Eur. Phys. J. D **32**, 39–43 (2005)
DOI: 10.1140/epjd/e2004-00182-3

THE EUROPEAN PHYSICAL JOURNAL D

Characterization of atomic avoided crossings by means of Fisher's information

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Received 14 June 2004 / Received in final form 14 October 2004
Published online 7 December 2004 –

Abstract. Atomic avoided crossings in strong magnetic and electric fields are usually identified by the energy level repulsion and by the sharp extremal value of the Shannon's entropy of the two involved states. In this work the proposal of a new information-theoretic parameter, the continuous Fisher information, for the prediction and characterization of these nonlinear phenomena is done. For just around the irregular region it is found that Fisher's informations of the two states cross over and show that the states exchange their informational character. Moreover, the state Fisher information sum keeps constant through the avoided crossing. This is illustrated for some hydrogenic excited states in strong magnetic fields as well as in parallel magnetic and electric fields.

PACS. 32.30.-r Atomic Spectra – 32.60.+i Zeeman and Stark effects – 89.70.+c Information theory and communication theory

1 Introduction

The avoided crossing phenomena have been analyzed in both collision and spectroscopic contexts since the early days of quantum mechanics [1] up until now [2,3]. The main reason that they are so important and so frequently studied is in their applicability: they provide an efficient tool to estimate in a physically transparent manner the atomic transitions caused by a slowly varying perturbation. Moreover the avoided crossing phenomena is a mechanism for the state energy reordering, what it is manifest by the energy level repulsion [1]: neighbouring energy levels with the same symmetry do not cross each other, but rather come close and they repel in an avoided crossing.

Recently the authors [4,5] have begun to explore an alternative picture of the avoided crossing phenomena based on the use of information-theoretic measures of the probability densities of the involved states. They have shown that the Shannon's information entropy [6] manifest that the state informational exchanging appearing in the avoided crossing phenomenon is indeed a mechanism. This is illustrated by the sharp extremal value of the Shannon entropy just around this irregular region, as well as by the entropy exchange between the involved states in going through the avoided crossing.

Here we pursue this emerging information theory approach with the proposal of a new parameter for the characterization of the avoided crossing phenomena, the continuous Fisher information [7], which measures the spatial distribution of the quantum-mechanical probability cloud of a state in a qualitatively different but complementary manner as Shannon's entropy. Both quantities characterize the information-theoretic content of the probability density $\rho(\mathbf{r})$ describing a given physical state. Moreover, both are able to measure the disorder of the system at that state, i.e. the degree of smoothness of the probability density. However the analytical properties of the two information quantities are quite different. The Shannon entropy is a logarithmic functional of the density, so that it is a global measure of disorder [8]. The Fisher information is a gradient functional of the density (see Eq. (1) below), so it has a property of locality because it is sensitive to local rearrangements of $\mathbf{r}$. See [9–11] for further discussions about the relative comparison between these two information measures.

The hydrogen atom in external fields, shown to have a spectrum with an intricate array of narrow avoided crossings [2,3], is a good laboratory system to illustrate the Fisher characterization. We analyze some avoided crossings between high-lying excited states of the hydrogen atom in the presence of a strong magnetic field, and in the presence of parallel electric and magnetic fields from both dynamics and information theory standpoints. This is done by studying in detail the ionization energy and Fisher's information of the involved states when the

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external magnetic field strength is varied, by means of a hybrid non-perturbative computational approach [12].

The concentration of the probability density distribution of an electronic excited state, $\rho(\mathbf{r}) = |\psi(\mathbf{r})|^2$, is most appropriately described by the Fisher information [7], given by

$$I_\rho = \int [\nabla\rho(\mathbf{r})]^2/\rho(\mathbf{r})d\mathbf{r} = 4\int [\nabla\rho^{1/2}(\mathbf{r})]^2 d\mathbf{r}. \qquad (1)$$

This quantity is an information-theoretic measure of the spatial concentration of the electronic cloud. The higher this quantity is, the more localized is the state wavefunction $\psi(\mathbf{r})$, the smaller the uncertainty and the higher the accuracy is in predicting the localization of the electron [7,13]. On the other hand, the Fisher information is closely connected with other density functionals which characterize various macroscopic properties [14,15], and it has been used for the description of numerous physical phenomena [10,11,16].

Here we show that the Fisher information of the states involved in an avoided crossing quantitatively measures the informational character exchange which takes place in this phenomenon, although differently as Shannon's entropy does [4,5]. One should keep in mind that Shannon's entropy and Fisher's information measure the "spreading" and the "concentration", respectively, of the electronic cloud. This is because the Shannon logarithmic functional best takes into account the tails of the probability distribution [8], while the Fisher gradient functional is more sensitive to local variations of the position of the electron. Moreover, we find that the sum of the Fisher informations of the two states keeps approximately constant through this irregular region.

This work is organized as follows. Firstly we describe the non-relativistic Hamiltonian of the system and briefly indicate the computational approach used. Then, we use this approach to obtain and describe the ionization energies, the wavefunctions and the Fisher informations of the excited states with azimuthal quantum number $m = 0$ involved in some avoided crossings when the magnetic field strength is varied. Finally, some concluding remarks and various open problems are pointed out.

2 Hamiltonian and computational method

The motion of the hydrogen atom in the presence of uniform magnetic $\mathbf{B}$ and electric $\mathbf{F}$ fields, both directed along the z-axis, is governed by the non-relativistic Hamiltonian

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

where atomic units have been used, 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 $F_0 = \alpha^3 m_e^2 c^3/e\hbar \approx 5.142 \times 10^{11}$ 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 [17] for magnetic fields below 1000 a.u., and the spin-orbit coupling is small for excited states with $n > 0.126B^{-1/3}$ [18]. Besides, we assume that the nucleus has infinite mass. For vanishing electric field (i.e. $F = 0$), the spherical symmetry of the hydrogen atom is broken by the contribution of the strong magnetic field. The states can only be described by means of the magnetic quantum number m and the z-parity. An additional parallel electric field breaks the symmetry with respect to reflection on the xy-plane, and hence the z-parity is no longer conserved. Thus, only the magnetic quantum number remains as a rigorous quantum number. Solely $m = 0$ states are considered. Moreover, to simplify the discussion the principal and orbital quantum numbers n and l of the field-free states are frequently used to refer to the states in the field, although they are not any longer good quantum numbers.

To solve this fully non-integrable two-dimensional problem a non-perturbative technique is necessarily required [2,3,12,19]. We have used a hybrid computational approach [12] 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. For a detailed description of the computational algorithm and its extension to the three-dimensional case, we refer to [12]. Let us also mention that the radial and angular integrals involved in the Fisher information (1) are computed by means of a Gauss-Legendre quadrature in the corresponding variables.

3 Results and discussion

To begin with we consider the avoided crossing appearing for the pair of states $(3p_0, 3d_0)$ of the hydrogen atom in parallel electric $\mathbf{F}$ and magnetic $\mathbf{B}$ fields when the magnetic field strength varies on the range 0.0087 a.u. $< B <$ 0.00882 a.u., and for fixed $F = 10^6$ V/m. The ionization energy and Fisher's information of these two states are given in Figures 1a and 1b, respectively, as a function of the magnetic field strength. For completeness, the Fisher information $I_{\rho_{3p_0}}(0)$ and $I_{\rho_{3d_0}}(0)$ for the diamagnetic case, i.e. when $F = 0$, are also included in Figure 1b, and the corresponding ionization energies were given in reference [5].

In the adiabatic limit of vanishing fields $3d_0$ is a quasi-circular state ($3d_2$ would be circular) and those states are stronger localised than the non-circular ones. Therefore in the adiabatic limit the corresponding Fisher entropy should be higher, which explains the different values from the very beginning. In case both states involved in an avoiding crossing would have very similar Fisher entropies in the adiabatic field-free limit it would be much harder to see any significant behaviour whence the states run through its avoided crossing.

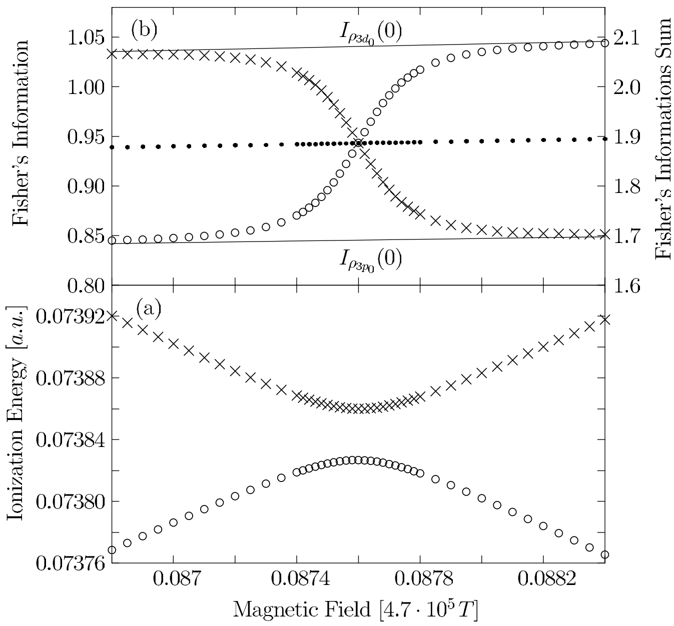

Fig. 1. The ionization energy (a), and Fisher's information (b), of the states $3p_0(\circ)$ and $3d_0$ $(\times)$ of the hydrogen atom in parallel electric and magnetic fields in terms of the magnetic field strength and $F = 10^6$ V/m. The sum of the Fisher informations is included in Figure 2b (•). Besides, the Fisher informations for the pure diamagnetic states (full lines) are also drawn in (b).

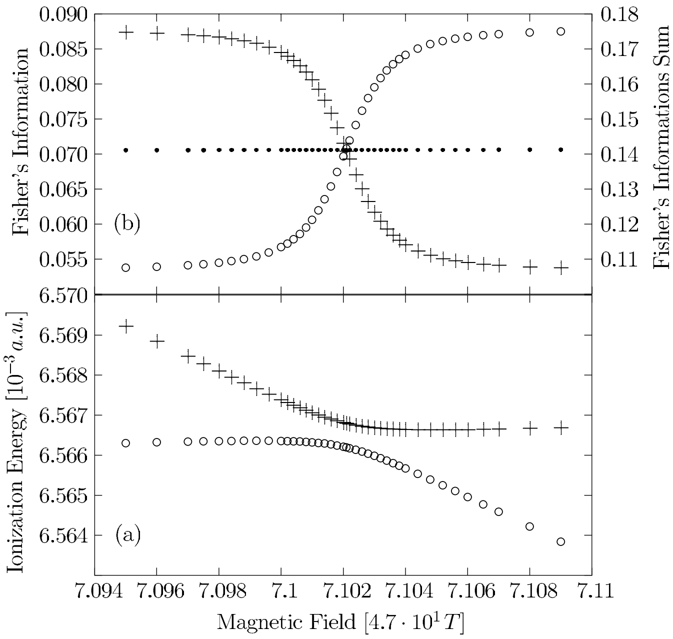

Fig. 2. First avoided crossing between states with $m = 0$ and positive z-parity evolving from field-free states with principal quantum numbers $n = 8$ (+) and $n = 9$ (∘). Figures (a) and (b) show the ionization energies and the Fisher information and their sum (•), respectively, in terms of the magnetic field strength.

From Figure 1a we notice that the presence of the electric field breaks the degeneracy of the states giving rise to an avoided crossing when the magnetic field strength $B \sim B_c \approx 0.00876$ a.u. In this region, both states strongly mix up and finally repel each other, keeping their relative spectral positions unaltered. The closest distance between the levels $\Delta E \approx 3.4 \times 10^{-5}$ a.u. occurs for the critical strength B_c.

Let us first discuss the Fisher information I_ρ in the absence of the electric field. This quantity for $3d_0$ is always bigger than that for $3p_0$ for all B values, what indicates that the electronic cloud is more localized in the former state, having both information quantities a monotonically increasing behavior as the magnetic field is increased. This is the confinement or concentration effect of the magnetic field on the electronic cloud.

An additional electric field drastically modifies the evolution of the Fisher information in going through the avoided crossing. For magnetic fields much smaller or larger than B_c the quantities $I_{\rho_{3d_0}}$ and $I_{\rho_{3p_0}}$ have values very close to those of the corresponding states of the diamagnetic hydrogen atom. As the magnetic field strength gets closer to B_c, $I_{\rho_{3d_0}}$ ($I_{\rho_{3p_0}}$) monotonically decreases (increases), keeping this behaviour all over the irregular region.

Moreover, the information difference $\Delta I = I_{\rho_{3d_0}} - I_{\rho_{3p_0}}$, which is always positive for the pure diamagnetic case, changes its sign in the avoided crossing region. Indeed, it is positive for $B < B_c$, and negative when $B > B_c$, having its smallest value $\Delta I \approx 10^{-4}$ for the critical strength $B_c \approx 0.0876$ a.u. 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 $3d_0$ have practically exchanged their localization properties when the magnetic field adiabatically changes its value between 0.087 a.u. and 0.088 a.u. Indeed, the state of the pair initially (i.e. for $B < B_c$) more localized becomes more spread for $B > B_c$. As the Shannon entropy [4,5], the Fisher information provides a quantitative manifestation of the information-theoretic character exchange taking place between the two states involved in the avoided crossing region.

As a second example we have investigated the narrow avoided crossing between the two energetically adjacent states evolving from field-free states with principal quantum numbers $n = 8$ and $n = 9$, with $m = 0$ and positive z-parity, when the field strength is varied on the range 7.094×10^{-4} a.u. $< B < 7.11 \times 10^{-4}$ a.u. The ionization energies are shown in Figure 2a, where we observe how the irregular phenomenon appears. The neighbouring states monotonically approach each other when B is enhanced up to a critical value B_c (in this case $B_c \approx 7.1021 \times 10^{-4}$ a.u.), then being very close one to another ($\Delta E \approx 6.1 \times 10^{-7}$ a.u.); however, they can not cross over because both have the same symmetry and the von Neumann-Wigner non-crossing rule [1] operates, and they repel each other yielding an avoided crossing, so that for $B > B_c$ the states monotonically separate out more and more.

More interesting is the evolution of the Fisher information with the external field illustrated in Figure 2b. The information of the two involved states have the opposite behaviour within the range of variation of the field strength, $I_{\rho_{n=8}}$ decreases monotonically as the field increases, whereas $I_{\rho_{n=8}}$ increases monotonically. Again, the information difference $\Delta I = I_{\rho_{n=8}} - I_{\rho_{n=9}}$, changes its sign in this irregular region, being positive for $B < B_c$ and negative for $B > B_c$. The closest value between both information-theoretic quantities is reached at B_c with $\Delta I \approx 3 \times 10^{-4}$. We observe that the informational character of the two involved states has been adiabatically exchanged because the corresponding wavefunctions strongly mix up in that region.

Furthermore, we have numerically observed that the sum of Fisher's informations of the two states involved in an avoided crossing keeps constant through this irregular region. Taken on the scaling of the right vertical axis for the sum of the Fisher informations, this result is shown in a dotted form in Figures 1b and 2b, where $I_{\rho_{3d_0}} + I_{\rho_{3p_0}}$ and $I_{\rho_{n=8}} + I_{\rho_{n=9}}$ are respectively included, illustrating that the total amount of information and localization of the two states keeps constant in this irregular region.

4 Concluding remarks and open problems

It is well-known that pairs of states interchange their character as they go through an avoided crossing. This was firstly discovered by von Neumann and Wigner already in 1929 in studying the dynamics of this phenomenon, proving the repulsion of the associated energy levels. Later on, numerous authors have rediscovered this repulsion feature and shown its applicability in collision theory and in atomic and molecular spectroscopy [2,3]. Recently, we have begun to analyze the avoided crossings by means of some elements of the information theory, showing that the Shannon entropy (see Refs. [4,5]) is a very appropriate tool for the prediction and characterization of the avoided crossings.

In this work we have found that Fisher's information manifests the information-theoretic character exchange between the two states involved in an avoided crossing. Both states keep their relative spectral positions but they do exchange their respective spatial localization or informational properties across the avoided crossing region. The state with higher (smaller) values of ionization energy and Fisher's information gets more (less) localized in going through that region. Furthermore, we have observed that the total information, i.e. the sum of the Fisher informations of both states stays constant through the avoided crossing region.

We are aware of the fact that our results are only based on the analysis of some hydrogenic avoided crossings in external magnetic fields, as well as parallel electric and magnetic fields, with strengths typical of some astrophysical objects and semiconductors [2,3]. To show that Fisher's characterization of the phenomenology of avoided crossings is more widely applicable, a more systematic study is required for other atoms (e.g. Rydberg) and molecules in the presence of external fields with arbitrary strength and mutual orientation, but this is beyond the scope of this project.

In summary we have shown that the Fisher information is a new information-theoretic parameter which may be used for the prediction and characterization of avoided-crossing phenomena at the same level as Shannon's entropy. Although for the system here considered (hydrogen in strong magnetic and electric fields) the physics manifested by the Fisher parameter is similar to that of Shannon indicator because of the so well-behaved character of the corresponding wavefunction, this is not always so. Indeed, sometimes the use of Shannon's entropy is not adequate for quantum problems [20]. It has been argued that this is related to the fact that there is no principle of entropy conservation [21] while certainly there is a principle of extremum physical information (a principle of minimum Fisher information) which has recently led to the fundamental equations of the non-relativistic quantum mechanics [10,11].

Finally the information theory approach which seems to emerge from these works needs a further investigation for obtaining the topology of the avoided crossings and their application to the transitions dynamics. In this sense let us point out a few observations. The diabatic states do not follow the von-Neumann-Wigner rule according to which the eigenstates of the adiabatic Hamiltonian having the same symmetry do not cross; that is, they usually cross there where the adiabatic states have avoided crossings and preserve their character through a crossing, still describing the same transitions physics. This behaviour is similar to that of Fisher's information measure shown in this work. Thus, a clear and exciting problem naturally appears: to study the diabatic physics by means of information-theoretic ideas and techniques. We feel that this connection is even more natural and direct than in the adiabatic case.

This work was supported by the Alexander von Humboldt Foundation (R.G.F.), the MCYT project BFM2001-3878-C02-01 as well as the NATO collaborative grant PST.CLG.979738. The authors belong to the JA group FQM-207.

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