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LETTER TO THE EDITOR

Analysis of classical motion on the Wannier ridge

K Richter† and D Wintgen‡

† Fakultät für Physik, Universität Freiburg, Hermann-Herder-Straße 3, 7800 Freiburg, West Germany

‡ Max-Planck-Institut für Kernphysik, Postfach 103980, 6900 Heidelberg, West Germany

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Abstract. We study the classical electronic motion of a two-electron atom on the Wannier ridge. Stability properties of certain periodic orbits are calculated. The analysis shows that the helium atom is not ergodic. Semiclassical implications of the classical analysis are discussed.

The failure of a Bohr–Sommerfeld like quantisation of the helium atom was a cornerstone in the evolution of quantum mechanics. Einstein (1917) recognised the reason for the failure: only for integrable systems is a multi-dimensional Bohr–Sommerfeld quantisation possible, but the helium atom is non-integrable. Nowadays there is a revival of semiclassical methods, in particular in connection with chaotic motion and topological quantisation (Eckhardt 1988, Friedrich and Wintgen 1989). Even though the general concepts of quantum mechanics are developed, the three body Coulomb problem is still an unsolved basic problem of the theory (Fano 1983). Current interest in atomic physics (experimentally and theoretically) is focused on correlated electronic motion far away from independent particle models (Sandner 1987). Examples are 'planetary atoms' (Leopold and Percival 1980) with both electrons highly (but asymmetrically) excited or 'Wannier ridge states' with symmetrical electron excitations (Rost and Briggs 1989).

In this letter we focus on the classical properties of such states. There are only a few rigorous results about general three body Coulomb systems. Up to now it is even unknown whether their motion is ergodic or not. To prove non-ergodicity it is sufficient to find a periodic orbit which is linearly stable in *all* directions. The reason for the lack of popularity of quantitative classical studies is obvious: the equations of motion are multi-dimensional, non-integrable, and singular, hence far away from an easy-to-do-job. In addition, the independent particle case $1/Z = 0$ (Z is the nuclear charge) is completely degenerated, which prohibits an application of the KAM theory to derive an 'independent particle' limit (Eckhardt and Wintgen 1990). Nevertheless, a classical analysis is the necessary input for a semiclassical treatment.

An essential ingredient for the classical analysis of the three body Coulomb problem is the regularisation of the motion. For a nucleus with charge Z and infinite mass the Hamiltonian reads (in atomic units, $e = m_e = 1$):

$$H = \frac{p_1^2 + p_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}. \tag{1}$$

In (1) the electron–nucleus distances are given by r_j, $j = 1,2$ and the distance between the electrons is r_{12}. Whenever an interparticle distance vanishes (particle collision) the potential energy diverges. There is a striking difference in the topology of the various collisions. In analogy to the motion of the electron in the hydrogen atom, the motion can be regularised for binary collisions, where only one interparticle distance vanishes. However, the triple collision ($r_1 = r_2 = r_{12} = 0$) cannot be regularised, e.g. these solutions have branch points of infinite order (Siegel 1941).

The potential appearing in (1) is homogeneous. Hence the equations of motion can be scaled and we can put the total energy E equal to -1 in (1). The period T of any periodic trajectory equals half its action S, $T = S/2$. Bounded classical motion is possible for $Z - \frac{1}{4} > 0$. In this letter we concentrate on the motion, where both electrons are confined to a common plane of the three-dimensional configuration space, $\boldsymbol{r}_j = (x_j, y_j, 0)$. This means that the total angular momentum $\boldsymbol{J}$ of the electrons points perpendicular to the plane. Such a planar system describes the general motion for the case of $\boldsymbol{J} = 0$. Besides the conservation of the total angular momentum $\boldsymbol{J}$, the Hamiltonian possesses further discrete symmetries. If we define θ as the angle between $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, then θ remains constant if (θ, p_θ) equals $(0,0)$ or $(\pi, 0)$. The motion then reduces by one degree of freedom and resembles that of a collinear atom. If we define α as the hyperangle between r_1 and r_2, $\tan(\alpha) = r_1/r_2$, then α remains constant if (α, p_α) equals (0,0), ($\pi/4$,0), or ($\pi/2$,0). For $\alpha = 0$ and $\alpha = \pi/2$ the motion is reduced to that of a single electron atom. The solution $\alpha = \pi/4$ defines the Wannier ridge of collective motion, where both electron-nucleus distances are the same for all times (Fano 1983). To regularise the binary collisions we follow a procedure of Aarseth and Zare (1974), which is essentially a double Kustaanheimo–Stiefel transformation together with a modified Levi-Civita regularisation. This approach (originally applied to celestial mechanics) regularises two of the three binary collisions. However, this is enough for our purpose, since the binary collision $r_{12} = 0$ is forbidden in Coulombic systems because of energy conservation (the r_{12} collision corresponds to the repulsive part of the potential). The transformation to regularised coordinates $\boldsymbol{R}_j = (X_j, Y_j, 0)$ and conjugate momenta $\boldsymbol{P}_j$ reads (ignoring the particle indices j):

$$
\begin{aligned}
&x = X^2 - Y^2 \qquad y = 2XY \\
&p_x = (XP_X - YP_Y)/2R^2 \qquad p_y = (YP_X + XP_Y)/2R^2.
\end{aligned} \tag{2a}
$$

After the (non-canonical) time transformation

$$
\mathrm{d}t = {R_1}^2 {R_2}^2 \mathrm{d}T \tag{2b}
$$

the new Hamiltonian h is given by

$$
h = 0 = \frac{{P_1}^2 {R_2}^2}{8} + \frac{{P_2}^2 {R_1}^2}{8} - Z({R_1}^2 + {R_2}^2) + {R_1}^2 {R_2}^2 \left(1 + \frac{1}{{R_{12}}^2}\right) \tag{3}
$$

where ${R_{12}}^2$ is the inter-electron distance r_{12} in the new coordinates (2a).

The stability of a periodic orbit is measured by the Liapunov exponents λ_i, each of which is the logarithm of an eigenvalue of the monodromy matrix for the linearised equations of motion perpendicular to the orbit after one period (Friedrich and Wintgen 1989). An orbit is linearly stable with respect to variations in i if λ_i is imaginary, and the orbit is unstable if λ_i is real. The case of a complex Liapunov exponent, $\lambda_i = a + \mathrm{i}b$, $a, b \neq 0$, is possible only for motion off the symmetry planes. We have studied the structure of the classical phase space and the properties of the periodic orbits for the non-trivial symmetry planes $(\theta, p_\theta) = (0,0)$ and $(\pi/2, 0)$, and $(\alpha, p_\alpha) = (\pi/4, 0)$ and their dependence on the angular momentum $\boldsymbol{J} = (0,0,J)$ and on the nuclear charge Z. Detailed results of these calculations will be published in a separate paper. Here we will give our results for the two fundamental orbits on the Wannier ridge $\alpha = \pi/4$, the so called 'Langmuir' orbit (Langmuir 1921) and the 'Wannier' orbit, for which also $\theta \equiv \pi$ is constant. The latter notation is somewhat unfortunate, since *all* motion with $\alpha \equiv \pi/4$ takes place on the Wannier ridge. However, the special orbit with $\theta \equiv \pi$ has been intimately connected with the existence of quasi-bound Wannier ridge resonances of doubly excited atoms (Rost and Briggs 1989) and with the Wannier exponent of the three-particle breakup (Fano 1983). The Langmuir orbit is shown for $J = 0$ in figure 1(*a*), while figure 1(*b*) shows the Wannier orbit for $0 < J < J_{\max} = 2(Z - \frac{1}{4})$. For $J = 0$ the Wannier orbit degenerates to the straight line motions of the collinear atom including the triple collision with the nucleus. For $J = J_{\max}$ the two ellipses become identical circles with the electrons being on opposite sides. In this case the stability properties of the orbit can be calculated analytically (Poirier 1989).

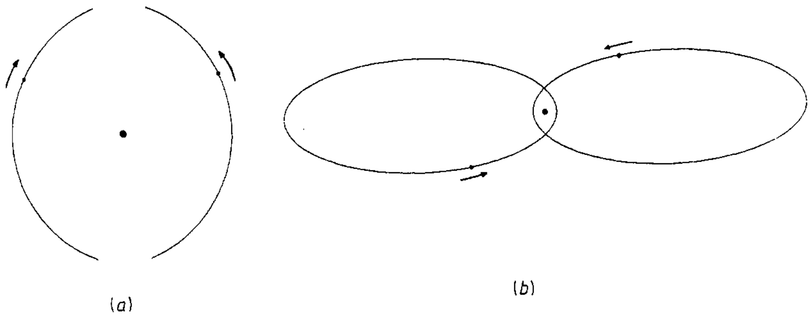

Figure 1. Schematic view of the two fundamental motions on the Wannier ridge, the Langmuir orbit (*a*) and the Wannier orbit with non-zero angular momentum (*b*).

The action S of the Wannier orbit is independent of J and is given by $S = 4\pi(Z - \frac{1}{4})$. The stability properties of the orbit have been analysed so far only for $J = J_{\max}$ (Poirier 1989). Our calculations show that the motion is always unstable with respect to the coordinate α, and λ_α behaves asymptotically ($J \to 0$) as

$$\lambda_\alpha \sim -A(Z) \lg J \tag{4}$$

with $A(Z) > 0$. This is shown in figure 2(*a*), where we plotted λ_α against $\lg J^2_{\mathrm{scal}}$, where $J_{\mathrm{scal}} = J/J_{\max}$. From (4) we find that for J=0 the Liapunov exponent λ_α becomes infinite, which reflects the non-regularisibility of the triple collision. Note that J is the angular momentum for the energy $E = -1$. Rescaling yields the *real* angular momentum J_E for an arbitrary energy, $J_E = J/\sqrt{-E}$. This means that independent of the real angular momentum, the scaled angular momentum J always goes to zero if we approach the double ionisation threshold $E \to 0$.

The stability properties with respect to deviations in θ vary somewhat capriciously with Z and J. For fixed Z the orbit becomes infinitely often stable and unstable when J goes to zero, and the number of conjugate points of the trajectory increases by two after each stability/instability change. This is illustrated in figure 2(*b*), where we plotted the hyperbolic cosine of λ_θ against $\lg J^2_{\mathrm{scal}}$ for $Z = 0.3$. For $|\cosh(\lambda_\theta)| < 1$

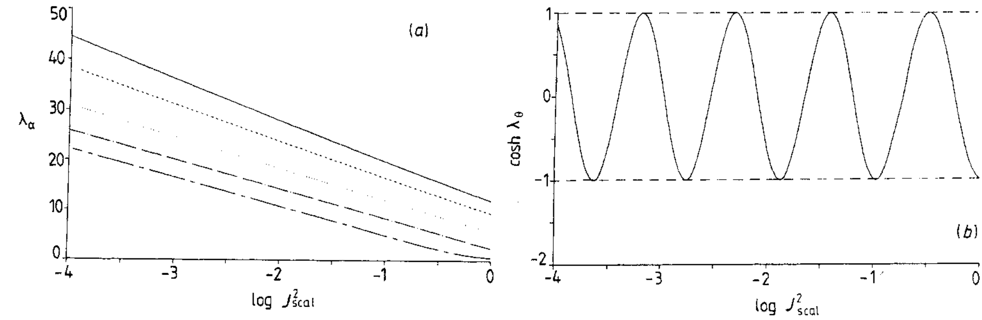

Figure 2. Dependence of the Liapunov exponents for the Wannier orbit on the angular momentum for λ_α and various Z-values, $Z = 0.4, 0.5, 1, 5, 100$ (from above) (a), and for λ_θ and $Z = 0.3$. In (b) the regime of stability is marked by broken lines. The curve touches the upper broken line, but crosses the lower one.

the orbit is stable and unstable otherwise. Qualitatively the behaviour shown in figure 2(b) does not change with Z, but the frequency scale of the near-periodicities depends strongly on Z. For example, for $Z = 1$ the observed near-periodicity has a scale of $\Delta \lg J^2_{\rm scal} \approx 4.2$. In addition, the relative intervals of instability become larger with increasing Z. Similar behaviour in the stability properties of certain orbits has been observed for various systems, one prominent example is the hydrogen atom in a uniform magnetic field (Friedrich and Wintgen 1989).

The stability properties of the Langmuir orbit are summarised in figure 3. Part (a) shows the hyperbolic cosine of the Liapunov exponent λ_1. The index 1 denotes the local coordinate perpendicular to the orbit and perpendicular to α, which in this case does not coincide with the static θ-coordinate alone. The orbit is stable up to $Z - \frac{1}{4} \approx 5.35$ and very weakly unstable for larger Z-values. At $Z - \frac{1}{4} = 0.176\,931\ldots$ the Liapunov exponent becomes zero and the orbit bifurcates with the birth of another periodic orbit. Part (b) shows the hyperbolic cosine of λ_α. The α-motion is unstable for all integer Z, except for $Z = 2$. Since also λ_1 is imaginary for $Z = 2$ we find that the electronic motion of the helium atom posesses stable motion and hence is *not* ergodic.

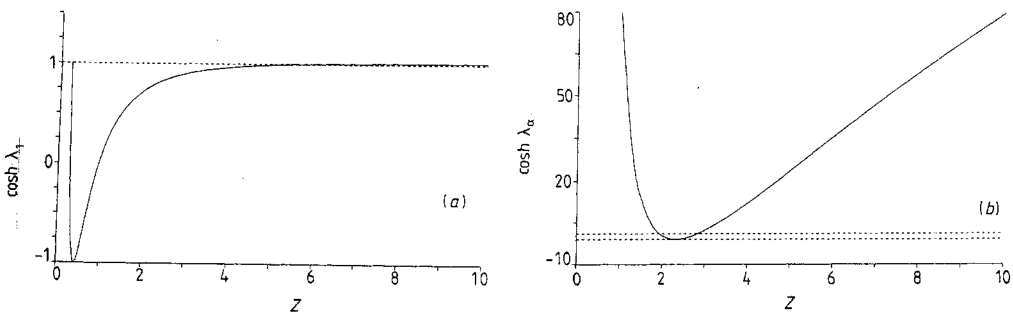

Figure 3. Dependence of the Liapunov exponents λ_1 (a) and λ_α (b) on the nuclear charge Z for the Langmuir orbit ($\boldsymbol{J} = 0$). The regime of stability is marked by broken lines.

What are the consequences of the classical analysis for the quantised motion, e.g. the real atoms? Gutzwiller (1971) has shown how to connect the classical periodic orbits with the quantal density of states by a semiclassical expansion of Feynman's path integral formalism. For the (chaotic) hydrogen atom in a magnetic field the applicability of this theory has been shown in a very convincing way (Friedrich and Wintgen 1989). The classical analysis presented here then suggests the following semiclassical predictions.

(i) Absence of resonant structures related to the Wannier orbit. This follows from the diverging Liapunov exponent λ_α of the Wannier orbit. The classical analysis presented here may explain why these resonances haven't been found in recent laser experiments (Camus *et al* 1989, Eichmann *et al* 1990). The resonances were predicted by adiabatic quantum calculations (Fano 1983, Rost and Briggs 1989). Unfortunately no *full* quantum calculations exist for high lying doubly excited states, which then could prove or disprove this hypothesis. Further experimental data may help to solve this controversy.

(ii) For helium we predict a double Rydberg series of very narrow resonances associated with the stability island around the Langmuir orbit. Semiclassically these states are exactly bound, but they can decay quantum mechanically by dynamical tunnelling through the boundary of the stability island. The number of states N associated with the stability island is approximately given by the island's volume in phase space (Berry 1983). However, this volume is presumably small and even though it scales with the energy as $(-2E)^{-3/2}$, N becomes large only for energies close to the double ionisation threshold. Unfortunately it will be hard to detect these states experimentally. The associated wavefunctions will have a very small overlap with low lying states, from which laser excitations normally occur.

In conclusion, we have studied the classical electronic motion of a two-electron atom. For small angular momentum the Wannier orbit becomes extremely unstable, which implies the absence of associated resonant structures in quantum spectra. For helium the Langmuir orbit is a simple periodic trajectory, which is linearly stable in all directions. This proves the non-ergodicity of the helium atom and implies the existence of a double Rydberg series of long living resonances.

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