Calculation of Langmuir States in Doubly Excited Helium

Jörg Müller[1] and Joachim Burgdörfer[1],[2]
[1]*Department of Physics, University of Tennessee, Knoxville, Tennessee 37996-1200*
[2]*Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6377*
(Received 20 November 1992)

We have identified a class of high-lying doubly excited resonances in helium which are directly linked to a classical orbit first proposed by Langmuir for the quantization of helium. The projection of the wave function onto three mutually orthogonal planes is shown to trace the Langmuir orbit. This class of resonances forms the top of the intrashell manifold, and are long-lived compared to other members of the same manifold. In the limit $Z \to \infty$, the wave function traces the modified, asymmetric Langmuir orbit generated by bifurcation of the Langmuir orbit.

PACS numbers: 31.50.+w, 03.65.Sq, 31.20.Tz

The internal structure of resonances in the isoelectronic sequence of helium have become the paradigm for our understanding of the three-body Coulomb problem, one of the most fundamental "simple," and yet nonseparable few-body problems. Since the experimental identification of low-lying doubly excited states in helium [1], it was recognized [2] that their existence hinges on a highly correlated motion of the two electrons maintaining a delicate balance of repulsive and attractive fields. The strength of electron-electron correlation prevents a description in terms of a perturbation theory for weakly perturbed independent particle states. Considerable progress has been achieved since in the experimental identification [3], classification [4,5], and calculation [6,7] of low-lying doubly excited states.

The interpretation and analysis of the internal structure of doubly excited states have frequently involved classical pictures for the strongly correlated ("collective") motion. A quantitative test of their validity was, however, difficult since the de Broglie wavelength of the electronic motion is for low-lying states comparable to the size of the orbit, $\langle r \rangle$, thereby preventing an unambiguous classical-quantum correspondence. This situation has dramatically changed with the recent advent of multiphoton laser excitation experiments [8], where high-lying doubly excited states with both electrons at large principal quantum numbers N,n of 10 and higher can be accessed. Here we use the notation N (n) for smaller (larger) of the two principal quantum numbers. In this regime where $\langle r \rangle \gtrsim 100Z^{-1}$, the quantum wave function begins to mimic the underlying classical dynamics. Classical models for correlated electron motion can be directly tested against properties of quantum states.

The structure of the classical phase space, in particular, the properties of periodic orbits [9,10] and their semiclassical (i.e., Bohr-Sommerfeld) quantization played an important role in the "old quantum theory" of helium [11]. Several orbits had been suggested in the early 1920s, one of which is due to Langmuir [12] and which corresponds to a planar configuration with two electrons performing bending vibrations as a possible classical realization of a two-electron orbit with total quantum number $L=0$ [Fig. 1(a)]. This periodic Langmuir orbit (LO) represents a collective, completely correlated motion of two equivalent electrons with $|r_1| = |r_2|$, distinctly different from any independent particle motion on (distorted) Kepler orbits.

Only recently Richter and Wintgen [13] discovered that the phase space near the LO is stable. For the stable island around the LO a rigorous torus (Einstein-Brillouin-Keller, EBK) quantization can be carried out [14]. It results in a double Rydberg series with energies

$$E(N) = S_L^2/(N-\mu_L)^2, \tag{1}$$

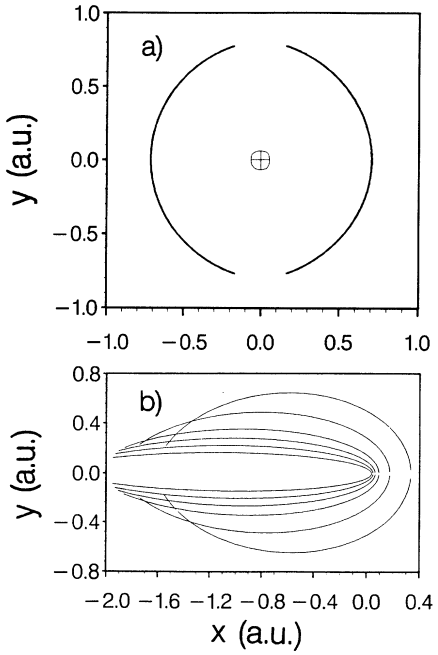

FIG. 1. (a) Langmuir orbit at $Z=2$; (b) asymmetric Langmuir orbit after the bifurcation at $Z=5.60$ for $Z=10$, 20, 50, 100, 200, and 500. The energy for each trajectory is $-Z$ in a.u., so the length scales become comparable.

© 1993 The American Physical Society

where S_L is the classical action along the Langmuir orbit at the energy $E=-1$ a.u. and μ_L is a quantum defect which depends on classical winding numbers. For helium, i.e., $Z=2$ we find $S_L \approx 1.35$ and $\mu_L \approx 0.27$ [14]. These "Langmuir states," which reside on tori, are classically stable; i.e., they decay only via tunneling or radiative processes. This implies the existence of a double Rydberg series of narrow resonances extremely close to the double ionization threshold.

The semiclassical quantization permits the identification of quantum numbers of the 3-torus: Langmuir states represent a realization of the maximum bending vibration $K=-(N-1)$ in the $(NnKT)^A$ classification scheme for doubly excited states [4], with $N=n$, $A=+$, and $T=0$ (for ^1S states). They describe two electrons "atop each other" [15]. The latter follows from the fact that the electrons spend most of their time near the turning point [Fig. 1(a)]. Langmuir states are the highest-lying state within an intrashell manifold. Semiclassical EBK quantization is, however, rigorously valid only when the classically stable island has a phase space volume of $\hbar$ necessary for accommodating at least one quantum state. This requirement is only satisfied for principal quantum numbers $N>500$, currently out of reach for experiments as well as quantum calculations.

The identification of the top edge of the intrashell manifold with Langmuir states in the semiclassical limit $N\rightarrow\infty$ suggests that corresponding quantum states at intermediate N should bear the signatures of the LO. In the following, we present a first evidence that full quantum mechanical wave functions for higher-lying states begin, indeed, to trace the Langmuir orbit, thereby confirming the original conjecture by Langmuir of some 70 years ago.

Our *ab initio* calculation employs standard stabilization-complex rotation techniques [7,16–18]. Briefly, we expand the ^1S wave function in terms of coupled Sturmian functions, $S_n^l(x)$, as

$$\psi_i(r_1,r_2,\theta;\sigma)=\sum_{(n,n_2,l)}^{M} e^{-\sigma(r_1+r_2)}(r_1r_2)^{-1}S_{n_1}^{l_1}(\sigma r_1) \times S_{n_2}^{l_2}(\sigma r_2)P_l(\cos\theta)\,. \quad (2)$$

The complex Hamiltonian for the three-body Coulomb problem

$$H(\beta)=\frac{1}{2}(\nabla_1^2+\nabla_2^2)e^{-2i\beta}+e^{-i\beta}\left(-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{1}{r_{12}}\right) \quad (3)$$

is diagonalized in the basis (2); the angle of complex rotation is denoted by β. In (3) we treat the nuclear mass to be infinite thereby neglecting mass polarization effects. Approximate complex eigenvalues are obtained from the conditions $dE/d\sigma\approx 0$, $dE/d\beta\approx 0$, and $dE/M\approx 0$ where M is the dimension of the basis (up to 2000). We include configurations with $1\le n_{1,2}\le 19$, $0\le l_{1,2}\le 18$. In addition, we also consider asymmetric configurations with $20\le n_{1,2}\le 25$, $n_{2,1}\le 12$, $l_{1,2}\le 11$. As usual, the real part of E describes the position while the negative imaginary part describes the half-width of the resonance. The expansion in terms of single-particle orbitals rather than Hylleraas-type basis has the drawback that a larger basis size is required for representing wave functions with significant density at small interelectronic distances $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$. Because of the Coulomb repulsion, the weight of this regime is, however, small for highly excited states. Even for the Langmuir orbit, where the two electrons suffer a head-on collision [Fig. 1(a)], the distance of closest approach at, for example, an energy corresponding to $N\simeq 10$ is $r_{12}\simeq 50$ a.u. On the other hand, the expansion (2) has the advantage to converge rapidly in the limit $Z\rightarrow\infty$ to be discussed below. Moreover, it permits the straightforward decomposition into single-particle angular momentum components l of the wave function. The latter feature has proven to be extremely helpful in identification of resonances in the region of overlapping manifolds. For moderately excited resonances our results can be checked against the pioneering calculations by Ho [7], and more recent calculations of Richter and Wintgen for "planetary states" [19] representing asymmetric excitations with $\langle r_1\rangle\approx\langle r_2\rangle/3$. We typically find agreement to three significant digits with Ref. [7] results and to six digits with Ref. [19] for the positions of the resonances. Larger deviations occur for the width.

The key point in the search for Langmuir states is the extrapolation of the semiclassical WKB-type energy formula [Eq. (1)] as a first step in identifying possible "candidates" for intrashell resonances in the regime of overlapping manifolds. In the second step, we determine the single-particle l distribution which is distinctly different for different classes of resonances. LO states $K=-(N-1)$ are characterized by a large weight at high angular momenta ($l\approx N$), which contrasts with the angular momentum distribution for $K=N-1$ states, where the high l components are exponentially suppressed [15]. Finally, we project the density of the wave function $P(R,\alpha,\theta)=|\phi(R,\alpha,\theta)|^2$ where $\theta=\cos^{-1}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)$, $R=(r_1^2+r_2^2)^{1/2}$, $\alpha=\tan^{-1}(r_2/r_1)$ are hyperspherical coordinates, onto the three mutually orthogonal planes (α,θ), (R,θ), and (r_1,r_2) by integrating over R, α, and θ, respectively.

The projections of the density of the $N=n=10$, $K=-9$ state (Fig. 2) traces, indeed, the LO in remarkable detail. The density is strongly enhanced near the classical turning point ($\theta=24°$). Furthermore, the distortion of the semicircular orbit due to the interelectronic Coulomb repulsion, which leads to a slight increase of the hyperradius R near the turning point, is accurately reproduced by the quantal density distribution (see the R-θ plane). Another feature in the α-θ plane is worth noting: While the dominant part of the probability density, which is located at $\theta<90°$, is peaked at $\alpha=45°$, it spreads out over $\alpha=45°\pm\delta$ for $\theta>90°$, where $\delta\approx 15°$ for $N=10$.

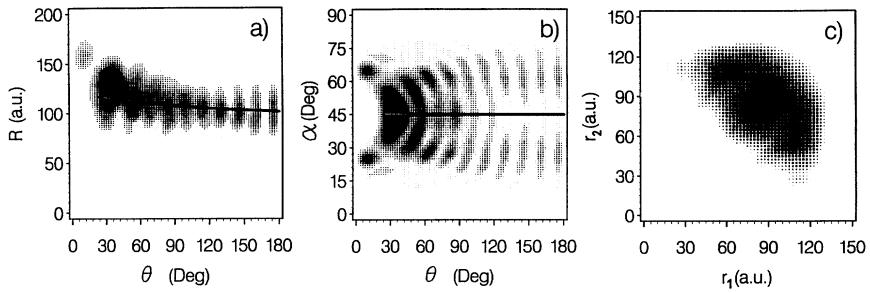

FIG. 2. Langmuir state ($^1S^e$) $N=n=10$, $K=-9$ for helium ($Z=2$) projected onto (a) R-θ, (b) α-θ, and (c) r_1-r_2 planes. The solid line shows the projection of the Langmuir orbit.

With increasing N, δ decreases and in the semiclassical limit $\lim_{N\to\infty}\delta=0$. This behavior reflects the semiclassical dynamics near the saddle in the effective potential in the α direction and will be discussed elsewhere [14].

The present findings that for sufficiently large N Langmuir states form the top of the intrashell manifold can be easily reconciled with the recent observation that "planetary" states, i.e., states where the outer electron is bound in a well formed by Coulomb attraction at large distances and a repulsive dipole barrier at small distances form the top of the manifold for lower N states. The key point is that the semiclassical energy for planetary states [19]

$$E_{\text{planetary}}(N)=-2.22/(N+0.01)^2, \tag{4}$$

where $N-1$ equals the number of nodes along the so-called "planetary orbit," becomes almost degenerate with the WKB energies of the Langmuir orbit [Eq. (1)] for $N=3$-5. For low N, the $K=-(N-1)$ wave function represents a mixture of a planetary component with density near $\langle r_1\rangle\simeq\langle r_2\rangle/3$ and $\alpha\approx 20°$ and a Langmuir component with density at $\langle r_1\rangle\simeq\langle r_2\rangle$ and $\alpha\approx 45°$. Only as N becomes large the quasidegeneracy is lifted and "pure" Langmuir and planetary states start to develop. Planetary states lie energetically below Langmuir states and are not intrashell states in the sense of symmetric excitation, $\langle r_1\rangle\simeq\langle r_2\rangle$.

For the width of the Langmuir resonances we find an approximate scaling rule

$$\Gamma(N)\approx 2.0N^{-4}\ \text{a.u.} \tag{5}$$

The estimate (5) is derived from an interpolation between the width calculated by complex rotation for $N=7$-11 and the classical lifetime of phase space distributions representing a quantum state near the Langmuir orbit for energies corresponding to $N>100$. The uncertainty of (5) is considerably larger than the extrapolation of the EBK estimates for position of resonances [Eq. (1)], which reproduces the full quantum results remarkably well. Note that for $N\gtrsim 500$, semiclassically $\Gamma=0$ as a quantum state fits inside the stable island. The width due to tunneling for $N>500$ will decay exponentially as a function of N rather than with a power law [Eq. (5)]. Another possible decay channel would be radiative deexcitation. However, since both electrons are far from the nucleus (i.e., $\langle p\rangle$ small), radiative decay rates are presumably exceedingly small.

For small Z, Langmuir resonances are embedded in overlapping intershell as well as intrashell manifolds, thereby making their identification very difficult. In the limit $Z\to\infty$, on the other hand, different manifolds remain well separated and the group-theoretical O(4) DESB states [4] provide an approximate representation of intrashell states. We have investigated the shape of the wave functions at the top of the manifold for large N using both the basis expansion [Eq. (2)] and the DESB. The density distribution (Fig. 3) *does not* resemble the Langmuir orbit [Fig. 1(a)] but the modified, asymmetric Langmuir orbit [Fig. 1(b)]. The latter is a direct signature of the bifurcation of the classical phase space structure. At $Z=5.60$ the Langmuir orbit bifurcates into the asymmetric Langmuir orbit where the electrons follow to semielliptic trajectories. In the limit $Z\to\infty$, this asymmetric Langmuir orbit degenerates to a "symmetric stretch" mode, however, with both electrons on the *same side* of the nucleus. Accordingly, the wave function is

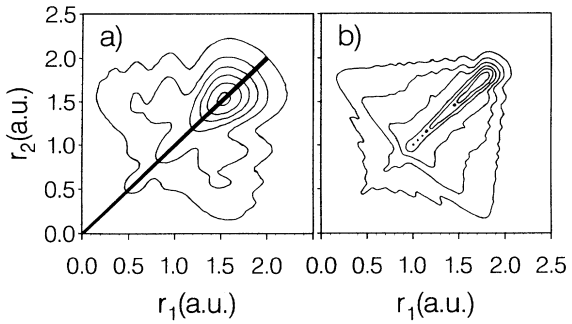

FIG. 3. Projection of the probability density of the $K=-(N-1)$ states in the limit $Z\to\infty$ in the r_1-r_2 plane. (a) $N=7$ using basis expansion [Eq. (2)]. (b) $N=28$ (DESB state). In (a) we also show the projection of the asymmetric Langmuir orbit in the limit $Z\to\infty$. (The low density close to the nucleus is due to the high velocity of the electrons in this region.)

aligned along the direction of the hyperradius R with fixed $\alpha=45°$ or $\theta=0°$, in complete accord with predictions of classical dynamics. This motion could also properly be described as "riding on the Wannier ridge," since the motion perpendicular to the ridge (along the α direction) is reduced to zero-point fluctuations. With increasing N and shorter wavelength, the condensation along the Wannier ridge becomes more pronounced (Fig. 3).

In summary, we have investigated high-lying resonances at the top of the intrashell manifold $[K=-(N-1)]$ in both helium ($Z=2$) as well the limit of nonoverlapping manifolds ($Z\rightarrow\infty$). We find wave functions for helium closely resembling Langmuir's model for correlated two-electron motion while in the limit $Z\rightarrow\infty$ the wave function traces a modified asymmetric Langmuir orbit originating from a bifurcation of the Langmuir orbit with increasing $Z\rightarrow\infty$. We also find that for lower $N(<6)$, the $K=-(N-1)$ states lose the signature of a single classical orbit but appear to reflect a mixture of a planetary and a Langmuir orbit. The latter is expected in view of the near degeneracy of the energy as predicted by a WKB-type quantization and in view of the increase of the de Broglie wavelength which tends to destroy a direct classical-quantum correspondence.

One of us (J.M.) acknowledges discussions with K. Richter and D. Wintgen and is grateful to R. J. Jelitto for his encouragement. This work was supported in part by the National Science Foundation and by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract No. DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc.

[1] R. P. Madden and K. Codling, Phys. Rev. Lett. **10**, 516 (1963).

[2] J. W. Cooper, U. Fano, and F. Prats, Phys. Rev. Lett. **10**, 518 (1963).

[3] P. G. Harris *et al.*, Phys. Rev. Lett. **65**, 309 (1990); M. Domke *et al.*, Phys. Rev. Lett. **66**, 1306 (1991).

[4] C. E. Wulfman, in *Group Theory and Its Application*, edited by M. Loebl (Academic, New York, 1971); D. R. Herrick *et al.*, Phys. Rev. A **11**, 97 (1975); K. Molmer and K. Taulbjerg, J. Phys. B **21**, 1739 (1988).

[5] C. D. Lin, Phys. Rev. A **29**, 1019 (1984); Adv. At. Mol. Phys. **22**, 77 (1986).

[6] J. H. Macek, J. Phys. B **1**, 831 (1968); A. Bhatia and A. Temkin, Phys. Rev. A **11**, 2018 (1975); N. Koyama, H. Fukuda, T. Motoyama, and M. Matsuzawa, J. Phys. B **19**, L331 (1986); J. M. Rost, J. S. Briggs, and J. M. Feagin, Phys. Rev. Lett. **66**, 1642 (1991); H. R. Sadeghpour, C. H. Greene, and M. Cavagnero, Phys. Rev. A **45**, 1587 (1992).

[7] Y. K. Ho, Phys. Rev. A **34**, 4402 (1986); J. Phys. B **23**, L71 (1990).

[8] W. E. Cooke and T. F. Gallagher, Phys. Rev. Lett. **41**, 1648 (1978); P. Camus, T. F. Gallagher, J. M. Lecomte, P. Pillet, and J. L. Provost, Phys. Rev. Lett. **62**, 2365 (1989); U. Eichmann, V. Lange, and W. Sandner, Phys. Rev. Lett. **68**, 21 (1992).

[9] M. C. Gutzwiller, *Chaos in Classical and Quantum Mechanics* (Springer, New York, 1990); G. E. Wesenberg, D. W. Noid, and J. B. Delos, Chem. Phys. Lett. **118**, 369 (1985).

[10] G. Ezra, K. Richter, G. Tanner, and D. Wintgen, J. Phys. B **24**, L413 (1991).

[11] J. L. Van Vleck, Philos. Mag. **44**, 842 (1922).

[12] I. Langmuir, Phys. Rev. **17**, 339 (1921).

[13] K. Richter and D. Wintgen, J. Phys. B **23**, 1197 (1990).

[14] J. Müller, J. Burgdörfer, and D. W. Noid, Phys. Rev. A **45**, 1471 (1992); J. Müller and J. Burgdörfer (unpublished).

[15] A. R. P. Rau, Rep. Prog. Phys. **53**, 181 (1990).

[16] E. Holoien and J. Midtdal, J. Chem. Phys. **45**, 2209 (1966).

[17] H. S. Taylor, Adv. Chem. Phys. **18**, 91 (1970).

[18] Y. K. Ho, Phys. Rep. **99**, 1 (1983); W. P. Reinhardt, Annu. Rev. Phys. Chem. **33**, 223 (1982); B. R. Junker, Adv. At. Mol. Phys. **18**, 208 (1982).

[19] K. Richter and D. Wintgen, J. Phys. B **24**, L565 (1991).