# Appendix 1.

# Phase and Group Velocities

In the simplest case, the propagation of a wave packet is characterized by the temporal evolution of its peak and accompanying changes in its shape, typically broadening and distortion. The situation can be more complicated in molecular dynamics, where elecron wave packets can split into two or more components, each of which propagates on a different part of a potential energy surface. These components may experience separate fates, such as yielding different sets of reaction products, or they may recombine at a later time and interfere. Moreover, as a wave packet propagates it may spread and/or distort so much that it loses its identity as a packet. The possibilities are legion.

## Electromagnetic Waves

The propagation of electromagnetic waves is usually easier to describe mathematically than the propagation of particle waves, so we shall start here. In vacuum, the relationship between $\omega$ and $k$ is trivial: $\omega = ck$, where $c$ is the speed of light. This has the consequence that a uniform plane wave (*i.e.*, single $k$ value) traveling in vacuum, say in the $x$-direction, can be expressed in complex form as

$$e^{i(kx-\omega t)} = e^{ik(x-ct)}. \tag{1}$$

The $x$-direction is used here, though propagation can take place in any direction. Trade $kx$ for $\vec{k}\cdot\vec{r}$ if you like.

Now consider an electromagnetic wave packet comprised of such waves. Regardless of the number of $k$ values present in the packet, in vacuum each constituent wave ($k$ value) travels at speed $c$ and therefore the packet propagates without changing its shape, leaving aside broadening due to diffraction in the plane perpendicular to the direction of propagation. On the other hand, when an electromagnetic wave propagates in a dispersive medium, $\omega(k)$ can be complicated. In this case, the packet propagates more slowly than in vacuum (*i.e.*, the speed of light is $c/n$, where $n$ is the index of refraction), and how its shape changes as it propagates is dictated by the variation of $\omega$ with $k$.

## Phase Velocity

The phase velocity of the 1D wave indicated in eqn (1) is the velocity with which the phase advances in the $+x$ direction. It is obtained by finding the velocity one must travel to perceive the phase as constant. Consequently, the time derivative of the phase, $\varphi = kx - \omega t$, is set equal to zero

$$\dot{\varphi} = \frac{d}{dt}\left(kx - \omega t\right) = 0, \tag{2}$$

which yields

$$\dot{x} = \omega / k = v_p, \tag{3}$$

where $v_p$ is the magnitude of the phase velocity. In other words, the phase advances in the $x$-direction with speed $v_p$.

Phase velocities do not, in general, correspond to the transport of energy. An example is the approach of waves to a shore. Here, the phase velocity is the velocity of the point of intersection of incoming wave fronts with the shore, as indicated in Fig. 1. As the wave front moves toward the shore, the point of intersection travels in a direction parallel to the shore. For small θ values, the point of intersection travels much more quickly than does the incident wave. Phase velocities can exceed the speed of light, as they do not involve the velocity of matter, and therefore there is no conflict with special relativity.

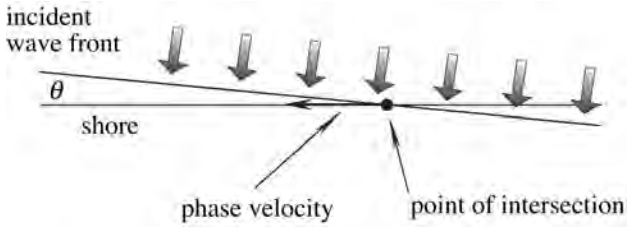



Figure 1. A wave approaches the shore with angle θ between the shore and the wave front. The time rate of change of the intersection point that travels to the left is a phase velocity. As θ goes to zero, this phase velocity goes to infinity.

## Group Velocity and Dispersion

In packets of the kind under consideration here, each $k$ value can have a different phase velocity. Though $v_p$ is independent of $k$ as long as $\omega$ is equal to a constant times $k$, in a dispersive medium this is not the case. The variation of $\omega$ with $k$ is not linear, and therefore $v_p$ depends on $k$. Thus, despite the fact that phase velocity is well defined for each $k$ value, it need not be well defined for a wave packet.

Transport of energy takes place with a velocity called the group velocity, $v_g$, which is the velocity with which a packet travels. For a particle in the classical limit, the packet becomes a point, and $v_g$ is simply the particle velocity. Except in pathological cases, $v_g$ corresponds to the transport of energy. Pathological behavior can happen near a resonance, where distortion of the packet is so severe that $v_g$ loses its meaning. In other words, it cannot be defined. For example, near a resonance part of the incident packet can be reflected, while another part is absorbed – to be emitted in a vastly different form, typically exponential decay of the quasibound level created through absorption of the incident packet. This confounds our ability to define a group velocity.

Were one to observe propagation, $v_g$ would be the motion of the peak, assuming this is well defined, or its "center-of-mass" if the packet is somewhat unkempt. As mentioned above, in the classical limit, the packet becomes a point and $v_g$ is just $p/m$.

The group velocity is obtained mathematically by determining when the amount of destructive interference is a minimum. This occurs when the phase $\varphi$ has the smallest amount of variation with respect to $k$:

$$\frac{d\varphi}{dk} = 0.$$

This condition indicates where the constituent waves add constructively, thereby forming the peak of the spatial distribution. It is called the stationary phase condition.

To maintain generality for the case of electromagnetic waves, it is assumed that $\omega(k)$ is an arbitrary function of $k$, and a Taylor expansion of $\omega(k)$ is carried out about the peak of the distribution of $k$ values. The $k$ value at this peak is denoted $k_0$, and $\omega(k)$ is given by

$$\omega(k) \approx \omega(k_0) + (\partial\omega/\partial k)_{k_0}(k-k_0) + \tfrac{1}{2}(\partial^2\omega/\partial k^2)_{k_0}(k-k_0)^2 \ldots . \tag{4}$$

The condition that gives maximum constructive interference, $d\varphi/dk = 0$, is now applied:

$$\frac{d}{dk}(kx-\omega t) \implies x = (\partial\omega/\partial k)\,t = \left\{(\partial\omega/\partial k)_{k_0} + (\partial^2\omega/\partial k^2)_{k_0}(k-k_0)\ldots\right\} t. \tag{5}$$

The terms inside the bracket determine the propagation characteristics. Retaining just the first term yields: $x = v_g t$, where $v_g$ is defined as

$$\boxed{v_g = (\partial\omega/\partial k)_{k_0}\ .} \tag{6}$$

The fact that $x$ does not depend on $k$ when just the first term in the bracket in eqn (5) is retained tells us that when this approximation is valid the packet travels without distortion. This can also be seen by considering the general form of the packet obtained using a plane wave basis and integrating over a continuous distribution of $k$ values:

$$\psi(x,t) = (2\pi)^{-1/2}\int_{-\infty}^{+\infty} dk\ \phi(k)\, e^{i(kx-\omega t)}\ . \tag{7}$$

The factor $(2\pi)^{-1/2}$ is included for consistency with the most common Fourier transform convention. In replacing $\omega$ with the first two terms of its expansion given by eqn (4), the phase in the exponent in eqn (7) becomes

$$kx - \omega(k_0)t - (k-k_0)v_g t = \left(k_0 v_g t - \omega(k_0)t\right) + k(x - v_g t)\,. \tag{8}$$

Because the term in large parentheses on the right hand side of eqn (8) does not depend on $k$, it can be removed from the integral in eqn (7), yielding

$$\psi(x,t) = e^{i\left(k_0 v_g t - \omega(k_0)t\right)} (2\pi)^{-1/2} \int_{-\infty}^{+\infty} dk\, \phi(k)\, e^{ik(x - v_g t)} \,. \tag{9}$$

Thus, despite the fact that the packet is displaced by $v_g t$ as it propagates, it experiences no distortion, as the phase factor $e^{i\left(k_0 v_g t - \omega(k_0)t\right)}$ plays no role in $|\psi(x,t)|$.

Referring to eqn (5), distortion is due to the second derivative and higher terms. When they are retained, the equation for $x$ becomes: $x = v_g t + (\partial^2\omega/\partial k^2)_{k0}(k - k_0)t$ .... In this case, the interference that takes place among the constituent waves does not preserve the initial shape, as the phases of the constituent waves vary nonlinearly with $k$. You can get an idea of how this works by going back to eqn (8), but this time including the second derivative term in the expansion of $\omega(k)$ given by eqn (4).

## Particle Wave Packets

For particle waves, propagation in free space takes place with significant dispersion because the phase is given by

$$\varphi = kx - Et/\hbar = kx - \hbar k^2 t/2m \tag{10}$$

The difference between particle and electromagnetic waves is considerable. For example, a free particle packet cannot propagate without changing its shape. It may propagate for a significant distance and appear, to the satisfaction of an observer, to have retained its shape. However, if the packet continues to propagate eventually its shape must change. The broadening of a Gaussian packet is illustrated in Fig. 2. The Gaussian shape is retained as $t$ increases. The horizontal axis is distance in arbitrary units.

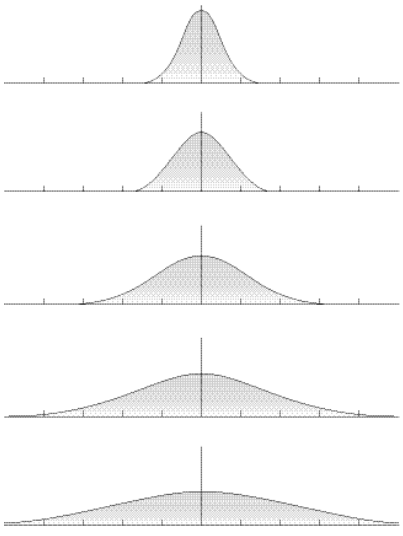


Figure 2. From top to bottom, the panels show the spreading of a Gaussian particle wave packet with time. The entries are snapshots of the spatial distribution at different times. The Gaussian shape is retained throughout the packet's evolution.

Group velocity is obtained in the same way as with electromagnetic packets. Specifically, the condition that corresponds to maximum constructive interference is used:

$$0 = \frac{d\varphi}{dk} = \frac{d}{dk}\left(kx - Et/\hbar\right) = \frac{d}{dk}\left\{kx - \left(E(k_0) + \left(\partial E/\partial k\right)_{k_0}(k-k_0)\ldots\right)\frac{t}{\hbar}\right\}. \tag{11}$$

This yields: $x = v_g t \ \ldots$, where the group velocity is

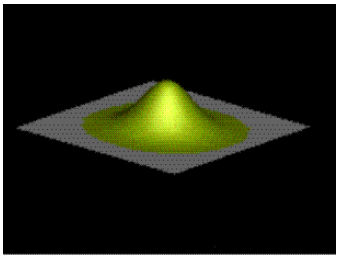
$$\boxed{v_g = \frac{1}{\hbar}\left(\partial E/\partial k\right)_{k_0} = \frac{\hbar k_0}{m}}, \tag{12}$$

where $E = (\hbar k)^2/2m$ has been used.

Note that $E(k)$ has been expanded about $k_0$ in order to identify the group velocity. For free particle wave packets, the expansion given by eqn (11) truncates after the second derivative term because $E = (\hbar k)^2/2m$ gives $\partial^2 E/\partial k^2 = \hbar^2/m$, and all higher order derivatives clearly vanish.

As with electromagnetic waves, the physical content of this result is explored by going back to the wave packet and inserting the above result, which is done below for the important case of the propagation of a Gaussian wave packet.

## Gaussian Wave Packets



Let's now examine a Gaussian packet that propagates in free space. There is no purely scientific reason that Ican think of for using a Gaussian shape. It is a convenient (and often realistic) form that can be used to model a number of physical situations. An example of a 2D Gaussian is shown on the right.

Because the Fourier transform of a Gaussian is another Gaussian, the momentum function $\phi(k)$ is of the form

$$\phi(k) = Ae^{-\left((k-k_0)x_0^2/2\right)}, \tag{13}$$

where $A = x_0^{1/2}\pi^{-1/4}$ is a normalization constant such that the integration of $|\phi(k)|^2$ over all $k$ gives unity. The function $\phi(k)$ is peaked about $k_0$, and only positive $k$ need to be included, as $k_0$ is positive. The functional form of $\psi(x, t=0)$ is obtained by inserting eqn (13) into eqn (7) and integrating:

$$\psi(x, t=0) = A(2\pi)^{-1/2}\int_0^\infty dk\, e^{ikx}e^{-\left((k-k_0)x_0^2/2\right)}. \tag{14}$$

Completing the square in the exponent and carrying out the integration yields

$$\psi(x,t=0) = (A/x_0)\,e^{ik_0x}e^{-x^2/2x_0^2}\ . \tag{15}$$

This Gaussian is centered at $x=0$. It is normalized in the sense that $|\psi(x,t=0)|^2$ integrated over all space gives unity.[1] Its spatial extent is $\sim x_0$. To obtain the wave packet's time development, eqn (13) is inserted into eqn (7):

$$\psi(x,t) = A(2\pi)^{-1/2}\int_0^\infty dk\; e^{\left((k-k_0)^2x_0^2/2\right)}e^{ikx}e^{-i\hbar tk^2/2m} \tag{16}$$

Completing the square and other manipulations (left as an exercise) yield

$$\psi(x,t) = \frac{A}{x_0\left(1+i(v_0t/k_0x_0^2)\right)^{1/2}}\exp\left\{-\frac{\left((x-v_0t)/x_0\right)^2}{2\left(1+i(v_0t/k_0x_0^2)\right)}+ik_0x-i\tfrac{1}{2}k_0v_0t\right\} \tag{17}$$

where $v_0 = \hbar k_0/m$ is the speed of the center of the packet (the group velocity). The direction of travel can be discerned from the terms $+ik_0x$ (the momentum is in the $+x$ direction), and $(x-v_0t)^2$ (the packet peaks at $x = v_0t$).

For large negative $t$, $\psi(x,t)$ is centered at large negative $x$. As time increases the packet advances with speed $v_0$. It has its minimum width at $t=0$, as seen from $|\psi(x,t)|^2$ .

$$|\psi(x,t)|^2 = \frac{(A/x_0)^2}{\left(1+(v_0t/k_0x_0^2)^2\right)^{1/2}}\exp\left\{-\frac{\left((x-v_0t)/x_0\right)^2}{1+(v_0t/k_0x_0^2)^2}\right\} \tag{18}$$

To achieve a minimum width at $t=0$, it is necessary for the packet to be spread out at negative times and compress as $t\to 0$. Free space packets either spread or compress with time, because they contain momentum distributions. It is possible to obtain compression using coherent optical methods to prepare packets that become more localized as they evolve in time until a minimum width is achieved, after which they broaden. The packet can be made to peak anywhere on the $x$-axis at $t=0$ by letting $x\to x-x'$ in the argument of the exponential, in which case the packet peaks at $x'$ at $t=0$.

The long-time limit of eqn (18) displays the packet's broadening in the regime where the initial width is small compared to the amount of broadening that has occurred. In this limit, $|\psi(x,t)|^2$ is

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[1] Parseval's theorem states that if $\phi(k)$ is normalized, *i.e.*, the integral of $|\phi(k)|^2$ over all $k$ is unity, its Fourier transform is likewise normalized. In other words, the integral of $|\psi(x)|^2$ over all $x$ is automatically unity.

$$|\psi(x,t)|^2 = A^2 \frac{k_0}{v_0 t} \exp\left\{-\left(\frac{(x-v_0 t)\,k_0 x_0}{v_0 t}\right)^2\right\} \tag{19}$$

$$= A^2 \frac{m}{\hbar t} \exp\left\{-\left(\frac{x-v_0 t}{\hbar t/m x_0}\right)^2\right\} \tag{20}$$

The width at long times is proportional to time and inversely proportional to the initial spatial width of the packet. The latter dependence is due to the fact that the width of the momentum distribution is inversely proportional to the spatial width, and it is the momentum that causes the spreading.

The above example illustrates the spreading of a well-behaved wave packet whose group velocity is easily identified: $v_g = v_0 = \hbar k_0 / m$ .

# Appendix 2.

## Classical Mechanics Including Vector Potential

Classical mechanics can be formulated on the basis of minimization of an important quantity that is referred to as the action, $S$.[1] In the case of particles, this means

$$0 = \delta S = \delta \int_{t_1}^{t_2} dt\, L = \int_{t_1}^{t_2} dt\, \delta L\,. \tag{1}$$

Integration end points are fixed as the paths that connect the end points are varied. With $L = L(q,\dot{q})$ (1D and no explicit time dependence), eqn (1) yields

$$0 = \int_{t_1}^{t_2} dt \left( \frac{\partial L}{\partial q}\delta q + \frac{\partial L}{\partial \dot{q}}\frac{d}{dt}\delta q \right) \tag{2}$$

$$= \int_{t_1}^{t_2} dt \left( \frac{\partial L}{\partial q} - \frac{d}{dt}\frac{\partial L}{\partial \dot{q}} \right) \delta q\,. \tag{3}$$

In writing eqn (2), the fact that the order of variation and differentiation can be interchanged has been used: $\delta(dq/dt) = d(\delta q)/dt$. Also, integration by parts of the second term in eqn (2) eliminates the integrated term because the variation vanishes at the integration end points. Equation (3) must be true for all $\delta q$ at each point in time, so the parenthetic term vanishes. This yields the Euler-Lagrange equation. When there is more than a single coordinate, each $q_i$ is treated separately, and we have

$$\partial_{q_i} L - \frac{d}{dt}\left( \frac{\partial L}{\partial \dot{q}_i} \right) = 0 \tag{4}$$

The Euler-Lagrange equation, including its extension to field theory, is widely used in physical science. The term $\partial_{q_i} L$ is called the canonical momentum $p_i$.

The Lagrangian is sometimes expressed as $T - U$, where $T$ is kinetic energy and $U$ is a potential. $U$ can be (but is not limited to) a scalar function whose gradient yields the force that an object experiences. For example, the classical dynamics of a polyatomic molecule can be described using a potential energy surface, $V(q_i)$, where $q_i$ denotes $N-6$ internal

[1] The term *action* can be traced to Maupertuis: "Nature is thrifty in all its actions." Mathematical justification of the principle of stationary action is credited mainly to Lagrange and Euler.

(ignoring rotation) nuclear coordinates. The gradients of $V(q_i)$ give the forces that the nuclei experience, for example, expressed in the space defined by the multidimensional $q_i$. In general, $U$ can be velocity dependent. Such a velocity dependent potential has nothing to do with $V(q_i)$. Isolated molecules are conservative systems, and if $V(q_i)$ contained a term linear in velocity this would correspond to dissipation. A velocity dependent $U$ pertains to magnetic interactions. Putting $L = T - U$ into the Euler-Lagrange equation shows that $U$ satisfies an equation for a generalized force, with components

$$0 = \underbrace{-\partial_{q_i} U + \frac{d}{dt}\left(\frac{\partial U}{\partial \dot{q}_i}\right)}_{:= F_i} + \partial_{q_i} T - \frac{d}{dt}\frac{\partial T}{\partial \dot{q}_i} . \tag{5}$$

The second term on the right can be nonzero when $U$ is velocity dependent. The generalized force $F_i$, which is defined as the first two terms, also satisfies

$$F_i = \frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}_i}\right) - \partial_{q_i} T . \tag{6}$$

When $U$ is not velocity dependent and $T$ has no explicit coordinate dependence, eqns (5) and (6) yield the usual situation: force is mass time acceleration, which is equal to minus the gradient of a potential. Effects of electromagnetic fields on charged particles are accounted for with the Lorentz force (using $c = 1$):

$$\vec{F}_L = q\left(\vec{E} + \vec{v} \times \vec{B}\right) . \tag{7}$$

Combining $\vec{F}_L$ with eqn (5) gives an expression for $U$ and therefore $L$. The fact that the Lagrangian has no explicit time dependence leads to an important result. Namely, a conserved quantity called the Hamiltonian is revealed. With $L$ in hand, the Hamiltonian is

$$H = p_i \dot{q}_i - L . \tag{8}$$

Repeated indices indicate summation. The Hamiltonian yields equations of motion via Hamilton's canonical equations. One is obtained from eqn (8) by taking the partial derivative with respect to $p_i$, and the other is obtained by using $\partial_{q_i} H = -\partial_{q_i} L = -p_i$.

$$\partial_{p_i} H = \dot{q}_i \qquad \partial_{q_i} H = -\dot{p}_i \tag{9}$$

## Adding the Electromagnetic Field

The approach presented here is one of brute force. The momentum in Hamilton's equations is the canonical momentum. In a simple case it is $m\dot{q}$, but when electromagnetic fields are present, this is not so. In terms of the potentials, the Lorentz force is

$$\vec{F}_L = q\left(-\nabla\phi - \partial_t \vec{A} + \vec{v}\times\nabla\times\vec{A}\right), \tag{10}$$

where $\phi$ and $\vec{A}$ are the scalar and vector potentials, $q$ is the charge, and $c = 1$ is used.

The first term inside the large parentheses has an obvious counterpart in eqn (5): the first term on the right hand side, whereas the other terms do not have immediately obvious counterparts. To make the connection to eqn (5), let us manipulate the third term inside the large parentheses in eqn (10) into a more recognizable form. It will turn out that this also results in cancellation of the partial derivative term $-\partial_t \vec{A}$.

To proceed, the $x$-component of $\vec{v}\times\nabla\times\vec{A}$ is written in a suggestive form, and from this an expression for the generalized potential $U$ is obtained

$$\left(\vec{v}\times\nabla\times\vec{A}\right)_x = v_y\left(\partial_x A_y - \partial_y A_x\right) - v_z\left(\partial_z A_x - \partial_x A_z\right) \tag{11}$$

$$= \left(v_x\partial_x A_x + v_y\partial_x A_y + v_z\partial_x A_z\right) - \left(v_x\partial_x A_x + v_y\partial_y A_x + v_z\partial_z A_x\right). \tag{12}$$

In writing eqn (12), the term $v_x\partial_x A_x$ has been both added (first parentheses) and subtracted (second parentheses). The net effect is zero, but this gives a desirable form. The contents of the second parentheses can be expressed in terms of time derivatives

$$\frac{dA_x}{dt} = \partial_t A_x + \left(v_x\partial_x A_x + v_y\partial_y A_x + v_z\partial_z A_x\right). \tag{13}$$

Thus, the second parenthetic term in eqn (12) equals a total derivative minus a partial derivative. The first parenthetic term in eqn (12) also can be expressed in a desirable form. Using the fact that $\vec{v}$ is not an explicit function of position, we have

$$v_x\partial_x A_x + v_y\partial_x A_y + v_z\partial_x A_z = \partial_x\left(\vec{v}\cdot\vec{A}\right). \tag{14}$$

Equations (13) and (14) are used to replace the parenthetic terms in eqn (12), yielding

$$\left(\vec{v}\times\nabla\times\vec{A}\right)_x = \partial_x\left(\vec{v}\cdot\vec{A}\right) - \frac{dA_x}{dt} + \partial_t A_x. \tag{15}$$

This enables eqn (10) to be written in a way that makes it easy to identify the potential $U$ used in eqn (5). We see that the partial derivatives with respect to time cancel one another. The $x$-component of the force given by eqn (10) is

$$F_{L,x} = q\left(-\partial_x\left(\phi - \vec{v}\cdot\vec{A}\right) - \frac{d}{dt}\left(\partial_{v_x}\left(\vec{v}\cdot\vec{A}\right)\right)\right), \tag{16}$$

where $A_x$ is written $\partial_{v_x}(\vec{v}\cdot\vec{A})$ in anticipation of the result. Equation (16) is of the form

$$F_{L,x} = -\partial_x U + \frac{d}{dt}\left(\partial_{v_x} U\right) \tag{17}$$

where

$$U = q\left(\phi - \vec{v}\cdot\vec{A}\right), \tag{18}$$

and the fact that $\phi$ has no explicit velocity dependence has been used. Now that the potential $U$ has been obtained, the Lagrangian, $L = T - U$, can be written

$$L = T - q\left(\phi - \vec{v}\cdot\vec{A}\right) \tag{19}$$

and the components of the canonical momentum are obtained from $L$ by using

$$p_i = \frac{\partial L}{\partial \dot{q}_i} = m\dot{q}_i + qA_i = \pi_i + qA_i\,. \tag{20}$$

Note that the canonical momentum $\vec{p}$ whose components are given above is not the same as the momentum associated with the particle's velocity. The latter is the kinetic momentum, $\vec{\pi} = m\dot{\vec{q}}$. It is the canonical momentum $\vec{p}$ that becomes $-i\hbar\nabla$ in quantum mechanics, not $\vec{\pi}$. When $\vec{A}$ is equal to zero, $\vec{p} = \vec{\pi}$, but when $\vec{A}$ is not equal to zero, $\vec{p} \neq \vec{\pi}$. The Hamiltonian is now obtained in a few steps. Starting with its definition:

$$H = \sum_i \dot{q}_i p_i - L\,, \tag{21}$$

eqn (19) is put into eqn (21), yielding

$$H = \sum_i \dot{q}_i p_i - T + q\phi - q\,\vec{v}\cdot\vec{A} \tag{22}$$

$$= \left( \sum_i \frac{\pi_i}{m} p_i \right) - \frac{\vec{\pi} \cdot \vec{\pi}}{2m} + q\phi - \frac{q}{m} \vec{\pi} \cdot \vec{A} \,. \tag{23}$$

Equation (20) is now used to write

$$H = \sum_i \left( \frac{p_i - qA_i}{m} \right) p_i \; - \frac{(\vec{p} - q\vec{A}) \cdot (\vec{p} - q\vec{A})}{2m} + q\phi - \frac{q}{m} \left( \vec{p} - q\vec{A} \right) \cdot \vec{A} \,. \tag{24}$$

Several lines of tedious algebra yields

$$\boxed{H = \frac{\left( \vec{p} - q\vec{A} \right)^2}{2m} + q\phi \,.} \tag{25}$$

# Appendix 3.

## Flux Quantization in Superconductivity

"In the past few weeks my colleagues and I have been asked many times: What are the practical uses of your theory? Although even a summary inspection of the proceedings of conferences on superconductivity and applications would give an immediate sense of the experimental, theoretical and developmental work in this field as well as expectations, hopes and anticipations – from applications in heavy electrical machinery to measuring devices of extraordinary sensitivity and new elements with very rapid switching speeds for computers – I, personally, feel somewhat uneasy responding. The discovery and the development of the theory is a vast work to which many scientists have contributed. In addition there are numerous practical uses of the phenomena for which theory rightly should not take credit. A theory (though it may guide us in reaching them) does not produce the treasures the world holds. And the treasures themselves occasionally dazzle our attention; for we are not so wealthy that we may regard them as irrelevant.

But a theory is more. It is an ordering of experience that both makes experience meaningful and is a pleasure to regard in its own right. Henri Poincarè wrote: *Le savant doit ordonner; on fait la science avec des faits comme une maison avec des pierres; mais une accumulation de faits n'est pas plus une science qu'un tas de pierres n'est une maison.*[1]

One can build from ordinary stone a humble house or the finest chateau. Either is constructed to enclose a space, to keep out the rain and cold. They differ in the ambition and resources of their builder and the art by which he has achieved his end. A theory, built of ordinary materials, also may serve many a humble function. But when we enter and regard the relations in the space of ideas, we see columns of remarkable height and arches of daring breadth. They vault the fine structure constant, from the magnetic moment of the electron to the behavior of metallic junctions near the absolute zero; they span the distance from materials at the lowest temperatures to those in the interior of stars, from the properties of operators under time reversal to the behavior of attenuation coefficients just beyond the transition temperature.

I believe that I speak for my colleagues in theoretical science as well as myself when I say that our ultimate, our warmest pleasure in the midst of one of these incredible structures comes with the realization that what we have made is not only useful but is indeed a beautiful way to enclose a space."

Leon Cooper
Nobel Lecture, 1972
(co-recipients John Bardeen and Robert Schrieffer)

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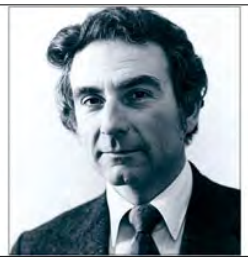
[1] Translation: The scientist must order; science is made with facts as a house with stones; but an accumulation of facts is no more a science than a heap of stones is a house.

Heike Kammerlingh-Onnes
(1853 - 1926)

John Bardeen
(1908 - 1991)



Leon Cooper
(1930 - )

Bob Schrieffer
(1931 - )

## Superconductivity: The Early Years

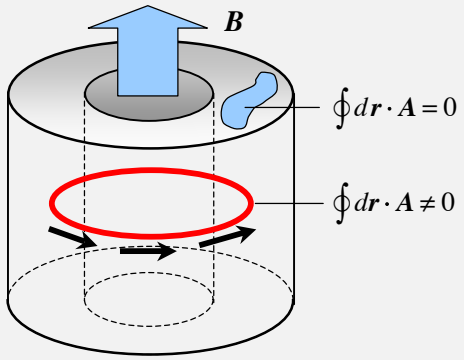
While carrying out research on the electrical properties of low temperature metals, Heike Kammerlingh-Onnes discovered that his mercury sample displayed an apparent absence of *dc* resistance at temperatures lower than 4.2 K. In fact, the drop in resistance as 4.2 K was approached from higher temperatures was precipitous, decreasing by three orders of magnitude in 0.1 K. The year was 1911. Though quantum mechanics had yet to be developed, talk of fundamental inconsistencies and the need for new theories was gaining momentum. Four years earlier Kammerlingh-Onnes had achieved a technological breakthrough. His *tour de force* preparation of liquid helium enabled him to embark on a number of scientific projects in this previously inaccessible temperature regime. And now this amazing effect of essentially zero resistance lay before him.[2] Amused, he introduced the term superconductivity.

Subsequent generations of experimentalists and theorists have succumbed to the lure of superconductivity. After a century it remains a subject rife with intellectual challenge, affording numerous opportunities in basic research. It is also of great technological importance, notably in NMR, ESR, FMRI, and the like.

Here we shall discuss flux quantization, focusing on its close relationship to the Aharonov-Bohm effect. An overview will cover type I superconductors, whose physics is more straightforward than that of the more technologically important type II superconductors. An excellent introductory level discussion of superconductivity is given in Hook and Hall: *Solid State Physics*.

[2] In a remarkable demonstration of the lack of resistance, Kammerlingh-Onnes in 1914 carried a sample containing superconducting current (with no electrical input) from Leiden to Cambridge.

Figure 1. A solid cylinder surrounds a hollow annular region. A closed circular path (red) encircles the flux Φ contained within the annulus. The region enclosed by the red path is not simply connected: the path cannot be continuously deformed to a point. Other paths can be taken within the body of the cylinder that do not enclose flux, such as the blue one shown on the top face. They are simply connected; they can be continuously deformed to a point.




To begin, consider the situation that exists inside a superconductor, *i.e.*, as opposed to at/near its surface. Static $\boldsymbol{E}$ and $\boldsymbol{B}$ are excluded, whereas $\boldsymbol{A}$ can be nonzero. Closed line integrals of $\boldsymbol{A}\cdot d\boldsymbol{r}$ vanish as long as the integral encloses no flux. That is, the region is simply connected. On the other hand, closed line integrals of $\boldsymbol{A}\cdot d\boldsymbol{r}$ do not, in general, vanish in multiply connected regions. For example, consider a circular loop that goes around a cylinder's symmetry axis, enclosing an annular region, as indicated in Fig. 1. In this case, $\boldsymbol{B} = 0$ within the body of the cylinder, though $\boldsymbol{B} \neq 0$ (fat arrow) inside the annular region. Consequently, $\boldsymbol{A}$ must be nonzero within the body of the cylinder, as its circuit integral encloses flux.

It is easy to accept the fact that static $\boldsymbol{E}$ is zero, because, by definition, no *dc* electric potential difference can exist in a perfect conductor. Though superconductors are richer in their physics than perfect conductors, they also display remarkably low resistance. There are reports of currents persisting for years with no energy input to maintain them. It has been estimated that the lifetime of a circulating current can be $\sim 10^5$ years.

## Meissner Effect and the London Equation

The fact that $\boldsymbol{B}$ is excluded from the interior of a superconductor deserves further consideration. This situation differs from that of a perfect conductor, as indicated in Fig. 2. The phenomenon in which $\boldsymbol{B}$ is excluded from a superconductor's interior is called the Meissner effect. Walter Meissner and Robert Ochsenfeld discovered it in 1933. In 1935 the London brothers (Fritz and Heinz) published the phenomenological explanation, based on elementary electrodynamics and Maxwell's equations, presented below. This effect lends itself to clever demonstrations of the uniqueness of superconductivity.

Suppose $\boldsymbol{E}$ is present. It cannot be present within the bulk of a perfect conductor, but it can have a nonzero value at/near the surface of the conductor. The superconducting electrons are responsible for nearly all of the current because their scattering lengths are very large compared to those of the normal electrons. Because of these large scattering lengths, it is assumed that the superconducting electrons are accelerated without dissipation, in which case their acceleration is given by

$$m\dot{\boldsymbol{v}} = -e\boldsymbol{E} \tag{1}$$

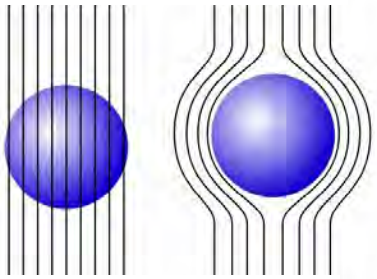


Figure 2. Meissner effect: (right) $\boldsymbol{B}$ is excluded from the interior. Were it inside before lowering the temperature below its critical value, it would be expelled. (left) In a normal conductor, no matter how low the resistance, $\boldsymbol{B}$ penetrates with impunity.

Recall that the Lorentz force on the electron is $\boldsymbol{F} = -e\left(\boldsymbol{E} + (\boldsymbol{v}/c)\times\boldsymbol{B}\right)$. In other words, the electron's acceleration, $m\dot{\boldsymbol{v}}$, is affected by the magnetic term $(\boldsymbol{v}/c)\times\boldsymbol{B}$ in addition to $\boldsymbol{E}$. However, this term has been neglected in writing eqn (1). The reason is twofold: First, its contribution is small when the velocity is small, and we are concerned here with low electron velocities. Second, $\boldsymbol{E}$ generates a current density that in turn generates $\boldsymbol{B}$. Consequently $\boldsymbol{B}$ is small. The superconducting current density is $\boldsymbol{j}_s = -en_s\boldsymbol{v}$, where $\boldsymbol{v}$ and $n_s$ are the superconducting electron velocity and number density, respectively. Putting this into eqn (1) yields

$$\frac{d\boldsymbol{j}_s}{dt} = \frac{n_s e^2}{m}\boldsymbol{E}\,. \tag{2}$$

Taking the curl of eqn (2) and using $\nabla\times\boldsymbol{E} = -\partial_{ct}\boldsymbol{B}$ yields

$$\frac{\partial}{\partial t}\left(\nabla\times\boldsymbol{j}_s + \frac{n_s e^2}{mc}\boldsymbol{B}\right) = 0. \tag{3}$$

**Exercise**: In going from eqn (2) to eqn (3) a total derivative has been replaced by a partial derivative. What, if anything, is the justification?

Were the quantity within the parentheses time independent but nonzero, eqn (3) would be satisfied, but $\boldsymbol{B}$ could have a nonzero constant value throughout the sample, in conflict with the observation of Meissner and Ochsenfeld. To make eqn (3) consistent with the Meissner effect, in which $\boldsymbol{B}$ is not just constant but it is excluded from the bulk, the London brothers set the contents of the bracket equal to zero:

$$\nabla\times\boldsymbol{j}_s + \frac{n_s e^2}{mc}\boldsymbol{B} = 0. \tag{4}$$

This is called the *London equation*. It was introduced because it is consistent with the Meissner effect. Later, it will be derived from a microscopic model. Together with $\nabla \times \boldsymbol{B} = \boldsymbol{j}_s/c$, eqn (4) predicts a penetration depth associated with the exponential decay of $\boldsymbol{B}$ within the superconductor. In other words, $\boldsymbol{B}$ can exist at the surface, but it decays as $e^{-x/\lambda}$ within the material. In writing $\nabla \times \boldsymbol{B} = \boldsymbol{j}_s/c$, the displacement current $\partial_{ct}\boldsymbol{E}$ is omitted because it is small relative to $\boldsymbol{j}_s/c$, and, most importantly, we are concerned with a static $\boldsymbol{B}$ field. This quasi-static approximation uncouples Maxwell's equations such that they do not yield a wave equation for the propagation of electromagnetic energy.

To obtain the exponential decay of the $\boldsymbol{B}$ that penetrates the material, use the identity: $\nabla \times \nabla \times \boldsymbol{B} = \nabla(\nabla \cdot \boldsymbol{B}) - \nabla^2 \boldsymbol{B}$. Because $\nabla \cdot \boldsymbol{B} = 0$, the right hand side is equal to $-\nabla^2 \boldsymbol{B}$. Thus, $\nabla^2 \boldsymbol{B} = -\nabla \times \boldsymbol{j}_s/c$. Combining this with eqn (4) gives

$$\nabla^2 \boldsymbol{B} = \frac{n_s e^2}{mc^2} \boldsymbol{B} . \tag{5}$$

The same equation is obtained for $\boldsymbol{j}_s$. Namely, taking the curl of eqn (4) and making the assumption that time derivative terms vanish yields

$$\nabla^2 \boldsymbol{j}_s = \frac{n_s e^2}{mc^2} \boldsymbol{j}_s . \tag{6}$$

As indicated in Fig. 3, both $\boldsymbol{B}$ and $\boldsymbol{j}_s$ decay exponentially into the material starting from its surface with the penetration depth $\lambda$ given by

$$\lambda^2 = \frac{mc^2}{n_s e^2} . \tag{7}$$

Now let's go back and examine the electric field, starting with eqn (2). This time, $\boldsymbol{E}$ is left alone and $\boldsymbol{j}_s$ is altered:

$$\begin{aligned} \frac{n_s e^2}{m} \boldsymbol{E} &= \frac{d\boldsymbol{j}_s}{dt} \\ &= c^2 \nabla \times \partial_{ct} B \\ &= -c^2 \nabla \times \nabla \times \boldsymbol{E} , \end{aligned} \tag{8}$$

which can be written

$$\nabla^2 \boldsymbol{E} = \frac{n_s e^2}{mc^2} \boldsymbol{E} . \tag{9}$$

The electric field decays into the superconductor in exactly the same way as do $\boldsymbol{B}$ and $\boldsymbol{j}_s$. In other words, everything is restricted to the penetration depth, as indicated in Fig. 3.

In terms of the vector potential $\boldsymbol{A}$, eqn (4) is

$$\nabla \times \left( \boldsymbol{j}_s + \frac{n_s e^2}{mc} \boldsymbol{A} \right) = 0 \qquad (10)$$

Thus, the quantity $\boldsymbol{j}_s + \left(n_s e^2/mc\right)\boldsymbol{A}$ can be expressed as the gradient of a scalar. It is also possible to use

$$\boldsymbol{j}_s = - \frac{n_s e^2}{mc} \boldsymbol{A} \qquad (11)$$

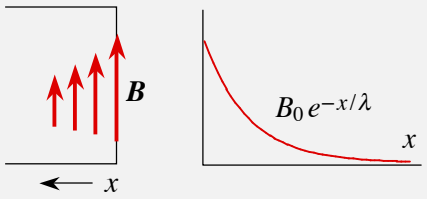



Figure 3. A steady magnetic field on the surface of a superconductor decays exponentially going inward. The electric field and superconducting current density do likewise.

as long as it is understood that the $\boldsymbol{A}$ in this expression has already taken into account the addition of the gradient of a scalar to the above equation. Indeed, the gauge transformation: $\boldsymbol{A} \rightarrow \boldsymbol{A} + \nabla\zeta$ leaves $\boldsymbol{B}$ unaffected, so assigning $\nabla\zeta$ to $\boldsymbol{A}$ is natural. When charge density is conserved ($\nabla \cdot \boldsymbol{j}_s = -\dot{\rho} = 0$), the Coulomb gauge $\nabla \cdot \boldsymbol{A} = 0$ is required. Thus, $\zeta$ must satisfy Laplace's equation: $\nabla^2\zeta = 0$, subject to boundary conditions.

At first glance eqn (11) does not appear to be gauge invariant: if $\nabla\zeta$ is added to $\boldsymbol{A}$ there is a corresponding change in $\boldsymbol{j}_s$. Equation (10) is fine with adding $\nabla\zeta$ because $\nabla \times \nabla\zeta = 0$, but not eqn (11). The continuity requirement $\nabla \cdot \boldsymbol{A} = 0$ dictates that only the transverse part of $\boldsymbol{A}$ is to be used, so if we include this condition in setting the gauge there will be no problem. For a simply connected body, if the normal component of $\nabla\zeta$ is known on the surface of a volume, $\zeta$ is determined everywhere to within a constant that has no physical consequence. So eqn (11) places a restriction on the gauge. In a body that is not simply connected, like rings and cylinders, knowing the normal component of $\nabla\zeta$ does not specify $\boldsymbol{A}$. Rather, $\boldsymbol{A}$ is determined by the flux within the ring or cylinder.

The bottom line is that the Meissner effect ensures that $\boldsymbol{B}$ and $\boldsymbol{j}_s$ are excluded from the bulk interior of a superconductor. Currents flow near the surface.

## BCS Theory

A breakthrough in the microscopic theory came with the 1957 paper of Bardeen, Cooper, and Schrieffer that established what is called the BCS theory of superconductivity. At the time, theory and experiment were being pursued avidly, and important breakthroughs had already been achieved. Fröhlich and Bardeen had independently suggested that phonons facilitate the pairing of electrons, and Schafroth had pointed out that paired electrons act as bosons, an insight that proved pivotal. London had predicted flux quantization and he introduced the flux quantum, $hc/e = \Phi_L$, where $h$ is the Planck constant and the subscript L refers to London. Onsager realized that superconducting current is carried by electron pairs rather than single electrons, so he suggested that the flux quantum should be $\Phi_0 = \Phi_L/2$. Experiments had uncovered an important isotope effect: the

nuclear mass in a crystal obeyed the scaling relationship $T_c M^{1/2}$ = constant. This implicated phonons, rekindling an earlier interest of Bardeen. Cooper had introduced a theory of electron pairing. Many other scientists made important contributions as well. Enthusiasm reigned. The stage was set.

In BCS theory, electrons near the Fermi surface form Cooper pairs. In simple terms, an electron passing through the crystal leaves in its wake a distorted lattice (a region of net positive charge), and another electron is attracted by this positively charged wake. It can be said that the electrons create and annihilate phonons. Formally, electron pairs are stabilized by the exchange of a phonon (Fig. 4). Screening is achieved through the sea of electrons near the Fermi surface, making electron-electron repulsion weak. In addition, the average separation of electrons in a Cooper pair is large, usually > 1000 Å, which helps. Though electron-electron repulsion is weak, it must be overcome to stabilize the pair. The binding energy of a Cooper pair is so weak that it would not survive were it alone. Fortunately, there is significant Pauli repulsion between the rest of the electrons and the electrons in the pair, stabilizing the latter.

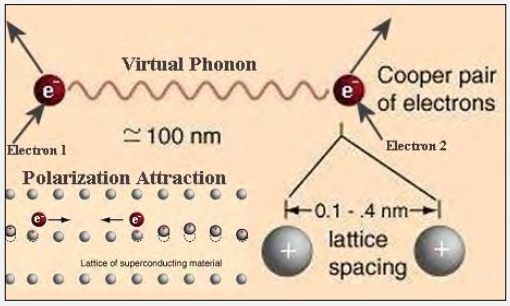



Figure 4. Graphics regarding Cooper pairs, the Meissner effect, etc. are available online.

Only ~ $10^{-4}$ of the electrons near the Fermi surface participate in the superconducting current. If the binding energy is ~ $kT_c$, where $T_c$ is the critical temperature below which the system is superconducting, this energy is ~ $\delta(p^2/2m)$ at the Fermi surface, which is ~ $v_F \delta p$, where $v_F$ is the electron velocity at the Fermi surface. Using $\delta x \delta p \sim \hbar$ dictates that the size $\delta x$ of a Cooper pair is enormous, say $10^3 - 10^4$ Å. Thus, the pair is much larger than the average spatial separation between superconducting electrons, and one cannot think of the pairs as isolated from one another. They are interleaved. [3]

[3] An analogy attributed to J. Robert Schrieffer and communicated to the author by Stephan Haas is that of Cooper pairs and couples on a dance floor. Imagine a large dance floor, a modern dance, and a pair of skilled partners. Throughout the dance, the partners maintain a large average distance between themselves, say, a dozen meters. They are sensitive to each other's movements, however subtle and nuanced, and they each respond in synchrony with the music that couples their motions, whirling and moving in one direction or another, as one might visualize a Cooper pair near a superconducting surface responding to magnetic and electric fields. The dancers' respective motions are correlated, and it is clear to any observer that the two of them are dancing together as a pair. Other dancers can pass between and around our designated couple. The other dancers also are paired in couples of the same persuasion as our designated couple. In fact, the entire dance floor is filled with such pairs in which two paired individuals, on average, remain far from one another, yet clearly they are dancing together. Strong correlations among the (boson) couples are due to correlations between the (fermion) individuals. The latter correlations derive from the common courtesy — that an individual avoids bumping into others on the dance floor. In response to the music, all of the couples whirl around in circles or move toward one side or another of the floor, remaining correlated throughout. Though the ensemble of couples has strong pair-pair correlations, each couple responds to the music with its own styled nuances. They are Cooper pairs.

The pairs consist of spin-up and spin-down electrons, resulting in a singlet. With the pairs acting as bosons, they are able to form a macroscopic ground state. Because the pair-pair separation is much smaller than the size (correlation length) of a pair, and because the normal electrons outnumber the superconducting ones by a factor of $\sim 10^4$, there is considerable Pauli repulsion due to the fermion nature of the individual electrons. As mentioned above, this stabilizes the pairs, which are strongly correlated among each other. Thus, the superconducting electrons comprise a collective state whose spatial dimension is large but whose momentum distribution is condensed. A resulting energy gap inhibits excitations from entering or leaving a state when the temperature is below $T_c$.

## Cooper Pairs and the London Equation

Strong correlations among Cooper pairs lead to a macroscopic state that is separated by an energy gap from higher states. Being bosons, individual pairs can each be put into the same state. The total current density is obtained by computing it for a single pair and multiplying this times the pair density $n_s/2$. With the pairs each entering the same state, the phase of the state becomes a well-defined, essentially classical, quantity. Another case in which a large number of bosons enter the same state is the electromagnetic field. The phases of two uncorrelated distinct photons have no bearing on one another. On the other hand, when photons have the same propagation direction $\boldsymbol{k}$ and frequency $\omega$, they can enter the same field mode, yielding a macroscopic electric field $\boldsymbol{E}(\boldsymbol{k},\omega)$ whose measurable phase has unambiguous meaning.

The expression for the total superconducting current density is

$$\boldsymbol{j}_s = \tfrac{1}{2} N_s (-2e) \psi^* \boldsymbol{v} \psi \ , \tag{12}$$

where $N_s$ is the number of superconducting electrons, as distinct from the *number density* of superconducting electrons, $n_s$. Volume is accounted for in the normalization of the wave function. Using the kinetic momentum operator yields

$$\boldsymbol{j}_s = -\frac{N_s e}{2m} \psi^* \frac{2e}{c} \psi \ . \tag{13}$$

The above equations reflect the facts that for Cooper pairs: the charge is $-2e$, the number of superconducting electron pairs is $N_s/2$, and the mass is twice that of an electron. The spatial variation of the wave function is given by $e^{i\eta}$, where $\eta$ depends on spatial coordinates. Thus, eqn (13) becomes

$$\boldsymbol{j}_s = -\frac{n_s e\hbar}{2m} \nabla\eta - \frac{n_s e^2}{mc} \boldsymbol{A} \, . \tag{14}$$

Note that with $\psi^*\psi = V^{-1} e^{-i\eta} e^{i\eta} = V^{-1}$, the number density $n_s$ has been recovered. Taking the curl of eqn (14) eliminates the gradient of the scalar, $\nabla\eta$, yielding

$$\nabla \times \boldsymbol{j}_s + \frac{n_s e^2}{mc}\boldsymbol{B} = 0 \tag{15}$$

This is none other than the London equation that was introduced earlier on phenomenological grounds.

## Flux Quantization

A fascinating consequence of the superconducting state is flux quantization. It has a great deal in common with the Aharonov-Bohm (AB) effect, which is exactly why it is being examined in this appendix. They each involve interplay between electromagnetic fields and phases of quantum mechanical particle waves. Superconducting electrons travel large distances without undergoing inelastic scattering. This is not surprising in light of the fact that Cooper pairs condense into a ground state that is separated from the lowest excited state by a sizable energy gap. Though distances are macroscopic, quantum mechanical effects can nonetheless be pronounced. Figure 5 indicates a current flowing in a superconducting wire loop. The diameter of the wire is much smaller than the radius of the loop, so the particle-on-a-ring (POR) model can be applied. What is new compared to atomic /molecular models is the scale: the dimensions are macroscopic. The distance over which an electron can maintain a well-defined phase is larger than the circumference of the loop.

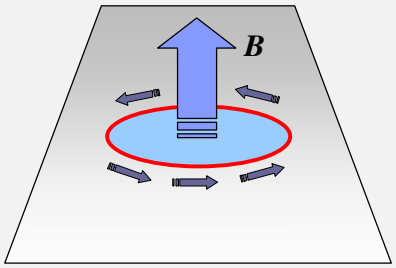



Figure 5. Superconducting loop: the wire diameter is much less than the loop radius. Current flows near the superconductor surface; the penetration depth is much less than the wire diameter.

Satisfying $\psi(0) = \psi(2\pi)$ results in quantization of the enclosed flux. The $\boldsymbol{B}$ field inside the ring is large because it is due to the superconducting current. The small amount of $\boldsymbol{B}$ that penetrates the wire near its surface has a negligible effect. We shall consider the boundary condition $\psi(0) = \psi(2\pi)$ for the wave function of a single electron, keeping in mind that the same argument applies to all of the electrons. Thus, the flux enclosed by the loop is quantized according to the quantization requirement for the wave function of a single electron. Flux quantization is distinct from the AB effect only in that $\boldsymbol{B}$ need not be external. We will examine cases with $\boldsymbol{B}_{\text{ext}} = 0$, as well as those with $\boldsymbol{B}_{\text{ext}} \neq 0$.

The superconducting current cannot be at odds with $\boldsymbol{B}$. In other words, flux quantization derives from consistency. The quantization of electron levels guarantees the quantization of the associated flux $\Phi$. Thus, it can be said that the AB effect accounts for flux quantization.

To see how $\Phi$ is quantized, we start with single electron states. Using these, Cooper pairs are constructed and the collective effect of many pairs is taken into account. This will yield a flux quantum $\Phi_0$ that is half as large as London's prediction of $\Phi_L = hc/e$.

There are alternate ways to derive flux quantization and two will be presented. Again, this material is extremely close to the POR system used to introduce the AB effect. You might find it useful to review the latter, as most of the details given there are not repeated below.

The energies for an electron interacting with $\boldsymbol{A}$ are obtained from its time independent Schrödinger equation:

$$E\psi = H\psi = \frac{1}{2m}\left( p_\phi + \frac{e}{c}A_\phi \right)^2 \psi = \frac{1}{2m}\left( \frac{-i\hbar}{r_0}\frac{\partial}{\partial\phi} + \frac{e}{c}\frac{\Phi}{2\pi r_0} \right)^2 \psi \tag{16}$$

where $r_0$ is the ring radius, and $A_\phi = \Phi / 2\pi r_0$ has been used. The electron under consideration interacts with the $\boldsymbol{A}$ that is created by all of the electrons. To satisfy $\psi(0) = \psi(2\pi)$ requires $\psi = (2\pi)^{-1/2} e^{in\phi}$, where $n$ is an integer. Thus, eqn (16) yields

$$E_n = B_{rot}\left( n + \Phi/\Phi_{\mathrm{L}} \right)^2 \tag{17}$$

where $B_{rot} = \hbar^2 / 2mr_0{}^2$, and $\Phi_{\mathrm{L}} = hc/e$.

The presence of $\boldsymbol{A}$ removes the twofold degeneracy that exists when $\boldsymbol{A} = 0$. This is also discussed in Chapter 3. The quantity $\Phi/\Phi_{\mathrm{L}}$ assumed any value because $\Phi$ was controlled externally. Here, $\Phi$ is due to the electron current in the superconductor, and the electron current and $\Phi$ must be consistent. The one-electron states ($n$ and $n'$) that combine to form a Cooper pair must be degenerate and have the same value of $\Phi$. One member has spin-up while the other has spin-down, making the pair a singlet. Referring to eqn (17), the degeneracy condition is

$$\left| n + \Phi/\Phi_{\mathrm{L}} \right| = \left| n' + \Phi/\Phi_{\mathrm{L}} \right| \tag{18}$$

It is not possible to create a pair in which $n$ and $n'$ have the same value. The potential that binds the electrons cannot be independent of $\phi$. The angular variation of the potential requires that the states have different quantum numbers if there is to be a nonzero matrix element between them. In addition, there is a requirement based on angular momentum conservation. Current does not flow within the bulk of a superconductor, only near its edge. Yet, if the angular momentum in the center of the wire is calculated, it is found that it is nonzero, as discussed later. This is explained by having the Cooper pairs rotate about their respective centers-of-mass in the center of the wire.

With $n \neq n'$, the only way to satisfy eqn (18) is:

$$n + \Phi/\Phi_{\mathrm{L}} = -\left( n' + \Phi/\Phi_{\mathrm{L}} \right) \tag{19}$$

where $n \neq n'$. Thus, $n + n'$ is equal to $-2\Phi/\Phi_{\mathrm{L}}$, and because $\Phi_{\mathrm{L}} = 2\Phi_0$, $n + n'$ is equal to $-\Phi/\Phi_0$. In other words, because $n + n'$ is an integer, so is $\Phi/\Phi_0$. Consequently, $\Phi$ is quantized according to

$$\Phi = n_\Phi \Phi_0 \tag{20}$$

The flux quantum is $\Phi_0 = hc/2e = \Phi_L/2$, and the flux quantum number $n_\Phi$ assumes integer values (Fig. 6). Flux quantization arises from the degeneracy requirement for participating single electron states. Referring to Fig. 6, it is not possible to displace the parabola horizontally except in half-integer steps. For example, eqn (17) can be written:

$$E_n = B_{rot}\left(n + \tfrac{1}{2} n_\Phi\right)^2 \tag{21}$$

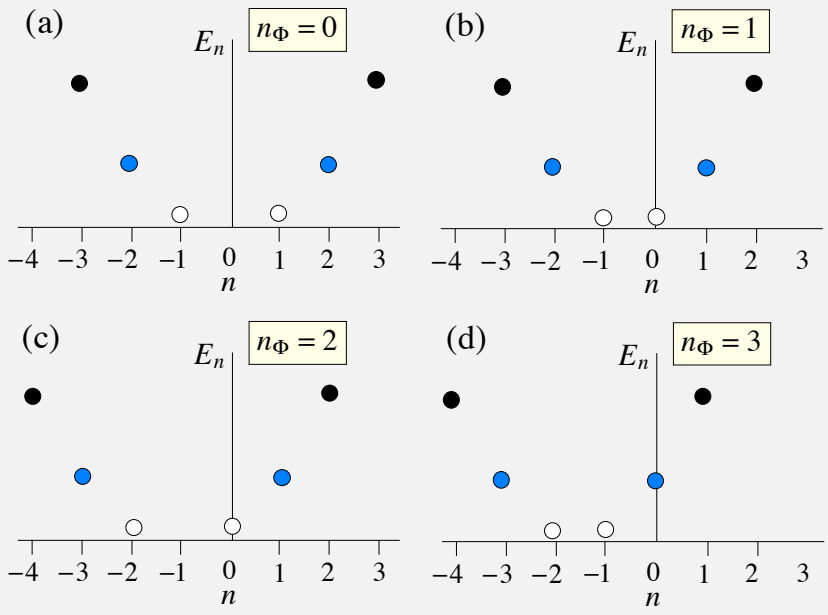



Figure 6. Single-electron energies are given for the specified values of $n_\Phi$. The allowed $E_n$ values lie on parabolas defined by eqn (21). Because of the $n \neq n'$ restriction, states at the bottoms of the parabolas are excluded. Entries (a) and (c) differ by horizontal displacement; likewise with (b) and (d). Adapted from Schrieffer.

It is clear that for a given value of $n_\Phi$ there are two $n$ values that have the same energy. For example, for $n_\Phi = 0$, we have the pairs $(n, n') = (1, -1), (2, -2)$, etc., while for $n_\Phi = 1$, we have $(0, -1), (1, -2)$, etc., and so on for the other $n_\Phi$.

Referring to Fig. 6, the states indicated in (a) and (c) differ only by a phase factor. Therefore they are related by a gauge transformation; likewise for the states in (b) and (d). Note that (a) and (c) have the same $\Delta n$ values for a given $E_n$. For example, $\Delta n = 4$ and 6 for the blue and black dots, respectively, in (a) and (b). Likewise, (b) and (d) have the same $\Delta n$ values for a given $E_n$. On the other hand, the $\Delta n$ values for a given $E_n$ of

the (a)/(c) pair differ from those of the (b)/(d) pair at the same $E_n$. Because the states that combine have the same energy, the eigenstates are 50/50 mixtures.

Now consider the pairs $n = \pm 1$ ($n_\Phi = 0$) and $n = 0, -2$ ($n_\Phi = 2$). With the first pair, $\psi \sim e^{i\phi} \pm e^{-i\phi}$, whereas with the second pair, $\psi \sim 1 \pm e^{-i2\phi} = e^{-i\phi}(e^{i\phi} \pm e^{-i\phi})$. The gauge transformation $e^{-i\phi}$ implies the presence of a vector gauge field, as discussed at length in Chapter 3. This gauge field is the $A_\phi$ in eqn (16). Experimental verifications of flux quantization followed the predictions. Data from the 1961 paper of Deaver and Fairbank are shown in Fig. 7.

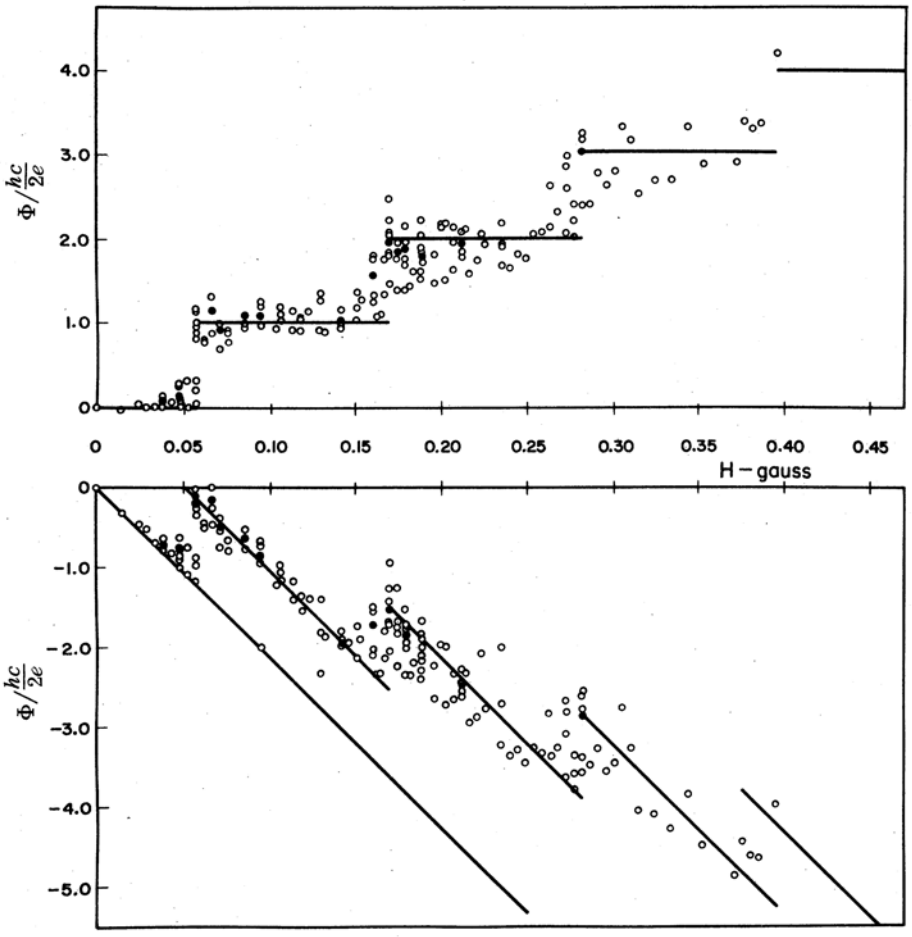



Figure 7. From Deaver and Fairbank: "(upper) Trapped flux in cylinder as a function of magnetic field; the cylinder was cooled below the superconducting transition temperature. The open circles are individual data points. The solid circles represent the average value of all data points at a particular value of applied field including all the points plotted and additional data which could not be plotted due to severe overlapping of points. Approximately two hundred data points are represented. The lines are drawn at multiples of $h/2e$. (lower) Net flux before turning off the applied field in which it was cooled as a function of the applied field. Open and solid circles have the same significance as above. The lower line is the diamagnetic calibration to which all runs have been normalized. The other lines are translated vertically by successive steps of $h/2e$."

## External *B*

In the above derivation, it was assumed that there is no externally applied $\boldsymbol{B}$ field. In this case, $\boldsymbol{A}$ that results from $\boldsymbol{j}_s$ must produce a phase shift consistent with the ring's cyclic boundary condition, $\psi(0) = \psi(2\pi)$. This boundary condition must be met regardless of the source of $\boldsymbol{A}$, so we now consider external $\boldsymbol{B}$ and how it affects quantization.

The flux quantization condition is $\Phi = n_\Phi \Phi_0$, and $\Phi$ has two sources, one the external field, $\boldsymbol{B}_{\text{ext}}$, the other the $\boldsymbol{B}$ field that arises from the current density $\boldsymbol{j}_s$ in the ring. Suppose we vary $\boldsymbol{B}_{\text{ext}}$. Then $\boldsymbol{j}_s$ must vary, which happens by having the number of Cooper pairs vary. For a given quantum number $n_\Phi$, increasing $\boldsymbol{B}_{\text{ext}}$ will cause the superconducting current density $\boldsymbol{j}_s$ to decrease until it is ~ zero. At that point, $\boldsymbol{j}_s$ undergoes an abrupt increase because $n_\Phi$ increases by one. This sequence will repeat for progressively higher values of $n_\Phi$. This is confirmed in the lower entry of Fig. 7, though I do not understand the author's caption for the lower entry.

## Easy Routes

In addition to yielding flux quantization, the above derivation provides information about Cooper pairs: the single-electron states that combine; how some of the pairs are related to one another by a gauge transformation while others are not (Fig. 6); and how the energies of the different kinds of pairs differ. The flux quantization condition alone can be derived more easily. Let us do this.

The center-of-mass of a Cooper pair can be carried around the loop indicated in Fig. 5 with the boundary condition $\psi_{\text{pair}}(0) = \psi_{\text{pair}}(2\pi)$ enforced upon completion of the circuit. In Chapter 3 an expression was derived for a wave function in the presence of $\boldsymbol{A}$. Applying this gives

$$\psi = \psi_0 \exp\left( -i \frac{2\pi}{\Phi_0} \oint d\boldsymbol{r} \cdot \boldsymbol{A} \right) \tag{22}$$

The gauge field $\boldsymbol{A}$ is the connection between $\psi_0$ and $\psi$, and its closed line integral gives the holonomy (geometric phase). Thus, flux quantization is readily understood in the context of geometric phase. The $\boldsymbol{A} = 0$ solution is $\psi_0$ which, by definition, satisfies $\psi_0(0) = \psi_0(2\pi)$. The exponential factor in eqn (22) contains the closed-circuit geometric phase, which is gauge invariant.

We need only consider the phase factor in eqn (22) and insure that it satisfies the boundary condition. The closed-circuit integral of $d\boldsymbol{r} \cdot \boldsymbol{A}$ gives $\Phi$, so the quantization condition $\Phi = n_\Phi \Phi_0$ is obtained immediately from eqn (22).

## Gauge Invariance

Assuming that the $\boldsymbol{A}$ in eqn (22) is integrated in a region where its curl is zero (*i.e.*, $\boldsymbol{B} = \nabla \times \boldsymbol{A} = 0$), it can be expressed as the gradient of a scalar, $\nabla\zeta$. The fact that $\boldsymbol{A}$ can be altered by the addition of $\nabla\zeta$ raises the amusing specter of eliminating $\boldsymbol{A}$ completely, as was discussed in some detail in Chapter 3. In other words, add to $\boldsymbol{A}$ its negative. Making $\boldsymbol{A}$ vanish by a gauge transformation is legal mathematically, but what happens?

The outcome is, of course, gauge invariant. The wave function is altered by its concomitant phase transformation such that there is no net effect. Let us see how this works by recalling eqn (14), which gives the current density $\boldsymbol{j}_s$ for a wave function whose phase factor is $e^{i\eta}$:

$$\boldsymbol{j}_s = -\frac{n_s e\hbar}{2m}\nabla\eta - \frac{n_s e^2}{mc}\boldsymbol{A}. \tag{14}$$

Adding and subtracting $(n_s e^2/mc)\nabla\zeta$ on the right hand side gives

$$\boldsymbol{j}_s = -\frac{n_s e\hbar}{2m}\nabla\left(\eta - \frac{2\pi}{\Phi_0}\zeta\right) - \frac{n_s e^2}{mc}(\boldsymbol{A} + \nabla\zeta). \tag{22}$$

$$\frac{2\pi}{\Phi_0} = \frac{hc}{2e}$$

Thus, we see that the phase of the new wave function has been altered according to

$$\eta_{\text{new}} = \eta_{\text{old}} - \frac{2\pi}{\Phi_0}. \tag{23}$$

As a result, there is no net change. When $\nabla\zeta$ is added to $\boldsymbol{A}$ to create $\boldsymbol{A}_{\text{new}} = 0$, the wave function acquires a phase that preserves the effect of the original $\boldsymbol{A}$. Current density and geometric phase are invariant with respect to gauge transformation.

## $\boldsymbol{j}_s = 0$ whereas $\boldsymbol{L} \neq 0$

Finally, it is pointed out that the quantization condition given by eqn (20) can be inferred from the fact that the superconducting current is restricted to the wire's surface; it is zero in the center. In the center, the kinetic momentum $\boldsymbol{\pi} = \boldsymbol{p} + (2e/c)\boldsymbol{A}$ is equal to zero, and therefore the canonical momentum $\boldsymbol{p}$ of a Cooper pair is equal to $-(2e/c)\boldsymbol{A}$. This enables us to integrate the canonical angular momentum, $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$, around the loop:

$$\int_0^{2\pi} \boldsymbol{L}\, d\phi = -\int_0^{2\pi} \left( \boldsymbol{r} \times \frac{2e}{c} \boldsymbol{A} \right) d\phi \tag{24}$$

The magnitude of the left hand side is $2\pi n\hbar$, where $n$ is any integer. The magnitude of the right hand side is equal to $-(2e/c)\Phi$. Thus, eqn (20) is obtained.

The picture is that in the center of the wire the pairs whirl around their centers of mass but they do not progress around the azimuth. They have angular momentum but they do not constitute a current around the wire.

# Appendix 4.

## Time Reversal Symmetry and Intersection Conditions

"People often ask themselves the right questions. Where they fail is in answering the questions they ask themselves, and even there they do not fail by much. A single avenue of reasoning followed to its logical conclusion would bring them straight home to the truth. But they stop just short of it, over and over again. When they have only to reach out and grasp the idea that would explain everything, they decide that the search is hopeless. The search is never hopeless. There is no haystack so large that the needle in it cannot be found. But it takes time, it takes humility and a serious reason for searching."

Time Will Darken It
William Maxwell

# Contents

## Time Reversal and Motion Reversal

Here we consider a symmetry that, for all practical purposes, is rigorous. *Time reversal symmetry* is applicable to all of the systems under consideration and it has a number of important consequences.[1] It is rigorous in the sense that any matrix element that would break it is too small to be of concern. Interactions such as spin-orbit, hyperfine, derivative coupling, etc. preserve it, whereas an external magnetic field breaks it. The introduction of external magnetic fields will be avoided, and the earth's magnetic field is too small to affect, to any measurable extent, a molecule's nonadiabatic dynamics. The only other interactions that break it lie within the realm of particle physics. As far as we are concerned time reversal symmetry is robust.

As with any symmetry, time reversal places restrictions on Hamiltonian matrix elements, causing some to vanish and defining relationships between others. Our goal is to derive these restrictions and use them to determine the number of independent conditions that must be met to achieve an intersection of two or more potential energy surfaces. Other things being equal, on statistical grounds, an increase in the number of independent conditions that must be met to achieve an intersection results in the intersection being less probable. We shall quantify this relationship to the extent possible.

To begin, consider time itself. We exist in a world in which the parameter we call time always increases. Neither reversible nor absolute, it submits to definition only in relative terms. Witness the ubiquitous enlistment of the $t = 0$ reference in the vernacular. What is meant by time reversal symmetry needs to be established at the outset.

All dynamical processes advance into their futures, and this is how we must treat time – asforever increasing. Yet, for systems in which energy is conserved and there are no external magnetic fields,[2] dynamical processes possess a certain forward-backward symmetry. They can proceed in what appears to be either direction, for example, as with a pendulum that swings to and fro, retracing paths used earlier.

Even a complicated trajectory of intricately coupled objects will retrace itself if it is stopped, its constituent momenta are reversed, and it is then allowed to continue. In other

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[1] Time reversal symmetry is the basis of microscopic reversibility, which in turn is the basis of detailed balance.

[2] When interaction with an external magnetic field $\boldsymbol{B}$ is present, time reversal symmetry is broken because the Hamiltonian is no longer a quadratic function of the momenta. For example, consider $H_{int} \propto \boldsymbol{B} \cdot \boldsymbol{J}$, where $\boldsymbol{J}$ is angular momentum. Because $H_{int}$ depends on the orientation of the angular momentum, the interaction energy changes sign for a particular state if the direction of its angular momentum is reversed. Another example involves a practical device, the Faraday isolator. These are used in CD players and to protect microwave tubes. They make use of a steady magnetic field to rotate the polarization of an electromagnetic wave that passes through the device. Reflected waves, though traveling backward relative to the incident waves, have their polarizations rotated by the device *in the same direction* as was the case for the incident waves, that is, rather than reversing the direction of rotation of the incident polarization. This enables reflected radiation to be rejected efficiently by using polarizers. The magnetic field has broken the isotropy of space.

words, its motion has been reversed. It will proceed, however, with time continuing to increase, even though it may *appear* to an observer as if time is receding into the past. Thus, time reversal is a perception, and an illusory one at that. It will appear to recede into the past only if one agrees to use the original trajectory as a reference. Otherwise there is ambiguity concerning which trajectory has been reversed. We shall see that this forward-backward symmetry ensures that in quantum mechanical systems there is at most only a phase difference between dynamical quantities evaluated in the forward and reverse directions.

In the classical world, it is easy to conjure an image of motion that has been reversed at some instant. Suppose a runner was filmed as she ran around a track during a training session. Later, when viewing the film, it is stopped at an arbitrary place. It is then played in reverse at the same speed. This is an example of what time reversal looks like: motion has been reversed or, alternatively, it appears as if time is running backward. Of course, in the case of the runner, time reversal could not really *happen*, because the system is not conservative; there is dissipation. Even if the runner's motion had been reversed at some instant, she would not have been able to retrace her original path unless she had exceptional memory and motor skills.

In the present context, time reversal symmetry has meaning for systems in which energy is conserved. In this case, the classical equations of motion work just as well with $t$ replaced by $-t$. With $\boldsymbol{r}(t)$ changed to $\boldsymbol{r}(-t)$, the velocity of a particle, $\boldsymbol{v}(t) = d\boldsymbol{r}(t)/dt$, becomes $\boldsymbol{v}(-t) = d\boldsymbol{r}(-t)/d(-t) = -d\boldsymbol{r}(-t)/dt$, and acceleration becomes $d^2\boldsymbol{r}(-t)/d(-t)^2 = d^2\boldsymbol{r}(-t)/dt^2$. See Fig. 1, where $\boldsymbol{r}_2, \boldsymbol{v}_2, t_2$ is replaced by $\boldsymbol{r}_2, -\boldsymbol{v}_2, -t_2$. Thus, as long as the particle's dynamics are governed by

$$m\frac{d^2\boldsymbol{r}}{dt^2} = -\nabla V(\boldsymbol{r}), \tag{1}$$

where $V(\boldsymbol{r})$ is a scalar potential, the substitution $t \rightarrow -t$ has no effect, because the equation contains only a second derivative with respect to time. One can obtain the solution to the time reversed problem [*i.e.*, $\boldsymbol{r}(-t)$] by taking the trajectory $\boldsymbol{r}(t)$ and making the substitution $t \rightarrow -t$. Trajectories retrace themselves in what amounts to *motion reversal*.

Motion reversal is not possible if eqn (1) contains an additional term that is proportional to $\boldsymbol{v}$, because then the substitution $t \rightarrow -t$ does not leave eqn (1) unaltered except for $\boldsymbol{r}(t)$ going to $\boldsymbol{r}(-t)$. In other words, the presence of a first derivative with respect to time breaks the symmetry with respect to $t \rightarrow -t$.

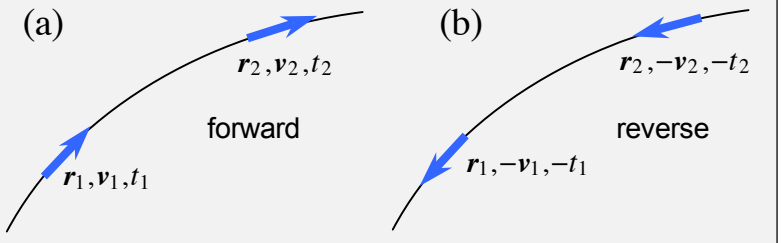


Figure 1. (a) A trajectory proceeds from $\boldsymbol{r}_1(t_1)$ to $\boldsymbol{r}_2(t_2)$. (b) In the motion reversed trajectory, the system proceeds from $\boldsymbol{r}_2(-t_2)$ to $\boldsymbol{r}_1(-t_1)$ with time increasing. Note that $-t_2 < -t_1$, so time increases in going from $-t_2$ to $-t_1$.

For example, the magnetic force on a charge $q$ is given by $q\boldsymbol{v}\times\boldsymbol{B}$, where $\boldsymbol{B}$ is the magnetic field and $\boldsymbol{v}$ is the particle's velocity. This force reverses its direction under motion reversal ($\boldsymbol{v}\rightarrow-\boldsymbol{v}$, with external $\boldsymbol{B}$ unchanged), whereas $-\nabla V(\boldsymbol{r})$ does not.

Figure 1 illustrates motion reversal. In (a), the trajectory proceeds from $t_1$ to $t_2$. In (b), reversed version is indicated. At $t=-t_2$, the velocity is $-\boldsymbol{v}_2$. It is directed oppositely to the velocity $\boldsymbol{v}_2$ in (a) at $t_2$. Likewise, the reversed trajectory at $t=-t_1$ has velocity $-\boldsymbol{v}_1$.

Even though time has been reversed in the sense that $t_2$ has been replaced by $-t_2$ and $t_1$ has been replaced by $-t_1$, the trajectories in (a) and (b) each proceed with time increasing. Specifically, in (a), $t_1<t_2$, so in going from $t_1$ to $t_2$ time increases. In (b), $-t_2<-t_1$, so in going from $-t_2$ to $-t_1$ time also increases. The trajectory in (b) is the motion-reversed version of the trajectory in (a).

In examining Fig. 1 further, we see that the state denoted $\boldsymbol{r}_1,-\boldsymbol{v}_1,-t_1$ in (b) could also have been obtained from $\boldsymbol{r}_2,\boldsymbol{v}_2,t_2$ in (a) by letting time run backwards, that is, going from $t_2$ to $t_1$ and then reversing the direction of the velocity. This is shown in Fig. 2. It is subtler than the motion reversal shown in Fig. 1. In Fig. 2, keep in mind that, as time recedes into the past, the velocity continues to point in the forward direction. The velocity is reversed at $\boldsymbol{r}_1$ (by letting $t\rightarrow-t$) after time has decreased from $t_2$ to $t_1$.

Thus, time (motion) reversal followed by propagation into the future gets us to the same place as propagation into the past followed by time (motion) reversal. This is an example from classical mechanics of what is called time reversal symmetry.

That this symmetry *must* exist follows from special relativity, which treats space and time on equal footing. Spatial symmetry operations include inversion (parity), in which coordinates are inverted according to $\boldsymbol{r}\rightarrow-\boldsymbol{r}$. The equivalent time operation is $t\rightarrow-t$. In other words, parity and time reversal are the same symmetry in 4D spacetime.

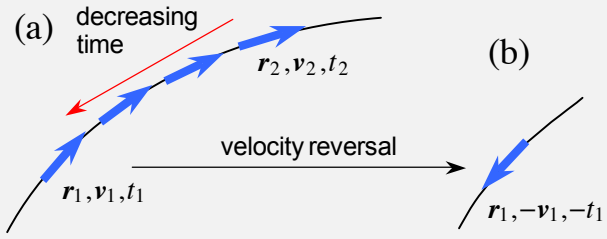


Figure 2. (a) From upper right to lower left, time recedes into the past. At each instant, the velocity points in the forward direction. (b) At $t=t_1$, time reversal causes the velocity to reverse direction. The net effect is the same as the motion reversed case in Fig. 1, *i.e.*, $\boldsymbol{r}_1,-\boldsymbol{v},-t_1$.

## Schrödinger Equation

As noted above, classical systems are symmetric with respect to time reversal in the sense that there exist essentially identical solutions to the equations of motion in the forward and reverse directions, except for the reversal of the directions of the momenta. This augurs for a corresponding quantum mechanical symmetry. In nearly all cases, symmetries that appear in classical mechanics have a quantum counterpart. Quantum mechanically, the time reversal illustrated in Figs. 1 and 2 still applies, though how it manifests remains to be seen. In addition, it will be necessary to deal with spin.

To examine the Schrödinger equation *vis-à-vis* time reversal, a cue is taken from Figs. 1 and 2. Ignoring momentum reversal for the time being, let us replace $t$ with $-t$

$$H\psi(\boldsymbol{r},-t) = i\frac{\partial\psi(\boldsymbol{r},-t)}{\partial(-t)} = -i\frac{\partial\psi(\boldsymbol{r},-t)}{\partial t} \tag{2}$$

where $\hbar = 1$ is used here and hereafter. It is assumed that $H$ is time independent, in which case energy is conserved.

This obviously does not work because the sign in front of $i$ is wrong. $H$ is unchanged by the transformation $t \rightarrow -t$ because it does not contain time explicitly. It contains only coordinates and momenta: $H = H(\boldsymbol{r},\boldsymbol{p})$. The rightmost term, however, changes sign because $\partial(-t) = -\partial t$. Consequently, $\psi(\boldsymbol{r},-t)$ is not a solution of the Schrödinger equation. Thus, the transformation $t \rightarrow -t$ alone does not work. The fact that something else is needed comes as no surprise, because nothing was done to reverse the directions of the momenta. In classical mechanics this happens automatically because the transformation $t \rightarrow -t$ converts $d/dt$ to $d/d(-t) = -d/dt$, thereby reversing the direction of the velocity. In quantum mechanics the operator $\boldsymbol{p} = -i\nabla$ does not depend on time.

This is remedied if the substitution $t \rightarrow -t$ is accompanied by complex conjugation. Equation (2) then becomes

$$H\psi^*(\boldsymbol{r},-t) = i\frac{\partial\psi^*(\boldsymbol{r},-t)}{\partial t}. \tag{3}$$

$H = H^*$ has been used, because for conservative systems $H$ only contains terms that are real. Hereafter it is assumed that $H = H^*$.

Referring to eqn (3), a time reversed Schrödinger equation has been obtained in which $\psi^*(\boldsymbol{r},-t)$ is the wave function. In other words, if $\psi(\boldsymbol{r},t)$ is a solution of the Schrödinger equation, then $\psi^*(\boldsymbol{r},-t)$ is also a solution. The nature of the difference between $\psi(\boldsymbol{r},t)$ and $\psi^*(\boldsymbol{r},-t)$, and under what conditions it is significant, remains to be seen. The prescription used to obtain eqn (3) is based on the classical analog used in Figs. 1 and 2. For example, the use of complex conjugation is intuitive because it reverses the sign of the momentum operator $-i\nabla$, thereby carrying out the transformation $\boldsymbol{p} \rightarrow -\boldsymbol{p}$. Likewise, angular momenta that have classical counterparts ($\boldsymbol{r} \times \boldsymbol{p}$) have their directions reversed under $\boldsymbol{p} \rightarrow -\boldsymbol{p}$. Though we are not yet ready to deal with spin, it is anticipated that its direction will also be reversed.

The above manipulations provide clues. They indicate that the operator for time reversal must carry out complex conjugation, which is a central feature in the development. For cases in which a spatial wave function is used, the prescription given above is complete; it yields the time-reversed wave function.[3] Spin on the other hand, having no spatial wave function, must be treated differently. An operator is needed that operates in the spin (ket) space. For that matter, we should be able to work in the ket space of the

[3] We shall avoid discussion of duality of $[\hat{x},\hat{p}] = i$ in which $\hat{x} = x$ and $\hat{p} = -i\partial_x$ is equivalent to $\hat{x} = i\partial_p$ and $\hat{p} = p$.

other observables as well, *e.g.*, operating on $|l,m\rangle$ rather than on $Y_{l,m}(\theta,\phi)$. Thus, the operation of complex conjugation must be augmented by operations carried out in the ket space that reverse the momenta.

The requirement of complex conjugation is incompatible with having the time reversal operator be either unitary or linear. In addition, the basis functions that are needed to describe an arbitrary wave function span the space of the $H\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r})$ eigenvalue problem, and consequently the time reversed system is describable using the same complete set. Time reversed wave functions are therefore related to the original (non-time-reversed) ones by a unitary transformation. Thus we anticipate that a unitary transformation is involved in time reversal. These and related features are discussed below.

## Time Reversal Operator

A time reversal operator, *T*, is now constructed, and properties of time reversed states and their matrix elements are then examined. The vanishing of, and relationships between, matrix elements yields the number of independent conditions that must be met for potential energy surface intersections to be possible. We start with the action of *T* on the ket $|\alpha\rangle$, yielding the time-reversed ket $|\alpha'\rangle$:

$$|\alpha'\rangle = T|\alpha\rangle . \tag{4}$$

The kets $|\alpha\rangle$ and $|\alpha'\rangle$ are taken to be time dependent, with the understanding that *T* acts at some instant of time. Time reversed quantities are labeled with primes. In keeping with the understanding that all momenta are to be reversed, $|\alpha'\rangle$ corresponds to such a state, the only arbitrariness being a phase factor, $e^{i\delta}$. For example, if $|\alpha\rangle = |\boldsymbol{p}\rangle$, where $\boldsymbol{p}$ is the momentum of a free particle, $|\alpha'\rangle = |-\boldsymbol{p}\rangle e^{i\delta}$.

In eqns (2) and (3), $|\alpha\rangle$ has been assigned a wave function $\psi(\boldsymbol{r},t)$ and the action of *T* on $\psi(\boldsymbol{r},t)$ is that of complex conjugation. The operator *T* does not itself include time evolution. When *T* acts on $\psi(\boldsymbol{r},t)$ it yields $\psi^*(\boldsymbol{r},t)$. It also instructs us to replace *t* with –*t*, thereby yielding the time-reversed state $\psi^*(\boldsymbol{r},-t)$. Likewise, *T* acting on $|\alpha\rangle$ does so at some particular time, say $t_0$. It is understood that the system undergoes time evolution before and after $t_0$, with the nature of the evolution changing abruptly at $t_0$ due to the application of *T*.

To obtain an expression relating the order in which *T* and *H* are applied, thereby revealing the commutator $[H,T]$, the time evolution operator in the Schrödinger picture, $e^{-iHt}$,[4] is applied to a ket that has been time reversed at $t = 0$

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[4] For a time independent Hamiltonian and a small time interval $\delta t$, the Schrödinger equation is:

$$\delta\psi = -iH\psi_0\delta t$$

where $\psi_0 = \psi(t=0)$. Thus, $\psi = (1 - iH\delta t)\psi_0$. For an arbitrary time interval *t*, $\psi(t)$ becomes:

$$\psi(t) = \lim_{N\to\infty}\left(1 - iHt/N\right)^N \psi_0 = e^{-iHt}\psi_0$$

This identifies the time evolution operator in the Schrödinger picture.

$$e^{-iHt}T|\alpha, t=0\rangle\,. \tag{5}$$

Equation (5) yields the time evolution of the time-reversed ket: $T|\alpha, t=0\rangle = |\alpha', t=0\rangle$. This is the quantum version of the trajectory in Fig. 1(b), whose momentum at $-t_2$ is the reverse of that shown in Fig. 1(a) at $t_2$ (albeit with $t_2$ set to zero here), and with propagation taking place from $-t_2$ to $-t_1$, namely, with time increasing.

For a short time interval $\delta t$, eqn (5) can be written

$$(1-iH\delta t)T|\alpha\rangle\,, \tag{6}$$

where $t = 0$ is understood in $|\alpha\rangle$. Time reversal symmetry demands that this state is the same as the one obtained by propagating $|\alpha\rangle$ for a negative time $-\delta t$, and then applying $T$. This is expressed as

$$T(1-iH(-\delta t))|\alpha\rangle\,. \tag{7}$$

By getting to the same place via the alternative routes indicated in (6) and (7), we have brought to the foreground the order in which $H$ and $T$ act. Equating (6) and (7) yields

$$-iH\delta tT|\alpha\rangle = TiH\delta t|\alpha\rangle\,. \tag{8}$$

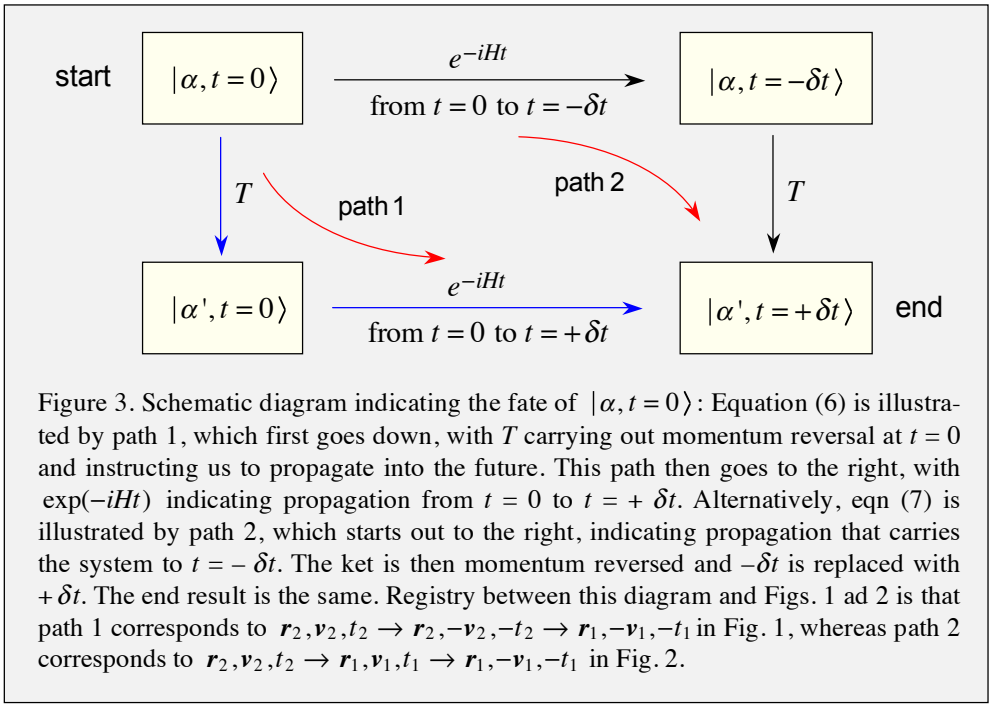


Figure 3. Schematic diagram indicating the fate of $|\alpha, t=0\rangle$: Equation (6) is illustrated by path 1, which first goes down, with $T$ carrying out momentum reversal at $t = 0$ and instructing us to propagate into the future. This path then goes to the right, with $\exp(-iHt)$ indicating propagation from $t = 0$ to $t = +\delta t$. Alternatively, eqn (7) is illustrated by path 2, which starts out to the right, indicating propagation that carries the system to $t = -\delta t$. The ket is then momentum reversed and $-\delta t$ is replaced with $+\delta t$. The end result is the same. Registry between this diagram and Figs. 1 ad 2 is that path 1 corresponds to $\boldsymbol{r}_2, \boldsymbol{v}_2, t_2 \to \boldsymbol{r}_2, -\boldsymbol{v}_2, -t_2 \to \boldsymbol{r}_1, -\boldsymbol{v}_1, -t_1$ in Fig. 1, whereas path 2 corresponds to $\boldsymbol{r}_2, \boldsymbol{v}_2, t_2 \to \boldsymbol{r}_1, \boldsymbol{v}_1, t_1 \to \boldsymbol{r}_1, -\boldsymbol{v}_1, -t_1$ in Fig. 2.

Figure 3 illustrates the two paths that arrive at the same place. Equation (8) is valid for an arbitrary ket, and $\delta t$ can be cancelled, so it reduces to

$$iHT + TiH = 0. \tag{9}$$

Referring to eqn (9), notice that we have been careful to not move *i* to the left of *T* in the term *TiH*. We know from the previous discussion that *T* brings about complex conjugation of the quantity to its right. Had we assumed that *TiH* is equal to *iTH*, an unacceptable result would have been obtained: $HT = -TH$ (anti-commutation). In this case, letting $HT = -TH$ act on an eigenket of *H* would have yielded:

$$HT|E_n\rangle = -TH|E_n\rangle = -E_nT|E_n\rangle \tag{10}$$

which makes no sense. According to eqn (10), the time reversed state of a free particle has a negative kinetic energy that is unbounded in the negative direction. However, kinetic energy is always positive real, and therefore eqn (10) is incorrect, *i.e.*, $TiH \neq iTH$. Rather, eqn (9) must yield

$$[H, T] = 0, \tag{11}$$

in which case *TiH* must be equal to $-iTH$. This is obvious because $Ti = -iT$.

The fact that $[H, T]$ must be zero follows from the fact that *T* reverses the direction of $\boldsymbol{p}$, whereas *H* (a scalar) is independent of the direction of $\boldsymbol{p}$, *i.e.*, it is a function of the scalar $\boldsymbol{p}\cdot\boldsymbol{p} = p^2$. Because *T* brings about complex conjugation it is a unique operator. This feature prevents it from being linear and unitary, as discussed below.

## *T* is Antiunitary

The fact that the time reversal operator *T* is neither linear nor unitary means that some of the manipulations we are familiar with in quantum mechanics need to be reconsidered. After doing this, matrix elements of *H* will be examined.

The definition of a general linear operator *L* is that it has the property

$$L(c_1|1\rangle + c_2|2\rangle + ...) = c_1L|1\rangle + c_2L|2\rangle + .... \tag{12}$$

where $|1\rangle$, $|2\rangle$, etc. are arbitrary kets and the $c_i$ are constants that are in general complex. On the other hand, a general antilinear operator *A* obeys the rule

$$\boxed{A(c_1|1\rangle + c_2|2\rangle + ...) = c_1^*A|1\rangle + c_2^*A|2\rangle + ....} \tag{13}$$

This property, in which the antilinear operator carries out complex conjugation, identifies $T$ as antilinear. From eqn (13) it follows that the product of two antilinear operators is a linear operator

$$A_1A_2\left(c_1|1\rangle + c_2|2\rangle + ...\right) = c_1A_1A_2|1\rangle + c_2A_1A_2|2\rangle + .... \tag{14}$$

Extending this, the product $A_1A_2...A_n$ is a linear operator if $n$ is even, whereas it is an antilinear operator if $n$ is odd. Obviously, $A_1L$ is antilinear, $A_1A_2L$ is linear, etc.

The definition of an *antiunitary* operator is that it is antilinear and satisfies $|\langle\alpha'|\beta'\rangle| = |\langle\alpha|\beta\rangle|$. It preserves the norm of the scalar product. The prime denotes a state that is transformed by an antiunitary operator. The phase relationship between $\langle\alpha'|\beta'\rangle$ and $\langle\alpha|\beta\rangle$ is yet to be determined.

## Complex Conjugation Revisited

In its simplest form, $T$ can be taken to be the complex conjugation operator $K$ plus the rule $t \rightarrow t'$. This preserves the norms of state vectors and satisfies eqn (13). Applying $K$ to the Schrödinger equation yields

$$HK\psi(\boldsymbol{r},t) = -i\,\frac{\partial K\psi(\boldsymbol{r},t)}{\partial t}, \tag{15}$$

and with $K\psi(\boldsymbol{r},t) = \psi^*(\boldsymbol{r},t)$ and $t$ replaced by $-t$, this becomes

$$H\psi^*(\boldsymbol{r},-t) = i\frac{\partial\psi^*(\boldsymbol{r},-t)}{\partial t}. \tag{16}$$

In this case, in which the state ket is represented in a position basis (with a spatial wave function) $K$ does all of the work. An example is the momentum eigenfunction $\exp\left(i(kx-\omega t)\right)$. The momentum points in the $\boldsymbol{e}_x$ direction, and as $t$ increases the wave advances with a phase velocity $\omega/k$. Applying $K$ yields $\exp\left(-i(kx-\omega t)\right)$, and replacing $t$ with $-t$ yields $\exp\left(-i(kx+\omega t)\right)$. The momentum of the transformed wave points in the $-\boldsymbol{e}_x$ direction, and as $t$ increases the wave advances with a phase velocity of $-\omega/k$, *i.e.*, in the $-\boldsymbol{e}_x$ direction. The wave function $\exp\left(-i(kx+\omega t)\right)$ is the time-reversed version of $\exp\left(i(kx-\omega t)\right)$.

## Unitarity

As mentioned earlier, $T$ in general must be able to carry out a unitary transformation, for example, when operating in the ket space. Thus, $T$ is written

$$T = UK, \tag{17}$$

where $U$ is a unitary operator. Note that, in general, $UK \neq KU$.

The $U$ in eqn (17) is not to be taken as the unitary time evolution operator $e^{-iHt}$. Recall that the latter was used to propagate a time-reversed state, as well as to propagate a state prior to its time reversal. This gave us eqns (6) and (7). The $U$ in eqn (17) is used to carry out a transformation that takes us from the original state to the time reversed one.[5] In the case of the wave function $\psi(\boldsymbol{r},t)$, $K$ plus $t \rightarrow t'$ does everything so $U$ equals one.

The role played by the time evolution operator $e^{-iHt}$ can be illustrated by applying it to a time reversed system. The application of $T$ at $t=0$ to a Hermitian operator $Op$ acting on $|\alpha\rangle$ gives $TOp(0)|\alpha\rangle = TOp(0)T^{-1}T|\alpha\rangle$, which identifies the time reversed operator $TOp(0)T^{-1}$. Applying $e^{-iHt}$ then yields

$$e^{-iHt}TOp(0)T^{-1}e^{iHt}. \tag{18}$$

If we now move $T$ and $T^{-1}$ through the exponentials (commutes with $H$), *i.e.*, to the left and right, respectively, the expression given by eqn (18) becomes

$$Te^{iHt}Op(0)e^{-iHt}T^{-1} = Te^{-iH(-t)}Op(0)e^{iH(-t)}T^{-1}. \tag{19}$$

The right hand side represents the time reversal of an operator $Op$ that has evolved backward in time from $t = 0$ to $-t$. Again, we see the equivalence of the two ways to arrive at the same place.

In the construction of $T$ given by $T = UK$, the individual roles played by $U$ and $K$ are in general basis dependent. Of course the product $UK$ cannot depend on the basis. Thus, $U$ and $K$ can each depend on the basis, as long as they do so in such a way that their product $UK$ does not.

The role of the operator $K$ is transparent; it takes the complex conjugate of entities to its right. If it operates on a wave function it yields the complex conjugate of the wave function, including any expansion coefficients, *e.g.*, $K(c_1\psi_1 + c_2\psi_2) = c_1^*\psi_1^* + c_2^*\psi_2^*$. In this case, the action of $K$ automatically reverses the momenta. Following the application of $K$, the operator $e^{-iHt}$ propagates the system forward in time but in the reverse direction, *i.e.*, yielding the motion reversed state.

As mentioned earlier, when $K$ operates on a spatial wave function, rather than its corresponding ket, it automatically reverses the momenta. (Momentum does not appear explicitly in $\psi(\boldsymbol{r},t)$; it is manifest in the spatial variation of $\psi(\boldsymbol{r},t)$, which changes upon complex conjugation.) This is why $K$ acting alone did everything that was needed to obtain the time-reversed wave function in eqn (16). All we had to do was make the substitution $t \rightarrow -t$.

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[5] The operator $U$ can be expressed as: $\sum_n |n'\rangle\langle n|$, where $|n'\rangle$ is the time reversed ket corresponding to $|n\rangle$. The sum is interpreted as having one index ($n$), not two ($n$ and $n'$). The prime denotes the time-reversed counterpart. When $n$ changes, $n'$ changes along with it. The $|n\rangle$ basis is complete, spanning the same space as the $|n'\rangle$ basis. Often the same basis is used for both. $U$ serves to transform a given vector into its time-reversed counterpart.

When dealing with the corresponding kets, $U$ is needed to reverse momenta. A simple example is $|l,m\rangle \rightarrow |l,-m\rangle$, where $m \rightarrow -m$ reverses the direction of the angular momentum. $K$ acting on the ket $|l,m\rangle$ does nothing, because the ket is a vector in Hilbert space whose indices $l$ and $m$ denote quantum numbers. Therefore, $|l,m\rangle$ is real to within a multiplicative global phase factor that plays no significant role and can be neglected, and the action of $K$ on $|l,m\rangle$ just gives $|l,m\rangle$. The role of the unitary transformation $U$ is then to convert $|l,m\rangle$ to $|l,-m\rangle$ so that $UK$ gives the time-reversed state. Had $|l,m\rangle$ been expressed in the position basis $Y_{l,m}(\theta,\phi)$ prior to applying $T$, the application of $K$ would have given $Y_{l,m}(\theta,\phi)^*$. However, the spherical harmonics obey the relationship

$$Y_{l,m}(\theta,\phi)^* = (-1)^m Y_{l,-m}(\theta,\phi). \tag{20}$$

In this case $K$ does everything, whereas $U$ does nothing (multiplication by one).

For kets that can be assigned a position representation, the operations $K$ and $U$ can be carried out with either the kets or their corresponding wave functions. With spins, however, there is no such option. We must work with the kets.

To express these ideas in general terms, we say that $K|i\rangle = |i\rangle$, where $|i\rangle$ denotes a member of the basis, and the subsequent application of $U$ that is needed to transform $|i\rangle$ to its time reversed counterpart is given by

$$\boxed{U|i\rangle = \sum_n |n'\rangle\langle n|i\rangle = |i'\rangle.} \tag{21}$$

Whereas $K$ does nothing to $|i\rangle$, $U$ does everything, changing $|i\rangle$ to $|i'\rangle$. Carrying this further, when $K$ operates on a ket $|\alpha\rangle$ that is a linear combination of basis kets, it takes the complex conjugate of the expansion coefficients:

$$K|\alpha\rangle = \sum_j |j\rangle\langle j|\alpha\rangle^*. \tag{22}$$

If $U$ is now applied we have:

$$UK|\alpha\rangle = U\sum_j |j\rangle\langle j|\alpha\rangle^* = \sum_{n,j} |n'\rangle\langle n|j\rangle\langle j|\alpha\rangle^* = \sum_j |j'\rangle\langle j|\alpha\rangle^*. \tag{23}$$

It is assumed that $|n\rangle$ and $|j\rangle$ bases are the same, in which case $\langle n|j\rangle = \delta_{nj}$. In this case, both $K$ and $U$ did something. The ket $|\alpha\rangle$ is completely general. It can be a base ket (*e.g.* an eigenket) or a linear combination of base kets.

The above examples illustrate the fact that, for a given basis, $K$ may do nothing to an eigenfunction, whereas for a different basis $K$ may alter the same eigenfunction. To illustrate this, consider spin ½. In the $s_z$ basis $|+\rangle$ and $|-\rangle$, the $s_y$ eigenkets are

$$|s_y \pm\rangle = \tfrac{1}{\sqrt{2}}\big(|+\rangle \pm i|-\rangle\big) \tag{24}$$

and operating with $K$ yields

$$K|s_y +\rangle = |s_y -\rangle \qquad K|s_y -\rangle = |s_y +\rangle \tag{25}$$

Thus, $K$ has carried out momentum reversal, so $U$ does not have to do this. Its role instead is to produce a needed phase change. This is left as an exercise.

## Fundamental Commutator Relations

In the 1D quantum version of the classical system indicated in Fig. 1, the position operator $x$ is unchanged by time reversal, whereas the direction of its canonically conjugate momentum operator $p$ is reversed:

$$x' = T\,x\,T^{-1} = x \qquad p' = T\,p\,T^{-1} = -p \tag{26}$$

Thus, we anticipate that the commutator: $[x,p] = i$, undergoes a sign change under time reversal. Sure enough: $T\,i\,T^{-1} = -i$ and $T\,[x,p]T^{-1} = [TxT^{-1}, TpT^{-1}] = [x',p']$. Note that the wave function $\psi$ that is understood when we write $[x,p] = i$ is now $T\psi$ when we write $[x',p'] = -i$ because $T$ that acts on $i$ moves to the right of $i$ after it has acted:

$$T\,[x,p]\psi = T\,i\psi \implies \big(TxT^{-1}, TpT^{-1}\big)T\psi = -iT\psi$$

In the time-reversed system, the fundamental commutator relation has changed sign. This occurs because $[x,p] = i$ is written with respect to the reference system of $x$ and $p$. Quantities obtained by using $[x,p] = i$ will differ by phase factors when viewed from the time reversed reference system, where $p$ has been transformed to $p' = -p$. We can assure ourselves that there cannot be more than a phase difference by recalling the ambiguity that exists concerning the labeling of the reversed and non-reversed systems. The matrix elements that describe dynamical processes cannot have different magnitudes in the time reversed and non-time-reversed systems, that is, $|\langle\alpha|Op|\beta\rangle| = |\langle\alpha'|Op'|\beta'\rangle|$. They can, however, have different phases.

This feature also appears in the theory of angular momentum. The angular momentum of a rotating object obeys the commutator relation $[J_x, J_y] = iJ_z$, where the angular momentum is defined relative to a lab-fixed axis system. Applying time reversal yields

$$\big[J_x', J_y'\big] = -iJ_z'. \tag{27}$$

This differs in sign from the usual relation $[J_x, J_y] = iJ_z$. One might wonder why there is a sign difference. What does this correspond to physically?

The primed system corresponds to the reference system given by the molecular axes. The rotating entity has the counter-clockwise sense of rotation shown in Fig. 4 , with its angular momentum aligned parallel to the *z*-axis. If one were sitting on the molecule (stationary relative to its axes), it would appear as if the angular momentum vector was rotating around the molecule, but in the reverse sense, *i.e.*, clockwise. The relative motion of the object and its angular momentum vector would appear to be reversed in the molecule and lab reference frames.

Figure 4. An object rotates in a lab reference system. Its angular momentum ***J*** lies parallel to the *z*-axis.

I need help with the graphics here!

## Matrix Elements

As stated earlier, a necessary condition on the time reversal operator is that it preserves the norms of all matrix elements. This ensures that dynamical processes proceeding in the reverse direction are the same (except for the motion reversal itself) as those proceeding in the forward direction. In the material that follows, this stipulation will be shown to yield a phase relationship. In addition, relationships between matrix elements will be revealed that limit the number of intersection conditions that derive from the requirements: (i) that all diagonal matrix elements have the same value, and (ii) that all off-diagonal matrix elements vanish.

The antilinear property of $T$ leads to subtle relationships between matrix elements, including those that couple time reversed and non-time-reversed states. We have become accustomed to writing matrix elements in the form $\langle\alpha|L|\beta\rangle$, where $L$ is a general linear operator, without worrying about whether $L$ operates to its right or its left. It does not matter. No difference results from operating in one direction versus the other. Thus, there is no need to use parentheses to distinguish $\big(\langle\alpha|L\big)|\beta\rangle$ from $\langle\alpha|\big(L|\beta\rangle\big)$. This is not the case for the general antilinear operator $A$.

Let us express $|\beta\rangle$ as

$$|\beta\rangle = c_{b1}|b_1\rangle + c_{b2}|b_2\rangle . \tag{28}$$

The coefficients $c_{b1}$ and $c_{b2}$ are complex and the kets $|b_1\rangle$ and $|b_2\rangle$ are real. The use of more than a single term on the right hand side of eqn (28) is to ensure generality. Following eqn (13), $A$ acting on $|\beta\rangle$ yields

$$A|\beta\rangle = c_{b1}{}^{*}A|b_1\rangle + c_{b2}{}^{*}A|b_2\rangle . \tag{29}$$

Likewise, $A$ acting on $|\alpha\rangle$ yields

$$A|\alpha\rangle = c_{a1}{}^{*}A|a_1\rangle + c_{a2}{}^{*}A|a_2\rangle\,, \tag{30}$$

whose adjoint is

$$\big(A|\alpha\rangle\big)^{\dagger} = \big(c_{a1}{}^{*}A|a_1\rangle + c_{a2}{}^{*}A|a_2\rangle\big)^{\dagger} = c_{a1}\big(\langle a_1|A\big) + c_{a2}\big(\langle a_2|A\big) \equiv \big(\langle\alpha|A\big)\,. \tag{31}$$

Thus, the inner product $\big(\langle\alpha|A\big)|\beta\rangle$ is given by

$$\begin{aligned}\big(\langle\alpha|A\big)|\beta\rangle &= c_{a1}c_{b1}\big(\langle a_1|A\big)|b_1\rangle + c_{a1}c_{b2}\big(\langle a_1|A\big)|b_2\rangle \\ &+ c_{a2}c_{b1}\big(\langle a_2|A\big)|b_1\rangle + c_{a2}c_{b2}\big(\langle a_2|A\big)|b_2\rangle\,.\end{aligned} \tag{32}$$

The parentheses are now removed because the kets are real. In other words, with nothing for *A* to complex conjugate, it is welcome to operate in either direction.

$$\begin{aligned}\big(\langle\alpha|A\big)|\beta\rangle &= c_{a1}c_{b1}\langle a_1|A|b_1\rangle + c_{a1}c_{b2}\langle a_1|A|b_2\rangle \\ &+ c_{a2}c_{b1}\langle a_2|A|b_1\rangle + c_{a2}c_{b2}\langle a_2|A|b_2\rangle\,.\end{aligned} \tag{33}$$

Thus, *A* behaves as a linear operator in matrix elements $\langle a_i|A|b_j\rangle$. Its antilinear property is used to take complex conjugates of the expansion coefficients $c_{a1}$ and $c_{a2}$, for example according to eqn (30). The analogous expression for *A* operating to the right is

$$\begin{aligned}\langle\alpha|\big(A|\beta\rangle\big) &= c_{a1}{}^{*}c_{b1}{}^{*}\langle a_1|A|b_1\rangle + c_{a1}{}^{*}c_{b2}{}^{*}\langle a_1|A|b_2\rangle \\ &+ c_{a2}{}^{*}c_{b1}{}^{*}\langle a_2|A|b_1\rangle + c_{a2}{}^{*}c_{b2}{}^{*}\langle a_2|A|b_2\rangle\end{aligned} \tag{34}$$

In comparing eqns (33) and (34), we see that $\big(\langle\alpha|A\big)|\beta\rangle$ differs from $\langle\alpha|\big(A|\beta\rangle\big)$ only by complex conjugation

$$\big(\langle\alpha|A\big)|\beta\rangle = \langle\alpha|\big(A|\beta\rangle\big)^{*}\,. \tag{35}$$

Thus, setting $A = T$ yields: $\langle\alpha'|\beta\rangle = \langle\alpha|\beta'\rangle^{*}$.

Let us now consider matrix elements of a general Hermitian operator in the time-reversed system $\langle\alpha'|Op'|\beta'\rangle$. Using $T = UK$ and $K = K^{-1}$ this becomes

$$\langle\alpha'|Op'|\beta'\rangle = \langle\alpha|KU^{-1}UKOpKU^{-1}UK|\beta\rangle\,. \tag{36}$$

The rightmost *K* operating on $|\beta\rangle$ yields: $c_{b1}{}^{*}|b_1\rangle + c_{b2}{}^{*}|b_2\rangle$. Likewise, leftmost *K* operating on $\langle\alpha|$ yields $c_{a1}\langle a_1| + c_{a2}\langle a_2|$. The *K* to the left of *Op* operates on *Op* and

passes to its right, where it meets another $K$. They annihilate because $K^2 = 1$. The unitary operators also disappear ($U^{-1}U = 1$). Introducing these facts into the right hand side of eqn (36) yields:

$$\langle \alpha' | Op' | \beta' \rangle = \langle \alpha | Op | \beta \rangle^* . \tag{37}$$

Thus, using $Op = H$ yields for the (real) diagonal matrix elements: $H_{\alpha\alpha} = H_{\alpha'\alpha'}$. For off-diagonal elements, the fact that $H_{\alpha'\beta'} = H_{\alpha\beta}^*$ limits the number of independent parameters that need to be varied to bring about an intersection. Finally, we can use $Op = 1$ to write:

$$\langle \alpha' | \beta' \rangle = \langle \alpha | \beta \rangle^* \tag{38}$$

Together with the antilinear property, this identifies $T$ as an antiunitary operator.

Given that the time reversal operator changes the signs of the momenta, $Op$ is either even or odd with respect to time reversal: $Op' = \pm Op$, with the sign depending on the power to which the momenta appear in $Op$. For example, if $Op$ is proportional to $\boldsymbol{p}$, then $Op' = -Op$. The Hamiltonian, being a scalar, is always even, *i.e.*, $H' = H$.

## Action of *T* on Kets

When applying $T$ an even number of times, all observables must be returned to their original values and the original ket must be recovered to within a phase factor that we shall call $c$. Let us determine the possible values that $c$ can assume, and the nature of the states to which these $c$ values correspond. For example, applying $T$ twice in succession yields

$$T^2 |\alpha\rangle = |\alpha''\rangle = c|\alpha\rangle \tag{39}$$

The double prime indicates the application of $T^2$, and we see that $|c| = 1$. Because the $|\alpha\rangle$ in eqn (39) is arbitrary, it can be replaced by its time reversed counterpart $|\alpha'\rangle$, in which case $T^2|\alpha'\rangle = c|\alpha'\rangle$. However, because $T^2|\alpha'\rangle = T|\alpha''\rangle = Tc|\alpha\rangle = c^*|\alpha'\rangle$, we see that: $c^*|\alpha'\rangle = c|\alpha'\rangle$, *i.e.*, $c$ is real. Also, because its magnitude is one, it has just two possible values, $+1$ and $-1$.

Equation (38), with $|\beta\rangle = |\alpha'\rangle$, can be used to write

$$\langle \alpha' | \alpha \rangle = \langle \alpha' | \alpha'' \rangle = c \langle \alpha' | \alpha \rangle . \tag{40}$$

Consider $c = +1$ with $|\alpha\rangle$ non-degenerate. In this case, eqn (40) indicates that $\langle \alpha' | \alpha \rangle \neq 0$. Otherwise, it would not be possible to assign the value $+1$ to $c$. Thus, $|\alpha\rangle$ and $|\alpha'\rangle$ cannot be mutually orthogonal, nor can they be made mutually orthogonal. Also, to see that $|\alpha\rangle$ and $|\alpha'\rangle$ have the same energy, let $T$ act on $H|\alpha\rangle = E|\alpha\rangle$:

$$TH|\alpha\rangle = TE|\alpha\rangle \tag{41}$$

The fact that $TH = HT$ and $E$ is real enables eqn (41) to be written:

$$H|\alpha'\rangle = E|\alpha'\rangle \tag{42}$$

In consideration of the facts that: (i) $|\alpha\rangle$ is non-degenerate; (ii) $|\alpha\rangle$ and $|\alpha'\rangle$ have the same energy; and (iii) $|\alpha\rangle$ and $|\alpha'\rangle$ cannot be chosen to be orthogonal to one another for any choice of $|\alpha\rangle$, they must be the same state, differing by at most a global phase factor. Moreover, wave functions associated with $|\alpha\rangle$ and $|\alpha'\rangle$ differ by complex conjugation, and therefore the wave functions of the reversed and non-reversed states must be real functions that can differ only by a multiplicative phase factor that is independent of the coordinates. This is the origin of the fact that the off-diagonal matrix elements can be assumed real for $c = +1$. Soon we shall identify the nature of the $c = +1$ states.

When the system is degenerate, the identification made above, namely, that $|\alpha'\rangle$ and $|\alpha\rangle$ are the same state, does not hold. The inner product $\langle\alpha'|\alpha\rangle$ can vanish with $E_\alpha = E_{\alpha'}$. An example is the spherical harmonics $Y_{l,m}(\theta,\phi)$, which are complex. When they are eigenstates, there is spatial isotropy and consequent degeneracy, with $E_{l,m} = E_{l,m'}$. In this case, the time reversed and non-time-reversed states (*i.e.*, $m$ and $m' = m$) are orthogonal to one another. Another way to think of this is to enlist the fact that degeneracy arises from symmetry. In the case of the isotropy of space, this symmetry provides good quantum numbers ($m$) and orthogonal states ($Y_{l,m}$ and $Y_{l,m'}$).

It remains to examine matrix elements $H_{\alpha\beta'}$. This is easily accomplished for $c = \pm 1$. Equation (37) with $|\beta\rangle$ replaced by $|\beta'\rangle$ and $Op = H$ gives:

$$H_{\alpha\beta'} = \langle\alpha'|H|\beta''\rangle^* = cH_{\alpha'\beta}{}^* \tag{43}$$

where $c$ can be $+1$ or $-1$. For $c = +1$, we have $|\alpha'\rangle = |\alpha\rangle$ and $|\beta'\rangle = |\beta\rangle$. Thus, eqn (43) reduces to $H_{\alpha\beta} = H_{\alpha\beta}{}^*$, *i.e.*, off-diagonal matrix elements are real.

This completes our derivation of relationships that exist among the Hamiltonian matrix elements due to time reversal symmetry. Figure 5 lists results for two intersecting surfaces $|\alpha\rangle$ and $|\beta\rangle$ and their time reversed counterparts $|\alpha'\rangle$ and $|\beta'\rangle$. The list of conditions in Fig. 5 is incomplete, as restrictions due to point group symmetry need to be added. This includes combined effects of point group and time reversal symmetries. Some of the entries in the lower two boxes will be obtained in subsequent sections, but they are included here *vide infra* in order to have them all in one place.

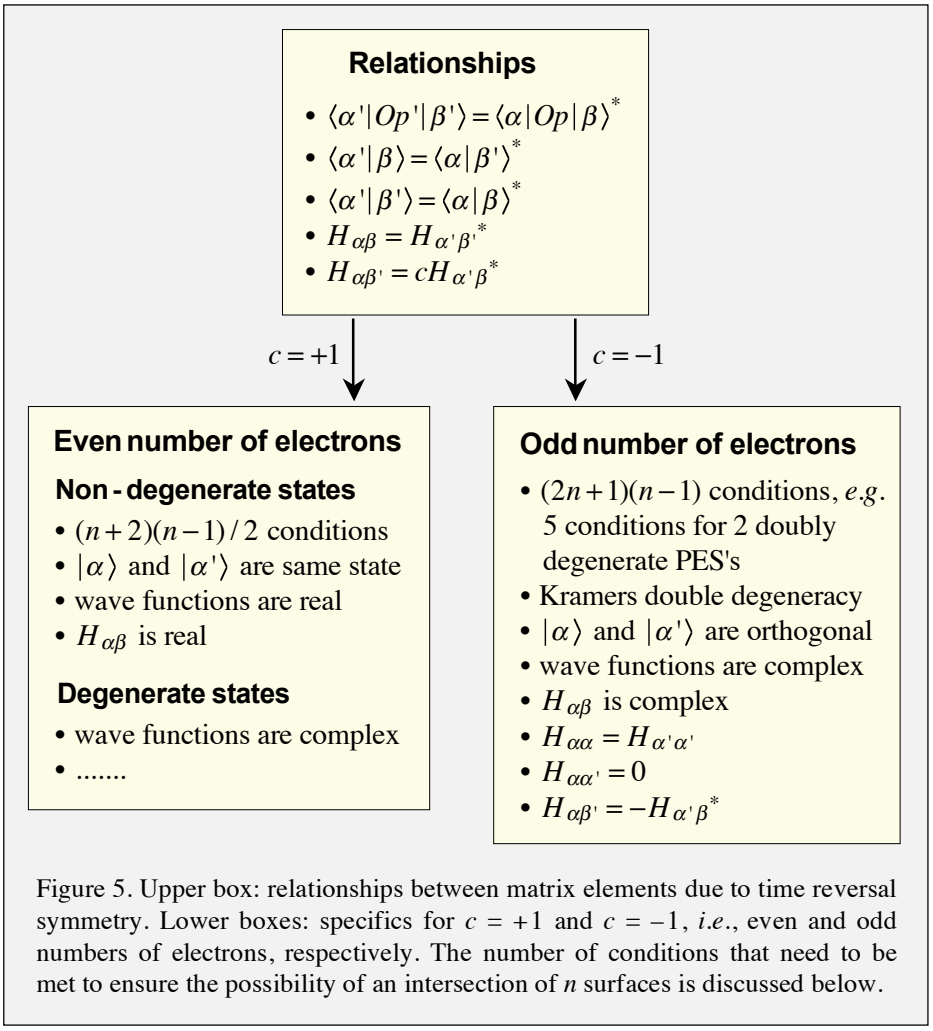


Figure 5. Upper box: relationships between matrix elements due to time reversal symmetry. Lower boxes: specifics for $c = +1$ and $c = -1$, *i.e.*, even and odd numbers of electrons, respectively. The number of conditions that need to be met to ensure the possibility of an intersection of $n$ surfaces is discussed below.

## Kramers Degeneracy

As shown above, for $c = +1$ and non-degenerate states, $\langle\alpha|\alpha'\rangle$ does not vanish regardless of the choice of $|\alpha\rangle$. Therefore $|\alpha\rangle$ and $|\alpha'\rangle$ each represent the same state. On the other hand, referring to eqn (40), for $c = -1$, $\langle\alpha|\alpha'\rangle$ is equal to zero for every possible choice of $|\alpha\rangle$. Thus, $|\alpha'\rangle$ is always orthogonal to $|\alpha\rangle$ and therefore these states are distinct. Given that they are also degenerate, this result, which is valid for all systems that obey time reversal symmetry, illustrates the fact that $c = -1$ is associated with a double degeneracy that is independent of spatial coordinates. The only way to remove this degeneracy is to eliminate time reversal symmetry, which can be achieved through the introduction of an external magnetic field.

For the case $c = -1$, the fact that applying $T$ twice in succession changes the sign of the ket implicates spin ½. Namely, it is well known that a $2\pi$ rotation in coordinate space

of a spin ½ ket results in its sign change. Participation of spin ½ is also suspected on the basis of the fact that the twofold degeneracy is removed through the application of an external magnetic field, *i.e.*, recall that when $H$ is proportional to $\boldsymbol{s}\cdot\boldsymbol{B}$, where $\boldsymbol{B}$ is an external magnetic field, there is a spin doublet.

The time reversal operator inverts the directions of all angular momenta. Thus, it carries out a rotation about the $y$-axis, through an angle $\pi$, of the ket $|J,M\rangle$. This yields $|J,-M\rangle$, where the quantum number $J$ can be either integer or half-integer. The $y$-axis is chosen, rather than the $x$-axis, in accord with the convention for spin ½, in which the matrix elements of the operator for rotation about the $y$-axis are purely real. Applying $T$ a second time returns $\boldsymbol{J}$ to its original orientation and yields a ket that is either the same as the original one (*i.e.*, in the case of integral angular momentum) or reversed in sign (*i.e.*, in the case of half-integral angular momentum).

To illustrate this, some results from the theory of angular momentum will be used. The general theory is discussed in many books. A good one is Thompson.

## Rotation

The rotation of a ket through an angle $\phi$ about an arbitrary axis whose direction is parallel to the unit vector $\boldsymbol{e}_n$ is achieved by using the unitary operator $R_n(\phi)$:

$$R_n(\phi) = \exp\left(-i\phi\boldsymbol{J}\cdot\boldsymbol{e}_n\right), \tag{44}$$

where $\boldsymbol{J}$ is the total angular momentum. As mentioned above, we shall use $\boldsymbol{e}_n = \boldsymbol{e}_y$. In this case, $\phi$ is replaced by $\theta$ to be consistent with the standard notation for the polar angle relative to the $z$-axis (Fig. 6). Thus, eqn (44) becomes:

$$R_n(\theta)|J,M\rangle = \exp\left(-i\theta J_y\right)|J,M\rangle \tag{45}$$

To transform $|J,M\rangle$ into $|J,-M\rangle$, the polar angle $\theta$ in eqn (45) is set equal to $\pi$, in which case $R_n(\theta)$ becomes $\exp\left(-i\pi J_y\right)$. If $|J,M\rangle$ has associated with it a multiplicative phase factor $e^{i\delta}$ (so that it can be written $e^{i\delta}|J,M\rangle$, with $|J,M\rangle$ real), applying the operator $T = UK$ (with $U = R_y$) to $e^{i\delta}|J,M\rangle$ yields:

$$T\,e^{i\delta}|J,M\rangle = \exp\left(-i\theta J_y\right)Ke^{i\delta}|J,M\rangle = \exp\left(-i\pi J_y\right)e^{-i\delta}|J,M\rangle \tag{46}$$

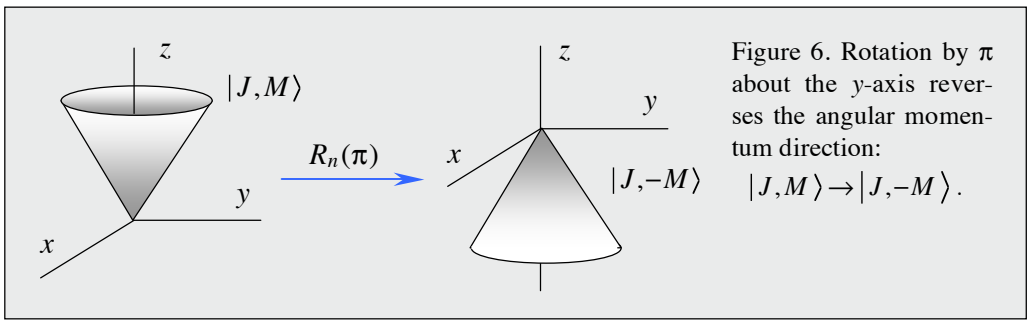


Figure 6. Rotation by $\pi$ about the $y$-axis reverses the angular momentum direction: $|J,M\rangle \rightarrow |J,-M\rangle$.

Applying $T$ again yields:

$$T^2 e^{i\delta}|J,M\rangle = \exp\left(-i2\pi J_y\right)e^{i\delta}|J,M\rangle \tag{47}$$

The fact that $K$ commutes with $\exp(-i\theta J_y)$ has been used. The phase factor $e^{i\delta}$ of the original ket, *i.e.*, $e^{i\delta}|J,M\rangle$, is seen to play no role. Thus, we see that, as far as $T^2$ is concerned, the ket can have associated with it an arbitrary phase factor without affecting the $T^2$ operation.

This provides insight into the fact that $T^2|\alpha\rangle = \pm|\alpha\rangle\,|\alpha\rangle$. The sign associated with $T^2$ is determined by the transformation property of $|\alpha\rangle$ with respect to the operation $R_n(\theta)$. Let us illustrate this for cases: (i) spin ½; (ii) even $J$ whose wave functions are spherical harmonics; and (iii) even $J$ associated with integral spin. Starting with spin ½, we write:

$$T|+\rangle = \exp\left(-i\pi s_y\right)|+\rangle \tag{48}$$

With $\boldsymbol{s} = \tfrac{1}{2}\boldsymbol{\sigma}$, where the $\sigma_i$ are the Pauli matrices represented in the $s_z$ basis, eqn (48) assumes a simple form:

$$T|+\rangle = \exp\left(-i\pi\tfrac{1}{2}\sigma_2\right)|+\rangle = \left(1+\left(-i\pi\tfrac{1}{2}\sigma_2\right)+\tfrac{1}{2}\left(-i\pi\tfrac{1}{2}\sigma_2\right)^2+\ldots\right)|+\rangle\,. \tag{49}$$

With a little algebra, this becomes

$$T|+\rangle = -i\sigma_2|+\rangle\,. \tag{50}$$

Going from eqn (49) to (50) is left as an exercise. Time reversal has caused $|+\rangle$ to become $-i\sigma_2|+\rangle = |-\rangle$:

$$-i\sigma_2|+\rangle = -i\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = \begin{pmatrix}0\\1\end{pmatrix} = |-\rangle\,. \tag{51}$$

Upon applying $T$ again, $|-\rangle$ is rotated through an angle $\theta = \pi$

$$T^2|+\rangle = (-i\sigma_2)(-i\sigma_2)|+\rangle = -i\sigma_2|-\rangle = -i\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} = -|+\rangle\,. \tag{52}$$

This shows that reversing the direction of the spin twice in succession (which is equivalent to a $2\pi$ rotation of the ket about the $y$-axis) reverses the sign of the ket. For the case of even $J$ and spherical harmonics, applying $T$ is equivalent to applying $K$

$$T\,Y_{l,m}(\theta,\phi) = Y_{l,m}(\theta,\phi)^* = (-1)^m Y_{l,-m}(\theta,\phi)\,. \tag{53}$$

Recall that $K$ does everything and $U$ plays no significant role. Thus,

$$T^2\,Y_{l,m}(\theta,\phi) = (-1)^{2m} Y_{l,m}(\theta,\phi) = Y_{l,m}(\theta,\phi)\,, \tag{54}$$

because $m$ is an integer. This illustrates the case $c = +1$. The wave functions $Y_{l,m}(\theta,\phi)$ are complex because the system is degenerate. Applying $T$ twice in succession recovers the original wave function.

When $J$ is even and built from spin ½ objects (in which case there is no spatial wave function), the transformation property of its ket can be found by considering spin ½, and using the fact that the total spin ket $|S,M_S\rangle$ is comprised of products of spin ½ kets. There must be an even number of these kets, each obeying eqn (52). The net effect is that $T^2|S,M_S\rangle = |S,M_S\rangle$. Carrying this reasoning a step further, for systems whose angular momentum is *either* integer or half-integer, the transformation rule is given by

$$T^2|J,M\rangle = (-1)^{2M}|J,M\rangle \tag{55}$$

This can also be expressed in alternate ways. For example, note that $(-1)^{2M} = (-1)^{2J}$.

This completes our foray into time reversal symmetry. It has given us relationships between matrix elements of the Hamiltonian that can be used to derive the number of independent conditions that need to be met if intersection is to be possible.

## Intersection Conditions

We have seen that point group and time reversal symmetries impose restrictions on Hamiltonian matrix elements, causing some to vanish and revealing relationships between others. In order for surfaces to intersect, their diagonal matrix elements must all have the same value, and the off-diagonal matrix elements between them must vanish. A careful consideration of the matrix elements, including whether they are real or complex, will reveal the number of independent conditions that must be met in order to make an intersection possible.

If the intersection conditions are to be satisfied, the Hamiltonian must depend on at least an equal number of parameters that can be treated as being independent of one another. If the number of independent parameters is less than the number of required conditions, the situation is like that of the diatom, *i.e.*, except for species of different symmetry, crossings are avoided. These independent parameters reside in the $\boldsymbol{R}$-space of the molecular "internal" nuclear degrees of freedom. These degrees of freedom exclude overall translation and rotation. The relevant nuclear degrees of freedom can be thought of as vibrations, including internal rotation such as the rotation of a methyl group relative to the rest off the molecule.

One can say that there exists a mapping of the space of matrix elements onto a subspace of the $\boldsymbol{R}$-space of the molecule's internal nuclear coordinates, the dimension of the

subspace being the number of intersection conditions. For example, if two conditions must be met in order to make an intersection possible, and the molecule has an $\boldsymbol{R}$-space whose dimension is three (a triatom), it is possible for the intersection conditions to be satisfied by varying just two nuclear degrees of freedom. There is no guarantee that an intersection *will* occur, but it is not forbidden in the sense of the avoided crossing of levels of the same symmetry that applies to diatomic molecules. Namely, in polyatomic molecules, surfaces of the same symmetry can cross without avoidance. If, in fact, intersection does occur, it can always be assigned to two nuclear degrees of freedom, not three. This leaves one degree of freedom for the intersection coordinate subspace (ICS).

Let us begin by using the results obtained for time reversal symmetry and derive the number of required conditions for some important cases. We will then add restrictions that are due to point group symmetry. Restrictions are added in order to maintain the point group, and restrictions are relaxed when the point group symmetry dictates that off-diagonal matrix elements vanish identically. These arguments will then be extended to restrictions that are relaxed due to the combined effects of time reversal and point group symmetries, specifically, for the $C_s$ point group. Going through these examples will clarify the role of the nuclear degrees of freedom of a polyatomic molecule insofar as intersection conditions are concerned.

## Molecules with an Even Number of Electrons

Consider the general case of the intersection of $n$ surfaces. For molecules that have an even number of electrons ($c = +1$, no Kramers degeneracy) the off-diagonal matrix elements are real, and the levels are assumed to be non-degenerate. The task is to establish the conditions that are required to bring about degeneracy. For $n$ such levels, the Hamiltonian matrix is written

$$\begin{pmatrix} H_{11} & H_{12} & .. & H_{1n} \\ H_{12} & H_{22} & .. & H_{2n} \\ .. & .. & .. & .. \\ H_{1n} & H_{2n} & .. & H_{nn} \end{pmatrix}, \tag{56}$$

where $H_{ij} = H_{ji}$ has been used.

To make the $n$ diagonal matrix elements equal requires that $n-1$ diagonal matrix elements are varied until all $H_{ii}$ have the same value. This imposes $n-1$ conditions that can be met through the variation of $n-1$ nuclear degrees of freedom. Of the $n(n-1)$ off-diagonal matrix elements, only half are independent because $H_{ij} = H_{ji}$. Consequently, there are $\frac{1}{2}n(n-1)$ independent off-diagonal matrix elements. In light of the fact that all of the matrix elements are real for an even number of electrons, $\frac{1}{2}n(n-1)$ conditions must be met in addition to the $n-1$ that arise from the requirement that the diagonal matrix elements are equal. Thus, the total number of conditions that must be met to satisfy time reversal symmetry is given by

$$M_{tr} = \tfrac{1}{2}(n+2)(n-1)\,. \tag{57}$$

For the intersection of two surfaces (*i.e.*, $n = 2$), eqn (57) indicates that two conditions must be met. This fact was introduced earlier, where these two conditions were identified with the energy difference, $H_{11} - H_{22}$, and the coupling matrix element, $H_{12}$. It is now seen that this applies to molecules having an even number of electrons, regardless of their multiplicity (*e.g.*, singlet or triplet). On the other hand, it excludes species that have an odd number of electrons, which accounts for most free radicals.

Referring to eqn (57), to have three surfaces intersect (*i.e.*, $n = 3$) requires that 5 conditions be met. If these are independent, it is not possible to have a triple intersection in a triatom for essentially the same reason that curves of the same symmetry do not cross in a diatomic molecule. Though the above arguments can be used with $n > 3$, there comes a point, with increasing $n$, where the description of such intersections in terms of diabats and adiabats is of questionable value, and alternate descriptions should be considered.

## Molecules with an Odd Number of Electrons

For molecules/radicals with an odd number of electrons (*i.e.*, $c = -1$), levels come in degenerate pairs (Kramers doublets) in which $|\alpha\rangle$ and $|\alpha'\rangle$ are distinct states. The intersection of two surfaces becomes an intersection of four surfaces when this is taken into account. Rather than $|\alpha\rangle$ and $|\beta\rangle$, we now have $|\alpha\rangle$, $|\alpha'\rangle$, $|\beta\rangle$, and $|\beta'\rangle$. Thus, instead of a $2 \times 2$ Hamiltonian matrix the relevant matrix is now $4 \times 4$.[6] Time reversal symmetry imposes restrictions on the matrix elements: some vanish and there are relationships between others. Referring Fig. 5, the $4 \times 4$ matrix is

$$\begin{array}{c} \begin{matrix} \alpha & \alpha' & \beta & \beta' \end{matrix} \\ \begin{pmatrix} H_{\alpha\alpha} & 0 & H_{\alpha\beta} & H_{\alpha\beta'} \\ 0 & H_{\alpha\alpha} & -H^*_{\alpha\beta'} & H^*_{\alpha\beta} \\ H^*_{\alpha\beta} & -H_{\alpha\beta'} & H_{\beta\beta} & 0 \\ H^*_{\alpha\beta'} & H_{\alpha\beta} & 0 & H_{\beta\beta} \end{pmatrix} \end{array}. \tag{58}$$

At the point of intersection, $H_{\alpha\alpha}$ and $H_{\beta\beta}$ must be equal. Because they are real, this constitutes one condition. The off-diagonal matrix elements $H_{\alpha\beta'}$ and $H_{\alpha\beta}$ are complex. For them to vanish, their real and imaginary parts must vanish separately. This constitutes four conditions. Thus, the total number of conditions required for an intersection of the Kramers doublets is five. Extending this to $n = 3$ is left as an exercise.

The matrix in eqn (58) has terms that couple time-reversed and non-time-reversed states. Nonetheless, Kramers degeneracy survives, as it can only be removed by the appli-

[6] In this discussion, numerical subscripts are used for $2 \times 2$ matrices (*e.g.*, $H_{12}$), while Greek subscripts are used for $4 \times 4$ matrices (*e.g.*, $H_{\alpha\beta}$).

cation of an external magnetic field. It can be shown that the eigenvalues of eqn (58) remain doubly degenerate as the off-diagonal elements range from very small to very large.

When spin-orbit interaction is negligible, spin can be assumed to be a good quantum number. Time-reversed states can then be treated separately from non-time-reversed states, as there are no interactions between these groups. The matrix element $H_{\alpha\beta'}$ is zero when there is no spin-orbit interaction. Consequently the remaining elements are all real because for each group of states the situation is the same as for the case of an even number of electrons. The $4 \times 4$ matrix is seen to reduce to two identical $2 \times 2$ matrices, one for $|\alpha\rangle$ and $|\beta\rangle$, and the other for $|\alpha'\rangle$ and $|\beta'\rangle$.

$$\begin{pmatrix} H_{\alpha\alpha} & 0 & H_{\alpha\beta} & 0 \\ 0 & H_{\alpha\alpha} & 0 & H_{\alpha\beta} \\ H_{\alpha\beta} & 0 & H_{\beta\beta} & 0 \\ 0 & H_{\alpha\beta} & 0 & H_{\beta\beta} \end{pmatrix} = \begin{pmatrix} H_{\alpha\alpha}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & H_{\alpha\beta}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\ H_{\alpha\beta}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & H_{\beta\beta}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \end{pmatrix} = \begin{pmatrix} H_{\alpha\alpha} & H_{\alpha\beta} \\ H_{\alpha\beta} & H_{\beta\beta} \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad (59)$$

where $\otimes$ denotes direct product.[7] Equation (59) uses: $H_{\alpha\alpha} = H_{\alpha'\alpha'}$, $H_{\beta\beta} = H_{\beta'\beta'}$, and $H_{\alpha\beta} = H_{\alpha'\beta'}$, with $H_{\alpha\beta}$ real. This simplification to a $2 \times 2$ real matrix applies to radicals comprised of light atoms, where spin-orbit interaction is negligible.

## Nuclear Degrees of Freedom

The numbers of intersection conditions derived above (*i.e.*, two for $n = 2$ and $c = +1$, five for $n = 3$ and $c = +1$, five for $n = 2$ and $c = -1$, and so on) are based solely on time reversal symmetry. A nonlinear polyatomic molecule with $N$ atoms has $M = 3N - 6$ nuclear degrees of freedom that can be varied to meet these conditions.[8] If the molecule remains bound, these degrees of freedom can be described as vibrational, though internal rotors are sometimes appropriate. If dissociation occurs, the situation is more subtle, but $3N - 6$ can still be used.

Consider $n = 2$, $c = +1$, for which two intersection conditions must be met. In the absence of restrictions that arise because of symmetries other than time reversal, these two conditions can be met by varying independently two nuclear degrees of freedom. Thus, for molecules that have an even number of electrons, $M - 2$ nuclear degrees of freedom can vary any which way while maintaining the degeneracy. This defines the dimension of the ICS for the case of an even number of electrons in which there are no additional symmetry requirements beyond those due to time reversal.

In the situation described above, no restrictions have been placed on the positions of the nuclear coordinates. As used here, the term "no restrictions" is equivalent to saying

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[7] With $\boldsymbol{L}\cdot\boldsymbol{S} = L_z S_z + (L^+ S^- + L^- S^+)/2$ there are, in general, nonzero matrix elements that connect $|+\rangle$ and $|-\rangle$ with their time reversed counterparts $|-\rangle$ and $|+\rangle$, respectively.

[8] Vibration-rotation interaction is neglected. Linear molecules have $3N - 5$ nuclear degrees of freedom.

the molecule is free to assume its lowest symmetry, which is $C_s$ for triatomic molecules and $C_1$ for tetratomic and larger molecules.

When the nuclear coordinates are constrained such that a higher symmetry point group applies, the number of degrees of freedom that can vary independently is less than $M$. If the number of degrees of freedom needed to maintain a particular point group is $M_{pg}$, then the molecule has $M - M_{pg}$ degrees of freedom that can vary freely with the point group maintained. Thus, when the intersecting surfaces are of the same symmetry, the dimension of the ICS is $M - M_{pg} - 2$ for molecules that have an even number of electrons. When the intersecting surfaces have different symmetries, the ICS is of dimension $M - M_{pg} - 1$. The change from $-2$ to $-1$ is due to the fact that the coupling matrix element vanishes identically, in which case no nuclear degree of freedom needs to be tuned to cause the coupling matrix element to vanish.

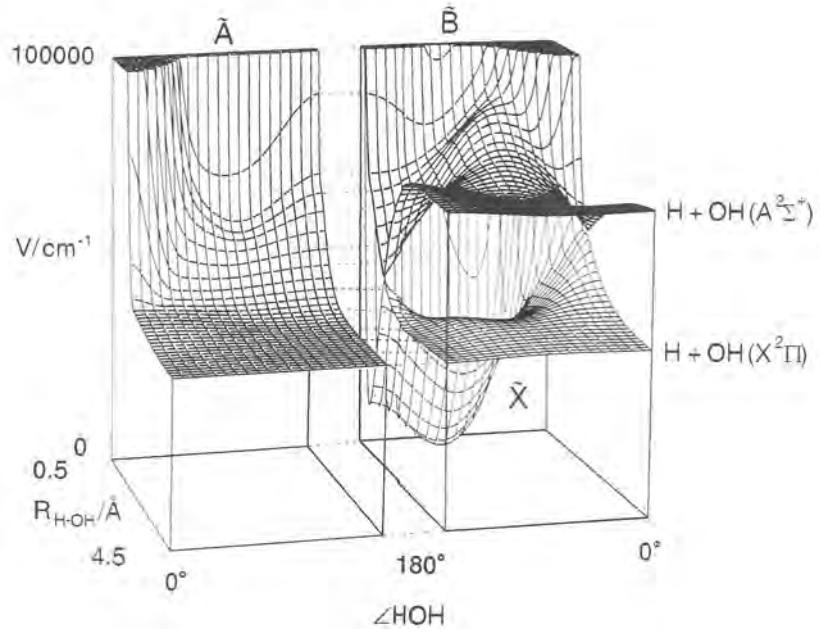


Figure 7. Portions of the 3 lowest adiabats are indicated. The ground state is $^1A_1$ in $C_{2v}$ symmetry. Note the equilibrium geometry: $\angle HOH = 118°$ and $R_{H\text{-}OH} = 1.1$ Å. The ground state is $^1A'$ in $C_s$ symmetry and $^1\Sigma$ in $C_{\infty v}$ or $D_{\infty v}$. States $\tilde{B}$ and $\tilde{A}$ are degenerate at 180 °. Note the conical intersection at this angle.

Let us return to the $H_2O$ example. Figure 7 (which is identical to Fig. 1.6) shows $\tilde{X}$, $\tilde{A}$, and $\tilde{B}$. One OH length is held at its equilibrium value, while the HOH angle and the other OH length are varied. The repulsive $\tilde{A}$ state is shown on the left. It correlates with $H+OH(X^2\Pi)$ and it is degenerate with $\tilde{B}$ at 180°, as they arise from a common $\Pi$ state.

The $\tilde{X}$ and $\tilde{B}$ states are shown on the right. They intersect conically at 180° (HOH) and 0° (HHO), where $\tilde{X}$ and $\tilde{B}$ are of $^1\Sigma^+$ and $^1\Pi$ symmetries, respectively. This is a subtle point. Referring to Fig. 7, we see that at 180°, $\tilde{X}$ is $^1\Sigma^+$ for $R_{H-OH}$ values smaller than that of the intersection. For $R_{H-OH}$ values larger than that of the intersection, $\tilde{X}$ correlates diabatically to the excited surface that leads to $H + OH(A^2\Sigma^+)$. On the other

hand, it correlates adiabatically (*i.e.*, on the lower cone of the conical intersection) to ground state products $H + OH(X^2\Pi)$.

Referring to Fig. 7, note that vertical projection from the ground state accesses the $\tilde{B}$ surface in a region where the gradients of the potential guide the nuclei toward the conical intersection. When $\tilde{B}$ is accessed at sufficiently high energies, a modest amount of flux goes along the ridge that leads to $H + OH(A^2\Sigma^+)$.

The $\tilde{X}$ and $\tilde{B}$ surfaces can cross/intersect over a wide range of linear configurations because they are of different symmetries at linear geometries, *i.e.*, $^1\Sigma^+$ and $^1\Pi$, respectively. The $\tilde{B}$ state correlates adiabatically with $H + OH(A^2\Sigma^+)$ in $C_s$ symmetry and it correlates with $H + OH(X^2\Pi)$ via the conical intersections at 180° and 0°. In the $C_s$ point group, the $\tilde{B}$ and $\tilde{X}$ surfaces are each of $A'$ symmetry, and they undergo avoided crossings near the intersection points shown in figure 10, *i.e.*, in the vicinities of 180° and 0°.

Figure 7 shows the HOH $\tilde{B}/\tilde{X}$ intersection point that corresponds to 180° and a fixed value of 1.8 $a_0$ for one of the OH bonds. Figure 8 indicates that there is a 1D intersection seam for the linear configurations at 180° and a family of values of $r_1$ and $r_2$. Deviations from linearity (*i.e.*, $180° \pm \delta\theta$) result in avoided crossings in the lower symmetry $C_s$ point group, where $\tilde{B}$ and $\tilde{X}$ are each $A'$.

When the molecule is linear, there are four vibrational degrees of freedom, two of which are needed to maintain linearity.[9] It is not necessary to maintain $D_{\infty h}$ symmetry, as this is overly restrictive. Rather, $C_{\infty v}$ applies. Thus, $M = 4$ and $M_{pg} = 2$, and the dimension of the ICS is $M - M_{pg} - 1 = 1$ for linear configurations.

For the molecule to maintain $C_{2v}$ symmetry, we have $M_{pg} = 1$, whereas for $C_s$ symmetry, we have $M_{pg} = 0$. In the case of $H_2O$, there are no additional intersections in either $C_{2v}$ or $C_s$. These are not forbidden in the sense that the number of intersection conditions exceeds the number of nuclear degrees of freedom. They just do not happen.

In general, even when there are only two intersecting adiabats, there can be confluences of seams, for example, one occurring for a symmetric geometric configuration and surfaces that have different symmetries, and another occurring for a geometric configuration of lower symmetry, where the states have the same symmetry. This arises in $O_3$.

Of course, the same rules apply to tetratomic and larger molecules. In these cases, the lowest symmetry point group is $C_1$, and if $M_{pg}$ degrees of freedom are needed to maintain a higher symmetry point group, then there are $M - M_{pg}$ nuclear degrees of freedom that can vary while still maintaining the higher symmetry point group.

The above considerations also apply to molecules that have an odd number of electrons ($c = -1$). For example, for $n = 2$, five conditions must be met to achieve an intersection on the sole basis of time reversal symmetry. To meet these conditions, at least five nuclear degrees of freedom must be available to be varied independently. Thus, for a system having $M$ nuclear degrees of freedom, the ICS is of dimension $M - 5$ for the case of the $C_1$ point group. To maintain a higher symmetry point group imposes a requirement that the ICS is of dimension $M - M_{pg} - 5$ for intersecting surfaces of the same symmetry.

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[9] As the non-linear molecule straightens (the HOH angle goes to 180°), *a*-axis rotation and the (non-degenerate) bend combine to give the twofold degenerate bend of the linear molecule. Being degenerate, the bend has angular momentum about the axis.

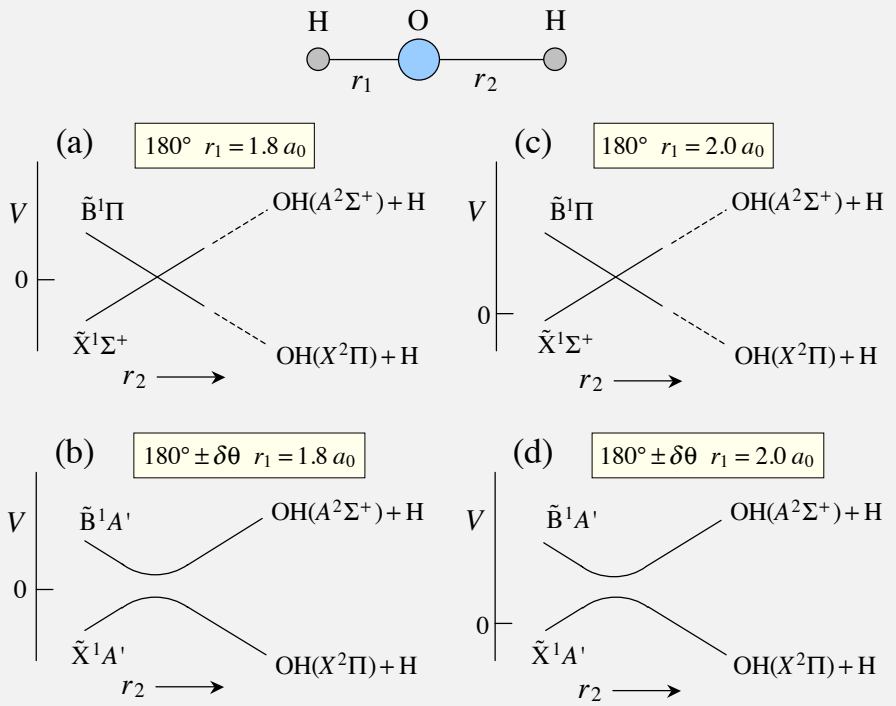



Figure 8. The $\tilde{X}$ / $\tilde{B}$ seam spans a range of linear configurations. For linear $H_2O$, $X^1\Sigma^+$ correlates diabatically to H + OH($A^2\Sigma^+$), whereas $\tilde{B}^1\Pi$ correlates diabatically to H + OH($X^2\Pi$). The surfaces cross at linearity because they are of different symmetry, as indicated in (a) and (c). In $C_s$ symmetry, the surfaces are each $^1A'$ and their crossings are avoided, as indicated in (b) and (d). By convention, the upper part [$V > 0$ in (a) and (b)] is referred to as the $\tilde{B}$ adiabat, even at linear geometries, where the surfaces cross. In (c) and (d), $r_1$ is larger than in (a) and (b), and crossing and avoided crossing occur at higher energy. The 1D seam is the continuum of $r_1$,$r_2$ combinations for which the surfaces intersect.

The situation thus appears to be quite restrictive, eliminating any possibility of an intersection in triatoms ($M = 3$) and presenting a stringent requirement for tetratomics ($M = 6$). We shall see that this extreme view is overly simplistic. For example, for $C_s$ symmetry the $-5$ becomes $-3$ because of the combined effect of time reversal and $C_s$ symmetries. In addition, in examining the role of spin-orbit interaction, we will see that it is central to the entire intersection issue for odd-electron molecules: when it is small enough to be neglected, the system approaches the simple $c = +1$ case. Otherwise, it is dealt with on a case-by-case basis.

## Time Reversal Symmetry and the $C_s$ Point Group

In the material presented above, conditions that must be met for an intersection to be possible have been derived. This was achieved by considering Hamiltonian matrix ele-

ments as well as the geometrical constraints (restricted nuclear configurations) needed to maintain a particular point group. Point group symmetry causes some matrix elements to vanish, and time reversal symmetry causes some matrix elements to vanish and dictates relationships between others. These considerations are central to obtaining the number of independent conditions that must be met to make intersection possible, and consequently the number of nuclear degrees of freedom available to be tuned to achieve degeneracy.

It is also necessary to consider possible *combined effects* of time reversal and point group symmetry that place restrictions on the matrix elements. Specifically, do time reversal and a particular point group taken together result in further vanishing of, and/or relationships between, the matrix elements? This is important because reducing the number of independent nonzero off-diagonal elements lowers accordingly the number of conditions that must be met, thereby facilitating intersection. For example, for $n = 2$ and $c = -1$, we have seen that the dimension of the ICS is $M - M_{pg} - 5$ for surfaces of the same symmetry. The 5 conditions that arise through considerations of the matrix elements make it impossible for a triatomic to have an intersection, and there is a stringent requirement on tetratomic species, for which $M = 6$. On the other hand, as mentioned above, if one of the (complex) off-diagonals becomes zero due to the combination of time reversal and point group symmetries, 5 is lowered to 3, which is a significant difference.

Here, we shall examine the combined effect of time reversal and $C_s$ symmetries for molecules that have an odd number of electrons. The relevant spatial symmetry element is the reflection plane. Higher symmetry may be present (*e.g.*, $D_{2h}$ contains $C_s$), but we are interested only in the plane of symmetry. The reason is that reflection through this plane is related intimately to the time reversal operation, which reverses the directions of all angular momenta. Symmetry operations other than reflection through the plane need not be considered. The linear point group $C_{\infty v}$ can be treated as a special case of $C_s$, as discussed below.

Because the Hamiltonian commutes with the reflection operator $\hat{\sigma}$, the eigenstates are assigned a $\hat{\sigma}$ label and they have $\hat{\sigma}$ eigenvalues of $\pm 1$. The reflection operator $\hat{\sigma}$ acts on both space and spin coordinates. Thus, the operators $\hat{\sigma}_r$ and $\hat{\sigma}_s$ are introduced: $\hat{\sigma}_r$ acts on spatial wave functions and $\hat{\sigma}_s$ acts on spin kets. Though $\hat{\sigma}_r$ and $\hat{\sigma}_s$ do not, in general, commute separately with the Hamiltonian because of spin-orbit interaction, they can nonetheless be useful.

The goal is to establish how the plane of $C_s$ symmetry affects matrix elements of the form $H_{\alpha'\beta}$, *i.e.*, between time reversed and non-time-reversed states. It will be shown (assuming $H_{\alpha\beta} \neq 0$) that $H_{\alpha'\beta}$ vanishes identically.

## Without Spin-Orbit Interaction

When spin-orbit interaction is weak enough to be neglected, the operator $\hat{\sigma}$ is equivalent to $\hat{\sigma}_r$. With spin absent from the Hamiltonian, it plays no role beyond that of a bookkeeping device for the Pauli exclusion principle, pairing spin-up with spin-down. The overall spin has good quantum numbers for its projection onto any space-fixed axis, and these projections are degenerate in the absence of an external magnetic field. They constitute the Kramers doublet for systems that have an odd number of electrons.

Molecular orbitals are expressed as symmetrized combinations of products of spatial functions times spin kets. Each eigenstate is expressed as a collection of such spin-orbitals whose individual symmetries are $A'$ or $A''$. The overall spatial symmetry is $A'$ or $A''$, with respective $\hat{\sigma}_r$ eigenvalues of $+1$ and $-1$, as shown in Fig. 9.

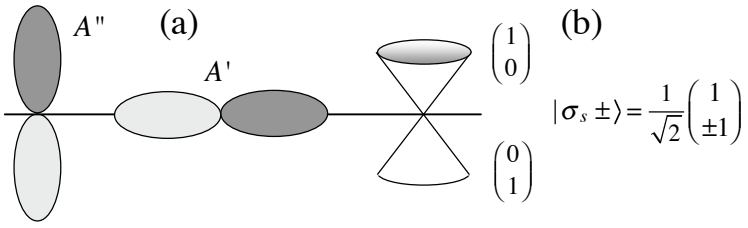



Figure 9. The $C_s$ plane is perpendicular to the page (horizontal line). (a) $A'$ and $A''$ have $\hat{\sigma}_r$ eigenvalues + 1 and – 1, respectively. (b) eigenkets of $\hat{\sigma}_s$.

Now let's turn to spin. The fact that the direction of the spin angular momentum is arbitrary in the absence of spin-orbit interaction means that any convenient basis can be used for its representation without complicating matters. However, because spin-orbit interaction relates spin to spatial coordinates, it is inevitable that the planar geometry of the $C_s$ point group will enter in the choice of spin basis when spin-orbit interaction is included. Thus, spin kets are chosen to be eigenkets of $\hat{\sigma}_s$, *i.e.*, symmetric and antisymmetric with respect to the plane:

$$|\sigma_s \pm\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\\pm 1\end{pmatrix} \tag{60}$$

with the $z$-axis perpendicular to the plane (Fig. 9). The $|\sigma_s \pm\rangle$ are eigenkets of $\hat{\sigma}_s$, with eigenvalues + 1 and – 1, as $\hat{\sigma}_s$ merely exchanges the $\hat{s}_z$ eigenkets $|+\rangle$ and $|-\rangle$:

$$\hat{\sigma}_s|\sigma_s \pm\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix}\begin{pmatrix}1\\\pm 1\end{pmatrix} = \pm\frac{1}{\sqrt{2}}\begin{pmatrix}1\\\pm 1\end{pmatrix} = \pm|\sigma_s \pm\rangle \tag{61}$$

Note that $\hat{\sigma}_s$ is the Pauli matrix $\sigma_1$.

The role of $T$ acting on $A'$ and $A''$ spatial wave functions is simple – it has no effect. That is, because the $A'$ and $A''$ states are non-degenerate, their wave functions are real, and therefore complex conjugation leaves them unchanged. Thus, $T$ commutes with $\hat{\sigma}_r$, and our task is reduced from one of examining the commutator $[T, \hat{\sigma}_s]$ to one of examining the commutator $[T, \hat{\sigma}_s]$, *i.e.*, determining how $T$ affects the $\hat{\sigma}_s$ eigenkets.

As we have seen earlier, the time reversal operator rotates spin ½ kets such that $T|+\rangle \rightarrow|-\rangle$ and $T|-\rangle \rightarrow -|+\rangle$.[10] Thus, $T$ can be expressed as

[10] The phase convention used here does not result in a symmetric treatment of the action of $T$ on $s_z$ eigenkets. This can be altered in appearance with phase factors, but the fact that the action of $T^2$ on a spin ½ ket must change its sign *requires* this asymmetry. For example, if an arbitrary phase factor is assigned: $e^{i\delta}|+\rangle$, then $Te^{i\delta}|+\rangle = e^{-i\delta}T|+\rangle$. Applying $T$ again gives $Te^{-i\delta}T|+\rangle = e^{i\delta}T^2|+\rangle$. Thus, $T^2|+\rangle$ gives $-|+\rangle$, independent of the phase factor $e^{i\delta}$.

$$T = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \tag{62}$$

which is equal to $-i\sigma_2$. As mentioned earlier, $T$ can contain a phase factor that does not affect the outcome of $T^2$ operating on a state.

Clearly, $T$ and $\hat{\sigma}_s$ do not commute, as $T = -i\sigma_2$ and $\hat{\sigma}_s = \sigma_1$:

$$[T, \hat{\sigma}_s] = -i[\sigma_2, \sigma_1] = -2\sigma_3 \tag{63}$$

To see how this affects the problem at hand, consider $T$ operating on $|\sigma_s +\rangle$:

$$T|\sigma_s +\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = -\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} = -|\sigma_s -\rangle \tag{64}$$

Application of $T$ has converted the even state $|\sigma_s +\rangle$ into the odd state $|\sigma_s -\rangle$. A minus sign also appears, but this is not important. Likewise, $T$ operating on $|\sigma_s -\rangle$ gives

$$T|\sigma_s -\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ -1 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = |\sigma_s +\rangle . \tag{65}$$

We see that the odd spin state $|\sigma_s -\rangle$ has been turned into the even spin state $|\sigma_s +\rangle$. Thus, the time reversal operator is seen to exchange the symmetries of the $\hat{\sigma}_s$ eigenkets. Consequently, when the matrix element $H_{\alpha\beta}$ is nonzero, the matrix element $H_{\alpha'\beta}$ vanishes identically. That is: when $|\alpha\rangle$ and $|\beta\rangle$ have the same $\hat{\sigma}_s$ eigenvalue, $|\alpha'\rangle$ and $|\beta'\rangle$ have different $\hat{\sigma}_s$ eigenvalues.[11]

This result could have been stated at the outset. Without spin-orbit interaction, there is no coupling between primed and unprimed states, and the situation is essentially the same as for $n = 2$ and $c = +1$. Spin has good quantum numbers and the Kramers doublet corresponds to spin-up and spin-down. The $A'$ and $A''$ states are non-degenerate, so the off-diagonal matrix element is real.

The considerations presented above set the stage for the case presented below in which spin-orbit interaction is taken into account.

## With Spin-Orbit Interaction

The inclusion of spin-orbit interaction changes the above scenario. Spin operators enter the Hamiltonian, removing the separate spatial and spin symmetries that apply in

[11] Recall that in time reversal symmetry there is ambiguity concerning the state that is time reversed: who is to say which path was the original one. We have shown that if $H_{\alpha\beta}$ is non-zero then $H_{\alpha'\beta}$ vanishes. It can also be stated that if $H_{\alpha'\beta}$ is nonzero then $H_{\alpha\beta}$ vanishes. Either way, one of the off-diagonal matrix elements vanishes.

their absence. The reflection operator $\hat{\sigma}$ still commutes with $H$, but $\hat{\sigma}_r$ and $\hat{\sigma}_s$ no longer commute separately with $H$.

The eigenstates can be expressed as linear combinations of products of the spatial and spin functions presented above. For example, the product of a spatial function of $A'$ symmetry times $|\sigma_s -\rangle$ is antisymmetric with respect to $\hat{\sigma}$. Likewise, the product of a spatial function of $A''$ symmetry times $|\sigma_s +\rangle$ is also antisymmetric with respect to $\hat{\sigma}$. Clearly, a state that is a linear combination of these antisymmetric products has a $\hat{\sigma}$ eigenvalue of $-1$, though neither $\hat{\sigma}_r$ nor $\hat{\sigma}_s$ are, by themselves, good labels.

The general expression for an eigenstate, say with a $\hat{\sigma}$ eigenvalue of $+1$, is given by:

$$\psi(\sigma+) = \sum_i \psi_{A'}^i |\sigma_s +\rangle + \sum_j \psi_{A''}^j |\sigma_s -\rangle \tag{66}$$

Sums indicate the participation of eigenfunctions of the non-relativistic Hamiltonian that serve here as a basis. Spin-orbit interaction has mixed together states that have good $\hat{\sigma}_r$ and $\hat{\sigma}_s$ quantum numbers when spin-orbit interaction is suppressed.

Let us now examine the action of $T$ on $\psi(\sigma+)$:

$$T\psi(\sigma+) = \sum_i \left(T\psi_{A'}^i\right)\left(T|\sigma_s +\rangle\right) + \sum_j \left(T\psi_{A''}^j\right)\left(T|\sigma_s -\rangle\right) \tag{67}$$

On the right hand side, $T$ acts only within the respective parentheses. $T$ leaves $\psi_{A'}^i$ and $\psi_{A''}^j$ unaffected because they are real. By using eqns (64) and (65), eqn (67) becomes:

$$T\psi(\sigma+) = -\sum_i \psi_{A'}^i |\sigma_s -\rangle + \sum_j \psi_{A''}^j |\sigma_s +\rangle \tag{68}$$

We see that $T\psi(\sigma+)$ is an eigenfunction of $\hat{\sigma}$, but with eigenvalue $-1$. The even state has been turned into an odd state, *i.e.*, the terms within the sums are all odd with respect to $\hat{\sigma}$. Likewise, $T\psi(\sigma-)$ is an eigenstate of $\hat{\sigma}$, but with eigenvalue $+1$. The odd state has been turned into an even state. Thus, when $T$ acts on an eigenfunction of $\hat{\sigma}$, it turns it into one that is orthogonal to it.

As a result, as in the case of no spin-orbit interaction, matrix elements of the form $H_{\alpha'\beta}$ vanish identically. Namely, when $|\alpha\rangle$ and $|\beta\rangle$ are of the same symmetry, $|\alpha'\rangle$ and $|\beta\rangle$ are always of different symmetry. This eliminates some off-diagonal matrix elements, thereby reducing the number of conditions that must be met to make an intersection possible. The case $n = 2$ is illustrated below

$$\begin{matrix} \alpha & \alpha' & \beta & \beta' \end{matrix}$$
$$\begin{pmatrix} H_{\alpha\alpha} & 0 & H_{\alpha\beta} & H_{\alpha\beta'} \\ 0 & H_{\alpha\alpha} & -H_{\alpha\beta'}^* & H_{\alpha\beta}^* \\ H_{\alpha\beta}^* & -H_{\alpha\beta'} & H_{\beta\beta} & 0 \\ H_{\alpha\beta'}^* & H_{\alpha\beta} & 0 & H_{\beta\beta} \end{pmatrix} \rightarrow \begin{matrix} \alpha & \alpha' & \beta & \beta' \end{matrix} \begin{pmatrix} H_{\alpha\alpha} & 0 & H_{\alpha\beta} & 0 \\ 0 & H_{\alpha\alpha} & 0 & H_{\alpha\beta}^* \\ H_{\alpha\beta}^* & 0 & H_{\beta\beta} & 0 \\ 0 & H_{\alpha\beta} & 0 & H_{\beta\beta} \end{pmatrix}. \tag{69}$$

For intersection to be possible one condition must be met for the diagonal elements and two must be met for the complex off-diagonal element. This differs from the case of no spin-orbit interaction. There, the off-diagonal element was real; here it is complex.

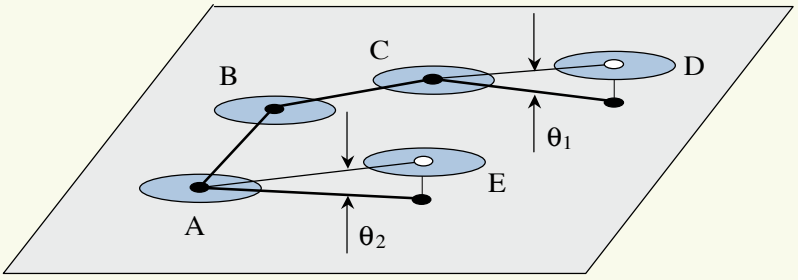



Figure 10. Atoms A, B, and C, as well as black dots and heavy lines, all lie in the plane. For D and E to lie in the plane, the angles $\theta_1$ and $\theta_2$ must be zero. This requires one degree of freedom per atom. To maintain $C_s$ symmetry, each additional atom beyond three increases $M_{pg}$ by

In summary, when the system has $C_s$ symmetry, the fact that matrix elements that couple primed and unprimed states all vanish reduces the number of restrictions from 5 to 3. For $n = 3$, the number of restrictions is reduced from 14 to 8, and so on for larger $n$. As discussed earlier, to achieve $C_s$ symmetry in a polyatomic molecule, $M_{pg}$ increases by one for each atom beyond three. This is illustrated in Fig. 10.

## Summary of Intersection Conditions

Table I illustrates with examples the derivations and arguments of the previous sections. Dimensions of ICS's are obtained for a few simple molecules using the formula:

$$M_{ICS} = M - M_{pg} - M_{tr} + M_{relax} \tag{70}$$

where $M$, $M_{pg}$, and $M_{tr}$ have been defined previously, and $M_{relax}$ is the number of intersection conditions that are relaxed on the basis of the symmetries of the surfaces that cross. Namely, when symmetry dictates that an off-diagonal matrix element vanishes, no nuclear degree of freedom needs to be tuned to make the matrix element vanish.

Interpretation of eqn (70) is as follows. For a given point group, $M_{pg}$ is the number of nuclear degrees of freedom needed to maintain this point group. If the point group is of the lowest possible symmetry (*i.e.*, $C_1$, except for triatoms in which case $C_s$ is the lowest possible symmetry), then $M_{pg}$ is zero. Otherwise, $M_{pg}$ must be worked out on a case-by-case basis. For example, for $H_2O$ to maintain a $C_{2v}$ geometry requires that one degree of freedom is held fixed. Thus, for a molecule that has $M$ degrees of freedom, $M - M_{pg}$ of them are available to vary any which way while maintaining the point group.

The number of restrictions that arise on the basis of time reversal symmetry is $M_{tr}$. For molecules that have an even number of electrons, the intersection of two surfaces gives $M_{tr} = 2$. If the intersecting surfaces are of different symmetry the off-diagonal elements are zero. In this case, the number of restrictions is one lower because the (real) off-diagonal element is zero. The parameter value $M_{relax} = 1$ accounts for this.

| | | point group | $M$ | $M_{pg}$ | $M_{tr}$ | $M_{relax}$ | $M_{ICS}$ |
|---|---|---|---|---|---|---|---|
| $H_2O$ | $\tilde{B}^1\Pi / \tilde{X}^1\Sigma^+$ | $C_{\infty v}$ | 4 | 2 | 2 | 1 | 1 |
| | $C_{2v}$ | | 3 | 1 | 2 | | |
| | $2^1A' / 1^1A'$ | $C_s$ | 3 | 0 | 2 | 0 | 1 |
| $CH_2$ | | $C_{\infty v}$ | 4 | 2 | 2 | 1 | 1 |
| | $C_{2v}$ | | 3 | 1 | 2 | | |
| | $2^3A'' / 3^3A''$ | $C_s$ | 3 | 0 | 2 | 0 | 1 |
| $NO_2$ | | $C_{\infty v}$ | 4 | 2 | 5 | 2 | – |
| | | $C_{2v}$ | 3 | 1 | 5 | 2 | – |
| | | $C_s$ | 3 | 0 | 5 | 2 | 0 |
| $CH_2OH$ | | $C_1$ | | | | | |

Table I. The dimension of the ICS is given by: $M_{ICS} = M - M_{pg} - M_{tr} + M_{relax}$. The conditions listed above do not say anything about whether or not an intersection will occur, only if it is possible. In the case of $NO_2$, an intersection is impossible except at a point. Though $NO_2$ is known to have strong nonadiabatic coupling, there is no contradiction, as spin-orbit interaction is modest.

For an odd number of electrons and two intersecting surfaces, $M_{tr}$ is five, arising from one diagonal and two complex off-diagonal matrix elements, $H_{\alpha\beta}$ and $H_{\alpha'\beta}$. The off-diagonals are subject to the symmetries of $|\alpha\rangle$ and $|\beta\rangle$. If they differ, $H_{\alpha\beta}$ vanishes and the number of intersection conditions lowers by two.

The issue of $H_{\alpha'\beta}$ is subtler. If the symmetry operations of the point group commute with $T$, this matrix element vanishes as well, lowering the number of intersection conditions by another two. If they do not commute, it may be possible to have $H_{\alpha'\beta} \neq 0$ at the same time that $H_{\alpha\beta} = 0$. Recall the case of $C_s$. When $|\alpha\rangle$ and $|\beta\rangle$ have the same $\hat{\sigma}$ eigenvalues, $H_{\alpha'\beta}$ vanishes. Alternatively, when $|\alpha\rangle$ and $|\beta\rangle$ have different $\hat{\sigma}$ eigenvalues, $H_{\alpha\beta}$ vanishes but $H_{\alpha'\beta}$ in general does not. In both cases, $M_{relax}$ is two.

Referring to Table I, for triatoms having an even number of electrons, the dimension of the ICS is always one, unless one invokes $D_{\infty h}$ symmetry, which is unreasonably restrictive. For triatoms having an odd number of electrons and non-negligible spin-orbit interaction, one might conclude, on the basis of the math, that intersections are impossible. Though true in the strictest sense, we have seen that when spin-orbit interaction is small enough to be safely neglected the system behaves in the same way as a molecule having an even number of electrons. Thus, the issue is one of degree rather than kind.

## Effect of Spin-Orbit Interaction

In the previous sections, it has been assumed that the off-diagonal matrix elements of the spin-orbit term in the Hamiltonian are, in general, complex for molecules that have an odd number of electrons. This is easy to accept because, in contrast to the case of molecules that have an even number of electrons, there is no reason to suspect that the off-diagonal matrix elements might be real. In other words, in the absence of evidence to the contrary, it must be assumed that off-diagonal Hamiltonian matrix elements are complex.

It is instructive, nonetheless, to see how this complex nature comes about. We shall do this by examining an idealized model in which spatial symmetry and the use of identical nuclei enable a result to be obtained quickly. This result is then generalized to include less symmetrical arrangements.

To proceed, a simple one-electron model is introduced, in which the spin-orbit matrix elements turn out to be imaginary. As mentioned above, use is made of a symmetrical arrangement of the nuclei, as indicated in Fig. 11. This facilitates the math, and it will be shown that distortion away from the symmetrical configuration introduces terms into the Hamiltonian matrix that make the off-diagonal matrix elements complex.

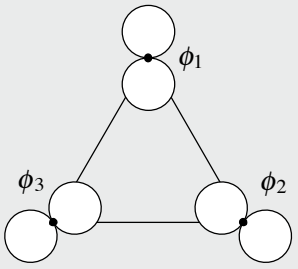



Figure 11. Identical nuclei form an equilateral triangle. Each has a *p*-orbital that lies in the plane.

Referring to Fig. 11, consider three identical nuclei arranged in an equilateral triangle. On each nucleus there is a *p*-orbital that lies in the plane defined by the nuclei. In light of the fact that we plan to generalize the results to dissimilar atoms, the nuclei are assumed to be distinguishable, in which case permutations need not be considered, at least here. Molecular orbitals are obtained by combining the atomic *p*-orbitals $\phi_1$, $\phi_2$, and $\phi_3$. The molecular orbitals that form a basis for the doubly degenerate irreducible representation are

$$\psi_1 = \tfrac{1}{\sqrt{6}}\left(2\phi_1 - \phi_2 - \varphi_3\right) \tag{71}$$

$$\psi_2 = \tfrac{1}{\sqrt{2}}\left(\phi_2 - \varphi_3\right). \tag{72}$$

Because we are concerned with a one-electron problem, interactions of the privileged electron with other electrons are suppressed, and the orbitals $\psi_1$ and $\psi_2$ are taken as wave functions that describe states of the system. Their energies can be assumed to differ slightly, being $-\delta$ and $+\delta$, respectively, relative to some energy $E_0$.

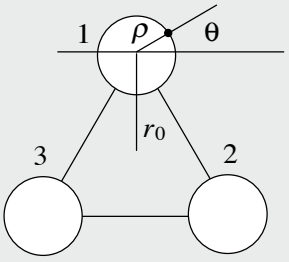



Figure 12. Nuclei circulate on small circular orbits of radii $\rho$. Though they remain localized at their respective equilibrium sites, angular momentum arises through this synchronous motion, which is akin to a distortion wave circulating on the periphery.

Likewise, two degenerate normal modes (coordinates $Q_a$ and $Q_b$) belong to the same irreducible representation. The coupling of electron and nuclear motions that takes place in this system is an example of the Jahn-Teller effect, in which the 3-fold symmetry is lowered through the coupling of the degenerate electronic states to one another via the $Q_a$ and $Q_b$ displacements. Figure 12 illustrates the synchronized nuclear motions that give rise to an angular momentum of ½.

For the case in Fig. 11, the original $D_{3h}$ symmetry goes to $C_{2v}$. Detailed descriptions of the Jahn-Teller effect are available in books and the literature. Here, we consider the fate of a single electron *vis-à-vis* the states given by eqns (71) and (72) and the spin-orbit term

$$V_{\rm so} = \left(\xi(r_1)\boldsymbol{l}_1 + \xi(r_2)\boldsymbol{l}_2 + \xi(r_3)\boldsymbol{l}_3\right)\cdot\boldsymbol{s}\,, \tag{73}$$

where $r_i$ is the distance between the electron and the $i^{th}$ nucleus. When $V_{\rm so}$ operates on $\psi_1$ or $\psi_2$ it alters their $p$-orbitals. To see how this works, consider one of the $\boldsymbol{l}_i\cdot\boldsymbol{s}$ terms in eqn (73), say $\boldsymbol{l}_1\cdot\boldsymbol{s}$. With $\boldsymbol{l}_1\cdot\boldsymbol{s}$ expressed as

$$\boldsymbol{l}_1\cdot\boldsymbol{s} = l_{1z}s_z + \tfrac{1}{2}\left(l_1^{+}s^{-} + l_1^{-}s^{+}\right), \tag{74}$$

the matrix elements $\langle\psi_1|(l_1^{+}s^{-} + l_1^{-}s^{+})|\psi_2\rangle$ vanish because $l_1^{+}$ and $l_1^{-}$ convert $p$-orbitals that lie in the plane into ones that are perpendicular to the plane.[12] Of course the same argument applies to $\boldsymbol{l}_2\cdot\boldsymbol{s}$ and $\boldsymbol{l}_3\cdot\boldsymbol{s}$. On the other hand, the matrix elements $\langle\psi_1|l_{1z}s_z|\psi_2\rangle$ do not vanish, because $l_{1z}$ operating on a $p$-orbital, say $p_{1x}$, gives

$$l_{1z}p_{1x} = l_{1z}\tfrac{1}{\sqrt{2}}\left(Y_{1,1} - Y_{1,-1}\right) = \hbar\tfrac{1}{\sqrt{2}}\left(Y_{1,1} + Y_{1,-1}\right) = i\hbar\,p_{1y}\,. \tag{75}$$

The resulting $p_{1y}$ orbital lies in the plane, so $\langle\psi_1|l_{1z}s_z|\psi_2\rangle$ does not vanish. Moreover, it is purely imaginary: $\pm i\gamma$, where $\gamma$ is real. The effect of $l_{1z}$ operating on $p_{1x}$ is to rotate it by 90° and add a phase of $\pi/2$. Distortion from the symmetric configuration in Fig. 11 can be expressed in terms of the coordinates … As the system has a threefold symmetry axis, the spin-orbit term in the Hamiltonian commutes with a rotation of 120°:

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{12}^{*} & H_{22} \end{pmatrix}\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} - \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}\begin{pmatrix} H_{11} & H_{12} \\ H_{12}^{*} & H_{22} \end{pmatrix} = 0 \tag{76}$$

This yields $H_{11} = H_{22}$ (which can be set equal to zero for convenience) and $H_{12}^{*} + H_{12} = 0$, indicating that $H_{12}$ is imaginary. Use was made of this in the Landau-Zener model including spin-orbit interaction.

[12] The $p$-orbitals are combinations of $|1,1\rangle$ and $|1,-1\rangle$, and the action of $l_1^{+}$ and $l_1^{-}$ on these kets can only convert them into $|1,0\rangle$, whose $Y_{1,0}$ wave function is perpendicular to the plane.

# Appendix 5.

## Classical Geometric Phase

A quantum mechanical eigenstate that evolves adiabatically under the influence of slowly varying external parameters remains in this state throughout its evolution. However torturous and/or lengthy the path in parameter space might be, the system does not undergo transitions to other states. What is referred to here as an eigenstate is defined by a set of quantum numbers that are appropriate to the *fast time scale*. The relatively *slow time scale* of adiabatic evolution is ignored in obtaining these quantum numbers. In other words, the system is frozen at successive sets of external parameters when calculating the eigenstates during the adiabatic evolution. Though the quantum numbers are preserved, the energy can change throughout the adiabatic evolution. In the corresponding classical system, it is the integrals of motion that are preserved.

In both classical and quantum mechanics the issue of phase remains at large. For example, the quantum system retains its original quantum numbers, but what about its phase? How does it progress along the path in parameter space?

Figure 1. A sphere suspended with a thin steel wire follows a straight-line path that passes across the center of the circular area. The oscillation plane slowly precesses (clockwise in the northern hemisphere, counterclockwise in the southern hemisphere) about a vertical line from the center of the circular area to the support high above. (photo by H. Reisler)

In addition to an eigenstate's *dynamic phase*, $-\omega_n t$ , there is another phase that accumulates along an adiabatic path. It depends on the external parameters whose variations are responsible for adiabatic evolution. Namely, it depends on geometric properties of these parameters, hence the name geometric phase. Whereas the dynamic phase is due to the duration of the trip, the geometric phase is due to the route taken.

In this appendix, two classical systems are examined in which a geometric phase is identified: the Foucault pendulum, and the parallel transport of a vector on the surface of a sphere. It is seen that, insofar as geometric phase is concerned, these systems are for all practical purposes identical. This phase is independent of how quickly or slowly a system changes, as long as it does so adiabatically. It is seen that the amount of phase is equal to the solid angle subtended by a closed path on the surface of a sphere. These classical cases are closely related to quantum geometric phase.

We shall begin with the Foucault pendulum. It has been around for over a century and a half, and it is a clear example of an adiabatic separation. It can be understood in terms of what is called the Coriolis force. Referring to Fig. 1, a heavy metal sphere is suspended from a stable support using a thin steel wire. The support is high and the heavy metal sphere almost touches the ground at the lowest point of its travel. The sphere swings to-and-fro along a straight-line path that slowly precesses. Leon Foucault built one with a 67-meter support and a sphere that weighed 28 kg. The historical sketch below is courtesy of Karl S. Kruszelnicki (Karl Sven Woytek Sas Konkovitch Matthew Kruszelnicki).

The Foucault pendulum was invented by accident. In 1848 Jean-Bernard-Leon (Leon) Foucault was setting up a long, skinny metal rod in his lathe. He twanged it, and the end proceeded to go up and down. If you treat the chuck of the lathe like a clock, the end vibrated from 12 o'clock down to 6 o'clock, and back to 12 o'clock, and so on. He slowly rotated the chuck by 90°. But the end of the rod vibrated back and forth between 12 and 6 o'clock.

This set Leon thinking. He set up a small pendulum in his drill press. He set the pendulum oscillating, and then started the drill press. Once again, the pendulum kept swinging in its original plane, and ignored the fact that its mounting point was rotating. He then constructed a 2-meter long pendulum with a 5 kg ball in his workshop in his cellar. Before the amplitude of the swing died away, he saw that the weight on the end of the pendulum appeared to rotate clockwise. Now that he was convinced of the principle, he built a second pendulum with an 11-meter wire in the Paris Observatory, and it too rotated clockwise.

He was asked to construct something impressive for the Paris Exhibition, so he built a 67-meter pendulum in the Pantheon, a Parisian church also known as the church of Saint Geneviève. He made sure the wire was symmetrical, and he used a 28 kg cannon ball. A stylus was placed under the ball, and sand was scattered under the path, so the stylus would cut a trace in the sand. The ball was pulled to one side and held in place with a string. With much ceremony, the string was set alight, and the ball descended in a straight (non-elliptical) path. Within a few minutes, the pendulum had begun to swing a little clockwise and the previous narrow straight-line in the sand had widened to look like a twin bladed propeller. Success! The earth rotated under his pendulum.


Figure 2. The Foucault pendulum in the chorus of the church of Saint Martin des Champs in Paris is the one used in the 1855 Paris exposition. The photo is from the web site of the Musée des Arts et Métiers.

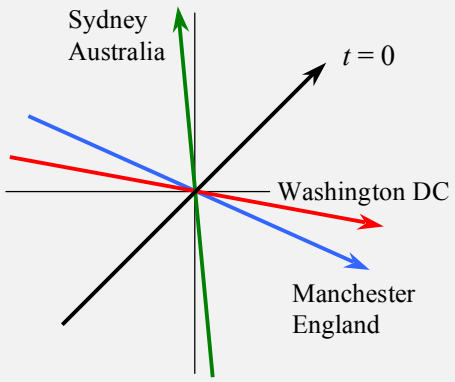
So it was possible, way back in 1850, to do an experiment inside a room that had no view of the outside world and prove that the earth rotated. The next year Foucault repeated his experiment, but this time with a massive, spinning weight. He showed that this weight, like the pendulum, ignored local effects and lined itself up with the stars. He had invented the gyroscope. In 1955, the Dutch Foreign Minister presented to the United Nations a Foucault pendulum for the entrance hall of the United Nations building in New York. In October 1995, the original pendulum was reinstalled in the Pantheon, using the original lead-coated brass ball.

## Foucault Pendulum

Everyone is familiar with the kind of pendulum you place on a table or hold with one hand. For small displacements, it swings to and fro with harmonic regularity. Its uses are legion. Were the pendulum shown in Fig. 1 like this, it would be possible – being careful with initial displacements to not inadvertently give the pendulum sideways momentum, and adding a small amount of momentum along the straight-line path during each cycle to make up for frictional loss – for it to oscillate indefinitely along a trajectory that passes through the vertical and never changes its orientation relative to the earth. In other words, the plane in which the pendulum swings would remain fixed relative to its surroundings.

This does not happen. The plane in which the pendulum oscillates slowly twists (precesses) about the vertical. The rate of precession is constant and the plane of oscillation eventually gets back to the starting point. Interestingly, the precession period depends on the location of the pendulum on the earth, varying from one day at the north and south poles to infinity at the equator, where it does not precess at all. Moreover, it turns in the clockwise direction in the northern hemisphere and in the counterclockwise direction in the southern hemisphere, as noted in Fig. 3.

Figure 3. Arrows indicate planes in which pendula in different cities swing. In each case the plane precesses slowly about a vertical line that extends from the midpoint of the swing up to the support. In the figure, this line is normal to the page, passing through the origin. The pendula are synchronized such that they all start at $t = 0$ in the black direction. In six hours, the one in Manchester has precessed 72° clockwise, the one in Washington has precessed 54° clockwise, and the one in Sydney has precessed 50.4° counterclockwise.




## How it Works

The earth is not an inertial reference system because it rotates relative to the fixed stars. This is interesting in itself. When we say an object rotates, it is assumed it rotates relative to something. In the present example, the stars are the likely suspects. But what if all of space were empty except for the earth? Would it then be possible to define rotation? Such queries were bantered about during the last part of the nineteenth century. They led ultimately to general relativity – one of the greatest theories of all time, or, more aptly, all time until the present.

Because of the earth's rotation, equations of motion that describe the dynamics of objects moving on the surface of the earth contain what appears to be a force (the Coriolis force) that accounts for the earth's rotation. When this force is included in the mathema-

tical description of the Foucault pendulum that uses the earth as the reference frame, the oscillation plane is found to precess relative to the earth. The math is given in the box below. Discussions of this and related phenomena that arise from dynamical processes in non-inertial reference frames can be found in books on classical mechanics.

The effect is most pronounced at the north and south poles, where the precession of the pendulum plane covers $2\pi$ in one day, synchronous with the earth's rotation. At the equator, there is no effect; the pendulum does not precess. As shown in the box, the precession period varies between these extremes in a predictable way. That is, the amount of rotation per day is $2\pi\cos\theta_0$, where $\theta_0$ is the polar angle for given latitude.[1]

## Coriolis Force

An observer on the surface of a rotating sphere perceives a force acting on a mass $m$:

$$\boldsymbol{F}_{eff} = \boldsymbol{F} - m\ddot{\boldsymbol{R}} - m\dot{\boldsymbol{\omega}}\times\boldsymbol{r} - m\boldsymbol{\omega}\times(\boldsymbol{\omega}\times\boldsymbol{r}) - 2m\boldsymbol{\omega}\times\boldsymbol{v} \qquad \text{(i)}$$

where $\boldsymbol{R}$ is from the origin of an inertial reference frame to the origin of the sphere, $\boldsymbol{r}$ is from the origin of the sphere to a point on its surface, $\boldsymbol{v} = \dot{\boldsymbol{r}}$, and $\boldsymbol{F}$ is the external force acting on $m$, including gravity. Equation (i) is derived in Marion and Thornton.

The term $-m\ddot{\boldsymbol{R}}$ is the translational acceleration of the rotating frame relative to the inertial frame, which is assumed fixed in space. This term is of no concern in the problem at hand because the non-inertial frame only rotates; it has no translational motion relative to an inertial frame. Therefore, $-m\ddot{\boldsymbol{R}}$ is zero. The term $-m\dot{\boldsymbol{\omega}}\times\boldsymbol{r}$ is the angular acceleration of the rotating frame. It also is of no concern because the earth rotates at constant angular velocity $\boldsymbol{\omega}$, in which case, $-m\dot{\boldsymbol{\omega}}\times\boldsymbol{r}$ is zero.

The term $-m\boldsymbol{\omega}\times(\boldsymbol{\omega}\times\boldsymbol{r})$ is the centrifugal force. When $\boldsymbol{\omega}$ and $\boldsymbol{r}$ are perpendicular to one another (as on the equator), $-m\boldsymbol{\omega}\times(\boldsymbol{\omega}\times\boldsymbol{r})$ reduces to $m\omega^2 r\hat{\boldsymbol{r}}$, which is directed radially outward. When $\boldsymbol{\omega}$ and $\boldsymbol{r}$ are not perpendicular to one another, the magnitude of the centrifugal force is $m\omega^2 r\sin\Theta$, where $\Theta$ is the angle between $\boldsymbol{\omega}$ and $\boldsymbol{r}$. This force is perpendicular to the $\boldsymbol{\omega}$ axis and $|\,\boldsymbol{r}\,|$ changes little, so it is not important.

The term $-2m\boldsymbol{\omega}\times\boldsymbol{v}$ is the Coriolis force. It accounts for the precession. Like the centrifugal force, it is not a real force. It appears when we solve equations of motion relative to a set of axes fixed to the rotating sphere. It accounts for many phenomena, from the circulatory motions of air masses in the northern and southern hemispheres to effects observed in the high-resolution spectroscopy of rotating molecules.

Let's now apply the Coriolis force to a Foucault pendulum on the earth at polar angle $\theta_0$. To examine the pendulum's motion, axes are chosen such that $\hat{\boldsymbol{z}}$ is perpendicular to the tangent plane and $\hat{\boldsymbol{x}}$ lies in the plane containing $\boldsymbol{\omega}$ and $\boldsymbol{r}$ (Fig. 4). The gravitational force is $-g\hat{\boldsymbol{z}}$. The angular frequency vector $\boldsymbol{\omega}$ of the earth's rotation has components $\omega_z = \omega\cos\theta_0$, $\omega_y = 0$, and $\omega_x = -\omega\sin\theta_0$.

[1] The polar angle $\theta_0$ is measured relative to the line that goes through the north and south poles, with the center of the earth being the origin. What is referred to in the vernacular as latitude is the complement of this angle, *e.g.*, $90° - \theta_0$ in the northern hemisphere.

The tension $\boldsymbol{T}$ in the suspension system exerts a force on the ball, with components: $T_z = mg$, $T_x = -mg(x/l)$, and $T_y = -mg(y/l)$, where $l$ is the length of the pendulum. The equation of motion:

$$\ddot{x}\hat{\boldsymbol{x}} + \ddot{y}\hat{\boldsymbol{y}} = \boldsymbol{T}/m - 2\boldsymbol{\omega}\times\boldsymbol{v} \tag{ii}$$

yields

$$\ddot{x} - 2\omega_z\dot{y} + \omega_0{}^2 x = 0 \tag{iii}$$

$$\ddot{y} + 2\omega_z\dot{x} + \omega_0{}^2 y = 0 \tag{iv}$$

where $\omega_0{}^2 = g/l$ is the pendulum's angular frequency. The solution of eqns (iii) and (iv) follows a standard procedure. Let $x(t) = xe^{i\alpha t}$ and $y(t) = ye^{i\alpha t}$, with the understanding that the real parts of $x(t)$ and $y(t)$ are taken after they have been determined. Putting these into eqns (iii) and (iv) yields

$$-\alpha^2 x - 2i\alpha\omega_z y + \omega_0{}^2 x = 0 \tag{v}$$

$$-\alpha^2 y + 2i\alpha\omega_z x + \omega_0{}^2 y = 0 \tag{vi}$$

These equations can be reduced to a single equation by multiplying eqn (vi) by $i$, adding it to eqn (v), and defining $z = x + iy$. This yields

$$\alpha^2 + 2\alpha\omega_z - \omega_0{}^2 = 0 \tag{vii}$$

The roots are

$$\alpha = -\omega_z \pm (\omega_0{}^2 + \omega_z{}^2)^{1/2} \tag{viii}$$

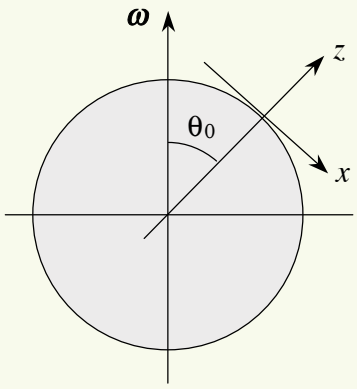


Figure 4. The $xy$ tangent plane touches the earth at the polar angle $\theta_0$. The $xz$-plane is in the plane of the paper.

Thus, there are two frequencies: one fast (essentially the natural frequency of the pendulum), and one slow (the precession). To see this, use $x(t) \propto e^{i\alpha_1 t} \pm e^{i\alpha_2 t}$ with the values of $\alpha$ given by eqn (viii):

$$x(t) \propto \exp\left\{-i\omega_z t + i\sqrt{\omega_0{}^2 + \omega_z{}^2}\, t\right\} \pm \exp\left\{-i\omega_z t - i\sqrt{\omega_0{}^2 + \omega_z{}^2}\, t\right\} \tag{ix}$$

If we assume that $|x(t)|$ is maximum at $t = 0$, the plus sign is used, giving

$$x(t) \propto \exp\{-i\omega_z t\} \cos\sqrt{\omega_0{}^2 + \omega_z{}^2}\, t \tag{x}$$

Taking the real part gives $x(t) \propto \cos\omega_z t \cos[(\omega_0{}^2 + \omega_z{}^2)^{1/2} t]$. Because $x(t)$ and $y(t)$ have a phase difference of $\pi/2$, $y(t) \propto \sin\omega_z t \cos[(\omega_0{}^2 + \omega_z{}^2)^{1/2} t]$. These expressions show that the pendulum precesses with angular frequency $\omega_z = \omega\cos\theta_0$. Thus, in one day the amount of precession is

$$\omega_z T = \text{ precession for one day } = 2\pi\cos\theta_0 \tag{xi}$$

This is one way to explain the Foucault pendulum.

When the earth undergoes its complete revolution in one day, the Foucault pendulum does not come back to its starting point unless it is located at the North or South Pole. Though the external parameters that are responsible for the adiabatic evolution of the pendulum have completed a closed circuit, the pendulum does not follow suit. The system is said to be non-holonomic or anholonomic. The dynamical quantity of interest, in this case the plane in which the pendulum swings, does not return to its original orientation relative to its surroundings when the variables that define the rotation of the earth relative to the heavens return to their original values.

The variation of the orientation of the pendulum plane depends on the that the variables take, namely, the latitude at which the pendulum is located. Phase can be defined such that no precession (*i.e.*, the pendulum is at the equator) corresponds to a phase of zero, while a precession period that is synchronous with the earth's rotation (*i.e.*, at the north or south pole) corresponds to a phase of $\pm 2\pi$. Other locations have phases whose magnitudes lie between zero and $\pm 2\pi$, according to the formulas in the above box.

It is interesting that the phase does not depend on the period of the earth's rotation. It depends only on the location of the pendulum on the surface of the earth. For a given location, if the earth were to double its rotational frequency, the phase change of the pendulum (as measured relative to its initial orientation) *per revolution of the earth* would not be affected. In other words, the pendulum precesses twice as quickly, but it does so for half as long in completing a cycle. This is an example of geometric phase. The dynamic phase, on the other hand, corresponds to the to and fro oscillation of the pendulum. This phase simply accumulates with time.

With the Coriolis force included in the equations of motion, the solution of the dynamics problem is straightforward, as shown in the above box. This yields the precession angle, which is a phase. It is a quite different phase than that of the pendulum's to and fro oscillation, which is of much higher frequency. The precessing vector *turns* relative to its original orientation. Note that when it has precessed by $\pm \pi$, the overall effect is to add $\pm \pi$ to the dynamic phase.

It will now be shown that the precession of the Foucault pendulum can be determined from geometrical arguments alone, *i.e.*, without solving the equations of motion given in the above box. To proceed, replace the plane of the pendulum by a vector that lies in the plane of the pendulum and is tangent to the surface. Though the initial orientation of the vector is arbitrary, it is advisable to use a *vector* rather than a *straight line* to avoid ambiguity about integer multiples of $\pi$. This vector is then transported on the surface of a sphere in a manner that is equivalent to how the rotation of the earth transports the Foucault pendulum.

The situation is approached through the mathematics of *parallel transport* of a unit vector $\boldsymbol{e}$ on the surface of a unit sphere (*i.e.*, one whose radius $\boldsymbol{r}$ has a magnitude of one). We shall now examine this, though not in depth. The excellent book by Henderson and Taimina (an introduction to non-Euclidean geometry) makes this material accessible to the non-specialist.

## Parallel Transport of a Vector on a Sphere

Transporting a vector on the surface of a sphere requires care if one has been imprinted with the intuition of a flatlander. The geometry is non-Euclidean,[2] and formulas and rules for angles, triangles, polygons, etc. on flat surfaces need to be reconsidered for the curved surface of the sphere. A good pedagogical strategy requires that you obtain a large (inexpensive) ball and non-permanent marker pens of different colors, as recommended by Henderson and Taimina. You are to draw on the ball (lines, circles, angles, etc.) to facilitate visualization of the geometrical constructs. Attempting to follow the discussion below without making sketches on your sphere might be frustrating.

The earth will be used as an example from time to time because references to latitudes, longitudes, the equator, and the north and south poles are intuitive. It is understood, however, that we are now transporting the vector ourselves, rather than having the earth's rotation do it, as with the Foucault pendulum. Though the "earth" treated here is non-rotating, it will nonetheless be possible to draw correspondence between this example and the Foucault pendulum. Namely, the latter can be modeled as a vector being transported on the surface of a non-rotating sphere. This will illustrate the geometric, rather than dynamic, nature of the precession of the Foucault pendulum.

On a flat surface, defining a straight line is trivial, whereas on a sphere, even this seemingly simple matter requires thought. Though there are no straight lines on a sphere, we are interested in the equivalent, for example, the shortest distance between two points, or a path in which our right and left legs travel the same distance without our body twisting relative to the chosen path. This leads to geodesics, which are paths that are intrinsically straight. The geodesics on a sphere are segments of great circles, *i.e.*, circles whose origins coincide with the sphere's origin. This is easily verified with your sphere. Take two points on it and stretch a string between them. It will be a geodesic – a segment of a great circle. As used here, intrinsic means that the paths are straight to someone on the sphere, according, say, to the criteria mentioned above. Of course, extrinsically, *i.e.*, observed from outside the sphere, there are no straight lines on the surface of a sphere.

Using geodesics, we can make triangles and polygons. Lines drawn on the sphere that are not geodesics cannot be used to make these objects. Because such lines are not intrinsically straight, it makes no sense to make triangles by using them. They are just lines that we draw and to which we assign with our imaginations degrees of straightness. Thus, we cannot make a triangle out of two longitudes and one latitude, whereas we can make a triangle with two longitudes and the equator.[3]

Now consider the parallel transport along a geodesic of a *unit vector* $\boldsymbol{e}$ that is tangent to the surface. Moving a vector around on the surface of a sphere can be subtle, and the meaning of *parallel transport*, particularly insofar as rotation is concerned, needs to be

---

[2] In a non-Euclidean space, it is not possible to choose a set of Cartesian coordinates. The simplest example is the surface of a sphere.

[3] Latitudes are not intrinsically straight. Recall that the shortest distance between two cities on the same latitude does not follow the latitude, but a geodesic. This is used in airplane flight paths.

established. For parallel transport, one of the conditions is that $\boldsymbol{e}$ must remain tangent to the surface of the sphere throughout the process, whether $\boldsymbol{e}$ is moved from one point on the sphere to another, or along a path that completes a closed circuit. Thus, we have:

$$\boldsymbol{e} \cdot \boldsymbol{r} = 0 \tag{1}$$

where the *unit vector* $\boldsymbol{r}$ is directed outward from the origin to the point on the sphere where $\boldsymbol{e}$ is tangent. In addition, parallel transport requires that $\boldsymbol{e}$ does not twist around $\boldsymbol{r}$ as it is transported on a geodesic. In other words, transport takes place with the angle between the unit vector $\boldsymbol{e}$ and the geodesic (at the point of tangency) remaining constant.

If we choose a closed path consisting solely of geodesics, it is easy to follow parallel transport because the angle that the vector makes with the path remains constant as the vector is transported on a given geodesic. When the path switches to a different geodesic, the angle between the vector and the new geodesic is preserved as the vector is parallel transported along the new geodesic.

Use your model sphere to trace the transport of a vector initially at the North Pole: (i) down a longitude to the equator; (ii) around the equator by some distance; and (iii) back to the North Pole. Referring to Fig. 5, along path (i) the vector is assumed, with no loss of generality, to lie parallel to the path. Along the equator it lies perpendicular to the path, and along its return to the North Pole it lies parallel to the path. At the North Pole, the returned vector is at an angle relative to its initial direction that is exactly the azimuthal angle $\phi$ of the equatorial geodesic segment. Parallel transport has resulted in an angle $\phi$ that arises because of the fact that the surface is curved.

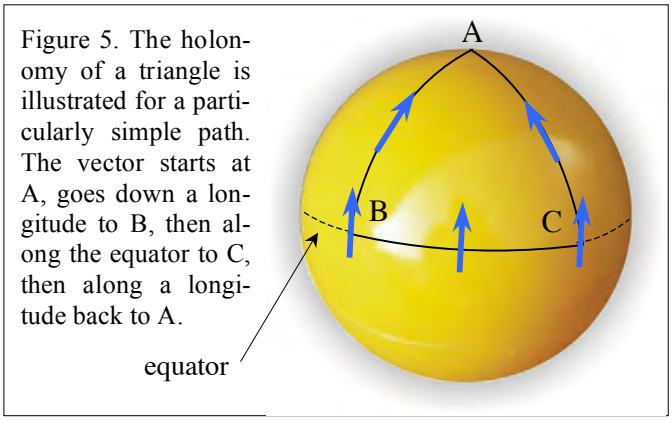



Figure 5. The holonomy of a triangle is illustrated for a particularly simple path. The vector starts at A, goes down a longitude to B, then along the equator to C, then along a longitude back to A.

This can also be illustrated by moving one of your arms. Hold your fully extended (straight at the elbow) right arm above your head with the thumb pointing horizontally to the left. Move it down in an arc to your right until it is shoulder high; the thumb now points vertically upwards, with your fully extended arm horizontal on your right side. Now move your arm in an arc until it is straight in front of you; the thumb still points upwards. Finally, raise your fully extended arm above your head. Your thumb now points behind you. There is an angle of 90° between its initial and final directions.

The angle between the vector at its start and finish is called the holonomy, $\mathcal{H}$. Figure 5 uses an easy path. However, we can just as easily choose three geodesics that constitute the most general case and compute the holonomy. This yields the general formula for the holonomy of a triangle on the surface of a sphere in terms of the three angles of the triangle. Figure 6 and the following discussion show how this is done.

Referring to Fig. 6, the vector remains tangent to the surface as it is transported along the indicated path. At **A** the vector lies at an angle $\theta_1$ relative to the geodesic **AB** along which it is about to be parallel transported. It moves along this geodesic to **B** with $\theta_1$ held constant. At **B** it makes an angle $\theta_2 = \pi - \beta_2 - \theta_1$ with respect to the geodesic **BC** upon which it is going to be parallel transported. It moves along this geodesic to **C**; as before, $\theta_2$ does not change. At **C** the vector makes an angle $\theta_3 = \beta_3 - \theta_2$ with the geodesic **CA** upon which it is going to be parallel transported. The vector is brought back to **A** along the last geodesic. The angle between its initial and final directions is

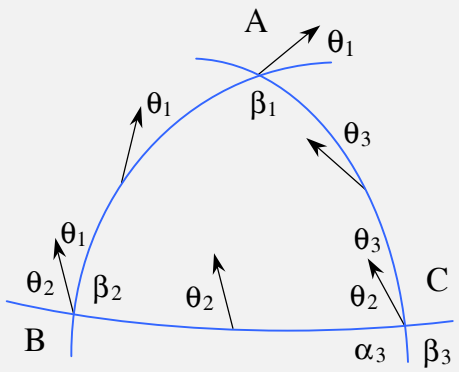



Figure 6. A vector tangent to the surface of a sphere is transported around a closed path consisting of three geodesics. The vector does not twist as it is transported on the geodesics. All angular changes occur at the apices.

$$\begin{aligned}\beta_1 - \theta_1 + \theta_3 &= \beta_1 - \theta_1 + \beta_3 - \theta_2 \\ &= \beta_1 - \theta_1 + \beta_3 - \pi + \beta_2 + \theta_1 \\ &= \beta_1 + \beta_2 + \beta_3 - \pi.\end{aligned}$$

Make sure you are comfortable with this, as careful bookkeeping is required. Thus, the holonomy of the triangle is

$$\mathcal{H}(\Delta) = \beta_1 + \beta_2 + \beta_3 - \pi \tag{2}$$

where the $\beta_i$ are the interior angles of the triangle, and $\Delta$ signifies the triangle. In terms of the exterior angles, $\alpha_i$ (see Fig. 6), the holonomy is: $\mathcal{H}(\Delta) = 2\pi - (\alpha_1 + \alpha_2 + \alpha_3)$.

We shall now obtain the Gauss-Bonnet formula for triangles, which is central to the subject of geometric phase. First, let us obtain an expression for the area of a triangle on a unit sphere. Using your model sphere, draw three great circles that give an easily recognized triangle (Fig. 7). Two great circles always intersect, creating areas called lunes, as seen in the figure. Imagine cutting an orange into segments. You might find it helpful to shade the two *easily recognized triangles*, which are on opposite sides of the sphere.

By adding together the areas of the enclosed regions, you will find that the area of the unit sphere ($4\pi$) is given by:

$$4\pi = 2(A_{\beta_1} + A_{\beta_2} + A_{\beta_3}) - 4A = 2A + 2(A'_{\beta_1} + A'_{\beta_2} + A'_{\beta_3}) \tag{3}$$

A prime denotes an area of a lune minus the area of interest, $A$. In other words, the area of the lune whose angle is $\beta_1$ is $A_{\beta_1}$, and therefore $A'_{\beta_1} = A_{\beta_1} - A$. Equation (3) is easily confirmed by visualizing the respective contributions on your model sphere. Likewise, an

equation can be written for the areas of the three lunes, each of which obeys the relation: $A'_{\beta_i} + A = 2\beta_i$. When the equations for $i = 1 - 3$ are added together we get

$$3A + A'_{\beta_1} + A'_{\beta_2} + A'_{\beta_3} = 2(\beta_1 + \beta_2 + \beta_3) \tag{4}$$

Make sure you understand the relationship $A'_{\beta_i} + A = 2\beta_i$, *e.g.*, by using your sphere. Eliminating the common term $(A'_{\beta_1} + A'_{\beta_2} + A'_{\beta_3})$ from eqns (3) and (4) yields

$$\boxed{A = \beta_1 + \beta_2 + \beta_3 - \pi} \tag{5}$$

The area $A$ on the unit sphere is, by definition, the solid angle subtended from the origin of the sphere. From eqns (2) and (5), we see that this solid angle is equal to the holonomy.


Figure 7. Three great circles create the triangle shown in the figure with internal angles $\beta_1, \beta_2$, and $\beta_3$. Two great circles always intersect, creating lunes (crosshatch), which are like slices of an orange.

The above exercise was carried out for a triangle. It is not difficult to extend the derivation to arbitrary shapes. This is left as an exercise. Polygons can be built from triangles, and a general shape can be approximated by a polygon. For any closed path, it is possible to approximate the path with a series of segments, connected one to the next, each of which is an arc segment of a geodesic. Thus, any path on the surface can be represented using a combination of geodesic segments. The result is that, for an arbitrary surface area on the sphere, the holonomy is given by the solid angle it subtends from the origin of the sphere:

$$\boxed{\mathcal{H} = \Omega} \tag{6}$$

where $\Omega$ is the solid angle. This is a great formula.

## Relationship to the Foucault Pendulum

Returning to the Foucault pendulum, we now identify its precession at different latitudes with corresponding cases of parallel transport of a vector on a sphere. In so doing, we are able to use eqn (6) to obtain the pendulum's precession (holonomy) directly, that is, without recourse to the Coriolis force. To begin, consider the case in which the pendu-

lum is located at the North Pole, where it remains fixed relative to the distant stars while the earth rotates beneath it. This is an admission that the earth rotates relative to *something*. Were the earth the ultimate reference system, it would be inertial and there would be no meaning to the phrase "while the earth rotates beneath it."

When the pendulum is at the North Pole, the parallel transport equivalent is to follow the path shown in Fig. 5, with the turning of the earth replaced by transport around the equator. No matter where the pendulum is located on the earth, the parallel transport equivalent includes going to the equator and then transporting the vector around the equator, as this constitutes the earth's rotation around an axis that goes through the north and south poles. When the pendulum is located at the north pole, the holonomy in one day is simply the solid angle of the upper hemisphere, $2\pi$. A person watching the pendulum at the North Pole sees the pendulum precess clockwise at the same rate as the earth's rotation, while a person observing it from a distant solar system sees the pendulum as stationary while the earth rotates counterclockwise. Repeating for the South Pole gives $-2\pi$. The pendulum precesses counterclockwise relative to the earth.

When the pendulum is near the equator, say a bit to the north, the enclosed area is just the thin strip above the equator. As the pendulum is brought closer to the equator, this area vanishes and the holonomy becomes zero. To an observer on earth a pendulum located at the equator does not precess. Of course, the most interesting situation is when the pendulum is located at latitude intermediate between the equator and the North Pole, as indicated in Fig. 8. In the case of a complete (one-day) rotation of the earth ($\Delta\phi = 2\pi$), the enclosed area $A$ is given by


Figure 8. The surface of interest is bounded by two longitudes, the equator, and the latitude defined by the polar angle $\theta_0$.

$$A = 2\pi \int_{\theta_0}^{\pi/2} d\theta \sin\theta = 2\pi \cos\theta_0 \tag{7}$$

where $\theta_0$ is the polar angle at which the pendulum is located.

The enclosed area $A$ on the unit sphere is equal to the solid angle $\Omega$, which is equal to the holonomy. This is exactly the precession angle obtained using the Coriolis force to solve any dynamics problem. It has been obtained, however, without solving the dynamics problem. The phase angle for the precession of the pendulum is seen to be a purely geometrical effect that arises because of the curved surface upon which transport occurs.

## Summary of the Foucault Pendulum

Let us reflect on what has been learned. The fact that the rotating earth is a non-inertial reference frame leads to an apparent force – the Coriolis force – that enters the equations of motion when solving dynamics problems on the surface of an assumed locally flat earth. This enables the precession of the Foucault pendulum to be obtained by a simple calculation.

More importantly, the precession angle (phase) can be obtained from a purely geometrical construction. This geometric phase is due to the non-Euclidean nature of the spherical surface, and it is equal to the subtended solid angle. In general, dynamics problems that involve adiabatic separation are not as easy as the Foucault pendulum, so exact solutions are not available. The corresponding vector transport, however, *is* readily available and yields the geometric phase without the need to solve the dynamics problem. This has far-reaching consequences in systems where an adiabatic separation is used to obtain solutions, such as the Born-Oppenheimer approximation.

We shall now generalize the above result to the parallel transport of complex vectors, finishing with (complex valued) quantum mechanical state vectors, where transport is brought about by terms in a Hamiltonian.

## Parallel Transport of a Complex Vector

The above development is easily generalized to the transport of a complex vector by introducing a third unit vector ***e***' that is perpendicular to both ***e*** and ***r***. The ***e*** and ***e***' vectors can be used to represent the real and imaginary parts of the complex vector. As mentioned earlier, this is a step in the direction of extending the results to include Hilbert vectors, thereby making the transition to quantum geometric phase.

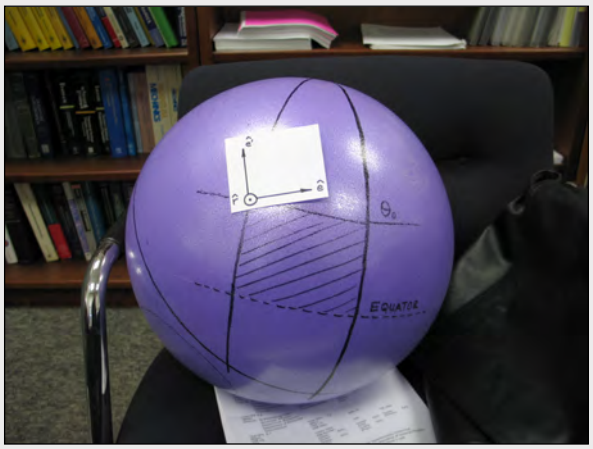



Figure 9. A triad of orthogonal unit vectors (***e***, ***e***', and ***r***) is located on the surface of a sphere. The vectors ***e*** and ***e***' lie in the tangent plane, while ***r*** lies normal to the tangent plane and points outward from the origin of the sphere. Parallel transport means that ***e*** and ***e***' do not twist around ***r*** as the triad is transported on a geodesic.

Referring to Fig. 9, the following dimensionless unit vectors are used to define a set of orthogonal axes: ***e***, which is tangent to the surface of the sphere; ***r***, whose direction is from the origin to the point on the sphere where ***e*** is tangent; and ***e***', which is orthogonal to both ***r*** and ***e***:

$$\boldsymbol{e}' = \boldsymbol{r} \times \boldsymbol{e} \tag{8}$$

Like $\boldsymbol{e}$, the unit vector $\boldsymbol{e}'$ lies in the plane that is tangent to the surface at the point where the tip of $\boldsymbol{r}$ touches the surface. Hereafter, this plane will be referred to as the tangent plane. The origin of the set of orthogonal axes given by $\boldsymbol{e}$, $\boldsymbol{r}$, and $\boldsymbol{e}'$ lies at the tangent point. The condition that neither $\boldsymbol{e}$ nor $\boldsymbol{e}'$ twists around $\boldsymbol{r}$ during parallel transport is stated mathematically as

$$\boldsymbol{\omega} \cdot \boldsymbol{r} = 0 \tag{9}$$

where $\boldsymbol{\omega}$ is the instantaneous rotational angular frequency of the set of axes (reference frame) given by the triad of unit vectors $\boldsymbol{e}$, $\boldsymbol{r}$, and $\boldsymbol{e}'$.

Though this set of axes rotates as a whole about the sphere's origin when the tip of $\boldsymbol{r}$ traces a path on the surface of the sphere along a geodesic, there cannot be a component of $\boldsymbol{\omega}$ that lies along $\boldsymbol{r}$. Were this component non-zero, it would constitute what we referred to earlier as twisting around $\boldsymbol{r}$. Namely, if viewed along the $\boldsymbol{r}$ direction, the $\boldsymbol{e}/\boldsymbol{e}'$ axes would rotate. If these axes twisted, they would change their angles with respect to the geodesic along which transport is occurring, and we would not have parallel transport.

The vector $\boldsymbol{\omega}$ has no nonzero component along $\boldsymbol{r}$. It lies in the tangent plane, and it is given by

$$\boldsymbol{\omega} = \boldsymbol{r} \times \dot{\boldsymbol{r}} \tag{10}$$

Because the component of $\boldsymbol{\omega}$ along $\boldsymbol{r}$ is zero, the vector $\boldsymbol{e}$ can only change in a direction that is perpendicular to the tangent plane. If it moved *in* the tangent plane, $\boldsymbol{\omega}$ would have a component along $\boldsymbol{r}$. Thus, $\dot{\boldsymbol{e}}$ lies perpendicular to the tangent plane and is given by

$$\dot{\boldsymbol{e}} = \boldsymbol{\omega} \times \boldsymbol{e} \tag{11}$$

The vectors $\boldsymbol{e}'$ and $\boldsymbol{e}$ are equivalent insofar as the conditions imposed on them by parallel transport are concerned. In the constraints given above for the triad of unit vectors, it is necessary to have both of these vectors to ensure that the requirements of 3D space are fulfilled, but their directions in the plane are arbitrary, except that they must be orthogonal to one another. They can be combined into the complex unit vector $\boldsymbol{\psi}$ to facilitate manipulations:

$$\boldsymbol{\psi} = \tfrac{1}{\sqrt{2}}\left(\boldsymbol{e} + i\boldsymbol{e}'\right) \tag{12}$$

The complex vector $\boldsymbol{\psi}$ satisfies the parallel transport requirements because $\boldsymbol{e}$ and $\boldsymbol{e}'$ separately satisfy these requirements. You might question why this particular combination has been chosen. Why not use $0.8\,\boldsymbol{e} + i\,0.6\,\boldsymbol{e}'$ or some other combination for which $|\boldsymbol{\psi}| = 1$? It will be shown that how the real and imaginary parts are apportioned does not

matter. Here, $(\boldsymbol{e}+i\boldsymbol{e}')/\sqrt{2}$ is introduced because it is convenient. The conditions indicated by eqns (9) – (11) can be expressed in terms of $\boldsymbol{\psi}$ and its time derivative by writing

$$\boldsymbol{\psi}^* \cdot \dot{\boldsymbol{\psi}} = \tfrac{1}{2}(\boldsymbol{e}-i\boldsymbol{e}')\cdot(\dot{\boldsymbol{e}}+i\dot{\boldsymbol{e}}') \tag{13}$$

$$= \tfrac{1}{2}\left(\boldsymbol{e}\cdot\dot{\boldsymbol{e}}+\boldsymbol{e}'\cdot\dot{\boldsymbol{e}}'+i(\boldsymbol{e}\cdot\dot{\boldsymbol{e}}'-\boldsymbol{e}'\cdot\dot{\boldsymbol{e}})\right) \tag{14}$$

The terms $\boldsymbol{e}\cdot\dot{\boldsymbol{e}}$ and $\boldsymbol{e}'\cdot\dot{\boldsymbol{e}}'$ each vanish because $\boldsymbol{e}$ and $\dot{\boldsymbol{e}}$ (likewise $\boldsymbol{e}'$ and $\dot{\boldsymbol{e}}'$) are orthogonal, for example, see eqn (11). Because $\boldsymbol{e}$ and $\boldsymbol{e}'$ are real, the imaginary part of $\boldsymbol{\psi}^*\cdot\dot{\boldsymbol{\psi}}$ is $(\boldsymbol{e}\cdot\dot{\boldsymbol{e}}'-\boldsymbol{e}'\cdot\dot{\boldsymbol{e}})/2$. This also vanishes, because $\dot{\boldsymbol{e}}$ and $\dot{\boldsymbol{e}}'$ are each perpendicular to the tangent plane that contains $\boldsymbol{e}$ and $\boldsymbol{e}'$. Thus,

$$\mathrm{Im}\left(\boldsymbol{\psi}^*\cdot\dot{\boldsymbol{\psi}}\right)=0 \tag{15}$$

or, equivalently,

$$\mathrm{Im}\left(\boldsymbol{\psi}^*\cdot d\boldsymbol{\psi}\right)=0 \tag{16}$$

where $d\boldsymbol{\psi}$ is due to $d\boldsymbol{r}$ (*i.e.*, $d\boldsymbol{\psi}/dt=(\dot{\boldsymbol{r}}\cdot\nabla)\boldsymbol{\psi}$ and $d\boldsymbol{\psi}=(d\boldsymbol{r}\cdot\nabla)\boldsymbol{\psi}$). Equation (16) can also be written $\mathrm{Im}(\boldsymbol{\psi}^*\cdot\nabla\boldsymbol{\psi})=0$. The real part of $\boldsymbol{\psi}^*\cdot\dot{\boldsymbol{\psi}}$ is also equal to zero, but unlike eqn (16), this does not lead to the useful expression derived below.

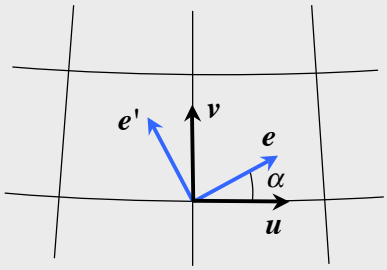



Figure 10. Unit vectors (axes) $\boldsymbol{u}$ and $\boldsymbol{v}$ are local basis vectors. The orthogonal pair $\boldsymbol{e}$ and $\boldsymbol{e}'$ lies at angle $\alpha$ relative to $\boldsymbol{u}$ and $\boldsymbol{v}$. The radius vector $\boldsymbol{r}$ (not shown) is directed outward from the origin intercepting the unit sphere at the $\boldsymbol{u}$, $\boldsymbol{v}$ (and $\boldsymbol{e}$, $\boldsymbol{e}'$) origin.

We shall now obtain an expression for the extent to which the vector $\boldsymbol{e}$ becomes rotated (without *twisting* around $\boldsymbol{r}$) as it moves about on the surface of the sphere under the constraint of parallel transport. A local basis of orthogonal axes on the sphere is introduced to keep track of the phase, which is defined locally as the direction of $\boldsymbol{e}$ relative to one of the axes (Fig. 10). Unit vectors $\boldsymbol{u}$ and $\boldsymbol{v}$ lie along the latitudes and longitudes of the sphere, respectively.

Analogous to the complex unit vector $\boldsymbol{\psi}$, which is a combination of the real unit vectors $\boldsymbol{e}$ and $\boldsymbol{e}'$, the complex unit vector $\boldsymbol{n}$ is introduced. It is made from the real unit vectors $\boldsymbol{u}$ and $\boldsymbol{v}$:

$$\boldsymbol{n}=\tfrac{1}{\sqrt{2}}\left(\boldsymbol{u}+i\boldsymbol{v}\right) \tag{17}$$

Referring to Fig. 10, the angle $\alpha$ is used to express the relationship between $\boldsymbol{\psi}$ and $\boldsymbol{n}$:

$$\boldsymbol{\psi} = \tfrac{1}{\sqrt{2}}\left(\boldsymbol{e} + i\boldsymbol{e}^{\prime}\right) \tag{18}$$

$$= \tfrac{1}{\sqrt{2}}\left((\boldsymbol{u}\cos\alpha + \boldsymbol{v}\sin\alpha) + i(\boldsymbol{v}\cos\alpha - \boldsymbol{u}\sin\alpha)\right) \tag{19}$$

$$= \tfrac{1}{\sqrt{2}}\left((\boldsymbol{u} + i\boldsymbol{v})\cos\alpha - i(\boldsymbol{u} + i\boldsymbol{v})\sin\alpha\right) \tag{20}$$

$$= \tfrac{1}{\sqrt{2}}(\boldsymbol{u} + i\boldsymbol{v})(\cos\alpha - i\sin\alpha) \tag{21}$$

$$= \boldsymbol{n}\, e^{-i\alpha} \tag{22}$$

Thus, $d\boldsymbol{\psi} = e^{-i\alpha}\, d\boldsymbol{n} - i\boldsymbol{n}e^{-i\alpha}\, d\alpha$. Dotting $d\boldsymbol{\psi}$ with $\boldsymbol{\psi}^* = \boldsymbol{n}^* e^{i\alpha}$ yields

$$\boldsymbol{\psi}^* \cdot d\boldsymbol{\psi} = \boldsymbol{n}^* e^{i\alpha} \cdot \left(e^{-i\alpha}\, d\boldsymbol{n} - i\boldsymbol{n}e^{-i\alpha}\, d\alpha\right) \tag{23}$$

$$= \boldsymbol{n}^* \cdot d\boldsymbol{n} - i\, d\alpha \tag{24}$$

Referring to eqn (16), because the imaginary part of $\boldsymbol{\psi}^* \cdot d\boldsymbol{\psi}$ is equal to zero, integrating the imaginary part of eqn (24) yields

$$\int_C d\alpha = \mathrm{Im} \int_C \boldsymbol{n}^* \cdot d\boldsymbol{n} \tag{25}$$

where $C$ is the path. If the path is closed, the accumulated phase $\alpha(C)$ is given by

$$\boxed{\alpha(C) = \mathrm{Im} \oint_C \boldsymbol{n}^* \cdot d\boldsymbol{n}} \tag{26}$$

Because $\alpha$ is the angle between the vector $\boldsymbol{\psi}$ and the local basis $\boldsymbol{n}$, eqns (25) and (26) have the same interpretation as the parallel transport discussed earlier. The arbitrary path $C$ can be approximated with small geodesic segments. Transport on each of these segments maintains a constant angle between the vector and the geodesic, which can be taken as parallel to one of the local basis vectors. Transport on a geodesic takes place with $\Delta\alpha = 0$ and $\Delta\boldsymbol{n} = 0$. Upon switching to the next geodesic segment, the angle $\alpha$ and local basis $\boldsymbol{n}$ change, so there are non-zero increments $\Delta\alpha$ and $\Delta\boldsymbol{n}$ that occur at this transition point. Transport along the new geodesic then occurs with $\Delta\alpha = 0$ and $\Delta\boldsymbol{n} = 0$ until the next transition point is reached, and so forth. Figure 6 shows how this works for a triangle, and generalization to the arbitrary curve $C$ has been discussed earlier.

## Gauge Transformation

It is intuitive that the result given by eqn (26) does not depend on the choice of basis. Were it basis dependent, it would not have physical significance. To see this independence mathematically, rotate the basis by using the transformation:

$$\boldsymbol{n} \rightarrow \boldsymbol{n}\, e^{i\mu(\boldsymbol{r})} \tag{27}$$

The degree of rotation $\mu(\boldsymbol{r})$ in general depends on $\boldsymbol{r}$. With this transformation, complex conjugation gives $\boldsymbol{n}^* \rightarrow \boldsymbol{n}^* e^{-i\mu(\boldsymbol{r})}$, and $d\boldsymbol{n}$ becomes $e^{i\mu(\boldsymbol{r})} d\boldsymbol{n} + i\boldsymbol{n} e^{i\mu(\boldsymbol{r})} d\mu(\boldsymbol{r})$. Putting these into the right hand side of eqn (26) yields

$$\alpha(C) = \mathrm{Im} \oint_C \boldsymbol{n}^* e^{-i\mu(\boldsymbol{r})} \cdot \left( e^{i\mu(\boldsymbol{r})} d\boldsymbol{n} + i\boldsymbol{n} e^{i\mu(\boldsymbol{r})} d\mu(\boldsymbol{r}) \right) \tag{28}$$

$$= \mathrm{Im} \oint_C \boldsymbol{n}^* \cdot d\boldsymbol{n} + \mathrm{Im} \oint_C i\, \boldsymbol{n}^* \cdot \boldsymbol{n}\, d\mu(\boldsymbol{r}) \tag{29}$$

$$= \mathrm{Im} \oint_C \boldsymbol{n}^* \cdot d\boldsymbol{n} + \oint_C d\mu(\boldsymbol{r}) \tag{30}$$

In going from eqn (29) to eqn (30), use has been made of the fact that $\boldsymbol{n}^* \cdot \boldsymbol{n} = 1$ and $\mu(\boldsymbol{r})$ is real. The integral of $d\mu(\boldsymbol{r})$ in eqn (30) vanishes because $\mu(\boldsymbol{r})$ is a scalar that is continuous along the path. Thus, there is no net change in the local basis upon completion of a closed path. That is, the basis is the same at the starting and ending points because the path is closed. We see that the local gauge transformation that rotates the basis has no effect on the geometric phase.

## Summary of Classical Geometric Phase

The Foucault pendulum is an example of a system in classical physics in which there is an obvious adiabatic separation between the time scales of the pendulum's oscillation and its precession. It reveals a geometric phase, and it is equivalent mathematically to the transport of a vector on the surface of a sphere. The geometric phase is the angle between the initial vector (before transport begins) and the vector after the transport process has been completed. This is of most interest when the path is closed, in which case the vector returns to its starting location, but with an angle $\alpha(C)$ between the initial and final vectors. In mathematics this is called the holonomy. It is also frequently called the anholonomy, so don't get excited about the presence or absence of the prefix *an*.

It has been shown from a simple geometrical construction that the geometric phase $\alpha(C)$ is equal to the solid angle of the closed path $C$ subtended from the origin of the sphere upon which transport takes place, independent of the shape of the path. Because

any path can be approximated as a series of geodesic segments, the Gauss-Bonnet formula yields the relationship $\alpha(C) = \Omega$ without need for further elaboration.

This result is the foundation of quantum geometric phase. We have shown that it is easily extended to the transport of two orthogonal vectors that lie in the plane that is tangent to the point of intersection. Thus, the result applies to complex vectors, because the real vectors $\boldsymbol{e}$ and $\boldsymbol{e}'$ can be combined into $\boldsymbol{\psi} = (\boldsymbol{e} + i\boldsymbol{e}')/\sqrt{2}$, with $\boldsymbol{\psi}$ automatically satisfying the requirements of parallel transport. The use of the Greek letter $\boldsymbol{\psi}$ to describe the vector $(\boldsymbol{e} + i\boldsymbol{e}')/\sqrt{2}$ is with purpose, as we shall now extend the result to vectors in Hilbert space, making the connection to quantum mechanics. It is obvious that $\alpha(C)$ cannot depend on the local basis vectors used to describe $\boldsymbol{e}$ and $\boldsymbol{e}'$. Thus, $\alpha(C)$ is invariant with respect to rotation of the $\boldsymbol{u}, \boldsymbol{v}$ basis. In the quantum counterpart, geometric phase is invariant with respect to a gauge transformation that alters the state vector.

## Generalization to Quantum Mechanical Vectors

Let us now proceed to quantum geometric phase. The vector that was used previously, $\boldsymbol{\psi} = (\boldsymbol{e} + i\boldsymbol{e}')/\sqrt{2}$, is replaced by $|\psi\rangle$. You are familiar with Hilbert space, but less so with the associated *ray space* that appends a phase factor to a state ket. Our state ket $|\psi\rangle$ is therefore written: $|n\rangle e^{i\gamma}$.

The phase $\gamma$ is the quantum version of $\alpha$. With the Foucault pendulum, transport is due to the earth's rotation, and with parallel transport we move the vector around on the sphere. In the case of quantum mechanics, the vector evolves adiabatically as a consequence of the Hamiltonian. Adiabatic change ensures that the state retains its quantum numbers. If the index $n$ denotes a set of quantum numbers, these quantum numbers will be preserved as the terms in the Hamiltonian responsible for the adiabatic evolution change slowly. The number of such terms in the Hamiltonian will turn out, for a number of cases of interest, to be $\leq 3$. This enables us to retain the 3D representation, avoiding differential geometry for spaces of dimension greater than three.

From the classical parallel transport result $\alpha(C) = \Omega$, we might be inclined to jump to the quantum version $\gamma(C) = \Omega$. In the quantum version, $\Omega$ is the solid angle subtended from the origin of a sphere in a space in which Cartesian axes represent the parameters responsible for the Hamiltonian's adiabatic evolution. The parameters can always be scaled to make a sphere (*e.g.*, rather than an ellipsoid) to preserve the direct correspondence. However, it is necessary to be careful about spin. Rotating a spin-$1/2$ ket by $2\pi$ yields a sign change, so non-integer angular momentum and problems that can be represented with spin-$1/2$ mathematics need to be looked at carefully.