Entanglement, Berry Phases, and Level Crossings for the Atomic Breit-Rabi Hamiltonian

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Abstract

The relation between level crossings, entanglement, and Berry phases is investigated for the Breit-Rabi Hamiltonian of hydrogen and sodium atoms, describing a hyperfine interaction of electron and nuclear spins in a magnetic field. It is shown that the entanglement between nuclear and electron spins is maximum at avoided crossings. An entangled state encircling avoided crossings acquires a marginal Berry phase of a subsystem like an instantaneous eigenstate moving around real crossings accumulates a Berry phase. Especially, the nodal points of a marginal Berry phase correspond to the avoided crossing points.

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I. INTRODUCTION

Energy levels, eigenvalues of a Hamiltonian, play the most primary role in determining properties of a quantum system. When energy levels cross or avoided cross as parameters of a Hamiltonian vary, various interesting phenomena happen. For example, if two instantaneous energy levels of a time-dependent Hamiltonian are avoided crossing, the non-adiabatic tunneling called the Landau-Zener tunneling between them takes place [1]. Closely related to this, the runtime of adiabatic quantum computation is inversely proportional to the square of the energy gap between the ground and first exited levels [2]. An eigenstate encircling adiabatically degeneracy points accumulates a Berry phase in addition to a dynamical phase [3, 4]. In quantum chemistry, a conical intersection of electronic energy surfaces of molecules plays a key role in understanding ultrafast radiationless reactions [5, 6]. A quantum phase transition, a dramatic change in a ground state as parameters of a system vary, is related with crossings or avoided crossings of two lowest energy levels [7]. Kais et al. have shown that the finite size scaling method can be used for studying the critical behavior, i.e., the level degeneracy or absorption, of a few-body quantum Hamiltonian \( H(\lambda_1, \cdots, \lambda_k) \) as a function of a set of parameters \( \{\lambda_i\} \) [8, 9]. These parameters could be the external fields, inter-atomic distances, nuclear charges for stability of negative ions, cluster size, and optical lattice parameters such as the potential depth [10]. Thus, it is important to develop a way of finding level crossings and to understand how eigenstates or relevant physical quantities change at crossing or avoided crossings.

Recently Bhattacharya and Raman presented a powerful algebraic method for finding level crossings without solving an eigenvalue problem directly [11]. Along with this mathematical way, it is necessary to understand what physical quantities can be used to detect or characterize crossings or avoided crossings. First of all, the measurement of a Berry phase could be a good way to detect level crossings because it due to level crossings. It is well known that avoided crossings or glancing intersections are not the source of Berry phases [5]. Is there any way that Berry phases can detect avoided level crossings? Here we show that the marginal Berry phase of an entangled state could be an indicator to avoided level crossings.

The entropy is another indicator to level crossings. Since level crossing or avoided crossings are accompanied with a drastic change in eigenstates, any contents of information
on relevant eigenstates may also vary. The Shannon entropy of the electron density measures
the delocalization or the lack of structure in the respective distribution. Thus the Shannon
entropy is maximal for uniform distribution, that is, for an unbound system, and is minimal
when the uncertainty about the structure of the distribution is minimal [12]. González-Férez
and Dehesa showed that the Shannon entropy could be used as an indicator of avoided cross-
ings [13]. The von Neumann entropy, the quantum version of the Shannon entropy, is a good
entanglement measure for a bipartite pure state. In quantum information, much attention
has been paid to the relation between entanglement and quantum phase transitions [14, 15].
Recently one of the authors investigated the relation between entanglement, Berry phases,
and level crossings for two qubits with the XY-type interaction and found that the level
crossing is not always accompanied with the abrupt change in entanglement [16].

In this paper, in order to study how entanglement and Berry phases vary at level crossings,
we consider the Breit-Rabi Hamiltonian describing a hyperfine interaction of electron and
nuclear spins in a uniform magnetic field [17]. It is shown that the von Neumann entropy of
the electron (or nuclear) spin is maximum at avoided crossings. It is demonstrated that the
significant changes in Berry phases and entanglement are closely related to level crossings.
We show that the marginal Berry phase of the electron (or nuclear) spin could be a good
indicator to avoided level crossings. The marginal Berry phase has nodal points at the
avoided crossing points.

The paper is organized as follows. In Sec. II the Breit-Rabi Hamiltonian is introduced.
In Sec. III as a specific application of the Breit-Rabi Hamiltonian, we consider a hyperfine
interaction between a nuclear spin 1/2 and an electron spin 1/2 of a hydrogen atom in a
magnetic field. We analyze the close relation between entanglement, Berry phases, and level
crossings. In Sec. IV we make a similar analysis for a sodium atom with a nuclear spin
3/2 and an electron spin 1/2. In Sec. V we summarize the main results.

II. BREIT-RABI HAMILTONIAN

Let us consider an atom with a single valence electron in the ground state with orbital
angular momentum \( L = 0 \). In the presence of a uniform magnetic field \( B \) in the \( z \) direction,
its atomic spectrum is described by the Breit-Rabi Hamiltonian [17], which is given by the
sum of the hyperfine interaction between a nuclear spin \( I \) and an electron spin \( S \) and their
Zeeman couplings to the magnetic field

\[ H = A \mathbf{I} \cdot \mathbf{S} + (aS_z + bI_z)B, \]  

(1)

where \( A \) is the hyperfine coupling constant, \( a = \gamma_e \hbar \) and \( b = \gamma_n \hbar \). Here \( \gamma_e \) and \( \gamma_n \) are the electron and nuclear gyromagnetic ratios, respectively. The electron spin operator \( \mathbf{S} \) and the nuclear spin operator \( \mathbf{I} \) are measured in the unit of \( \hbar \).

The Breit-Rabi Hamiltonian \( (1) \) is well studied to describe double resonance in nuclear magnetic resonance \([18]\) and the muon spin rotation in semiconductors \([19]\). Although simple and well understood, it still continues to provide new insights. Recently Bhattacharya and Raman found a new class of invariants of the Breit-Rabi Hamiltonian \([11]\). As will be shown here, it is a prime example for showing the close relation between level crossings, entanglement, and geometric phases. Also it is related to a Hamiltonian of electron spin qubits in quantum dots \([20]\) where the Heisenberg interaction between two electron spins can be turned on and off to implement the controlled-not gate.

Before applying the Hamiltonian \( (1) \) to specific systems, let us look at its general properties. If \( B = 0 \), then \( H \) commutes with both the square of the total spin operator \( \mathbf{J}^2 \) and \( J_z \), where the total spin operator is defined by \( \mathbf{J} \equiv \mathbf{I} + \mathbf{S} \). However, for \( B \neq 0 \), due to the fact that \( a \neq b \), the Hamiltonian \( (1) \) no longer commutes with \( \mathbf{J}^2 \), but still commutes with \( J_z \). So the eigenvalue \( m \) of \( J_z \) is a good quantum number for the Breit-Rabi Hamiltonian. With ladder operators, \( S_\pm = S_x \pm iS_y \) and \( I_\pm = I_x \pm iI_y \), the Hamiltonian \( (1) \) can be rewritten as

\[ H = AI_zS_z + A^2 (S^+I^- + S^-I^+) + B(aS_z + bI_z). \]  

(2)

Let us use a simple notation \( |m_S, m_I\rangle \) to represent the product state \( |S, m_S\rangle \otimes |I, m_I\rangle \), where \( |S, m_S\rangle \) is an eigenstate of \( \mathbf{S}^2 \) and \( S_z \), and \( |I, m_I\rangle \) is an eigenstate of \( \mathbf{I}^2 \) and \( I_z \). The first and third terms in Eq. \( (2) \) give the diagonal matrix elements

\[ \langle m_S m_I | H | m_S m_I \rangle = f(m_S, m_I) = Am_S m_I + m_S aB + m_I bB. \]  

(3a)

The second term in Eq. \((2)\) corresponds to the off-diagonal matrix elements

\[ \langle m'_S m'_I | S_+ I_- | m_S m_I \rangle \]

\[ = \sqrt{(S - m_S)(S + m_s + 1)} \sqrt{(I + m_I)(I - m_I + 1)} \delta_{m'_S, m_S+1} \delta_{m'_I, m_I-1}. \]  

(3b)

Since \( m'_S - m_S = 1 \) and \( m'_I - m_I = -1 \) (or vice versa), one has the selection rule, \( \Delta m = (m'_S + m'_I) - (m_S + m_I) = 0 \), that is, the magnetic quantum number \( m = m_S + m_I \) is conserved.
This implies that the Hamiltonian (1) is block diagonal in the basis set \( \{|m_S, m_I]\} \) ordered by \( m \).

### III. THE HYDROGEN ATOM IN A UNIFORM MAGNETIC FIELD

#### A. Eigenvalues and Eigenstates

As a simple but real system described by the Hamiltonian (1), let us consider the interaction between the nuclear spin \( I = 1/2 \) and the electron spin \( S = 1/2 \) of a hydrogen atom in a uniform magnetic field. Since \( H \) commutes with the \( z \)-component of the total spin operator, \( J_z = S_z + I_z \), it is convenient to arrange the product basis \( \{|m_S, m_I]\} \) in the decreasing order of the magnetic quantum number \( m \) of \( J_z \) as \( \{|1/2, 1/2\}, |1/2, -1/2\}, |1/2, 1/2\}, \ldots\} \). By means of Eqs. (3), the Breit-Rabi Hamiltonian for a hydrogen atom can be written in the ordered basis

\[
H = \frac{1}{4} \begin{pmatrix}
A + 2(a + b)B & 0 & 0 & 0 \\
0 & -A + 2(a - b)B & 2A & 0 \\
0 & 2A & -A - 2(a - b)B & 0 \\
0 & 0 & 0 & A - 2(a + b)B
\end{pmatrix}.
\]

The Hamiltonian (4) is block diagonal, so it is straightforward to obtain its eigenvalues and eigenvectors. The subspace of \( m = \pm 1 \) is spanned by \( \{|1/2, 1/2\}, |1/2, -1/2\}\). The block Hamiltonian on this subspace is already diagonal and has its eigenvalues and eigenvectors

\[
E_{\pm 1} = \frac{A}{4} \pm \frac{1}{2}(a + b)B, \quad |E_{\pm 1}\rangle = |\pm \frac{1}{2}, \pm \frac{1}{2}\rangle,
\]

where the subscripts ‘\( \pm 1 \)’ in \( E_{\pm 1} \) denote the magnetic quantum number \( m = \pm 1 \). The block Hamiltonian with \( m = 0 \) is defined on the subspace of \( \{|1/2, -1/2\}, |1/2, -1/2\}\) and is written as

\[
H_{m=0} = \frac{1}{4} \begin{pmatrix}
-A + 2(a - b)B & 2A \\
2A & -A - 2(a - b)B
\end{pmatrix}.
\]

One can interpret the Hamiltonian \( H_{m=0} \) as that of a spin in an effective magnetic field in the \( x-z \) plane, \( B_{\text{eff}} \equiv (A/2, 0, (a - b)B/2) \). The eigenvalues and eigenvectors of \( H_{m=0} \) can
be written easily as

\[ E_0^\pm = -\frac{A}{4} \pm \frac{1}{2} \sqrt{(a-b)^2 B^2 + A^2}, \quad (7a) \]

\[ |E_0^+\rangle = \cos \frac{\alpha}{2} \left| \frac{1}{2}, -\frac{1}{2} \right\rangle + \sin \frac{\alpha}{2} \left| -\frac{1}{2}, \frac{1}{2} \right\rangle, \quad (7b) \]

\[ |E_0^-\rangle = -\sin \frac{\alpha}{2} \left| \frac{1}{2}, -\frac{1}{2} \right\rangle + \cos \frac{\alpha}{2} \left| -\frac{1}{2}, \frac{1}{2} \right\rangle, \quad (7c) \]

where \( \tan \alpha \equiv \frac{A}{(a-b)B} \). In a weak magnetic field limit (so called the Zeeman region), the Zeeman energy is smaller than the hyperfine coupling. At \( B = 0 \), i.e., \( \alpha = \pi/2 \), the ground eigenstate \( |E_0^-\rangle \) becomes the singlet state, \( |E_0^-\rangle = \frac{1}{\sqrt{2}} \left( \left| -\frac{1}{2}, \frac{1}{2} \right\rangle - \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \right) \). In a strong magnetic field called the Paschen-Back region, the Zeeman couplings are dominant. That is, in limit of \( B \to \infty \), one has \( \alpha \to 0 \) and \( |E_0^-\rangle \to -\left| -\frac{1}{2}, \frac{1}{2} \right\rangle \).

The eigenvalues and eigenstates of the Breit-Rabi Hamiltonian for a hydrogen atom, Eqs. (5) and (7) depend on two parameters: the hyperfine constant \( A \) and the magnetic field \( B \). The hyperfine constant \( A \) of the hydrogen atom in vacuum is positive. However, if a hydrogen atom is in an inert gas, the hyperfine constant \( A \) could be negative \[21\], resembling the spin-spin coupling constant in a Heisenberg model. We assume that \( A \) as well as \( B \) varies and can be negative. To this end, \( A \) in Eqs. (5) and (7) is replaced by \( f A \) with \( -1 \leq f \leq 1 \), so \( A \) is still kept the positive constant in vacuum. If \( f \) is negative, so the hyperfine constant.

Depending on \( f \) and \( B \), the ground state of the Hamiltonian (4) is given either by \( |E_{\pm 1}\rangle \) or by \( |E_0^-\rangle \). It is convenient to plot the energy levels normalized by \( A \). Then, Eqs. (5) and (7) become \( E_{\pm 1}/A = \frac{f}{4} \pm \frac{1}{2} (a'+b')B \) and \( E_0^\pm/A = -\frac{f}{4} \pm \frac{1}{2} \sqrt{(a'-b')^2 B^2 + f^2} \), where \( a' \equiv a/A \approx 19.767 \) \( \text{T}^{-1} \) and \( b' \equiv b/A \approx -0.03 \) \( \text{T}^{-1} \) are taken from Ref. \[22\], and \( B \) is measured in the unit of tesla. The energy levels \( E_m/A \) are plotted as functions of \( B \) for \( f = 1 \) in Fig. 1 (a) and for \( f = -0.5 \) in Fig. 1 (b). For \( f > 0 \), the ground level is \( E_0^- \). For \( f < 0 \), two levels, \( E_0^+ \) and \( E_{\pm 1} \), with different magnetic quantum numbers cross at \( f = \frac{2a'b'}{a'-b'}|B| \). Fig. 2 (a) shows the energy gap \( \Delta/A \) between the ground and first exited states as a function of \( f \) and \( B \), where we take \( a' = 0.1 \) \( \text{T}^{-1} \) and \( b' = -0.01 \) \( \text{T}^{-1} \) to see clearly the phase diagram of the ground state of the Hamiltonian (4) determined by the magnetic quantum number \( m \). As shown in Fig. 2 (a), the energy gap \( \Delta/A \) vanishes along the lines defined by \( f = \frac{2a'b'}{a'-b'}|B| \) and the negative \( f \) axis. In the region of \( f < \frac{2a'b'}{a'-b'}|B| \), the ground state becomes either \( |E_{+1}\rangle \) or \( |E_{-1}\rangle \) with the magnetic quantum number \( m = 1 \) or \( m = -1 \), respectively. On the other hand, the ground state in the region defined by
$f > \frac{2\sqrt{\lambda}}{a_0 - b_0} |B|$ is given by $|E_0^-\rangle$ with the magnetic quantum number $m = 0$. One can see that the magnetic quantum number $m$ of the ground state changes abruptly at the level crossing points.

B. Entanglement

Let us discuss the relation between level crossings and entanglement. Entanglement refers to the quantum correlation between subsystems and has no classical analog [23, 24]. When level crossing happens as the parameter of the Hamiltonian varies, the ground state changes drastically. Entanglement as a physical quantity may also undergo a significant change. However, entanglement is not always a good indicator to level crossing as shown in Ref. [16].

First, let us examine the relation between entanglement and level crossings for each eigenstate. The von Neumann entropy $S$ of a subsystem is a good entanglement measure for a pure bipartite system. If $|\psi_{AB}\rangle$ is a quantum state of a system composed of two subsystems $A$ and $B$, the entanglement between $A$ and $B$ is measured by the von Neumann entropy of the subsystem, $S(\rho_A) = -\text{tr}(\rho_A \log \rho_A) = S(\rho_B) = -\text{tr}(\rho_B \log \rho_B)$, where the reduced density matrix $\rho_A$ of the subsystem $A$ is obtained by tracing out the degrees of freedom of $B$ as $\rho_A = \text{tr}_B(|\psi_{AB}\rangle \langle \psi_{AB}|)$. If the ground state is given by $|E_{\pm 1}\rangle$, i.e., a product state, then the von Neumann entropy $S$ of the electron (or nuclear) spin is zero. On the other hand, for the quantum state $|E_0^\pm\rangle$ of the electron and nuclear spins, the von Neumann entropy of the electron (or nuclear) spin can be written as

$$S(\rho_A) = -\frac{1 + \cos \alpha}{2} \log_2 \frac{1 + \cos \alpha}{2} - \frac{1 - \cos \alpha}{2} \log_2 \frac{1 - \cos \alpha}{2}.$$  (8)

Fig. 1 (c) shows the von Neumann entropy of the electron (or nuclear) spin for each eigenstate as a function of $B$. For the eigenstates $|E_0^\pm\rangle$, it is maximum at $B = 0$, i.e., at the avoided crossing point. This is analogous to the sharp change in Shannon entropy at avoided crossing in Ref. [13].

Now, let us look at how entanglement changes at level crossings as the parameters of the Hamiltonian vary. Fig. 2 (b) plots the von Neumann entropy $S$ of the electron (or nuclear) spin for the ground state as a function of $f$ and $B$. Across the level crossing line, $f = \frac{2\sqrt{\lambda}}{a_0 - b_0} |B|$, the von Neumann entropy changes abruptly. For $f > 0$, $S$ becomes 1 as $B$ goes to 0. Along the line of $f = 0$, the von Neumann entropy $S$ vanishes even though there
is no level crossing.

C. Berry Phase

An instantaneous eigenstate encircling the energy level crossing points acquires the Berry phase in addition to the dynamical phase. The information on the level crossings is encoded in the Berry phase. At $B = 0$ and $f = 1$, the two levels $E_{\pm 1}$ cross and the other two levels $E_{\pm 0}$ are avoided crossing. Also $E_{\pm 1}$ and $E_{\mp 0}$ cross at $f = \frac{2a\omega'}{a - B|B|}$. Here we focus on the Berry phase due to the level crossing or avoided crossing at $B = 0$.

Due to the fact that $a \gg |b|$, an electron spin rotates much faster than a nuclear spin. We assume the magnetic field $B$ is rotated slowly enough for both the electron and nuclear spins to evolve adiabatically. The magnetic field $B = B\hat{n}$ in the direction of $\hat{n} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$ is constructed starting from $B = B\hat{z}$. First, it is rotated about the $y$ axis by angle $\theta$. And it is subsequently rotated about the $z$ axis by angle $\phi$. By applying SU(2) rotations corresponding to the above SO(3) rotations on the Hamiltonian (1), one obtains the Breit-Rabi Hamiltonian in the magnetic field $B = B\hat{n}$

$$H(\theta, \phi) = A\mathbf{I} \cdot \mathbf{S} + a\mathbf{B} \cdot \mathbf{S} + b\mathbf{B} \cdot \mathbf{I}. \tag{9}$$

The hyperfine interaction $A\mathbf{I} \cdot \mathbf{S}$ is spherical symmetric, so the eigenvalues and eigenvectors of the Hamiltonian (9) are identical to those of the Hamiltonian (1) except replacing $|\pm \frac{1}{2}\rangle$ by $|\hat{n}; \pm \frac{1}{2}\rangle$. Here $|\hat{n}; \pm \frac{1}{2}\rangle$ are eigenstates of $\hat{n} \cdot \mathbf{S}$ or $\hat{n} \cdot \mathbf{I}$. If the magnetic field $B$ is rotated slowly about the $z$ axis by $2\pi$ to make a cone with a solid angle $\Omega = 2\pi(1 - \cos \theta)$, then the instantaneous eigenstate $|\hat{n}; \pm \frac{1}{2}\rangle$ follows it and accumulates the Berry phase $\beta_\pm = \mp \frac{1}{2} \Omega$. The total Berry phase $\beta$ of electron and nuclear spins is the sum of two phases acquired by each one. It depends on the magnetic quantum number $m$

$$\beta = \begin{cases} \mp \Omega & \text{for } m = \pm 1, \\ 0 & \text{for } m = 0. \end{cases} \tag{10}$$

As expected, the Berry phase is nonzero only for real crossings, i.e., $m = \pm 1$. Fig. 2(c) plots the total Berry phase as a function of $B$ and $f$ and shows that the total Berry phase jumps at the level crossings. The zero Berry phase of the eigenstates $|E_{\mp 0}(\theta, \phi)\rangle$ can be understood in two ways. First, two levels $E_{\mp 0}$ are avoided crossing at $B = 0$, so it is zero. Another view
is as follows. Since \( |E_0^\pm \rangle \) is a superposition of \( |\frac{1}{2}, -\frac{1}{2} \rangle \) and \( | -\frac{1}{2}, \frac{1}{2} \rangle \), the Berry phase of the electron spin is opposite to that of the nuclear spin and they cancel each other.

Although the entangled states \( |E_0^\pm \rangle \) of electron and nuclear spins accumulates no Berry phase, each subsystem (electron spin or nuclear spin) can get nonzero marginal Berry phases of mixed states. Following the studies on geometric phase of mixed states [25, 26] and the relation between entanglement and marginal Berry phases [26, 27, 28], we investigate the relation between avoided level crossings, marginal Berry phases, and entanglement. For an adiabatic cyclic evolution parameterized by \( x \), an instantaneous eigenstate of a bipartite system \( AB \) can be expressed in a Schmidt decomposition

\[
\psi(x) = \sum_{i=1}^{M} \sqrt{p_i} |e_i(x)\rangle \otimes |f_i(x)\rangle,
\]

where \( \{|e_i(x)\rangle\}_{i=1}^{N_A} \) is an orthonormal basis for a subsystem \( A \), \( \{|f_i(x)\rangle\}_{i=1}^{N_B} \) for a subsystem \( B \), \( M \leq \min\{N_A, N_B\} \), and \( \sum_{i=1}^{M} p_i = 1 \). Here our attention is restricted to the case that the Schmidt coefficients \( \sqrt{p_i} \) are independent of \( x \). After an adiabatic cyclic evolution implemented by \( x(0) = x(T) \), the total Berry phase of the bipartite system \( AB \) is given by

\[
\beta = \sum_{i=1}^{M} p_i (\beta_i^A + \beta_i^B),
\]

where \( \beta_i^A = \int_C dx \cdot \langle e_i(x) | \nabla_x | e_i(x) \rangle \). Then the marginal mixed state Berry phase \( \Gamma_A \) of a subsystem \( A \) is defined by

\[
\Gamma_A = \arg \sum_i p_i \exp \left( i \beta_i^A \right).
\]

With Eqs. (11) and (12), let us analyze how the total Berry phase and the marginal Berry phase of \( |E_0^-\rangle \) depend on \( B \). The two Schmidt coefficients are given by \( p_1 = \sin^2 \Omega/2 \) and \( p_2 = \cos^2 \Omega/2 \). It is easy to obtain the marginal Berry phase of the electron spin \( \Gamma_e = \arctan \left( \cos \alpha \tan \frac{\Omega}{2} \right) \) and the average Berry phase of the electron spin \( \beta_e \equiv p_1 \beta_1^e + p_2 \beta_2^e = \frac{\Omega}{2} \cos \alpha \). In the limit of \( B \gg 1 \), i.e., \( \alpha \to 0 \), one has \( |E_0^-\rangle \to | -\frac{1}{2}, \frac{1}{2} \rangle \) and \( \beta_e = \Omega/2 \). Also the marginal Berry phase of the electron spin is given by \( \Gamma_e = \Omega/2 \) for \( 0 \leq \theta < \frac{\pi}{2} \). Fig. 3 plots \( \Gamma_e \) as a function of \( B \) and the azimuthal angle \( \theta \). The marginal Berry phase of the electron spin jumps at \( \theta = \pi/2 \) and \( B = 0 \). The node at \( B = 0 \) corresponds to the avoided crossing.
IV. THE SODIUM ATOM IN A UNIFORM MAGNETIC FIELD

A. Energy Spectrum

Now we consider an $^{23}\text{Na}$ atom in its $3S_{1/2}$ ground state in the presence of a uniform magnetic field $B$ along the $z$ axis. The nuclear and electron spins of an $^{23}\text{Na}$ atom are $I = 2/3$ and $S = 1/2$, respectively. As in Sec. III it is convenient to arrange the product basis $\{ |m_S, m_I\rangle \}$ in the decreasing order of the magnetic quantum number $m$ of $J_z$ as follows.

$\{ |\frac{3}{2}, \frac{3}{2}\rangle, |\frac{1}{2}, \frac{1}{2}\rangle, |\frac{3}{2}, -\frac{3}{2}\rangle, |\frac{1}{2}, -\frac{1}{2}\rangle, |\frac{3}{2}, -\frac{3}{2}\rangle, |\frac{1}{2}, -\frac{1}{2}\rangle, |\frac{3}{2}, -\frac{3}{2}\rangle \}$, and $\{ |\frac{1}{2}, \frac{1}{2}\rangle, |\frac{3}{2}, -\frac{3}{2}\rangle \}$. For example, $\{ |\frac{1}{2}, \frac{1}{2}\rangle, |\frac{3}{2}, -\frac{3}{2}\rangle \}$ spans the subspace of $m = 1$. In this ordered basis set, the Hamiltonian for the sodium atom can be represented by a block-diagonal matrix

$$H = \begin{pmatrix}
f(\frac{3}{2}, \frac{3}{2}) & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & f(\frac{1}{2}, \frac{1}{2}) & \frac{\sqrt{2}}{2} A & 0 & 0 & 0 & 0 & 0 \\
0 & \frac{\sqrt{2}}{2} A & f(\frac{1}{2}, \frac{1}{2}) & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & f(\frac{1}{2}, -\frac{1}{2}) & \frac{A}{2} & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{A}{2} & f(\frac{1}{2}, \frac{1}{2}) & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & f(\frac{1}{2}, -\frac{3}{2}) & \frac{\sqrt{2}}{2} A & 0 \\
0 & 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{2} A & f(\frac{1}{2}, -\frac{1}{2}) & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & f(\frac{1}{2}, -\frac{3}{2})
\end{pmatrix}, \quad (13)$$

where $f(m_S, m_I) \equiv A m_S m_I + m_S aB + m_I bB$. Each block is at most a $2 \times 2$ matrix and can be easily diagonalized. First, consider the subspace of $m = \pm 2$. The corresponding eigenvalues and eigenvectors can be written as

$$E_{\pm 2} = \frac{3}{4} A \pm \frac{1}{2} (a + 3b) B, \quad (14a)$$

$$|E_{\pm 2}\rangle = |\pm \frac{1}{2}, \pm \frac{3}{2}\rangle. \quad (14b)$$

Notice that Eqs. (14) are comparable to Eqs. (13). Second, in the subspace with $m = 1$ spanned by $\{ |\frac{1}{2}, -\frac{1}{2}\rangle, |\frac{1}{2}, \frac{3}{2}\rangle \}$, one obtains the eigenvalues and eigenvectors,

$$E_{\pm 1}^+ = -\frac{A}{4} + bB \pm \frac{1}{2} \sqrt{(A + (a - b)B)^2 + 3A^2}, \quad (15a)$$

$$|E_{\pm 1}^+\rangle = \cos \frac{\alpha_1}{2} |\frac{1}{2}, \frac{1}{2}\rangle + \sin \frac{\alpha_1}{2} |\frac{1}{2}, \frac{3}{2}\rangle, \quad (15b)$$

$$|E_{\pm 1}^+\rangle = -\sin \frac{\alpha_1}{2} |\frac{1}{2}, \frac{1}{2}\rangle + \cos \frac{\alpha_1}{2} |\frac{1}{2}, \frac{3}{2}\rangle, \quad (15c)$$
where \( \tan \alpha_1 \equiv \frac{\sqrt{3}}{A + (a - b)B} \). Third, the Hamiltonian of \( m = -1 \) is defined on the subspace spanned by \( \{ \left| \frac{1}{2}, -\frac{3}{2} \right>, \left| -\frac{1}{2}, -\frac{1}{2} \right> \} \). Its eigenvalues and eigenstates are given by

\[
E_{\pm 1}^\pm = -\frac{A}{4} - bB \pm \frac{1}{2} \sqrt{(A - (a - b)B)^2 + 3A^2},
\]

(16a)

\[
\left| E_{\pm 1}^\pm \right> = \cos \frac{\alpha_2}{2} \left| -\frac{1}{2}, -\frac{1}{2} \right> + \sin \frac{\alpha_2}{2} \left| \frac{1}{2}, -\frac{3}{2} \right>,
\]

(16b)

\[
\left| E_{-1}^- \right> = -\sin \frac{\alpha_2}{2} \left| -\frac{1}{2}, -\frac{1}{2} \right> + \cos \frac{\alpha_2}{2} \left| \frac{1}{2}, -\frac{3}{2} \right>,
\]

(16c)

where \( \tan \alpha_2 \equiv \frac{\sqrt{3}}{A - (a - b)B} \). Note that Eqs. (16) can be obtained from Eqs. (15) by replacing \( B \) with \(-B\). Finally, the subspace of \( m = 0 \) is spanned by \( \{ \left| \frac{1}{2}, -\frac{1}{2} \right>, \left| \frac{1}{2}, -\frac{1}{2} \right> \} \). The corresponding eigenvalues and eigenvectors are given by

\[
E_{0}^\pm = -\frac{A}{4} \pm \frac{1}{2} \sqrt{(a - b)^2B^2 + 4A^2},
\]

(17a)

\[
\left| E_{0}^+ \right> = \cos \frac{\alpha_0}{2} \left| -\frac{1}{2}, -\frac{1}{2} \right> + \sin \frac{\alpha_0}{2} \left| \frac{1}{2}, \frac{1}{2} \right>,
\]

(17b)

\[
\left| E_{0}^- \right> = -\sin \frac{\alpha_0}{2} \left| -\frac{1}{2}, -\frac{1}{2} \right> + \cos \frac{\alpha_0}{2} \left| \frac{1}{2}, \frac{1}{2} \right>,
\]

(17c)

where \( \tan \alpha_0 \equiv \frac{A}{(a - b)B} \). As expected, Eqs. (17) is very similar to Eqs. (7) in the case of a hydrogen atom.

**B. Entanglement**

Let us examine the relation between entanglement and level crossings or avoided crossings for a sodium atom. With the values of the parameters \( A, a, \) and \( b \) of the \( ^{23}\text{Na} \) atom in Ref. [22], energy levels \( E_m/A \) are plotted in Fig. 4 (a). The von Neumann entropies of the electron (or nuclear) spin for each eigenstates are shown in Fig. 4 (b). The ground state is given by \( \left| E_{+1}^- \right> \) for \( B > 0 \) and \( \left| E_{-1}^- \right> \) for \( B < 0 \). Two levels, \( E_{+1}^+ \) and \( E_{+1}^- \), are avoided crossing and maximally entangled at \( A - (a - b)B = \sqrt{3}A \). Another two levels, \( E_{-1}^+ \) and \( E_{-1}^- \), are avoided crossing and maximally entangled at \( A + (a - b)B = \sqrt{3}A \). Two levels with \( m = 0, E_0^\pm \) are avoided crossing and maximally entangled at \( B = 0 \). Two levels \( E_4^\pm \) show real crossing at \( B = 0 \) and have zero von Neumann entropies. Again one can see that the eigenstate is maximally entangled at the avoided crossing point. This is analogous to the results in Ref. [13], where Shannon entropy is used as an indicator of avoided crossings.
C. Berry phase

As in Sec. III C, let us consider an adiabatic cyclic evolution of nuclear and electron spins of a sodium atom by rotating the magnetic field $B \hat{n}$ slowly. For an adiabatic rotation keeping the azimuthal angle $\theta$ constant and varying the polar angle $\phi$ from 0 to $2\pi$, the instantaneous eigenstates accumulates the total Berry phases proportional to the magnetic quantum number $m$, $\beta = \mp m\Omega$. In contrast to a hydrogen atom, the ground state is given either by $|E_{+1}\rangle$ or by $|E_{-1}\rangle$ with $m = \pm 1$, so it acquires the total Berry phase $\beta = \mp \Omega$.

Let us analyze how the marginal Berry phase of the entangled state is related to the avoided crossings. We focus on the eigenstate, $|E_{-1}\rangle$. It has two Schmidt coefficients, $p_1 = \sin^2 \frac{\alpha_1}{2}$ and $p_2 = \cos^2 \frac{\alpha_1}{2}$. With Eq. (11), one obtains the total phase as a sum of the Berry phases acquired by nuclear and electron spins with weights of the Schmidt coefficients,

$$\beta = \sin^2 \frac{\alpha_1}{2} \left(-\frac{\Omega}{2} - \frac{\Omega}{2}\right) + \cos^2 \frac{\alpha_1}{2} \left(\frac{\Omega}{2} - \frac{3\Omega}{2}\right) = -\Omega. \quad (18)$$

From Eq. (12), one obtains the marginal Berry phases of an electron spin $\Gamma_e$ and of nuclear spin $\Gamma_n$

$$\Gamma_n = \arg \left[ \sin^2 \frac{\alpha_1}{2} e^{-i\Omega/2} + \cos^2 \frac{\alpha_1}{2} e^{-i3\Omega/2} \right], \quad (19a)$$

$$\Gamma_e = \arctan \left[ \cos \alpha_1 \tan \frac{\Omega}{2} \right]. \quad (19b)$$

Fig. 5 plots the marginal Berry phase of a nuclear spin $\Gamma_n$ as a function of $B$ and the azimuthal angle $\theta$. In the limit of $B \gg 1$, i.e., $\alpha_1 \to 0$, one has $|E_{+1}\rangle \to |\frac{1}{2}, \frac{3}{2}\rangle$, $\Gamma_e = \Omega/2$, and $\Gamma_n = -3\Omega/2$. It is clearly seen that the node of the marginal Berry phase of a nuclear (or electron) spin corresponds to the avoid crossing at $A + (a - b)B = \sqrt{3}A$. Thus it could be expected that the marginal Berry phase of a subsystem for an entangled state has a node at avoided crossings.

V. CONCLUSIONS

We have considered the Breit-Rabi Hamiltonians for hydrogen and sodium atoms, describing the hyperfine interaction between a nuclear spin and an electron spin in the presence of a magnetic field. We have examined the relation between level crossings, entanglement, and Berry phases. It is shown that entanglement between nuclear and electron spins is maximum
at avoided crossing points. The Berry phase and the von Neumann entropy change abruptly at level crossings as the parameters of the Breit-Rabi Hamiltonian for a hydrogen atom vary. An entangled state encircling the avoided crossing acquires the marginal Berry phase of an electron (or nuclear) spin like an eigenstate moving around the real crossing accumulates a Berry phase. We have shown that the nodal points of the marginal Berry phase of an entangled state corresponds to the avoided crossing points.

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FIG. 1: (Color online) Energy levels $E_m/A$ of the Breit-Rabi Hamiltonian for a hydrogen atom as functions of the magnetic field $B$ with (a) $f = 1$ and (b) $f = -0.5$. (c) the von Neumann entropy $S$ of the electron (or nuclear) spin for each eigenstate. Here $a' = 19.767 \, \text{T}^{-1}$ and $b' = -0.03 \, \text{T}^{-1}$ are taken from Ref. 22.
FIG. 2: (Color online) (a) Energy gap $\Delta / A$ between the ground and first exited states, (b) the von Neumann entropy $S$ of the electron (or nuclear) spin, and (c) the Berry phase $\beta / \Omega$ of the ground state for a hydrogen atom as a function of $f$ and $B$. Here $a' = 0.01 \, \text{T}^{-1}$ and $b' = -0.1 \, \text{T}^{-1}$ are taken to see the jumps clearly at the level crossings.

FIG. 3: (Color online) Marginal Berry phase $\Gamma_e$ of the electron spin for the entangled eigenstate $|E_0^-\rangle$ of a hydrogen atom as a function of $B$ and the azimuthal angle $\theta$. Here we take $f = 1$, $a' = 19.767 \, \text{T}^{-1}$, and $b' = -0.03 \, \text{T}^{-1}$.
FIG. 4: (Color online) (a) Energy levels $E_m/A$ and (b) the von Neumann entropy $S$ of the electron (or nuclear) spin for the eigenstates of the sodium atom as a function of $B$. The two parameters of a sodium atom, $a' = 32.091 \text{ T}^{-1}$ and $b' = -0.012709 \text{ T}^{-1}$ are taken from Ref. [22].

FIG. 5: (Color online) Marginal Berry phase of the nuclear spin $\Gamma_n$ for the eigenstate $|E_{+1}^-\rangle$ as a function of $B$ and $\theta$. 