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The hydrogen atom in electric and magnetic fields : Pauli's 1926 article

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Abstract

The results obtained by Pauli in his 1926 article on the hydrogen atom made essential use of the quantum dynamical $so(4)$ symmetry of the bound states. Pauli used this symmetry to compute the perturbed energy levels of an hydrogen atom in a uniform electric field (Stark effect) and in uniform electric and magnetic fields. Although the Stark effect on hydrogen has been studied experimentally, Pauli's results in mixed fields have been studied only for Rydberg states of rubidium atoms in crossed fields and for lithium atoms in parallel fields.

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1 Introduction

In 1926 there appeared nearly simultaneously two articles by Schrödinger [1] and Pauli [2] that solved one and the same central problem of the newly discovered quantum mechanics: the computation of the hydrogen atom spectrum. In most textbooks on quantum mechanics the eigenvalue problem is solved using Schrödinger's approach with spherical coordinates and simultaneously diagonalizing the set of operators H_0, $\vec{L}^{\,2}$, L_z. The main benefit of this approach is that one can deal, in principle, with any central potential and that the eigenstates have definite parity, which is of practical importance in the study of the selection rules for radiative transitions. However, a simple problem like the Stark effect, is quite cumbersome to deal with perturbatively, except for the low lying states.

An essential aspect of the Coulomb problem is that the Schrödinger equation is also separable in parabolic coordinates [4]. This super-separability is related to the conservation of an additional vector $\vec{m}$, the so-called Runge-Lenz (RL) vector, which is specific to the Coulomb potential. Despite its name, the discovery of this conserved vector in Newtonian mechanics goes back to Hermann in the 18th century, as noted by Goldstein [5], who mentions also early works by Laplace and Hamilton.

Pauli succeeded in defining a quantum extension $\vec{M}$ of the RL vector which is an observable, that is, an hermitian operator, and commutes with the Hamiltonian H_0. This success enabled him to calculate the spectrum of the hydrogen atom by an abstract approach. The quantum extension of the RL vector was used to obtain the dynamical $so(4)$ symmetry of the bound states. This symmetry, combined with the general theory of angular momentum allows to express the energies of the hydrogen atom [6].

The main drawbacks of Pauli's approach are that it works only for a Coulomb potential and that the eigenstates have, in general, no definite parity. However, in the same article, Pauli gave two non-trivial applications of his ideas: the first order perturbation of the energy levels under a uniform electric field (Stark effect) and in the more complicated case of uniform electric and magnetic fields. Guided by an analogous relation from classical mechanics, Pauli guessed the following crucial relation between quantum expectation values :

$$\langle\, 2H_0\, \vec{R}\rangle = \frac{3}{2}\,\langle \vec{M}\rangle, \tag{1}$$

where $\vec{R}$ is the position operator and the expectation value should be taken in any eigenstate of the Hamiltonian H_0. It is natural to call Eq. (1) Pauli's identity and we will later discuss its origin.

Textbooks that discuss more advanced topics related to the quantum RL vector (see Refs. [7]-[9]), do not treat these interesting applications. The main aim of this note is to popularize Pauli's results. In Sec. II we introduce the quantum RL vector and use it to derive the spectrum of the hydrogen atom [10]. In Sec. III we present a new derivation of the crucial identity

$$2H_0\,\vec{R} = \frac{3}{2}\,\vec{M} + \frac{1}{i\hbar}\,[H_0, \vec{T}], \tag{2}$$

which implies Eq. (1). It is interesting to note that Eq. (2) was first derived by a clever calculation of commutators by Becker and Bleuler [11] fifty years after Pauli's article. Our derivation will make apparent that it is the natural quantum extension of a classical relation. In Sec. IV we consider the hydrogen atom in the presence of uniform electric and magnetic fields. We then use Pauli's elegant approach to obtain the first-order perturbed levels. We conclude with a short account of the experimental checks, some of which are quite recent.

2 Background material

To set our notation (we stick closely to those of [7]), let us recall the basic properties of the quantum RL vector. As far as possible, we will use upper case letters for quantum operators. We will write the hamiltonian of the hydrogen atom

$$H_0 = \frac{\vec{P}^2}{2\mu} - \frac{\kappa}{R}, \qquad \kappa = \frac{q^2}{4\pi\epsilon_0}, \tag{3}$$

where μ is the reduced mass, q is the proton charge and $\kappa = q^2/4\pi\epsilon_0$. Although going from the classical angular momentum $\vec{l} = \vec{r} \wedge \vec{p}$ to the operator $\vec{L} = \vec{R} \wedge \vec{P}$ is not ambiguous and leads to an hermitian operator $\vec{L}$, the situation is somewhat more complicated for the RL vector. Classically its definition

$$\vec{m} = \frac{1}{\mu}\,\vec{p} \wedge \vec{l} - \kappa\,\frac{\vec{r}}{r} \tag{4}$$

shows that there are quantization ambiguities due to the lack of commutativity of the operators $\vec{P}$ and $\vec{L}$. There are two possible (but non-hermitian) corresponding operators, $\vec{P} \wedge \vec{L}$ and $(\vec{P} \wedge \vec{L})^\dagger = -\vec{L} \wedge \vec{P}$. Pauli observed that the simplest choice for $\vec{M}$ so that it is hermitian is

$$\vec{M} = \frac{1}{2\mu}(\vec{P} \wedge \vec{L} - \vec{L} \wedge \vec{P}) - \kappa\,\frac{\vec{R}}{R}. \tag{5}$$

From these definitions we can check that both $\vec{L}$ and $\vec{M}$ are conserved at the quantum level, that is, that they commute with H_0.

The classical Poisson brackets involving $\vec{l}$ and $\vec{m}$ generalize to commutators of $\vec{L}$ and $\vec{M}$:

$$\begin{aligned} [L_i, L_j] &= i\hbar\,\epsilon_{ijk}\,L_k, \\ [L_i, M_j] &= i\hbar\,\epsilon_{ijk}\,M_k, \\ [M_i, M_j] &= \left(\frac{-2H_0}{\mu}\right) \cdot i\hbar\,\epsilon_{ijk}\,L_k, \end{aligned} \tag{6}$$

Two further important relations should be noted:

$$\begin{aligned} \vec{L} \cdot \vec{M} &= \vec{M} \cdot \vec{L} = 0, \\ \vec{M}^{\,2} &= \left(\frac{2H_0}{\mu}\right)(\vec{L}^{\,2} + \hbar^2) + \kappa^2. \end{aligned} \tag{7}$$

The checks of the conservation of the RL vector and of Eqs. (6) and (7) are quite involved: a detailed calculation may be found in Ref. [8] (p. 462) and in Ref. [9] (p. 265).

Let us restrict ourselves to the subspace of the Hilbert space spanned by the bound states $|\psi\rangle$ with energy $E < 0$. H_0^{-1} and $(-H_0)^{-1/2}$ can be defined by

$$H_0^{-1}\,|\psi\rangle = E^{-1}\,|\psi\rangle, \qquad (-H_0)^{-1/2}\,|\psi\rangle = (-E)^{-1/2}\,|\psi\rangle.$$

We also define

$$\vec{M}\,' = \left(-\frac{\mu}{2H_0}\right)^{1/2} \vec{M}. \tag{8}$$

Because $\vec{L}$ and $\vec{M}$ commute with H_0, the algebra in Eq. (6) becomes

$$\begin{aligned}
[L_i, L_j] &= i\hbar\,\epsilon_{ijk}\,L_k, \\
[L_i, M'_j] &= i\hbar\,\epsilon_{ijk}\,M'_k, \\
[M'_i, M'_j] &= i\hbar\,\epsilon_{ijk}\,L_k,
\end{aligned} \tag{9}$$

which we recognize as an $so(4)$ algebra with generators $\vec{L}$, $\vec{M}'$. For further use we define the generators

$$\begin{aligned}
\vec{I} &= \tfrac{1}{2}(\vec{L} + \vec{M}\,'), \\
\vec{K} &= \tfrac{1}{2}(\vec{L} - \vec{M}\,').
\end{aligned} \tag{10}$$

Their commutation rules are quite instructive :

$$\begin{aligned}
[I_i, I_j] &= i\hbar\,\epsilon_{ijk}\,I_k, \\
[K_i, K_j] &= i\hbar\,\epsilon_{ijk}\,K_k, \\
[I_i, K_j] &= 0,
\end{aligned} \tag{11}$$

because they show that the operators $\vec{I}$ generate an $so(3)_I$ Lie algebra, while the operators $\vec{K}$ generate an $so(3)_K$ Lie algebra. Furthermore these two algebras are completely independent (commuting), and their Casimir operators (i. e. operators commuting with the whole algebra) are $\vec{I}^{\,2}$ for $so(3)_I$ and $\vec{K}^{\,2}$ for $so(3)_K$.

The correspondence given in (10) between $\vec{L}$, $\vec{M}'$ and $\vec{I}$, $\vec{K}$ gives just the change of basis that displays the isomorphism $so(4) \sim so(3)_I \oplus so(3)_K$. From the general theory of quantum angular momentum [7], we can find a basis common to the operators $\vec{I}^{\,2}$, $\vec{K}^{\,2}$, I_z, K_z such that

$$\begin{cases}
\vec{I}^{\,2}\,|i, m_i; k, m_k\rangle = i(i+1)\hbar^2\,|i, m_i; k, m_k\rangle \\
\quad I_z|i, m_i; k, m_k\rangle = m_i\,\hbar\,|i, m_i; k, m_k\rangle \\
\vec{K}^{\,2}\,|i, m_i; k, m_k\rangle = k(k+1)\hbar^2\,|i, m_i; k, m_k\rangle \\
\quad K_z|i, m_i; k, m_k\rangle = m_k\,\hbar\,|i, m_i; k, m_k\rangle,
\end{cases} \tag{12}$$

with $i, k = 0, \frac{1}{2}, 1, \ldots$ $m_i \in [-i, \ldots, +i]$, and $m_k \in [-k, \ldots, +k]$. The first relation in (7) implies that the operators $\vec{I}$ and $\vec{K}$ are constrained by

$$\begin{aligned}
\vec{L} \cdot \vec{M}\,' &= 0 \\
\vec{I}^{\,2} &= \vec{K}^{2}
\end{aligned} \tag{13}$$

while the second relation can be written as :

$$-\frac{1}{2}\mu\kappa^2 (H_0)^{-1} = 2(\vec{I}^{\,2} + \vec{K}^{\,2}) + \hbar^2, \tag{14}$$

showing that the states $|i, m_i; i, m_k\rangle$, are also hamiltonian eigenstates. At the level of the eigenvalues, the operator relation in Eq. (14) gives

$$-\frac{1}{2}\mu\kappa^2 \frac{1}{E_n^{(0)}} = 4i(i+1)\hbar^2 + \hbar^2 = (2i+1)^2\hbar^2, \tag{15}$$

so that the inverse energies are given by the eigenvalues of the Casimir operators of $so(4)$. Up to the identification of the principal quantum number $n = 2i + 1$, we obtain for the energy eigenvalues

$$E_n^{(0)} = -\frac{\mu\kappa^2}{2\hbar^2 n^2}, \tag{16}$$

where $n = 2i + 1 = 1, 2, \ldots$ The eigenstates $|i, m_i; i, m_k\rangle$ are such that $m_i \in [-i, \ldots + i]$ and $m_k \in [-i, \ldots + i]$. The degeneracy is easily seen to be $(2i + 1)^2 = n^2$.

These states are not eigenstates of $\vec{L}^{\,2}$. Indeed the relation $\vec{L} = \vec{I} + \vec{K}$ shows that l may take any value between 0 and $2i = n - 1$, in agreement with the Schrödinger approach. Note that the complete set of commuting observables diagonalized here are H_0, I_z, and K_z while in Schrödinger's approach one takes H_0, $\vec{L}^{\,2}$, and L_z. Note also that the angular momentum $\vec{L}$ is axial, while $\vec{M}$ is a true vector, so that $\vec{I}$, $\vec{K}$ have no definite parity, and hence their eigenstates cannot have any definite parity. This absence of a definite parity is also obvious from the fact that the states $|i, m_i; i, m_k\rangle$ have no definite value for the orbital angular momentum l. Let us conclude that even for parity invariant potentials the eigenstates need not be of definite parity as can be seen in the discussion of the simpler case of a particle in a box, given in Ref. [12] (p.328).

3 From classical to quantum Pauli's identity

Equation (1) has a classical content, because it involves mean values. Indeed, for any classical periodic trajectory, the mean value of a dynamical quantity $f(\vec{r})$, is defined by

$$\langle f\rangle = \frac{1}{T}\int_0^T f\,dt = \frac{\mu}{\lambda T}\int_{-\pi}^{+\pi} f\; r^2\,d\phi, \tag{17}$$

where T is the period and $\lambda = \mu r^2 d\phi/dt$ is the angular momentum. For the Coulomb case, we have

$$\begin{aligned} \frac{r_0}{r} &= 1 + e\,\cos\phi, \\ e &= \sqrt{1 + 2\frac{\mathcal{E}\lambda^2}{\mu\kappa^2}}, \\ T &= 2\pi\frac{\mu r_0^2}{\lambda(1-e^2)^{3/2}}, \end{aligned} \tag{18}$$

where $r_0 = \lambda^2/\mu\kappa$, $\mathcal{E}$ is the total energy and e the eccentricity of the orbit. We can show that the classical RL vector, lying in the trajectory plane, is directed from the origin to the perihelion, which lies on the x-axis. Its components (see Ref. [8] (p. 460) for the details) are given by

$$m_x = \kappa e, \qquad\qquad m_y = m_z = 0. \tag{19}$$

TIf we take $f = \vec{r}$, we have

$$\begin{aligned} \langle x\rangle &= \frac{\mu\, r_0^3}{\lambda T}\int_{-\pi}^{+\pi}\frac{\cos\phi}{(1+e\cos\phi)^3}\,d\phi = -\frac{3\pi\mu e r_0^3}{\lambda T(1-e^2)^{5/2}}, \\ \langle y\rangle &= \frac{\mu\, r_0^3}{\lambda T}\int_{-\pi}^{+\pi}\frac{\sin\phi}{(1+e\cos\phi)^3}\,d\phi = 0, \qquad \langle z\rangle = 0. \end{aligned} \tag{20}$$

Some algebra leads to

$$2\mathcal{E}\,\langle x\rangle = \frac{3}{2}\,\kappa e, \qquad\qquad \langle y\rangle = \langle z\rangle = 0. \tag{21}$$

If we compare Eqs. (19) and (21) and identify the total energy with the classical hamiltonian h_0, we obtain Pauli's relation in classical mechanics

$$2h_0\,\langle\vec{r}\rangle = \frac{3}{2}\,\vec{m}. \tag{22}$$

Equation (22) is an equality between mean values of classical physical quantities, because the RL vector is conserved. It follows that the difference between these two classical physical quantities must be a total derivative (whose mean-value necessarily vanishes). So we need to find some vector $\vec{\tau}$ such that

$$2h_0\,\vec{r} = \frac{3}{2}\,\vec{m} - \frac{d}{dt}\vec{\tau}. \tag{23}$$

Since on dimensional grounds the sought vector has dimension of momentum $\times$(length)^2, it must have the structure

$$\vec{\tau} = a\,(\vec{r}\cdot\vec{p})\,\vec{r} + b\,\vec{r}^{\,2}\,\vec{p}. \tag{24}$$

The coefficients a and b, fixed by enforcing relation (23), give for $\vec{\tau}$ the expression

$$\vec{\tau} = \frac{1}{2}\,(\vec{r}\cdot\vec{p})\,\vec{r} - \,\vec{r}^{\,2}\,\vec{p}, \tag{25}$$

which can be written more suggestively, using a Poisson bracket as

$$2h_0\,\vec{r} = \frac{3}{2}\,\vec{m} + \{h_0,\vec{\tau}\}, \qquad\qquad \{f,g\} = \sum_s \frac{\partial f}{\partial x_s}\,\frac{\partial g}{\partial p_s} - \frac{\partial f}{\partial p_s}\,\frac{\partial g}{\partial x_s}. \tag{26}$$

The above relations involve classical (commuting) quantities ; to generalize Eq. (26) to the quantum level, we try the following quantum extension

$$2H_0\,\vec{R} = \frac{3}{2}\,\vec{M} + \frac{1}{i\hbar}\,[H_0,\vec{T}], \tag{27}$$

where the quantities involved are now operators and $\vec{T}$ is the unknown quantum extension of the classical quantity $\vec{\tau}$. We point out that in the left hand side of Eq. (27), the position of the hamiltonian operator with respect to $\vec{R}$ is important. In this case $\vec{T}$ can be written in terms of three vector operators

$$\vec{T} = a\,\vec{R}\,(\vec{R}\cdot\vec{P}) + b\,(\vec{R}\cdot\vec{R})\,\vec{P} + i\hbar\,c\,\vec{R}. \tag{28}$$

If we require Eq. (27) to be satisfied, we obtain the result [13]

$$\vec{T} = \frac{1}{2}\,\vec{R}\,(\vec{R}\cdot\vec{P}) - (\vec{R}\cdot\vec{R})\,\vec{P} + i\hbar\,\vec{R}. \tag{29}$$

Pauli's relation (1) follows from Eq. (27) when we take its expectation value between eigenstates of H_0. We can write

$$\langle 2H_0\,\vec{R}\rangle = 2\,E_n^{(0)}\,\langle\vec{R}\rangle = \frac{3}{2}\,\langle\vec{M}\rangle. \tag{30}$$

For further use we will write Eq. (30) as

$$\vec{R} \sim \frac{3}{2}\,(2\,E_n^{(0)})^{-1}\;\vec{M}, \tag{31}$$

The symbol $\sim$ indicates that the equality holds only when expectation values between eigenstates (with energy $E_n^{(0)}$) of the unperturbed hamiltonian are calculated.

4 Electric and magnetic fields

In the approximation of an infinitely heavy nucleus, $\mu = m$ the electron mass. If we also neglect the diamagnetic terms, the perturbation due to the uniform electric field $\vec{E}$ and magnetic field $\vec{B}$ writes

$$H_1 = q\,\vec{E}\cdot\vec{R} + \frac{q}{2m}\,\vec{B}\cdot\vec{L}, \tag{32}$$

where q is the proton charge. For the first order computation we need the matrix elements $\langle i, m_i'; i, m_k'|H_1|i, m_i; i, m_k\rangle$ for states of definie energy $E_n^{(0)}$ where $i = (n-1)/2$ has some fixed value. Its first piece, using Pauli's identity, in the form given by Eq. (31), we have

$$\vec{E}\cdot\vec{R} \sim \frac{3}{2}\,(2E_n^{(0)})^{-1}\,\vec{E}\cdot\vec{M} = -(-2mE_n^{(0)})^{-1/2}\,\vec{E}\cdot\vec{M}\,' = -\frac{3}{2}\,n\,\frac{a_0}{\hbar}\,\vec{E}\cdot\vec{M}\,', \tag{33}$$

with $a_0 = \hbar^2/\mu\kappa$. It is then sufficient to use

$$\vec{M}\,' = \vec{I} - \vec{K}, \qquad\qquad \vec{L} = \vec{I} + \vec{K}, \tag{34}$$

to obtain

$$H_1 \sim \left(-\frac{3}{2}\,n\,\vec{\mathcal{E}} + \vec{\mathcal{B}}\right)\cdot\frac{\vec{I}}{\hbar} + \left(\frac{3}{2}\,n\,\vec{\mathcal{E}} + \vec{\mathcal{B}}\right)\cdot\frac{\vec{K}}{\hbar}, \tag{35}$$

with $\vec{\mathcal{E}} = qa_0\,\vec{E}, \vec{\mathcal{B}} = \mu_B\,\vec{B}$, and $\mu_B = q\hbar/2m$. Notice that dimensional analysis shows that $\vec{\mathcal{E}}$ and $\vec{\mathcal{B}}$ have the same dimensions as energy.

Let us now define

$$\vec{\nu}_\pm = \frac{\pm\frac{3}{2}\,n\,\vec{\mathcal{E}} + \vec{\mathcal{B}}}{\left|\left|\pm\frac{3}{2}\,n\,\vec{\mathcal{E}} + \vec{\mathcal{B}}\right|\right|}, \qquad E_\pm = \left|\left|\pm\frac{3}{2}\,n\,\vec{\mathcal{E}} + \vec{\mathcal{B}}\right|\right| = \sqrt{\frac{9}{4}\,n^2\;\vec{\mathcal{E}}^{\,2} \pm 3\,n\,\vec{\mathcal{E}}\cdot\vec{\mathcal{B}} + \vec{\mathcal{B}}^{\,2}}, \tag{36}$$

so that the perturbation can be written as

$$H_1 \sim \frac{E_-}{\hbar}\,(\vec{\nu}_-\cdot\vec{I}) + \frac{E_+}{\hbar}\,(\vec{\nu}_+\cdot\vec{K}). \tag{37}$$

This perturbation is made up of two completely independent (commuting) pieces which can be diagonalized separately. Indeed, one can check the relation [14]

$$\vec{\nu}\cdot\vec{I} = e^{\frac{i}{\hbar}\theta\vec{\mu}\cdot\vec{I}}\,I_z\,e^{-\frac{i}{\hbar}\theta\vec{\mu}\cdot\vec{I}}, \tag{38}$$

with

$$\vec{\nu} = \sin\theta(\cos\phi\,\vec{\imath} + \sin\phi\,\vec{\jmath}) + \cos\theta\,\vec{k}, \qquad\qquad \vec{\mu} \equiv \frac{\vec{\nu}\wedge\vec{k}}{||\vec{\nu}\wedge\vec{k}||} = \sin\phi\,\vec{\imath} - \cos\phi\,\vec{\jmath},$$

which states that a rotation of angle θ around the axis $\vec{\mu}$ transforms the vector $\vec{\nu}$ into the unit vector $\vec{k}$ along the z axis. It can be checked using the well-known identity

$$e^{iA}\,B\,e^{-iA} = B + i\,[A,B] + \frac{i^2}{2!}\,[A,[A,B]] + \cdots$$

and the $so(3)_I$ algebra for the generators $\vec{I}$. It follows that the operator $\vec{\nu}\cdot\vec{I}$ has the same eigenvalues as I_z, i.e. $m_i\hbar$. Similar results are also valid for $\vec{K}$. If we adapt this result to the perturbation given by Eq. (37) we can write

$$\begin{cases} \vec{\nu}_-\cdot\vec{I} = e^{\frac{i}{\hbar}\theta_-\vec{\mu}_-\cdot\vec{I}}\, I_z\, e^{-\frac{i}{\hbar}\theta_-\vec{\mu}_-\cdot\vec{I}}, & \cos\theta_- = \vec{\nu}_-\cdot\vec{k}, \qquad \vec{\mu}_- = \dfrac{\vec{\nu}_-\wedge\vec{k}}{||\vec{\nu}_-\wedge\vec{k}||}, \\ \vec{\nu}_+\cdot\vec{K} = e^{\frac{i}{\hbar}\theta_+\vec{\mu}_+\cdot\vec{K}}\, K_z\, e^{-\frac{i}{\hbar}\theta_+\vec{\mu}_+\cdot\vec{K}}, & \cos\theta_+ = \vec{\nu}_+\cdot\vec{k}, \qquad \vec{\mu}_+ = \dfrac{\vec{\nu}_+\wedge\vec{k}}{||\vec{\nu}_+\wedge\vec{k}||}, \end{cases} \tag{39}$$

and we obtain the first order correction to the energies

$$\Delta\, E_n^{(1)} = m_i\cdot E_- + m_k\cdot E_+. \tag{40}$$

Recall that the quantum numbers m_i and m_k take all integer or half-integer values between $-(n-1)/2$ and $+(n-1)/2$.

4.1 The first order Stark effect

For vanishing magnetic field, we can take the electric field along the z axis. From Eq. (35) we obtain the first order perturbed energies

$$\Delta\, E_n^{(1)} = -\frac{3}{2}\, qa_0\, |\vec{E}|\, n(m_i - m_k). \tag{41}$$

The levels are split into $2n-1$ sub-levels, each with residual degeneracy $n-|m|$. Eq. (41) is the celebrated first-order Stark effect formula, which was obtained in 1926 simultaneously by Waller [15], Wentzel [16], and Epstein [17] by perturbation calculations in parabolic coordinates. A more handy reference is Ref. [4], where perturbative results up to second order. The reader is urged to compare these extensive calculations (even in first order) with the elegance of Pauli's.

The experimental results from Ref. [18] are given in figure 1 for the hydrogen atom. The low lying states exhibit a nearly linear field dependence up to a value of 10^{-5} au (atomic unit), but this value decreases with increasing n. This linear regime accounts also for some crossings of the energy levels corresponding to different values of n. The second order corrections are also sizeable in this region for some levels. For higher field values the situation is much more complicated since the states are broadened by tunnelling effects or even ionized, and cannot be accounted for by perturbation computations around the bound states! This complicated region lies to the right of the solid curve.

4.2 First order Zeeman effect

For vanishing electric field, we can take the magnetic field along the z axis and we are back to the Zeeman energies

$$\Delta E_n^{(1)} = \mu_B\, |\vec{B}|\, m, \tag{42}$$

where $m = m_i + m_k$. As for the Stark effect the energy levels are split up into $2n-1$ levels, each with residual degeneracy $n-|m|$.

4.3 Parallel versus crossed fields

Pauli's result simplifies for the special case of crossed electric and magnetic fields, i. e. such that $\vec{E} \cdot \vec{B} = 0$. The perturbed energies become

$$\Delta E_n^{(1)} = E_\perp \cdot m, \quad \text{with} \quad E_\perp = \sqrt{\frac{9}{4} n^2 \, (q a_0 \, \vec{E})^2 + (\mu_B \, \vec{B})^{\, 2}}. \tag{43}$$

In some sense the system is still in a Zeeman-like regime, with the same splitting pattern, but with a more complicated mixed field dependence appearing in the factor $E_\perp$. Equation (43) has been checked for Rydberg states of rubidium atoms (large principal quantum number $n = 34$), which are essentially hydrogen-like [19]. The experimental results, taken from Ref. [19], are reproduced in Fig. 2. The different lines correspond to different values of m. Note how small the window is for the electric field (between 0 and 20 V/cm) and for the magnetic field (between 0 and 6 10^{-2} T) to observe Pauli's quantization, but the results are in good agreement with (43) for weak fields.

An experiment dealing with parallel electric and magnetic fields has been described in Ref. [20] for lithium atoms. These results are quite interesting, since the symmetry breaking is completely different from the crossed case, with no left over degeneracy. A quite large set of references to theoretical as well as experimental work may be found in [21].

The second order perturbative computation was done quite recently [22],[23]. The most interesting aspects cover now the non-perturbative transition to chaos ($B \gtrsim 10T$) which is quite harder to deal with. The interested reader should consult Ref. [23].

Acknowledgments : We discovered Pauli's quantization in the very nice problem given in [24] (p. 57). For the hydrogen atom, the perturbative computation is worked out for the states with $n = 2$ in polar coordinates. We are happy to thank A. Laverne and J. Letessier for kind help in dealing with the figures, O. Betbeder for a critical reading of the manuscript, D. Delande for the recent references on the subject and the Referees for useful suggestions.

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FIGURE CAPTIONS :

Figure 1: Stark effect for the hydrogen atom. An atomic unit (au) corresponds to an electric field of $5,14\ 10^9$ v/cm. From Ref. [18]

Figure 2: Rydberg states of rubidium atoms in crossed electric and magnetic fields. The electric field unit is 1 V/cm and the magnetic field unit 10^{-2} T. From Ref. [19]

Figure 1

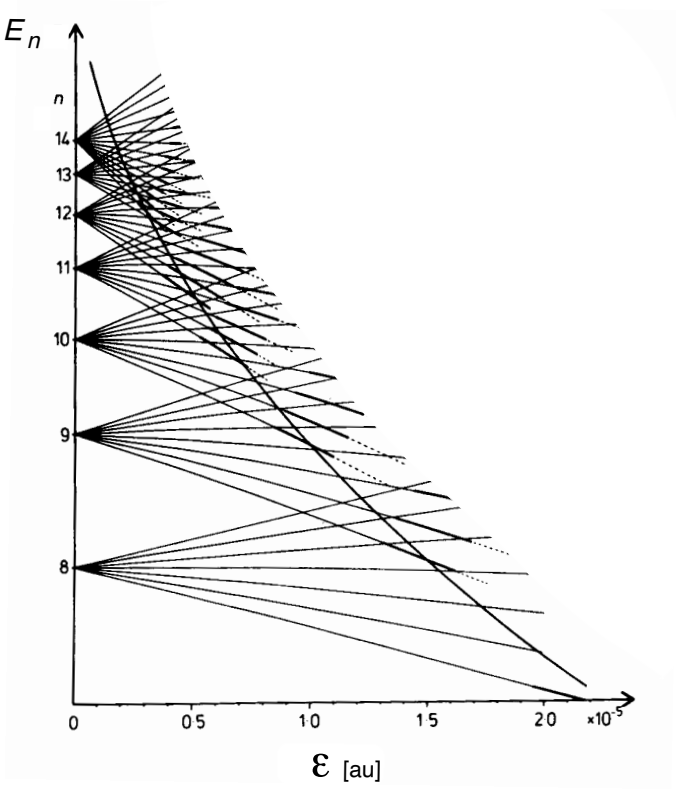

Figure 2