

LETTER TO THE EDITOR

The hydrogen atom in a magnetic field. Spectrum from the Coulomb dynamical group approach

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Abstract. We present some sample results for the problem of the hydrogen atom in a magnetic field. The energies have been computed for a typical Rydberg situation of atomic physics interest using limited computer facilities. The use of the Coulomb dynamical group allows a complete description of the symmetries and a rational choice of a Sturmian type basis set. Moreover, comparison with Rayleigh-Schrödinger perturbative expansions of the energies is performed.

During the last few years, the behaviour of atoms in strong magnetic fields has been the subject of experimental and theoretical investigation (for a review, see Gay 1985).

Up to now, accurate theoretical predictions have been available only for the lowest excited states of hydrogen, while experiments have been done on the Rydberg states of atoms. Except for the work of Clark and Taylor (1980, 1982) using a large Sturmian basis (and a Cray-I computer), no accurate numerical values exist for the Rydberg states of hydrogen.

The purpose of this letter is to illustrate how the use of group theory affords a complete analysis of the symmetry properties extending previous low-field considerations (Herrick 1982) and leads to a rational choice of basis for computation (saving both CPU time and memory). This is exemplified by numerical predictions of the spectrum in the Rydberg region.

We first recall the group properties of the hydrogen atom. The symmetry properties are then used to define a proper basis set with convenient symmetry. This allows us to deduce Rayleigh-Schrödinger perturbative (RSPT) expansions of the energy. Finally, we compare numerical predictions and experimental results.

The symmetry group of the non-relativistic hydrogen atom is known to be SO(4). It has been used in the magnetic problem by Herrick (1982) and allows a classification of the spectrum in the low-field limit. We generalise this approach using the non-invariance group SO(4, 2) of the Coulomb problem which by construction accounts for the whole structure of the problem whatever the energy (Englefield 1971).

The method has been introduced in a previous paper (Delande and Gay 1984). Here we just recall some of its basic features[‡].

As L_z is a constant of the motion in the magnetic problem, we use the SO(2, 2) non-invariance subgroup of SO(4, 2).

We define the semi-parabolic coordinates

$$\mu = (r+z)^{1/2} \quad \nu = (r-z)^{1/2} \quad (1)$$

[†] Associated with CNRS, UA18.

[‡] In the paper of Delande and Gay (1984), a different definition of the coordinates μ and ν is used, but the generators of the group are essentially the same.

and the set of operators depending on the parameter α

$$S_z^{(\alpha)} = \frac{1}{4} \left[\pm \alpha \left(\frac{\partial^2}{\partial \mu^2} + \frac{1}{\mu} \frac{\partial}{\partial \mu} - \frac{M^2}{\mu^2} \right) + \frac{1}{\alpha} \mu^2 \right]$$

$$S_y^{(\alpha)} = \frac{i}{2} \left(1 + \mu \frac{\partial}{\partial \mu} \right).$$
(2)

These operators fulfil the commutation relations of an $SO(2, 1)$ Lie algebra. Together with the $T^{(\alpha)} = (T_x^{(\alpha)}, T_y^{(\alpha)}, T_z^{(\alpha)})$ operators (which act in the same way on the ν coordinate), they are the generators of a non-invariance group $SO(2, 1) \otimes SO(2, 1) = SO(2, 2)$. With M denoting the z component of the angular momentum and E the energy, the choice $\alpha = (-2E)^{-1/2}$ is particularly convenient as the Schrödinger equation reduces to

$$[S_z^{(\alpha)} + T_z^{(\alpha)} - (-2E)^{-1/2}] \Psi(\mu, \nu) = 0. \quad (3)$$

Hence, the eigenfunctions of the hydrogen atom are just direct products of those of $S_z^{(\alpha)}$ and $T_z^{(\alpha)}$.

The eigenbasis of $S_z^{(\alpha)}$ is labelled with a non-negative integer number n_1 (n_2 for $T_z^{(\alpha)}$)

$$S_+^{(\alpha)} |n_1, M\rangle^{(\alpha)} = (n_1 + |M| + \frac{1}{2}) |n_1 + 1, M\rangle^{(\alpha)}. \quad (4)$$

In this basis, $S_{\pm}^{(\alpha)} = S_x^{(\alpha)} \pm i S_y^{(\alpha)}$ are ladder operators such that

$$S_+^{(\alpha)} |n_1, M\rangle^{(\alpha)} = [(n_1 + 1)(n_1 + |M| + 1)]^{1/2} |n_1 + 1, M\rangle^{(\alpha)}$$

$$S_-^{(\alpha)} |n_1, M\rangle^{(\alpha)} = [n_1(n_1 + |M|)]^{1/2} |n_1 - 1, M\rangle^{(\alpha)}. \quad (5)$$

Combining (3) and (4) we find

$$\Psi(\mu, \nu) = |n_1, M\rangle^{(\alpha)} \otimes |n_2, M\rangle^{(\alpha)}$$

$$(-2E)^{-1/2} = n_1 + n_2 + |M| + 1 = n \quad \text{or} \quad E = -1/2n^2.$$

n_1 and n_2 are the usual parabolic quantum numbers for the Coulomb problem.

The set of states

$$\{|n_1, M\rangle^{(\alpha)} \otimes |n_2, M\rangle^{(\alpha)} | \alpha = n_1 + n_2 + |M| + 1; n_1 = 0, 1, 2, \dots, \infty; n_2 = 0, 1, 2, \dots, \infty\}$$

coincides with the usual parabolic eigenstates for the bound Coulomb spectrum†. (Notice that α is varying with n_1 and n_2 and takes every integer value $|M| + 1, |M| + 2, \dots, \infty$.) For a fixed α value, the set $\{|n_1, M\rangle^{(\alpha)} \otimes |n_2, M\rangle^{(\alpha)}\}$ is an eigenbasis of $S_z^{(\alpha)}$ and $T_z^{(\alpha)}$ which we call 'parabolic Sturmian' basis. Other bases can be obtained by mixing the μ and ν coordinates. For instance, we can consider the coupling scheme $U = S + T$ that is

$$U_i^{(\alpha)} = S_i^{(\alpha)} + T_i^{(\alpha)} \quad i = x, y, z. \quad (6)$$

The $(U_x^{(\alpha)}, U_y^{(\alpha)}, U_z^{(\alpha)})$ set of operators generates an $SO(2, 1)$ non-invariance algebra and the U operators commute with the total angular momentum L^2 (Englefield 1971).

Thus, the eigenbasis associated with the U coupling scheme is an eigenbasis of spherical type. The family generated by varying $\alpha = |M| + 1, |M| + 2, \dots, \infty$ is the usual Coulomb spherical basis.

For fixed α values, the family of eigenfunctions of $U_z^{(\alpha)}$ generates the usual Sturmian basis which has been used by Clark and Taylor (1982) for their computations‡.

† Positive energy states are just eigenstates of $(S_x^{(\alpha)}, T_x^{(\alpha)})$ with $\alpha = (2E)^{-1/2}$.

‡ Our parameter α is connected to the ξ parameter of Clark and Taylor by $\xi = 2/\alpha$.

One can consider as well another coupling scheme:

$$\begin{aligned} V_x^{(\alpha)} &= S_x^{(\alpha)} - T_x^{(\alpha)} & V_y^{(\alpha)} &= S_y^{(\alpha)} - T_y^{(\alpha)} \\ V_z^{(\alpha)} &= S_z^{(\alpha)} + T_z^{(\alpha)}. \end{aligned} \quad (7)$$

($V_x^{(\alpha)}$, $V_y^{(\alpha)}$, $V_z^{(\alpha)}$) are the generators of an $SO(2, 1)$ Lie algebra as can be established from their commutation relations. Instead of commuting with L^2 (as in the previous case), the generators ($V_x^{(\alpha)}$, $V_y^{(\alpha)}$, $V_z^{(\alpha)}$) commute with λ^2 , an angular momentum introduced by Labarthe (1981) and Herrick (1982). The eigenbasis associated with this V coupling scheme with $\alpha = (-2E)^{-1/2} = |M| + 1, \dots, \infty$ builds the hydrogenic basis of λ type which in the framework of the $SO(4)$ analysis has been shown to be well suited to deal with the magnetic problem in the low-field limit (when various n manifolds are not merging) (Herrick 1982). Hence, this V coupling scheme approach is a generalisation to the strong mixing regime of the Herrick analysis affording mixing of the various Coulomb manifolds.

We will call the eigenbasis for fixed α in the V coupling scheme the ' λ -Sturmian basis'.

The Hamiltonian of the hydrogen atom in a magnetic field is (using the cylindrical gauge) in atomic units ($\gamma = B/B_c$ with $B_c = 2.35 \times 10^5$ T)

$$H = \frac{p^2}{2} - \frac{1}{r} + \frac{\gamma}{2} L_z + \frac{\gamma^2}{8} (x^2 + y^2). \quad (8)$$

L_z is a constant of the motion which means that the paramagnetic term $\frac{1}{2}\gamma L_z$ may be ignored.

Reexpressed in the $SO(2, 2)$ framework (using (1) and (2)), the Schrödinger equation takes the algebraic form

$$\begin{aligned} [S_z^{(\alpha)} + T_z^{(\alpha)} + \frac{1}{2}\gamma^2 \alpha^4 (S_z^{(\alpha)} + S_x^{(\alpha)}) (T_z^{(\alpha)} + T_x^{(\alpha)}) (S_z^{(\alpha)} + S_x^{(\alpha)} + T_z^{(\alpha)} + T_x^{(\alpha)}) \\ - \frac{1}{2}(1 + 2E\alpha^2)(S_z^{(\alpha)} + S_x^{(\alpha)} + T_z^{(\alpha)} + T_x^{(\alpha)}) - \alpha] |\Psi\rangle = 0. \end{aligned} \quad (9)$$

We present two methods for solving this equation.

Solving equation (6) by making use of the spherical Coulomb basis (eigenbasis of $U_z^{(\alpha)}$ with $\alpha = |M| + 1, \dots, \infty$) is not a good strategy. This requires the calculation of matrix elements between eigenstates of α -dependent operators, which is feasible but complicated. In addition, no selection rule exists and the basis cannot be counted (because of the positive energy states) which makes truncation hazardous.

On the other hand, a Sturmian basis (fixed value of α) can be counted and the matrix elements of the operators involved in (6) are easy to calculate using formulae (4) and (5) (they are just combinations of the generators of the group). In addition, the generators connect a given state to only a finite number of states. The matrix representing (6) in a Sturmian basis will then be a band matrix allowing efficient truncation and diagonalisation. Solving (6) is not a real eigenvalue problem, but rather a generalised eigenvalue problem of the type

$$(A - \lambda B)|\Psi\rangle = 0$$

where A and B are fixed operators and λ and $|\Psi\rangle$ the required eigenvalue and eigenvector respectively.

After Clark and Taylor (1982), we solved the problem using the Crawford algorithm (Crawford 1973). However, the previous analysis provides us with several possible choices of a Sturmian basis which may differently respect the inner symmetries of the

problem to be solved. From Herrick (1982), the low-field limiting symmetries are of Λ or parabolic types and naturally extend into the strong mixing regime with the non-invariance group description as confirmed from a classical study of the motion (Delande and Gay 1985). Hence the choice of the V coupled basis (Ridge states) or decoupled (S, T) basis (well states) will be considerably more efficient than using the U coupled spherical Sturmian basis (Clark and Taylor 1982) which does not comply with the low-field symmetry and thus requires a tremendous number of channels to be incorporated.

Table 1 shows the sample results obtained for the ($n = 33, M = 3, K = 1$) (upper level of the hydrogenic manifold) for various values of the coupling parameter γn^3 which represents the ratio of the Lorentz force acting on the electron over the Coulomb force of the nucleus. The strong-field regime lies around $\gamma n^3 \approx 1$.

Using a V coupled basis conveniently truncated, accurate values of the energies up to $\gamma n^3 \approx 1$ are obtained with less than 100 Sturmian states (instead of 1000 to 2000 states in the U coupled basis). Indeed, the calculations can be held typically on a microcomputer instead of a Cray-I.

The problem of convergence will be discussed later.

The band structure of equation (6) makes it convenient for perturbation expansions. Indeed, the infinite series involved in non-degenerate or degenerate perturbation theory in the usual Coulomb basis here becomes finite while the computation of matrix elements from the generators of the group is straightforward.

We have thus calculated the Rayleigh-Schrödinger expansion of the energy levels as a function of γ^2 . Details of the calculations will be published elsewhere.

The ground-state situation has previously been extensively studied (Le Guillou and Zinn-Justin 1983) and some of the lowest excited states also (Galindo and Pascual 1976, Silverstone and Moats 1981). Our results agree with those of Cizek and Vrscay (1982) and Silverstone and Moats (1981) for the ground state (at 36th order) and for the 3s-3d states (87th order).

For the first time, expansions up to the 60th order have been possible in a typical Rydberg situation ($n = 30-60$). However, the calculation of 30 orders turns out to be sufficient in the present approach. The $rsPT$ series is found always to alternate with a convergence radius 0. Approximate convergence can be obtained using Padé approximants up to the strong field regime ($\gamma n^3 \approx 1$) only.

By 'approximate convergence', we mean that the values obtained do not tend to a well defined value, but rather are spread around an average value. The increase of the order of the Padé approximant does not reduce this spread.

We believe that this phenomenon is the high-field counterpart of the anticrossing patterns in the low-field regime. The Padé approximants, being smooth functions, diabatically 'cross' the anticrossings, the spread of the values thus giving the width of the anticrossing.

Table 1 displays the energy of the ($n = 33, M = 3, K = 1$) Rydberg state as a function of the magnetic field up to the strong-mixing regime. Calculations have been performed using three methods.

- (i) Diagonalisation in the U Sturmian basis (Clark and Taylor method).
- (ii) Diagonalisation in the V Sturmian basis.
- (iii) Padé approximants on the $rsPT$ series.

Accurate predictions can be obtained up to $\gamma n^3 = 1.2$. For higher values, the spread in the Padé- $rsPT$ method increases very rapidly and destroys convergence; in the same way, eigenvalues obtained in the U or V Sturmian basis do not converge.

Table 1. Calculated energy of the $n = 33$, $M = 3$, $K = 1$ state (upper state of the manifold) as a function of the magnetic field (paramagnetic shift not taken into account). γ is the reduced magnetic field $\gamma = B/B_c$ ($B_c = 2.35 \times 10^5$ T). (a) Diagonalisation in U Sturmian basis. Typical size of the basis is 1000 functions. (b) Diagonalisation in V Sturmian basis. The sizes of the basis are respectively 52, 52, 93, 120. (c) Padé approximant built on the RSPT expansion of the energy. Convergence is obtained respectively at orders 4, 10, 24, 24.

B (T)	$\gamma(33)^3$	Energy (au)		
		(a)	(b)	(c)
0.654	0.1	$-4.563\ 6975 \times 10^{-4}$	$-4.563\ 6975 \times 10^{-4}$	$-4.563\ 6975 \times 10^{-4}$
3.270	0.5	$-3.956\ 6688 \times 10^{-4}$	$-3.956\ 6688 \times 10^{-4}$	$-3.956\ 6688 \times 10^{-4}$
6.998	1.070 203 96	$-2.179\ 43(2) \times 10^{-4}$ ^a	$-2.179\ 40(5) \times 10^{-4}$	$-2.179\ 41(2) \times 10^{-4}$
7.847	1.2		$-1.689\ 6(5) \times 10^{-4}$	$-1.690\ 1(9) \times 10^{-4}$

^a Courtesy C W Clark (private communication).

There are strong clues that this phenomenon is associated with the onset of chaos in the classical system (Delande and Gay 1985). Chaos destroys the symmetries of the system and is expected to produce strong avoided crossings in the energy diagram (Berry 1981), thus inhibiting the convergence of Padé approximants.

The RSPT expansion needs quite a long CPU time to be calculated, but only a few milliseconds are needed to compute the value of the Padé approximant. The method is convenient for predicting the energy of a given state at various field strengths. On the contrary, diagonalisation in a conveniently symmetrised Sturmian basis is quite fast, but should be done for each field value. The accuracy of the two methods is comparable while they require limited computer resources.

Table 2. Comparison between selected experimental values of the energy of the ($M = 3$, $K = 1$) quasi-hydrogenic states of caesium (upper state of each manifold) and theoretical calculations. The paramagnetic contribution is included. The agreement is excellent over the whole range of magnetic field. The small discrepancies (about $2 \times 10^{-3} \times$ zero field energy) are due to the non-hydrogenic corrections in caesium Rydberg atoms (about 1.5×10^{-3}), the uncertainty on the strength of the magnetic field (about 10^{-3}) and the Doppler width of the lines (about 10^{-3}).

Principal quantum number n	B (T)	γn^3	E_{exp} (cm ⁻¹)	E_{calc} (cm ⁻¹)
48	0.653	0.307	-44.39	-44.37
46	1.154	0.478	-44.11	-44.12
44	1.682	0.610	-43.82	-43.75
42	2.265	0.714	-43.49	-43.56
40	2.972	0.809	-43.10	-43.17
38	3.829	0.894	-42.62	-42.72

Table 2 displays comparison between the experimental values of the energy obtained on quasi-hydrogenic states of caesium ($M = 3$, $K = 1$ states with V type approximate symmetry) (Gay *et al* 1980) and the theoretical predictions. The agreement is clearly excellent (better than 2×10^{-3} of the zero field energy) for the whole range of magnetic field.

What is required now is to extend this type of analysis to the high-field regime up to the Landau limit.

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