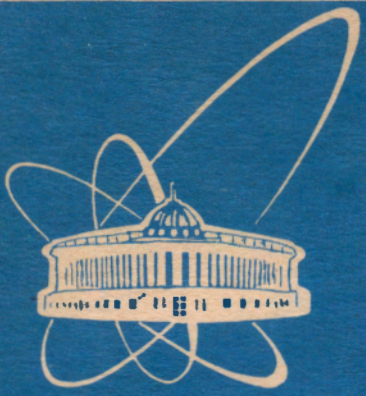

ОБЪЕДИНЕННЫЙ
ИНСТИТУТ
ЯДЕРНЫХ
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Дубна

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NON-PERTURBATIVE BEHAVIOUR OF HYDROGEN ATOM IN VAN DER WAALS FIELD

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The problem of a hydrogen atom in the generalized van der Waals field [1-3]

$$\Delta V(x,y,z) = \gamma(x^2 + y^2 + \beta^2 z^2) \tag{1}$$

(where $\gamma > 0$ and β are constants and (x,y,z) are the coordinates of an electron relative to a nucleus) has a broad interest in physics. A large number of recent publications deal with different aspects of the well-known particular case, $\beta = 0$, of the problem (the quadratic Zeeman effect [4]). Another physically interesting limit, as an example of a confining potential [5], is the spherical quadratic Zeeman interaction ($\beta = 1$) [6]. The case, $\beta = \sqrt{2}$, corresponds to the instantaneous van der Waals interaction between an atom and metal surfaces [7] and is a subject of extensive discussions so far [8]. Note also the connection which was found in [2] between the problem (1) and a set of two coupled sextic anharmonic oscillators and the recent analysis of the chaos-order-chaos transitions in this system (see [2],[9],[10] and Refs. therein).

In the paper [1] a general consideration (for arbitrary $0 \leq \beta \leq 2$), based on the adiabatic invariant

$$\Lambda = (4 - \beta^2)A^2 + 5(\beta^2 - 1)A_z^2 \tag{2}$$

(where $\vec{A}$ is the Runge-Lenz vector [4]), has been suggested for the weak perturbation ΔV (1). This generalization for an arbitrary β of the result $\Lambda = 4A^2 - 5A_z^2$, obtained in [11],[12] for the special case $\beta = 0$, has permitted a reducing of the weak perturbation (1) to a simple effective operator withing the manifold $n = const$

$$\Delta V = \frac{1}{2}\gamma n^2[\Lambda - (\beta^2 - 1)L_z^2 + n^2(\beta^2 + 1) + \beta^2 + 3]. \tag{3}$$

By studying problem (1) as a function of β, one may analyze how the instantaneous van

der Waals ($\beta = \sqrt{2}$) and the well-studied diamagnetic ($\beta = 0$) cases are related one to another and connected with the adjacent dynamical symmetries found in [1] for certain values of β ($\beta = 1/2, 1$ and 2).

In this Letter I extend the consideration to the non-perturbative region of the problem. Highly excited states of a hydrogen atom subjected to interaction ΔV (1) are analyzed with the method of global approximation on a subspace grid [13] by using as an example the $n = 10, m = 0$ multiplet studied in paper [1] by the perturbative way. Problem (1) is reduced to the system of N differential equations [14]

$$\sum_{j}^{N}\{\delta_{kj}\frac{d^2}{dR^2} + 2(\delta_{kj}\varepsilon^N - V_{kj}(R))\}\psi_j(R) = 0. \qquad (4)$$

for the eigenvalue ε^N and eigenfuncion $\psi^N(R, \Omega_j) = \frac{1}{R}\cdot\{\psi_j(R)\}$ we are looking for on the subspace grid $\Omega_j = \{cos\theta_j\}_1^N$. Where

$$V_{kj}(R) = \{-\frac{1}{R} + \gamma R^2(sin^2\theta_k + \beta^2 cos^2\theta_k)\}\delta_{kj} + \frac{1}{2R^2}\cdot\sum_{l}^{N} l(l-1)P_{l-1}(\theta_k)P_{lj}^{-1}, \qquad (5)$$

$P_l(\theta)$ are the Legendre polynomials and P_{lj}^{-1} is the inverse matrix $N \times N$ to $\{P_l(\theta_j)\}$ defined on the grid $\Omega_j = \{cos\theta_j\}_1^N$. The summation index l takes the values 1,3, ..., 2N-1 and 2,4,...,2N for the respective states with positive or negative Z-parity, and the negative nodes of the 2N-point Gauss quadrature on [−1,1] are used as N grid points $\Omega_k = -cos\theta_k \in [-1, 0]$ ($k = 1, 2, ..., N$). (Interaction (1) permits the separation of the azimuthal variable ϕ in spherical coordinates (R, θ, ϕ)). Using the solution $\psi_j(R)$ of the system of equations (4) one can evaluate the wave function

$$\psi^N(R, \theta) = \frac{1}{R}\sum_{lj}^{N} P_l(\theta)P_{lj}^{-1}\psi_j(R), \qquad (6)$$

approximating the eigenfunction $\psi(R, \theta)$ of the initial problem (1) as $N \to \infty$. In my previous paper [14], devoted to the problem of a hydrogen atom in crossed fields, a fast convergence of the expansion (6) with respect to N was demonstrated and also the error analysis of the numerical integration of system (4) over R was given for the diamagnetic case ($\beta = 0$): low-lying excited states have been analyzed in the region of very strong fields, $1 \le H = \sqrt{8\gamma} \le 10^3$ ($10^{-3} \le \gamma \le 10^5$), and highly accurate binding energies for these states were obtained. In this Letter the consideration is extended to a highly excited atom ($n \sim 10$) perturbed by the interaction (1). The evaluation has been performed for two field strenghts, γ, from the region where the perturbation formulas [1] are still working well and where the system already exhibits considerable non-perturbative behaviour. Two such cases are demonstrated on Figs. 1(a,b) where the normalized energy shifts, $\Delta E = (\varepsilon + 1/(2n^2))/(\gamma n^4)$, of the states in the $n = 10, m = 0$ manifold calculated as a function of β are given for two fields $\gamma = 2\cdot 10^{-10}$ and $2\cdot 10^{-8}$. Note that in the diamagnetic limit ($\beta = 0$) the calculated spectrum represents the eigenstates of a hydrogen atom in the strong magnetic fields $H = \sqrt{8\gamma} \sim 10^5 G$ and $\sim 10^6 G$, respectively. The calculations with $N \le 6 (l \le 12)$ give the order of accuracy $\sim 10^{-3}$ for the shifts ΔE for $\gamma = 2\cdot 10^{-8}$ and more accurate evaluations for the weaker perturbation $\gamma = 2\cdot 10^{-10}$. The deviation of the shifts ΔE of the n=10-manifold presented on Fig.1(a) from the perturbation result [1] obtained by a diagonalisation of the operator (3) does not exceed the value $\sim 10^{-3}$ for the field $\gamma = 2\cdot 10^{-10}$. Rather unexpectedly the non-perturbative regime is already apparent for $\gamma = 2\cdot 10^{-8}$ in the region $\gamma n^4 \ll 1$. In this case (Fig.1(b)) the system exhibits considerable deviation of the spectrum ΔE from the perturbative behaviour as

in Fig.1(a). This effect is more evidently developed for oscillator strengths. This is demonstrated in Figs. 1 (c,d) , where the relative oscillator strengths (dipole transition probabilities $W_{1s}^{nL} = 3 \mid < \psi_{1s} \mid z \mid \psi_{nL} > \mid^2$) are given for $\beta = 2$ and $\sqrt{2}$, for γ from both perturbative and non-perturbative region. The calculated wave functions $\psi_L^N(R,\theta)$ of the multiplet $n = 10, m = 0$ are presented in Fig.2 for diamagnetic ($\beta = 0$) and instantaneous van der Waals ($\beta = \sqrt{2}$) perturbations. For labeling these wave functions I use the rotational quantum number L - a good quantum number of the rotationally invariant case $\beta = 1$ where the dynamical symmetry $O(4) \supset O(3)_L$ occurs, the square L^2 of the angular momentum is a constant of motion and $\Lambda = 3(n^2 - 1 - L^2)$ [1]. Applying to the calculated " correlative diagrams" given in Figs.1(a,b) one may use the L quantum number for labeling the spectrum of the van der Waals perturbed hydrogen atom (1) in the entire region $0 \leq \beta \leq 2$, although for deciphering the points of the calculated spectrum, which are far removed from the value $\beta = 1$, one needs to use the good quantum numbers of other dynamical symmetries of the system [1] , appropriate to the considered case of β. In the vicinity of the point $\beta = 1/2$ it is the eigenvalues $\eta(\eta + 1)$ of the square $\mathcal{L}^2$ of the operator $\mathcal{L} = (A_x, A_y, L_z)$ ($\Lambda = 15/4(A_x^2 + A_y^2)$ as $\beta = 1/2$ and the system exhibits the $O(4) \supset O(3)_\eta \supset O(2)_m$ symmetry). Near $\beta = 2$ the spectrum has a doublet structure since $\Lambda = 15A_z^2$ as $\beta = 2$, the A_z is a constant of motion with the eigenvalues $q = n_2 - n_1$ and the dynamical symmetry is $O(4) \supset O(2)_q \otimes O(2)_m$ (the problem becomes separable in parabolic coordinates).

Note that although a considerable violation of the analytical spectrum of the van der Waals perturbed atom (1) at the points of the dynamical symmetry [1]

$$2n^2 \Delta E_{n\Lambda m} = \begin{cases} \frac{15}{4}\eta(\eta+1) - \frac{3}{4}m^2 + \frac{5}{4}n^2 + \frac{13}{4}, & \beta = \frac{1}{2} \\ 5n^2 + 1 - 3L(L+1), & \beta = 1 \\ 15(n_2 - n_1)^2 - 3m^2 + 5n^2 + 7, & \beta = 2 \end{cases}$$

occurs for $\gamma = 2 \cdot 10^{-8}$, nevertheless the spectrum still preserves the rotational structure

near the points $\beta = 1/2$ and 1 and the doublet structure at the vicinity of $\beta = 2$ (see Figs.1). The states of the spectrum at the point $\beta = \sqrt{2}$ exhibit both neighbouring symmetries of $\beta = 1$ and 2, which is more sharply demonstrated by the picture of the dipole oscillator strengths (Fig.1(d)): the lines above $\Delta E = 2.5$ repeat the doublet structure of the $\beta = 2$ case (Fig.1(c)) and below this point are strongly suppressed as in the case of rotational symmetry $\beta = 1$.

In conclusion I would like to underline that non-perturbative behaviour of the hydrogen atom in the field ΔV (1) is found already in the region $\gamma_c n^4 \sim 10^{-4} \ll 1 (n \sim 10)$ and must be taken into account in the analysis of atomic spectra perturbed by strong magnetic fields or by the instantaneous van der Waals interaction with a metallic wall [8] when $\gamma \sim \gamma_c$ ($H_c = \sqrt{\gamma_c} \sim 10^6 G$ for $\beta = 0$) . Moreover, an evaluation for higher $n (\sim 30 - 40)$ shows a significant decrease of the critical field, γ_c, corresponding to a transition to the non-perturbative region.

Due to the fast covergence of the expansion (6), applying of the method of global approximation on a subspace grid [13],[14] offers highly accurate quantum computation of the van der Waals perturbed hydrogen atom. The key idea of this approach, the reduction of the initial multidimensional problem to the problem of type (4) on the subspace grid [13], has also successfully been exploited in the "discrete variable representation" [15], recently applied to the hydrogen atom in crossed fields[16], in the Lagrange-mesh calculations[17] and in the "pseudospectral method"[18].

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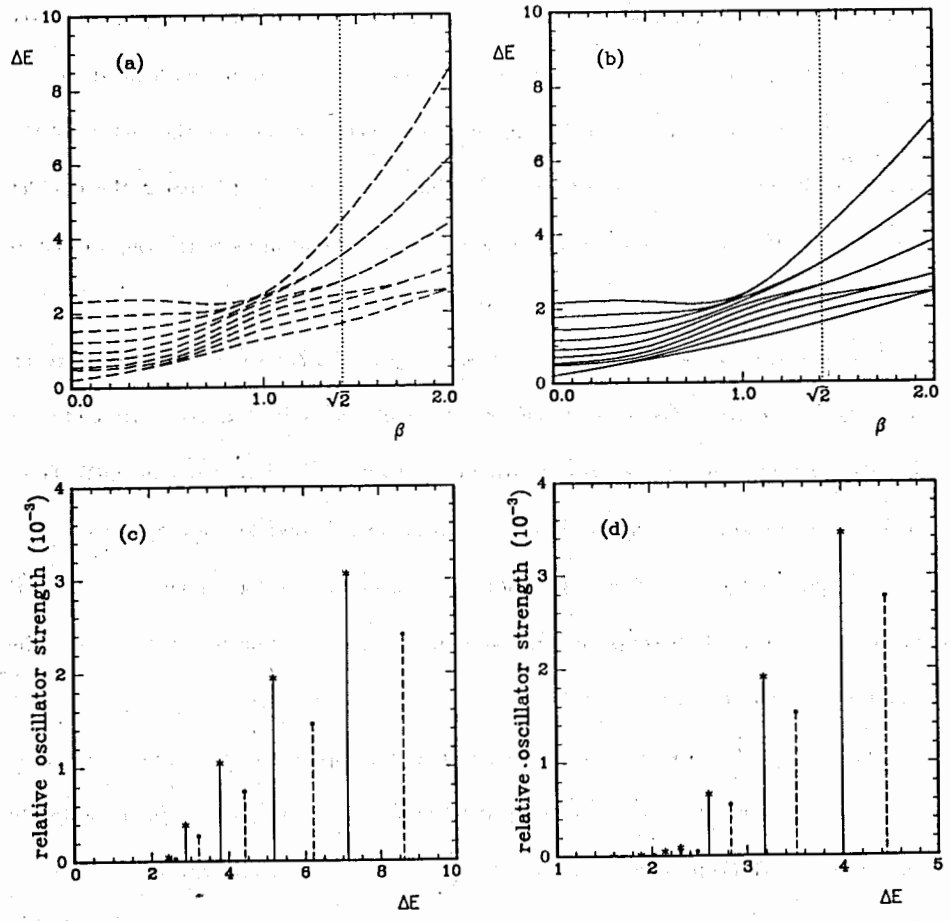


Fig. 1: (a)(b) Normalized level shifts ΔE of the multiplet $n = 10, m = 0$ calculated for two field strengths γ: dashed curves - perturbative region, $\gamma = 2 \cdot 10^{-10}$; solid curves- non-perturbative region, $\gamma = 2 \cdot 10^{-8}$. (c) The oscillator strengths from the ground state to the perturbed manifold $n = 10, m - 0$ for the case $\beta = 2$, dashed lines - perturbative region, $\gamma = 2 \cdot 10^{-10}$; solid lines - non-perturbative region, $\gamma = 2 \cdot 10^{-8}$. (d) Same as Fig. (c) but for $\beta = \sqrt{2}$.

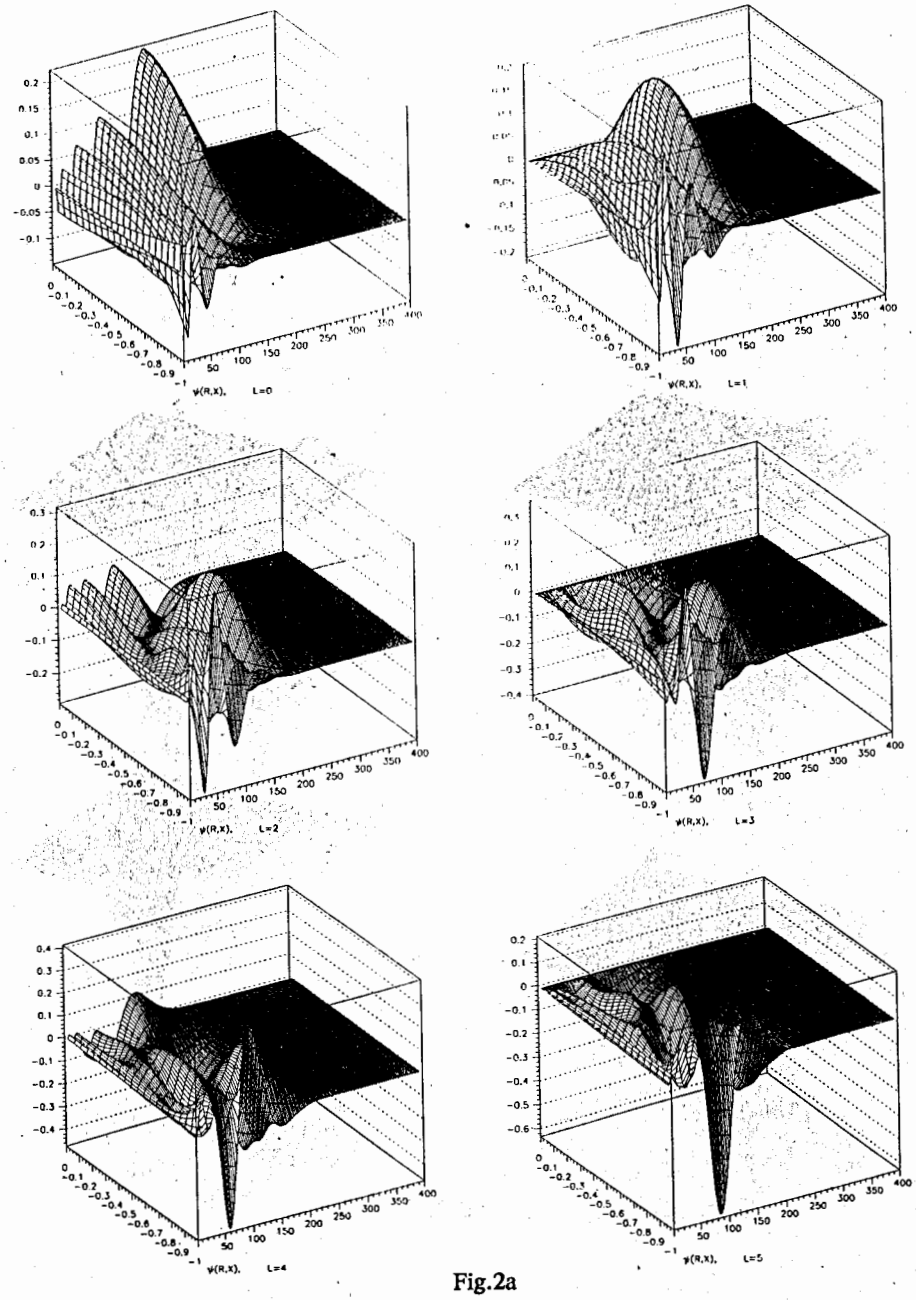
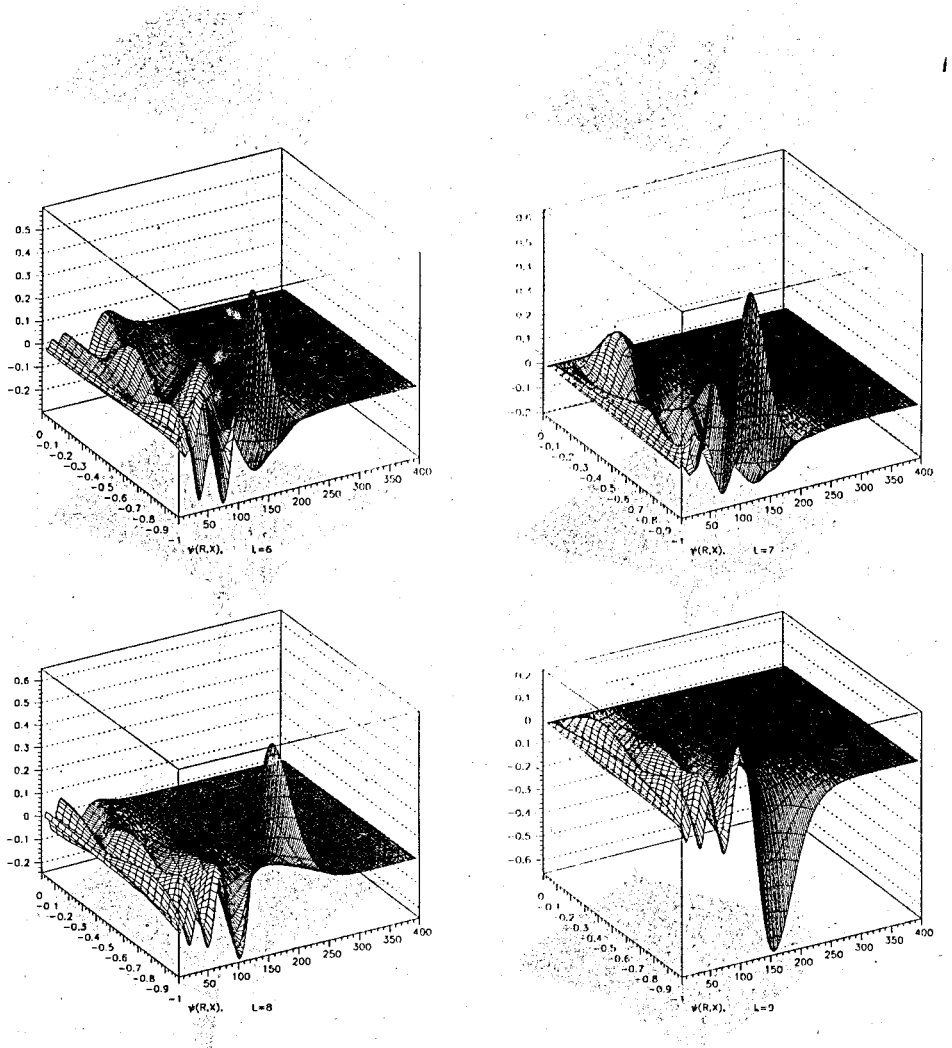


Fig.2a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ψ(R,X), L=7
ψ(R,X), L=8
ψ(R,X), L=9

Fig.2a

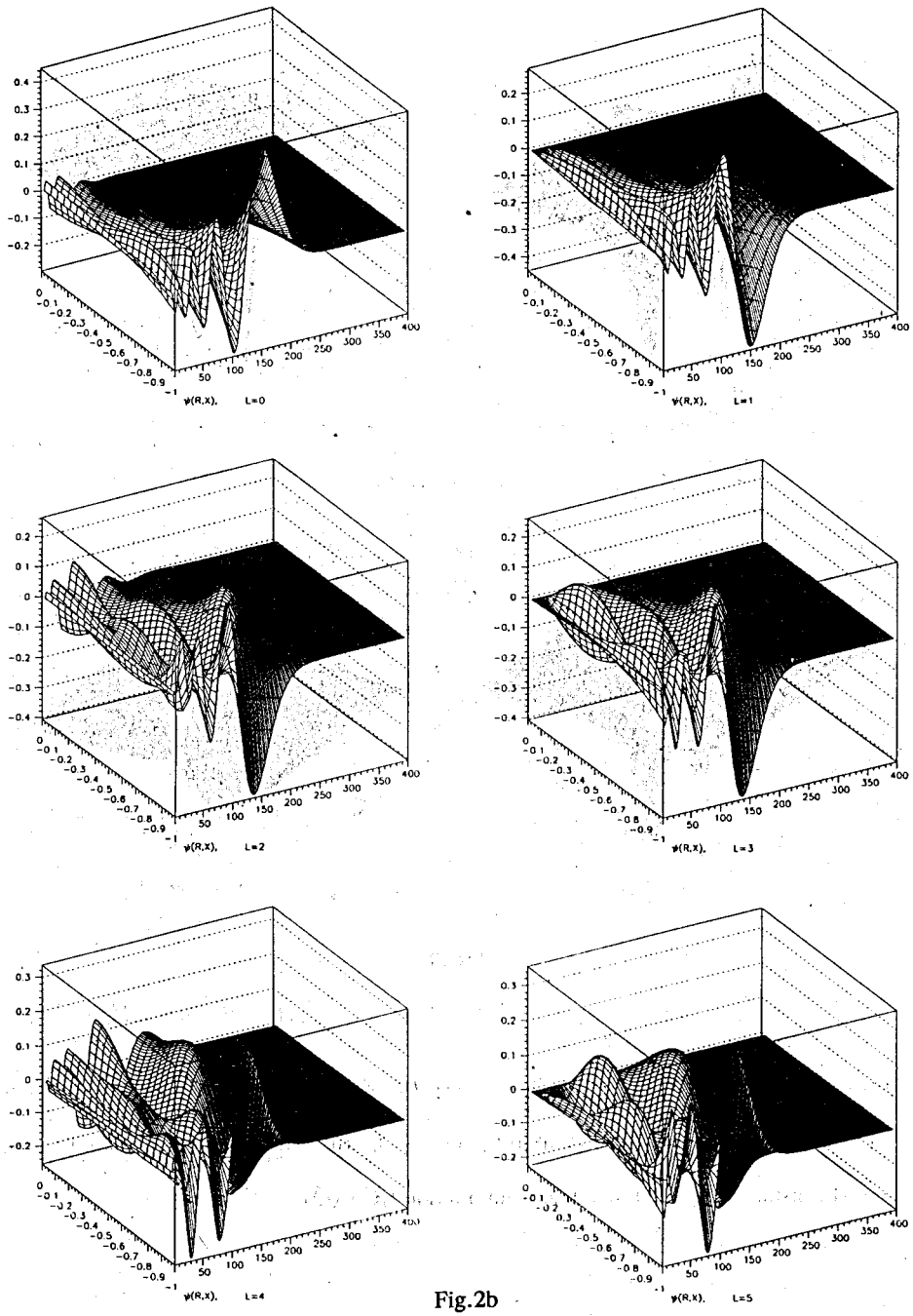
ψ(R,X), L=0
ψ(R,X), L=1
ψ(R,X), L=2
ψ(R,X), L=3
ψ(R,X), L=4
ψ(R,X), L=5

Fig.2b

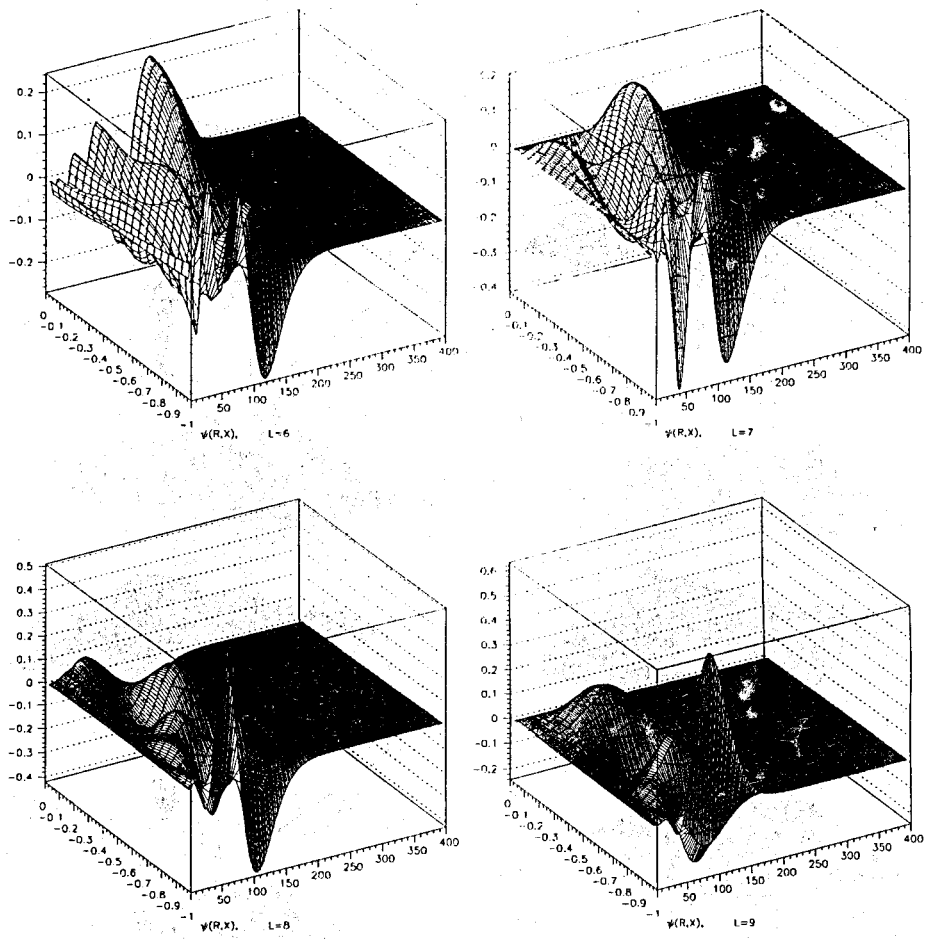

Fig.2b

Fig. 2: The wave functions, $\psi_L(R, x = -cos\theta)$, of the hydrogen atom multiplet, $n = 10, m = 0$, perturbed by the potential (1) for $\gamma = 2 \cdot 10^{-8}$: (a) diamagnetic case ($\beta = 0$) and (b) instantaneous van der Waals interaction ($\beta = \sqrt{2}$).

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Мележик В.С. Е4-95-67

Атом водорода в поле Ван дер Ваальса:
непертурбационные эффекты

С помощью непертурбационного метода глобальной аппроксимации на подпространственной сетке исследован спектр атома водорода, возмущенного обобщенным взаимодействием Ван дер Ваальса $\Delta V(x, y, z) = \gamma(x^2 + y^2 + \beta^2 z^2)$. Установлено существенное отклонение от теории возмущений и нарушение, в специальных точках $\beta = 1/2$, 1 и 2 динамической симметрии, аналитического спектра системы для напряженностей поля $H = \sqrt{8\gamma} \approx 10^{-3}$ а.е. $\approx 10^6 G$ из области $\gamma n^4 << 1 (n \approx 10)$.

Работа выполнена в Лаборатории ядерных проблем ОИЯИ.

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Melezhik V.S. E4-95-67

Non-Perturbatibe Behaviour of Hydrogen Atom
in Van der Waals Field

The spectrum of the hydrogen atom perturbed by the generalized van der Waals interaction $\Delta V(x, y, z) = \gamma(x^2 + y^2 + \beta^2 z^2)$ is analyzed with a non-perturbative method of global approximation on a subspace grid. Considerable deviation from the perturbation formulas and violation of the analytic spectrum, which the system exhibits in special cases of the dynamical symmetry $\beta = 1/2$, 1 and 2, have been found already for the field strength, $H = \sqrt{8\gamma} \approx 10^{-3}$ a.u. $\approx 10^6 G$, in the region $\gamma n^4 << 1 (n \approx 10)$.

The investigation has been performed at the Laboratory of Nuclear Problems, JINR.

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