Understanding Electron Spin

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Electron spin is of obvious importance in chemistry. It is therefore surprising that even textbooks with "Quantum" titles often make no attempt to provide an intelligible account thereof. It is more fashionable to introduce the concept as a mystery with its origin in either relativity or deep quantum theory.

This state of affairs is only partially explained by the fact that the Schrödinger equation was formulated (1) before the recognition of electron spin (2, 3) because several proposals outlining a physical basis of spin were published soon after (4, 5). The overriding consideration seems to be that a consistent mathematical description of the two-level spin system emerged for the first time in Dirac's relativistic wave equation (6). Thereby spin could be described as a relativistic effect without further elucidation.

Spin and Angular Momentum

In classical mechanics angular momentum is calculated as the vector product of generalized coordinates and momenta.

\[ \ell = \mathbf{q} \times \mathbf{p} \]

which in component form reduces to

\[ \ell_x = yp_z - zp_y, \quad \ell_y = zp_x - xp_z, \quad \ell_z = xp_y - yp_x \]

To convert this into a quantum-mechanical statement the momentum is represented by an operator

\[ \hat{p}_i = -i\hbar \frac{\partial}{\partial q_i} \]

operating on some \( \psi \), for example,

\[ \hat{L}_x \psi = -i\hbar \left( \frac{\partial \psi}{\partial y} - \frac{\partial \psi}{\partial z} \right) \]

Operating on this with \( \hat{L}_z \) gives

\[ \hat{L}_x \hat{L}_z \psi = -\hbar \left( y \frac{\partial^2 \psi}{\partial x \partial z} - z \frac{\partial^2 \psi}{\partial x \partial y} - x \frac{\partial^2 \psi}{\partial y \partial z} + x \frac{\partial \psi}{\partial z} + z \frac{\partial \psi}{\partial y} \right) \]

Likewise

\[ \hat{L}_y \hat{L}_z \psi = -\hbar \left( z \frac{\partial^2 \psi}{\partial y \partial x} - x \frac{\partial^2 \psi}{\partial y \partial z} - y \frac{\partial^2 \psi}{\partial x \partial z} + y \frac{\partial \psi}{\partial z} + x \frac{\partial \psi}{\partial x} \right) \]

Using

\[ \frac{\partial^2 \psi}{\partial x \partial y} = -\frac{\partial^2 \psi}{\partial y \partial x} \]

etc., by subtraction one has

\[ \hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x = -\hbar \left( x \frac{\partial \psi}{\partial x} + y \frac{\partial \psi}{\partial y} \right) \]

This defines the commutator

\[ [\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z \]

and in the same manner

\[ [\hat{L}_x, \hat{L}_z] = i\hbar \hat{L}_y, \quad [\hat{L}_y, \hat{L}_x] = i\hbar \hat{L}_z \]

The operator for the square angular momentum is constructed from

\[ \hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \]

Now, the angular-dependent part of the central-field Schrödinger wave function, in spherical polar coordinates, is an eigenfunction of \( \hat{L}^2 \).

\[ \hat{L}^2 \psi_{\ell m}(\theta, \phi) = \ell(\ell + 1) \hbar^2 \psi_{\ell m}(\theta, \phi) \]

\[ \ell = 0, 1, \ldots (n - 1) \]

\[ \hat{L}_\theta \psi_{\ell m}(\theta, \phi) = \hbar m \psi_{\ell m}(\theta, \phi) \]

The eigenvalues of \( \hat{L}_\theta \) are \((2\ell + 1)\)-fold degenerate. States with \( \ell = 0 \) should have zero angular momentum, contrary to experiment. Hydrogen \( s \) states \((\ell = 0)\) show fine structure in the form of doublet levels that represent an additional degeneracy of \( 2s + 1 \).

This remarkable state of affairs implies that, whereas classical angular momentum is a conserved quantity, the observable quantity associated with \( \hat{L}_\theta \) is not. The quantum-mechanical conserved quantity, implied by the rotational symmetry of space, is therefore associated with another operator (7),

\[ \hat{J} = \hat{L} + \hat{S} \]

where the commutators are defined by

\[ [\hat{S}_\ell, \hat{S}_m] = i\hbar \delta_{\ell m} \]

gtc., for \( \hat{L} \), but now \( \hat{S} \) cannot be expressed in terms of \( \hat{p} \) and \( \hat{q} \) operators. However, the following set of \( 2 \times 2 \) matrices (Pauli matrices) has the required property.

\[ \hat{S}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{S}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{S}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \]

The quantity corresponding to the eigenvalues of \( \hat{S}_s \),

\[ s = \pm \sqrt{\ell + 1} \]

is known as the spin of the system.

Quantum Mechanics of Spin

It follows from the foregoing that quantum theory in the traditional Schrödinger formulation is not complete. On the other hand, spin appears in Dirac's equation not because it is relativistic, but because the wave function has the correct transformation properties.

Instead of deriving a relativistic equation from the energy-momentum expression,
by substituting
\[ E^2 = c^2 p^2 + m^2 c^4 \]
by introducing the quantum operators
\[ E \rightarrow i \hbar \frac{\partial}{\partial t} \]
\[ p \rightarrow -i \hbar \frac{\partial}{\partial x} \]
without demonstrating that the form
\[ 2m \hbar \frac{\partial \psi}{\partial t} - \hbar^2 c^2 \psi = 0 \]
obeys the Galilean transformation
\[ x' = Rx + vt + a \]
\[ t' = t + b \]
The correct Galilean invariance can be ensured by following the same linearization procedure as Dirac. This means finding the linear classical form that yields the correct quantum formulation, that is,
\[ (AE + Bp + C)\psi = 0 \]
To match eq 1 this requires \( A^2 = AB = BC = C^2 = 0 \) and \( AC + CA = 2m \) with \( B^2 = 1 \). Because \( B \) is a vector, we can clearly formulate the required condition in terms of Pauli and other matrices as
\[ B_i = \begin{pmatrix} 0 & 0 \\ 0 & \sigma_i \end{pmatrix} \]
\[ A = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \]
\[ C = \begin{pmatrix} 0 & 2m \\ 0 & 0 \end{pmatrix} \]
and the wave function as a column vector,
\[ \psi = \begin{pmatrix} \phi \\ \chi \end{pmatrix} \]
Thus,
\[ (AC + CA)E + B^2 p^2 \psi = 0 \]
The linearized Schrödinger equation in this form is
\[ (AE + Bp + C)\psi = 0 \]
that is,
\[ \begin{pmatrix} 0 & 0 \\ 0 & E \end{pmatrix} \begin{pmatrix} \sigma p & 0 \\ 0 & \sigma p \end{pmatrix} \begin{pmatrix} \phi \\ \chi \end{pmatrix} + \begin{pmatrix} 0 & 2m \\ 0 & 0 \end{pmatrix} \psi = 0 \]
which is
\[ \begin{pmatrix} \sigma p & 2m \\ E & \sigma p \end{pmatrix} \begin{pmatrix} \phi \\ \chi \end{pmatrix} = 0 \]
or
\[ \sigma p \phi + 2m \chi = 0 \]
\[ E\phi + (\sigma p)\chi = 0 \]
Because \( \sigma^2 = 1 \), it follows that
\[ \phi = \frac{(\sigma p)\chi}{E} = \frac{2m\chi}{(\sigma p)} \]
that is,
\[ (p^2 - 2mE)\chi = 0 \]
and likewise for \( \phi \).
Both \( \phi \) and \( \chi \) therefore satisfy the Schrödinger equation with the same eigenvalue \( E = p^2/2m \).
To describe an electron in an electromagnetic field represented by a scalar potential \( V \) and vector potential \( A \), the quantum operators become
\[ E \rightarrow \left( \hbar \frac{\partial}{\partial t} - V \right) \]
\[ p \rightarrow \left( -i \hbar \nabla - \frac{eA}{c} \right) \]
into
\[ 2mE\phi = (\sigma p)(\sigma p)\phi \]
that is,
An Absolute Direction

where \( V(i\sigma A) = V \times A = \text{curl } A = B \)

where \( B \) is the magnetic field.

The equation reduces to

\[
\frac{\partial \psi}{\partial t} = \frac{\hbar^2}{2m} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} \right) - \frac{\hbar e}{2mc} \left( (V_{Ax} + eA_x) \frac{\partial \psi}{\partial x} + (V_{Ay} + eA_y) \frac{\partial \psi}{\partial y} \right)
\]

where

\[
V(i\sigma A) = V \times A = \text{curl } A = B
\]

which corresponds to an equation ascribed to Pauli (9) and obtained by empirically adding an operator to the Schrödinger Hamiltonian to account for electron spin.

The importance of this equation lies in the term that reflects an intrinsic magnetic moment

\[
\mu = \frac{\hbar e}{2mc}
\]

which is exactly as required to explain the fine structure of electronic spectra in terms of a spin angular momentum of \( \sigma/2 \) and a Landé factor of 2.

The Physical Basis of Spin

Conservation of Angular Momentum

The two-valuedness of electron spin reflected here by the matrix nature of \( \sigma \) appears to be a strict quantum property, but this has never been demonstrated conclusively. This question probably cannot be addressed without examining the conservation of angular momentum in more detail. It occurs as a consequence of the isotropy or spherical rotational symmetry of space. This is easily demonstrated (10) for rotation around an axis \( z \) in the \( x, y \) plane, at a distance

\[
r = (x^2 + y^2)^{1/2}
\]

from the origin. The angular momentum with respect to the origin is

\[
M = m(x\dot{y} - y\dot{x})
\]

and the time rate of change follows as

\[
\frac{dM}{dt} = m(x\ddot{y} - y\ddot{x})
\]

Because \( m\dot{x} \) and \( m\dot{y} \) are components of force,

\[
\frac{dM}{dt} = -x \frac{\partial V}{\partial y} + y \frac{\partial V}{\partial x}
\]

Now,

\[
\frac{\partial V}{\partial y} = \frac{dV}{dr} \frac{y}{r} \frac{dV}{d\theta}
\]

Thus,

\[
\frac{dM}{dt} = \left( \frac{xy}{r} + \frac{yx}{r} \right) = 0
\]

An Absolute Direction

This conservation law can be stated in another way, in terms of a nonobservable (11), which in this case is an absolute spatial direction. Whenever an absolute direction is observed, the conservation no longer holds. This could mean that in the quantum domain, space cannot be assumed to be rotationally symmetrical and the special direction corresponds to the observed spin alignment.

Simple Electrodynamic Effect

Alternatively it could be viewed as a simple electrodynamic effect like the instantaneous magnetic interaction between two like charges approaching at right angles. By the right-hand rule the forces between the charges are, as shown in the figure, equal but not opposite as required to conserve momentum. The missing momentum has been transferred to the field, and only when the field momentum is added to the mechanical momentum of the charges does conservation of momentum prevail (12).

Similar considerations apply to angular momentum (13). In this instance conservation requires that the field acquires angular momentum, in addition to the mechanical angular momentum that a particle may have. In the case of a quantum-mechanical particle this statement is equivalent to the suggestion (5, 14) that spin should be regarded as a circulating flow of momentum density in the electron field, of the same kind as carried by the fields of a circularly polarized electromagnetic wave. This means that spin is not associated with the internal structure of the electron, but rather with the structure of its wave field.

The Hamilton-Jacobi Equation

Both of the foregoing interpretations imply that an electron wave function has more than mathematical significance and refers to a physically real wave as proposed by De Broglie (15) and later more fully developed by Bohm (16) and others (17) in terms of the quantum potential (16) and the quantum torque (17). To understand these concepts the spinor wave function is written in terms of the Euler angles (18),

\[
\psi = R e^{i\theta/2} \left[ e^{-i\phi/2} \cos \theta/2 \right] = R e^{i\phi/2}
\]

and substituted into the Pauli equation (see above), to produce a generalized Hamilton-Jacobi (HJ) equation.

\[
\frac{\hbar^2}{2} \left( \frac{\partial^2 \psi}{\partial r^2} + \frac{\partial^2 \psi}{\partial \theta^2} + \frac{1}{r} m^2 \frac{\partial^2 \psi}{\partial \phi^2} + Q + Q_s + \frac{2}{R} \mathbf{B} \cdot \mathbf{S} + eA_\theta + V = 0 \right)
\]

The spin vector is

\[
\mathbf{S} = \frac{\hbar}{2} (\sin \theta \sin \phi, \sin \theta \cos \phi, \cos \theta)
\]

The HJ equation differs from the classical equation for a spinning particle by two extra terms, the usual quantum potential,

\[
Q = -\frac{\hbar^2 R^2}{2mR}
\]

and a spin-dependent quantum potential,

\[
Q_s = \frac{\hbar^2}{8m} \left( (V_\theta)^2 + \sin^2 \theta (V_\phi)^2 \right)
\]

Both of these terms are inversely proportional to particle mass, which is thereby identified as the parameter that distinguishes between quantum and classical systems.

In terms of the spin vector,

\[
\frac{d\mathbf{S}}{dt} = \mathbf{T} + \frac{2}{\hbar} \mathbf{B} \times \mathbf{S}
\]
where \( T \) is an additional quantum torque, which introduces a nonclassical precession of the spin vector along a trajectory. Whereas classically an attempt to align a spin vector with an inhomogeneous magnetic field results in a torque \((S \times B)\) that makes the spin precess about the field, the quantum torque produces an extra rotation that actually aligns the spin vector in one direction or the other (\( \Theta = 0 \) or \( \pi \)).

The term
\[
\frac{\hbar}{2m} \left( \frac{\partial \Theta}{\partial t} + \cos \Theta \frac{\partial \phi}{\partial t} \right)
\]
is a spin-dependent contribution to the energy and although it contains \( \hbar \) does not vanish as a function of the particle mass. In this sense electron spin is not a quantum-mechanical entity, as already pointed out on other grounds by Ohanian (14).

In an Electromagnetic Field

One final issue to settle is the possibility that electron spin is manifest only in an electromagnetic field. As first demonstrated by Gordon (4), however, the probability current density according to the Dirac equation separates into two components. They are associated with a magnetic moment per unit volume,
\[
M = -\frac{e}{2m} \psi^* \gamma^\alpha \psi = \frac{e}{m} \gamma^\alpha S
\]
and an electric dipole moment per unit volume, which vanishes for a stationary electron.
\[
P = \frac{ie\hbar}{2mc} \psi^* \gamma^\alpha \gamma^\beta \psi
\]
\( S \) is a spin vector per unit volume. More precisely, a magnetic moment operator
\[
\hat{m} = \frac{e}{m} \gamma^\alpha S
\]
defines the usual spin operator for the electron.

The spin current density is nonzero, even in the rest frame of the electron. Ohanian (14) interprets this as final evidence that a circulating current flowing in the wave field, even of a stationary electron, is responsible for the additional angular momentum called spin.

This decomposition is not possible in the standard nonrelativistic formulation when calculating probability current as the time rate of change of the probability density\(^2\) (19).
\[
\frac{\partial}{\partial t}[\psi^* \psi] = \frac{ie\hbar}{2mA} \left( \psi^* (\nabla \psi^*) - (\nabla \psi^*) \psi \right)
\]
However, in the Galilean invariant form of Lévy-Leblond (8) the probability current density separates into
\[
j = \frac{ie\hbar}{2m} \left[ \psi^* (V \psi^*) - (V \psi^*) \psi \right] - \frac{he}{2m} \psi \times (\psi^* \gamma^\beta \psi)
\]
where the second term is the spin current.

Conclusion

This enquiry has demonstrated that spin is neither a relativistic effect nor a purely quantum one. Like a classical wave, an electron has angular momentum associated with its wave field. The fundamental difference (14) is that the spin of a classical wave is a continuous macroscopic parameter, which is quantized in the case of electron spin. The possibility noted that electron spin could be induced by an applied field has also been dispelled. It persists even to be associated with a stationary electron.

Spin is not a property of an electron but a manifestation of the interaction between an electron and the vacuum, which here represents the medium that carries the quantum potential and its associated field. There is a special direction in space—time, evidenced by the quantum torque that aligns the electron spin in the absence of an applied field. This also accounts for the violation of angular-momentum conservation, experienced as the emergence of spin.

Like the familiar notion of up/down alignment of spin, the special direction that breaks the rotational symmetry should not be thought of as a direction in three-dimensional space, unless it is so projected by an applied magnetic field. On the purely speculative level the quantum potential can be viewed as generated by the vacuum, constituting an interface between time domains (20). In this sense spin would be directed either into or out of the interface to define a two-level system. This two-valuedness occurs only for systems that respond to the interfacial quantum potential and is preserved during any projection into lower dimensions.

Literature Cited