Explicit Spin Coordinates

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Abstract

The recently established existence of spherical harmonic functions, \( Y^m_\ell(\theta, \phi) \) for half-odd-integer values of \( \ell \) and \( m \), allows for the introduction into quantum chemistry of explicit electron spin-coordinates; i.e. spherical polar angles \( \theta_s, \phi_s \), that specify the orientation of the spin angular momentum vector in space.

In this coordinate representation the spin angular momentum operators, \( S^2, S_z \), are represented by the usual differential operators in spherical polar coordinates (commonly used for \( L^2, L_z \)), and their electron-spin eigenfunctions are \( \sqrt{\sin \theta_s} \exp(\pm \phi_s/2) \).

This eigenfunction representation has the pedagogical advantage over the abstract spin eigenfunctions, \( \alpha, \beta \), that “integration over spin coordinates” is a true integration (over the angles \( \theta_s, \phi_s \)). In addition they facilitate construction of many electron wavefunctions in which the electron spins are neither parallel nor antiparallel, but inclined at an intermediate angle. In particular this may have application to the description of EPR correlation experiments.

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1 The Coordinate Representation of Spin

The nature of the electron remains an enigma [1]; however (and notwithstanding the Pauli and Dirac representations of spin [2]) the closest physical model is a spherically symmetric distribution of charge rotating around an axis [3, p.55]. This internal rotation is known as the electron’s spin; its quantized angular momentum component is known to be $\pm \hbar/2$ (associated with a magnetic moment $\hbar e/(2mc)$).

In the coordinate representation of spin, the direction of the electron’s axis of rotation may be specified by two spherical polar angles: $\theta_s, \phi_s$; the subscript, $s$, distinguishes these angles from the $\theta, \phi$ that describe the angular position of the electron relative to the nucleus in the Schrödinger theory of the hydrogen atom; the $\theta, \phi$ coordinate system has its origin at the nucleus, whereas the $\theta_s, \phi_s$ coordinate system has its origin at the electron.

The recent discovery of spherical harmonics, $Y^m_\ell(\theta, \phi)$, for half-odd-integer values of $\ell$ and $m$ [4], provides the basis for a coordinate representation of electron spin, the coordinates being the two spherical polar angles $\theta_s, \phi_s$.

In this representation the operators for the square of the total spin angular momentum, $S^2$, and its $z$-component, $S_z$, are expressed in terms of the spherical polar angles [5, p.207], [6, p.95] by:

$$S^2 = -\hbar^2 \left\{ \frac{1}{\sin \theta_s} \frac{\partial}{\partial \theta_s} \left( \sin \theta_s \frac{\partial}{\partial \theta_s} \right) + \frac{1}{\sin^2 \theta_s} \frac{\partial^2}{\partial \phi_s^2} \right\}$$

$$S_z = \hbar \frac{\partial}{\partial \phi_s}$$

The eigenfunctions of these operators, $\alpha(\theta_s, \phi_s)$, $\beta(\theta_s, \phi_s)$, corresponding to the known spin-states of an electron are ??:

$$\alpha(\theta_s, \phi_s) = \frac{1}{\pi} \sqrt{\sin \theta_s} e^{i(\phi_s/2)} \quad \text{for } m_s = +1/2$$

$$\beta(\theta_s, \phi_s) = \frac{1}{\pi} \sqrt{\sin \theta_s} e^{i(-\phi_s/2)} \quad \text{for } m_s = -1/2$$

where $m_s$ is the well-known spin quantum number, and the factor of $1/\pi$ normalizes the functions with respect to integration over $\theta_s$ and $\phi_s$ (see below).

Application of the operators (1) to the functions (2) shows that both of these functions are eigenfunctions.
• of $S^2$ with eigenvalue $3\hbar^2/4$, and
• of $S_z$ with eigenvalues of $m_s\hbar = \pm\hbar/2$.

The functions (2) are normalized in the sense that:

$$\int_0^{2\pi} \sin(\theta_s) d\theta_s = 1 \quad (3)$$

in which $^*$ denotes the complex conjugate, and $Y(\theta_s, \phi_s)$ is one of $\alpha(\theta_s, \phi_s)$ or $\beta(\theta_s, \phi_s)$. They are also orthogonal in the sense that:

$$\int_0^{2\pi} \alpha^*(\theta_s, \phi_s) \beta(\theta_s, \phi_s) d\phi_s = \int_0^{2\pi} \alpha(\theta_s, \phi_s) \beta^*(\theta_s, \phi_s) d\phi_s = 0 \quad (4)$$

The normalization (3) is the one usually used for the spherical harmonics. However, it should be noted that the Fermion functions (2) are only single-valued when $\phi$ is considered to have the range of a double circle: $0 \leq \phi_s \leq 4\pi$; this $4\pi$ symmetry is a well known property of fermion wavefunctions [7, p.21 & p.138]. Alternatively, if the range of $\phi_s$ is regarded as that of a single circle, $0 \leq \phi_s \leq 2\pi$, they are double-valued functions in the sense that:

$$Y(\theta_s, \phi_s + 2\pi) = -Y(\theta_s, \phi_s)$$

The double-valuedness is admissible because the probability density, $Y^*(\theta_s, \phi_s) Y(\theta_s, \phi_s)$ is single-valued and positive. The alternative of basing the normalization upon $0 \leq \phi_s \leq 4\pi$ would simply introduce a factor of $\sqrt{2}$ into the normalization constant.

## 2 Previous Representation of Spin

The history of intrinsic (spin) angular momentum is a fascinating story [8]. The spin of an electron has been represented most simply by eigenfunctions, $\alpha$ and $\beta$, which are abstract in the sense that they are not functions of any coordinates; they are defined to be eigenfunctions of $S^2$ and $S_z$ with eigenvalues of $\hbar^2 s(s+1)$ and $\hbar m_s$, with $s = \frac{1}{2}$ and $m_s = \pm\frac{1}{2}$ [5, 300]:

$$S^2 \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \hbar^2 \frac{1}{2}(\frac{1}{2} + 1) \begin{bmatrix} \alpha \\ \beta \end{bmatrix} \quad S_z \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \begin{bmatrix} + \hbar/2 \\ - \hbar/2 \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} \quad (5)$$
Different authors handle the abstract nature of the spin eigenfunctions, $\alpha$ and $\beta$, differently. In presenting the orthonormality relations:

\begin{align*}
\langle \alpha | \alpha \rangle &= \langle \beta | \beta \rangle = 1 \\
\langle \alpha | \beta \rangle &= \langle \beta | \alpha \rangle = 0
\end{align*}

Dykstra [9, p.185] avoids explicit consideration of the functional dependence of the “abstract functions” $\alpha$ and $\beta$ on the “abstract spin coordinate”, and likewise avoids explicit consideration of the integration “over the spin coordinate” implicit in (6) and (7).

In this purely abstract interpretation of $\alpha$ and $\beta$ the simplest concept is to define them by the eigenvalue equations (5) with normalization defined by (6) (their orthogonality, (4), follows from (5) because they are eigenfunctions of $S_z$ with different eigenvalues).

Expectation values such as $\langle \alpha | S^2 | \alpha \rangle$, $\langle \beta | S^2 | \beta \rangle$, $\langle \alpha | S_z | \alpha \rangle$, and $\langle \beta | S_z | \beta \rangle$, and (6) are likewise abstract - they do not have to refer to “integration over the spin coordinate”.

Other authors [10, p.15], [11, p.14], [12, p.253], [2, p.233], invoke the Pauli $2 \times 2$ matrix representation of electron spin to infer that the spin coordinate/variable spans a discrete space of just 2 values, which are $\{1, 0\}$ for $\alpha$ and $\{0, 1\}$ (or $\{0, -1\}$ [10]) for $\beta$. Calais then correctly says that:

“integration over spin space . . . is a misnomer for summation over spin space”

In the Pauli matrix representation this summation (in (6,7)) is the scalar product of the transpose of $\alpha, \beta$ (\{1, 0\}, \{0, 1\}) with the $2 \times 1$ column vectors. Identifying the 2 elements of the column-vector eigenfunctions of the Pauli representation as a space of 2 points spanned by the “spin coordinate”, is a dubious concept, for as Schiff shows [2, pp.144-147] the number of points of the spin-space increases with the total angular momentum quantum number, $j$: it is $2j + 1$ for $j = 1/2, 1, 3/2$, etc.

In many electron wavefunctions one must designate which electron is in a spin eigenstate, $\alpha, \beta$. This is commonly indicated by $\alpha(s_1), \beta(s_2)$ etc, or simply $\alpha(1), \beta(2)$ etc. This notation indicates that $\alpha(s_1)$ denotes an $\alpha$ spin function for electron 1, and some authors (naturally) refer to $s_1, s_2$, etc, as the “spin coordinate” of electron 1, 2, etc. In this context these electron designators are really specifying labels rather than coordinates. Similar
designators will be needed in our spin-coordinate representation of many-electron wavefunctions; different angles, \( \theta_s, \phi_s, (j = 1, 2, \ldots) \) must be used for each electron.

## 3 Discussion

Heretofore no scalar representation in terms of the explicit (angular) coordinates of the spin motion has been used, and yet such positional coordinates are believed to have a privileged role in the interpretation of quantum mechanics [13].

The logical steps in the derivation of the Fermion Spherical Harmonics [4] parallel the arguments used to derive the abstract eigenfunctions and eigenvalues of angular momentum, which (as is well-known) lead to both integer and half-odd-integer values of \( \ell \) and \( m \) [14, §5.4,p.115]. It was the belief that the wavefunction (rather than the probability) must be single-valued that inhibited discovery of these functions for so many years.

We hope that the explicit coordinates, \( \theta_s, \phi_s \), for the orientation of the spin vector of each electron will be adopted in the teaching of quantum chemistry, for they will make “integration over spin coordinates” a true integration entirely comparable with integration over the positional coordinates of each electron (such as \( r, \theta, \phi \) for an atomic electron), and the spin eigenfunctions \( \alpha, \beta \) will have an explicit functional dependence upon the angles \( \theta_s, \phi_s \) as shown explicitly in (2).

Apart from their pedagogical value, these angular dependent spin eigenfunctions will facilitate the construction of wavefunctions in which the orientation of a particular spin vector is neither parallel to, nor anti-parallel to, another spin vector or to an external magnetic field.

One possible application is to the theory of Nuclear Magnetic Resonance (NMR), where the spins of different nuclei will, in general, be neither parallel nor anti-parallel.

Another example is the Einstein-Podolski-Rosen gedanken experiment, in which two electrons go away from a source in opposite directions towards spin-orientation detectors which are inclined at any angle, \( \theta \) (when parallel, \( \theta=0 \), or anti-parallel, \( \theta=\pi \)). The experiment measures correlations between detections at the two detectors as a function of their angle of inclination, \( \theta \); further detail is beyond the scope of this article [15, Ch.4,p.35].
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References


