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LETTER TO THE EDITOR

Semiclassical cycle expansion for the helium atom

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Abstract. We analyse the classical dynamics of near-collinear electron configurations in helium. The dynamics turns out to be fully chaotic. An application of periodic orbit quantization techniques yields the energy of doubly excited states with high accuracy. The analysis shows that near-collinear intra-shell resonances are associated with an asymmetric stretch like motion of the electron pair rather than the symmetric stretch motion along the Wannier ridge.

The failure of the Copenhagen School (see e.g. van Vleck 1922) to obtain a reasonable estimate of the ground-state energy of the helium atom was a cornerstone in the evolution of quantum mechanics. Nowadays we know the essential shortcomings of the old quantum theory (Leopold and Percival 1980, section 3.4 in Gutzwiller 1990):

(i) the role of conjugate points along classical trajectories and their importance for the approach to wave mechanics were not properly accounted for;

(ii) the precise role of periodic trajectories when the classical dynamics are non-integrable or even chaotic was unknown.

Even though it is widely known that the old quantum theory failed in the early days of quantum mechanics, it is less well known that the principal obstacles to the determination of the ground-state energy of the helium atom were overcome about a decade ago (Leopold and Percival 1980). Nevertheless, a proper semiclassical treatment of the helium atom is still an outstanding problem of the basic theory (as is a proper quantum description). The helium atom therefore remains the essential touchstone of semiclassical mechanics, even though considerable progress has been achieved very recently in applications for other chaotic atomic systems (Friedrich and Wintgen 1989, Cvitanović and Eckhardt 1989, Tanner *et al* 1991).

The purpose of this letter is threefold. We first analyse the classical dynamics for near-collinear arrangements of the two electrons in the helium atom. We find strong evidence that the resulting motion is fully chaotic *in* the corresponding symmetry plane whereas the linearized motion *off* the plane is stable. We then apply modern semiclassical techniques to quantize the chaotic dynamics and obtain the energies of certain doubly excited states. Finally, our results (together with numerically highly accurate quantum mechanical calculations) unambiguously show that the widely accepted viewpoint of electron pair propagation along the Wannier ridge for doubly excited

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intra-shell resonances is simply wrong. The wavefunctions of (near-collinear) intra-shell states are instead clearly localized along classical orbits associated with asymmetric stretch like motion of the electrons.

For a nucleus with charge Z and infinite mass the Hamiltonian reads (atomic units used)

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

The electron–nucleus distances are given by r_j, $j=1,2$ and the distance between the electrons is r_{12}. The energy E and the total angular momentum $\boldsymbol{L}$ are constants of motion. The potential appearing in (1) is homogeneous and the equations of motion can be scaled to energy-independent form. The accumulated action along a classical path is then $\tilde{S}(E)=2\pi zS$ with $z=(-E)^{-1/2}$ and $2\pi S$ the action at energy $E=-1$.

Here we shall focus on total angular momentum $\boldsymbol{L}=0$, for which the motion of the electrons is confined to a space-fixed plane in configuration space. This removes three of the total of six degrees of freedom, and we take the three inter-particle distances r_i as dynamical variables. It is convenient to replace these by the perimetric coordinates (James and Coolidge 1937)

$$x=r_1+r_2-r_{12} \qquad y=r_1-r_2+r_{12} \qquad z=-r_1+r_2+r_{12} \tag{2}$$

with $x, y, z \geqslant 0$. The Hamiltonian (1) possesses discrete symmetries which are readily identified as symmetry planes in the perimetric coordinate set. Collinear motion with both electrons on different sides of the nucleus is confined to the $x\equiv 0$ plane. Collinear motion with both electrons localized on the same side of the nucleus is given by either $y\equiv 0$ or $z\equiv 0$. Finally, motion on the so-called Wannier ridge (Fano 1983) $r_1=r_2$ takes place in the $y=z$ plane. The electron motion in the symmetry planes becomes essentially two-dimensional.

The necessary ingredient for any semiclassical analysis is a proper understanding of the underlying classical dynamics. For the helium atom such quantitative analyses are being developed at present (Richter and Wintgen 1990a, b, Kim and Ezra 1991, Blümel and Reinhardt 1991, Eckhardt 1991). Dynamics in the different symmetry planes differs quite dramatically. The system is nearly integrable for collinear arrangements where both electrons are on the side of the nucleus (Richter and Wintgen 1990b), whereas motion on the Wannier ridge shows a rather complicated pattern (Richter and Wintgen 1990a) with mixed regular and irregular orbits and strong sensitivity to the nuclear charge Z. Collinear motion with the electrons on different sides of the nucleus turns out to be fully chaotic for all practical purposes, as we will now show.

A system is 'chaotic' if all periodic orbits (PO) are linearly unstable and their number proliferates exponentially with their action. The exponential proliferation becomes obvious if the PO can be mapped onto a tree of symbols as e.g. for the anisotropic Kepler problem (AKP) (Gutzwiller 1990) or the diamagnetic Kepler problem (DKP) (Eckhardt and Wintgen 1990). Our numerical results on the collinear motion of the helium suggest that the PO obey a binary coding.

In figure 1 we show equipotential lines for the collinear electron arrangement $x\equiv 0$. The perimetric coordinates y, z then coincide (apart from a factor of 2) with the inter-particle distances r_1, r_2. The system ionizes if either $r_1\to\infty$ or $r_2\to\infty$. To characterize the motion we introduce a symbolic description of the trajectories by recording the sequence $\ldots i_1 i_2 i_3 \ldots$ of electron collisions with the nucleus, i.e. $r_i=0$. The PO shown

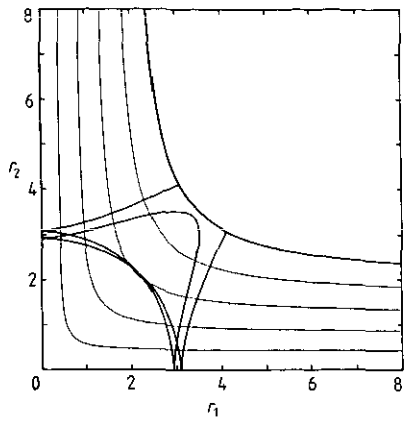

Figure 1. Equipotential lines and boundary of the classical allowed region for the collinear electron configuration in helium. A typical periodic trajectory is also shown.

in figure 1 is then coded by the periodically continued string of symbols ... 21211212 .... There appears to be no restriction on allowed symbol sequences, but for a PO the length of the periodic symbol sequence must be even. This rule can be overcome by de-symmetrizing the motion and considering the motion in the fundamental domain (Cvitanović and Eckhardt 1989, Eckhardt and Wintgen 1990). A collision is then denoted by the symbol '+' if the previous collision was by the *same* electron, and by the symbol '−' if the collision before was by the *other* electron. The PO of figure 1 is then coded '+−−−'. This orbit has (topological) length 4, because its code consists of repetitions of a string of four symbols. As usual in such de-symmetrizations the orbit shown is already periodic after four collisions in the fundamental domain, but the corresponding configuration space segment is only half of the full period. We now assume that the collinear PO not involving triple collision ($r_1 = r_2 = r_{12} = 0$) can be mapped one-to-one onto the binary symbols $\{+, -\}$. This conjecture is supported by numerical results summarized in table 1, where we list all PO up to symbol length 6, and also by similar results obtained independently by Blümel and Reinhardt (1991).

Apart from the missing orbit '+' (which parallels the AKP and the DKP problem) all the symbol sequences in table 1 exist and we did not find any orbit which does not fit the coding scheme. The coding takes care automatically of the discrete symmetries of PO. The maximal number of conjugate points of a PO is given by its symbol length, and the Morse index α by twice the symbol length. The type of fixed point is determined whether the number of the symbols '−' in the sequence is odd or even. All stability exponents u listed in table 1 are strictly positive, i.e. all the orbits are unstable with respect to the motion in the collinear plane $x \equiv 0$. The linearized motion *off* the symmetry plane is however stable and characterized by the winding number γ (Eckhardt and Wintgen 1991).

The missing orbit '+' can be formally assigned to a PO for which one electron is removed to infinity whereas the second electron is moving on a degenerate Kepler ellipse. Note also that the 'symmetric stretch' orbit $r_1 \equiv r_2$ (i.e. the Wannier configuration of the electrons) is missing from the list. Inclusion of this orbit as a *fundamental* orbit (i.e. an orbit of symbolic length 1) would lead to a complete ternary coding equivalent to that for the DKP problem (Eckhardt and Wintgen 1990). It has however been shown

Table 1. Various properties of the collinear periodic orbits of the helium atom. u is the stability exponent, i.e. the Liapunov exponent times the action S of the orbit. The Morse index α for the motion in the symmetry plane and the winding number γ for the motion off the plane are given in the next columns. The type of fixed point (FX) is denoted by H for hyperbolic orbits and by IH for hyperbolic orbits with reflection.

No	Code	S	u	γ	α	FX
1	+	—	—	—	2	H
2	−	1.829 00	0.6012	0.5393	2	IH
3	+−	3.618 25	1.8622	1.0918	4	IH
4	++−	5.326 15	3.4287	1.6402	6	IH
5	+−−	5.394 52	1.8603	1.6117	6	H
6	+++−	6.966 77	4.4378	2.1710	8	IH
7	++−−	7.041 34	2.3417	2.1327	8	H
8	+−−−	7.258 49	3.1124	2.1705	8	IH
9	++++−	8.566 19	5.1100	2.6919	10	IH
10	+++−−	8.643 07	2.7207	2.6478	10	H
11	++−+−	8.937 00	5.1563	2.7292	10	H
12	++−−−	8.946 19	4.5932	2.7173	10	IH
13	+−+−−	9.026 90	4.1765	2.7140	10	IH
14	+−−−−	9.071 79	3.3424	2.6989	10	H
15	+++++−	10.138 74	5.6047	3.2073	12	IH
16	++++−−	10.216 74	3.0324	3.1594	12	H
17	+++−+−	10.570 67	6.1393	3.2591	12	H
18	+++−−−	10.576 29	5.6766	3.2495	12	IH
19	++−+−−	10.706 99	5.3252	3.2520	12	IH
20	++−−+−	10.706 99	5.3252	3.2520	12	IH
21	++−−−−	10.743 04	4.3317	3.2332	12	H
22	+−+−−−	10.878 55	5.0002	3.2626	12	H
23	+−−−−−	10.910 15	4.2408	3.2467	12	IH

previously (Richter and Wintgen 1990a) that the stability exponent for the Wannier orbit is infinite due to the occurrence of a non-regularizable triple collision, so that the Wannier orbit and related closed orbits beginning and ending in triple collision will not contribute to the semiclassical periodic orbit sum (see below) for the density of states.

Gutzwiller (1990) has derived a semiclassical theory in which the periodic orbits of the classical system are intimately connected to the eigenvalues of the quantized Hamiltonian. The formal theory is divergent, however, and re-summation techniques must be used to overcome this deficiency. The cycle expansion method was proposed (Artuso *et al* 1990, Cvitanović 1991) and successfully applied to a chaotic scattering system (Cvitanović and Eckhardt 1989) and—in combination with a functional equation—to some bounded systems (Tanner *et al* 1991).

Applied to the present system the Gutzwiller formula for the spectral Euler product reads (ignoring renormalization (Berry and Keating 1990) of the LHS)

$$\prod_n (E - E_n) \sim \prod_{\text{PPO}} \prod_{k=0}^{\infty} \prod_{m=0}^{\infty} (1 - t_{\text{PPO}}^{(k,m)}). \tag{3}$$

The weight $t_{\text{PPO}}^{(k,m)}$ of each prime (i.e. non-repeated) periodic orbit (PPO) is given by

$$t_{\text{PPO}}^{(k,m)} = (\pm 1)^k a^j \exp[2\pi i z S - i\alpha\pi/2 - (k+\tfrac{1}{2})u - 4\pi i(m+\tfrac{1}{2})\gamma] \tag{4}$$

where all classical quantities are given in table 1. The plus sign applies to hyperbolic PO and the minus sign to hyperbolic PO with reflection. The bookkeeping indices a, j are only introduced for convenience, j equals $(2k+1)$ times the symbol length and a will be set to unity. The idea of the cycle expansion is to expand the infinite product (3) into a power series of the bookkeeping index a. For $k = m = 0$ this reads

$$\prod_{\text{PPO}} (1 - t_{\text{PPO}}) = 1 - t_+ - t_- - (t_{+-} - t_+ t_-) - (t_{++-} + t_+ t_{+-}) - \dots . \tag{5}$$

Except for the fundamental orbits '+' and '−' each orbit contribution is accompanied by a compensating term pieced together from shorter orbits. Thus terminating the expansion at a given symbol length effectively means a re-summation of *all* orbits, with the approximation that the longer orbits are shadowed to increasing accuracy by the shorter ones. The zeros of the cycle expanded product are the energy eigenvalues in the semiclassical approximation to Green function traces.

The present calculations were carried out for $m = 0$ and all orbit contributions up to $j = 6$. In table 2 we show our results for some doubly excited $^1S^e$ states. We use the $N(K, T)n$ classification, where N, n roughly correspond to the principal quantum numbers of the electrons and $K = N - 1$, $T = 0$ (for a detailed description of the approximate labels K, T see, e.g., Rost and Briggs 1991). The quantum results are taken from a compiled list of highly accurate helium resonances (Wintgen 1991), which completes and improves available data (Ho 1986). It is more natural in this context to compare the effective quantum numbers $N_{\text{eff}} = 1/\sqrt{E}$ than the binding energies E themselves, but both values are given. We find that the cycle expansion results are mostly good to within 1% or better. This is rather better than might be expected; in

Table 2. Total binding energies E and effective quantum number N_{eff} for the $N(K, T)n$ $^1S^e$ states ($K = N - 1$, $T = 0$) obtained by WKB quantization of the fundamental orbit, by the cycle expansion and by full quantum solutions.

		N_{eff}			Energies	
N	n	WKB	Cycle	QM	Cycle	QM
1	1	0.568	0.584	0.587	2.932	2.904
2	2	1.115	1.134	1.134	0.778	0.778
2	3		1.308	1.302	0.585	0.590
3	3	1.662	1.684	1.682	0.353	0.354
3	4		1.883	1.886	0.282	0.281
4	4	2.208	2.243	2.231	0.199	0.201
4	5		2.456	2.456	0.166	0.166
4	6		2.574	2.575	0.151	0.151
5	5	2.755	2.783	2.780	0.129	0.129
5	6		3.025	3.020	0.109	0.110
5	7		3.154	3.159	0.101	0.100
6	6	3.302	3.343	3.329	0.0895	0.0902
6	7		3.586	3.580	0.0778	0.0780
6	8		3.733	3.733	0.0717	0.0718
7	7	3.849	3.903	3.883	0.0657	0.0663
7	8		4.140	4.138	0.0583	0.0584
7	9		4.305	4.301	0.0540	0.0541
8	8	4.395	4.429	4.411	0.0510	0.0514
8	9		4.689	4.686	0.0455	0.0455
8	10		4.865	4.865	0.0423	0.0423

fact, accurate quantum results for the very high lying doubly excited states ($N > 6$) are not available in the literature despite enormous efforts by various theoretical groups. For published data the results are comparable or even superior to elaborate (adiabatic) hyperspherical calculations (Koyama *et al* 1986).

Generally, the energies obtained in the cycle expansion (as well as in the quantum mechanical calculations) are complex valued and we have only tabulated the real part of these energies (the imaginary parts are close to zero). However, the widths of the resonances (i.e. the imaginary part of their energies) are still smaller than the semiclassical error in the real part and there is likely no reason why the imaginary part should be more accurate.

The choice $m = 0$ in our calculations means that the associated semiclassical wavefunctions are localized in the $x = 0$ plane with only a zero-point motion perpendicular to it. This approach is justified by the stability of the classical motion perpendicular to the plane. In fact, the quantum wavefunctions show the same behaviour (Wintgen 1991). Putting $m \neq 0$ gives states with $K = N - 2m$, but the linearization of the motion perpendicular to the plane becomes a rather crude approximation if $N \gg m$ does not hold.

We also list in table 2 the results of the simplest cycle approach including only the fundamental PO '—', which is nothing but a WKB quantization of the orbit (but including a zero-point motion perpendicular to the orbit). Quantization of the fundamental asymmetric stretch PO gives rather accurate results for the doubly excited intra-shell resonances $N = n$. For the other states $N \neq n$ the inclusion of all the orbits of table 1 is essential and the simplified WKB approach cannot yield them. However, these results indicate that the intra-shell resonances are associated with the asymmetric stretch like motion of the fundamental periodic orbit rather than the symmetric stretch motion along the Wannier ridge. This conclusion is in striking contrast to the common viewpoint expressed in the literature (see, e.g., Fano 1983, Rau 1983, Watanabe and Lin 1986, Sadeghpour and Greene 1990, Harris *et al* 1990) but in line with recent suggestions (Richter and Wintgen 1990a, Kim and Ezra 1991, Rost *et al* 1991). An inspection of the intra-shell wavefunctions obtained by accurate solutions of the full Schrödinger equation, however, confirms the above conclusion. In figure 2 we show, e.g., the

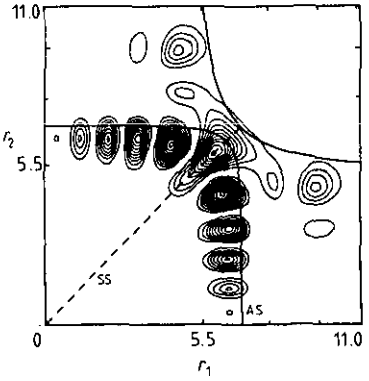

Figure 2. Probability distribution $|\Psi_{Nm}(x, y, z)|^2$ for the intra-shell wavefunction $N = n = 6$ in the $x = 0$ plane corresponding to the collinear arrangement $r_{12} = r_1 + r_2$. The axes have a quadratic scale to account for the wave propagation in Coulombic systems, where nodal distances increase quadratically. The fundamental orbit '—' (AS) as well as the symmetric stretch motion (SS) along the Wannier ridge are overlayed on the figure.

probability distribution of the $N = n = 6$ state which is clearly localized along the fundamental orbit and *not* along the Wannier ridge $y \equiv z$. The classical probability along the trajectory is largest (as well as the quantal wavefunction) where it passes the Wannier saddle point, but the motion is directed perpendicular to the ridge.

The WKB treatment of the fundamental orbit also provides the dynamical origin of the double Rydberg formula (Rau 1983)

$$E_N = -(Z-\sigma)^2/(N-\mu)^2 \tag{6}$$

for the intra-shell resonances. We find $Z - \sigma = S_-$ and $\mu = 1 - \gamma_- - \alpha_-/4$ (i.e. $\sigma = 0.1710$ and $\mu = -0.0393$) which fits well with the semi-empirically derived values of $\sigma = 0.1795$ and $\mu = -0.0597$ (Molina 1989).

In summary, we have shown that the classical dynamics of the collinear helium atom is fully chaotic. An application of modern semiclassical periodic orbit quantization techniques for the full three-dimensional problem yields a number of resonances with high accuracy. The analysis shows that highly excited intra-shell resonances are—contrary to common belief—not associated with the symmetric stretch motion along the Wannier ridge but with an asymmetric stretch like motion of the electron pair.

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