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Hydrogen atom in the instantaneous van der Waals potential: Pitchfork bifurcation and ro-vibrational structure of the energy spectrum

N.S. Simonović [a,1], J.P. Salas [b,*]

[a] *Max Planck Institut für Physik komplexer Systeme, Nöthnitzer Str. 38, 01187 Dresden, Germany*
[b] *Area de Física Aplicada, Universidad de La Rioja, Edificio Politécnico, C/Luis de Ulloa 20, 26004 Logroño, Spain*

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Abstract

We present a semiclassical study of the energy spectrum of a Rydberg hydrogen atom in the instantaneous van der Waals potential. The results are in good agreement with those obtained by the first-order quantum perturbation theory. Both the semiclassical and the quantum calculations show that vibrational energy levels disappear when the magnetic quantum number $|m|$ increases. This fact is well explained in the framework of classical dynamics of this system for which the pitchfork bifurcation takes place at critical value $|m|/n = \sqrt{5/7}$. © 2001 Elsevier Science B.V. All rights reserved.

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We consider the problem of a hydrogen atom at a large distance from a metal surface (i.e., for $d \gg r$, where r and d are the electron–nucleus and nucleus–surface distances, respectively) under the approximation of the instantaneous van der Walls interaction. The corresponding potential can be obtained as the quadratic approximation of the exact atom-surface potential within the electrostatic image model [1,2]. Using cylindrical coordinates (ρ, z, φ) and atomic units, the Hamiltonian of the system takes the form

$$\mathcal{H} = \frac{p^2}{2} - \frac{1}{r} - \frac{1}{16d^3}\left(r^2 + z^2\right), \tag{1}$$

where $r = (\rho^2 + z^2)^{1/2}$ and $p^2 = p_\rho^2 + L_z^2/\rho^2 + p_z^2$. Owing to the cylindrical symmetry, the z-component of angular momentum L_z is conserved and the φ-motion is separated from that in the (ρ, z) plane. Thus, the system reduces to the problem with two degrees of freedom. In our recent paper we have considered the case $L_z = 0$ [3]. Here we analyse the effects of nonzero L_z and present the results.

From the point of view of the classical mechanics, for sufficiently large d, system (1) is nearly integrable [2]. Hence, we are handling with a perturbed Coulombian system which can be treated by using classical perturbation methods. Following previous works on similar perturbed systems [4–6], we normalize our problem by applying a Lie transformation [7]. After this process, we get an integrable Hamiltonian where only one degree of freedom is left.

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[*] Corresponding author.
E-mail address: josepablo.salas@dq.unirioja.es (J.P. Salas).

[1] Permanent address: Institute of Physics, P.O. Box 57, 11001 Belgrade, Yugoslavia.

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We perform the normalization in the Delaunay variables $(I_1, I_2, I_3, \phi_1, \phi_2, \phi_3)$, where the action I_3 is the principal Delaunay action, I_2 is the magnitude of the total angular momentum $\mathbf{L}$, and $I_1 = L_z$, i.e., the z-component of the angular momentum I_2. The actions (I_3, I_2, I_1) correspond to the principal, orbital and magnetic quantum numbers (n, l, m), respectively. For a more complete explanation of the geometrical meaning of the Delaunay variables, we refer the reader to [8]. The Delaunay normalization [9] is a canonical transformation $(I_1, I_2, I_3, \phi_1, \phi_2, \phi_3) \rightarrow (I_1', I_2', I_3', \phi_1', \phi_2', \phi_3')$ which converts $\mathcal{H}$ into a function $\mathcal{H}'$ that does not depend on the averaged mean anomaly ϕ_3'. As consequence of this reduction, the new Hamiltonian admits the principal action I_3' as an integral. In the following, for the sake of simplicity, we drop the primes on the new action–angle variables.

Carry out the reduction to first order, the normalized Hamiltonian (*normal form*) $\mathcal{H}'$ comes as the sum $\mathcal{H}' = -1/(2I_3^2) + \mathcal{H}_1'$, where

$$\mathcal{H}_1' = -\frac{I_3^4}{32d^3}\left(3 - \frac{I_1^2}{I_3^2} + \Lambda\right), \tag{2}$$

Λ being the dynamical part of the normalized Hamiltonian:

$$\Lambda = \left[2 + \frac{5}{2}\left(1 - \frac{I_1^2}{I_2^2}\right)(1 - \cos 2\phi_2)\right] \times \left(1 - \frac{I_2^2}{I_3^2}\right). \tag{3}$$

Since I_1 and I_3 are constants of the motion, the Hamiltonian $\mathcal{H}'$ reduces to Λ. We note that Λ is the generalized approximate Solov'ev constant [10]. The phase portrait of the normalized system, for a given values of I_1 and I_3, are the maps of Λ on the cylinders (ϕ_2, I_2). It is worthwhile noting that this map is singular because it excludes the circular orbits $(I_2 = I_3)$ and the equatorial orbits $(I_2 = I_1)$. This singularity disappears when the system is treated in the following variables:

$$\xi_1 = \frac{2\eta e \sin i \cos\phi_2}{(1 - \beta^2)}, \qquad \xi_2 = \frac{2\eta e \sin i \sin\phi_2}{(1 - \beta^2)},$$

$$\xi_3 = \frac{2}{(1 - \beta^2)}\left[\eta^2 - \frac{1}{2}(1 + \beta^2)\right], \tag{4}$$

where $e = \sqrt{1 - I_2^2/I_3^2}$ and $i = \cos^{-1}(I_1/I_2)$ are, respectively, the eccentricity and the inclination of the electronic orbits. We have introduced the dimensionless quantities $\eta = I_2/I_3$ and $\beta = I_1/I_3$. In this variables (ξ_1, ξ_2, ξ_3), owing that $\xi_1^2 + \xi_2^2 + \xi_3^2 = 1$, the phase space is an sphere of unit radius. Given the values of I_3 and I_1 (i.e., the value of β), the north pole of the sphere represents the circular orbits ($e = 0$), while the south pole represents the equatorial orbits $(i = 0)$.

The dynamics emerging from Λ has been studied by Elipe and Ferrer [11]. These authors have shown that the averaged system shows four equilibrium points that we denote by $E_{1,2,3,4}$. The equilibrium E_1 (E_2) is located at the north (south) pole, while the equilibria $E_{3,4}$ are at the meridian $\xi_1 = 0$. The equilibria $E_{1,2}$ are, respectively, absolute and local maxima of $\mathcal{H}'$, while the equilibria $E_{3,4}$ are absolute minima of $\mathcal{H}'$ with equal energy. [2]

The most important feature of this dynamical system is that it undergoes a pitchfork bifurcation at a critical value $\beta = \sqrt{5/7}$. We observe this fact in Fig. 1 where the phase flow evolution in the cylinders (ϕ_2, η) as well as in the unit sphere is shown for $\beta = 0.7$, 0.8 and 0.9.

When $\beta < \sqrt{5/7}$ (Figs. 1(a)–(d)), we observe that there exist three families of classical levels (orbits). The two families of *vibrational* levels V_1 (V_2) around the equilibria E_3 (E_4) and the family of *rotational* levels R around E_1. These two kind of levels are kept apart by a separatrix passing through E_2.

As the parameter β reaches the critical value $\sqrt{5/7}$, the separatrix shrinks and, at the same time, the equilibria $E_{3,4}$ migrate to the southern hemisphere. This fact indicates that the vibrators are gradually replaced by rotators. Finally, when $\beta > \sqrt{5/7}$, the pitchfork bifurcation has taken place: only the equilibria $E_{1,2}$ survive and there are only rotational levels (Figs. 1(e) and (f)).

As it has been shown for a Rydberg hydrogen atom in external field [12,13] and for this problem in the polar case $\beta = 0$ [3], the classical families of vibrators and rotators are connected to the quantum states of the system. In this way, each classical phase space trajectory with appropriately quantized value of the

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[2] For a discussion about the stability of these equilibria, we refer the reader to [11].

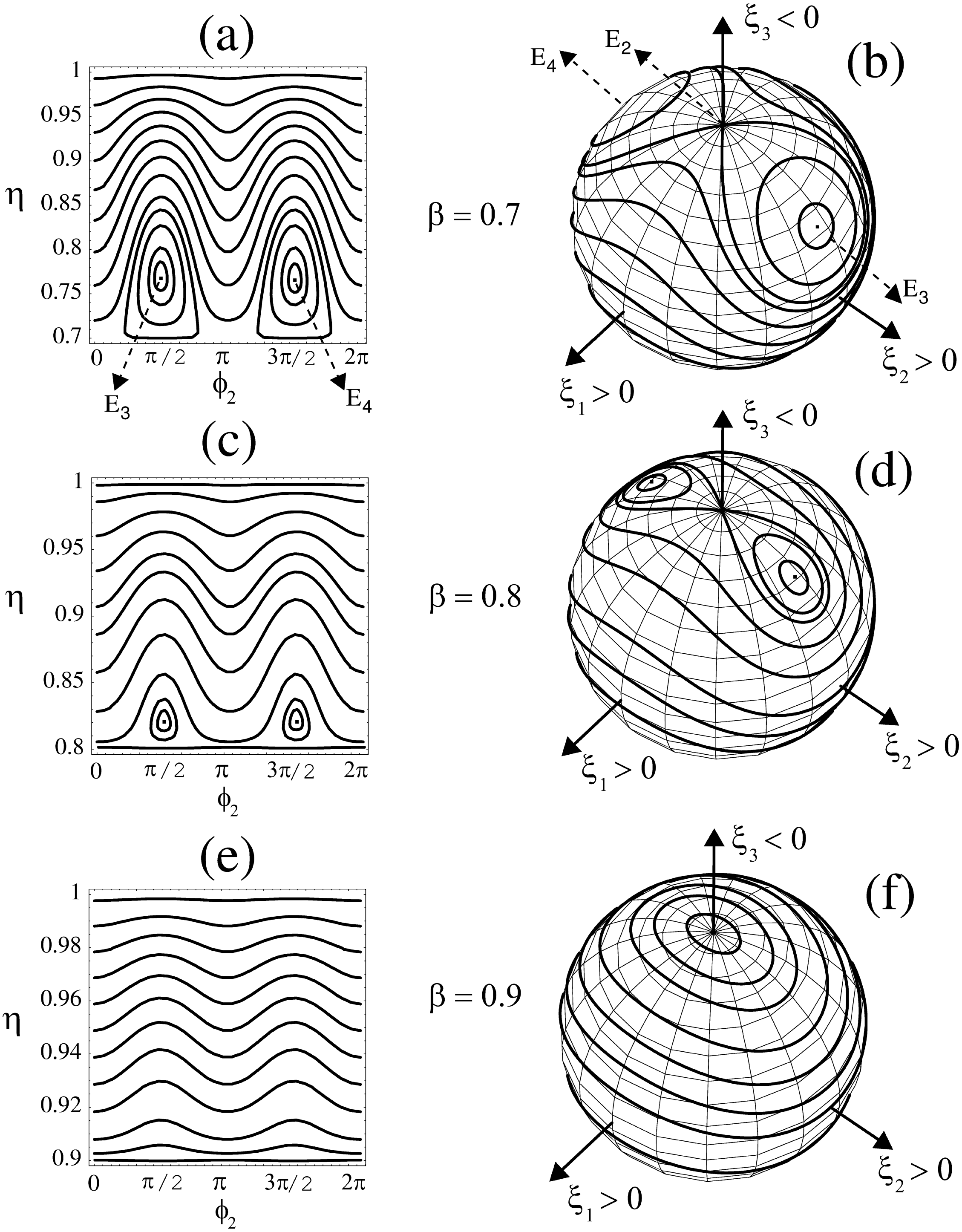

Fig. 1. Phase flow evolution of the normalized Hamiltonian $\mathcal{H}'$ for $\beta = 0.7$ ((a) and (b)), $\beta = 0.8$ ((c) and (d)) and $\beta = 0.9$ ((e) and (f)). The left panel corresponds to the phase flow on the cylinders (ϕ_2, η), while the right one corresponds to the phase flow on the unit sphere (ξ_1, ξ_2, ξ_3).

action corresponds to a quantum state. Hence, while the quantum states corresponding to vibrational levels are degenerated and have the lower energies, those corresponding to rotational levels are nondegenerate and have the higher energies. This is the fundamental qualitative level structure information arising from the classical picture which is difficult to obtain from quantum mechanics.

Since the system determined by the normal form (2) is integrable, it can be quantized by applying the EBK rules to the action variables (I_1, I_2, I_3). As we have mentioned above, I_1 and I_3 are exact and approximate constants of the motion, respectively, and they can be quantized as in the unperturbed Kepler problem, i.e., $I_1 = m,\ I_3 = n$. However, because of the presence of the instantaneous van der Waals interaction, the angular momentum I_2 is not a constant of the motion and the appropriate quantization rules is [12]

$$A = \frac{1}{2\pi} \oint_C I_2 \, d\phi_2 = k + \frac{1}{2}, \tag{5}$$

where k is the semiclassical quantum number. For vibrators, A is $1/2\pi$ times the area enclosed by the loop in the map (ϕ_2, I_2), while for a rotator, it is $1/2\pi$ the area between the rotator line and the $I_2 = I_3$ line in the same map.

We evaluate the latest action integral by using the Solov'ev constant Λ, which takes the values $0 < \Lambda < \Lambda_{\mathrm{max}} = 7(1 - \sqrt{5/7}\,\beta)^2$ and for separatrix $\Lambda_{\mathrm{sep}} = 2(1-\beta^2)$. We remark that the separatrix in the (ϕ_2, I_2) representation corresponds to the line $I_2 = I_3$. Note that (3) is a biquadratic equation in terms of I_2, giving (positive) solutions $I_2^{\pm} = [(-b \pm \sqrt{b^2 - 4ac})/2a]^{1/2}$, where $a = 4 + 5\Phi$, $b = -2I_3^2(2 - \Lambda) - 5(I_1^2 + I_3^2)\Phi$, $c = 5I_1^2 I_3^2 \Phi$, and $\Phi = 1 - \cos 2\phi_2$. The action integrals A for rotational and vibrational motions are then

$$A_{\mathrm{rot}} = \frac{1}{2\pi} \int_0^{2\pi} I_2^+ \, d\phi_2, \quad 0 < \Lambda < \Lambda_{\mathrm{sep}}, \tag{6}$$

$$A_{\mathrm{vib}} = \frac{1}{2\pi} \int_{\phi_2^0}^{\pi - \phi_2^0} \left(I_2^+ - I_2^-\right) d\phi_2, \qquad \Lambda_{\mathrm{sep}} < \Lambda < \Lambda_{\mathrm{max}}, \tag{7}$$

where

$$\phi_2^0 = \frac{1}{2} \arccos\Bigl(1 - \frac{2}{5} I_3^2 \Bigl\{(\Lambda + 2) I_1^2 + (\Lambda - 2) I_3^2 + 2I_1 \sqrt{\Lambda\bigl[2I_1^2 + (\Lambda - 2) I_3^2\bigr]}\Bigr\} \Big/ \bigl(I_3^2 - I_1^2\bigr)^2\Bigr).$$

Semiclassical values for the energy level shifts are found by solving iteratively equation $A(I_1, I_3, \Lambda) = k + 1/2$ for Λ and inserting these values (with the conditions $I_1 = m$ and $I_3 = n$) in Eq. (2):

$$\Delta E_{nmk} = -\frac{n^4}{32 d^3} \left(3 - \frac{m^2}{n^2} + \Lambda_{nmk}\right). \tag{8}$$

We apply the above formula for $d = 100$ nm and $n = 10$. The vibrational (doubly degenerate in k) levels may exist for $k = 0, 1, 2$, whereas the rotational for $k = 6, 7, 8, 9$ (see Table 1). Additionally, all levels with $|m| \neq 0$ are also doubly degenerate in m. The levels shown in the brackets ((n, m, k) equal $(10, 1, 6)$ and $(10, 6, 7)$) are nonessential (unphysical) and they appear due to the vicinity of the separatrix. Because of the same reason the levels $(10, 4, 6)$ and $(10, 7, 7)$ are missing in the rotational submanifold, however their values (labeled in Table 1 by asterisks) are estimated by the formula

$$\Delta E_{nmk^*} \approx \Delta E_{nm}^{\mathrm{sep}} = -\frac{n^4}{32 d^3} \left(5 - 3\frac{m^2}{n^2}\right), \tag{9}$$

which is obtained by using the Λ-value for the separatrix.

The effects of the instantaneous van der Waals interaction to the energy spectrum of the hydrogen atom can be calculated also quantum-mechanically by using the first-order degenerate perturbation theory. The eigenstates can be expressed as a function of the pure hydrogenic basis by using the expansion over the orbital quantum number l:

$$\Psi_{nm\kappa}(r, \vartheta, \varphi) = \sum_{l=|m|}^{n-1} c_l^{nm\kappa} R_{nl}(r) Y_l^m(\vartheta, \varphi), \qquad \kappa = |m|, \ldots, n-1, \tag{10}$$

since m and n are exact and within the first-order theory good quantum numbers, respectively. The coefficients $c_l^{nm\kappa}$ follow after solving the secular problem

Table 1

The energy level shifts (in GHz) for the $n = 10$ manifold at $d = 100$ nm — semiclassical and quantum-mechanical results

$\lvert m\rvert$	0		1		2		3		4	
k	SC	QM	SC	QM	SC	QM	SC	QM	SC	QM
		−2.7173		−2.4057		−2.1188		−1.8567		−1.6205
0	−2.7052		−2.3935		−2.1064		−1.8441		−1.6067	
		−2.7173		−2.4057		−2.1188		−1.8566		−1.6189
		−2.1437		−1.9074		−1.6995		−1.5286		
1	−2.1313		−1.8946		−1.6841		−1.5022			
		−2.1437		−1.9071		−1.6954		−1.5032		
		−1.7262		−1.5872						
2	−1.7101		−1.5572							
		−1.7209		−1.5527						
6	−1.5168	−1.5051	(−1.5094)		−1.4866	−1.4763			−1.3774*	−1.3884
7	−1.3920	−1.4047	−1.3864	−1.3889	−1.3695	−1.3829	−1.3410	−1.3417	−1.3001	−1.3165
8	−1.2243	−1.2325	−1.2199	−1.2287	−1.2065	−1.2146	−1.1841	−1.1930	−1.1524	−1.1599
9	−1.0248	−1.0335	−1.0213	−1.0300	−1.0109	−1.0196	−0.9934	−1.0020	−0.9690	−0.9775

$\lvert m\rvert$	5		6		7		8		9	
k	SC	QM	SC	QM	SC	QM	SC	QM	SC	QM
		−1.4141		−1.2392						
0	−1.3948		−1.2105							
		−1.4032		−1.2023						
7	−1.2457	−1.2423	(−1.1751)		−1.0757*	−1.0788				
8	−1.1109	−1.1200	−1.0589	−1.0646	−0.9948	−1.0056	−0.9148	−0.9142		
9	−0.9374	−0.9456	−0.8985	−0.9065	−0.8520	−0.8594	−0.7976	−0.8045	−0.7343	−0.7375

The vibrational (doubly degenerate in k) levels appear for $k = 0, 1, 2$, whereas the levels with $k = 6, 7, 8, 9$ are the rotational. The values shown in the brackets are unphysical and they appear in the semiclassical calculations due to the vicinity of the separatrix. Because of the same reason the values labeled by the asterisks are missing in direct calculation, and these values are estimated by formula (9).

for the perturbation, which involves the diagonalization of a matrix of rank $n - |m|$ obtained by representing the operator $r^2 + z^2$ in the hydrogenic basis $\{|nlm\rangle;\ l = |m|, \ldots, n-1\}$. If we denote the eigenvalues of this matrix by $(r^2 + z^2)_{nm\kappa}$, the energy shifts are

$$\Delta E_{nm\kappa} = -\frac{1}{16d^3}\left(r^2 + z^2\right)_{nm\kappa}. \tag{11}$$

The corresponding values for the $n = 10$ manifold are given in Table 1 for comparison with the semiclassical results. (Note that the quantum number κ is not defined uniquely, so we prefer the semiclassical quantum number k for labeling the states.)

We can observe from the table that the semiclassical results are in good agreement with the quantum mechanical. The tiny splitting of the degeneracy appearing in the quantum-mechanical values of the vibrational energy levels near the classical separatrix is a consequence of tunneling between vibrational states V_1 and V_2 in the vicinity of the separatrix. This splitting does not appear in the semiclassical energy levels because the EBK rules do not incorporate tunneling effects. It is important to remark that in both semiclassical and quantum calculations, the degenerate vibrational levels disappear when $|m|$ increases. This fact is the semiclassical/quantum reflex of the pitchfork bifurcation that takes place in the classical counterpart. The classical criterion for this disappearance is $|m| > [\sqrt{5/7}\,n]$, where the term on the left side is the integer part of $\sqrt{5/7}\,n$. Then, for $n = 10$ this takes place for $|m| > 8$. However, from the Table 1 we can see that the degenerate levels have disappeared still when $|m| > 6$. This happens due to the fact that, although for $|m| = 7, 8$ the vibrational regions in phase space exist (see Fig. 1), the corresponding actions $A_{\mathrm{vib}} < 1/2$ and there are no vibrational levels (rule (5)). Thus, an empirical criterion is $|m| > [\sqrt{5/7}\,n] - 2$, which is valid for $5 \leqslant n \leqslant 21$. Hence, the quantum/semiclassical threshold of disappearance of the degenerate levels might be roughly evaluated from the pure classical results. Once again, the classical mechanics proves to be a powerful tool which provides a compact geometric picture of the energy level structure of the perturbed Rydberg systems.

References

[1] K. Ganesan, K.T. Taylor, J. Phys. B: At. Mol. Opt. Phys. 29 (1996) 1293.

[2] N.S. Simonović, J. Phys. B: At. Mol. Opt. Phys. 30 (1997) L613.

[3] J.P. Salas, N.S. Simonović, J. Phys. B: At. Mol. Opt. Phys. 33 (2000) 291.

[4] S.L. Coffey, A. Deprit, B.R. Miller, C.A. Williams, Ann. NY Acad. Sci. 497 (1986) 22.

[5] A. Deprit, V. Lanchares, M. Iñarrea, J.P. Salas, J.D. Sierra, Phys. Rev. A 54 (1996) 3885.

[6] J.P. Salas, A. Deprit, S. Ferrer, V. Lanchares, J. Palacián, Phys. Lett. A 242 (1998) 83.

[7] A.J. Lichtemberg, M.A. Lieberman, Regular and Stochastic Motion, Springer, Berlin, 1992.

[8] B. Goldstein, Classical Mechanics, 2nd ed., Addison-Wesley, Reading, MA, 1980.

[9] A. Deprit, Celest. Mech. 26 (1981) 9.

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

[11] A. Elipe, S. Ferrer, Phys. Rev. Lett. 72 (1994) 985.

[12] R.L. Waterland, J.B. Delos, M.L. Du, Phys. Rev. A 35 (1987) 5064.

[13] P. Cacciani, E. Luc-Koenig, J. Pinard, C. Thomas, S. Liberman, Phys. Rev. Lett. 56 (1986) 1467.