RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 52, NUMBER 5 NOVEMBER 1995

Nonperturbative behavior of a hydrogen atom in a van der Waals field

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(Received 5 December 1994)

The spectrum of the hydrogen atom perturbed by the generalized van der Waals interaction $\Delta V(x,y,z)=\gamma(x^2+y^2+\beta^2z^2)$ is analyzed with a nonperturbative 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 $\beta=\frac{1}{2}$, 1, and 2, have already been found for the field strengths $H=\sqrt{8\gamma}\sim10^{-3}$ a.u. $\sim10^6$ G, in the region $\gamma n^4\ll1$ $(n\sim10)$.

PACS number(s): 31.10.+z, 03.65.Fd, 32.60.+i, 03.65.Ge

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

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

[where $\gamma>0$ and β are constants and (x,y,z) are the coordinates of an electron relative to a nucleus] is of 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 has been a subject of extensive discussions so far [8]. Note also the connection that 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 references therein).

In the paper [1] a general consideration (for arbitrary $0\leq\beta\leq2$), 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 $\beta=1$, has permitted a reduction of the weak perturbation (1) to a simple effective operator within the manifold $n=\text{const}$,

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

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 to one another and connected with the adjacent dynamical symmetries found in [1] for certain values of β ($\beta=\frac{1}{2}$, 1, and 2).

In this paper I extend the consideration to the nonperturbative region. Highly excited states of the problem (1) are analyzed with the method of global approximation on a subspace grid [13]. The Schrödinger equation in spherical coordinates (R,θ,ϕ) is reduced to the system of N differential equations for the eigenvalue ε^N and eigenfunction $\psi^N(R,\Omega_j)=\psi_j(R)$ defined on the subspace grid $\Omega_j=\{\cos\theta_j\}_1^N$ [14]. With the calculated vector $\{\psi_j(R)\}_1^N$ one can evaluate the wave function

$$\psi^N(R,\theta)=\sum_{lj}^{N} P_l(\theta)P_{lj}^{-1}\psi_j(R), \tag{4}$$

approximating the eigenfunction $\psi(R,\theta)$ of the initial problem (1) as $N\to\infty$. Here $P_l(\theta)$ are the Legendre polynomials and P_{lj}^{-1} is the inverse matrix $N\times N$ to $\{P_l(\theta_j)\}$.

In my previous paper [14], devoted to the problem of a hydrogen atom in crossed fields, a fast convergence of the expansion (4) with respect to N was demonstrated for the diamagnetic case ($\beta=0$): low-lying excited states had been analyzed in the region of very strong fields, $1\leq H=\sqrt{8\gamma}\leq10^3$ $(10^{-1}\leq\gamma\leq10^5)$, and highly accurate binding energies of these states were obtained. In this paper the consideration is extended to a highly excited atom $(n\sim10)$ perturbed by the interaction (1). The evaluation has been performed for two field strengths γ, from the region where the perturbation formulas [1] are still working well and where the system already exhibits considerable nonperturbative behavior. Two such cases are demonstrated in Figs. 1(a) and 1(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 $\gamma=2\times10^{-10}$ and 2×10^{-8}. Note that in the diamagnetic limit ($\beta=0$) the calculated spectrum represents the eigenstates of a hydrogen atom in the strong magnetic fields $H=\sqrt{8\gamma}\sim10^5$ and $\sim10^6$ G, respectively. The calculations with $N\leq6$ $(l\leq12)$ give the order of accuracy $\sim10^{-3}$ for the shifts ΔE for $\gamma=2\times10^{-8}$ and more accurate evaluations for the weaker perturbation $\gamma=2\times10^{-10}$. The deviation of the shifts ΔE of the $n=10$ manifold presented in Fig. 1(a) from the perturbation result [1] obtained by a diagonalization of the operator (3) does not exceed the value $\sim10^{-3}$ for the field $\gamma=2\times10^{-10}$. Rather unexpectedly the nonperturbative regime is already apparent for $\gamma=2\times10^{-8}$ in the region $\gamma n^4\ll1$. In this case [Fig. 1(b)] the system exhibits considerable deviation of the spectrum ΔE from the perturbative behavior, as in Fig. 1(a). This effect is more evidently devel-

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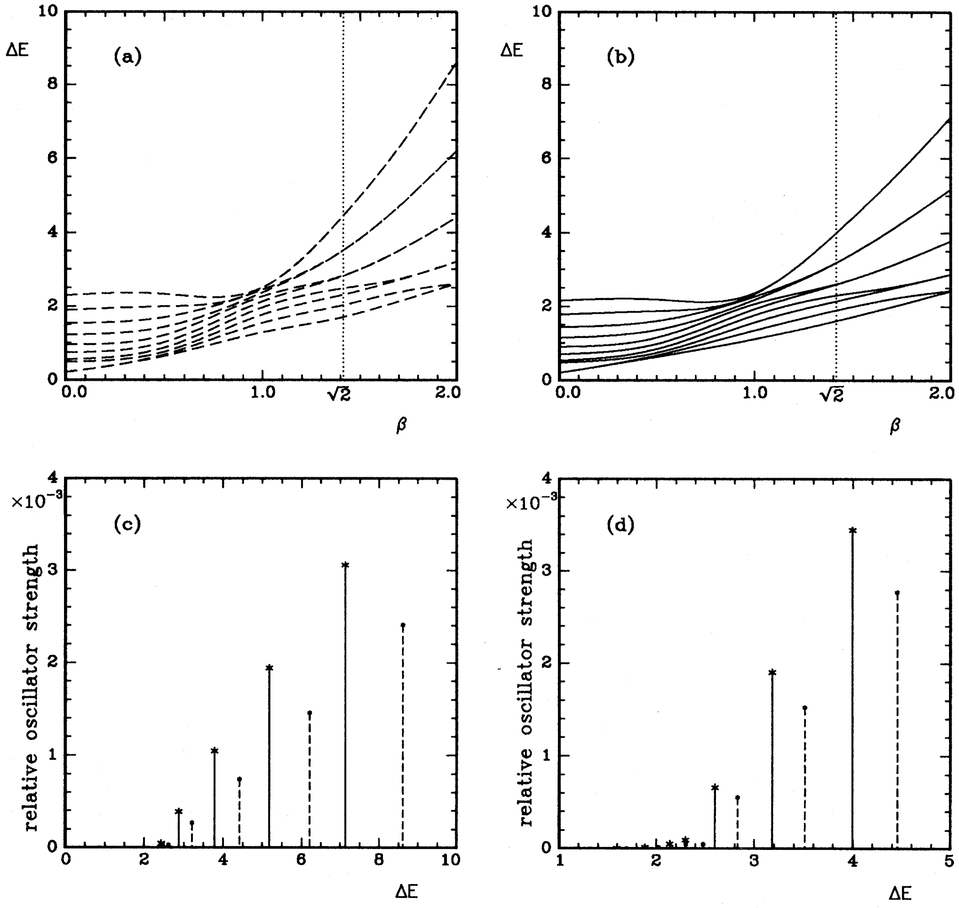

FIG. 1. (a) and (b) Normalized level shifts ΔE of the multiplet $n=10$, $m=0$ calculated for two field strengths γ: dashed curves, perturbative region $\gamma=2\times10^{-10}$; solid curves, nonperturbative region $\gamma=2\times10^{-8}$. (c) The oscillator strengths from the ground state to the perturbed manifold $n=10$, $m=0$ for the case $\beta=2$: dashed lines, perturbative region $\gamma=2\times10^{-10}$; solid lines, nonperturbative region $\gamma=2\times10^{-8}$. (d) Same as (c) but for $\beta=\sqrt{2}$.

oped for oscillator strengths. This is demonstrated in Figs. 1(c) and 1(d), where the relative oscillator strengths (dipole transition probabilities $W_{1s}^{nL}=3|\langle\psi_{1s}|z|\psi_{nL}\rangle|^2$) are given for $\beta=2$ and $\sqrt{2}$ for γ from both the perturbative and nonperturbative regions. A few calculated wave functions $\psi_L^N(R,\theta)$ of the multiplet $n=10$, $m=0$ are presented in Fig. 2 for the instantaneous van der Waals ($\beta=\sqrt{2}$) perturbation. 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 calculated "correlative diagrams" given in Figs. 1(a) and 1(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 $0\leqslant\beta\leqslant2$, 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] that are appropriate to the considered case of β. In the vicinity of the point $\beta=\frac{1}{2}$ they are the eigenvalues $\eta(\eta+1)$ of the square $\mathscr{L}^2$ of the operator $\mathscr{L}=(A_x,A_y,L_z)$ [$\Lambda=\frac{15}{4}(A_x^2+A_y^2)$ as $\beta=\frac{1}{2}$ 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 $\gamma=2\times10^{-8}$, the spectrum still preserves the rotational structure near the points $\beta=\frac{1}{2}$ and 1 and the doublet structure at the vicinity of $\beta=2$ (see Fig. 1). The states of the spectrum at the point $\beta=\sqrt{2}$ exhibit both neighboring 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 struc-

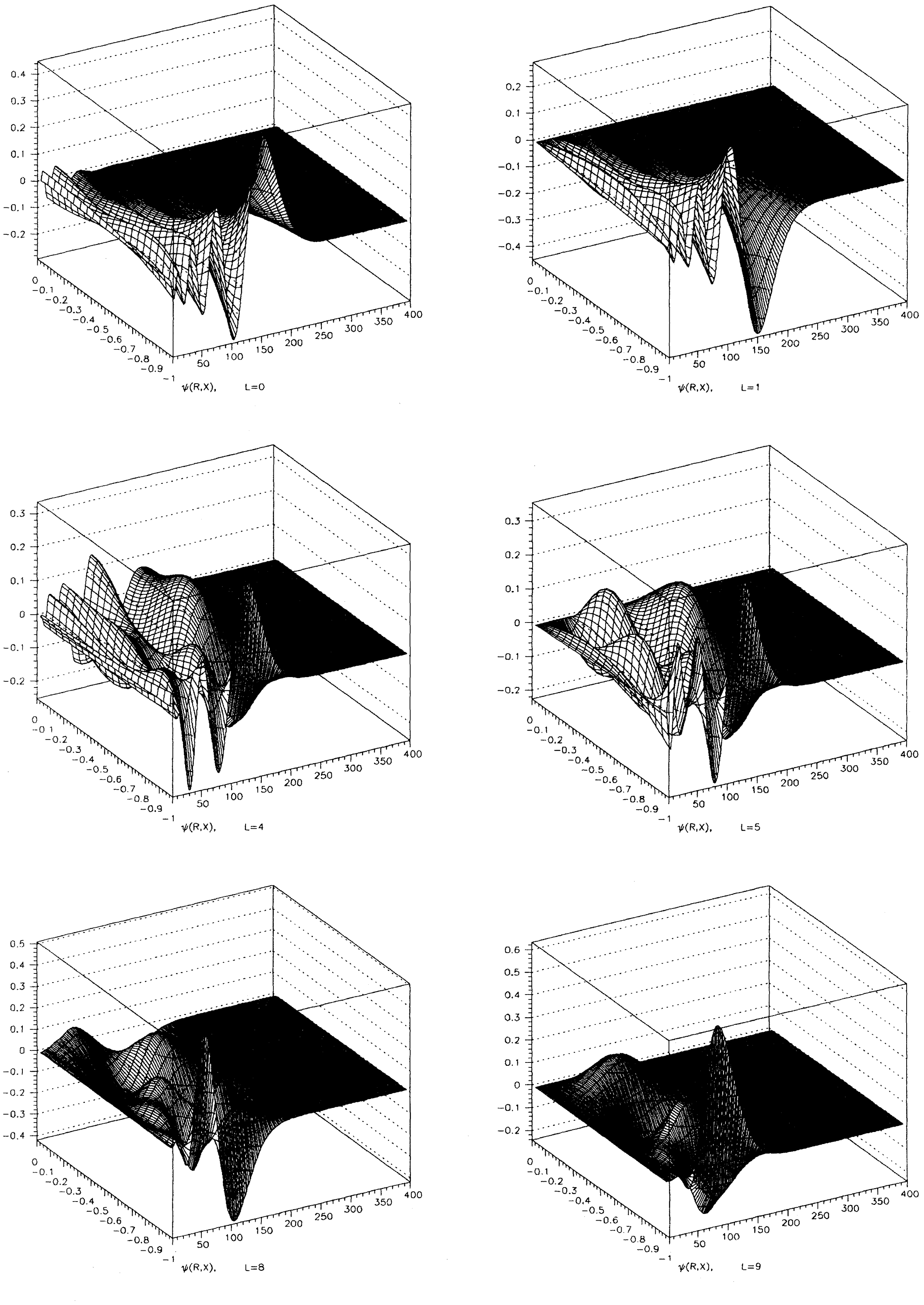

FIG. 2. Wave functions $\psi_L(R,x=-\cos\theta)$ of the hydrogen atom multiplet $n=10$, $m=0$, perturbed by the instantaneous van der Waals interaction (1) ($\beta=\sqrt{2}$) for $\gamma=2\times10^{-8}$.

ture 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 underscore the fact that nonperturbative behavior of the hydrogen atom in the field ΔV (1) is already found 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 nonperturbative region.

Due to the fast convergence of the expansion (4), applying the method of global approximation on a subspace grid [13,14] offers a 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 on $\{R,\theta\}$ to the problem on the subspace grid $\{R,\theta_i\}$ [13], has also been successfully exploited in the "discrete variable representation" [15], which was recently applied to the hydrogen atom in crossed fields [16], in the Lagrange-mesh calculations [17], and in the "pseudospectral method" [18]. It also looks promising to adapt a shooting-relaxation technique [19] for improvement of the reported results.

The work has been supported by the National Science Foundation, Grant No. PHY-9115407, and the International Scientific Foundation, Grant No. MJR300.

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