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Knotted Zeros in the Quantum States of Hydrogen

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Complex superpositions of degenerate hydrogen wavefunctions for the nth energy level can possess zero lines (phase singularities) in the form of knots and links. A recipe is given for constructing any torus knot. The simplest cases are constructed explicitly: the elementary link, requiring $n \geqslant 6$, and the trefoil knot, requiring $n \geqslant 7$. The knots are threaded by multistranded twisted chains of zeros. Some speculations about knots in general complex quantum energy eigenfunctions are presented.

1. INTRODUCTION

In view of the high esteem that Martin Gutzwiller enjoys among quantum physicists, it might seem inappropriate—disrespectful, even—that I should celebrate his 75th birthday by writing about nothing. Yet "nothing," in the form of zeros of functions, the structure of the vacuum, etc., is important in physics as well as mathematics. There have been recent attempts to convince the nonscientific public of this,[1,2] and Martin certainly appreciates it, as we know from his study of the zeros of the Riemann zeta function[3] (see also Ref. 4).

The "nothing" I will concentrate on here is the geometry of zeros of scalar quantum wavefunctions for bound states in three-dimensional space. I will explore an aspect of the generic case, where there is no time-reversal symmetry and the wavefunctions ψ are complex. Then the zeros, which have codimension two ($\mathrm{Re}\,\psi = 0$ and $\mathrm{Im}\,\psi = 0$), are lines. The aspect to be explored is the possibility that the zero lines can form knots and links. Rigorous mathematical investigation seems difficult and I have not attempted it. Instead, I will demonstrate that knots and links can occur in a very special case, by constructing them explicitly.

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The special case is the wavefunctions of the hydrogen atom. Although this system has time-reversal symmetry, which usually implies that the wavefunctions of stationary states are real, the degeneracy resulting from its spherical and other symmetries makes it possible to construct complex superpositions that are also stationary states. (A familiar one-dimensional example is the hindered rotator, that is waves on a ring where there is a real potential V depending periodically on the angle ϕ: the stationary states are real and nondegenerate, except for the case $V=\text{constant}$ when the states $\cos m\phi$ and $\sin m\phi$ can be combined into the angular momentum eigenfunctions $\exp(\pm im\phi)$.)

One reason why zeros of complex waves are interesting is that, as has been known for a long time in the case of propagating waves, they are singularities (dislocations) of the phase $\operatorname{Im}\log\psi$[5–7] or vortices in the current $\operatorname{Im}\psi^*\nabla\psi$.[8–10] Recently there has been an upsurge of interest in these singularities, experimental[11–14] as well as theoretical,[15, 16] in zeros of propagating waves, especially in optics. It has been established that experimentally-constructible beams can possess zeros that can be knotted or linked,[17] and my purpose here is to apply the same methods to the bound states of hydrogen.

2. PRINCIPLES OF THE CONSTRUCTION

The following strategy, devised by Berry and Dennis in Ref. 17 and explained there, enables the construction of any torus knot, specified by its winding integers p, q. If p and q are coprime, the knot is a single loop (e.g., the trefoil $p=2$, $q=3$), and if p and q have a common factor N the "knot" consists of N linked copies of the primitive knot p/N, q/N (e.g., $p=q=2$ corresponds to two linked unknotted loops).

The strategy is first to construct a singular wave ψ_0 with high symmetry, consisting of a circular line zero L_p of order p, threaded by an axial line zero A_q of order q. Then a perturbation ψ_1 is added, that does not itself possess zeros threading the loop L_p. In the total wave $\psi=\psi_0+\psi_1$, L_p unfolds into the desired p, q torus knot, for topological reasons explained in Ref. 17, and A_q unfolds into a q-stranded twisted chain. Both ψ_0 and ψ_1 will be constructed from the degenerate states with energy $E_n\propto -1/n^2$, where n is the principal quantum number.

At a line zero, the Schrödinger equation satisfied by ψ reduces to Laplace's equation in the cartesian coordinates ξ, η transverse to the line, so near a zero of order p ψ must have the form

$$\psi=K_+(\xi+i\eta)^p+K_-(\xi-i\eta)^p \tag{1}$$

If $K_+ > K_-$, the zero has singularity strength $+p$, and if $K_+ < K_-$ the strength is $-p$ (strength is defined[7, 15] as phase change/2π during a positive circuit of the zero).

In the three-dimensional space with polar coordinates $\{r, \theta, \phi\}$, L_p will be constructed in the equatorial plane $\theta = \pi/2$, and A_q will lie along the polar axis $\theta = (0, \pi)$. The ingredients in the construction are the (un-normalized) hydrogen states

$$\psi_{nlm} = r^l \exp(-\tfrac{1}{2}r)\, L_{n-l-1}^{2l+1}(r)\, P_l^m(\cos\theta) \exp(im\phi) \tag{2}$$

where r is measured in units of $n/2$ Bohr radii and L and P denote the Laguerre and Legendre polynomials. For present purposes, the important features of these states are that they are even/odd about the equatorial plane (i.e., as a function of $\cos\theta$ or the cartesian z coordinate) if $l-m$ is even/odd, and they possess $n-l-1$ radial nodal surfaces.

States ψ that are torus-knotted will be built from superpositions of the ψ_{nlm} with fixed n; this guarantees that the knots will be stationary. To build the unperturbed wave ψ_0, it suffices to use states with fixed m, since these states all possess an axial zero A_m, of the desired form (1) with $p = m$ and $K_- = 0$. For fixed n and m, the states with $l = m, m+1, \ldots, n-1$ (that is, a number $n-m$ of states) are available to be superposed to create the pth order circular zero L_p at some fixed radius r^* in the equatorial plane. The general requirements for creating such a zero have been discussed before.[17] Here I show the construction explicitly for the simplest cases.

3. EXPLICIT EXAMPLES: THE SIMPLE LINK AND THE TREFOIL KNOT

These are the link, $m = 2$, $p = 2$, and the trefoil knot, $m = 3$, $p = 2$. In both, the need is to make a second-order equatorial zero loop L_2. From (1), this requires

$$\psi = 0, \qquad \partial_r \psi = 0, \qquad \partial_z \psi = \frac{1}{r}\partial_\theta \psi = 0 \qquad \text{at} \quad r = r^*, \quad \theta = \frac{1}{2}\pi \tag{3}$$

where ∂ denotes derivatives. The first two requirements can be satisfied with a superposition of two states with $l-m$ even, by adjusting the coefficient of one of them to make two radial zeros coincide at some radius r^*. The third requirement can be satisfied with a superposition of two states with $l-m$ odd, by adjusting the coefficient of one of them to move a simple radial zero into coincidence with the double zero at r^*. For concordance with (1), the two superpositions must be out of phase by $\pi/2$. Therefore four states are needed, so $n-m \geqslant 4$, that is $n \geqslant m+4$. Thus, the creation of the 2,2 link requires at least the $n=6$ energy level, and the 2,3 trefoil requires at least the $n=7$ level.

For the link, we therefore write the unperturbed state as

$$\psi_{0,\,\text{link}} = \psi_{622} + a\psi_{642} + iC(\psi_{652} + b\psi_{632}) \tag{4}$$

where a, b and r^* to be adjusted. Since the number of radial nodes is three for ψ_{622}, one for ψ_{642}, two for ψ_{632}, and zero for ψ_{652}, the procedure just outlined is feasible, and indeed can easily be implemented numerically, with the result

$$\begin{gathered} a = -0.0156013\ldots; \qquad b = 0.0517186\ldots \\ r^* = 4.825198\ldots = 14.475594\ldots \text{ Bohr radii} \end{gathered} \tag{5}$$

For the trefoil, the same argument gives

$$\psi_{0,\,\text{trefoil}} = \psi_{733} + a\psi_{753} + iC(\psi_{743} + b\psi_{763}) \tag{6}$$

with constants

$$\begin{gathered} a = -0.008644\ldots; \qquad b = 0.0219055\ldots \\ r^* = 6.5800481 = 23.030168 \text{ Bohr radii} \end{gathered} \tag{7}$$

There is a redundancy in these link and trefoil functions, embodied in the free real parameter C, which corresponds to the ratio K_+/K_- in (1). Note also that in both cases r^* is considerably smaller than the expectation value ($n(n+1/2)$ Bohr radii) of the radius of the most compact state with energy E_n: the loops L_2, and the knots soon to be constructed from them, lie well within the electron clouds.

For the perturbations creating the knots from these singular states, convenient choices are the spherically symmetric states

$$\psi_1 = \varepsilon\psi_{n00}; \qquad n=6 \text{ (link)}, \quad n=7 \text{ (trefoil)} \tag{8}$$

To show that these do indeed create the desired structures, we approximate the total wave $\psi_0 + \psi_1$ near the loop L_2 using (1), to obtain the equation for the zero in cylindrical polar coordinates R, z, ϕ:

$$\begin{aligned} &A[(R-r^*)^2 - z^2] + 2iB(R-r^*)\,z \\ &\quad = -\varepsilon\psi_{n00}(r^*)\exp(-im\phi) \qquad (m=2,\ n=6,\ \text{link};\ m=3,\ n=7,\ \text{trefoil}) \end{aligned} \tag{9}$$

where $A = K_+ + K_-$ and $B = (K_+ - K_-)/2$ are constants. In plane polar coordinates ρ, γ centered on L_2, the zeros are

$$\arg(A\cos 2\gamma + iB\sin 2\gamma) = \pi - m\phi, \qquad \rho = \sqrt{\frac{\varepsilon\,|\psi_{n00}(r^*)|}{A^2\cos^2 2\gamma + B^2\sin^2 2\gamma}} \tag{10}$$

For each azimuth ϕ, there are two solutions γ differing by π, corresponding to the two strands of the knot or link. In two rotations of the z axis, that is as ϕ increases by 4π, each solution γ changes by $2m\pi$, that is the strands of the knot twist m times. This establishes that the perturbation does split L_2 into the desired torus link ($m = 2$) and knot ($m = 3$). (The torus on which the knots lie has an elliptic cross section, given by the second equation in (10).)

Under the perturbation ψ_1, the axial zero A_m splits into m simple zero lines, whose form can be determined by making use of the observation that $P_l^m(\cos\theta) \propto \theta^m$ for $\theta \ll 1$. Thus in cylindrical polars the unperturbed wave near A_m has the form

$$\psi_0 \approx R^m \exp(im\phi)\, D(z) \tag{11}$$

where $D(z)$ is a complex function with no zeros. Adding the perturbation gives the zero lines as

$$R^m \exp(im\phi) = -\varepsilon\,\frac{\psi_{n00}(z)}{D(z)} \tag{12}$$

This describes an m-stranded twisted chain whose links are connected where the radius shrinks to zero at the $n-1$ zeros of $\psi_{n00}(z)$; the twist arises from the changing phase of $D(z)$. (For the propagating waves studied by Ref. 17, the perturbation did not possess axial zeros, so the "chain" was an m-stranded helix.)

The unfolded link and knot, and the chains threading them, are illustrated in Figs. 1 and 2. In both cases, the states possess additional zero lines outside the region shown, in the form of simple loops surrounding the axial chain.

4. CONCLUDING REMARKS

These torus knots and links of phase singularity, created by superposing the quantum states of hydrogen, can surely be generated with other sets of degenerate states in three dimensions, such as the spherically symmetric

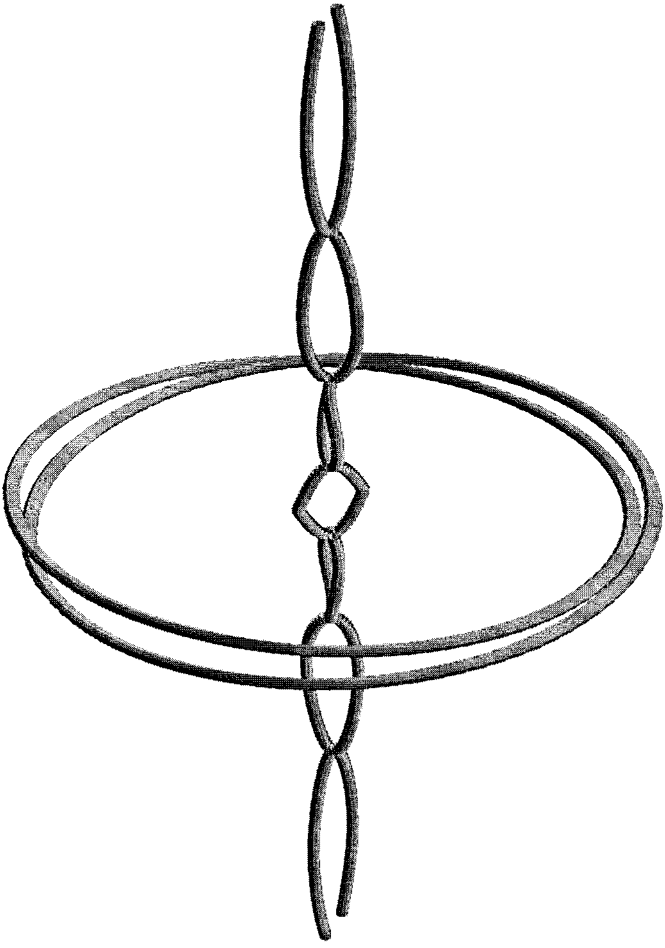

Fig. 1. Zero lines in the form of two linked loops threaded by a two-stranded chain, calculated as the superposition of ψ_0 [Eqs. (4) and (5) with $C = 0.1$] and the perturbation ψ_1 [Eq. (8)] with $\varepsilon = 10$.

harmonic oscillator. More interesting is the question of whether knotted zeros exist in typical three-dimensional eigenfunctions, where there is no time-reversal or other symmetry so the states are nondegenerate. There are two causes for optimism: the structural stability of the knots (that is, their persistence under perturbation by an arbitrary complex wavefunction), and the redundancy of the construction, embodied in the constant C in (4) and (6). From the first, we conclude that there must be complex hermitian operators, close to the Coulomb hamiltonian, for which our knots and

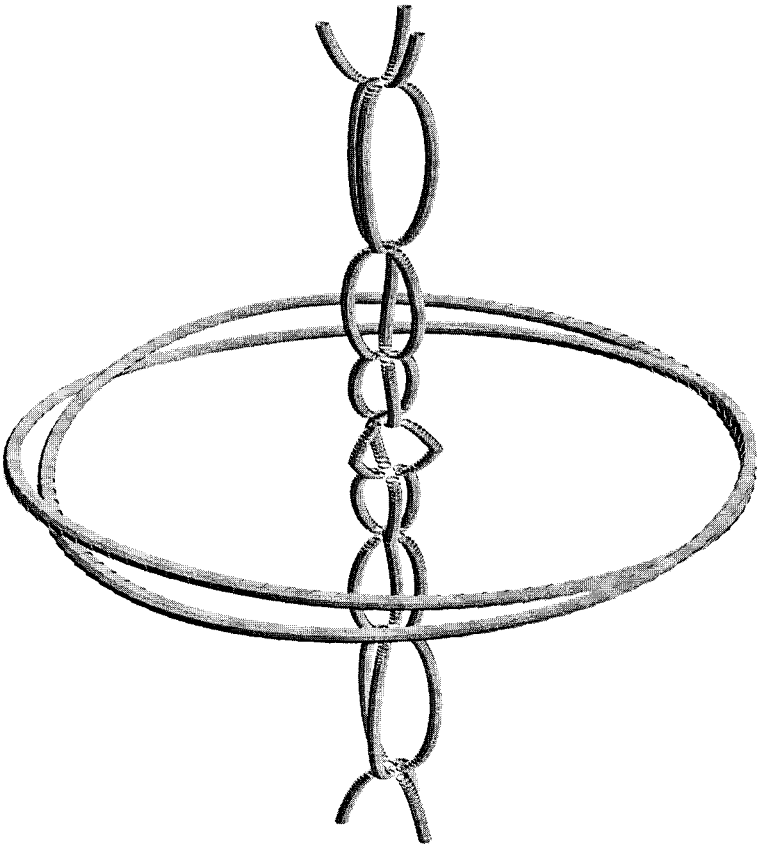

Fig. 2. Zero lines in the form of a trefoil knot threaded by a triple-stranded chain, calculated as the superposition of y_0 [Eqs. (6) and (7) with $C=0.1$] and the perturbation ψ_1 [Eq. (8)] with $\varepsilon=400$.

links occur in nondegenerate eigenstates (an analogous situation is the splitting of the degeneracy of the free-rotator states $\exp(\pm im\phi)$ on a ring, by the addition of a constant azimuthal vector potential, corresponding to threading the ring by an Aharonov–Bohm flux line). From the second, we conclude that there are many such nearby hamiltonians.

Given that knots do exist in generic complex energy eigenfunctions, two types of further investigation could repay further study. First, one can take a given system—for example a charged particle moving in a box containing a uniform magnetic field in a direction not parallel to any symmetry direction of the box—and ask at which energy level E_n the first knot or link occurs, analogous to the $n=6$ and $n=7$ constructions for hydrogen.

(This is somewhat analogous to the question of the lowest degeneracy, not related to symmetry, in the spectra of planar triangular billiards.[18])

Second, one can consider the class of all three-dimensional magnetic billiards whose classical motion is chaotic, and ask about the statistics of knots and links in high excited states. A precise question is: what is the average number of p, q torus knots for excited states near the nth, as $n \to \infty$? I conjecture that the number will be proportional to n, and independent of the magnetic field strength, provided this is large enough. Getting the constant of proportionality seems hard. The result could probably be found by averaging over an ensemble of complex Gaussian random waves in three dimensions.[19, 20] However, this too involves a difficult calculation in statistical topology.

These speculations can be extended to topologies of phase singularity that are not included in the class of torus knots. For example, one can ask whether quantum states can contain zero lines in the form of Borromean rings,[21] where three unknotted loops are connected even though no two are linked.

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