Editors' Suggestion

Defect in the Joint Spectrum of Hydrogen due to Monodromy

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In addition to the well-known case of spherical coordinates, the Schrödinger equation of the hydrogen atom separates in three further coordinate systems. Separating in a particular coordinate system defines a system of three commuting operators. We show that the joint spectrum of the Hamilton operator, the z component of the angular momentum, and an operator involving the z component of the quantum Laplace-Runge-Lenz vector obtained from separation in prolate spheroidal coordinates has quantum monodromy for energies sufficiently close to the ionization threshold. The precise value of the energy above which monodromy is observed depends on the distance of the focus points of the spheroidal coordinates. The presence of monodromy means that one cannot globally assign quantum numbers to the joint spectrum. Whereas the principal quantum number n and the magnetic quantum number m correspond to the Bohr-Sommerfeld quantization of globally defined classical actions a third quantum number cannot be globally defined because the third action is globally multivalued.

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What could possibly be said about the hydrogen atom that is new? The hydrogen atom is conceivably the best studied system in quantum mechanics, alongside its classical counterpart the Kepler problem in classical mechanics. These systems are of paramount importance for our fundamental understanding of atomic physics and astronomy, respectively. Using their separability in spherical coordinates these systems are solved in any introductory physics course. Separable systems are special examples of integrable systems. A *quantum integrable system* (QIS) is a collection of f independent commuting operators $\mathcal{H} = (\hat{H}_1, \ldots, \hat{H}_f)$, where say $\hat{H}_1$ is the Hamilton operator. In addition, we require that the classical limits $(H_1, \ldots, H_f)$ of these operators have pairwise vanishing Poisson brackets, and thus constitute a Liouville integrable system with each H_i a constant of motion (or integral for short). Geometrically this means that $(H_1, \ldots, H_f)$ defines the *energy momentum map*, from the $2f$-dimensional classical phase space to $\mathbb{R}^f$ and that the pre-image of a regular value of this map is a union of f-dimensional tori (if compact) in the neighbourhood of which one can construct action angle variables following the Liouville-Arnold theorem [1]. The semiclassical Bohr-Sommerfeld quantization of actions shows that the joint spectrum $(\lambda_1, \ldots, \lambda_f) \in \mathbb{R}^f$, where $\hat{H}_i\psi = \lambda_i\psi$ for $i = 1, \ldots, f$ with joint eigenstate ψ locally has the structure of a lattice $\mathbb{Z}^f$ and can hence be locally labeled by quantum numbers.

Because of defects this local lattice may not be extendable to a global lattice and hence a global assignment of quantum numbers to quantum states may be impossible [2–4]. This is the quantum mechanical manifestation of an obstruction to the global construction of action angle variables referred to as Hamiltonian monodromy and first introduced by Duistermaat [5] and then studied quantum mechanically jointly with Cushman [6]. Now many examples of systems displaying (quantum) monodromy are known, see, e.g., Ref. [7] and the references therein, and generalizations have been discovered [8,9]. Quantum monodromy explains, e.g., problems in assigning rovibrational spectra of molecules [10–12] or electronic spectra of atoms in external fields [13,14] (also see Refs. [15,16]) and it provides a mechanism for excited-state quantum phase transitions [17,18]. The generalization of monodromy to scattering systems leads to similar defects in the lattice of transparent states in planar central scattering [19]. It has been shown that monodromy can also play a role in spatiotemporal nonlinear wave systems [20]. Dynamical manifestations of monodromy have recently been studied in Ref. [21].

Both the Schrödinger equation for the hydrogen atom and the Kepler problem have the property that they can be separated in four coordinate systems [22]: spherical [23], parabolic [23], prolate spheroidal [24–26] (which contains the first two as singular limiting cases [27]) and spheroconical coordinates [28]. Whereas there is, in principle, complete freedom in the choice of the coordinates for the computation of the spectrum of hydrogen the measurement of the spectrum can single out one particular choice by the experimental setup. For example, parabolic coordinates also separate the Schrödinger equation of the hydrogen atom in the presence of an external electric field, the so-called Stark problem, and prolate ellipsoidal coordinates allow for separation also in the presence of an additional

charge. Likewise, the wave functions resulting from the most familiar choice of spherical coordinates give the atomic orbitals. Neglecting the electron-electron interactions these form the basis of the atomic orbital model and the rules on how the corresponding states are filled for multielectronic atoms explain the periodic table.

Technically speaking, each separating coordinate system for the hydrogen atom gives a set of different separation constants which in turn define different sets of three commuting operators. In the case of spherical coordinates this gives the very well known QIS $\mathcal{H} = (\hat{H}, \hat{\mathbf{L}}^2, \hat{L}_z)$, which has the joint spectrum $(-1/(2n^2), \ell(\ell+1), m)$ with quantum numbers $n = 1, 2, 3, \ldots$, $l = 0, 1, 2, \ldots, n-1$ and $m = -l, -l+1, \ldots, l$. Here $\hat{L}_z$ is the z component of the angular momentum operator $\hat{\mathbf{L}}$ and, as in the rest of this Letter, we use atomic units. In the case of separation in prolate spheroidal coordinates a different QIS is obtained as $\mathcal{G} = (\hat{H}, \hat{G}, \hat{L}_z)$ with $\hat{G} = \hat{\mathbf{L}}^2 + 2a\hat{e}_z$, where $\hat{e}_z$ is the z component of the quantum Laplace-Runge-Lenz or eccentricity vector and the positive parameter a is half the distance between the focus points of the prolate spheroidal coordinates, see, e.g., Ref. [29].

In this Letter we show that the spectrum of joint eigenvalues (E, g, l_z) of $\mathcal{G}$ has quantum monodromy in the limit of sufficiently large principal quantum number n. The joint spectrum of $\mathcal{G}$ for a large but fixed principal quantum number n is shown in Fig. 1. Locally the spectrum has a lattice structure. Globally, however, it has a defect as can be seen from moving a fundamental lattice cell about the isolated singular value of the energy momentum map marked by the red dot in Fig. 1. As a consequence, globally defined quantum numbers cannot exist. Even though separability of the hydrogen atom in prolate spheroidal coordinates has been known for a long time, this is the first time that quantum monodromy in the hydrogen atom is described. Our work serves as a reminder that the physical reality of the orbitals of hydrogen is not invariantly defined, but depends on the choice of a quantum integrable system via the choice of a separating coordinate systems, and shows that the choice can entail the impossibility to globally label the spectrum by quantum numbers.

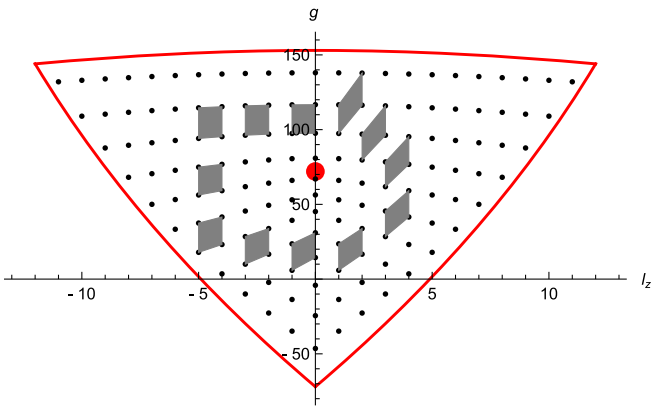

FIG. 1. Quantum lattice formed by the joint spectrum (black dots) for the commuting operators ($\hat{L}_z$, $\hat{G}$) for fixed principal quantum number $n = 12$ and $a = 144/5$, illustrating the monodromy of a fundamental cell transported around the isolated critical value of the classical energy momentum map (red dot).

Super-integrable systems.—Before we discuss the details of the hydrogen atom we want to elucidate the general structure underlying our analysis. Given a Hamiltonian operator $\hat{H}$ it is exceptional to be able to find a QIS $\mathcal{H}$ that contains $\hat{H}$—most Hamiltonians are nonintegrable. It is even more exceptional to be able to find nontrivially distinct QIS $\mathcal{H}$ and $\mathcal{G}$ that both contain the same $\hat{H}$. This implies, but is not equivalent to, that the system is superintegrable, see, e.g., the review [30]. Important examples are systems that are separable in different coordinate systems. Schwarzschild [31] was the first to point out that if the Hamilton-Jacobi equation of H can be separated in more than one coordinate system, the quantum energy eigenvalues of $\hat{H}$ are degenerate. Such a Hamiltonian operator $\hat{H}$ is called multiseparable, and is, hence, included in nonequivalent QIS $\mathcal{H}$ and $\mathcal{G}$. The simplest multiseparable systems are the free particle, the harmonic oscillator, and the Kepler problem. A multiseparable system is superintegrable, because if both $\mathcal{H}$ and $\mathcal{G}$ contain $\hat{H}$, then we have found more than $f-1$ operators that commute with $\hat{H}$. An important class of 3-dimensional superintegrable and multiseparable systems is classified in [32].

The classical geometry of superintegrable systems is well understood. Fixing the integrals defines tori of lower dimension than in the Liouville-Arnold theorem and Nekhoroshev showed that one can construct lower dimensional action angle coordinates in a generalization of the Liouville-Arnold theorem [33]. More global aspects have been studied in Refs. [34,35]. From the classical geometric point of view considering tori with half the dimension of phase space in a superintegrable system appears somewhat arbitrary. However, from the quantum point of view it is prudent to study all possible sets of commuting observables, because these tell us what can be measured simultaneously as the uncertainty principle is trivial in this case. Thus we are going to study a particular set of collections of Kepler ellipses that form 3-tori in phase space, and we will show that the joint quantum spectrum associated to these tori has quantum monodromy.

The Kepler problem and the hydrogen atom.—To fix our notation let $\mathbf{r} = (x, y, z)^t$ be the position of the electron in $\mathbb{R}^3$ and $\mathbf{p} = (p_x, p_y, p_z)$ its momentum. The nucleus is at the origin. The Hamiltonian is $H = \frac{1}{2}|\mathbf{p}|^2 - 1/r$, where $r = |\mathbf{r}|$, the angular momentum is $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, and the Laplace-Runge-Lenz vector is $\mathbf{e} = \mathbf{p} \times \mathbf{L} - \mathbf{r}/r$. The components of $\mathbf{L}$ and $\mathbf{e}$ all have vanishing Poisson brackets with H, but are not all independent because of the relations $\mathbf{L} \cdot \mathbf{e} = 0$ and $|\mathbf{e}|^2 = 1 + 2H|\mathbf{L}|^2$. Hence, there are five

independent integrals and the system is maximally superintegrable; i.e., fixing the five integrals on the six-dimensional phase space of the Kepler problem for negative energies defines one-dimensional tori. These one-dimensional tori simply are the periodic orbits given by the Kepler ellipses. Introducing $\mathbf{K} = n\mathbf{e}$, where $H = -1/(2n^2)$ (assuming $H < 0$) the components of $\mathbf{L}$ and $\mathbf{K}$ satisfy the commutator relations of the algebra so(4) with Casimir functions $\mathbf{L} \cdot \mathbf{K} = 0$ and $\mathbf{L}^2 + \mathbf{K}^2 = n^2$. In the quantum version similarly operators $\hat{H}$, $\hat{\mathbf{L}}$ and $\hat{\mathbf{K}}$ are defined and satisfy the same commutation relations of the so(4) algebra. We note that the SO(4) symmetry was already used by Pauli in his 1926 paper [36] to determine the spectrum of hydrogen.

Separation in prolate spheroidal coordinates and monodromy.—Prolate spheroidal coordinates (ξ, η, ϕ) with focus points at $\pm\mathbf{a} = (0, 0, \pm a)$ on the z axis are defined by $\xi = (r_1 + r_2)/(2a)$, $\eta = (r_1 - r_2)/(2a)$, where $r_1 = |\mathbf{r} - \mathbf{a}|$ and $r_2 = |\mathbf{r} + \mathbf{a}|$ and ϕ is the angle about the z axis. The surfaces of constant ξ and η are prolate ellipsoids and two-sheeted hyperboloids, respectively, with focus points $\pm\mathbf{a}$. For $a \to 0$, spherical coordinates are recovered, while for $a \to \infty$, parabolic coordinates are found. Assuming the hydrogen nucleus to be located at the focus point $\mathbf{a}$, the separation of the Schrödinger equation $(-\frac{1}{2}\nabla^2 - 1/r_1)\psi = E\psi$ with the ansatz $\psi(\mathbf{r}) = \psi_\xi(\xi)\psi_\eta(\eta)\psi_\phi(\phi)$ leads to three separated equations. The equation for ϕ gives the angular momentum eigenvalues $l_z = m = 0, \pm 1, \pm 2, \ldots$, and the equations for ξ and η give the same equation

$$-\frac{d}{ds}(s^2 - 1)\frac{d}{ds}\psi_s(s) = \frac{P(s)}{s^2 - 1}\psi_s(s), \tag{1}$$

where $P(s)$ is the polynomial

$$P(s) = (2a^2E(s^2 - 1) + 2as - g)(s^2 - 1) - l_z^2. \tag{2}$$

For $s = \xi$, Eq. (1) is considered on the interval $[1, \infty)$ and for $s = \eta$, Eq. (1) is considered on $[-1, 1]$. The separation constant g is the eigenvalue of the operator

$$\hat{G} = \hat{\mathbf{L}}^2 + 2a\hat{e}_z, \tag{3}$$

where $\hat{e}_z$ is the z component of the quantum Laplace-Runge-Lenz vector which in position representation reads

$$\hat{e} = \frac{1}{2}(\hat{\mathbf{p}} \times \hat{\mathbf{L}} - \hat{\mathbf{L}} \times \hat{\mathbf{p}}) - \frac{1}{r_1}(\mathbf{r} - \mathbf{a}). \tag{4}$$

In Eqs. (3) and (4) $\hat{\mathbf{p}} = -i\nabla$ and $\hat{\mathbf{L}} = -i(\mathbf{r} - \mathbf{a}) \times \nabla$ are the standard momentum and angular momentum operators defined relative to the point $\mathbf{a}$. The operators $\hat{H}$, $\hat{L}_z$, and $\hat{G}$ mutually commute; i.e., $\mathcal{G} = (\hat{H}, \hat{G}, \hat{L}_z)$ defines a QIS.

The joint spectrum and the corresponding eigenfunctions or orbitals of $(\hat{H}, \hat{G}, \hat{L}_z)$ can be computed in a variety of ways. We use an algebraic approach that goes back to Coulson and Robinson [37]. As explained in the Supplemental Material [38] each spheroidal eigenfunction is a finite linear combination of spherical harmonics. Figure 4 shows the 49 degenerate eigenfunctions with principal quantum number $n = 7$, arranged by the position of the eigenvalues in the joint spectrum. Eigenfunctions with large g are similar to the standard eigenfunctions from separation in spherical coordinates, while those with small g are similar to eigenfunctions obtained from separation in parabolic coordinates. The eigenfunctions near the isolated singular point of the energy momentum map are roughly interpolating between these two limiting behaviors. The red curves in Fig. 3 show the classical caustics, i.e., the boundaries of the configuration space projections of the invariant tori in phase space that have constants of motion corresponding to the quantum mechanical eigenvalues. This presentation illustrates how the eigenstates are localized on the classical tori.

A standard WKB ansatz shows that the joint spectrum can be computed semiclassically from a Bohr-Sommerfeld quantization of the actions according to $I_\phi = (1/2\pi)\oint p_\phi \mathrm{d}\phi = l_z = m$, $I_\eta = (1/2\pi)\oint p_\eta \mathrm{d}\eta = n_\eta + \frac{1}{2}$ and $I_\xi = (1/2\pi)\oint p_\xi \mathrm{d}\xi = n_\xi + \frac{1}{2}$ with $m \in \mathbb{Z}$ and non-negative quantum numbers n_η and n_ξ. Here the momenta p_η and p_ξ are given by $p_s^2 = P(s)/(s^2 - 1)$, where $P(s)$ is again the polynomial in Eq. (2) which implies that the actions I_η and I_ξ are given by elliptic integrals. It turns out that I_η and I_ξ are not smooth functions of the eigenvalues (E, g, l_z)—from a study of the elliptic integrals in the complex plane it can be shown that they have a discontinuous derivative at $l_z = 0$ (this can be seen as a special case of the computation in Ref. [39]). This indicates that the lattice of eigenvalues formed by the joint spectrum might have a defect. Using the calculus of residues one finds that the sum of the actions $I_\eta + I_\xi + |I_\phi|$ is equal to $1/\sqrt{-2E}$ and, hence, is in particular smooth for energies $E < 0$. In fact the quantization of the sum can be identified with the principal quantum number n from which we then obtain $E = -1/(2n^2)$. The magnetic quantum number m and the principal quantum number n are the only good quantum numbers—no third quantum number can be globally defined for the QIS $\mathcal{G}$. This is what we see in Fig. 1 which shows a layer of the lattice of the joint spectrum of constant principal quantum number n. The defect is caused by a singular value of codimension two of the classical energy momentum map which is located on the g axis at $g = 2a$.

For (E, g, l_z) at this singularity, the polynomial $P(s)$ in Eq. (2) has a double root at 1. Because of this, the separated classical motions in the η and ξ degrees of freedom both have a turning point at 1. The corresponding orbits in configuration space are given by a two-parameter family of Kepler ellipses which have a common mutual intersection point at the focus point $-\mathbf{a}$. In the left panel of Fig. 2 we show the one-parameter subfamily of these ellipses

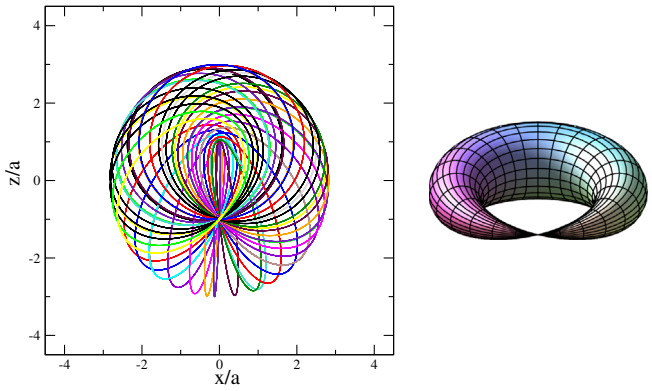

FIG. 2. Kepler ellipses corresponding to the isolated singular value of the energy momentum map (left) and pinched 2-torus (right).

contained in the $(x\ z)$ plane. The full two-parameter family is obtained from rotation about the z axis. In phase space the two-parameter family topologically forms a pinched 2-torus times a circle. In fact in order to prove monodromy it is sufficient to show that the corresponding classical system has a pinched torus [3] and this is what we do in the Supplemental Material [38]. The two-parameter family of these Kepler ellipses contains the degenerate ellipse consisting of the line segment given by the interval $[a + 1/E, a]$ on the z axis. This is a periodic collision orbit that runs along the symmetry axis and bounces back and forth between the nucleus at $\mathbf{a}$ and the turning point $a + 1/E$ on the z axis. For E greater than $-1/(2a)$, which is the value of the potential energy at the focus point $-\mathbf{a}$, the turning point of this periodic orbit on the z axis is below the focus point $-\mathbf{a}$. This is the condition for the isolated value for the energy momentum map to come into existence as we show in the Supplemental Material [38]. This means that the layers of the joint spectrum for constant principal quantum number n have a defect for $n > \sqrt{a}$ and no defect for $n < \sqrt{a}$, which is illustrated in Fig. 4.

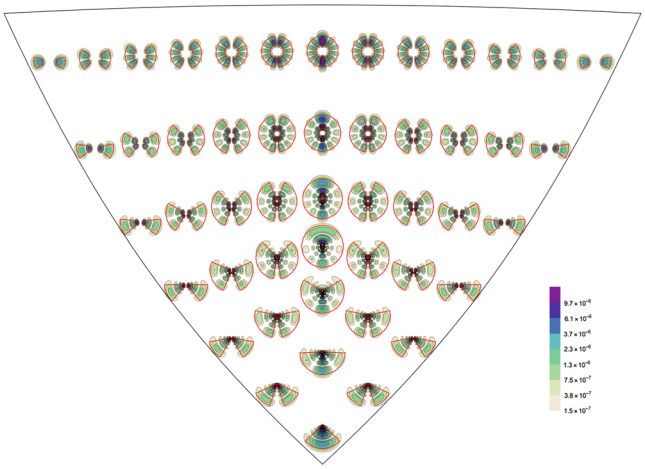

FIG. 3. Eigenfunctions (or orbitals) with $n = 7$ and $a = 7.72$. Shown is the probability density $|\psi|^2$ of the normalised wave function on a slice $\phi = \pi/2$. Overlaid as red curves are the classical caustics. The eigenfunctions are arranged by the position of the eigenvalues in the (l_z, g) plane as in Fig. 1. The fourth state from below (or equivalently above) with $l_z = 0$ is located approximately on the isolated singular point of the energy momentum map.

Conclusions.—We have shown that the joint spectrum associated with the separation of the hydrogen atom in prolate spheroidal coordinates has a lattice defect due to quantum monodromy. The quantum integrable system $\mathcal{G}$ obtained from this separation has two global quantum numbers n and m, but a third global quantum number does not exist due to the lattice defect. This monodromy is different from the one that is described in Refs. [13–16], since there an electromagnetic field is added to the system. In the limit of vanishing fields their monodromy vanishes and does not limit to the monodromy that we describe here for the bare hydrogen atom without external fields.

Spherical and parabolic coordinates can be considered to be limiting case of prolate ellipsoidal coordinates for $a \to 0$ and $a \to \infty$, respectively. In Fig. 4 the left and right images are close to these limiting situations. For $a \to \infty$, the condition $n > \sqrt{a}$ cannot be satisfied, so there is no monodromy. For $a \to 0$, the focus point collides with the boundary, and after extracting the square root of the diagram we recover the standard spectrum of $\mathcal{H}$ again without monodromy. This leaves the spheroconical coordinate system. Preliminary computations show that this QIS does not have monodromy. However, the spectrum does have an unexpected structure in that there is an additional separatrix. This Letter raises the fascinating question whether an experiment can be designed which measures simultaneously the values of the three observables of $\mathcal{G}$ associated with prolate spheroidal coordinates and also the corresponding orbitals (see Fig. 3). To this end it is important to note that monodromy persists under perturbations [40,41], such that the effect remains if, e.g., spin-orbit coupling or the fine structure is taken into account. In recent years various experimental techniques have been developed to measure molecular orbitals [42–45], and using, e.g., electron-ion recollision processes, also atomic orbitals [46]. Using photoionization microscopy it has been shown that one can measure the orbitals associated with the Stark states of hydrogen [47]. These experiments do not particularly depend on the strength of the electric field and can be considered to realize the measurement of the orbitals and spectrum associated with the separation in parabolic coordinates. Even though the

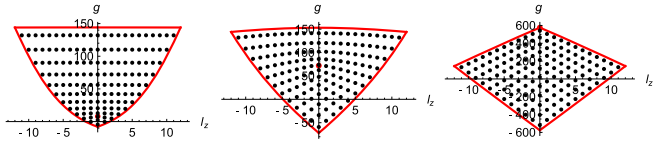

FIG. 4. Classical critical values (red) in (l_z, g), for $n = 12$, $a = 4$, 36, 288 and corresponding joint spectrum (black dots).

latter experiment makes use of the fact that the hydrogen atom in an electric field is an open system such experiments indicate in general that it may be possible that also the spectrum and orbitals of hydrogen associated with separation in prolate spheroidal coordinates can be measured at some point in the future.

We note that a similar type of analysis as presented in this Letter can be done in other multiseparable systems. In particular, we have already obtained preliminary results for the isotropic harmonic oscillator which show that there is a QIS that contains this Hamiltonian for which the joint spectrum has monodromy. This will be presented in a forthcoming paper [48].

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