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LETTER TO THE EDITOR

Calculations of planetary atom states

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Abstract. We prove the existence of a new type of resonance formation in highly doubly excited atoms and ions. The resonant states represent the quantum analogue of a stable planetary atom configuration discovered recently in classical mechanics. The energies and total decay widths of the resonances are calculated quantum mechanically by solving the full three-body Coulomb problem without any approximation. The resonance energies and the structure of the associated wavefunctions coincide with expectations derived from simple semiclassical models. We discuss excitation schemes which should allow an experimental observation of these strongly correlated electron states.

The structure and the formation of highly correlated electronic states in doubly excited atoms and ions is of topical interest in spectroscopy (Camus *et al* 1989, Eichmann *et al* 1990, Kilgus *et al* 1990, Harris *et al* 1990, Domcke *et al* 1991) and atomic physics (Fano 1983, Herrick 1983). Nevertheless, a global understanding and characterization of these states is still lacking because of the non-separability of the problem. The search for approximate symmetries for the three-body Coulomb problem using group-theoretical or adiabatic methods was partially successful for doubly excited intrashell resonances (Herrick 1983, Feagin and Briggs 1986, 1988, Rost *et al* 1991a) and approximate quantum numbers were introduced to classify the multitude of resonances occurring (for a recent review see Rost and Briggs 1991). However, the first stringent test of such models on the basis of accurate *ab initio* calculations were performed only recently and only for a certain class of states (Rost *et al* 1991b, Ezra *et al* 1991). In this letter we report on large scale *ab initio* calculations for planetary helium states (Leopold and Percival 1980), where both electrons are highly excited. We focus on a new class of extremely correlated states, for which the existing classification schemes turn out to be inapplicable. The existence of such states was predicted recently on classical grounds and represents the quantum analogue of a stable classical planetary atomic configuration (Richter and Wintgen 1990). The general mechanism for the formation of this type of long-lived resonance is the existence of a stable periodic orbit, which allows for an (approximate) torus quantization of the nearby phase space region (Miller 1975).

The non-relativistic Hamiltonian of a two-electron atom (or ion) is given by (atomic units used)

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

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r_1 and r_2 are the electron distances from the nucleus having charge Z and infinite mass and r_{12} is the interelectron distance. The restriction to infinite mass is only for convenience; inclusion of mass polarization terms is straightforward for the present approach and does not alter our conclusions.

Recently we reported on the existence of classically stable planetary configurations, where the electrons arrange themselves around a collinear mode (periodic orbit) with both electrons localized on the same side of the atom (Richter and Wintgen 1990). The periodic orbit represents a strongly asymmetric configuration, the ratio of the radial extents of the electrons being approximately 1 : 3. In addition, the outer electron is *dynamically* localized near some fixed radial distance. For this reason we label the orbits as *frozen planet configurations.* A semiclassical treatment of the classical motion suggests the existence of a Rydberg series of resonances converging to the three-particle breakup threshold (Richter and Wintgen 1990)

$$E_{nkl} = -\frac{S^2}{[n+\frac{1}{2}+2(k+\frac{1}{2})\gamma_1+(l+\frac{1}{2})\gamma_2]^2}. \tag{2}$$

$S = 1.4915$ is the (scaled) action of the periodic orbit for helium ($Z = 2$), and $\gamma_1 = 0.4616$, $\gamma_2 = 0.0677$ are the classical winding numbers. The Rydberg series is characterized by three quantum numbers n, k, l, which are to be interpreted as nodal excitations along the orbit (n) and along the two directions perpendicular to the orbit,the bending degree of freedom (k) and the motion perpendicular to the orbit preserving collinearity (l). In the lowest semiclassical approximation these states are bound, but they can autoionize by dynamical tunnelling (Davis and Heller 1981). The resonances appear as doublet states, each of which has an odd/even symmetry under electron exchange (Pauli principle). Dynamical tunnelling again lifts this doublet degeneracy. Both processes are suppressed exponentially with the nodal excitation n along the orbit similarly to 'static' tunnelling through potential barriers, i.e. the total decay widths and the doublet splitting energies decrease exponentially with n.

We emphasize that the frozen planet configurations (and the corresponding quantum mechanical solutions described below) represent highly correlated electron motion in the sense that *all* parts of the Hamiltonian (1) are essential and of equal importance. The minimal nuclear charge to bind an outer electron in this type of collinear configuration is $Z = 1+\varepsilon$ (otherwise the outer electron potential is purely repulsive), but in addition $1/Z$ *must* be non-zero, i.e. the repulsive electron–electron interaction is of crucial importance for the formation of these states. The helium atom (or presumably any other neutral atom) possesses an 'optimal' value of the nuclear charge for which the experimental verification of these states should be most straightforward. Note that the requirement of finite charge Z implies a failure of independent particle models to describe the states on the basis of $1/Z$ perturbation theory. A familiar example of such a model is the (K, T) classification scheme of Herrick (1983), in which (moderate) electron correlations are introduced via degenerate perturbation theory. In contrast, the configurations discussed here are of highly non-perturbative nature.

A detailed description of our method to solve the Schrödinger equation for the Hamiltonian (1) will be published elsewhere. Briefly, we rewrite equation (1) in *perimetric coordinates* (James and Coolidge 1937) defined by

$$x = r_1+r_2-r_{12} \qquad y = r_1-r_2+r_{12} \qquad z = -r_1+r_2+r_{12}. \tag{3}$$

In these coordinates the analytic structure of the Schrödinger equation becomes simple (Pekeris 1958), even though we have to deal with a non-separable system in three

dimensions (we focus on total angular momentum $L=0$ in this letter). We expand each degree of freedom (x, y, z) in a complete set of Sturmian functions and implement scaling techniques, which were already proven to be extremely powerful for other highly excited Coulombic systems (Wintgen and Friedrich 1987, Wintgen *et al* 1987). The calculation of the matrices requires mostly simple integer arithmetic. The resulting matrix equation is of banded, sparse structure and allows for efficient diagonalization. The complex rotation method (Reinhardt 1982, Ho 1983) is used to evaluate resonance positions and widths. The stationary energy eigenvalues are evaluated using optimized non-linear parameters in the Sturmian basis. This ensures that the calculated eigenfunctions always fulfill the virial theorem $\langle V\rangle = -2\langle T\rangle$ (Ho 1983). The calculations were done on a Micro VAX computer, where it was possible to include about 5530 basis states. Convergence of the (complex) eigenvalues was checked by systematically varying the basis size. More than one hundred resonances were calculated, the results of which will be published in a separate paper.

Table 1 summarizes the positions of the resonances ($n, k=0, l=0$) with n ranging from 2 to 10 together with the predictions of the simple semiclassical formula (2). The quantum results are converged to all digits quoted. Only the lowest two states of $^1S^e$ symmetry have been calculated so far, but with less accuracy (Ho 1986). The states listed in table 1 are by far the highest excited ones ever calculated for any three-body Coulomb complex.

Table 1. Energies E_{nkl} and total decay widths $\Gamma/2$ (atomic units) for planetary states with total angular momentum $L=0$ and nodal quantum numbers $k=l=0$. They are given for both even ($^1S^e$) and odd exchange parity ($^3S^e$). Numbers are truncated, not rounded. The predictions of the semiclassical formula (2) are also given (E_{scl}).

	$^1S^e$		$^3S^e$		
n	$-E$	$\Gamma/2$	$-E$	$\Gamma/2$	$-E_{scl}$
2	0.257 371 61	0.000 010 57	0.249 964 61	0.000 006 78	0.247 92
3	0.141 064 15	0.000 011 63	0.140 088 48	0.000 004 40	0.139 35
4	0.089 570 80	0.000 002 02	0.089 467 82	0.000 000 17	0.089 145
5	0.062 053 55	0.000 000 56	0.062 041 27	0.000 000 03	0.061 887
6	0.045 538 66	0.000 000 20	0.045 539 24	0.000 000 37	0.045 458
7	0.034 842 64	0.000 000 36	0.034 843 85	0.000 000 14	0.034 798
8	0.027 517 59	0.000 001 18	0.027 519 28	0.000 000 02	0.027 491
9	0.022 284 57	0.000 000 54	0.022 283 66	0.000 000 03	0.022 265
10	0.018 411 98	0.000 000 05	0.018 411 89	0.000 000 03	0.018 400

Considering the many approximations inherent in the semiclassical treatment leading to equation (2), the agreement with the exact quantum results is very good. The semiclassical error of the formula (2) for the effective quantum number $N_{eff} = S/\sqrt{-E}$ (the denominator in equation (2)) is proportional to $1/n$ and vanishes in the semiclassical limit $n\to\infty$ (Richter *et al* 1991a).

As predicted by the semiclassical theory, the energy splittings $\Delta E_\pm$ between the parity doublets listed in table 1 indeed decrease exponentially. The number of equal significant digits roughly increase by one for each additional node in n. More precisely we find $\ln|\Delta E_\pm| \approx 1.4n$. The widths of the resonances also decrease exponentially but they fluctuate rather largely around this general trend. The exponential stability of the

quantum states is remarkable considering the vastly increasing number of open channels into which the states can decay. The $(n, k, l) = (10, 0, 0)$ state, e.g., is coupled to 55 continuum channels. The extreme stability against particle decay is a direct consequence of the semiclassical nature of these states.

The semiclassical theory also accounts for the correct nodal structure of the associated wavefunctions. Figure 1(a) shows a plot of the conditional wavefunction probability corresponding to the collinear arrangement $r_{12} = r_1 - r_2$ for the state with quantum numbers $(n, k, l) = (6, 0, 0)$. Note that it is energetically allowed for one electron to escape to infinity ($r_1 \to \infty$ or $r_2 \to \infty$). The classical frozen planet periodic orbit is a nearly straight-line motion with $r_1 \approx 120$ and its location is indicated in the figure. Obviously the wavefunction is localized along this orbit. The wavefunction falls off exponentially across the orbit without any nodal excitation. This is also the case for the density perpendicular to the collinear symmetry plane, which is not shown in the figure. Such behaviour is consistent with the assignment of the quantum numbers $k = l = 0$. Figure 1(d) shows the same wavefunction, but the axes now have a quadratic scale instead of a linear one. This accounts for the usual wave propagation in Coulombic systems, where nodal distances increase quadratically. We can now easily count the number of nodal excitations along the orbit and indeed find $n = 6$. Thus the semiclassical picture not only accounts for the energy of the resonances, but also gives a good description of the wavefunction involved.

We strongly emphasize that the set of quantum numbers (n, k, l) used to classify our states should not be confused with independent particle (hydrogenic) quantum numbers (n_i, l_i, m_i). A rough estimate via expectation values for the $(10, 0, 0)$ state yields appreciable contributions of single particle configurations with $n_1 \approx 13$, $n_2 \approx 17$ and population of all single particle angular momenta l_i. In addition, because of the highly non-hydrogenic nature of the wavefunctions for the outer electron the states do not fit into existing classification schemes.

Not much energy is needed to excite the outer 'frozen' electron, as can be seen from the small value of the winding number γ_2. For the series of states with $n = 8$, $k = 0$ we find differences in the effective quantum numbers ΔN_{eff} of 0.062, 0.052 and 0.043 for the frozen-electron excited states $l = 0$ up to $l = 3$. Again, the agreement with the simple semiclassical prediction $0.068 = \gamma_2$ is more than fair. Figure 1(b) and (c) show the states with $n = 6$ (as in (a)), but with one and two additional nodes perpendicular to the frozen planet orbit, i.e. excitations of the outer electron. The structure of the wavefunctions coincides with the semiclassical expectation. Particularly, the figure demonstrates that the outer electron has a vibrational structure around its classical localization point instead of a hydrogenic-like wavefunction as for the inner electron. The wavefunctions do explore more of the region off the periodic orbit, which is the reason for the slight decrease of the differences in N_{eff} cited above. A proper semiclassical torus quantization would presumably account for such differences.

In this letter we presented highly accurate quantum mechanical calculations, but we would like to point out that comparable results (even quantitatively) can be obtained within a single channel adiabatic approximation for the outer electron (Richter *et al* 1991a). In such an approach the outer electron is trapped inside a potential well, while the wavefunction of the inner electron is described by a highly polarized molecular type wavefunction localized along the axis connecting the nucleus and the frozen electron. Within this approximation the quantum numbers n, k do correspond one-to-one to molecular type quantum numbers of the inner electron, while the quantum number l describes the degree of (harmonic) excitation of the outer electron in the

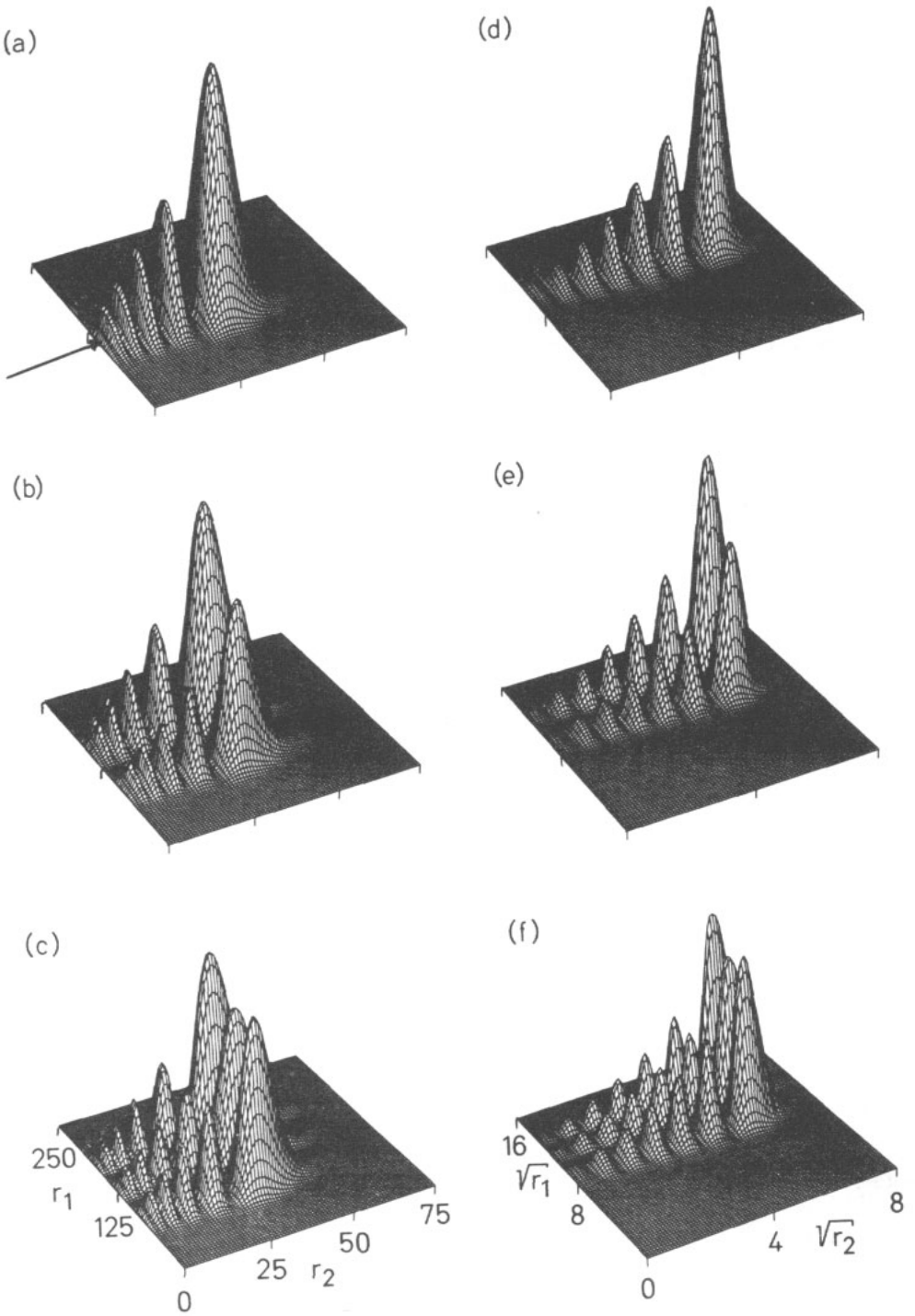

Figure 1. Conditional probability density of frozen-planet states $n=6$, $k=0$ and $l=0$ (a), $l=1$ (b), $l=2$ (c). In (a) the classical frozen-electron distance is indicated with an arrow. (d)-(f) show the same wavefunctions as in (a)-(c), but on a quadratic scale.

potential well. Such a simple model can be used to complement the qualitative semiclassical arguments (Richter and Wintgen 1990) about restrictions on the quantum numbers n, k, l. The adiabatic description has also been used to propose a mechanism for the production of long-lived anti-protonic states in atoms (Richter *et al* 1991b, Iwasaki *et al* 1991).

So far, the frozen planetary states have not been identified in experiments. Since they are nearly stable against autoionization it would be hard to detect them by the time reversed process, e.g. by dielectronic recombination in merged electron–ion beams (Kilgus *et al* 1990). In addition, because of the vast density of resonant states in the energy region close to the double ionization threshold a very high experimental resolution is necessary. The cross section for single photon absorption from the ground state (Domcke *et al* 1991) also vanishes because of the exponential localization of the outer electron at large radial distances. Stepwise laser excitations such as those reported by Camus, Gallagher T F, Lecomte J M, Pillet P, Pruvost L and Boulmer J (1989) and Eichmann *et al* (1990) are presumably the best way to populate these states. However, in such an experiment a proper polarization of the photons is of crucial importance. The dipole operator for circular polarized photons is proportional to the perimetric coordinate y and suppresses all structures in the $y=0$ plane, where the states are localized. The same linear polarization for all photons, however, amplifies the structures in this plane.

In summary, we showed within large scale *ab initio* calculations the existence of highly correlated electron states in helium, which form the quantum analogue of the classical frozen planet configurations discovered recently. The resonances are extremely stable, their lifetimes against autoionization increase exponentially with the degree of excitation. A simple semiclassical model based on quantizing the neighbourhood of the frozen-planet periodic orbit gives a proper description of the energies and wavefunctions involved and leads to new insight for the formation process of highly correlated states. Recent classical (and semiclassical) studies for three-body Coulomb systems already proved to be very successful in enlightening the (so-far often misinterpreted) role of electron-pair motion along the Wannier ridge (Ezra *et al* 1991). The present results again confirm that the structure of the three-body resonant states does reflect the underlying classical mechanics in the same way as has now been demonstrated in great detail, e.g., in the case of the complex spectra of a hydrogen atom in a magnetic field (Friedrich and Wintgen 1989).

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