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Approximate topology and the nonexistence of spin-symmetry species of hindered methyl groups

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The usual assumption of proton spin-symmetry species of hindered methyl groups is not consistent with the approximate nature of the multiply connected topology of rotation, which leads instead to a U(1) gauge theory in which wave packets transport three anyons around a void and gain phase due to a vector potential related to angular velocity. Though spin-symmetry species do not exist, some of their properties appear at low temperatures.

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The discussion of methyl rotation entails the introduction of a closed coordinate space ϕ with a range of 2π. The "approximate topology" in the title means that this multiply connected space has no fundamental status. It merely serves to separate what is observationally important in the motion from what is discarded because it is undetectable. Like any trio of atoms moving as part of a solid, the triangle of hydrogen atoms in a methyl group has a quantum state that is a superposition of many basis functions, and the motion of the atoms including the rotation of the group as a whole is contained in the set of evolving complex amplitudes. From this large set, two or three parameters are extracted to describe the evolution of measured observables, usually associated with the spatial distribution of components of the collective nuclear magnetism. By associating each basis function with a value of ϕ, the amplitudes are made to define a wave packet $\psi(\phi,t)$ which, if it happens to rotate without shape change, has the form $\psi(\phi-\omega t)$. After a time $2\pi/\omega$, the distribution of amplitudes with respect to ϕ is restored, but the state function is different because there are many basis functions for each value of ϕ. The methyl-group shape, for example, is not restored after a revolution, though the change is not directly detectable. In addition to its shape, a wave packet has a phase and, in general, this changes during one rotation. Since other coordinates have been discarded, the wave-packet phase carries the residual information that the true topology is simply connected. It is consequently the key to describing interactions with the environment and transformations to rotating frames.

Existing quantum theories of methyl dynamics (see [1]–[3] for bibliography) incorrectly assign a fundamental status to the multiply connected space. This is because they assume that rotation through $2\pi/3$ cyclically permutes three fermions identified with the nuclei of the three hydrogen atoms. From this they infer that the Pauli exclusion principle imposes the constraint $\psi(\phi,t)=\lambda\psi(\phi+2\pi/3,t)$, where $\lambda^3=1$, leading to the conclusion that the hindering potential has perfect threefold symmetry and that there are three species [4] of methyl group characterized by $\lambda=1$ or $\exp(\pm i2\pi/3)$, each with its own set of spin states. The constraint is inconsistent with wave packets, rotational phase, coordinate transformations, and exchange of angular momentum with an environment. It results from a confusion between fermions and quasiparticles. Fermion properties are satisfied by a basis of Slater determinants, which associate spin states x,y,z with three lattice sites 1,2,3. In each basis function (x,y,z), each fermion is equally distributed at all three sites and has all three spin states. Rotation replaces (x,y,z) with (z,x,y). If a quasiparticle is associated with each spin state, then rotation through $2\pi/3$ cyclically permutes quasiparticles and may be associated with a wave-packet phase change $2\pi\sigma/3$. Spin-symmetry species result from imposing the Pauli principle on the quasiparticles instead of the fermions.

The fact that σ may take any value has led to the term "anyons." Wilczek [5] defines them as quasiparticles confined to a plane and exchanging positions by winding around a hole, so changing a winding number in a system in which time-reversal symmetry is broken by rotation. Theories in which quasiparticles are required to be indistinguishable are restricted to delocalized states in which the quasiparticles are distributed equally amongst the three lattice sites, requiring the hindering potential to have threefold symmetry at all times. It is usually assumed that the dynamics of the environment is constrained to maintain this symmetry. Though this is commonly regarded as one of the fundamental differences between quantum and classical mechanics, it is really a symptom of two contradictory assumptions. The multiply connected topology implies dynamic isolation of the methyl group, while the influence of lattice fluctuations implies nonisolation. We may anticipate that with the near isolation of low temperatures, an approximate threefold symmetry and some of the properties of spin-symmetry species appear as a limiting case. Strictly, though, spin-symmetry species are incompatible with dynamics. Methyl rotation involves the least complicated nontrivial approximate topology [6–8], which it shares with the Aharonov-Bohm effect [9]. Three lines of argument based on topology, coordinate transformations, and dynamics demonstrate the existence of a vector potential [8,10] which, being equivalent to the rotational phase, is the essential element of rotation theory. It governs the angular velocity of a wave packet and the rotational inertia of the methyl group.

The motion of methyl protons is confined to a plane with a zone near the axis of the methyl group where the proton wave functions are almost zero. By notionally excluding the protons from this region, we convert the space on which they move to a multiply connected one. This is similar to the exclusion of the electron from the solenoid in the Aharonov-Bohm effect and results in what Shulman calls an approximate topology [6]. The true path of the complex of methyl group and environment is simply connected [11], but the decomposition into methyl rotation and environmental motion discards coordinates whose change counts rotations. They are replaced by a logically essential topological property of the artificial multiply connected rotation space. The paths of rotation divide into homotopy classes with different winding numbers [6–8]. Because of the hole, it is not possible to deform paths belonging to different classes into each other. This is linked to the absence of a cyclic boundary condition. A wave packet making one circuit of the space in a right- or left-handed sense changes its winding number, while its phase changes by $2\pi\sigma$, where σ is the average wave number of the wave packet, connected through the energy wave-number relation to the angular velocity [7]. A moving wave packet has a phase gradient σ from leading to trailing edges. The phase difference between leading and trailing edges is $2\pi\sigma$. In constructing the multiply connected space, we cause the leading edge of the wave packet on a circuit $n+1$ to follow immediately after the trailing edge on circuit n, resulting in an abrupt phase change of $2\pi\sigma$, due to the change of topology. At high temperature, σ and the methyl angular velocity have broad distributions. At high temperature, the simple classical hopping model of methyl rotation [12] ignores spin-symmetry species and introduces a distribution of angular velocities through the reciprocal of a correlation time. The quantum and classical theories are thus compatible.

Essential to the spin-symmetry-species assumption is a dynamic constraint in the form of a cyclic boundary condition

$$\psi(\phi+2\pi,t)=\psi(\phi,t)\ . \tag{1}$$

This is usually justified as ensuring the singlevaluedness of $\psi(\phi,t)$ on the multiply connected space, but in fact it cannot relate directly to that space on which ϕ and $\phi+2\pi$ do not both exist. It relates instead to the universal covering space [9], and its effect is to restrict σ, and hence angular velocity, to zero. Thus (1) is not consistent with the high-temperature hopping model. By showing that it is also inapplicable in the quantum domain, we eliminate spin-symmetry species and remove the source of incompatibility between the quantum and classical theories. Equation (1) is an extension of a time-independent condition

$$\psi(\phi+2\pi)=\psi(\phi)\ , \tag{2}$$

which selects eigenfunctions of a time-independent Hamiltonian and accounts for a discrete tunnel frequency as an interval between energy levels. In contrast, (1) refers to mobile wave packets. The elementary formulation of quantum mechanics in terms of stationary states of hypothetical conservative systems gives no indication of the generalizations that are necessary in introducing time. This explains the widespread omission of the topological quantum phase, which is associated with the closed geometry of the coordinate or Hilbert space upon which wave packets are deemed to evolve. The condition (1) is thus only a guess, and a poor one. It implies that dynamics contains no features that are not in statics as represented by (2). This leaves no room for inertia, torque, and angular velocity. It assumes that a symmetry property of a stationary state becomes a dynamical constraint when time is introduced. A simple pendulum illustrates how, on the contrary, a stationary (axial) symmetry is dynamically broken with the creation of a new (azimuthal) dynamical coordinate.

The correct generalization of (2), obtained using path-integration methods [8], shows that a wave packet making a rotational circuit without changing its form changes phase by $2\pi\sigma$, replacing (1) by

$$\psi(\phi,t+2\pi/\omega)=\psi(\phi,t)\exp(i2\pi\sigma)\ . \tag{3}$$

There is, however, another more physically meaningful representation of a rotating wave packet. This is on the universal covering space where the coordinate (written ϕ_c) is unbounded. On the ϕ_c,t plane, two important points are expressed, (a) the fact that the path of the methyl group (and environment) is really simply connected, while (b) our choice of coordinates forces an apparent change of topology. We choose in (3) to regard two points in space-time as the same point on a subspace at two different times. This approximation results in the concept of rotation, but it changes the relationship of space and time. It is useful to defer this step. The propagation of wave packets and coordinate transformations are therefore handled on the universal covering space, and then a mapping transfers the result to the multiply connected space-time ϕ,t. Whereas ϕ,t is a cylindrical surface with t parallel to the axis, (ϕ_c,t) is an infinite plane. A rotating wave packet occupies a strip 2π wide on this plane, so that $\psi_c(\phi_c\pm2\pi,t)=0$ if $\psi_c(\phi_c,t)\neq0$. It is transferred to ϕ,t by

$$\psi(\phi,t)=\sum_n \psi_c(\phi+2n\pi,t)\ . \tag{4}$$

As an example, we form a wave packet by superimposing two states $\exp[i\phi_c(\sigma\pm m)]$ of a quasi-free rotor for which the energies are $(\hbar^2/2I)(\sigma\pm m)^2$:

$$\begin{aligned}\psi(\phi_c,t)=&\exp\{i[(m+\sigma)\phi_c-(\Omega+m\omega)t]\}\\&+\exp\{i[(-m+\sigma)\phi_c-(\Omega-m\omega)t]\}\\=&\,2\cos[m(\phi_c-\omega t)]\exp[i(\sigma\phi_c-\Omega t)]\ ,\end{aligned} \tag{5}$$

where $\Omega=(\hbar/2I)(\sigma^2+m^2)$ and $\omega=(\hbar\sigma/I)$. The wave packet whose envelope is $2\cos[m(\phi_c-\omega t)]$ is confined to a 2π-wide strip by nodal boundaries

$$(2n\pi+\pi/2m)<\phi_c-\omega t<[(n+1)2\pi+\pi/2m]\ . \tag{6}$$

The effect of (4) is to roll this inclined strip into a cylinder with a helical seam that separates the leading and trailing edges of the rotating wave packet. The wave packet follows a helical path around the (ϕ,t) cylinder. The strip is inclined to the t axis of the ϕ_c,t plane at $\tan^{-1}(\omega)$. A rotational impulse at time t has the effect of bending the strip and changing the pitch of the helical path on (ϕ,t). Transformation to a rotating frame also changes the inclination of the strip by changing the m values and hence changing the angular velocity ω. For example, a transformation that changes m to $m-\sigma$ and $-m$ to $-m-\sigma$ stops the wave packet's rotation and removes the phase gradient. The ϕ_c,t plane can accommodate an infinite set of similar parallel strips with an infinite set of similar wave packets differing in their winding numbers and so belonging to different homotopy classes. Specifying the winding number of a particular wave packet selects one strip. Each strip covers ϕ,t, through (4). The operation $\phi_c \rightarrow \phi_c + 2\pi$ transforms to a new wave packet trajectory ψ'_c, which is displaced from the original wave packet on the covering space. Instead of (1), we have

$$\psi'_c(\phi_c + 2\pi, t) = \psi_c(\phi_c, t)\exp(i2\pi\sigma) \ . \tag{7}$$

In failing to discriminate between the multiply connected space and its simply connected covering space, or between wave packets of different winding numbers, (1) incorrectly assumes rotation to be fundamentally different from translation as represented on the universal covering space.

By choosing a reference frame in which the wave packet is stationary, the phase gradient σ is made equal to zero and the quantum numbers in the basis functions are retained as integers. Now σ appears in the angular-momentum operator for the relative motion of wave packet and lattice. The classical equation of motion for a nonconservative rotor $I\,d\omega/dt = T$ is derived from the Lagrangian

$$L = (I\omega^2/2) + \hbar\sigma\omega \ , \tag{8}$$

where $T = -\hbar\,d\sigma/dt$ and $\omega = d\phi/dt$. Transformation to an arbitrary rotating frame replaces σ by $\sigma - \mu$, and changes the integer quantum numbers m to $m + \mu$. The angular-momentum operator obtained from $dL/d\omega$ by the usual operator substitution is

$$\hbar[(-i\partial/\partial\phi) + \sigma - \mu] \ . \tag{9}$$

The effect of (9) on $\exp[i\phi(m+\mu)]$ is the same as $\hbar[(-i\hbar\partial/\partial\phi) + \sigma]$ operating on $\exp(im\phi)$, so the expectation value of the relative angular momentum is independent of the reference frame. The choice $\mu = 0$ leaves the integral of the torque as a vector potential in the propagating Hamiltonian, while the choice $\mu = \sigma$ makes it appear as a Doppler shift in the wave numbers of the basis functions. The former is most convenient.

The propagating Hamiltonian has the form

$$H = (\hbar^2/2I)\left[-i\frac{\partial}{\partial\phi} + \sigma \right]^2 - V\cos(3\phi) + W(\phi,t) \ . \tag{10}$$

The last term is the low-symmetry dynamic potential, which generates and accelerates wave packets. It declines at low temperature to leave the threefold term V. Then the eigenvalues separate into librational triplets with the ground-state tunnel splitting identifiable with 3Δ, where Δ is an overlap integral connecting functions localized in adjacent potential wells of $-V\cos(3\phi)$. The tendency of the wave packet to come to rest in the lattice frame is described by

$$\frac{d\sigma}{dt} = -\sigma/\tau + f(t) \ , \tag{11}$$

where $f(t)$ represents thermal fluctuations like W. At low temperature, $W \rightarrow 0$. The quasistationary states are combinations of localized functions, which are really amplitudes of Slater determinants. In terms of Slater determinants (x,y,z), etc., they are

$$\psi(k) = (\tfrac{1}{3})^{1/2}[(x,y,z) + \exp(i2\pi k/3)(z,x,y) + \exp(i4\pi k/3)(y,z,x)] \ , \tag{12}$$

where $k = 0$, 1, or -1, the energies being

$$E(k) = -2\Delta\cos[2\pi(k+\sigma)/3] \ . \tag{13}$$

The discrete tunnel splitting 3Δ, the Kramers degeneracy of $k = \pm 1$, and the approximate threefold symmetry of the hindering potential are thus characteristic of $\sigma = 0$ and the zero-temperature limit.

The functions (12) belong to the A, Ea, and Eb species of C_3. The spin functions (x,y,z) can be expanded in terms of eigenfunctions of the total spin, four of which correspond to a total spin $F = \frac{3}{2}$ and four to $F = \frac{1}{2}$, the latter dividing into two pairs. These sets of 4,2,2 belong respectively to A, Ea, and Eb. When the spin functions are inserted into (12), the coefficients are zero except for those having the form (A×A), (Ea×Eb), and (Eb×Ea), where the first symbol indicates the value of k and the second the permutation symmetry of the spin function. Thus $k = 0$ is associated with $F = \frac{3}{2}$ and the other two with $F = \frac{1}{2}$. These properties resemble those attributed to spin-symmetry species, but they have nothing to do with fermion indistinguishability, which is satisfied by the Slater-determinant form of the basis functions. They express the indistinguishability of the quasiparticles in a completely delocalized state, which distributes them equally amongst all three sites. The breaking of the threefold symmetry makes the quasiparticles distinguishable, which does not, of course, conflict with the Pauli principle.

Without the threefold-symmetry constraint and the boundary condition (1), the true nature of methyl dynamics as a U(1) gauge theory appears. There are two gradients of the wave-packet phase, the spatial gradient σ and the time gradient Ω. In electromagnetism, there are four gradients which together form a four-potential. Instead of the six electromagnetic-field components derived from the curl of the four-potential in the six planes of the four-dimensional space-time, there is only one component, the torque, because there is only one plane, (ϕ,t). Equating the torque to the single space-time component of the curl of the potential, one obtains

$$T = \hbar\left[-\frac{\partial\Omega}{\partial\phi} + \frac{\partial\sigma}{\partial t} \right] , \tag{14}$$

which can be compared with $E = -\mathrm{grad}(V) + \partial A/\partial t$. The analog of Maxwell's equations reduces to a single equation corresponding to Faraday's law, and this is the classical equation of motion, torque equals rate of change of angular momentum.

For a hindered group, ϕ is only sampled in the wells of $-V\cos(3\phi)$. Wave packets can be represented approximately by three complex amplitudes. The resulting three-vector (or equivalent density matrix) is propagated by a time-dependent 3×3 matrix with properties extracted from (10). There is an analogy with spin dynamics, though methyl dynamics is based on SU(3) operations rather than SU(2). The propagating matrix incorporates fluctuations of the hindering potential W, the tendency Δ to delocalize by tunneling, and the vector potential σ representing the inertial effect of previous torques. In the localized basis (x,y,z), (z,x,y), and (y,z,x), the propagator is

$$S(t)=\begin{bmatrix} W\cos(pt) & \Delta\exp(i\gamma) & \Delta\exp(-i\gamma) \\ \Delta\exp(-i\gamma) & W\cos(pt+2\pi/3) & \Delta\exp(i\gamma) \\ \Delta\exp(i\gamma) & \Delta\exp(-i\gamma) & W\cos(pt+4\pi/3) \end{bmatrix}, \tag{15}$$

where $\gamma=2\pi\sigma/3$. If $p=\omega$, the ripple W and the wave packet rotate quasisynchronously, and the ripple exerts a torque whose sign depends on their relative phase. If the ripple speeds up, it accelerates the wave packet, changing the vector potential in response to the torque. In the delocalized representation (12), S becomes

$$S'(t)=\begin{bmatrix} 2\Delta\cos(\gamma) & W\exp(ipt) & W\exp(-ipt) \\ W\exp(-ipt) & 2\Delta\cos(\gamma+2\pi/3) & W\exp(ipt) \\ W\exp(ipt) & W\exp(-ipt) & 2\Delta\cos(\gamma+4\pi/3) \end{bmatrix}. \tag{16}$$

The ripple term is resonant when $\hbar p$ is equal to one of the differences between a pair of diagonal elements. Then one of three types of two-component wave packet is excited. Differences between the diagonal terms in (16) govern the two modes of evolution of a wave packet, namely, rotation and shape changing. The evolution of a wave packet from pure tunneling motion (shape changing) to pure rotation can be compared with the trajectory of a pendulum changing from planar swinging to conical rotation. To show this, we form a localized three-component wave packet by superposing equal amplitudes of the functions $\psi(k)$. This may be done by first forming three two-component wave packets like (5) on the universal covering space, and then transferring them to ϕ,t using (4), where they interfere, giving

$$\psi(t)=[a_1,a_2,a_3]=a_1(x,y,z)+a_2(z,x,y)+a_3(y,z,x)\ , \tag{17}$$

$$a_n=1+\exp\{i[\omega_1 t+2(n-1)\pi/3]\} + \exp\{i[\omega_2 t-2(n-1)\pi/3]\}\ , \tag{18}$$

$$\hbar\omega_n=2\Delta[\cos(\gamma)-\cos(\gamma+2n\pi/3)]\ . \tag{19}$$

The trajectory is displayed by plotting the coordinates of the center of gravity of the wave packet on a plane defined by

$$X=(2a_1a_1^*-a_2a_2^*-a_3a_3^*)/3^{1/2} = \cos(\omega_1 t)+\cos(\omega_2 t)+\cos[(\omega_2-\omega_1)t]\ , \tag{20}$$

$$Y=(a_2a_2^*-a_3a_3^*) = -\sin(\omega_1 t)+\sin(\omega_2 t)-\sin[(\omega_2-\omega_1)t]\ . \tag{21}$$

When $\gamma=0$, this describes an oscillating linear path on the (X,Y) plane, like a swinging pendulum. Three points on the plane that form an equilateral triangle represent the three methyl orientations $\phi=0$ and $\pm 2\pi/3$, each labeled by the spin states associated with the lattice sites. The delocalized stationary states (12) are represented by a stationary point at the center of the triangle, the degree of localization being given by the distance from the center. The wave-packet trajectory changes smoothly from the linear path when $\gamma=0$, through rotating elliptical orbits like a Foucault pendulum, to a right- or left-handed circuit of the three orientations when $\gamma=\pm\pi/2$ and $\omega_1=-\omega_2$. The progressive development from delocalized stationary states to rotational trajectories of localized wave packets like those implicitly assumed to occur in high-temperature classical theories is similar to the excitation of a stationary pendulum to a conical orbit. In a rotational orbit, the spin states are transported around the lattice sites, modulating spin-dependent interactions and so enabling the rotation to be observed experimentally. Spin-symmetry species have concealed this evolution and had the effect of divorcing methyl rotation from other topics involving the dynamics of quasiparticles in condensed matter, with which it is closely allied. It has consequently been denied two roles for which it is well fitted, as a paradigm of coherent quantum molecular dynamics, mirroring the established role of coherent spin dynamics, and as a particularly clear example of the quantum to classical transition from localization in k space to localization in coordinate space. Elimination of the unphysical constraints removes a number of conceptual difficulties and makes redundant a number of bogus rationalizations of previous incompatibilities. It provides an alternative point of departure. Experimentally it opens perspectives for new types of experiment aimed at reproducing in molecular dynamics some elements of the coherent time-domain techniques of spin dynamics.

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