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LETTER TO THE EDITOR

Group theory applied to the hydrogen atom in a strong magnetic field. Derivation of the effective diamagnetic Hamiltonian

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Abstract. We present a formalism based on the non-invariance algebra for the Coulomb problem that allows us to deduce an effective Hamiltonian for a wide variety of perturbing potentials. Applications to the problem of the hydrogen atom in a magnetic field are performed. We especially derive the exact first- and second-order expressions of the effective diamagnetic Hamiltonian under a general operatorial form. Some of the consequences and further developments are briefly indicated.

During the last few years, renewed attention has been paid to the strongly magnetised hydrogen-atom problem. Numerous experiments on Rydberg states have especially confirmed the existence of regular features in the strong mixing regime of the motion (when the magnetic energy is comparable with the Coulomb binding energy). However, the theoretical understanding is still limited to approximate semi-classical calculations (Gay 1982, O'Connell 1982), except in the low-field limit. In this limit, the effective diamagnetic Hamiltonian in a given manifold has been derived in first order using classical perturbation theory (Solov'ev 1981), and also using group theory (Herrick 1982) using the Fock method in momentum space.

Our purpose is here to present a method based on the SO(4, 2) non-invariance algebra of the Coulomb problem which is more general, enabling us in particular to deduce an effective diamagnetic Hamiltonian at arbitrary orders in the magnetic field. Such an achievement requires us to include all the states in the Coulomb spectrum including continua which is done quite naturally with the present SO(4, 2) formalism. The present treatment is the rigorous re-formulation of previous works (Gay *et al* 1983). Some attempts along similar lines, but limited to the ground or first states of the hydrogen atom, have been reported by Bednar (1977) and Chen (1983). Here we succeed in obtaining the general development of the effective diamagnetic Hamiltonian under operatorial form at arbitrary n value.

We first recall the basic equivalence of the Coulomb problem with the one of a pair of two-dimensional harmonic oscillators (the so-called 'oscillator representation'). Next some properties of the SO(2, 1) and SO(4) Lie algebra will be discussed. Then this will be applied to the hydrogen atom in a magnetic field. The effective diamagnetic Hamiltonian exact up to fourth order in the B field will be deduced in terms of the generators (j_1, j_2) of the SO(4) Lie algebra for the Coulomb problem.

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The Hamiltonian for the non-relativistic hydrogen atom (assuming the proton is infinitely massive) is in atomic units ($\hbar = m = q = 4\pi\varepsilon_0 = 1$):

$$H_0 = p^2/2 - 1/r$$

$L_z = -\mathrm{i}\,\partial/\partial\varphi$ commutes with H_0. Let Ψ be an eigenfunction of H_0, with negative energy E and angular momentum $L_z = m$. Using the dilated semi-parabolic coordinates

$$\mu = (-2E)^{1/4}(r+z)^{1/2}$$

and

$$\nu = (-2E)^{1/4}(r-z)^{1/2}$$

$$\Psi(\boldsymbol{r}) = \exp(\mathrm{i}m\varphi)\Psi(\mu, \nu)/\sqrt{2\pi}$$

one gets the transformed Schrödinger equation:

$$\left(\frac{\partial^2}{\partial\mu^2} + \frac{1}{\mu}\frac{\partial}{\partial\mu} + \frac{\partial^2}{\partial\nu^2} + \frac{1}{\nu}\frac{\partial}{\partial\nu} - \frac{m^2}{\mu^2} - \frac{m^2}{\nu^2} - (\mu^2+\nu^2) + \frac{4}{\sqrt{-2E}}\right)\Psi(\mu, \nu) = 0. \tag{1}$$

This can be interpreted as the Schrödinger equation for a pair of uncoupled two-dimensional harmonic oscillators with the same angular momentum m and frequency $\omega = 1$, written in polar coordinates (μ or ν, φ).

How to generate the eigenstates for this two-dimensional oscillator at constant L_z is well established†. One can choose the set of Hermitean operators such that (Englefield 1971):

$$\begin{aligned} S_{\substack{x\\z}} &= \frac{1}{4}\left(\pm\frac{\partial^2}{\partial\mu^2} \pm \frac{1}{\mu}\frac{\partial}{\partial\mu} \mp \frac{m^2}{\mu^2} + \mu^2\right) \\ S_y &= \frac{\mathrm{i}}{2}\left(1 + \mu\frac{\partial}{\partial\mu}\right). \end{aligned} \tag{2}$$

They fulfil the commutation relations which are those of an SO(2, 1) Lie algebra:

$$[S_x, S_y] = -\mathrm{i}S_z \qquad [S_y, S_z] = \mathrm{i}S_x \qquad [S_z, S_x] = \mathrm{i}S_y. \tag{3}$$

Such an algebra is well known to be associated with the Lorentz group in three dimensions (including one time dimension), that is the group of real linear direct transformations preserving $x^2 + y^2 - t^2$.

The Casimir operator of SO(2, 1) is from (2) and (3):

$$S^2 = S_x^2 + S_y^2 - S_z^2 = \tfrac{1}{4}(1 - m^2). \tag{4}$$

S_z is nothing but *half the Hamiltonian* of the two-dimensional oscillator with angular momentum m. Then, the eigenstates of such an oscillator at fixed m span a unitary irreducible representation of SO(2, 1).

Obviously, the generators ($S_{\substack{x\\y}}$) do not commute with the Hamiltonian. Therefore SO(2, 1) is not a symmetry group but a non-invariance group for the two-dimensional harmonic oscillator with fixed angular momentum.

† The general analysis can be found in Cohen-Tannoudji *et al* (1973) and is based on the introduction of the set of four creation–annihilation operators (a_i^+, a_i) in a cartesian ($i = x, y$) or 'circular' ($i = +, -$) frame. The latter is especially convenient as $L_z = a_+^+a_+ - a_-^+a_- = n_+ - n_- = m$ is diagonal. The choice of (2) then comes from the relations $S^+ = a_+^+a_-^+$, $S^- = a_+a_-$, $S_z = \frac{1}{2}(a_+^+a_+ + a_-^+a_- + 1)$. This justifies equations (5) with $n = n_- = a_-^+a_-$ for $m > 0$ and $n = n_+ = a_+^+a_+$ for $m < 0$.

Turning back to the Coulomb problem and equation (1), the pair of two-dimensional oscillators at constant $L_z = m$ can be described in terms of the two sets (S_i), (T_i) of generators. The (T_i) are defined through (2) for the ν coordinate. As the two sets are commuting (the oscillators are independant), the non-invariance algebra associated with equation (1) is the direct sum $SO(2, 1) \oplus SO(2, 1)$ which is an SO(2, 2) Lie algebra.

Consequently, the solutions of equation (1) when E is not fixed span a unitary irreducible representation of SO(2, 2). The SO(2, 2) is the sub-algebra of the complete non-invariance algebra SO(4, 2) of the Coulomb problem, associated with fixed angular momentum m (Englefield 1971).

Here we recall some simple algebraic properties of the representations of SO(2, 1). We finally re-deduce the Coulomb spectrum.

SO(2, 1) being a non-compact group, the unitary irreducible representations are infinite dimensional. The representations realised for the oscillator problem are of D_k^+ type with $k = \frac{1}{2}|m| + \frac{1}{2}$. The states $|n, k\rangle$ are specified by a non-negative quantum number n. The actions of the S_i are (see Englefield 1971),

$$\begin{aligned} S^2|n, k\rangle &= k(1-k)|n, k\rangle = \tfrac{1}{4}(1-m^2)|n, k\rangle \\ S_z|n, k\rangle &= (k+n)|n, k\rangle \\ S^+|n, k\rangle &= (2k+n)^{1/2}(n+1)^{1/2}|n+1, k\rangle \\ S^-|n, k\rangle &= n^{1/2}(n+2k-1)^{1/2}|n-1, k\rangle \end{aligned} \tag{5}$$

where $S^{\pm} = (S_x \pm \mathrm{i}S_y)$, and then they provide convenient ladder operators at constant L_z (see previous footnote).

Equation (1) gives immediately:

$$(S_z + T_z)\Psi(\mu, \nu) = (-2E)^{-1/2}\Psi(\mu, \nu)$$

and is diagonal in the $|n_1, k\rangle \otimes |n_2, k\rangle$ basis associated with (S^2, T^2, S_z, T_z). From (5) one gets $E = -1/2n^2$ with $n = n_1 + n_2 + |m| + 1$. Then (n_1, n_2) are identical with the usual parabolic quantum numbers for the Coulomb problem.

The symmetry group of the hydrogen atom is $SO(4) = SO(3) \otimes SO(3)$. A representation of SO(4) can be explicitly given in terms of the angular momenta (j_1, j_2) such that (Bander and Itzykson 1966)

$$j_{\frac{1}{2}} = \tfrac{1}{2}(\boldsymbol{L} \pm \boldsymbol{A}) \tag{6}$$

where $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$ is the angular momentum and $\boldsymbol{A}$ the Runge–Lenz vector:

$$\boldsymbol{A} = (-2mH_0)^{-1/2}[(\boldsymbol{p} \times \boldsymbol{L} - \boldsymbol{L} \times \boldsymbol{p})/2 - e^2\boldsymbol{r}/r]$$

j_1 and j_2 commute both with each other and with H_0. Hence the eigenstates of fixed energy span a unitary irreducible representation of $SO(3) \otimes SO(3)$, which is SO(4).

Let us consider eigenstates of (H_0, j_{1z}, j_{2z}) with fixed values of n and m ($m = L_z = j_{1z} + j_{2z}$). There is an isomorphism between this set and the set of eigenstates of the oscillator representation with fixed values of n and m. More precisely, these two sets do coincide, but for a phase factor. The two representations that are linked through the isomorphism, satisfy:

$$\begin{aligned} j_{1z} + j_{2z} &= m \\ j_{1z} - j_{2z} &= n_1 - n_2 \\ j_1^2 = j_2^2 &= j(j+1) \qquad \text{with} \qquad n = 2j+1. \end{aligned} \tag{7}$$

Because the j are angular momenta, one can build operators that act on the (j_{1z}, j_{2z}) values but leave (n, m) invariant. For instance,

$$j_1^+ j_2^- |j_{1z}, j_{2z}\rangle = [j(j+1) - j_{1z}(j_{1z}+1)]^{1/2}[j(j+1) - j_{2z}(j_{2z}-1)]^{1/2}|j_{1z}+1, j_{2z}-1\rangle. \qquad (8)$$

The transform of such an operator in the oscillator representation connects the (n_1, n_2) and (n_1+1, n_2-1) states. It is then proportional to S^+T^-. The coefficient can be deduced from (7), (8) and (5), and is a phase factor (-1).

Finally, the isomorphism is expressed by:

$$\begin{aligned} &S^{\pm}T^{\mp} \leftrightarrow -j_1^{\pm} j_2^{\mp} \\ &S_z + T_z \leftrightarrow n = 2j+1 \\ &S_z - T_z \leftrightarrow j_{1z} - j_{2z} \\ &m \leftrightarrow j_{1z} + j_{2z}. \end{aligned} \qquad (9)$$

The Hamiltonian for the non-relativistic Coulomb problem in the symmetric gauge $(\mathscr{A} = \frac{1}{2}\boldsymbol{B} \times \boldsymbol{r})$, is (in atomic units):

$$H = \frac{p^2}{2} - \frac{1}{r} + \frac{\gamma}{2} L_z + \frac{\gamma^2}{8}(x^2 + y^2) \qquad (10)$$

with $\gamma = B/B_c (B_c = 2.35 \times 10^9$ G). L_z is a constant of the motion and we further ignore the role of the $\gamma L_z/2$ paramagnetic term. The use of dilated parabolic coordinates allows us to put (10) into a form analogous to (1), but with the additional $V(\mu, \nu)$ term which represents the diamagnetic interaction:

$$V(\mu, \nu) = \frac{\gamma^2}{8}(-2E)^{-2}(\mu^4\nu^2 + \mu^2\nu^4). \qquad (11)$$

Hence, the pair of two-dimensional oscillators with the same angular momentum m are now coupled through the diamagnetic interaction V. Expressing the latter in terms of the generators of the SO(2, 2) algebra leads, with $\mu^2 = 2(S_z + S_x)$, to:

$$[2(S_z + T_z) + V - 2(-2E)^{-1/2}]\Psi = 0$$

with

$$V = \gamma^2(-2E)^{-2}(S_z + S_x)(T_z + T_x)(S_z + T_z + S_x + T_x). \qquad (12)$$

Equation (12) holds exactly and puts on a firm basis the formal equivalence between the Coulomb problem in a $\boldsymbol{B}$ field and the one of a pair of coupled two-dimensional harmonic oscillators (Delande 1981, Gay 1982, Fano 1983).

The next step is to solve equation (12) perturbatively, assuming V is a small perturbation of the zero-field operator $(S_z + T_z)$.

At first order in γ^2, the effective Hamiltonian is $\tilde{H}_1 = P_n V P_n$ where P_n is the projector on the n level of the oscillator representation $(S_z + T_z = n)$. Obviously, V is a polynomial of degree three in the S_i, T_i $(i = x, y, z$ or $i = +, -, z)$. The restriction of V is readily derived by retaining those terms which preserve the n value. They are $S_z T_z^2$, $T_z S^+ S^-$, $S_z S^+ T^-$ ... while the terms $S_z^2 T^+$, $S^+ S^- T^-$ ... do not. One gets straightforwardly:

$$\tilde{H}_1 = \tfrac{1}{4}\gamma^2(-2E)^{-2}(S_z + T_z)(S^2 + T^2 + 6T_z S_z + 2S^+T^- + 2S^-T^+). \qquad (13)$$

Such an operator mixes the states of the two oscillators at constant n (principal quantum number). Consequently it preserves the SO(4) symmetry of the Coulomb problem.

In order to derive the first-order effective diamagnetic Hamiltonian H_1, one should be aware that (12) and (13) have an implicit dependence on the energy E which we expand as $E=-1/2n^2+H_1$. Further use of equations (9) leads immediately to:

$$H_1=\frac{\gamma^2 n^2}{16}(3n^2+1-4j_{1z}^2-4j_{2z}^2+4j_{1z}j_{2z}-4j_1^+j_2^--4j_1^-j_2^+) \tag{14}$$

or

$$H_1=\frac{\gamma^2 n^2}{16}(n^2+3+L_z^2+4A^2-5A_z^2). \tag{15}$$

This is the exact quantum result, the classical form of which has been obtained by Solov'ev (1981) using perturbation theory. An alternate quantum derivation has been given by Herrick (1982) using Fock's method on the R(4) hypersphere, in momentum space (see e.g. Bander and Itzykson 1966).

The present method based on the non-invariance algebra for the Coulomb problem has a first merit which is its physical clarity. It only requires the understanding of the physics of the harmonic oscillator in position space. A consequence is that the calculations are simple and allow for any generalisation. Especially, equation (13) is exact and allows us to account for any coupling due to the diamagnetic interaction which the method on the Fock hypersphere does not afford. Consequently, we do not have any difficulties, so far as the principles are concerned, in deducing an effective Hamiltonian at higher orders, while exactly accounting for the role of all the states of the Coulomb spectrum (including continua).

As an example, we deduce the effective Hamiltonian at second order in γ^2. Its expression in the oscillator representation is:

$$\tilde{H}_2=P_nV(1-P_n)[2n-2(S_z+T_z)]^{-1}(1-P_n)VP_n$$

where V is given by (12). The key point of the evaluation is to notice that V only has a finite number of non-zero matrix elements (selection rules are $|\Delta n_i|\leqslant 2$ $i=1$, 2 and $|\Delta(n_1+n_2)|\leqslant 3$). Thus the calculation of $\tilde{H}_2$ only involves finite summations (in contrast to what happens using the usual Coulomb basis). Once $\tilde{H}_2$ is obtained in terms of the (S_i, T_i) one turns back to the (j_1, j_2) representation using (9) and then deduces through iteration in (12) the exact expression at second order of the effective diamagnetic Hamiltonian. It is:

$$\begin{aligned}H_2=(\tfrac{1}{8}\gamma^2)^2\tfrac{1}{48}n^6\{&-223n^4-598n^2-27+192(j_{1z}^4+j_{2z}^4)+144j_{1z}^2j_{2z}^2-(176n^2+752)j_{1z}j_{2z}\\&+(j_{1z}^2+j_{2z}^2)(-32j_{1z}j_{2z}+284n^2+372)+8(j_1^+j_2^-+j_1^-j_2^+)\\&\times[53n^2+153+20(j_{1z}^2+j_{2z}^2)-12j_{1z}j_{2z}]\\&+208(j_1^+j_2^--j_1^-j_2^+)(j_{1z}-j_{2z})+48(j_1^{+2}j_2^{-2}+j_1^{-2}j_2^{+2})\}\end{aligned} \tag{16}$$

(which can be expressed as a function of $(j_1\cdot j_2)$ and $(j_{1z}j_{2z})$—see Gay *et al* (1983)).

Higher orders could be deduced (exactly) with the use of computer programs for algebraic manipulations. While the convergence of the expansion is an open problem, Padé approximants built on it lead to interesting results.

Equation (16) is the first expression of the second-order term under *operatorial form valid for any n and m values.* Limited comparisons with calculations for $n=1$ and 2 are possible. For the ground state, one gets $j=\frac{1}{2}(n-1)=0$ and $j_{1z}=j_{2z}=0$.

Then $E=\frac{1}{2}+\frac{1}{4}\gamma^2-\frac{53}{3}(\frac{1}{8}\gamma^2)^2+\ldots$ in agreement with Bednar (1977) and Chen (1983)†.

The present method can apply to any perturbation of the Coulomb problem that is a polynomial function of the components of S and T, of which polynomial potentials in z and r are a special case. But potentials lacking any rotational symmetry would require the use of the complete SO(4, 2) non-invariance algebra.

In such a formalism, the Stark effect is very simple to handle, as V is just the *sum* of two terms depending respectively on S and T and is thus separable (a feature associated with the Stark dynamical symmetry).

When the principal quantum number n tends to infinity, the effective Hamiltonian tends to its classical limit which can be obtained another way, quantising the Birkhoff–Gustavson normal form (Reinhardt and Farrelly 1982, Robnik 1984, Robnik and Schrüfer 1984).

Such a method allowing us to deduce an effective Hamiltonian in a *given n manifold* cannot (as various perturbative methods used or proposed) give an answer to the question of exponentially small anticrossings in the diamagnetic problem. This would require us to consider at all orders in B field the two levels which may cross (or within the present formalism to deduce an effective Hamiltonian valid for two, n and $n+1$ manifolds).

Although we will discuss elsewhere the numerous physical implications of the present method, one should remark that the eigenfunctions of the oscillator representation are closely connected with the usual Sturmian functions (through a recoupling). The fact that computations in such a basis have been successful for predicting the diamagnetic spectrum below threshold (Clark and Taylor 1980) just manifests how well it fits the underlying algebraic structure of the problem.

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† Various misprints exist in Chen (1983). But the (non-operatorial) form obtained for $n=3$ is definitely incorrect.