Oscillator strengths in the spectra of Rydberg atoms excited by the van der Waals interaction with a conducting surface

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Highly excited hydrogen atoms whose levels are split by the interaction with the electrostatic images in a conducting plane are analyzed. The classical model of a Rydberg atom and the semiclassical approximation are used. An analytic distribution of oscillator strengths in the spectra of the perturbed atom is found for transitions of the Lyman and Balmer series. Transitions from Rydberg states which correspond in the classical model to electron orbits which do and do not periodically degenerate into a straight line are analyzed separately. In the latter case, the probability for optical transitions to low-lying states is exponentially small.

INTRODUCTION

Rydberg atoms in a conducting cavity have been the subject of many recent studies. These systems have attracted much theoretical interest because they make it possible to see several subtle effects of quantum electrodynamics. These systems are also pertinent to several promising practical applications, e.g., a one-atom maser (see the reviews[1–3]).

The interaction with a conducting wall strongly affects a Rydberg atom even if the distance d from the atom to the wall is much greater than the average radius of the atom, n^2 (n is the principal quantum number of the valence electron). The operator representing the overall interaction of the atom with the wall is broken up into several terms, which play different roles at different values of d (Ref. 4). The most elementary interaction is the van der Waals interaction, which is dominant at distances which are not too large, and for which retardation can be ignored. Assuming that the surface is ideally conducting, and using the simple electrostatic model for the interaction of an atomic dipole with its image, we can write the following expression for the effective interaction operator (in atomic units):[2]

$$W=-\frac{1}{16d^3}(x^2+y^2+2z^2). \tag{1}$$

Here x, y, z are the coordinates of the electron with respect to the nucleus, which is at a distance d from the surface. We assume that the z axis runs normal to the surface (Fig. 1).

Perturbation (1) converts the n^2-fold degenerate level of the isolated atom into a multiplet (which we will be calling the "dipole–dipole multiplet"). A d^{-3} splitting depends on the distance from the atom to the surface; a force thereby arises and acts on the atom. The magnitude of this force differs for atoms in different sublevels; this variation has a strong effect on the behavior of the atoms under experimental conditions.[3] The multiplets generated by interaction (1) have an extremely unusual structure,[5] which is a bit reminiscent of the structure of quadratic Zeeman multiplets.[6–8]

For diagnostics of Rydberg atoms inside cavities, and for calculations of their lifetimes and other properties, it is important to know the oscillator strengths of the transitions from perturbed Rydberg states to low-lying excited atomic states. (The latter are incomparably less sensitive to external agents and can be regarded as the states of the free atom.) Calculations show that different components of a given dipole–dipole multiplet have probabilities for transition to the ground state which differ by several orders of magnitude. This interesting effect was explained at a qualitative level by Alhassid *et al.*[5]

In this paper we take a detailed theoretical look at the distribution of oscillator strengths for transitions from highly excited states of a hydrogen atom perturbed by the van der Waals interaction with a wall. We derive analytic expressions for probabilities of transitions to the ground and low-lying excited levels. These expressions turn out to agree almost exactly with the results of numerical calculations. We show that the distribution of oscillator strengths and the density of energy levels in a dipole–dipole multiplet are related by trivial relations. The analysis method is analogous to that used in Refs. 9 and 10 in the problem of the quadratic Zeeman and Stark–Zeeman effects in the spectra of highly excited atomic hydrogen.

1. EQUATION FOR THE COEFFICIENTS OF THE EXPANSION OF THE WAVE FUNCTION AND SOLUTION OF THIS EQUATION AT SMALL *l*

Cases of practical interest are those in which the splitting associated with the interaction W is small in comparison with the interval (n^{-3}) between adjacent unperturbed levels of the hydrogen atom. In this case the wave functions and energies of the atom can be found by perturbation theory. We write the wave function Ψ as a superposition of spherical orbitals $|nlm\rangle$ for a shell with a given n and with an unperturbed energy $E_n^{(0)}=-1/2n^2$. By virtue of the properties of perturbation (1), the superposition includes states with a fixed value of m (the projection of the angular momentum L_z), and the parity:

$$\Psi=\sum_l C_l|nlm\rangle\,. \tag{2}$$

The coefficients C_l and the corrections to the energy in the lowest order of our perturbation theory can be found from the equations

$$p_lC_{l-2}+(w_l-E^{(1)})C_l+p_{l+2}C_{l+2}=0, \tag{3}$$

where p_l and w_l, the matrix elements of the perturbation operator, are given by

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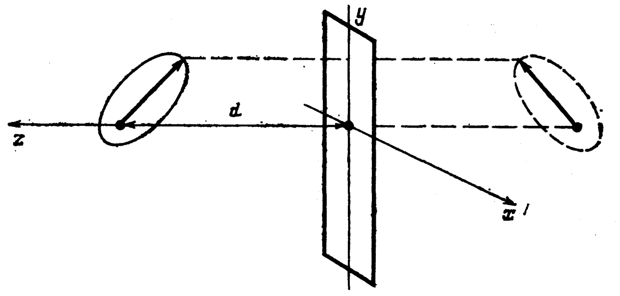

FIG. 1. Interaction of the dipole moment of the hydrogen atom with its image in a conducting plane.

$$w_l = W_{nlm}^{nlm} = -\frac{1}{16d^3} (r^2)_{nl}^{nl} [2 - (\sin^2\vartheta)_{lm}^{lm}],$$
$$p_l = W_{nlm}^{nl-2m} = \frac{1}{16d^3} (r^2)_{nl}^{nl-2} (\sin^2\vartheta)_{lm}^{-2m}. \tag{4}$$

The expressions for the matrix elements of the operators r^2 and $\sin^2\vartheta$ are[11]

$$(r^2)_{nl}^{nl} = \frac{5}{2} n^4 \left[1 + \frac{1 - 3l(l+1)}{n^2}\right],$$
$$(r^2)_{nl}^{nl-2} = \frac{5}{2} n^4 \left[\left(1 - \frac{l^2}{n^2}\right)\left(1 - \frac{(l-1)^2}{n^2}\right)\right]^{1/2},$$
$$(\sin^2\vartheta)_{lm}^{lm} = \frac{2(l^2 + l - 1 + m^2)}{(2l-1)(2l+3)}, \tag{5}$$
$$(\sin^2\vartheta)_{lm}^{l-2m} = -\left[\frac{(l^2 - m^2)((l-1)^2 - m^2)}{(2l+1)(2l-1)^2(2l-3)}\right]^{1/2}.$$

System of equations (3) has a tridiagonal matrix and is a trinomial recurrence relation for C_l.

We are interested in the probabilities for transitions to the ground level or low-lying excited levels of the hydrogen atom. These probabilities can be expressed in terms of the coefficients C_l with small l in an elementary way. For example, the oscillator strengths for transitions of the Lyman series are equal to the product of the oscillator strength for the $1s$–np transition in the isolated hydrogen atom and the quantity C_1^2. The distribution of oscillator strengths in a dipole–dipole multiplet is thus determined by the weight of the np orbital in the wave functions of the various sublevels. Correspondingly, the probabilities for transitions in the Balmer series are determined by the coefficients C_0, C_1, and C_2.

In line with our purpose here, we will consider only states with $n \gg 1$ and small values of $|m|$ (0, 1, 2). In this case the initial elements of the sequence C_l determined by trinomial recurrence relation (3) can easily be found analytically:

$$C_l = A\mathscr{P}_{lm}((|\varepsilon| - 1)^{1/2}), \quad l \ll n. \tag{6}$$

Here A is an unknown constant, which does not depend on l, and $\mathscr{P}_{lm}$ is the normalized Legendre function

$$\mathscr{P}_{lm}(x) = \left[\frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_{lm}(x). \tag{7}$$

Its argument is expressed in terms of the scaling correction to the energy:

$$\varepsilon = E^{(1)}/u_d, \tag{8}$$

where the quantity

$$u_d = \frac{1}{16d^3} \cdot \frac{5}{2} n^4 \tag{9}$$

is a characteristic energy of the interaction of the Rydberg atom with the surface. Since the perturbation W is negative, all the levels of the dipole–dipole multiplet lie below the unperturbed energy value; thus $E^{(1)}$ and ε are negative.

The result in (6) follows from the circumstance that under the condition $l \ll n$ diagonal and nondiagonal matrix elements of r^2 [Eqs. (5)] can be approximated by the same constant:

$$(r^2)_{nl}^{nl} \approx (r^2)_{nl}^{nl-2} \approx {}^5/_2 n^4. \tag{10}$$

The behavior of the coefficients C_l in the case $l \ll n$ is thus determined exclusively by the angular part of the matrix elements p_l and w_l. Using the known recurrence relation

$$x\mathscr{P}_{lm}(x) = \left[\frac{(l-m+1)(l+m+1)}{(2l+1)(2l+3)}\right]^{1/2} \mathscr{P}_{l+1m}(x) + \left[\frac{(l-m)(l+m)}{(2l-1)(2l+1)}\right]^{1/2} \mathscr{P}_{l-1m}(x) \tag{11}$$

twice to find the relationship between $\mathscr{P}_{lm}(x)$ and $\mathscr{P}_{l\pm 2m}(x)$, and comparing the result with what remains from trinomial recurrence relation (3) after substitution (10), we find Legendre solution (6). The physics underlying this approximation is discussed in Refs. 9 and 10.

To finally find C_l with $l \ll n$ we need to find the normalization constant A. To do this, we must know C_l with l comparable to n, in which case approximation (6) is not valid.

2. CLASSICAL MODEL

Because of the analogy between differential equations and trinomial recurrence relations, we can use an approximate solution of trinomial recurrence relation (3) by the WKB method.[7,12] It is convenient to first describe the purely classical picture of the van der Waals interaction of the atom with the surface. The fertility of classical ideas in problems involving perturbations of Rydberg atoms by external fields has been generally acknowledged since the work by Solov'ev.[6]

In the classical hydrogen atom the electron is moving along an elliptical orbit with a given energy $E_n^{(0)}$, a given angular momentum **L**, and a given Runge–Lenz vector **A**. The interaction with the surface causes the shape and orientation of the orbit to begin to evolve, so **L** and **A** are no longer constant. The effective Hamiltonian describing this evolution, $H^{(1)}$, can be found by averaging the perturbation W over the period of the circulation of the electron in its classical orbit.[6,13] However, the matrix elements of the operator W in the l representation are available, so the simplest way to find $H^{(1)}$ is to use the correspondence principle.[9]

We rewrite trinomial recurrence relation (3), expressing $C_{l\pm 2}$ in terms of C_l by means of operators which shift l:

$$\left[w(l) + p(l)\exp\left(-2\frac{d}{dl}\right) + p(l+2)\exp\left(2\frac{d}{dl}\right)\right] C(l) = E^{(1)} C(l). \tag{12}$$

We then go over to the classical limit, letting $n \to \infty$ and $l \to \infty$ in such a way that l/n remains finite. In this limit the quantity $L \equiv l + 1/2$ takes on the meaning of the classical angular momentum. (The classical angular momentum goes off to infinity in our case solely because of our use of the atomic system of units, with $\hbar = 1$.) The operator $-id/dl$ becomes the canonical "momentum" θ which is the conjugate of L. The expressions for w and p simplify dramatically in the classical limit. In particular, since we have $m \sim 1$, we can discard the terms containing m^2/n^2. We thus find

$$w \to w_{cl}(L) = -u_d \cdot \frac{3}{2}\left[1 - \frac{3}{5}\left(\frac{L}{n}\right)^2\right],$$
$$p \to p_{cl}(L) = -u_d \cdot \frac{1}{4}\left[1 - \left(\frac{L}{n}\right)^2\right] \qquad (13)$$

We find that in the classical limit the Hamiltonian of our problem [the operator in square brackets in Eq. (12)] corresponds to the following Hamiltonian:

$$H^{(1)}(L, \theta) = w_{cl}(L) + 2p_{cl}(L)\cos 2\theta. \qquad (14)$$

Ignoring the difference between $L_z \sim \hbar$ and zero, we assume that the plane of the classical orbit passes through the z axis and remains in a fixed spatial position. In this case the quantity θ, the conjugate of L, is the angle between the Runge–Lenz vector and the z axis (this would not be true if L_z were comparable to n; Ref. 14, for example). Analysis of the canonical equations

$$\dot{L} = \frac{\partial H^{(1)}}{\partial \theta} = -4p_{cl}(L)\sin 2\theta, \qquad (15a)$$

$$\dot{\theta} = -\frac{\partial H^{(1)}}{\partial L} = -u_d\frac{L}{n^2}\left[\frac{9}{5} + \cos 2\theta\right] \qquad (15b)$$

thus gives us a complete picture of the evolution of the Keplerian orbit.

The Hamiltonian in (14), which is a trigonometric function of the generalized momentum, is typical of problems in classical perturbation theory written in terms of action—angle variables. A qualitative picture of the motion of such systems can be drawn by working with diagrams of the "potential functions"

$$U^-(L) \equiv H^{(1)}(L, \theta)\,|_{\theta=0} = -u_d\left[2 - \frac{7}{5}\left(\frac{L}{n}\right)^2\right],$$
$$U^+(L) \equiv H^{(1)}(L, \theta)\,|_{\theta=\pi/2} = -u_d\left[1 - \frac{2}{5}\left(\frac{L}{n}\right)^2\right]. \qquad (16)$$

These functions play a role because of the following circumstances.

1. According to Eq. (15a), the generalized "velocity" $\dot{L}$ vanishes at $\theta = 0$ or $\pi/2$ (modulo π). Since the Hamiltonian $H^{(1)}(L,\theta)$ is constant and represents the correction to the energy $E^{(1)}$ for the interaction with the surface, we find that $\dot{L}$ vanishes if either $E^{(1)} = U^-(L)$ (in which case we have $\theta = 0$ or π) or $E^{(1)} = U^+(L)$ (in which case we have $\theta = \pi/2$). Consequently, the limits on the evolution of the angular momentum for a given correction to the energy $E^{(1)}$ are determined by the points at which the level $E^{(1)}$ intersects the plot of the function $U^{\pm}(L)$ (Fig. 2).

2. From the condition $|\cos 2\theta| \leqslant 1$ and the equality $H^{(1)} = E^{(1)}$ we conclude

$$U^-(L) \leqslant E^{(1)} \leqslant U^+(L). \qquad (17)$$

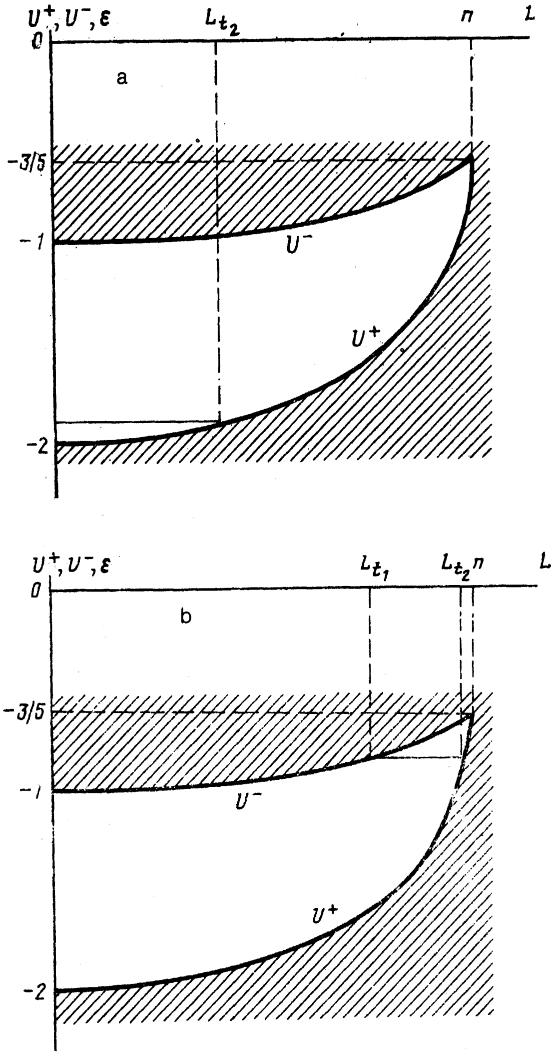

FIG. 2. Oscillations of the angular momentum of a hydrogen atom which is interacting with a conducting surface. a—$\varepsilon < -1$; b—$\varepsilon > -1$.

These results put restrictions on the values of $E^{(1)}$. According to Fig. 2, the energy $E^{(1)}$ obeys the inequalities

$$-2 \leqslant E^{(1)}/u_d \leqslant -^3/_5 \qquad (18)$$

[otherwise there is no L for which inequalities (17) are satisfied].

3. Eliminating θ from Eq. (15a) with the help of the condition $H^{(1)} = E^{(1)}$, we easily find a differential equation which relates $\dot{L}$ to $U^{\pm}(L)$:

$$\dot{L} = \pm 2[(U^+ - E^{(1)})(E^{(1)} - U^-)]^{1/2}. \qquad (19)$$

This result means that the classical angular momentum oscillates with a period

$$T = \int_{L_{t_1}}^{L_{t_2}} \frac{dL}{[(U^+ - E^{(1)})(E^{(1)} - U^-)]^{1/2}}. \qquad (20)$$

The quantities L_{t_1} and L_{t_2} in integral (20) are the minimum and maximum values of the angular momentum. The quantity L_{t_2} can be found as the root of the equation $E^{(1)} = U^-(L)$. With regard to L_{t_1}, the situation depends on the value of the energy correction.

We first assume $-1 \leqslant E^{(1)}/u_d \leqslant -3/5$ (Fig. 2b). The left turning point is then the root of the equation $E^{(1)} = U^+(L)$, with $0 < L_{t_1} \leqslant L \leqslant L_{t_2}$. Since L does not vanish, the quantity $\dot{\theta}$ does not change sign according to canonical equation (15b), while $|\theta|$ increases monotonically. This result corresponds to a rotation of the Runge–Lenz vector in the plane passing through the z axis. The absolute value $|\mathbf{A}|$ oscillates, reaching extrema at $\theta = 0$, π and $\theta = \pi/2$.

If $-2 \leqslant E^{(1)}/u_d \leqslant -1$, the situation is radically different (Fig. 2a). The left turning point is $L = 0$, in which case the orbit of the electron degenerates into a line. Simultaneously, the sign of $\dot{\theta}$ changes. In this case, there are two symmetric methods, corresponding to the same energy $E^{(1)}$, by which the orbit can evolve. These two methods correspond to oscillations of the Runge–Lenz vector near either the positive or negative direction along the z axis. One or the other of the two possible isolated symmetric classical trajectories $L = L(\theta)$ will be realized, depending on the initial conditions. The angular momentum reaches a maximum at $\theta = 0$ and π, respectively, and vanishes at the value of θ determined from the equation

$$H^{(1)}(L, \theta)\,|_{L=0} = E^{(1)}.$$

The picture of the evolution drawn here agrees with the results of Ref. 8, which were derived by a different (and considerably less graphic) method.

3. SEMICLASSICAL SOLUTION OF THE RECURRENCE RELATION

Returning to the quantum-mechanical problem, (3), we note that its eigenvalue spectrum is obviously limited by classical interval (18) (Ref. 12). We will not go into a discussion of the quantization conditions for the energy levels, but we would point out that in the part of the spectrum with $-2 < E^{(1)}/u_d < -1$ the existence of two symmetric isolated classical trajectories leads to an approximate twofold degeneracy of the eigenvalues. On the interval with $-1 < E^{(1)}/u_d \leqslant -3/5$, the levels are singlets.

In the classically allowed region of L values, the semiclassical solution of recurrence relation (3) is

$$C_l = \frac{A_{\mathrm{WKB}}}{v^{1/2}(L)} \cos(S(L) + \chi)\,|_{L=l+1/2}, \tag{21}$$

where A_{WKB} and χ are arbitrary constants, and $S(L)$ and v are the classical action and classical velocity, respectively, given as functions of L. Specifically,

$$S = \int \theta(L)\,dL, \qquad \theta = \frac{1}{2} \arccos\left(\frac{E^{(1)} - w_{cl}(L)}{2p_{cl}}\right) \tag{22}$$

and $v = \dot{L}$ [see (19)]. Expression (21) is the standard form of the WKB solution in an arbitrary (possibly discrete) representation. It is the same as the result of the solution of trinomial recurrence relation (3) in the asymptotic limit in n^{-1} (Ref. 12).

The normalization constant A_{WKB} is found from the condition

$$\sum_l C_l^2 = 1, \tag{23}$$

where the summation is over either even values of l or odd values. We then find that the constant A_{WKB} is, as usual, related to the classical oscillation frequency of the "coordinate" L:

$$A_{\mathrm{WKB}} = 2(\Omega/\pi)^{1/2}. \tag{24}$$

The quantity $\Omega = 2\pi/T$ can be calculated with the help of (20). This quantity is also equal to a quantity which can be determined experimentally, ΔE, the energy interval between adjacent levels of a given parity in a dipole–dipole multiplet.

4. OSCILLATOR STRENGTHS OF CLASSICALLY ALLOWED TRANSITIONS FROM STATES OF A DIPOLE–DIPOLE MULTIPLET

Let us use (21) to determine the normalization constant in Legendre solution (6). [The WKB method cannot be used directly to find C_l with l on the order of unity because of singularities in p_l and w_l in (3).]

We consider the levels in the interval $-2 < \varepsilon < -1\varepsilon = E^{(1)}/u_d$, in which case the classically allowed region of values of the angular momentum extends to $L = 0$ (Fig. 2a). We consider values of l such that the condition $l^2 - m^2 \gg 1$ holds, but the condition $l^2 \ll n^2$ also holds. The first of these inequalities justifies our use of WKB solution (21); the second makes it possible to simplify the functions in (21), under the assumption

$$\begin{aligned} S(L) &\approx L\theta(0) = L \arccos\,(|\varepsilon| - 1)^{1/2}, \\ v(L) &\approx v(0) = 2u_d[(2 - |\varepsilon|)(|\varepsilon| - 1)]^{1/2}. \end{aligned} \tag{25}$$

We can thus rewrite (21) as

$$C_l \approx \left\{\frac{2\Delta\varepsilon}{\pi[(2 - |\varepsilon|)(|\varepsilon| - 1)]^{1/2}}\right\}^{1/2} \times \cos\left[\left(l + \frac{1}{2}\right) \arccos(|\varepsilon| - 1)^{1/2} + \chi\right]. \tag{26}$$

Here $\Delta\varepsilon = \Delta\varepsilon/u_d$ is the reduced energy interval between levels of a given parity. We now note that under the condition $l^2 - m^2 \gg 1$ the Legendre function can be replaced by its asymptotic expression, so solution (6) can be written in the form

$$C_l \approx A\left[\frac{2}{\pi(2 - |\varepsilon|)^{1/2}}\right]^{1/2} \cos\left[\left(l + \frac{1}{2}\right) \arccos(|\varepsilon| - 1)^{1/2} - \frac{\pi}{4} + \frac{m\pi}{2}\right]. \tag{27}$$

Comparing (27) and (26), we find the value of the constant A. We thus find explicit expressions for the coefficients C_l in the expansion of the wave function of a level with a reduced energy ε:

$$C_l = \left[\frac{\Delta\varepsilon}{(|\varepsilon| - 1)^{1/2}}\right]^{1/2} \mathcal{P}_{lm}((|\varepsilon| - 1)^{1/2}), \quad l \ll n. \tag{28}$$

The quantity $\Delta\varepsilon$ varies along the multiplet, i.e., is a function of ε (Fig. 3). On the interval $-2 < \varepsilon < -1$, it is given by an

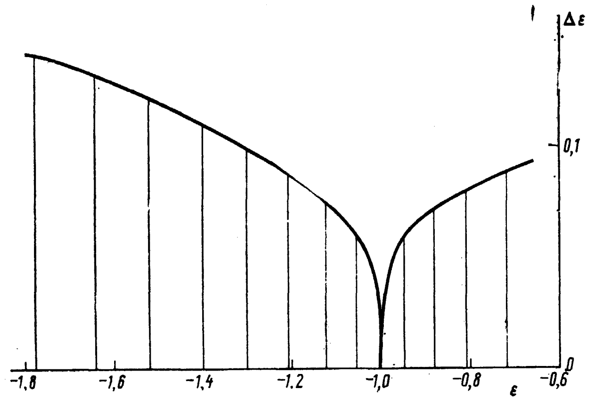

FIG. 3. Energy intervals in a dipole–dipole multiplet. Solid line—Analytic calculation from expression (29); vertical line segments—calculated through a numerical diagonalization of the perturbation matrix.

expression which follows from (20) (K is the complete elliptic integral of the first kind):

$$\Delta\varepsilon = \frac{2\pi}{n}\left[\frac{1}{(|\varepsilon|-{}^{3}/_{5})^{1/2}}\mathbf{K}(k)\right]^{-1}, \quad k=\left[\frac{2(2-|\varepsilon|)}{5|\varepsilon|-3}\right]^{1/2}. \tag{29}$$

From expression (28) we find explicit analytic expressions for the oscillator strengths for transitions of various series in the multiplet region with $-2<\varepsilon<-1$.

Lyman series. The oscillator strengths are proportional to one of the following quantities, depending on the magnetic quantum number of the upper level, m:

$$\begin{aligned} C_1^2 &= {}^{3}/_{2}(|\varepsilon|-1)^{1/2}\Delta\varepsilon, \quad m=0, \\ C_1^2 &= \frac{3}{4}\frac{(2-|\varepsilon|)}{(|\varepsilon|-1)^{1/2}}\Delta\varepsilon, \quad |m|=1. \end{aligned} \tag{30}$$

Balmer series. For transitions to $2s$ states, the oscillator strengths are proportional to one of the quantities in (30). For transitions to $2p$ states, they are instead proportional to one of the following quantities

$$\begin{aligned} C_2^2(\varepsilon) &= \frac{15}{16}\frac{(2-|\varepsilon|)^2}{(|\varepsilon|-1)^{1/2}}\Delta\varepsilon, \quad |m|=2, \\ C_2^2(\varepsilon) &= \frac{15}{4}(|\varepsilon|-1)^{1/2}(2-|\varepsilon|)\Delta\varepsilon, \quad |m|=1, \\ \left(\frac{5^{1/2}}{8}C_0+C_2\right)^2 &= \frac{45}{8}\frac{(|\varepsilon|-{}^{5}/_{4})^2}{(|\varepsilon|-1)^{1/2}}\Delta\varepsilon, \quad m=0, \quad \Delta m=0, \\ \left(-\frac{5^{1/2}}{4}C_0+C_2\right)^2 &= \frac{45}{8}\frac{(|\varepsilon|-{}^{3}/_{2})^2}{(|\varepsilon|-1)^{1/2}}\Delta\varepsilon, \quad m=0, \quad \Delta m=1. \end{aligned} \tag{31}$$

In the $m=0$ case, the transition probability amplitude consists of ($2p$–ns) and ($2p$–nd) terms. The coefficients $5^{1/2}/8$ and $5^{1/2}/4$ are the ratios of the corresponding transition amplitudes in the isolated hydrogen atom.[15]

Plots of the distributions of oscillator strengths (30) and (31) have completely different shapes (Fig. 4; the region from $\varepsilon=-2$ to $\varepsilon=-1$). In particular, in the limit $\varepsilon\to-1$ the intensity either increases sharply or tends toward zero, depending on the parity of the sum of indices $l+m$ of the Legendre function responsible for the observed intensity. For transitions of the Balmer series from $m=0$ states, the intensity dips to zero at $\varepsilon=-5/4$ ($\Delta m=0$; linear polarization of the emitted light) or at $\varepsilon=-3/2$ ($\Delta m=1$, circular polarization). Since expressions (30) and (31) are proportional to the same function $\Delta\varepsilon(\varepsilon)$ (the reciprocal of the density of energy levels), however, all these distributions can be found from each other by multiplication by simple functions of the energy.

Shown in Fig. 4 along with analytic expressions (30) and (31) are the results of a numerical solution of problem (3) for $n=30$ (the vertical line segments; the abscissa of a segment is determined by the energy of the perturbed state, and the height of the segment is determined by the transition probability). At the scale of these figures, the results of the numerical and analytic solutions coincide.

5. PROBABILITIES FOR CLASSICALLY ALLOWED TRANSITIONS

On the energy interval with $-1<E^{(1)}/u_d<-3/5$, the Keplerian orbit of an electron perturbed by the van der Waals interaction never becomes a straight line. Consequently, small values of the angular momentum are classically unattainable for the atomic electron. By virtue of the condition $\Delta l=1$, there are accordingly forbidden transitions to low-lying atomic states with a small angular momentum. More precisely, the probability for such transitions is exponentially small at $n\gg1$. To find the corresponding expression, we write the WKB solution of our recurrence relation (3) in the classically forbidden region, with $0<L<L_{t_1}$ (Fig. 2b). Using the results of Ref. 11, we find

$$C_l = \frac{A_{\mathrm{WKB}}}{2|v|^{1/2}}(-1)^{[l/2]} \times \exp\left[-\frac{1}{2}\int_L^{L_{t_1}} \operatorname{arch}\left(\frac{w_{cl}-E^{(1)}}{2p_{cl}}\right)dL\right]\Bigg|_{L=l+1/2} \tag{32}$$

[$(l/2)$ means the greatest integer in $l/2$]. This expression falls off exponentially as l decreases, simultaneously changing sign in each step.

In Legendre solution (6), the argument is purely imaginary in this energy interval. Using the appropriate asymptotic expression for the Legendre functions (formula 8.10.4 from the handbook in Ref. 16), we find, for $l^2-m^2\gg1$,

$$C_l = \frac{A}{(2\pi)^{1/2}}\frac{1}{(2-|\varepsilon|)^{1/4}}(-1)^{[l/2]}[(1-|\varepsilon|)^{1/2}+(2-|\varepsilon|)^{1/2}]^{l+1/2}. \tag{33}$$

Joining (32) with (33), and substituting in A_{WKB} from (24), we finally find

$$C_l = \left(\frac{\Delta\varepsilon}{(1-|\varepsilon|)^{1/2}}\right)^{1/2}\exp\left[-\frac{1}{2}\int_0^{L_{t_1}} \operatorname{arch}\left(\frac{w_{cl}-E^{(1)}}{2p_{cl}}\right)dL\right] \times |\mathscr{P}_{lm}(i(1-|\varepsilon|)^{1/2})|. \tag{34}$$

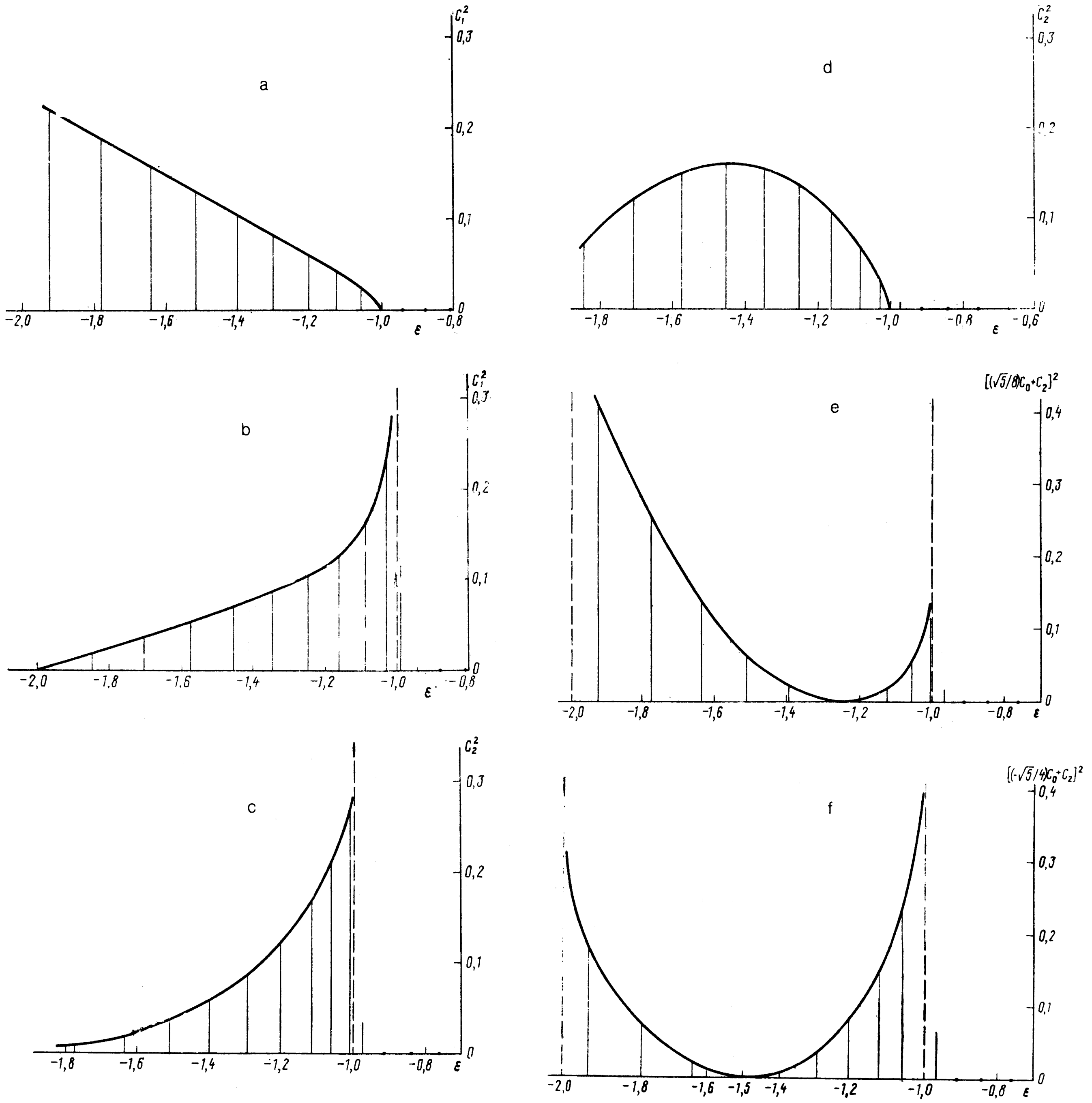

FIG. 4. Distributions of the oscillator strengths in a dipole–dipole multiplet (m is the magnetic quantum number of the upper level). a—Lyman series, $m = 0$; b—Lyman series, $m = 1$; c—Balmer series, $|m| = 2$; d—Balmer series, $|m| = 1$; e—Balmer series, $m = 0$, $\Delta m = 0$; f—Balmer series, $m = 0$, $\Delta m = 1$.

This result means that the distribution of oscillator strengths in the Lyman and Balmer series is given by expressions like (30) and (31), but with $|\varepsilon| - 1$ replaced by $1 - |\varepsilon|$, and with an additional factor which determines the probability for tunneling to a state with a zero angular momentum:

$$\bar{T} = \exp\left[-\int_0^{L_{t_1}} \operatorname{arch}\left(\frac{w_{cl} - E^{(1)}}{2p_{cl}}\right) dL\right]. \qquad (35)$$

The function $\Delta\varepsilon(\varepsilon)$ is also given by an expression which differs from (29):

$$\Delta\varepsilon = \frac{2\pi}{n}\left[\frac{2}{5}(2-|\varepsilon|)\right]^{1/2}\left[\mathbf{K}\left(\frac{1}{k}\right)\right]^{-1}, \qquad (36)$$

where the argument k is defined in (29). Expressions (34)–(36) have apparently been derived here for the first time.

To evaluate the accuracy of our analytic expressions, we give in Table I values of the square of the coefficient C_1, which determines the transition probabilities in multiplets of the Lyman series, for the cases $n = 30$, $m = 0$ and 1. The horizontal lines separate results corresponding to classically

TABLE I. Values of C_1^2 for $n = 30$ and $m = 0$ and 1.

ε	$m=0$		ε	$m=1$	
	$C^2_{1\,\mathrm{anal}}$	$C^2_{1\,\mathrm{num}}$		$C^2_{1\,\mathrm{anal}}$	$C^2_{1\,\mathrm{num}}$
−0,6253	$8,61\cdot 10^{-16}$	$8,47\cdot 10^{-16}$	−0,6251	$1,54\cdot 10^{-15}$	$1,58\cdot 10^{-15}$
−0,7189	$9,45\cdot 10^{-12}$	$8,97\cdot 10^{-12}$	−0,7187	$2,10\cdot 10^{-11}$	$2,08\cdot 10^{-11}$
−0,8041	$1,18\cdot 10^{-8}$	$1,12\cdot 10^{-8}$	−0,8038	$3,51\cdot 10^{-8}$	$3,48\cdot 10^{-8}$
−0,8800	$3,80\cdot 10^{-6}$	$3,57\cdot 10^{-6}$	−0,8797	$1,72\cdot 10^{-5}$	$1,71\cdot 10^{-5}$
−0,9454	$3,39\cdot 10^{-4}$	$3,11\cdot 10^{-4}$	−0,9447	$3,09\cdot 10^{-3}$	$3,14\cdot 10^{-3}$
			−0,9916	$1,86\cdot 10^{-1}$	$1,17\cdot 10^{-1}$
−1,0002	$6,42\cdot 10^{-4}$	$5,33\cdot 10^{-4}$			
−1,0556	$2,18\cdot 10^{-2}$	$2,04\cdot 10^{-2}$	−1,0284	$2,25\cdot 10^{-1}$	$2,26\cdot 10^{-1}$
−1,1233	$3,91\cdot 10^{-2}$	$3,87\cdot 10^{-2}$	−1,0874	$1,57\cdot 10^{-1}$	$1,60\cdot 10^{-1}$
−1,2037	$5,81\cdot 10^{-2}$	$5,84\cdot 10^{-2}$	−1,1616	$1,26\cdot 10^{-1}$	$1,27\cdot 10^{-1}$
−1,2960	$8,01\cdot 10^{-2}$	$7,99\cdot 10^{-2}$	−1,2480	$1,05\cdot 10^{-1}$	$1,05\cdot 10^{-1}$
−1,3997	$1,04\cdot 10^{-1}$	$1,03\cdot 10^{-1}$	−1,3460	$8,64\cdot 10^{-2}$	$8,67\cdot 10^{-2}$
−1,5143	$1,29\cdot 10^{-1}$	$1,29\cdot 10^{-1}$	−1,4552	$6,95\cdot 10^{-2}$	$6,96\cdot 10^{-2}$
−1,6399	$1,57\cdot 10^{-1}$	$1,57\cdot 10^{-1}$	−1,5753	$5,27\cdot 10^{-2}$	$5,29\cdot 10^{-2}$
−1,7762	$1,87\cdot 10^{-1}$	$1,87\cdot 10^{-1}$	−1,7063	$3,58\cdot 10^{-2}$	$3,58\cdot 10^{-2}$
−1,9233	$2,20\cdot 10^{-1}$	$2,20\cdot 10^{-1}$	−1,8480	$1,82\cdot 10^{-2}$	$1,83\cdot 10^{-2}$

allowed and forbidden transitions. Results calculated from analytic expressions (30) and (34) are given here and are compared with data found through a numerical solution of Eqs. (3). The agreement is good except near the singularity $\varepsilon = -1$.

CONCLUSION

We have analyzed the distribution of oscillator strengths in multiplets generated by a splitting of the levels of the hydrogen atom by the van der Waals interaction with a conducting surface. We have derived an analytic expression for the distribution of oscillator strengths. It has the form of the product of the energy separation of neighboring levels of a multiplet and the square of a Legendre function. The argument of this function is determined by the level energy. In the violet part of the multiplet, transitions to slightly excited states are classically forbidden. An additional barrier factor appears in the expression for the oscillator strength here.

Comparing our analysis with the case of diamagnetic perturbation,[9,10] we see that the intensity distribution in the spectra of the highly excited hydrogen atom perturbed by various external agents is actually described by the same universal formula. The distinctive nature of the perturbation is seen in a different energy dependence of the argument of the Legendre function and also in the properties of the function $\Delta\varepsilon(\varepsilon)$, which determines the interval between levels in various parts of the multiplet.

[1] I. M. Beterov and P. B. Lerner, Usp. Fiz. Nauk **159**, 665 (1989) [Sov. Phys. Usp. **32**, 1984 (1989)].

[2] S. Haroche, in *Atoms in Unusual Situations* (ed. J. P. Briand), Plenum, New York, 1986, p. 77.

[3] E. A. Hinds, Adv. At. Mol. Opt. Phys. **28**, 235 (1990).

[4] G. Barton, Proc. Roy. Soc. A **410**, 175 (1987).

[5] Y. Alhassid, E. A. Hinds, and D. Meschede, Phys. Rev. Lett. **59**, 1545 (1987).

[6] C. W. Clark and K. T. Taylor, J. Phys. B **13**, 737 (1980).

[7] E. A. Solov'ev, Pis'ma Zh. Eksp. Teor. Fiz. **34**, 278 (1981) [JETP Lett. **34**, 265 (1981)].

[8] P. A. Braun, Zh. Eksp. Teor. Fiz. **84**, 850 (1983) [Sov. Phys. JETP **57**, 492 (1983)].

[9] P. A. Braun, Zh. Eksp. Teor. Fiz. **97**, 1749 (1990) [Sov. Phys. JETP **70**, 986 (1990)].

[10] P. A. Braun, J. Phys. B **24**, 399 (1991).

[11] R. H. Garstang, Rep. Progr. Phys. **40**, 105 (1977).

[12] P. A. Braun, Teor. Mat. Fiz. **37**, 355 (1978).

[13] A. P. Kazantsev and V. L. Pokrovskiĭ, Zh. Eksp. Teor. Fiz. **85**, 1917 (1983).

[14] J. B. Delos, S. K. Knudsen, and D. W. Noid, Phys. Rev. A **28**, 7 (1983).

[15] H. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms*, Springer-Verlag, Berlin, 1957 (Russ. Transl. Fizmatgiz, Moscow, 1960).

[16] M. Abramowitz and I. A. Stegun (editors), *Handbook of Mathematical Functions*, Dover, New York, 1964 (Nauka, Moscow, 1979).

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