

QUASI-STATIONARY SPECTRUM OF HYDROGEN-LIKE ATOMS
NEAR A METAL SURFACE

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Abstract: The problem of quasi-stationary spectrum of a hydrogen-like atom near a metal surface is considered. A method for solving the corresponding boundary-value problem is applied which provides asymptotically exact result for the complex eigen-energies. The physical implications of the calculated quasi-stationary spectrum are discussed.

1. Introduction

One of the fundamental problems in theoretical studies of atom-metal surface interactions is the determination of the perturbed atomic energy spectrum. The discrete states of an atom, interacting with a metallic surface, are subject to a strong mixing with the continuum of metal states, becoming thus quasi-stationary in nature. The knowledge of the complex energy of these states is of greatest importance for understanding and for correct description of many resonance electron tunneling phenomena in the atom-metal system: resonant processes in slow atom-surface collisions, electron tunneling spectroscopy of adsorbed atoms, etc. Information about the energy level shift and broadening of perturbed atomic levels is necessary for determination of dipole moment of atom-metal complex, effective charge and binding energy of ad-atoms, in studies of virtual surface-impurity states, etc. The wide range of physical implications of quasi-stationary states in the atom-metal system has recently been reviewed by Gadzuk¹⁾.

Much theoretical work was devoted in the past decade to the problem of determining the complex energies of an atom interacting with a metal surface²⁻⁴⁾. The main feature of this activity was the use of a perturbational approach due to Fano⁵⁾, in which the mixing of a single atomic state with the metal continuum was accomplished within the lowest order only. In practice, the calculations of the

energy level shift ΔE and the level broadening Γ were reduced to calculation of matrix elements of the atom-metal interaction V_{am} between the unperturbed single-electron states

$$\Delta E = \langle a | V_{am} | a \rangle, \quad \Gamma \sim |\langle m | V_{am} | a \rangle|^2,$$

where $|a\rangle$ and $|m\rangle$ are the single-electron atomic and metallic wavefunctions, respectively.

However, the ordinary perturbational approach to problems with quasi-stationary spectrum suffers from some essential drawbacks⁶⁾. Namely, the unperturbed state functions in this case do not provide a good approximation to the problem in the whole domain of variation of variables. In the resonance electron tunneling phenomena, for example, the major contribution to the transition effect (or, equivalently, to the level broadening Γ) comes from the sub-barrier region, where the perturbational treatment is inapplicable at all⁷⁾.

In the present paper we consider the problem of determination of quasi-stationary spectrum of a hydrogen-like (or a highly excited) atom interacting with a metallic surface. The method we are going to apply in treating this problem is a modification of Cherry's comparison equation method⁸⁾, as elaborated by Slavyanov^{9,10)}. This modified comparison (or etalon) equation method enables one to obtain uniform asymptotic expansions for the eigen-functions and eigen-values of a Sturm-Liouville boundary problem containing a large parameter. With respect to the perturbational approach this method possesses some additional advantages^{9,10)}. The essential idea of the modified comparison equation method is to expand the argument of the etalon solution in an asymptotical series instead of multiplying the etalon solution by an asymptotic series, as accepted in standard versions of comparison equation method^{11,12)}.

In the next Section we give the Hamiltonian of our problem and separate the variables in the corresponding Schrödinger equation in the parabolic coordinates. In Section III we solve the »quasi-radial« part of the Schrödinger equation using the modified comparison equation method and calculate the complex energy spectrum. In Section IV we transform the imaginary energy part Γ from the parabolic quantum number representation to the more convenient angular momentum representation. Finally, in Section V we give some concluding remarks.

Atomic units ($m_e = \hbar = e^2 = 1$) will be used throughout this work.

2. Hamiltonian of the problem and separation of variables in Schrödinger equation

In the existing literature on atom-metal interaction it is customary to treat the metal within the Sommerfeld model and its electromagnetic polarization due to atomic charges to represent by electrostatic image forces. In the space outside the metal, where the image-force approximation is valid, the Hamiltonian of the atom-metal system is

$$H = H_0 + V_{ie} + V_{ic}, \quad (1)$$

where H_0 is the atomic Hamiltonian and V_{ie} and V_{ic} are the image potentials of the electron and atomic core, respectively.

Let us take the origin of the coordinate system in the center of atomic core (with a charge Z) and orient the z -axis perpendicularly and away from the surface. The metallic surface is assumed perfectly flat and placed at a distance $z = -R$ from the core. In this coordinate system the electronic Hamiltonian of our problem takes the form

$$H = -\frac{1}{2} \nabla^2 - \frac{Z}{r} - \frac{1}{4(z+R)} + \frac{Z}{\sqrt{x^2 + y^2 + (z+2R)^2}} \quad (2)$$

The interaction terms in the Hamiltonian (2) impose a pronounced axial symmetry to the problem. Moreover, for large atom-surface distances R , their dominant effect on the electronic motion is restricted to a relatively narrow cylindrical region around the z -axis. These circumstances enable one to separate the variables in the Schrödinger equation in the physically most important regions of electron motion, using parabolic coordinates. The solutions from these regions can be matched to provide a complete asymptotic solution¹³⁾.

Let us first consider the Schrödinger equation for our problem

$$H \Psi = E \Psi \quad (3)$$

in the region $r \ll R$. The image potentials V_{ie} and V_{ic} in this region can be represented by

$$V_{ie} = -\frac{1}{4(z+R)} = -\frac{1}{4R} + \frac{1}{4R^2} z + O(1/R^3), \quad (4a)$$

$$V_{ic} = \frac{Z}{\sqrt{x^2 + y^2 + (z+2R)^2}} = \frac{Z}{2R} - \frac{Z}{4R^2} z + O(1/R^3). \quad (4b)$$

The The Schrödinger equation (3) now gets the form

$$\left(\frac{1}{2} \nabla^2 + \tilde{E} + \frac{Z}{r} + \tilde{F}_z \right) \Psi = 0, \quad (5)$$

where

$$\tilde{E} = E - \frac{2Z-1}{4R}, \quad \tilde{F} = \frac{Z-1}{4R^2}. \quad (6)$$

Thus, in the region $r \ll R$, our problem is reduced to the hydrogen atom Stark problem in the external electric field \tilde{F} . Introducing parabolic coordinates

$$\begin{aligned} \xi &= r + z, & \eta &= r - z, & \Phi &= \arctan(y/x), \\ 0 &< \xi < \infty, & 0 &< \eta < \infty, & 0 &< \Phi < 2\pi, \end{aligned} \quad (7)$$

and representing the wavefunction Ψ in the form

$$\Psi = \frac{X(\xi) Y(\eta)}{\sqrt{2\pi \xi \eta}} \exp(\pm im \varphi), \quad (8)$$

the variables in Eq. (5) can readily be separated, giving the wellknown equations for $X(\xi)$ and $Y(\eta)$

$$X''(\xi) + \left[\frac{\tilde{E}}{2} + \frac{\beta_1}{\xi} + \frac{1-m^2}{4\xi^2} + \frac{\tilde{F}}{4} \xi \right] X(\xi) = 0, \quad (9a)$$

$$Y''(\eta) + \left[\frac{\tilde{E}}{2} + \frac{\beta_2}{\eta} + \frac{1-m^2}{4\eta^2} - \frac{\tilde{F}}{4} \eta \right] Y(\eta) = 0. \quad (9b)$$

The separation constants β_1 and β_2 in Eqs. (9) play the role of spectral parameters, and the energy spectrum is determined by the equation

$$\beta_1(E) + \beta_2(E) = Z. \quad (10)$$

From the boundary conditions

$$X(\xi)|_{\xi=0} = 0, \quad Y(\eta)|_{\eta=0} = 0, \quad (11)$$

associated with the Eqs. (9), one can obtain series expansions for β_1 and β_2 in terms of the small parameter \tilde{F} . Within the modified comparison equation method, such expansions have been derived by Slavyanov¹⁰⁾. Up to the first order we have

$$\beta_1 = k(-2\tilde{E})^{1/2} + \frac{\tilde{F}}{(-2\tilde{E})} \left(\frac{3}{2} k^2 + \frac{\tau}{2} \right) + O(\tilde{F}^2), \quad (12a)$$

$$\beta_2 = \kappa(-2\tilde{E})^{1/2} - \frac{\tilde{F}}{(-2\tilde{E})} \left(\frac{3}{2} \kappa^2 + \frac{\tau}{2} \right) + O(\tilde{F}^2), \quad (12b)$$

where $\tau = (1 - m^2)/4$ and k and κ are certain parameters discussed below. Inserting the expressions (6) for \tilde{E} and \tilde{F} in Eqs. (12) and expanding the result in series with respect to small parameter $1/R$, we obtain within the second order accuracy

$$\beta_1 = k(-2E)^{1/2} + \frac{k(2Z-1)}{4(-2E)^{1/2}} \frac{1}{R} - \frac{k(2Z-1)^2 + 4(-2E)^{1/2}(Z-1)(3k^2 + \tau)}{32(-2E)^{3/2}} \frac{1}{R^2} + O\left(\frac{1}{R^3}\right), \quad (13a)$$

$$\beta_2 = \kappa(-2E)^{1/2} + \frac{\kappa(2Z-1)}{4(-2E)^{1/2}} \frac{1}{R} - \frac{\kappa(2Z-1)^2 - 4(-2E)^{1/2}(Z-1)(3\kappa^2 + \tau)}{32(-2E)^{3/2}} \frac{1}{R^2} + O\left(\frac{1}{R^3}\right). \tag{13b}$$

The parameters k and κ in the above expressions for β_1 and β_2 are determined by the behaviour of electron wavefunction at large values of ξ and η , i. e. outside the region $r \ll R$. Examination of the interaction potentials included in the Hamiltonian (2) in the region outside the metal leads to conclusion that the image potentials are vanishingly small, for large ξ , so that the following boundary condition holds

$$X(\xi) \xrightarrow[\xi \rightarrow \infty]{} 0. \tag{14}$$

This condition immediately determines the values of the parameter $k^{(10)}$.

$$k = n_1 + \frac{m+1}{2}, \quad n_1 = 0, 1, 2, \dots, \tag{15}$$

where n_1 is the ordinary parabolic quantum number. Contrary to the case of $\eta\xi$ -direction, the image potentials in η -direction influence significantly the electronic motion at large η . From the standpoint of the quasi-stationary spectrum determination, the most important is the region around the negative z -axis. At large atom-surface distances this region gives dominant contribution to the electron transition effect in the atom-metal system. Assuming that this region is sufficiently narrow ($\xi \ll \eta$, $(\xi \eta)^{1/2} \ll R$), the image potentials V_{ie} and V_{ic} can be approximated by

$$V_{ie} = -\frac{1}{2(\xi - \eta + 2R)} \simeq -\frac{1}{2(2R - \eta)}, \tag{16a}$$

$$V_{ic} = \frac{Z}{\sqrt{\xi\eta + \left(\frac{\xi - \eta}{2} + 2R\right)^2}} \simeq \frac{2Z}{4R - \eta}, \tag{16b}$$

which again permits separation of variables in the Schrödinger equation (3) in (ξ, η) coordinates. The equation for the η -part of the electron wave function is then

$$Y''(\eta) + \left[\frac{E}{2} + \frac{\beta_2}{\eta} + \frac{1}{4(2R - \eta)} - \frac{Z}{4R - \eta} + \frac{1 - m^2}{4\eta^2} \right] Y(\eta) = 0. \tag{17}$$

We use the same notation for $Y(\eta)$ and β_2 as before since Equ. (17) is reduced to Eq. (9b) for $\eta \ll R$. The solution of the above equation should satisfy the following boundary conditions

$$Y(\eta)|_{\eta=0} = 0, \quad Y(\eta) \xrightarrow[\eta > \eta_1]{} \text{outgoing wave}, \tag{18}$$

where η_1 is the turning point of Equ. (17) closest to the metal surface at $\eta = 2R$.

Equations (17) and (18) define a boundary-value problem with complex «eigen-values» β_2 . This problem will be solved in the next section using the modified comparison equation method, and the quasi-stationary energy spectrum is then calculated from Eq. (10).

3. Determination of the quasi-stationary energy spectrum

It is convenient to transform the boundary-value problem (17) and (18) into an equivalent one by the following scaling transformation: $\eta = 2Rt$, $0 < t < 1$. Then we have

$$\frac{d^2 Y(t)}{dt^2} \left[-\frac{c^2}{4} + c \left(\frac{\lambda}{t} + \frac{\gamma}{4(1-t)} - \frac{\gamma Z}{2-t} \right) + \frac{\tau}{t^2} \right] Y(t) = 0, \quad (19)$$

$$Y(t)|_{t=0} = 0, \quad Y(t) \xrightarrow[t > t_1]{} \text{outgoing wave}, \quad (20)$$

where $t_1 = \eta_1/(2R) \simeq 1 - (\gamma/c)$ is the turning point closest to the surface (at $t = 1$), and

$$c = (-2E)^{1/2} 2R, \quad \lambda = \beta_2 (-2E)^{-1/2}, \quad \gamma = (-2E)^{-1/2}. \quad (21)$$

The parameter c is considered large and consequently Eq. (19) has a pole and close to it turning point at each of the endpoints of the interval $[0, 1]$. We shall find uniform asymptotic expansions for $Y(t)$ in two overlapping regions, each containing one of the endpoints $t = 0$ and $t = 1$. The matching condition for these two solutions in the intermediate region of t , together with the boundary conditions (20), will give the values of the spectral parameter λ .

Let us first consider the region around the point $t = 0$. If the condition $c \gg 4\lambda$ is satisfied (i. e. the extremely high excited states are excluded from consideration), then we have a turning point $t_0 = \frac{4\lambda}{c}$ close to the pole $t = 0$, and as etalon equation for Equ. (19) we can take the Whittaker equation

$$\frac{d^2 V(v)}{dv^2} + \left[-\frac{c^2}{4} + \frac{c\kappa}{v} + \frac{\tau}{v^2} \right] V(v) = 0, \quad (22)$$

where κ is a new spectral parameter and $v = v(t, c)$. The solution of Equ. (22), which is regular at $v = 0$, is

$$V(v) = \mathcal{M}_{\kappa, \frac{m}{2}}(cv). \quad (23)$$

In accordance with the modified comparison equation method we search for the solution $Y_0(t)$ of Equ. (19) in the vicinity of $t = 0$ in the form

$$Y_0(t) = [v'(t)]^{-1/2} V(v(t)). \tag{24}$$

Substituting this into Equ. (19) and using Equ. (22), we obtain a non-linear equation for $v(t)$

$$\begin{aligned} \frac{v'^2}{4} - \frac{1}{4} + \frac{1}{c} \left[\frac{\lambda}{t} + \frac{\gamma}{4(1-t)} - \frac{\gamma Z}{2-t} - \frac{\kappa v'^2}{v} \right] + \\ + \frac{\tau}{c^2} \left(\frac{1}{t^2} - \frac{v'^2}{v^2} \right) - \frac{1}{2c^2} \{v, t\} = 0, \end{aligned} \tag{25}$$

where

$$\{v, t\} \equiv \frac{v'''}{v'} - \frac{3}{2} \left(\frac{v''}{v'} \right)^2.$$

Now we assume that $v(t, c)$ and $\lambda(c)$ can be expanded in asymptotic series in inverse powers of c , i. e.

$$v(t, c) = \sum_{j=0}^{\infty} v_j(t) c^{-j}, \quad \lambda(c) = \sum_{j=0}^{\infty} \lambda_j c^{-j}. \tag{26}$$

The condition that Equ. (25) is satisfied for any power of c gives an infinite system of recurrence first-order differential equations for v_j

$$\begin{aligned} v_0'^2 &= 1, \\ v_0' v_1' &= 2 \left(\frac{\kappa v_0'^2}{v_0} - \frac{\lambda_0}{t} \right) - \frac{\gamma}{2(1-t)} + \frac{2\gamma Z}{2-t}, \\ v_0' v_2' &= -\frac{v_1'^2}{2} + \frac{2\kappa}{v_0} \left(2v_0' v_1' - \frac{v_1 v_0'^2}{v_0} \right) - \frac{2\lambda_1}{t} - \\ &\quad - 2\tau \left(\frac{1}{t^2} - \frac{v_0'^2}{v_0^2} \right) + \{v_0, t\}, \\ &\dots \end{aligned} \tag{27}$$

The condition that the transition points of Equ. (29) and Equ. (22) coincide is $v_0(0) = 0$. If we impose the initial conditions

$$v_j(0) = 0 \tag{28}$$

for the system (27), then the coefficients λ_j can be chosen so that $v'_j(t)$ are finite in the vicinity of $t = 0$. For λ_j we obtain

$$\begin{aligned} \lambda_0 &= \kappa v'_0(0), \\ \lambda_1 &= \kappa v'_1(0) + \tau \frac{v''_0(0)}{v'_0(0)}, \\ \lambda_2 &= \kappa v'_2(0) + \tau \left[\frac{v''_1(0)}{v'_0(0)} - \frac{v''_0(0) v'_1(0)}{v'^2_0(0)} \right], \\ &\dots \end{aligned} \tag{29}$$

Solving the system (27) with the initial conditions (28) and using (29) we obtain

$$v(t) = t + \frac{1}{c} \left[2\gamma Z \ln \left(\frac{2}{2-t} \right) + \frac{\gamma}{2} \ln(1-t) \right] + \frac{1}{c^2} v_2(t) + O\left(\frac{1}{c^3}\right), \tag{30}$$

$$\begin{aligned} \lambda = \kappa + \frac{1}{c} \frac{\gamma \kappa}{2} (2Z - 1) + \frac{1}{c^2} \left\{ -\frac{\gamma \kappa}{2} \left[\frac{\gamma \kappa}{4} (2Z - 1)^2 - \right. \right. \\ \left. \left. (Z - 1)(3\kappa^2 + \tau) \right] \right\} + O\left(\frac{1}{c^3}\right), \end{aligned} \tag{31}$$

where the term λ_2 in Equ. (31) is obtained using a Taylor expansion of $v_2(t)$ in the vicinity of $t = 0$

$$v_2(t) = \left[\frac{3}{2} (Z - 1) \kappa \gamma - \frac{1}{8} (2Z - 1)^2 \gamma^2 \right] t + O(t^2).$$

At this stage it is worthwhile to note that one can easily reproduce the expression (13b) for β_2 from Eqs. (31) and (21).

We turn now to solving Equ. (19) in the vicinity of the other endpoint, $t = 1$. If $c \gg \gamma$, then the pole at $t = 1$ and the turning point $t_1 \cong 1 - (\gamma/c)$ are close to each other and as etalon equation for Equ. (19) one can take

$$\frac{d^2 U(u)}{du^2} + \left[-\frac{c^2}{4} + \frac{c\gamma}{4u} \right] U(u) = 0, \tag{32}$$

where $u = u(t, c)$. The general solution of this equation can be represented as linear combination of the Whittaker functions $W_{\pm\alpha, \beta}(\pm z)$, i. e.

$$U(u) = D_1 W_{\frac{\gamma}{4}, \frac{1}{2}}(cu) + D_2 W_{-\frac{\gamma}{4}, \frac{1}{2}}(-cu). \tag{33}$$

We seek for the solution $Y_1(t)$ of Equ. (19) in the region around $t = 1$ in the following form

$$Y_1(t) = [u'(t)]^{-1/2} U(u(t)), \tag{34}$$

were the function $u(t)$ satisfies the non-linear equation

$$\begin{aligned} \frac{u'^2}{4} - \frac{1}{4} + \frac{1}{c} \left(\frac{\lambda}{t} + \frac{\gamma}{4(1-t)} - \frac{\gamma Z}{2-t} - \frac{\gamma u'^2}{4u} \right) + \\ + \frac{1}{c^2} \frac{\tau}{t^2} - \frac{1}{2c^2} \{u, t\} = 0 \end{aligned} \tag{35}$$

obtained from Eqs. (34), (32) and (19). Expanding $u(t, c)$ in an asymptotic series

$$u(t, c) = \sum_{i=0}^{\infty} u_i(t) c^{-i} \tag{36}$$

from Equ. (35) one obtains

$$\begin{aligned} u'^2 &= 1, \\ u'_0 u'_1 &= \frac{\gamma u_0'^2}{2u_0} - \frac{\gamma}{2(1-t)} - \frac{2\kappa}{t} + \frac{2\gamma Z}{2-t}, \\ &\dots \end{aligned} \tag{37}$$

Solving the system of equations (37) with the initial conditions $u_j(1) = 0$ and using Equ. (36) one finds

$$u(t) = 1 - t + \frac{1}{c} [2\kappa \ln t + 2\gamma Z \ln(2-t)] + O\left(\frac{1}{c^2}\right). \tag{38}$$

The solutions $Y_0(t)$ and $Y_1(t)$ should be matched in the region inside the barrier. Using the asymptotic expressions for the Whittaker functions¹⁴⁾ ($|c v| \gg 1, |cu| \gg \gg 1$), and equating the logarithmic derivatives of Y_0 and Y_1 one gets

$$D_1 2^{-2\gamma Z} c^{2\kappa + \gamma/2} e^{-c} e^{i\pi\left(\kappa - \frac{m+1}{2} - \frac{\gamma}{4}\right)} - D_2 \frac{\Gamma\left(\kappa + \frac{m+1}{2}\right)}{\Gamma\left(-\kappa + \frac{m+1}{2}\right)} = 0. \tag{39}$$

Another equation for the constants D_1 and D_2 can be obtained from the second of the boundary conditions (20). Using the asymptotic expressions for the Whittaker functions $W_{\pm \frac{\gamma}{4}, \frac{1}{2}}(\pm cu)$ when the first index is much larger than the argument^{1, 4)}, $\left(\frac{\gamma}{4} \gg cu, \frac{\gamma}{4} \gg 1\right)$ the mentioned condition gives

$$i D_1 e^{-i\pi\gamma/4} + D_2 \left(\frac{4e}{\gamma}\right)^{\gamma/2} = 0. \quad (40)$$

The condition that the homogeneous system of linear equations (39) and (40) has a non-trivial solution gives the following «dispersion relation» for the parameter κ

$$\frac{\cos \pi \left(\kappa - \frac{m}{2}\right)}{\pi} = i \frac{\left(\frac{4e}{\gamma}\right)^{\gamma/2} 2^{-2\gamma Z}}{\Gamma\left(\kappa + \frac{1+m}{2}\right) \Gamma\left(\kappa + \frac{1-m}{2}\right)} c^{2\kappa + \gamma/2} e^{-c} e^{i\pi\left(\kappa - \frac{m+1}{2}\right)} \quad (41)$$

where the relation $\Gamma\left(\frac{1}{2} + x\right) \Gamma\left(\frac{1}{2} - x\right) = \pi/\cos \pi x$ has been used. Solving the equation (41) by iteration we obtain

$$\kappa = \kappa_0 + \delta, \quad \kappa_0 \equiv n_2 + \frac{m+1}{2}, \quad n_2 = 0, 1, 2, \dots, \quad (42)$$

$$\delta = -i \frac{\left(\frac{4e}{\gamma}\right)^{\gamma/2} 2^{-2\gamma Z}}{n_2! (n_2 + m)!} c^{2\kappa_0 + \gamma/2} e^{-c} \left[1 + O\left(\frac{1}{c}\right)\right], \quad (43)$$

where n_2 is the second parabolic quantum number. The exponentially small imaginary correction in the parameter κ indicates that the obtained electronic states are quasi-stationary in nature. Inserting the above result for κ into Equ. (13b) we obtain a complex value for the separation constant β_2 . Using expressions (13) in Equ. (10) and solving it by iteration we obtain the following asymptotic expansion for the complex energy spectrum

$$E = E_0 + \Delta E(n_1, n_2, m) - \frac{i}{2} \Gamma(n_1, n_2, m), \quad (44)$$

where

$$E_0 = -\frac{Z^2}{2n^2}, \quad (45a)$$

$$\Delta E(n_1, n_2, m) = \frac{2Z-1}{4R} - \frac{3n(n_1 - n_2)(Z-1)}{8ZR^2} + O(1/R^3), \quad (45b)$$

$$\Gamma(n_1, n_2, m) = \frac{Z^2 \left(\frac{4eZ}{n}\right)^{n/2Z}}{2^{2n-1} n^3 n_2! (n_2 + m)!} \left(\frac{2ZR}{n}\right)^{\frac{n}{2Z} + 2n_1 + 1 + m} \times \quad (45c)$$

$$\times \exp \left[-\frac{2ZR}{n} + \frac{n(2Z-1)}{2Z} \right] \left[1 + O(1/R) \right],$$

where $n = n_1 + n_2 + m + 1$ is the principal quantum number. The above expressions for $\Delta E(n_1, n_2, m)$ and $\Gamma(n_1, n_2, m)$ are asymptotically correct, i. e. they are valid under the assumptions $R \gg n^2/Z^2$ and $\frac{n}{4Z} \gg 1$. We note that the perturbational method can give correct expression for ΔE , although in a much more laborious manner than presented here. However, the level broadening $\Gamma(n_1, n_2, m)$ cannot be obtained correctly within a perturbational approach. As calculations of Gadzuk^{3,4)} have shown, perturbational method fails to reproduce both the pre-exponential factor and the second exponential term in Equ. (45c). In a recent paper by Chaplik¹⁵⁾ the imaginary part of the complex energy has been calculated using the standart JWKB method (the case $Z = 1, m = 0$ only). However, Chaplik used a twice larger electron image potential in the Hamiltonian, which resulted in an incorrect pre-exponential factor and in an absence of the second exponential factor in $\Gamma(n_1, n_2, m)$.

To make a more direct comparison of the level broadening result of this paper with the corresponding perturbational calculations, one has to convert Γ from parabolic quantum representation. This representation will make it possible to extend our result for the level broadening to arbitrary (non-hydrogen-like) highly excited atoms within a first-order approximation.

4. Angular momentum representation of energy level broadening

In order to obtain the value of energy level broadening in the ordinary angular momentum representation (n, l, m) , one has to sum up $\Gamma(n_1, n_2, m)$ over the possible values of the parabolic quantum numbers n_1 and n_2 . Accordingly, we have

$$\Gamma(n, l, m) = \sum_{n_1 + n_2 = n - 1 - m} |\langle l | n_1 n_2 \rangle|^2 \Gamma(n_1, n_2, m), \quad (46)$$

where $\langle l | n_1 n_2 \rangle$ are the coefficients which connect the angular momentum and the Stark eigenstates. These coupling coefficients are simply related to the Clebsch-Gordan coefficients¹⁶⁾. Using the fact that $\Gamma(n_1, n_2, m)$ takes its maximum value

for $n_1 = 0, n_2 = n - 1 - m$ and using the symmetry $|\langle l | n_1 n_2 \rangle| = |\langle l | n_2 n_1 \rangle|$ of the coupling coefficients, the above sum can be written as

$$\Gamma(n, l, m) = \Gamma_0(n, l, m) \left[\sum_{s=0}^{n-l-1} A(s) F(s, n) + \sum_{\nu=l-1-m}^{n-1-m} B(\nu) F(\nu, n) \right], \quad (47)$$

$$(s + \nu = n - 1 - m),$$

where

$$\Gamma_0(n, l, m) = \frac{Z^2 |\langle l | 0, n - 1 - m \rangle|^2}{2^{2n-1} n^3 (n-1)! (n-1-m)!} \left(\frac{4eZ}{n} \right)^{n/2Z}. \quad (48)$$

$$\left(\frac{2ZR}{n} \right)^{\frac{n}{2Z} + 2n-1-m} e^{-\frac{2ZR}{n} + \frac{n(2Z-1)}{2Z}},$$

$$F(s, n) = \left(\frac{2ZR}{n} \right)^{-2s}, \quad (49)$$

and the coefficients $A(s)$ and $B(\nu) = A(s \rightarrow n - 1 - m - \nu)$ can be calculated by some recursion relations¹⁷⁾. Since the second term in (47) is of order of magnitude $O(1/R^2)$, it follows that within the accuracy with which $\Gamma(n_1, n_2, m)$ was calculated, only the first term in the sum (47) should be retained. Invoking the explicit relation between $\langle l | n_1 n_2 \rangle$ and the Clebsch-Gordan coefficients¹⁶⁾, one obtains the following expression for $\Gamma(n, l, m)$ ($A(0) = 1$)

$$\Gamma(n, l, m) = \frac{Z^2 e^n}{2^{2n-1} n^3 m! (n+l)! (n-l-1)! (l-m)!} \frac{(2l+1)(l+m)!}{(4Z/n)^{n/2Z} \left(\frac{2ZR}{n} \right)^{\frac{n}{2Z} + 2n-1-m} e^{-\frac{2ZR}{n}}}. \quad (50)$$

It is seen from this expression that the axially symmetric states ($m = 0$) give the main contribution to the energy level broadening. The contribution of the states with $m \neq 0$ is of the order of $O(1/R)$ or less. Having this in mind and averaging $\Gamma(n, l, m)$ over the projections of angular momentum on the z -axis, we obtain

$$\Gamma(n, l) = \frac{Z^2 e^n}{2^{2n-1} n^3} \frac{1}{(n+l)! (n-l-1)!} \left(\frac{4Z}{n} \right)^{n/2Z} \times \quad (51)$$

$$\times \left(\frac{2ZR}{n} \right)^{\frac{n}{2Z} + 2n-1} e^{-\frac{2ZR}{n}}.$$

In order to extend this result to excited states of an arbitrary atom within a single electron approximation, we take $Z = 1$ and $n = 1/\alpha$. Introducing further a Coulomb normalization constant for the excited electron wavefunction¹⁸⁾,

$$B = \frac{\alpha (2\alpha)^{1/\alpha}}{\left[\Gamma\left(\frac{1}{\alpha} + l + 1\right) \Gamma\left(\frac{1}{\alpha} - l\right) \right]^{1/2}}, \quad (52)$$

the expression (51) for $\Gamma(n, l)$ can be put in the form

$$\Gamma(\alpha, l) = B^2 \left(\frac{\alpha}{2}\right)^{1/\alpha} R^{\frac{2}{\alpha} + \frac{1}{2\alpha} - 1} e^{-2\alpha R}. \quad (53)$$

If the Coulomb approximation (52) for the wave function normalization constant of the active electron cannot be considered valid, then the constant B in Equ. (53) can be determined by joining the Coulomb-like asymptotics of the electron wavefunction with some more exact (e. g. variational or Hartree-Fock) wavefunction in the region where they both well represent the electronic motion. This procedure is explained in more details elsewhere¹¹⁾.

The expression (53) can be compared in a more direct way with the perturbational result of Gadzuk³⁾. The R -dependence of Gadzuk's result for ns -states is

$$\Gamma_G(\alpha, 0) \sim \alpha^4 R^3 e^{-2\alpha R} [1 + O(1/R^2)]. \quad (54)$$

As discussed in the Introduction, the perturbational method gives a quite different pre-exponential factor in Γ with respect to the asymptotical methods. This fact is now well established for other electron tunneling phenomena also^{6,19)}.

5. Concluding remarks

In the previous two sections we have presented the results of our calculations on the quasi-stationary energy spectrum of an atomic particle interacting with a metallic surface. The method of comparison equation, applied in this work, provides asymptotically exact results for the spectrum within the physical approximations adopted. In our case, the results on energy level shift and broadening are correct if the following conditions are satisfied: $R \gg (m/Z)^2$ (or $\alpha^2 R \gg 1$) and $\left(\frac{n}{4Z}\right) \gg 1$ (or $4\alpha \ll 1$). In principle, the modified comparison equation method gives a possibility to calculate also the corrective term in $\Gamma(n_1, n_2, m)$ which is of the order of $O(1/R)$. However, in most of the physical applications of the obtained quasi-stationary spectrum, the leading term of Γ may be considered sufficient.

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KVAZI-STACIONARNI SPEKTAR VODONIKU SLIČNIH ATOMA U BLIZINI POVRŠINE METALA

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Sadržaj

Razmotren je problem kvazi-stacionarnog spektra vodoniku sličnog atoma u blizini metalne površine.

Pomoću metoda etalonskih jednačina nađen je asimptotski egzaktni izraz za kompleksne energije sistema. Imaginarni deo energije određuje verovatnoću prelaska u jedinici vremena atomskog elektrona u kontinuum metalnih stanja. Izraz za verovatnoću prelaza dat je kako u reprezentaciji paraboličnih kvantnih brojeva tako i u reprezentaciji angularnog momenta.

Pokazano je da perturbacioni prilaz tom problemu daje nekorektan predekonjoncijalni faktor u izrazu za verovatnoću.