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ASYMMETRIC STRETCH COLLINEAR MODEL FOR HYDROGEN NEGATIVE ION

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Abstract. *We analyse the classical dynamics of collinear asymmetric stretching configuration of electrons in hydrogen negative ion. Approximative WKB quantization of the configuration yields the energies of doubly-excited intra-shell resonances comparable with quantum-mechanical values. The results indicate, as in the case of collinear configurations of helium atom, that the intra-shell resonances are associated with the asymmetric stretch like motion rather than the symmetric stretch motion along the Wannier ridge.*

Key words: *semiclassical, hydrogen negative ion, asymmetric-stretch*

1. INTRODUCTION

Calculations of quantum spectra of many-electron atoms are usually based on applying some approximate methods for solving the corresponding Schrödinger equation. However, in the region of highly-excited states, electron dynamics carries the features of classical moving particle (correspondence principle), what allows one to use semiclassical methods for calculation of the energy spectra in this region. In the last years the resonance structure of hydrogen and other negative ions has been the subject of extensive investigations using electron-impact detachment from the ions [1]. The main restriction in these investigations are due to the treatment of the ions within a one-electron approximation with a loosely bound electron moving in some effective core potential. By this approximation the possibility of transitions to a double-excited state of the negative ion is neglected. Here we consider a simple classical model for the hydrogen negative ion, which includes two-electron dynamics (full three-body Coulomb potential), providing a semiclassical calculation of energies for symmetrically doubly-excited (intra-shell) resonant states.

The semiclassical techniques for nonintegrable systems are usually based on the

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periodic-orbit (PO) theory of Gutzwiller [2], where the quantum level density is expressed in terms of contributions of classical periodic orbits (so-called trace formula). Ezra *et al* [3] applied the PO theory to calculate the energies of doubly-excited $^1S^e$ states of helium, taking into account the contributions of a number of collinear periodic orbits. The results obtained using collinear PO's are found to be in good agreement with quantum mechanical calculations. Also, they have shown that including only the contribution of the so-called *asymmetric stretch* (AS) orbit, it gives rather accurate results for the doubly-excited intra-shell resonant states. Recent investigations of symmetrically excited (intra-shell) resonant states of helium [4,5] have shown that both the states and associated classical configurations, which are extensions of the collinear AS orbit to the plane (including bending mode), are near-separable in the spheroidal coordinates. These results indicate that the intra-shell resonances of helium can be associated with classical AS-like motion.

Two fundamental PO's of a two-electron system are symmetric-stretch (SS) and asymmetric-stretch orbits (Fig. 1). They represent in-phase and out-of-phase motion, respectively. The first case appears if the motion is on the so-called Wannier ridge, i.e. when electron-nucleus distances are equal ($r_1 = r_2$) all the time. Otherwise the motion is out-of-phase and mostly off-Wannier ridge. Besides these, there is an infinite set of collinear periodic orbits, whose kinematics can be considered as mixtures of the two fundamental modes. This set covers all possible collinear configurations with the electrons located on different sides of the nucleus. The AS orbit is weakly unstable (quasistable), whereas SS orbit appears highly unstable [6], what from the classical point of view explains why the intra-shell resonances of helium are associated with AS like motion, rather than the SS motion along the Wannier ridge.

Fig. 1. Symmetric and asymmetric stretching collinear modes.

In this paper we use the AS model to calculate the energy spectrum of doubly-excited intra-shell resonances for hydrogen negative ion as it has been done for helium atom. The only (essential) difference between the helium atom and the hydrogen negative ion is the nuclear charge. However, since the electron-electron correlations are not changed, the results of semiclassical calculations for helium cannot simply be scaled. In the next section we consider the AS collinear model applied to the hydrogen negative ion. Then, in section 3, using approximate WKB quantization, we calculate semiclassical energies of doubly-excited $^1S^e$ intra-shell resonances and discuss the results in section 4.

2. THE CLASSICAL MODEL

2.1. The Hamiltonian

The Hamiltonian of the classical hydrogen negative ion reads ($m_e = e = 1$)

$$H = \frac{\mathbf{p}_1^2 + \mathbf{p}_2^2}{2} - \frac{1}{r_1} - \frac{1}{r_2} - \frac{1}{r_{12}}. \tag{1}$$

As is well known, differential equations of motion of a three-particle system are not amenable to analytical calculations, except for some particular class of configurations endowed with a simple symmetry, and one has to resort to numerical computations. Because of the singular character of Coulomb interaction, the regularization of differential
equations of motion is necessary.

Since equations of motion for Coulombic systems are invariant under a continuous similarity transformations (scaling invariance) [7]

$$\mathbf{p} \to \beta \mathbf{p}, \quad t \to \beta^{3/2} t, \quad E \to \frac{1}{\beta} E, \quad S \to \sqrt{\beta} S, \quad (\beta > 0) \tag{2}$$

it is sufficient to carry out all classical calculations at fixed energy $E = -1$, and then rescale all relevant quantities according to eqs. (2).

2.2. Regularization

Here we follow the procedure of Aarseth and Zare [8] to regularize the planar motion of the system given by the Hamiltonian (1) and introduce regularized coordinates and momenta Q_i, P_i, $i = 1,2,3,4$, instead of $\mathbf{r}_1 = (x_1, y_1)$, $\mathbf{r}_2 = (x_2, y_2)$, $\mathbf{p}_1 = (p_{x_1}, p_{y_1})$, $\mathbf{p}_2 = (p_{x_2}, p_{y_2})$, by means of the transformations [9,10]

$$\begin{aligned} x_1 &= Q_1^2 - Q_2^2, \quad y_1 = 2Q_1Q_2, \\ x_2 &= Q_3^2 - Q_4^2, \quad y_2 = 2Q_3Q_4, \\ p_{x_1} &= \frac{Q_1P_1 - Q_2P_2}{2r_1}, \quad p_{y_1} = \frac{Q_2P_1 - Q_1P_2}{2r_1}, \\ p_{x_2} &= \frac{Q_3P_3 - Q_4P_4}{2r_2}, \quad p_{y_1} = \frac{Q_4P_3 - Q_3P_4}{2r_2}, \end{aligned} \tag{3}$$

and the new time variable τ by

$$dt = r_1 r_2 d\tau, \tag{4}$$

where $r_1 = Q_1^2 + Q_2^2$, $r_2 = Q_3^2 + Q_4^2$. The regularized Hamiltonian reads

$$\tilde{H} = \frac{r_2 \mathbf{P}_1^2}{8} + \frac{r_1 \mathbf{P}_2^2}{8} - r_1 - r_2 + r_1 r_2 \left(\frac{1}{r_{12}} - E \right) = 0, \tag{5}$$

where $\mathbf{P}_1 = (P_1, P_2)$, $\mathbf{P}_2 = (P_3, P_4)$, and $r_{12} = [(Q_1^2 - Q_2^2 - Q_3^2 + Q_4^2)^2 + 4(Q_1Q_2 - Q_3Q_4)^2]^{1/2}$. Although the case $r_{12} \to 0$ is still singular, the AS orbit can be evaluated numerically because the triple collisions do not appear in this case.

2.3. Calculation of the AS orbit

The orbit can be obtained by the propagation method starting the electrons motion from initial positions $\mathbf{r}_1 = (1.5290478,0)$, $\mathbf{r}_2 \approx (0,0)$ at the total energy $E = -1$, using numerical (Runge-Kutta) integration of regularized equations of motion with constant step $\Delta\tau$. However, if we want to find 'exact' AS PO and its monodromy (stability) matrix, which determine the stability of the orbit, we have to apply the so-called *monodromy method*. This method starts from an approximate PO and iteratively, using a variant of the Newton-Raphson method, finds exact PO [11]. Here we use the AS orbit obtained by the propagation method, expressed in regularized coordinates, for the start of first iteration (i.e. as approximate PO). Since the AS orbit expressed in regularized coordinates becomes closed after two periods, it is necessary to take for 'approximate' PO the AS orbit of doubled period. Monodromy method applied to regularized two-electron systems and calculation of AS PO (for helium) is explained in more details in ref. [12]. The AS orbit for the hydrogen negative ion, calculated by this method at energy $E = -1$ has the period $T = 5.195$ and the full action along the orbit $S = 10.390$. The eigenvalues of the monodromy matrix (for two AS periods T) are $\mu_1 = 42.433$, $\mu_2 = 0.02357$, $\mu_{3,4} = 0.54877 \pm i0.83597$ and $\mu_{5,6,7,8} \approx 1$. Two real eigenvalues $\mu_{1,2}$ (nonvanishing Lyapunov exponents) indicate that one (radial) oscillatory mode of AS orbit is unstable. On the other hand, two complex conjugate eigenvalues $\mu_{3,4}$ are associated with stable (angular, bending) mode of a trajectory in the vicinity of this PO.

The frequency ratio (so-called *winding number*) with which neighbouring trajectories wind around the PO (here the AS orbit) in phase space

$$\gamma_{AS} = \frac{\omega_{ang}}{\omega_{AS}}, \tag{6}$$

is related to the complex conjugate eigenvalues $\mu_{3,4} = \exp(\pm 2\pi i \gamma_{AS})$. In our case it gives $\gamma_{2AS} = 0.34245 + k$, $k = 0, \pm 1, \pm 2, \ldots$, since the results above hold for AS orbit of doubled period, which imply that $\gamma_{AS} = \gamma_{2AS}/2$. Analysis of nearby periodic trajectories using a surface of section technique indicates that $1 < \gamma_{AS} < 20/17$, and consequently, $k = 2$ i.e. $\gamma_{AS} = 1.1712$.

3. WKB QUANTIZATION

As mentioned above, including only the contribution of the AS orbit in Gutzwiller trace formula (what is WKB quantization of the AS orbit, including a zero-point motion perpendicular to the orbit), it gives in the case of helium rather accurate results for the doubly-excited intra-shell resonant states. We shall assume that this holds also for hydrogen negative ion and apply this approximative semiclassical quantization in order to obtain the energy spectrum. Another technique which is applicable only for quantization of regular motion (so-called torus quantization) use Einstein-Brillouin-Keller (EBK) conditions [13,14]. Since AS orbit appear weakly unstable, approximate torus quantization is also available, yielding the same WKB formula as previous approach.

The mean value of the full action of an orbit in the vicinity of AS orbit over one

radial period is

$$S = S_{rad} + \gamma S_{ang}\,, \tag{7}$$

where S_{rad} and S_{ang} are (approximate) action integrals for radial and angular mode of the orbit, respectively, and $\gamma = \omega_{ang}/\omega_{rad}$ frequency ratio (winding number) of angular and radial motions. If the orbit is very close to the AS orbit, then $S_{ang} \to 0$, $S_{rad} \to S_{AS}$ and $\gamma \to \gamma_{AS}$. It is found that S is approximately constant for orbits near the AS orbit (in contrast to S_{rad} and S_{ang}). Then, the approximation of AS collinear model consists of taking $S \approx S_{AS}$ and $\gamma \approx \gamma_{AS}$ for all orbits in the vicinity of the AS orbit.

Because of the approximate separability of the radial and angular motion the quantization proceeds similar to that of the rovibrational motion of a triatomic molecule. If we use the spheroidal coordinates (λ, μ, φ) [4] to describe the collective electronic motion, the molecular orbital (MO) quantum numbers (n_λ, n_μ, m), together with quantum number ν for adiabatic variable R (interelectronic distance), can be used as semiclassical quantum numbers [5]. Maslov's indices are for three vibrational modes: $\alpha_\lambda = 2$ (two degenerate bending modes), $\alpha_\mu = 2$ (asymmetric stretch) and $\alpha_R = 2$ (symmetric stretch). In the present case of the AS configuration the latest mode is not excited ($\nu = 0$) and we have for the radial action to be $2\pi\hbar(n_\mu + \alpha_\mu/4)$ with the vacuum contribution $2\pi\hbar\alpha_R/4$. Then, the EBK quantum conditions for the actions S'_{rad} and S'_{ang} are ($\hbar = 1$)

$$S'_{rad} = 2\pi(n_\mu + 1)\,, \quad S'_{ang} = 2\cdot 2\pi(n_\lambda + \frac{1}{2}) \tag{8}$$

and according to (7) for S'

$$S' = 2\pi[n_\mu + 1 + \gamma(2n_\lambda + 1)]\,. \tag{9}$$

In order to satisfy the quantum conditions, the full action S, which is calculated for $E = -1$ has to be rescaled by using (2), what in the approximation of AS collinear model gives

$$E_{n_\mu, n_\lambda} = -\frac{S_{AS}^2}{4\pi^2[n_\mu + 1 + \gamma_{AS}(2n_\lambda + 1)]^2} \tag{10}$$

The results for *intra-shell* $^1S^e$ resonances using MO [4] and correlation quantum numbers ${}_N(K,T)_n^A$ [15] are given in the Table 1. They are compared with quantum mechanical calculations [16] and with the results due to Bohr's model (which underlies 'synchronous' two-electron kinematics [17])

$$E_N = -\frac{(1-1/4)^2}{N^2} \tag{11}$$

4. Discussion

We have presented the results of a semiclassical (WKB) calculation of the energies of doubly-excited $^1S^e$ intra-shell resonant states of the hydrogen negative ion, using an AS collinear model. Semiclassical energies are comparable with quantum-mechanical values

and this agreement is better than for semiclassical energies due to Bohr's model ('synchronous' two-electron configuration). In the last case (last column in Table 1) energy levels are degenerated for different values of the quantum number K (angular mode), what implies that we would obtain the same results using the SS collinear model (as a limiting case of Bohr's model with elliptic electron orbits degenerated to the straight lines). These results indicate, as in the case of helium, that the intra-shell resonances for hydrogen negative ion are associated with the AS like motion rather than the SS motion along the Wannier ridge.

Table 1. Energy levels for $^1S^e$ ($m = 0$, $A = +1$) intra-shell ($N = n$) resonant states of H^- classified using MO and correlation quantum numbers. Semiclassical results obtained using asymmetric stretch model (AS) are given together with the quantum mechanical results (QM) and the results due to Bohr's model (Bohr).

$(n_\mu,n_\lambda)_\nu$	N	n	K	T	E(AS)	E(QM)	E(Bohr)
$(0,0)_0$	1	1	0	0	-0.5801	-0.527	-0.5625
$(2,0)_0$	2	2	1	0	-0.1572	-0.149	-0.1406
$(0,1)_0$	2	2	-1	0	-0.1342		-0.1406
$(4,0)_0$	3	3	2	0	-0.0718	-0.069	-0.0625
$(2,1)_0$	3	3	0	0	-0.0645	-0.056	-0.0625
$(0,2)_0$	3	3	-2	0	-0.0582		-0.0625
$(6,0)_0$	4	4	3	0	-0.0410	-0.040	-0.0352
$(4,1)_0$	4	4	1	0	-0.0377		-0.0352
$(2,2)_0$	4	4	-1	0	-0.0349		-0.0352
$(8,0)_0$	5	5	4	0	-0.0264	-0.026	-0.0225
$(6,1)_0$	5	5	2	0	-0.0247	-0.024	-0.0225
$(4,2)_0$	5	5	0	0	-0.0232		0.0225
$(10,0)_0$	6	6	5	0	-0.0185	-0.018	-0.0156
$(8,1)_0$	6	6	3	0	-0.0175	-0.017	-0.0156
$(6,2)_0$	6	6	1	0	-0.0165	-0.015	-0.0156

Finally, we expect that a planar extension of the AS model (so-called 'asynchronous' model) for H^- would improve the results for semiclassical energies, as it has been obtained for helium [18].

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ASIMETRIČNO ISTEŽUĆI KOLINEARNI MODEL ZA NEGATIVNI JON VODONIKA

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Analiziramo klasičnu dinamiku kolinearne asimetrično istežuće konfiguracije elektrona u negativnom jonu vodonika. Aproksimativna WKB kvantizacija ove konfiguracije daje energije dvostruko pobuđenih 'intra-shell' rezonanci uporedive sa kvantno mehaničkim vrednostima. Ovi rezultati ukazuju da su, kao i u slučaju kolinearne konfiguracije atoma helijuma, 'intra-shell' rezonance pre povezane sa asimetrično istežućim tipom kretanja nego sa simetrično istežućim kretanjem duž Wannierovog grebena.

Ključne reči: *semiklasično, negativni jon vodonika, asimetrično istežuće*