantum numbers \( n \) and \( n' \) are the eigenvalues of the components of the commuting operators \( I_1 = \frac{1}{2} (\mathbf{I} + \mathbf{A}) \) and \( I_2 = \frac{1}{2} (\mathbf{I} - \mathbf{A}) \) along the vectors

$$a_1 = \frac{1}{2c} H - \frac{3n}{2Z_A} E, \quad a_2 = \frac{1}{2c} H + \frac{3n}{2Z_A} E.$$  

(10)

It is more convenient here to express the eigenfunctions \( \psi_{n,n'} \) in terms of the hydrogen-atom wave functions \( \psi_{n_1n_2} \), obtained when the variables are separated in a parabolic coordinate system with its axis along the z axis; in this case it is easier to go over from the rotating to the fixed system (in[12]), the axis of the parabolic system was directed along \( \mathbf{E} \). The quantum numbers \( l_1 \) and \( l_2 \) are simply related to the ordinary parabolic quantum numbers \( n_1, n_2, m_1, m_2, \) and \( m \):

$$l_1 = m + n_2 - n_1, \quad l_2 = m + n_1 - n_2, \quad m = m_1 + m_2, \quad m = m_1 + m_2.$$  

(11)

Using the same method employed in[11], we obtain the expansion in terms of the functions of the moving system:

$$\psi_{n,n'} = \sum_{(l,m)\in\mathbb{Z}} D_{l,n}^m(0,\beta_0,0) D_{l',n'}^m(0,\beta_0,0) \psi_{n,n'},$$

(12)

where the \( D_{l,n}^m \)'s are the well-known Wigner functions of the spherical top and \( \beta_0 \) and \( \beta_2 \) are the angles between the vector \( \mathbf{H} \) and the vectors \( \omega_1 \) and \( \omega_2 \). In our case

$$\beta_0 = -\beta = \beta, \quad \tan \beta = \frac{3nZ_A}{2Z_A}, \quad \beta = \frac{n}{2} < \beta < \pi.$$  

(13)

A similar expansion in terms of the fixed-basis functions has the form

$$\psi_{n,n'} = \sum_{(l,m)\in\mathbb{Z}} D_{l,n}^m(0,\beta,0) D_{l',n'}^m(0,\beta,0) \psi_{n,n'}.$$  

(14)
Let us now make the assumption that the angular momentum L is conserved in the motion of the heavy particles. Strictly speaking, only the total angular momentum L + 1 is conserved, and our assumption is admissible if we consider the angular momentum L to be large and neglect momentum transfer from the heavy particles to the electron, i.e., assume that L ≫ n. If now L = const, then in the moving system the functions ψni'ni'' do not depend on the time explicitly, and depend on the form of the trajectory R(t) only through the parameter L.

Let us seek the solution of Eq. (2) in the form
\[ ψ = \sum_{n'i'n''} c_{n'i'n''} e^{i\omega_{n'i'n''} t} \exp\left(-i\delta_{n'i'n''} t\right) \]
and introduce in place of the time t a new variable χ, which is the azimuthal angle. Then d/dt = (MR^2)^{-1}d/dχ, the term with R^2 cancels out on both sides of the equation (it is precisely here that the unique characteristic of the dipole interaction appears), the coefficients of the system do not, in general, depend on χ, and the system itself splits up into separate equations:
\[ i\frac{d\psi_{n'i'n''}}{d\chi} = \frac{M}{L} (n'i+n'n'')\psi_{n'i'n''}. \]

Thus, the time-evolution operator U(t₂, t₁) is diagonal in the n'−n" representation, its diagonal matrix elements being given by
\[ \langle n', n'' | U(t₂, t₁) | n, n \rangle = \exp\left[-iv(n' + n'')\chi(t₂ - t₁)\right], \]
with ν = MLC⁻¹, δX = χ(t₂) − χ(t₁).

In the moving parabolic basis ψ_{ni'i''}(exp(−1/2ε(νt))), we obtain
\[ \langle n'i'i''(0) | U | n'i'ni''(0) \rangle = \sum_{n'i'n''} D_{n'i'ni''}^{(n'i'i'')} (0, 0, 0)D_{n'i'i'ni''}^{(n'i'i'')} (0, 0, 0) \exp\left[-iv(n'i' + n'n'')\chi(t₂ - t₁)\right]. \]

Finally, the transition from the parabolic quantum numbers i₁ and i₂ to the spherical quantum numbers l and m is accomplished with the aid of the Clebsch-Gordan coefficients; in doing this, we must (as in the formula (9)) pay particular attention to the correct choice of the phases of the wave functions [9].

It is interesting that the operator U depends only on the angular momentum L and on the change ΔX in the azimuthal angle, and does not depend on the other characteristics of the trajectory of the particle motion.

As was explained in [1], upon the application of mutually perpendicular electric and magnetic fields the degeneracy of the energy levels of the hydrogen atom is not completely removed in first-order perturbation theory. In our nonstationary problem, this leads to a situation in which the operator U possesses special symmetry properties, in so far as
\[ \langle n'i'i'' | U | n'i'i'' \rangle = \langle n'i'i'' | U | n'i'i'' \rangle = \langle n'i'i'' | U | n'i'i'' \rangle = \langle n'i'i'' | U | n'i'i'' \rangle \]
\[ \delta_{n'i'n''} \langle n'i'i'' | U | n'i'i'' \rangle \]
\[ \delta_{n'i'n''} \langle n'i'i'' | U | n'i'i'' \rangle \]
\[ \delta_{n'i'n''} \langle n'i'i'' | U | n'i'i'' \rangle \]

The unitarity of U leads to additional relations between its matrix elements.

For the particular case when n = 2, we obtain
\[ \langle 2'i'i' | U | 2'i'i' \rangle = (1 - \frac{1}{2} \sin^2 \beta) \cos \omega t - i \cos \beta \sin \omega t + \frac{1}{2} \sin^3 \beta, \]
\[ \langle 2'i'i' | U | 2'i'i' \rangle = -i \sin \omega t - \frac{1}{2} \sin^3 \beta \]
\[ \langle 2'i'i' | U | 2'i'i' \rangle = \cos \omega t - \cos \beta \sin \omega t - \frac{1}{2} \sin^3 \beta \]
\[ \langle 2'i'i' | U | 2'i'i' \rangle = \sin^2 \beta \sin \omega t. \]

All the remaining matrix elements can be obtained with the aid of (18). We can show by means of simple transformations that the solution obtained by us for this case to the nonstationary electron problem coincides with the solution found by Chibisov [5]; (see also [6]) in spherical basis for the particular case of rectilinear flight.

3. The Case of Coulomb Interaction Between the Heavy Particles. The Limits of Applicability of the Method

If the trajectory R(t) of the nuclei is given, then the formula (17) allows the immediate determination of the probability of transition between any atomic states \( |ψ_i \rangle \) and \( |ψ_j \rangle \) with a given n:
\[ P_{n→m} = | \langle ψ_i | U(n→m) | ψ_j \rangle |^2. \]

Let us consider the case when Z_A ≠ 1. Then the motion of the heavy particles is determined largely by the Coulomb interaction
\[ V(R) = \frac{1}{r} (Z_A - 1) Z_B R. \]

Then the interaction of the charge Z_B with the dipole induced in the atom as a result of the linear Stark effect can be neglected in computing the trajectory if the condition
\[ ρ ≪ |n| Z_A (Z_A - 1), \]
where ρ is the impact parameter for the nuclei, is fulfilled. The scattering angle θ in the potential (21) is connected with the angular momentum by the relation
\[ L(θ) = \frac{1}{v} \langle Z_A - 1 \rangle Z_B |\sin \theta/2|, \]
where v is the relative velocity of the nuclei.

The cross section for scattering through an angle θ (in the center of mass system) that accompanies the transitions of the atom from the state \( |ψ_i \rangle \) to the state \( |ψ_j \rangle \) is equal to
\[ (dσ/dθ)_{n→m} = a(θ) P_{n→m}(θ), \]
where \( a(θ) \) is the cross section for scattering in the Coulomb potential (21):
\[ a(θ) = \left[ \frac{(Z_A - 1) Z_B}{4E} \right] \sin \theta \]

E = 1/2Mv^2. The quantity P_{n→m} in the formula (24) should be computed with the aid of the formulas (17) and (20), it being necessary to use (23) and set ΔX = π − ϵθ, where ϵ = sign[(Z_A - 1)Z_B], i.e., ϵ = 1 if V(R) is a repulsive potential and ϵ = −1 for the case of an attractive potential.

In the n = 2 case the relations between the states with spherical and parabolic quantum numbers is especially simple (see, for example, [10]). Using this relation, we obtain with the aid of (20) the total transition probability between the metastable 2s state and the 2p state:
\[ P_{n→p}(θ) = 4 \sin^2 \beta \sin^2 \frac{θ}{2} \left( 1 - \sin^2 \beta \sin^2 \frac{θ}{2} \right); \]
\[ \tan \beta = \frac{3Mv}{Z_A (Z_A - 1)} \frac{θ}{2}, \]
\[ v(θ) = (\epsilon - \epsilon_0) (\epsilon + \epsilon_0) \sin^2 \beta. \]

It follows from the formula (28) that for a sufficiently large value of Mv the probability P_{2s → 2p}(θ) oscillates between zero and unity as the angle θ varies. It is worth noting that the formula (26) for the transition probability does not explicitly contain Z_B, the charge of the incoming particle. The results for proton scattering by the ion He’(2s) are shown in Fig. 1.
Not allowed for in the paper is the fact that in reality an energy level with a given n is split by some small amount $\Delta_{rel}$ because of the presence of relativistic effects (the fine structure and the Lamb shift). If the condition

$$\rho/v < 1/\Delta_{rel},$$

(27)

is fulfilled, then in solving the nonstationary problem the indicated splitting need not be considered, and the transition probability between the fine-structure states can be found by simply computing the matrix elements of the above-obtained operator $U$ between these states. The transition probability for the transitions $2s_{1/2} \rightarrow 2p_{1/2}$ and $2s_{1/2} \rightarrow 2p_{3/2}$ then differs from the transition probability for the $2s \rightarrow 2p$ transition only by statistical factors (30), and we obtain for the $2p_{1/2} \rightarrow 2p_{3/2}$ transition probability the expression

$$P_{2p_{1/2} \rightarrow 2p_{3/2}}(\theta) = 2P_{2p_{1/2} \rightarrow 2p_{3/2}}(\theta) = \sqrt{2} \cdot \sin^2 \frac{\theta}{2} \cdot \cos \theta \cdot \left(1 - \cos \theta\right) \left(1 + \cos \theta\right)$$

(28)

For the case of rectilinear flight, we can derive from this formula the formula (13) of (14).

Let us discuss the limits of applicability of the other approximations made in the course of the solution of the problem. The dipole approximation for the interaction potential is valid for large impact parameters:

$$\rho > 3n^2/Z_0.$$  

(29)

This approximation does not allow the description of charge transfer, which is especially important in the symmetric ($Z_A = Z_B$) case. The neglect of charge transfer is valid in this case if the condition

$$\frac{2n^2 Z_0^4}{12n^2 v^2} \exp \left(-\frac{Z_0}{n} + n\right) < 1,$$

(30)

which becomes important at low collision velocities, is fulfilled.

In order for the transitions between states with different $n$ to be negligible, it is in any case necessary that the Stark splitting ($\Delta E \sim 3n^2 Z_0^2 Z^2_0$) of the energy levels due to the interaction with the charge $Z_0$ be significantly smaller than the spacing ($\Delta E \sim Z_0^2 n^2$) between levels with different $n$, whence

$$\rho > n^3 (3Z_0^2 - Z_0^4)n.$$  

(31)

Usually, this last limitation is stronger than (29). Further, estimating, according to (14), the transition probability for a nonadiabatic transition between levels with different $n$, and requiring that it be small, we obtain

$$\rho/v > n^3 Z_0^4.$$  

(32)

Finally, this same inequality guarantees a low probability of $n$ changing as a result of the rotation of the inter-nuclear axis $AB$ (such a coincidence is one of the consequences of the characteristics of the dipole potential, which is inversely proportional to the square of the distance).

The classical description of the nuclear motion for small-angle scattering is applicable in the case when the potential has a Coulomb asymptotic form for not too high velocities (17):

$$v < (Z_0 - 1)Z_0.$$  

(33)

We show in Fig. 2 on the example of the $H^+ + He^+$ scattering that there exist regions of the variables $E$ and $\theta$ in which all the conditions (22), (27), and (29)–(33) are satisfied and the above-employed approximations are applicable. In doing this, we allowed for the fact that, strictly speaking, the indicated estimates should contain not the impact parameter $\rho$, but the distance of closest approach of the nuclei during a collision. This circumstance becomes important at large scattering angles, and is the cause of the deviation in Fig. 2, of the boundaries of applicability of the approximations from straight lines. Notice also that the violation of some of the conditions of applicability of the theory should not lead to the complete disappearance of the obtained interference oscillations in the transition probability as a function of the scattering angle. In fact, the deviation at small $R$ from the dipole approximation only yields a shift in the positions of the maxima, while the violation of the condition (32) leads to some damping of the oscillations as a result of the transition of the atom to states with a different $n$.

4. CONCLUSION

Using the obtained formulas, we can easily predict the results of the simultaneous measurement of the direction of the scattered particle and the direction and polarization of the emitted $\gamma$ quantum. Notice that in
the case of the $2s \rightarrow 2p$ transition, the following selection rule is rigorously valid: the p state corresponding to the transition dipole moment perpendicular to the scattering plane (which contains the initial and final momenta of the scattered particle) is not populated. This leads to the linear polarization of the $L_2$ quanta emitted in directions lying in the scattering plane.

The total cross section for inelastic scattering for arbitrary $n$ can be computed by integrating over the angles the obtained differential cross sections. In order to remove the logarithmic divergence that arises in the integration, it is necessary to take into account at large impact parameters the relativistic splitting of the levels of the atom and match the corresponding solutions in the intermediate region, as was done in Chibisov's paper. Some difference between the results of this paper and our results arises because of the fact that the curvature of the trajectory has been taken into account in our expression for the transition probability.

It is of interest to consider in the framework of the quantum or semiclassical approximation the motion of the colliding particles themselves with allowance for the dipole term in the interaction. This is especially important for the computation of the angular distribution in the reaction $H^+ + H(2s) \rightarrow H^+ + H(2p)$.

The present problem is, in a sense, unique: it is thus far the only nontrivial and sufficiently realistic case, in which the dynamical problem of strong interaction between states can be solved exactly. This enables us to explicitly introduce the concept of dynamical terms, whose role in our problem is played by the quantity $\frac{y(n' + n)R^2}{n}$, and of the corresponding dynamical quasi-molecule wave functions $\psi_{nn'/n''}$, which depend on the angular momentum $L$ of the colliding particles.


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