Shannon Entropy as an Indicator of Atomic Avoided Crossings in Strong Parallel Magnetic and Electric Fields

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Avoided crossings are the most distinctive atomic spectroscopic features in the presence of magnetic and electric fields. We point out the role of Shannon's information entropy as an indicator or predictor of these phenomena by studying the dynamics of some excited states of hydrogen in the presence of parallel magnetic and electric fields. Moreover, in addition to the well-known energy level repulsion, it is found that Shannon's entropy manifests the informational exchange of the involved states as the magnetic field strength is varied across the narrow region where an avoided crossing occurs.

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The study of the spectroscopic properties of hydrogenic systems in the presence of a combination of external magnetic and electric fields with arbitrary orientation and arbitrary strengths has been the subject of permanent interest since the very early days of quantum mechanics from both fundamental and applied points of view [1–3]. Indeed, even for the case of parallel fields in which the system has two degrees of freedom and three different forces acting on the electron, it is still missing a fully analytical nonrelativistic solution of the problem [4,5]. Moreover, an increasing number of applications of these systems to astrophysics, plasma physics, solid state physics, and quantum chaos are being applied to the interpretation of numerous physical phenomena [2,3].

In this work we consider the hydrogen atom in the presence of strong parallel magnetic **B** and electric **F** fields. It is known that the competition among the Coulomb potential with spherical symmetry, the diamagnetic potential with cylindrical symmetry, and the electric field with parabolic symmetry governs the dynamics of the hydrogen atom, producing drastic changes in its internal structure which gives rise to a large variety of spectral manifestations. All the atomic states become quasibound because of the action of the electric field and field ionization occurs for sufficiently strong F values. Most distinctive is the intricate amount of narrow avoided crossings between levels [6,7] which show up in the energy spectrum for adiabatic changes of the magnetic field strength.

Our purpose is to study the dynamics of the diamagnetic hydrogen atom for a fixed electric field strength across the region where an avoided crossing takes place when the magnetic field strength is varied. This is done by means of the analysis of two quantities: the ionization energy and Shannon's information entropy of the two states involved in this irregular spectral feature. The spreading of the probability density distribution of an electronic excited state, $\rho(\mathbf{r}) = |\psi(\mathbf{r})|^2$, is best described by Shannon's information entropy [8], defined by

$$S_\rho = -\int \rho(\mathbf{r}) \ln\rho(\mathbf{r}) d\mathbf{r}. \tag{1}$$

This quantity is an information measure of the spatial delocalization of the electronic cloud. So, it gives the uncertainty of the localization of the electron. The lower this quantity is, the more concentrated is the wave function of the state, the smaller the uncertainty is, and the higher the accuracy is in predicting the localization of the electron.

It is found that these two quantities give the complementary physical insight of the dynamics of the system through the avoided crossing region. The repulsion of the states shown by the ionization energy illustrates how the avoided crossing phenomenon is a mechanism for state reordering with energy as B is adiabatically changed. This is a consequence of the celebrated von Neumann–Wigner noncrossing rule [9]. The behavior of Shannon's entropy shows that the states involved in this irregular feature exchange their informational character, so quantitatively estimating in a precise way the character exchange already pointed out by von Neumann and Wigner [9], and later on by other authors (see, e.g., Refs. [7,10]). These results are illustrated for some selected pairs of states by comparison of the behavior of the aforementioned quantities when B is varied for a fixed F value in the two following extreme cases: $F = 0$ and $F = 10^6$ V/m. The states involved in each selected pair are so that in the presence of a magnetic field they have the same azimuthal quantum number and different parity; thus they can be degenerate in energy (i.e., they can cross); the inclusion of an additional electric field breaks this degeneracy. In such a situation the associated neighboring energy levels do not cross each other, but rather they come close and then they repel one to another yielding to an avoided crossing.

The motion of the hydrogen atom in the presence of the uniform magnetic **B** and electric **F** fields, both directed along the z axis, is governed by the nonrelativistic Hamiltonian

$$H = -\frac{1}{2r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{2r^2}\mathbf{L}^2(\theta, \phi) - \frac{1}{r} + \frac{B^2}{2}r^2\sin^2\theta + Fr\cos\theta, \quad (2)$$

where we have chosen the atomic system of units ($\hbar = m = e = 1$), so that the magnetic field strength B is measured in units of $B_0 = 2\alpha^2 m_e^2 c^2/\hbar e \approx 4.701 \times 10^5$ T, and the electric field strength F in units of $F_0 = \frac{\alpha^3 m_e^2 c^3}{e\hbar} \approx 5.142 \times 10^{11}$ V/m. The operator $\mathbf{L}^2(\theta, \phi)$ denotes the squared angular momentum expressed in spherical coordinates. It is well-known that relativistic corrections are negligible [11] for magnetic fields below 1000 a.u., and the spin-orbit coupling is small for excited states with $n > 0.126B^{-1/3}$ [1]. In addition, the motion of the nucleus is not explicitly considered because for strong magnetic fields its effect may be accounted for by a constant shift in the energy which is exact for parallel fields [12]. For vanishing electric field (i.e., $F = 0$), the spherical symmetry of the hydrogen atom is broken by the diamagnetic contribution of the strong field to the Coulomb potential. The states can be described only by means of the magnetic quantum number m and the z parity. In the presence of an additional parallel electric field the symmetry of the system with respect to reflection on the xy plane is broken, and hence the z parity is no longer conserved. Thus, only the magnetic quantum number remains as a rigorous quantum number. This is the reason to disregard the paramagnetic term $B \cdot L_z$, where L_z is the z component of the angular momentum, in the Hamiltonian (2). Furthermore, only $m = 0$ states are considered.

To solve this fully nonintegrable two dimensional problem a nonperturbative technique is necessarily required. We have used a hybrid computational approach which combines the discrete variable representation and the finite element method to deal with the angular and radial variables, respectively, so transforming the Hamiltonian into a generalized symmetric eigenvalue problem which is solved with the help of a Krylov-type technique. The accuracy and efficiency of this approach has been shown to describe the spectrum of the level of various nonintegrable systems [13], including hydrogenic and some alkalilike atoms and ions [14]. For a detailed description of the computational algorithm and its extension to the three dimensional case, we refer to [13]. Let us also mention here that the radial and angular integrals involved in the Shannon entropy (1) are computed by means of a Gauss-Legendre quadrature in the corresponding variables.

We have investigated the ionization energy and the Shannon entropy of the hydrogenic states involved in the first avoided crossing of the pair $(3p_0, 3d_0)$ when B is varied and the electric field strength has the values 0 and 10^6 V/m [10]. Both quantities are computed with six converged digits. The quantum numbers n, l, and m, characteristic of a free hydrogen atom, will be frequently used to refer to the states in the presence of the fields in order to facilitate the discussion of their evolution; however, we should keep in mind that the only good quantum numbers are m and the z parity in the absence of electric field, and just m when there is an additional strong electric field.

Our computed results for the pair of states $(3p_0, 3d_0)$ of the diamagnetic hydrogen atom (i.e., with $F = 0$) are shown in Figs. 1(a) and 1(b) when the magnetic field strength varies on the range 0.0083 a.u. $< B <$ 0.0092 a.u.. The ionization energy is shown [see Fig. 1(a)] to have a monotonically increasing (decreasing) behavior for the state $3p_0$ ($3d_0$) when B is enhanced, so that these states cross each other at critical field strength $B_c \approx 0.008\,76$ a.u.; thus, they exchange their energy positions in the spectrum. From Fig. 1(b) some observations can be made. First, the entropy of $3d_0$ is always bigger than that of $3p_0$ for all B values, which indicates that the electronic cloud is more delocalized in the former state, so not depending on their respective energies. Second, the entropies of the two states have a similar global monotonically decreasing behavior all over the entire range of B values. This is a manifestation of the confinement of the electronic cloud induced in the two states by the enhancement of the magnetic field. Less known is the fact that, since the mixture between the two states is not allowed

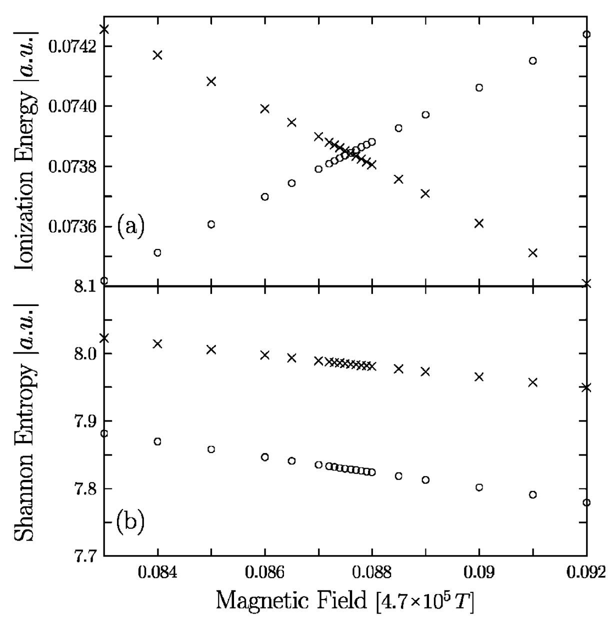

FIG. 1. The ionization energies (a) and Shannon entropies (b) of the states $3p_0$ (○) and $3d_0$ (×) of the diamagnetic hydrogen atom as a function of the magnetic field strength.

because of their different parity, the entropies are not disturbed at all by the energy crossing of the associated levels, showing a smooth behavior as the field is increased.

The presence of an additional parallel electric field with $F = 10^6$ V/m provokes that the z parity is no longer conserved, breaking the degeneracy of the two states of the pair due to the Pauli exclusion principle and making possible the appearance of irregular features called avoided crossings. This is explicitly shown in Figs. 2(a) and 2(b) for the pair $(3p_0, 3d_0)$ when the magnetic field strength varies over the range mentioned above. From Fig. 2(a) we observe that the ionization energy of the two states has the same behavior as in the case $F = 0$ previously discussed [see Fig. 1(a)] for increasing B values up to the region between 0.087 and 0.088 a.u. where both states strongly mix up and finally they repel each other, giving rise to an avoided crossing and keeping their respective energetic positions in the spectrum. The closest distance between the levels $\Delta E \approx 3.4 \times 10^{-5}$ a.u. occurs for the critical $B_c \approx 0.0876$ a.u. strength. For $B > B_c$ the energies of the two states have a smooth behavior but, contrary to what happens in the pure diamagnetic case, their spectral positions are not exchanged.

The variation of the Shannon entropy of the two states with the magnetic field strength, as shown by Fig. 2(b), allows us to gain a deeper physical insight into the dynamics of the system through the avoided crossing region. Indeed, the evolution of the entropies is drastically distorted by the presence of the avoided crossing. Both entropies behave similarly and smoothly till the system penetrates into the region where this phenomenon takes place, presenting a minimum at the critical B_c value. For magnetic fields much smaller than B_c the entropies $S_{\rho_{3d_0}}$ and $S_{\rho_{3p_0}}$ have values very close to those of the corresponding states of the diamagnetic hydrogen atom [see Fig. 1(b)], which means that the strong electric field hardly alters the shape of wave function, indicating that the electronic cloud is similarly localized in the two states. Moreover, it is observed that the entropy difference $\Delta S = S_{\rho_{3d_0}} - S_{\rho_{3p_0}}$ is positive as for the pure diamagnetic case. However, as the magnetic value approaches the critical strength B_c the entropies of both states suddenly change, so that not only their values strongly decrease reaching a minimum for $B = B_c$ but also the difference ΔS decreases, having the value 2×10^{-4} for this critical magnetic field strength. Then, for $B > B_c$ the entropies monotonically increase so that their difference enhances and its sign is negative. The latter is most remarkable because it is a clear and quantitative indication that the information-theoretic character of both states has been exchanged in going through the avoided crossing region. That is, the two states $3p_0$ and $3d_0$ practically exchange their localization properties when the magnetic field adiabatically changes its value between 0.087 and 0.088 a.u.

We have observed these results for other pairs of hydrogenic states with higher principal quantum numbers. Let us describe for completeness our analysis for the pair $(5p_0, 5d_0)$ of the diamagnetic hydrogen atom in the presence of a parallel electric field. The computations were performed when B is varied within the interval 0.0139–0.0141 a.u.. The results for the ionization energies and the Shannon entropy of these two states are shown in Figs. 3(a) and 3(b) in the absence of an electric

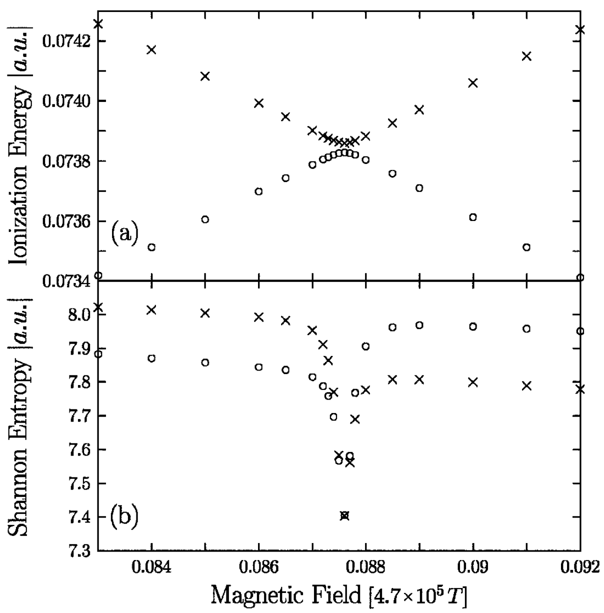

FIG. 2. The ionization energies (a) and Shannon entropies (b) of the states $3p_0$ (○) and $3d_0$ (×) of the hydrogen atom in parallel electric and magnetic fields as a function of the magnetic field strength. The electric field was fixed to $F = 10^6$ V/m.

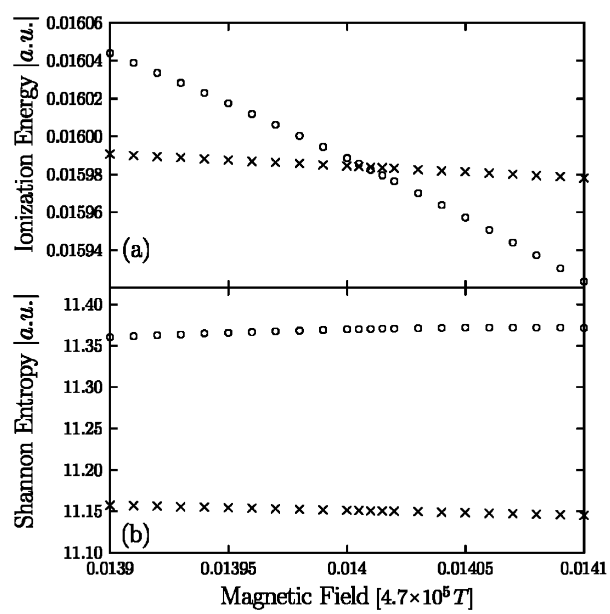

FIG. 3. The ionization energies (a) and Shannon entropies (b) of the states $5p_0$ (×) and $5d_0$ (○) of the diamagnetic hydrogen atom as a function of the magnetic field strength.

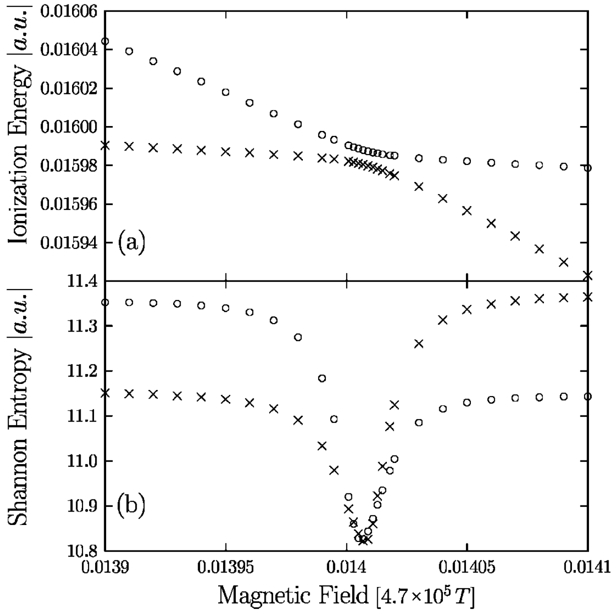

FIG. 4. The ionization energies (a) and Shannon entropies (b) of the states $5p_0$ ($\times$) and $5d_0$ ($\bigcirc$) of the hydrogen atom in parallel electric and magnetic fields as a function of the magnetic field strength. The electric field was fixed to $F = 5.1 \times 10^4$ V/m.

field, and in Figs. 4(a) and 4(b) for an electric field $F = 5.1 \times 10^4$ V/m. From Fig. 3 we observe once more that (i) the ionization energies of these two purely diamagnetic states have a smooth but opposite monotonic behavior when B is increased, so that they cross each other for the critical value $B_c \approx 1.4007 \times 10^{-2}$ a.u., and (ii) the entropies have a practically constant behavior, showing that the spread of the electronic cloud does not vary in both states all over the entire range of the values of the magnetic field. Moreover, the entropy difference $\Delta S = S_{\rho_{5d_0}} - S_{\rho_{5p_0}}$ is always positive, indicating the higher spatial delocalization of the state $5d_0$.

The presence of the electric field of strength F breaks the degeneracy in energy of the pair of states yielding an avoided crossing when the magnetic field strength $B = B_c$. This feature, which has a much narrower width than that of the previous pair, is clearly shown in (i) the ionization energy, by the apparent repulsion of levels in Fig. 4(a), and (ii) in the Shannon entropy, by the minimum which is encountered for the two states of the pair [see Fig. 4(b)]. It is found that the closest energetic distance and the entropy difference between these states are $\Delta E = 7 \times 10^{-6}$ a.u. and $\Delta S = 3.2 \times 10^{-3}$ a.u. at the critical magnetic field strength B_c.

In this work it is found that the existence of avoided crossings between states of a hydrogen atom in the presence of strong parallel magnetic and electric fields is manifest not only in the ionization energy, by means of the known repulsion of the associated energy levels, but also in Shannon's entropy, which shows (i) a sudden change for the two states at the critical value of the magnetic field strength, provoking a drastic confinement of the electronic cloud, and (ii) an informational exchange between the states, which includes the exchange of the spatial localization or information-theoretic properties of the electron in going through this chaotic region. In conclusion the role of Shannon's entropy as an indicator or predictor of irregular features of atomic spectra at the same and complementary level than the ionization energy is raised up for the first time, to our knowledge. We are aware of the fact that to set up this role on firm grounds, a more systematic study is required, including the calculation of these quantities for hydrogenic and Rydberg atoms in the presence of magnetic and electric fields of any strength and mutual orientation. Here we have analyzed only parallel fields with strong and intermediate strengths which are characteristic of astronomical compact objects (white dwarfs and neutron stars).

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