Image-Potential States in Small Metal Particles

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Electron states near the surface of small metal particle caused by an image charge (image-potential states) have been investigated. The wave functions were calculated and the energy spectrum of these states was found depending on particle size. To estimate the influence of static magnetic field on the image-potential states the model problem, in which electron is localized on a surface of a sphere in uniform magnetic field was solved. In this case the field dependence of the energy levels represents a complex level crossing structure.

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Numerous physical effects based on specific states of ions and electrons at a surface of conductor have been the subject of large number of theoretical and experimental works and find expanding practical applications. One of the effects is an existence of image-potential states (IP states) which are the electron states localized at a metal surface in the field of image charge [1]. In a case of massive samples an electron bound to its own image does not penetrate the metal surface because of peculiarities of energy-band structure of the metal. IP states were widely investigated by low-energy electron diffraction (LEED), inverse photoemission (IPES) [2] and scanning tunneling spectroscopy (STS) [3]. In work [4] the transient processes signals have been observed after action of short super high frequency pulse on a metal surface while static magnetic field was perpendicular to the surface. The origin and the properties of observed signals have been explained [5] in terms of combined magnetic resonance [6] of electrons localized in IP states.

Last decade a particular attention has been given to nanotechnologies. One of the systems widely used in micro- and nanoelectronics is an ensemble of small (nanosized) metal particles embedded into dielectrical or semiconducting matrix. In such a system electron states localized on the particle surface play significant role in particle interactions with surrounding matrix and interparticle interactions, in forming of system response to external electromagnetic radiation, in transfer of electrons throughout the system.

The aim of the present work is the investigation of electron IP states for small metal particle and their features determined by finite (nano) size of particle.

In the case of small spherical metal particle image potential causing an electron localization near particle surface can be approximated by the following formulae:

$$V_{image}(r) = \begin{cases} -\dfrac{\lambda a e^2}{r^2 - a^2}, & r \neq a \\ -\infty, & r = a \end{cases}, \tag{1}$$

where a is a radius of particle and λe is an effective image charge. To obtain energy spectrum and wave functions of electron IP states one must solve the Schrödinger equation for above mentioned potential

$$\left[-\frac{\hbar^2}{2m^*}\Delta + V_{image}(r)\right]\psi(r,\theta,\alpha) = E\psi(r,\theta,\alpha). \tag{2}$$

Here m^* is effective mass of electron in IP state. Due to spherical symmetry the wave function has the following form: $\psi(r,\theta,\alpha) = \psi^{(\ell)}(r)Y_{\ell m}(\theta,\alpha)$, where $\psi^{(\ell)}(r)$ is radial part of wave function and $Y_{\ell m}(\theta,\alpha)$ is the spherical function. Then the equation (2) is reduced to equation for radial function:

$$\frac{d^2\psi^{(\ell)}(\rho)}{d\rho^2} + \frac{2}{\rho}\frac{d\psi^{(\ell)}(\rho)}{d\rho} + \left[\tilde{\varepsilon} + \frac{b}{\rho^2 - 1} - \frac{c}{\rho^2}\right]\psi^{(\ell)}(\rho) = 0, \tag{3}$$

The dimensionless parameters in Eq. (3) are $\rho = r / a$, $\tilde{\varepsilon} = 2a^2E / e^2a_0$, $b = 2\lambda a / a_0$, $c = \ell(\ell+1)$, where a_0 is the Bohr radius and ℓ is orbital quantum number. The equation (3) can be solved by expansion of $\psi^{(\ell)}(r)$ in power series. The equation has two singular points: $\rho = 1$ - regular point, $\rho = \infty$ - essential singularity. The solution about a regular point ($\rho = 1$) can be written [7] in the form:

$$\psi_1^{(\ell)}(\rho) = A(\rho - 1)\left[1 + \sum_{n=1}^{\infty} a_n(\rho - 1)^n\right], \tag{4}$$

where A is a constant and a_n are coefficients satisfy to the recurrence equation

$$a_n = -\left[p_n + q_n + \sum_{m=1}^{n-1} a_{n-m}[(n-m+1)p_m + q_m]\right] / n(n+1), \qquad a_1 = -(p_1 + q_1)/2, \;\; n = 1,2,3,...,$$

with $\quad p_{m(\geq 1)} = 2(-1)^{m+1}, \quad q_2 = (\tilde{\varepsilon} - c - b/4), \quad q_{m(1,\geq 3)} = (-1)^m\left[c(1-m) - b/2^m\right].$

The solution about infinity can be represented [8] as a power asymptotic expansion:

$$\psi_2^{(\ell)}(\rho) \sim Be^{-\alpha\rho}\rho^{-1}\sum_{m=1}^{\infty} b_m\rho^{-m}, \tag{5}$$

where $\alpha = \sqrt{-\tilde{\varepsilon}}$, B is a constant and expansion coefficients b_m are determined by the following expression:

$$b_{m-1} = -\frac{1}{2\alpha(m-1)}\left[(m-1)(m-2)b_{m-2} + \sum_{p=1}^{q} Z_p b_{m-2p}\right] \quad \text{for} \quad m = 1,2,3,\ldots,$$

$$Z_1 = b - c, \qquad Z_{p(\geq 2)} = b, \;\; q = m/2 \;\; \text{for even } m \text{ and } \; q = (m-1)/2 \;\; \text{for odd } m$$

where b_0 is arbitrary constant. The asymptotic expansion (5) is the alternating series and so its maximal accuracy is achieved by cutting off the series on minimum module term [9].

Solutions (4) and (5) must be sewed at some point ρ^* in which the smoothness condition should be fulfilled:

$$\psi_1^{(\ell)}(\rho^*) = \psi_2^{(\ell)}(\rho^*), \qquad \psi_1^{(\ell)\prime}(\rho^*) = \psi_2^{(\ell)\prime}(\rho^*). \tag{6}$$

The set of equations (6) leads to the spectrum of IP states. The convergence of $\psi_1^{(\ell)}(\rho^*)$, $\psi_2^{(\ell)}(\rho^*)$ and their derivatives [7,10] at given point ρ^* strongly depends on particle radius a and dimensionless energy $\tilde{\varepsilon}$, orbital quantum number ℓ being of minor importance. For certain values of a and ℓ the series in set (6) will be convergent at point ρ^* only for $\tilde{\varepsilon}$ falls in some interval. The estimation made for limit case of metal plane [5] shows that $\tilde{\varepsilon} \in (-2363, 0)$. Below for definiteness the particle radius a was taken equal to 5 nm and $\ell = 0$. Then for $\rho^* = 1.4$ the solution convergence takes place when $\tilde{\varepsilon} \in [-2363, -250]$ and smoothness condition is fulfilled only for two values of energy: $\tilde{\varepsilon}_1 = -2185.4254$ and $\tilde{\varepsilon}_2 = -513.5375$ which are the first and second energy levels of IP state. The shift of point ρ^* to the value 1.7 leads to the interval $\tilde{\varepsilon} \in [-550, -200]$ and to $\tilde{\varepsilon}_2 = -513.5375$ and $\tilde{\varepsilon}_3 = -206.5863$. In similar way all energy levels of IP states may be calculated for given size of metal particle.

The first four energy levels ($n = 1, 2, 3, 4$) for different values of orbital number ℓ are presented in Fig 1.

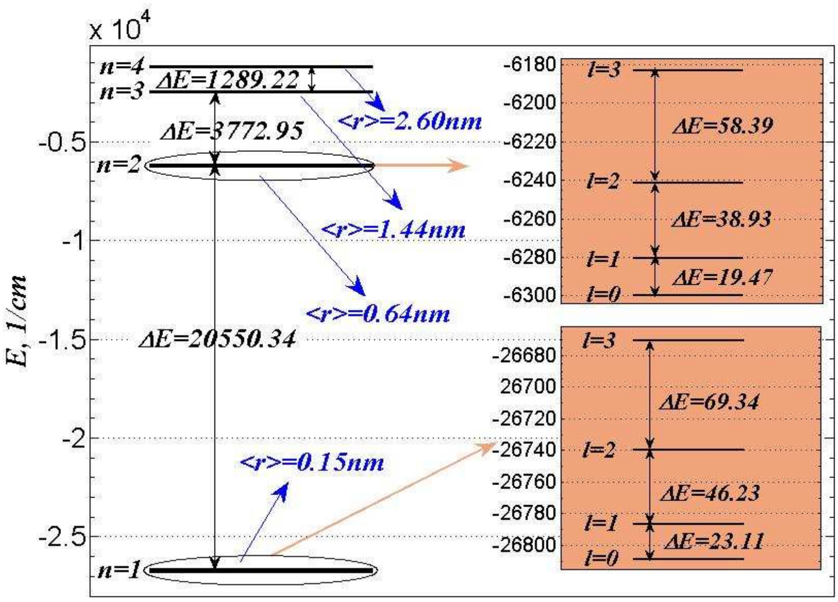

Fig.1. The energy diagram of IP states electron situated closed by spherically metal sample. The radius of particle is taken $a = 5nm$. Here n is the principal quantum number and ℓ is the orbital quantum number. The average distances from the surface are denoted by blue for each of the states and they are depended on ℓ weakly.

A special interest is the possibility of investigation of IP states by magnetic resonance methods, in particular combined magnetic resonance. For this purpose the influence of static magnetic field on IP state should be taken into account. This essentially hinders the solving of the problem. A simple model was considered to gain insight into the behavior of real system: the energy spectrum and wave functions were calculated for an electron whose motion is constrained to the surface of a sphere of radius a in the magnetic field. To restrict an electron motion the term corresponding to infinitely deep and narrow well at $r = a$ was included in Schrödinger equation. Because the radial motion is absent wave function can be expressed, as follows:

$$\psi(\theta,\varphi) = (1-x^2)^{n/2}\left[C_1\sum_{k=0}^{\infty} a_{2k}x^{2k} + C_2\sum_{k=0}^{\infty} a_{2k+1}x^{2k+1}\right]e^{i\varphi\ell_z}, \tag{7}$$

where $x = \cos\theta$, $n = |\ell_z|$ (ℓ_z is magnetic quantum number) and C_1, C_2 are the constants. Series coefficients satisfy the recurrence equation:

$$\lambda^2 a_{k-2} + (k+1)(k+2)a_{k+2} - \left[k(k+1) + 2nk - B\right]a_k = 0, \qquad k \geq 2, \tag{8}$$

$$a_0 = 1,\ \ a_1 = 1,\ B = 2ma^2E/\hbar^2 - \lambda^2 - 2\lambda\ell_z - n(n+1).$$

Here $\lambda = \Phi / 2\Phi_0$, where Φ is the flux through the equatorial plane and Φ_0 is a flux quantum.

From Eq. (8) one can obtain the continued fractions the roots of which give the energy spectrum of considered problem. Field dependence of energy levels leads to the complex level crossing structure [11]. The calculated dependence of several low-lying energy levels on magnetic field is presented in Fig.2. The similar behavior in magnetic field can be expected for energy levels of real IP states for small metal particles.

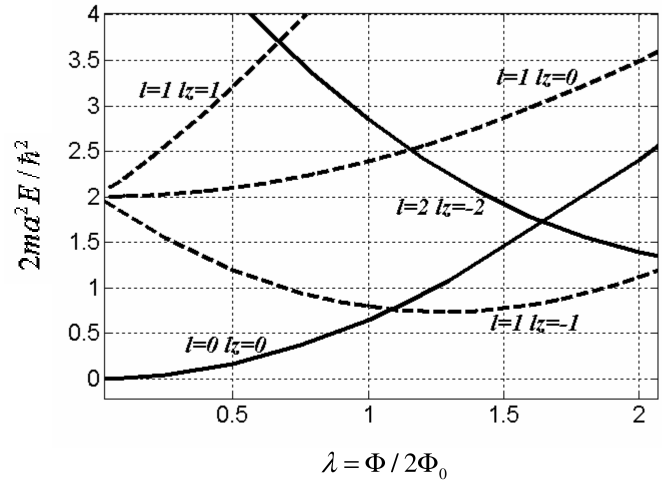

Fig.2. The energy spectrum of electron confined of sphere as function of magnetic field.

References

1. Straub D., Himpsel F. J. *Phys. Rev. Lett.* **52**, 1922 (1984).
2. Himpsel F. J., Ortega J. E. *Phys. Rev.* B **46**, 9719 (1992).
3. Yang S., Bartynski R.A., Kochanski G.P., Papdia S., Fonden T., Persson M. *Phys. Rev. Lett.* **70**, 849 (1993).
4. Smolakov B.P., Solovarov I.K. *JETP* **93**, 1039 (1987).
5. Zhikharev V.A., Kessel A.R. *Surface: Physics. Chemistry. Mechanics.* **5,** 13 (1988).
6. Rashba E.I., Sheka V.I. *SSP* **3**, 1863 (1961).
7. Whittaker E.T., Watson G.N. in *A course of modern analysis*, edited by F.V. Shirokov (Editorial URSS, Moscow, 2002), p.279.
8. Kamke E. in *Handbook of Ordinary Differential Equations*, (Lan, St. Petersburg, 2003), p.124.
9. Gradshteyn I. S., Ryzhik I. M. in *Tables of integrals, series and products*, (Fizmatlit, Moscow, 1962), p.32.
10. Erdelyi A. in *Asymptotic Expansions*, (Fizmatgiz, Moscow, 1962).
11. Kim J.H., Vagner I.D., Sundaram B. *Phys. Rev.* B **46**, 9501 (1992).