Two-level quantum systems have their ubiquitous presence in chemistry and physics—in the basic ideas of bonding of atoms based on the superposition of two quantum states; in quantum optics and laser physics; in magnetic resonance; and a multitude of other phenomena. The underlying theory is well-described in many textbooks. This article aims to go beyond textbooks and familiarize university students (and hopefully excite them) about several related topics of great contemporary interest in chemistry and physics of materials, remaining however within their accessible realm. These topics are of current research activity, including tunneling centers in solids, coherent preservation of quantum information in qubits, hybridization of orbitals in carbon leading to materials such as graphene, the Berry phase, and its implication for magnetic monopoles, topological solids, and Rashba spin-split bands, etc. In discussing these themes, references are made to textbooks of quantum mechanics, but the connection is provided to advanced areas in a manner that is pedagogical and not forbidding to students.

1. Introduction

In some sense, a two-state system is the opposite end of a continuum of a mechanical particle characterized by its position and momentum that live in an infinite-dimensional Hilbert space; the two-state system is discrete and just two-dimensional. In fact, it is the ‘most quantum mechanical’ in that it is the extreme case of a spin $s$—as $s (= |s|)$ becomes gradually large, the spin tends to be-

---

*Vol 26, No. 12, DOI: https://doi.org/10.1007/s12045-021-1279-9*
have more and more classically, because the spin-split levels are energy-separated by a term proportional to the Planck constant $\hbar$, and hence the energy levels become more or less continuous.

As it turns out, one-half of the elementary particles of nature are fermions endowed with $s = 1/2$, such as electrons, protons, neutrons, muons, and neutrinos. Solid-state chemistry and physics is replete with two-state entities that provide the probes, e.g., electron spin/paramagnetic resonance (ESR/EPR) that employs electrons, nuclear magnetic resonance (NMR) that uses protons, neutron (magnetic) scattering, muon spin rotation, to name a few. In section 2, we briefly recollect the essential algebraic properties of Pauli spin matrices, described in textbooks [1, 2], and collated in the Appendix of [3], and indicate their relevance in magnetic resonance experiments and other two-level atoms and molecules wherein the Pauli matrix connotes to not a real spin but a pseudospin [4]. Since the underlying algebra involves the manipulation of $2 \times 2$ matrices, it is well within the reach of even final year school students.

Section 3 is devoted to an assortment of application of two-level concepts—solid-state chemistry and physics—split into three sub-sections, in which the superposition of wave functions (‘bonding’ and ‘anti-bonding’) find their use. In 3.1, we employ the pseudospin formalism in describing coherent tunneling of a quantum particle in a symmetric double-well, again a textbook example [5], but having implications for solid-state devices. Similar considerations lead to an analysis of coherence in a quantum dot, as dealt with in 3.2. Our focus in 3.3 is on sp-hybridization, a mechanism of C-bonding that applies to acetylene [6]. The other form, namely sp2 hybridization, yielding covalent bonding of carbon leading to a tight-binding lattice of two-dimensional graphene, has been recently discussed in detail and is briefly touched upon here [3, 7, 8]. Our treatment in section 4—in a sense the most topical—is devoted to the seemingly intriguing aspect of the Berry phase [9], set up in the background of a generic two-level system. In subsection 4.1, we establish the connection between the Berry phase of a two-level system and the magnetic monopole. The ap-
plication of the Berry phase to two distinct but similar two-level systems of graphene and Rashba spin-split bands constitute subsection 4.2. Our principal conclusions are summarized in section 5.

2. Preliminaries

The most convenient formulation of spin one-half physics is in terms of Pauli matrices that originated in an essential form in the Dirac theory of relativistic electrons [8]. The Cartesian components of the Pauli spin $\sigma$ (= $2\hbar s$) have the following $2 \times 2$ matrix representation [1, 2]:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (1)$$

It is easy to verify by matrix multiplication that the two columns $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$, called the state-vectors, are the eigenstates of $\sigma_z$ with eigenvalues $+1$ and $-1$ respectively, corresponding to the two opposite orientations of the spin. It was Dirac who introduced compact notations for the state vectors and their conjugates as follows [10]:

$$|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}; \quad <+| = (1 \ 0), \quad <|-| = (0 \ 1), \quad (2)$$

which are called $ket$ and $bra$, respectively. While the above $ket$ and $bra$ vectors are the spin-states of a real spin-half object such as an electron, it is easy to let our imagination run and equally view them as the state vectors of any two-state system, thus giving rise to the notion of a pseudo-spin.

It is interesting to note that a suitable linear combination of the eigenstates of $\sigma_z$ can yield the eigenstate of any arbitrary component of $\sigma$, a special case of which is the eigenstate of $\sigma_x$, as can be verified by the following observation:

The most convenient formulation of spin one-half physics is in terms of Pauli matrices that originated in an essential form in the Dirac theory of relativistic electrons.
\begin{align*}
\sigma_x \begin{pmatrix} 1 \\ 1 \end{pmatrix} &= \sigma_x \begin{pmatrix} 1 \\ 0 \\ 0 \\ 1 \end{pmatrix} = +1 \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \\
\sigma_x \begin{pmatrix} 1 \\ -1 \end{pmatrix} &= \sigma_x \begin{pmatrix} 1 \\ 0 \\ 0 \\ -1 \end{pmatrix} = -1 \begin{pmatrix} 1 \\ -1 \end{pmatrix}, \\
\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} &= \frac{1}{\sqrt{2}} \left[ |+\rangle + |\rangle \right] = |S\rangle, \\
\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} &= \frac{1}{\sqrt{2}} \left[ |+\rangle - |\rangle \right] = |A\rangle,
\end{align*}

wherein, $|S\rangle$ and $|A\rangle$ are symmetric and anti-symmetric linear combinations of the eigenstates of $\sigma_z$ that turn out to be useful for tunneling and sp-bonding discussed in section 3.

We now come to sketch the solution of a time-dependent two-state problem that has the genesis of much of what we are going to say in sequel. The issue is that of a spin-half entity finding itself in a static magnetic field $B_0$ along the $z$-axis and a frequency-dependent rotating field of magnitude $B$ in the $xy$-plane. The point is, the field in the $xy$-plane couples to spin operators, which are off-diagonal in the representation in which $\sigma_z$ is diagonal, and therefore, causes resonant transitions when the frequency $\omega_0$ matches the Zeeman frequency due to the static field. It is amazing to recall how many Nobel Prizes were awarded to scientists who exploited the basic idea here, the notable being Rabi (1944) on molecular beams and NMR; Bloch and Purcell (1952) on B-field in atomic nuclei and nuclear magnetic moments; Townes, Basov, and Prochorov (1964) on masers, lasers, and quantum optics and Kastler (1966) on optical pumping [2].

Consider then the following Hamiltonian:

\begin{equation}
H_i = B_0 \sigma_z + B[\sigma_x \cos(\omega_0 t) + \sigma_y \sin(\omega_0 t)].
\end{equation}

where we have suppressed all pre-factors e.g., the g-factor, Bohr/nuclear magneton, etc., for the sake of simplicity in notation. As time $t$ progresses, the oscillatory field of frequency $\omega_0$ makes $B$ precess
around the z-axis in the counter-clockwise direction in a right-handed coordinate system by an angle $\omega_0 t$. Hence, if we imagine ourselves in a coordinate frame that also rotates around the z-axis with the same angular speed, we would expect the time-dependent field to be static. This can be formally achieved with the aid of a rotation operator [1, 2]

$$R(t) = \exp(-i\sigma_z\omega_0 t/2).$$  \hfill (5)

Under this rotation, the Hamiltonian in (4) transforms to a time-independent form:

$$H_o = R^\dagger(t)H(t)R(t) = B_0\sigma_z + B\sigma_x.$$  \hfill (6)

The Schrödinger equation reads (upon setting $\hbar = 1$)

$$i(\partial/\partial t) |\Psi(t)\rangle = H(t) |\Psi(t)\rangle = R(t) H_o R(t)^\dagger |\Psi(t)\rangle,$$  \hfill (7)

where we have used (6) and the fact that $R(t)R(t)^\dagger = I$, $I$ being the unit operator.

Introducing

$$|\Psi^\ast(t)\rangle = R(t) |\Psi(t)\rangle,$$  \hfill (8)

we deduce from (7)

$$i(\partial/\partial t) |\Psi^\ast(t)\rangle = H_0 |\Psi^\ast(t)\rangle - (\sigma_z\omega_0/2) |\Psi^\ast(t)\rangle$$

$$= [(B_0 - \omega_0/2)\omega_z + B\sigma_x] |\Psi^\ast(t)\rangle,$$  \hfill (9)

upon substituting the right hand side of (6). The above is a Schrödinger equation governed by a time-independent Hamiltonian whose solution reads

$$|\Psi^\ast(t)\rangle = \exp(-it[(B_0 - \omega_0/2)\sigma_z + B\sigma_x]) |\Psi(0)\rangle.$$  \hfill (10)
where we have noted the fact that (cf., (5) and (8)) $|\Psi^*(0)\rangle = |\Psi(0)\rangle$. Once we have (10) the actual Schrödinger wave function can be obtained from (8) as:

$$|\Psi(t)\rangle = R(t) \exp\left(-it[(B_0 - \omega_0/2)\sigma_z + B\sigma_x]\right) |\Psi(0)\rangle.$$  \hspace{1cm} (11)

It is interesting to note that while the last two terms in (11) involve wave function evolution under a time-independent ‘effective’ field (having incorporated the frequency), the prefactor $R(t)$, when operated upon a state vector, would introduce an additional phase factor (see (5)). This phase, normally unimportant such as in the derivation of (12) below, will turn out to be of relevance in our discussion of the Berry phase (section 4).

We are now all set to discuss 'spin-resonance'. Assuming that we start from the state $|+\rangle$ (for notation see (2)), the probability that the spin returns to that state after a time $t$ is

$$P_+(t) = |<+|\Psi(t)|+\rangle|^2 = |<+|\exp[-it[(B_0 - \omega_0/2)\sigma_z + B\sigma_x]]|+\rangle|^2.$$  \hspace{1cm} (12)

Using the form of exponentiated Pauli matrices [1, 2], it is easy to see that

$$P_+(t) = 1 - B^2/[(B_0 - \omega_0/2)^2 + B^2] \sin^2\{t[(B_0 - \omega_0/2)^2 + B^2]^{1/2}\}.$$  \hspace{1cm} (13)

Clearly,

$$P_-(t) = |<|-|\Psi(t)|-\rangle|^2 = 1 - P_+(t).$$  \hspace{1cm} (14)

Equations (13) and (14) embody the Rabi formula after I. I. Rabi, the founder of molecular beam methods [2]. It is clear that the amplitude of oscillation depicted by (13) exhibits a resonance, when $\omega_0 = 2B_0$, the separation of the two Zeeman-split levels.

As mentioned earlier, the discussion here is equally applicable to any two-level atom (e.g., lasers in quantum optics [4]) or molecule
(e.g., ammonia in a maser system [2, 11]). A remark is in order here about the two-level mapping. As the expansion of the acronym LASER—light amplification by stimulated emission of radiation—suggests, an optical pump is used to elevate an atom to an excited state (with a short lifetime), from which it quickly decays into an intermediate ‘stimulated’ level. The latter has a higher population than the ground level, implying ‘population inversion’, which further leads to the ‘amplification’ of emitted light. Thus, though there are three levels to start with, the lasing action actually involves the intermediate and the ground levels [4]. On the other hand, in a MASER—microwave amplification by stimulated emission of radiation—the two levels correspond to the two possible positions of the nitrogen atom in an ammonia molecule, somewhat akin to a defect tunneling in a double-well (see Figure 1), and it is the tunneling frequency that corresponds to the frequency of radiation [11]. For treating these problems, we will have to map the spin-state $|-\rangle$ into the lower level $|1\rangle$ and the state $|+\rangle$ into the upper level $|2\rangle$. Correspondingly, the Pauli matrices are to be replaced by

$$\sigma_z = |2\rangle \langle 2| - |1\rangle \langle 1|, \sigma_x = |2\rangle \langle 1| + |1\rangle \langle 2|, \sigma_y = (|2\rangle \langle 1| - |1\rangle \langle 2|)/i. \ (15)$$

The magnetic field $B_0$ has the interpretation of $(E_2 - E_1)/2$, where $E$’s are the respective energies of the two levels, while the transverse field $B$ measures the overlap energy, to be dubbed ‘tunneling’, in the next section.

3. Two-level Systems in the Solid State

3.1 Defect in a Symmetric Double-well

Imagine, ala Merzbacher [5], a symmetric double-well oscillator potential that may be viewed as juxtaposed two back-to-back one-dimensional harmonic oscillator potentials (Figure 1):

$$V(x) = (k/2)(|x| - a)^2, \quad (16)$$
Figure 1. The potential energy $V(x)$ for a double well, in which $x_L$ and $x_R$ are the so-called classical turning points. However, quantum tunneling allows penetration through the barrier of height $V_0$.

$k$ being the so-called spring constant. Evidently the potential is symmetric around $x = 0$, has two minima at $+a$ and $-a$, and has a barrier in the middle at $x = 0$ of height $V_0 = ka^2/2$.

A classical entity such as a marble ball, once placed at the bottom of the left or the right well, will be stuck there if there is no thermal motion. However, in quantum mechanics, the wave function will be spread all over—a phenomenon euphemistically referred to as tunneling. Therefore, the question arises: what do we expect physically as far as the wave functions are concerned? If $a = 0$, we have a single harmonic oscillator with well-known energy eigenvalues and eigenfunctions. On the other hand, if $a = \infty$, we have a double oscillator albeit infinitely far apart with zero communication between the two segments, as the barrier height grows very large. Thus, for a finite value of $a$, the two lowest eigenfunctions $\Psi_0(x)$ and $\Psi_1(x)$ qualitatively look like Figure 2. The ground state wave function $\Psi_0(x)$ mirrors the symmetry of the double-well, implying that a quantum particle is equally likely to be predominantly localized at the two minima where the probability amplitude is a maximum, with however, a non-zero probability of being at the middle at $x = 0$. On the other hand, the first excited state wave function $\Psi_1(x)$, from parity consideration [5], is anti-symmetric around $x = 0$, with zero probability at the middle but again equal probability ($= |\Psi_1(x)|^2$) at the two minima of the double-well.

The energy eigenvalues, as a function of dimensionless $a$, are
shown in Figure 3, again in conformity with our physical expectation—at $a = 0$, we have 'one-dimensional' eigenvalues, whereas for $a = \infty$, the eigenvalues pair-wise collapse into a doubly-degenerate value, reflecting the fact that now we have two independent oscillators. In-between (and not for a very large value of $a$) there is a finite energy-difference called tunnel splitting $\Delta$, which is due to the overlap of $\Psi_0(x)$ and $\Psi_1(x)$. A WKB estimate yields [5]:

$$\Delta = (8\omega V_0/\pi)^{1/2} \exp(-2V_0/\omega), \omega = (k/m)^{1/2}.$$  \hspace{1cm} (17)

$m$ being the mass of the particle. (Again we have set $\hbar = 1$.)

The tunneling phenomenon discussed here is of relevance to electron, positron, proton, muon, etc., trapped amongst two equivalent interstitial sites in a solid and thus constrained to move in a double-well potential. This situation is often encountered in ultra-low-temperature defect physics in the solid-state, molecular rotations in solids [12], or the ammonia maser problem where the nitrogen atom tunnels between two equivalent positions [11]. The reason for low temperatures being pertinent here is that un-
**Figure 3.** The energy eigenvalue $\gamma = (E/h\omega - 1/2)$ plotted versus $(m\omega/\hbar)^{1/4}a$, for the four lowest energy eigenvalues of the double well. The dashed curve shows the barrier height, for the sake of comparison.

Under only such conditions, the two lowest energy levels will be dominant, thus validating the ‘two-level’ description.

Referring again to Figure 1, we may designate the quantum state associated with the bottom of the left well as $|1\rangle$, which is then mapped into $|-\rangle$, an eigenstate of $\sigma_z$, which is however now a pseudo-spin-state (see (15)). Similarly, the bottom of the right well is designated as state $|2\rangle$ or $|+\rangle$. However, while these states are the ‘physical states’ in which we can find the quantum particle, tunneling mixes them as the tunneling states $\Psi_0(x)$ and $\Psi_1(x)$, shown in Figure 2, are the eigenstates of the underlying Hamiltonian. Indeed the latter states can be (approximately) considered as the symmetric and anti-symmetric states $|S\rangle$ and $|A\rangle$ respectively, that are the eigenstates of $\sigma_x$ (cf., (3)). Thus the Hamiltonian can be written as

$$ H = \Delta \sigma_x. \quad (18) $$

Interestingly, (18) may be seen as a limiting case of the generic
two-level Hamiltonian of (4), in which \( B_0 = \omega_0 = 0 \) and \( B = \Delta \), though the \( B_0 \) term will have to be inserted in certain realistic situations of asymmetric double-wells [12]. With this identification, we can now borrow the already-derived results of section 2. Thus we have

\[
P_+(t) = \cos^2(\Delta t), \tag{19}
\]

that measures the probability that the quantum particle can be found in the right well at time \( t \) given that it was localized there at \( t = 0 \). Such an oscillatory behavior, as depicted by (19), and indeed also in the time-dependent problem of resonance as discussed in section 2, is characteristic of quantum coherence. It leads to, for instance, tunneling peaks seen in the neutron scattering of hydrogen defects in a metal like Nb [12].

### 3.2 Coherence in a Quantum Dot

A very active area of research today is quantum information theory that finds relevance in the attempt to develop quantum computers. Such information can be stored, for instance, in a qubit that comprises two quantum dots—each dot may be realized in a molecular form of carbon, e.g., fullerene [13]. Here, we consider one realization of a solid-state qubit in which each quantum dot is characterized by a single energy level [14]. Thus, the qubit exists in a superposition of two dot-states that may be represented by \( |1\rangle > \) and \( |2\rangle > \), much akin to the left and right bottom of the double-well treated in subsection 3.1. The Hamiltonian of the qubit may be written as

\[
H_q = E_1 |1\rangle < 1| + E_2 |2\rangle < 2| + (\Delta_{12} |1\rangle < 2| + \Delta_{21} |2\rangle < 1|), \tag{20}
\]

where the tunneling \( \Delta \), in general, can be complex, obeying of course the hermiticity property of \( H_q \). Using the closure relation:

\[
|1\rangle < 1| + |2\rangle < 2| = I, \tag{21}
\]
and dropping a constant energy term, (20) can be exactly put in the form of (4) if we fix the time \( t \) at a constant epoch and rewrite

\[
\omega_0 t = \phi, \Delta_{12} = B e^{i\phi}, \Delta_{21}^* = B e^{-i\phi}, B_o = (E_2 - E_1)/2,
\]

(22)

and employ (15). We can therefore, re-express the qubit Hamiltonian as

\[
H_q = B_o \sigma_x + B[\sigma_x \cos \phi + \sigma_y \sin \phi].
\]

(23)

It can be easily checked that following are the eigenfunctions of \( H_q \):

\[
|u_+> = \begin{pmatrix} \cos \vartheta \\ \exp(i\varphi) \sin \vartheta/2 \end{pmatrix}, |u_-> = \begin{pmatrix} -\sin \vartheta/2 \\ \exp(i\varphi) \cos \vartheta/2 \end{pmatrix}, \tan \vartheta = B/B_o,
\]

(24)

corresponding to the energy eigenvalues \( \lambda_{\pm} = \pm (B_o^2 + B^2)^{\dagger} \). The reader may note that while the symbol \( \vartheta \) is usually reserved for the co-latitude angle in a three-dimensional spherical polar coordinate system, here it enters as a fictitious angle, simply defined by the ratio of the two magnetic field strengths (see the last entry in (24)). It will however transpire that \( \vartheta \) will have its customary meaning restored when, in section 4, we will discuss a different but mathematically equivalent Hamiltonian of (24).

In order to elucidate the meaning of coherence it is customary to consider the density operator [2, 10]

\[
\rho(t) = |\Psi(t)> <\Psi(t)| = \exp(-iH_qt)|\Psi(0)> <\Psi(0)|\exp(iH_qt),
\]

(25)

which can be easily computed using the technique discussed earlier in arriving at (12), in section 2. Coherence implies that the off-diagonal matrix element, e.g., \( <+|\rho(t)|- > \) stays non-vanishing as the time \( t \) proceeds to infinity. When both the off-diagonal elements vanish, we obtain a 'mixed' state indicating complete decoherence. It is the off-diagonal element that transports or carries

---

Coherence implies that the off-diagonal matrix element, e.g., \( <+|\rho(t)|- > \) stays non-vanishing as the time \( t \) proceeds to infinity. When both the off-diagonal elements vanish, we obtain a 'mixed' state indicating complete decoherence. It is the off-diagonal element that transports or carries
phase information, facilitated by tunneling, from one dot to the other, crucial for quantum computing.

3.3 Hybridization in Carbon

Carbon-based materials—molecules, clusters, nanorods, graphene, etc.,—are unique in their applications. Because of their immense technological uses, various allotropes of carbon, such as fullerene (a zero-dimensional molecule of 60 or 70 C atoms) and the two-dimensional graphene, which can be rolled into three-dimensional C nanotubes, have attracted two Nobel prizes—to Kroto, Curl and Smalley for fullerene (1996) and to Geim and Novoselov for graphene (2010) [8]. The uniqueness of these materials relates to the many possible electronic configurations of the carbon atom.

A free C atom has 6 electrons. Two of these are strongly bound core electrons in the quantum state designated as 1s, wherein the orbital quantum number l = 0 (s-state) and the principal quantum number n = 1. These core electrons need no further deliberation as they are so deep inside that they have no consequence for solid-state properties. That leaves us with 4 electrons, called valence electrons, that have to be accommodated in the n = 2 orbitals. As argued in [8], the ground state configuration of C may be written as: 2s\textsuperscript{1}2p\textsubscript{x}\textsuperscript{2}2p\textsubscript{y}\textsuperscript{1}2p\textsubscript{z}\textsuperscript{1}, with four unpaired electrons in separate orbitals.

Because the energy difference between the upper 2p energy levels and the lower 2s level is smaller than the binding energy of chemical bonds, the wave functions for these four electrons can readily mix, a process called hybridization. In carbon, three possible hybridizations occur sp, sp\textsuperscript{2} and sp\textsuperscript{3}. In sp hybridization, a linear superposition of the 2s orbital and one of the 2p orbitals, say 2p\textsubscript{x}, is constituted [6]. The resultant hybridized sp orbitals, denoted by |sp\textsubscript{>s} and |sp\textsubscript{>}\textsubscript{A} can be expressed as:

\begin{equation}
|sp\textsubscript{>}_s = \frac{1}{\sqrt{2}}[|2s > + |2p\textsubscript{x} >],
|sp\textsubscript{>}_A = \frac{1}{\sqrt{2}}[|2s > - |2p\textsubscript{x} >].
\end{equation}
Figure 4. sp hybridization in acetylene; the shaded regions indicate positive amplitude of the wave functions; \( |s_p >_S \) is elongated in the positive x-direction (upper sketch) while \( |s_p >_A \) is elongated in the negative x-direction (lower sketch).

where the subscripts in capital letters indicate symmetric and anti-symmetric combinations as in (3), also referred to as the ‘bonding’ and ‘anti-bonding’ states, in the present context [15].

Figure 4 provides a schematic glimpse of the directed valence of the \( |s_p >_S \) (upper diagram) and \( |s_p >_A \) (lower diagram) orbitals. The shaded portion indicates the positive amplitude of the wave function. The wave function \( |2s > + |2p_x > \) is elongated in the positive direction of x (x being chosen arbitrarily) whereas that of \( |2s > - |2p_x > \) is elongated in the negative direction of x. Therefore, when atoms lie on the x-axis, the overlap of \( |s_p >_S \) with \( |s_p >_A \) of a neighboring atom becomes large compared with the original \( |2p_x > \) function, giving rise to higher binding energy, and hence a covalent bond namely a \( \sigma \) bond.

A common example of sp hybridization is acetylene [6]: \( HC \equiv CH \) wherein \( \equiv \) denotes a triple bond between two carbon atoms. The acetylene molecule \( HC \equiv CH \) is a linear molecule with each atom placed in an equilibrium position on the x-axis and with each carbon atom displaying sp-hybridization. The two \( |2p_y > \) and \( |2p_z > \) wave functions of each carbon atom are normal to the \( \sigma \) bond, and they form weaker bonds called \( \pi \) bonds with the
$|2p_y\rangle$ and $|2p_z\rangle$ wave functions of the other carbon atom. Thus one $\sigma$ bond and two $\pi$ bonds lead to the triple bond structure: $HC \equiv CH$ of acetylene.

The ‘two-level story’ in graphene is somewhat different [3, 7, 8]. First, it is the combination of $|2s\rangle$, $|2p_x\rangle$ and $|2p_y\rangle$ orbitals that yields sp$^2$ hybridizations which are symmetrically situated at an angle of 120° with each other. Each of the three orbitals can find its twin brother in a neighboring C atom and form a covalent bond, which, in the valence-bond theory, is called a $\sigma$-bond. It is indeed fascinating to realize that it is the 120° orientations of the three (strongly) $\sigma$-bonded pairs of neighboring C atoms that yield the honeycomb structure of planar graphene in which each C atom finds itself three nearest neighbour C atoms at the vertices of an equilateral triangle [7, 8]. Once the structure is in place, it is the lone $2p_z$ electron of a C atom that can bind with a similar $2p_z$ electron of a nearby C atom, giving rise to a $\pi$-bond. As it turns out, it is this weakest bound electron that is responsible for all the spectacular properties of graphene.

The $\pi$ electron is shared by two nearest-neighbor sublattice sites of the honeycomb lattice of graphene and hence can be represented by a pseudo-spin-half. Thus, we are back at our two-state picture in which the states now correspond to the site-occupancy of the honeycomb lattice that can be treated in the tight-binding approximation [8].

4. The Berry Phase

The concept of the Berry phase is crucially significant for a whole host of modern phenomena in the electronic properties of solids such as the quantum Hall Effect and topological phase transitions—the importance of which has been acknowledged by the award of the Nobel Prize to K. von Klitzing (1985) as well as to R. B. Laughlin, H. L. Stormer and D. C. Tsui (1998), all for the quantum Hall effect; and D. J. Thouless, J. M. Kosterlitz and F. D. M. Haldane (2016) for topological and exotic phases.

Before we introduce this enigmatic topic, it is useful to consider
a two-level problem that is different from the one treated earlier (see (4) or (23)). Imagine an actual spin-half particle subjected to a three-dimensional magnetic field, characterized by its magnitude \( h \) and the polar angles \( \vartheta \) and \( \phi \). The Hamiltonian reads:

\[
H = (h_x \sigma_x + h_y \sigma_y + h_z \sigma_z), \quad h = (h_x^2 + h_y^2 + h_z^2)^{1/2}, \quad h_x = h \sin \vartheta \cos \phi, \\
h_y = h \sin \vartheta \sin \phi, \quad h_z = h \cos \vartheta.
\] (27)

It is a matter of a small exercise to verify that the following are the eigenfunctions of \( H \):

\[
| \uparrow \rangle = \begin{pmatrix} \exp(-i\varphi) \cos \vartheta / 2 \\ \sin \vartheta / 2 \end{pmatrix}, \quad | \downarrow \rangle = \begin{pmatrix} \exp(-i\varphi) \sin \vartheta / 2 \\ -\cos \vartheta / 2 \end{pmatrix}, \quad (28)
\]

corresponding to the energy eigenvalues \(+h\) and \(-h\), respectively. (The notation \(| \uparrow \rangle, \quad | \downarrow \rangle\) ought not to be confused with the eigenstates \(|+\rangle\) and \(|-\rangle\) of \( \sigma_z \) introduced earlier.)

It is interesting to note that (cf., (24) and (28))

\[
| \uparrow \rangle = \exp(-i\varphi)|u_+\rangle, \quad | \downarrow \rangle = \exp[-i(\varphi + \pi)]|u_-\rangle.
\]

Further, the eigenvalues are identical to that of the problem treated earlier if we identify \( h \) with \((B_0^2 + B^2)^{1/2}\). Indeed \(|u_+\rangle\) and \(|u_-\rangle\) could have equally well served as the eigenfunctions of \( H \)! This flexibility in the choice of the wave functions is what is called the gauge freedom, wherein lies the mystery of the Berry phase, much akin to the Aharonov–Bohm phase of electromagnetism, in combination with quantum mechanics [16].

Thus, although the problems posed by (23) and (27) refer to two distinct physical contexts of a spin—(i) in a magnetic field \( B_0 \) along the \( z \)-axis and another field of magnitude \( B \) in the \( xy \)-plane at an azimuthal angle \( \phi \), exhibiting cylindrical symmetry, and (ii) in a field of magnitude \( h \), arbitrarily oriented in three-dimensional space, the two problems are mathematically equivalent. The point
is, both the problems possess eigenfunctions characterized by the same number: two, of distinct parameters $-B/B_0$ and $\phi$ in (i), and $\theta$ and $\phi$ in (ii). It is this parameter-dependence of the eigenfunctions that is at the heart of the Berry phase. This means the Hamiltonian here has two dependencies, one on the dynamical variable: the spin and the other is a parametric one. The issue of the Berry phase occurs when the parameters are slowly (adiabatically) varied, as amplified below.

Let us assume that we begin from an instantaneous ground state function, which can be viewed as $|u_-\rangle$ or alternately $|\downarrow\rangle$, and rotate slowly and azimuthally at a rate $(d\phi/dt = \omega_0)$, as in the resonance problem (cf., (4)). However, $\omega_0$ is assumed so small that the associated energy cannot match the energy difference between the Zeeman-split levels, i.e., $\omega_0 \ll B_0$. (Clearly, we could have equally well begun from the excited state $|u_+\rangle$ and carried out the same procedure. The important point is, only one of the states would have to be made to undergo the cyclic rotation—an odd number of times—and then made to interfere with the unaltered state, with a finite phase-difference, so as to observe measurable effects.) The effect of rotation on the resultant wave function $|\psi(t)\rangle$ can be estimated from (11). First, considering that $\omega_0 \ll B_0$, the dynamic evolution approximately yields exp \[ -it(B_0\sigma_z + B_1\sigma_x)|u_-\rangle = exp(it\lambda_-)|u_-\rangle, \]

having used the fact that the concerned wave function is the ground state ket vector. The exponential involving $\lambda_-$ is, however, the dynamical phase associated with the Schrödinger time-evolution, which is not crucial for our present consideration. But we still have to take into account the effect of the counter-clockwise rotation triggered by the operator $R(\Delta t)$ that causes $\phi$ to change to $\phi - d\phi (= \phi - \omega_0\Delta t)$. The new wave function is then:

\[ |\psi(t + \Delta t)\rangle \approx \exp(it\lambda_-)[|u_-\rangle - d\phi (\partial/\partial \phi)|u_-\rangle]. \]

Taking the overlap with the bra vector $< u_- |$, we find

\[ < u - |\psi(t + \Delta t)\rangle = \exp(it\lambda_-)[1 - d\phi < u_- |(\partial/\partial \phi)|u_-\rangle]. \]  \tag{29}
Now, the adiabatic theorem [1] states that the wave function does not change from the original one of \( |u_-> \) but for a phase factor, which apart from the dynamical phase, depends on a distinct phase, which, for the infinitesimal change envisioned here, may be denoted as \( \Delta \gamma \). Thus, \( |\psi(t + \Delta t) > = exp(it\lambda_-)exp(-i\Delta \gamma)|u_-> \).

Taking the overlap then in (29)

\[
exp(-i\Delta \gamma) \sim [1 - d\phi < u_-|\partial / \partial \phi|u_->],
\]

where the right-hand side, upon re-exponentiation, yields \( exp[-d\phi < u - |(\partial / \partial \phi)|u_->] \). Hence,

\[
\Delta \gamma = -id\phi. < u - |(\partial / \partial \phi)|u_->.
\]  

(30)

Finally, taking \( \phi \) over a closed cycle the Berry phase can be written as:

\[
exp(-i\gamma) = exp[i \oint d\phi < u_-|\partial / \partial \phi|u_->].
\]  

(31)

Note that the adiabatic theorem precludes ‘level crossing’ along the closed cycle path, which is ensured by the condition \( \omega_0 \ll B_0 \). This means, the degeneracy point (\( \lambda_- = \lambda_+ \)) must be avoided.

At this stage, it is fair to point out that the present treatment has been restricted to just \( \phi \) being varied. We could have equally well-considered changes with respect to \( \theta \) or both \( \phi \) and \( \theta \). That motivates us to introduce the notation for the ‘Berry connection’, in analogy with the gauge or vector potential of electromagnetism:

\[
A_\phi = -i < u_-|\partial / \partial \phi|u_->, A_\theta = -i < u_-|\partial / \partial \theta|u_->,
\]  

(32)

which allows us to write the Berry phase in (31) in a form reminiscent of the Aharonov–Bohm phase [16]. In this case, however, with the cylindrical symmetry subsumed in the wave functions (24), it can be easily verified that
\[ A_\theta = 0, A_\phi = \cos^2(\theta/2). \] (33)

In further simile with electromagnetism, we may now define a 2-indexed ‘field-tensor’, named the ‘curvature of the connection’ as:

\[ F_{\phi \theta} = (\partial/\partial \phi)A_\theta - (\partial/\partial \theta)A_\phi = \frac{1}{2} \sin \theta. \] (34)

in the present case. To investigate the gauge-issue it is interesting to check on the Berry connection for the eigenvalues in (28). We find

\[ A_\theta = 0, A_\phi = -\sin^2(\theta/2). \] (35)

On the other hand, the Berry curvature is

\[ F_{\phi \theta} = \frac{1}{2} \sin \theta. \] (34*)

identical to the expression given in (34). This underscores the fact that while the Berry connection (or the gauge potential) is gauge-dependent, the Berry curvature (like the magnetic field—since (34) is like a ‘curl’) is not.

The discussion on the subtlety of the Berry phase has been illuminated here based on the simple paradigm of a two-level system. The reader may notice an intriguing classical analogy here in optics—the Pancharatnam phase due to interference of polarized light [18]. It is interesting to note that just two years after Pancharatnam’s classic paper, the appearance of the geometric phase—what chemists call the ‘Longuet–Higgins phase’—was pointed out by Longuet–Higgins and coworkers [19]. This was in the context of vibration-rotation spectra of molecules in which the nuclear coordinates play the role of ‘slow’ variables, while the ‘much faster’ electronic coordinates are enslaved by the occurrence of the geometric phase. Incidentally, to the illustrious list at the beginning of this section can be added the name of Herzberg.

It is interesting to note that just two years after Pancharatnam’s classic paper, the appearance of the geometric phase—what chemists call the ‘Longuet–Higgins phase’—was pointed out by Longuet–Higgins and coworkers.
who received the Nobel Prize in Chemistry in 1971, for his contribution to the electronic structure and geometry of molecules. A comprehensive review of the applications of the geometric phase to classical physics, optics, chemical physics, quantum physics, and mathematics can be found in a review article in *Physics Today* by Berry [20].

Referring back to the two-level case the Berry phase can in general be expressed as the closed line integral of the inner product of two vectors:

$$\exp(-i\gamma) = \exp(-i \oint d\Phi_j A_j),$$

which, upon further use of the Stokes theorem, can be rewritten as

$$\exp(-i\gamma) = \exp(-i \oint dS_{jk} \partial_j A_k) = \exp(-i \oint dS_{jk} F_{jk}),$$

in an explicitly gauge-invariant form.

### 4.1 The Magnetic Monopole Issue

Despite the great success of Maxwell’s electromagnetic theory, there is one disconcerting aspect namely, there is an asymmetry; whereas the existence of an electronic charge has been firmly established, the corresponding point charge for magnetism has eluded discovery. Theorists, however—in particular, Dirac [2], if not but for purely aesthetic reason—had considered the existence of a magnetic monopole, which leads to interesting features of singularities and topology.

We have implied earlier that the Berry phase also has a topological flavor, and, therefore, it is rather a queer coincidence to see a link between the Berry phase of a two-level system and the magnetic monopole. However, it turns out that this analogy—in the model analyzed here—is only manifested in the topological space of magnetic fields and not in the actual space as for the monopole.
In order to carry out this study, it is convenient to look anew, as we do now, at the two-level problem of a spin in a three-dimensional magnetic field as at the beginning of this section. In that context, the ground state eigenfunction (28) can be rewritten as:

\[ |\downarrow\rangle = \zeta \left( \frac{h_x - ih_y}{h + h_z} \right), \quad (28^*) \]

where

\[ \zeta = [1/2h(h + h_z)]^{1/2}, \quad (38) \]

and \( h \)'s have been defined earlier in (27).

As stated before, we will have to now take derivatives of functions with regard to not actual space coordinates but the \( h \)-fields. To this end we find:

\[ \frac{\partial}{\partial h_x} |\downarrow\rangle = -\zeta^2 h_x(2 + h_z/h)|\downarrow\rangle - \zeta \left( \frac{-1}{h_x/h} \right), \quad (39) \]

where the first prefactor occurs from the derivative of \( \zeta \). Hence, after a little algebra we arrive at:

\[ A_x = -i <\downarrow | \frac{\partial}{\partial h_x} |\downarrow\rangle = h_x\zeta^2. \quad (40) \]

Similarly we find,

\[ A_y = -h_x\zeta^2, \quad \text{but} \quad A_z = 0, \quad (40^*) \]

reflecting the axial symmetry of the underlying wave functions.

It is more meaningful of course to consider the Berry curvature or the gauge-invariant magnetic field (fictitious though, in the space of the \( h \)-fields) which, in the Cartesian system, can be written as:

\[ B = i \left( \frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} \right) + j \left( \frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} \right) + k \left( \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \right). \quad (41) \]
From (40) and after some algebra we conclude that:

$$B = (1/2\hbar^3)(\hbar_x + \hbar_y + \hbar_z) = \hbar/2\hbar^3.$$  

(42)

In this case, the so-called Chern C number, by definition an integer:

$$C = (1/2\pi) \oint dS_{jk}F_{jk},$$  

(43)

turns out to be exactly 1, as can be seen from (42) by carrying out the surface integral over a differential surface defined by its normal that lies along \( \mathbf{h} \).

Equation (42) suggests an inverse square Coulomb-type field, like in electrostatics. Astonishingly, this is just the monopole field, albeit in the space of \( \mathbf{h} \)-fields, with however a magnetic charge of \( \frac{1}{2} \) [2].

4.2 Application to Two-dimensional Quantum Solids

The case of graphene has been extensively discussed earlier in Current Science [3] and Resonance articles [7, 8, 9]. We recall that the two-dimensional lattice of graphene is well described by a tight-binding model wherein the two states, represented by a pseudo Pauli spin, correspond to the occupation of a \( \pi \)-electron in one of the sub-lattice sites of a honeycomb structure.

When the tight-binding Hamiltonian is expressed in the reciprocal wave vector-space, the energy spreads into two bands—valence and conduction. These bands, otherwise separated (and hence yielding a weak insulator sometimes referred to as a semi-metal), however, touch at two distinct points \( \mathbf{K} \) and \( \mathbf{K}^* \) in the Brillouin zone where the energy-difference between the valence and the conduction bands disappears, as the wave vector \( \mathbf{q} \) goes to zero, thus facilitating transport. Near the \( \mathbf{K} \) and \( \mathbf{K}^* \) points, the energy has a curious linear dependence on \( |\mathbf{q}| \), reminiscent of relativistic Dirac theory of spin-half particles.
Focusing on the \( \mathbf{K} \)-point, the Hamiltonian can be written as [3, 8]

\[
H_{\mathbf{k}}(\mathbf{q}) = v \mathbf{F} \mathbf{q}.
\]  

(44)

where \( v \) can be interpreted as the Fermi velocity. The reader will note that this is exactly in the form of (27) where the Cartesian components of the ‘magnetic field’ read

\[
h_x = v q_x, \ h_y = v q_y, \ h_z = 0,
\]  

(45)

as the \( \mathbf{q} \)-vector lies in the \( xy \)-plane reflecting the essential two-dimensional character of the solid. Clearly the energy eigenvalues are now given by:

\[
\lambda_{\pm} = \pm v |\mathbf{q}|,
\]  

(46)

which merge at the \( |\mathbf{q}| = 0 \) or the \( \mathbf{K} \)-point called the Dirac point. Given that this is also the point at which the ‘effective magnetic field’ in (45) vanishes, it identifies the location of the singularity point at which the magnetic monopole is situated (cf., section 4.1).

Following (28) the energy eigenfunctions are:

\[
|\uparrow_{\mathbf{q}}\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} \exp(-i\varphi_{\mathbf{q}}) \\ 1 \end{pmatrix}, \quad |\downarrow_{\mathbf{q}}\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} \exp(i\varphi_{\mathbf{q}}) \\ -1 \end{pmatrix},
\]  

(47)

where \( q \) is suffixed to underscore the fact that the parameters of the state now have an explicit \( q \)-dependence. The point is, unlike the previous example where the magnetic fields can be varied in the laboratory, here the \( \mathbf{q} \)-fields are intrinsic to the system. The question of the Berry phase and all the concomitant topological issues arise when the \( \mathbf{q} \)-fields change adiabatically \textit{vis a vis} the dynamic pseudo spin variables.

We now turn to a different example of a two-dimensional electronic solid that is characterized by the so-called Rashba interaction. Recall that in the special theory of relativity, an electric
field $\mathbf{E}$ in the laboratory creates, in a Lorentz frame moving with a velocity $\mathbf{v}$, a magnetic field $\mathbf{B}_L$ given by:

$$
\mathbf{B}_L = (\mathbf{v} \times \mathbf{E})/c^2,
$$

(48)
c being the speed of light.

If the $\mathbf{E}$-field points along the $z$-axis of the laboratory, the $\mathbf{B}_L$-field would lie in the $xy$-plane. Further, the $\mathbf{B}_L$-field is perpendicular to the velocity $\mathbf{v}(= \hbar k/m_e)$, that also lies in the $xy$-plane for a two-dimensional solid. Consequently, the Zeeman coupling between $\mathbf{B}_L$ and (now the real) spin $\sigma$—the reason behind spin-orbit coupling in free atoms [17]—can again be cast in the form of (27), but now:

$$
h_x = -\alpha q_y, h_y = \alpha q_x, \alpha = \hbar E/m_e c^2.
$$

(49)

Once again, like the Dirac solid of graphene, the two energy eigenvalues $\lambda_{\pm} = \pm \alpha |q|$, but now as a variant to (47), the energy eigenfunctions turn out to be

$$
|\uparrow q\rangle = \sqrt{2} \frac{1}{|\exp(i\varphi q)|} |\downarrow q\rangle = \frac{1}{\sqrt{2}} \left( \begin{array}{c}
1 \\
-i\exp(i\varphi q)
\end{array} \right).
$$

(50)

If we additionally apply a magnetic field $B_o$ along the $z$-axis, we are back to a situation similar to that described by (23) and (24). The energy eigenvalues now become $\lambda_{pm} = \pm (\hbar^2 0 + \alpha^2 |q|^2)^{1/2}$, implying that the spectrum has a gap at the Dirac point $|q| = 0$, with a gap energy that equals $2B_o$. The energy eigenfunctions are:

$$
|u_+\rangle = \left( \begin{array}{c}
\cos \vartheta/2 \\
\exp(i\varphi) \sin \vartheta/2
\end{array} \right),
|u_-angle = \left( \begin{array}{c}
\sin \vartheta/2 \\
-i\exp(i\varphi) \cos \vartheta/2
\end{array} \right),
\tan \vartheta = \alpha |q| / B_o.
$$

(51)

Once again the Berry phase finds all its ramifications here.
5. Concluding Remarks

In this article, we have employed the paradigm of a two-level scenario to illustrate myriads of phenomena in quantum chemistry and physics. These include certain well-researched subjects of magnetic resonance, tunneling, hybridized orbitals, etc. But dwelling on that platform, we have also discussed the topically important concepts of memory protection in quantum coherent devices and the exotic electronic transport in Dirac solids, e.g., graphene and Rashba spin-coupled systems. We have labored to explicitly exhibit all the diverse wave functions (albeit with the same eigenvalues, upon the trivial redefinition of symbols) in order to emphasize the gauge freedom inherently linked with the occurrence of the Berry phase.

The two-level tunneling centers, discussed in subsection 3.1, have been taken to new levels in recent times when the problem of decoherence has been dealt with in terms of what is dubbed as the spin-boson Hamiltonian; the extent of activity can be judged by the fact that a special issue of Chemical Physics has been dedicated to this theme [21].

The two-level physics in the Rashba setup indicated in (48) and (49) has been recently established in the interface of oxides by means of planar Hall resistivity measurements [22]. Further application of a transverse magnetic field leads to Landau diamagnetism [23]. The accompanying Shubnikov–de Haas oscillations in the magnetoresistance, and the essential influence of the Berry phase thereon, based on (50), have also been seen in experiments [24].

Acknowledgement

I am grateful to the Indian National Science Academy for support through their ‘Senior Scientist’ scheme. I would also like to thank Malay Bandyopadhyay for his help in the preparation of the manuscript. Special thanks are due to the reviewer who made me aware of the pioneering contributions to the geometric
phase in chemical physics made by H. C. Longuet-Higgins and collaborators.

Suggested Reading


Address for Correspondence
Sushanta Dattagupta
Uniworl City
Heights Tower 6, Flat 002
New Town (Action Area II)
Rajarhat, Kolkata 700 156
Email: sushantad@gmail.com