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LETTER TO THE EDITOR

# Hydrogen atom in a strong magnetic field: calculation of the energy levels by quantising the normal form of the regularised Kepler Hamiltonian

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**Abstract.** The energy levels of the hydrogen atom in a magnetic field are obtained by quantising the Birkhoff-Gustavson normal form of the diamagnetically perturbed, regularised Kepler Hamiltonian. The method enables us to go beyond the approximations quadratic in the field and to calculate quartic and higher terms in the power expansion for the energy levels. (We consider here only the case $m = 0$.) The result is equivalent to finding the field-dependent third integral of motion.

The Hamiltonian of an atom in a magnetic field contains field-independent terms (vacuum terms), terms linear in the field (paramagnetic interaction) and the quadratic terms (diamagnetic terms). Whereas the analysis of the linear Zeeman effect is complete, the quadratic Zeeman effect, which is essential to the atomic diamagnetism, is very difficult to treat because it is just the diamagnetic term that breaks the symmetries of the vacuum problem. This makes the system non-integrable, and there is no obvious choice of 'good quantum numbers'. New phenomena arise in this mixing regime of equally strong forces with different symmetries. This is the case for low lying states in the fields near the critical field strength $Z^2 B_0$, $B_0 = \alpha^3 e^2/r_0 = 2.35\,10^9$ G ($\alpha$ is the fine structure constant, $r_0 = e^2/m_e c^2$, the classical electron radius), or for highly excited atoms (Rydberg atoms) in relatively weak fields available in a laboratory, e.g. $B \approx 5 \times 10^4$ G. The general criterion is $N^3 B/B_0 \approx 1$, where $N$ is the main quantum number.

The interesting phenomena of nonlinear dynamics involved in the problem have attracted the attention of theoreticians, because of important astrophysical applications, and even more so because of the experimental motivation: with the advent of tunable dye lasers the experimental physicists are able to supply beautiful spectra of such a fully developed diamagnetic regime. A great number of papers have been published recently on this subject. It is impossible to give a complete list of all the references, but we refer the reader to a recent review article by Gay and Delande (1983) and the references therein.

The hydrogen atom in a magnetic field is the prototype for the study of atomic diamagnetism. It leads to important methodological problems and is also a realistic approximation for Rydberg atoms in strong fields. The purpose of this work is to further develop the ideas published earlier (Robnik 1981, 1982). This includes in

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particular the construction of the approximate, formal integral of motion. The field-independent integral has been constructed by Solovev (1981, 1982). The proposal to use the Birkhoff-Gustavson normal form for the quantisation has been independently followed by Reinhardt and Farrelly (1982). In the present work we apply the quantisation method recently developed by Robnik (1984). The results that we obtain—the power expansion of the levels as functions of the field—are conceptually equivalent to the construction of a *field-dependent* third *integral* of motion. In this sense we go beyond Solovev's work and provide analytic results that are different from those of Reinhardt and Farrelly (1982).

The dimensionless classical Hamiltonian of our system is

$$H = \tfrac{1}{2}p^2 - r^{-1} + \tfrac{1}{8}\gamma^2\rho^2 \tag{1}$$

where $\rho^2 := x^2 + y^2$, $r^2 := z^2 + \rho^2$, $\gamma := B/B_0$, the dimensionless magnetic field, while all coordinates are measured in units of Bohr radii, and the energy $E = H$ is measured in atomic units. In these units $\hbar = 1$. We treat here the naked quadratic Zeeman problem: infinite mass of the nucleus and no motion of the CM (i.e. no electric field). We also eliminated the paramagnetic term by considering the problem in a uniformly rotating Larmor frame, or by specialising to the case $m = 0$.

By transforming (1) to the parabolic coordinates $\xi$, $\eta$,

$$\xi := r - z \qquad \eta := r + z \tag{2}$$

we have

$$H = \frac{2\xi}{\xi+\eta}p_\xi^2 + \frac{2\eta}{\xi+\eta}p_\eta^2 + \frac{m^2}{2\xi\eta} - \frac{2}{\xi+\eta} + \frac{\gamma^2}{8}\xi\eta \tag{3}$$

where $m = p_\varphi$, the $z$ component of the angular momentum.

The next step is to regularise the Kepler Hamiltonian by the canonical transformation

$$\begin{aligned} \xi &= u^2 \qquad & p_\xi &= p_u/2u \\ \eta &= v^2 \qquad & p_\eta &= p_v/2v \end{aligned} \tag{4}$$

whence

$$2 = \tfrac{1}{2}[p_u^2 + p_v^2 + (-2E)(u^2+v^2)] + \frac{m^2}{2}\left(\frac{1}{u^2}+\frac{1}{v^2}\right) + \tfrac{1}{8}\gamma^2u^2v^2(u^2+v^2). \tag{5}$$

By stretching the variables

$$\begin{aligned} u(-2E)^{1/4} &\to u \qquad & v(-2E)^{1/4} &\to v \\ p_u/(-2E)^{1/4} &\to p_u \qquad & p_v/(-2E)^{1/4} &\to p_v \end{aligned} \tag{6}$$

we finally obtain the *effective Hamiltonian* $\mathcal{H}$,

$$\begin{aligned} \mathcal{H}(u, v, p_u, p_v) = \frac{2}{(-2E)^{1/2}} &= \tfrac{1}{2}(u^2 + p_u^2) \\ &+ \tfrac{1}{2}(v^2 + p_v^2) + \frac{m^2}{2}\left(\frac{1}{u^2}+\frac{1}{v^2}\right) + \tfrac{1}{8}Gu^2v^2(u^2+v^2) \end{aligned} \tag{7}$$

where

$$G = \gamma^2/(-2E)^2.$$

We consider only the case of vanishing angular momentum $m=0$. The Birkhoff-Gustavson normal form of the effective Hamiltonian (7) obtained by using a symbolic computer program (Schrüfer 1985) written in REDUCE (Hearn 1983) can be cast in the form (see Robnik 1984)

$$\tfrac{1}{2}\mathcal{H}=\frac{1}{(-2E)^{1/2}}=A+B\frac{\gamma^2}{(-2E)^2}+C\frac{\gamma^4}{(-2E)^4}+D\frac{\gamma^6}{(-2E)^6}+\dots \tag{8}$$

with

$$A=\tfrac{1}{2}(\tau_1+\tau_2) \tag{9a}$$

$$B=\tfrac{1}{32}(\tau_1+\tau_2)(3\tau_1\tau_2+K^2+K^{*2}) \tag{9b}$$

$$\begin{aligned}C=-\frac{\tau_1+\tau_2}{6144}[&\tau_1\tau_2(65\tau_1^2+423\tau_1\tau_2+65\tau_2^2)\\&+(K^2+K^{*2})(33\tau_1^2+220\tau_1\tau_2+33\tau_2^2)+27(K^4+K^{*4})]\end{aligned} \tag{9c}$$

$$\begin{aligned}D=\tfrac{1}{2}\tau_1\tau_2&\left(\frac{7}{2048}\tau_1^5+\frac{3529}{49152}\tau_1^4\tau_2+\frac{5225}{18432}\tau_1^3\tau_2^2+\frac{5225}{18432}\tau_1^2\tau_2^3+\frac{3529}{49152}\tau_1\tau_2^4+\frac{7}{2048}\tau_2^5\right)\\&+\tfrac{1}{2}(K^2+K^{*2})\left(\frac{479}{294912}\tau_1^5+\frac{533}{12288}\tau_1^4\tau_2+\frac{104639}{589824}\tau_1^3\tau_2^2\right.\\&\left.+\frac{104639}{589824}\tau_1^2\tau_2^3+\frac{533}{12288}\tau_1\tau_2^4+\frac{479}{294912}\tau_2^5\right)\\&+\tfrac{1}{2}(K^4+K^{*4})\left(\frac{2179}{294912}\tau_1^3+\frac{11461}{294912}\tau_1^2\tau_2+\frac{11461}{294912}\tau_1\tau_2^2+\frac{2179}{294912}\tau_2^3\right)\\&+\frac{389}{196608}\frac{(\tau_1+\tau_2)}{2}(K^6+K^{*6})\end{aligned} \tag{9d}$$

where in the normal variables we have the definitions

$$\begin{aligned}&\tau_1=\tfrac{1}{2}(u^2+p_u^2) \qquad \tau_2=\tfrac{1}{2}(v^2+p_v^2)\\&K=\tfrac{1}{2}(u+\mathrm{i}p_u)(v-\mathrm{i}p_v).\end{aligned} \tag{10}$$

We note that most of the normal terms vanish as a consequence of the 1:1 resonance and of the special structure of the diamagnetic perturbation as seen in equation (7): $A$ is the unperturbed harmonic part, i.e. it is of the second degree, $B$ is the sixth degree, $C$ is tenth degree, $D$ is fourteenth degree, etc. Therefore, in order to go beyond the quadratic approximation of equation (8) one must calculate the normal form to *at least tenth order.* We calculated the fourteenth degree, but in the following we shall use only the quartic or lower terms in (8), although it is a technical point to go higher if one wishes. One should notice that the effective normal Hamiltonian (8) depends on the total energy $E$, so that in quantising (8) we get an implicit relation for $E$.

Before embarking on the quantisation scheme we note that for vanishing magnetic field but arbitrary $m$ the usual WKB quantisation of (7) yields exactly the Coulomb spectrum

$$E_{n_1n_2m}=-\tfrac{1}{2}(n_1+n_2+m+1)^{-2} \tag{11}$$

where $n_1$, $n_2$ are the two non-negative integer quantum numbers. Let us now consider

the limiting case $m \to 0$. The simple setting of $\tau_1 = n_1 + \frac{1}{2}$ and $\tau_2 = n_2 + \frac{1}{2}$ obviously yields the wrong result, and does indeed lack a justification. The complication arises from the fact that $u$ and $v$ are restricted to the positive values, so we do not have two simple uncoupled harmonic oscillators for the underlying unperturbed system, but 'one-sided' oscillators instead. While the algebraic structure of the Hamiltonian is unchanged, its analytic structure has changed and we have to specify the boundary conditions at $u = 0$ and $v = 0$. Suppose we formally extend the Hamiltonians (7) and (8) to the negative values of $u$ and $v$. As $u$ and $-u$ in combination with any of $v$ and $-v$ correspond to the same point in the true configuration space we must require that the wavefunction $\psi(u, v)$ is an even function of $u$, and of $v$, so that all quadrants in the $u$, $v$ coordinate plane are equivalent. By formally treating the Hamiltonian (7) (with $m = 0$) as a two-dimensional harmonic oscillator we thus select only the even-even parity states, whence

$$\tau_1 = 2n_1 + \tfrac{1}{2} \qquad \tau_2 = 2n_2 + \tfrac{1}{2} \tag{12}$$

and

$$\begin{aligned} \hat{K}|2n_1, 2n_2\rangle &= [2n_1(2n_2+1)]^{1/2}|2n_1 - 1, 2n_2 + 1\rangle \\ \hat{K}^+|2n_1, 2n_2\rangle &= [(2n_1+1)2n_2]^{1/2}|2n_1 + 1, 2n_2 - 1\rangle. \end{aligned} \tag{13}$$

However, by doing the quantisation correctly we have now got the incorrect result for the ground state, as can easily be seen from (7). The reason is the non-commutation of classical canonical transformations and assignment of differential operators. As a consequence our case $m = 0$ actually corresponds to $m = \frac{1}{2}$, but this defect can be accounted for by the additive semiclassical correction terms equal to $\frac{1}{2}$ in equation (12), so that we have finally

$$\tau_1 = 2n_1 + 1 \qquad \tau_2 = 2n_2 + 1 \qquad n_1, n_2 = 0, 1, 2, \ldots . \tag{14}$$

Equations (13) and (14) constitute our quantisation scheme.

Strictly speaking, we must first quantise $\mathcal{H}$ and then solve for $E$, but within the semiclassical approximation these operations may be interchanged. We find the power expansion (up to the quartic terms)

$$E = H = -\frac{1}{2A^2}\left[1 - 2\gamma^2 A^4 \frac{B}{A} - \gamma^4 A^8 \left(5\frac{B^2}{A^2} + 2\frac{C}{A}\right) + O(\gamma^6)\right]. \tag{15}$$

In order to quantise (15) we insert $A$, $B$, and $C$ from (9$a$)-(9$c$)

$$\begin{aligned} E = -\frac{1}{2N^2}\{1 - \tfrac{1}{8}\gamma^2 N^4(3\tau_1\tau_2 + K^2 + K^{*2}) + \tfrac{1}{1536}\gamma^4 N^8[\tau_1\tau_2(65\tau_1^2 + 93\tau_1\tau_2 + 65\tau_2^2) \\ + (K^2 + K^{*2})(33\tau_1^2 - 40\tau_1\tau_2 + 33\tau_2^2) - 3(K^4 + K^{*4})]\}. \end{aligned} \tag{16}$$

By $N$ we have denoted the main quantum number, i.e.

$$N = A = n_1 + n_2 + 1 \tag{17}$$

so that the lowest term in (16) gives the unperturbed Coulomb spectrum. We can split the operator (16) as follows:

$$\hat{E} = -(1/2N^2) + \hat{E}_D \tag{18}$$

where $\hat{E}_D$ commutes with the Kepler Hamiltonian, i.e. it leaves $N$ manifolds invariant.

Therefore, to obtain the spectrum $E$ one has to diagonalise (18) within the $N$-manifold subspace. Writing explicitly

$$\hat{E}_D = \tfrac{1}{16}\gamma^2 N^2(3\tau_1\tau_2 + \hat{K}^2 + \hat{K}^{+2}) - \tfrac{1}{3072}\gamma^4 N^6[\tau_1\tau_2(65\tau_1^2 + 93\tau_1\tau_2 + 65\tau_2^2) + (\hat{K}^2 + \hat{K}^{+2})(33\tau_1^2 - 40\tau_1\tau_2 + 33\tau_2^2) - 3(\hat{K}^4 + \hat{K}^{+4})] \tag{19}$$

we have to solve

$$\det(\langle n_1 n_2|\hat{E}_D|n_1' n_2'\rangle - E_D\delta_{n_1 n_2 n_1' n_2'}) = 0 \tag{20}$$

for each $N$-manifold subspace such that $n_1 + n_2 + 1 = n_1' + n_2' + 1 = N$. This is straightforward. Let us consider some examples.

(*a*) *The ground state* $N = 1$. Obviously $\tau_1 = \tau_2 = 1$ and $\hat{E}_D$ is diagonal, i.e. from (16) follows

$$E_{00} = -\frac{1}{2} + \frac{3}{16}\gamma^2 - \frac{223}{3072}\gamma^4 + \dots . \tag{21}$$

(*b*) *The first excited state* $N = 2$. We have only two states $|0, 2\rangle$ and $|2, 0\rangle$. The matrix elements are given by

$$\langle 2, 0|\hat{E}_D|0, 2\rangle = \langle 0, 2|\hat{E}_D|2, 0\rangle = 9\gamma^2/4$$
$$\langle 2, 0|\hat{E}_D|2, 0\rangle = \langle 0, 2|\hat{E}_D|0, 2\rangle = 6^{1/2}\gamma^2/2$$

so that from (20) and (18) we have for the diamagnetic shifts of the 2s0 and 2p0 states

$$E_{2s0} = -\frac{1}{8} + \left(\frac{9}{4} + \frac{6^{1/2}}{2}\right)\gamma^2$$
$$E_{2p0} = -\frac{1}{8} + \left(\frac{9}{4} - \frac{6^{1/2}}{2}\right)\gamma^2. \tag{22}$$

The results are expected to be quite good for higher levels. It has been shown for some examples that the Birkhoff-Gustavson normal form can yield results very close to the quantum perturbation theory (Robnik 1984) and has the advantage that one has to deal only with finite matrices.

We turn now to the discussion of the results and note the following observation. If $|n_1, n_2\rangle$ is a state in the $N$-dim subspace of constant main quantum number $N = n_1 + n_2 + 1$, then the structure of the diamagnetic Zeeman operator $\hat{E}_D$ given in (1) implies that $\hat{E}_D|n_1, n_2\rangle$ is again in the same $N$ manifold. Thus $N$ manifolds are invariant subspaces of $\hat{E}_D$, which means complete absence of inter-$N$ mixing. Our approximate quantisation therefore predicts that levels differing in $N$ may cross.

The reason for this lies in the fact alone that the Kepler problem (1) can be mapped onto the harmonic oscillator by the regularisation procedure (1)-(5), and the perturbation of the former can be replaced by the purturbation of the latter. The existence of such a mapping simply is a consequence of the property that all Kepler orbits are closed (periodic), which is related to the existence of additional integrals of motion (Runge-Lenz vector). This is the key to the O(4) symmetry of the Kepler problem. So we again reach the conclusion pointed out first by Solovev (1982) and Herrick (1982) that O(4) symmetry of the Kepler problem is fundamental to the symmetry of the quadratic Zeeman interaction in the weak field limit. (For alternate treatments see

Clark and Taylor (1980, 1982) and Richards (1983).) *New* in our results is that this carries over to higher fields, and that the absence of inter-$N$ mixing is predicted *formally* to all orders in the field. This is in excellent agreement with the numerical calculations of Zimmerman *et al* (1980, 1982).

How can we then account for the exponentially small separations of order $\exp(-N)$ at the avoided crossings that are observed empirically (see Delande and Gay 1981, Zimmerman *et al* 1980)? Notice the stress on the word formally: the classical perturbation expansion *à la* Birkhoff-Gustavson given in equation (8) is a formal expansion. It will never converge. Similarly, the quantum perturbation theory (in the orthodox formulation) most probably diverges.

It is reasonable to expect that the exact non-perturbative treatment would explain the exponentially small splittings but only below some threshold corresponding to the classical critical energy for the onset of chaos, beyond which the approximate symmetry is invariably lost. An intuitive and qualitative explanation has been suggested (cf Solovev 1982, Robnik 1982): within the semiclassical approximation the wavefunctions are localised in non-overlapping regions prescribed by the classical invariant tori—as long as they exist. The small splitting of levels would correspond to the small overlap of exponentially decaying tails of the wavefunctions obtained if the corrections to the semiclassical approximation are taken into account.

Apart from the fine structure splittings at avoided crossings, the few lowest terms of the (quantised) Birkhoff-Gustavson normal form (8) are a good approximation as long as the ratio $r$ between two successive non-vanishing terms is small enough. We estimate this from (8) and (9), or from (16), to be of the order

$$r \simeq \gamma^2\tau^2/(-2E)^2 \simeq N^6\gamma^2.$$

If $r \ll 1$, then the approximation is fairly good because the inter-$N$ mixing is extremely weak. However, if $r \simeq 1$ (or equivalently $\gamma N^3 = BN^3/B_0 \simeq 1$), then the approximation fails, and the series starts to diverge at the very beginning. As has been pointed out (Robnik 1982), the criterion $\gamma N^3 \simeq 1$ is equivalent to the classical stochasticity criterion (for $N \gg 1$). Thus, the inter-$N$ mixing regime becomes fully developed just above the critical energy, $E_{\rm crit} = -(2N_{\rm crit}^2)^{-1} = -0.5\,\gamma^{2/3}$, beyond which the classical invariant tori are all destroyed. The caustics, and with them the localisation of wavefunctions, disappear. This is the basis of the prediction that *the law of exponentially small splittings must break down near* $\gamma N^3 \simeq 1$ and beyond this threshold. Hence, for $N \geqslant N_{\rm crit} \simeq \gamma^{-1/3}$ the inter-$N$ mixing is strong†, resulting in the usual avoided crossings and thereby building up the quasi-Landau regime eventually. Similar conclusions can be drawn from a recent group theoretical treatment by Delande and Gay (1984). The power series for the levels as a function of the field that they obtain is not known to converge, and it is most likely only an asymptotic series. It certainly does not describe the exponentially small splittings ($\exp(-N)$) at avoided crossings, consistent with its asymptotic nature. The coefficients in the power series are the same as those obtained from the quantum perturbation theory, and therefore more accurate than the semiclassical results of our present work.

Finally we should mention that we have done the calculations for the full four-dimensional KS transformation ($m$ arbitrary) and confirmed that the quality of the approximation is not improved. For example, for the ground state we found $E = -\frac{1}{2} + 5\gamma^2/16 + \ldots$.

† At the laboratory field strength, e.g. $B = 4.7 \times 10^4$ G ($\gamma = 2 \times 10^{-5}$), one has $N_{\rm crit} \simeq 37$.

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