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Rayleigh–Schrödinger perturbation theory with a strong perturbation: the quadratic Zeeman effect in hydrogen

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Abstract. The ground state energy of a hydrogen atom in a uniform magnetic field has been computed by means of low-order variational-perturbation theory. High accuracy is obtained for arbitrary field strengths up to 10^{12} G by the simple expedient of including the leading effect of the field in the zero-order model.

1. Introduction

The solution of Schrodinger's equation for a spinless non-relativistic hydrogen atom in a uniform magnetic field (HAMF) continues to attract considerable theoretical interest. The weak-field Rayleigh–Schrödinger (RS) perturbation theory (PT) energy coefficients are known accurately and to high order for both ground and excited states. However, the RSPT energy series are *divergent*, and there have been several efforts to devise summation techniques which are capable of providing high accuracy over the whole range of field strengths of interest (see, for example, Cizek and Vrscay 1982, Silverman 1983).

In spite of the fundamental importance of this analysis, it is intuitively clear that the weak-field RSPT expansion is not immediately suitable for describing the effect of an *intense* field; a more realistic description is provided by the *infinite*-field limit, which consists of a harmonic oscillator model with the Coulomb interaction playing the role of perturbation. In fact, Cohen and Herman (1981, to be referred to as CH) have shown that separate *suitably scaled* low-order RSPT treatments provide fairly accurate energies at low and high field strengths respectively. The CH calculations suffer from the need to treat the weak-field and intense-field limits separately, and there is also some inevitable loss of accuracy at intermediate field strengths. A more satisfactory zero-order model should clearly combine the essential features of both the weak- and strong-field limits. The resulting unified treatment may then be expected to be effective at all field strengths.

In the present work, we again employ the same basic methods as CH. Formally, our procedure may be summarised as follows. Given the Hamiltonian

$$H(p) = H_0 + pH_1 \tag{1}$$

in which p measures the strength of the perturbation while H_0, H_1 are *independent* of p, we write in place of (1)

$$H(p) = \lim_{q\to 1} \tilde{H}(p, q) \tag{2}$$

where

$$\tilde{H}(p, q) = \tilde{H}_0(p) + q\tilde{H}_1(p) \tag{3}$$

and allow $\tilde{H}_0$, $\tilde{H}_1$ to be p dependent. The *dummy* parameter q will be set equal to unity at the end of the calculation, so that convergence of the q-perturbation series needs to be established only for $0 \leq q \leq 1$. By contrast, the range of the *physical* parameter p is *infinite* ($0 \leq p < \infty$), so that we may expect convergence of the p-perturbation series *for all p of interest* only under very restricted conditions. But with a suitable choice of $\tilde{H}_0(p)$, we may hope to demonstrate the validity of the q expansion at $q = 1$ (numerically, if necessary). In practice, RSPT wavefunctions are calculated only through first order, but with an additional linear variational parameter. The resulting energies (some of which are *upper bounds*) show high accuracy, in spite of the simplicity of the model $\tilde{H}_0(p)$ adopted, and the resulting wavefunctions.

2. Strong-field wavefunctions and energies

The non-relativistic Hamiltonian of a spinless hydrogenic atom of nuclear charge Z, placed in a uniform magnetic field $\boldsymbol{B}$ in the z direction, is in atomic units (au)

$$H = -\tfrac{1}{2}\nabla^2 - Z/r + \tfrac{1}{2}\gamma L_z + \tfrac{1}{8}\gamma^2 r^2 \sin^2\theta. \tag{4}$$

The natural perturbation parameter γ is related to the field strength B by means of (cf Garstang 1977)

$$\gamma = B/B_0 \qquad B_0 = 2.3505 \times 10^9\ \text{G} \tag{5}$$

and L_z (the orbital angular momentum operator in the field direction) commutes with H for all γ, so that m is a good quantum number for all field strengths. For $m = 0$ states, $\langle L_z \rangle = 0$ and we have effectively

$$H = -\tfrac{1}{2}\nabla^2 - Z/r + \tfrac{1}{8}\gamma^2 r^2 \sin^2\theta. \tag{6}$$

We first adopted a simple *product* of the two functional forms described by CH, which after a suitable scaling transformation $r \to r/\alpha$ implies the following choice of approximate wavefunction:

$$\psi_0 = N \exp[-(r + \tfrac{1}{2}\mu r^2)]. \tag{7}$$

This allows us to construct $\tilde{H}_0$ and $\tilde{H}_1$ (for simplicity of presentation we suppress the physical parameter γ):

$$\tilde{H}_0 = -\tfrac{1}{2}\nabla^2 - 1/r + \mu r + \tfrac{1}{2}\mu^2 r^2 \tag{8}$$

and

$$\tilde{H}_1 = \lambda/r - \mu r + \tfrac{1}{2}(\nu - \mu^2)r^2 - \tfrac{1}{2}\nu r^2 P_2(\cos\theta), \tag{9}$$

where $P_2(\cos\theta)$ is the usual Legendre polynomial, and we have written for convenience

$$\lambda = 1 - Z/\alpha \qquad \mu = \beta/\alpha^2 \qquad \nu = \gamma^2/6\alpha^4. \tag{10}$$

The two parameters $\alpha(\gamma)$ and $\beta(\gamma)$ vary with the field strength, and it is expected that $\beta \to 0$ as $\gamma \to 0$ while $\alpha \to 0$ as $\gamma \to \infty$. We note here that ψ_0 approaches its correct limiting form as $\gamma \to 0$, but *not* as $\gamma \to \infty$; we will return to this point below.

Standard RSPT now yields energies in *scaled* (α^2) *au*

$$E_0 = -\tfrac{1}{2} + \tfrac{3}{2}\mu \tag{11}$$

and

$$E_1 = \lambda\langle 1/r\rangle_0 - \mu\langle r\rangle_0 + \tfrac{1}{2}(\nu - \mu^2)\langle r^2\rangle_0 \tag{12}$$

the calculation of the expectation values

$$\langle r^n\rangle_0 = 4\pi N^2 \int_0^\infty \exp[-(2r + \mu r^2)] r^{n+2}\, \mathrm{d}r \tag{13}$$

is deferred to appendix 1. The energy through first order is simply $\alpha^2(E_0 + E_1)$, and may be optimised by variation of α and β. The results naturally show some improvement over both single parameter models of CH and table 1 contains the optimal values of the parameters and corresponding energies. (We have set $Z = 1$ to facilitate comparison with earlier work.)

Table 1. Ground state energies of a hydrogen atom in a uniform magnetic field (in au), $\psi_0 = N\exp(-r - \frac{1}{2}\mu r^2)$.

			Perturbation sums					
γ	α	β	(1)	(2)	(3)	E_{var}	E_{geom}	Accurate†
0.1	0.9976	0.0049	−0.497 52	−0.497 53	−0.497 53	−0.497 53	−0.497 53	−0.497 53
0.2	0.9916	0.0182	−0.490 31	−0.490 38	−0.490 38	−0.490 38	−0.490 38	−0.490 38
0.5	0.9687	0.0872	−0.445 84	−0.447 05	−0.447 18	−0.447 19	−0.447 20	−0.447 21
1.0	0.9401	0.2385	−0.323 71	−0.330 02	−0.330 63	−0.330 65	−0.330 70	−0.331 17
2.0	0.9095	0.5793	0.009 09	−0.014 27	−0.020 46	−0.022 08	−0.022 69	−0.022 23
3.0	0.8934	0.9305	0.400 52	0.354 61	0.341 09	0.337 33	0.335 45	0.335 39
4.0	0.8729	1.306	0.824 67	0.754 11	0.732 61	0.726 69	0.723 14	0.719 13
5.0	0.8625	1.679	1.269 9	1.173 0	1.142 0	1.133 2	1.127 3	1.119 8
10.0	0.7923	3.458	3.680 1	3.472 4	3.385 2	3.344 0	3.322 1	3.256 4
100	0.5022	39.35	53.916	51.070	49.940	49.553	49.195	46.211

(1) First-order sum.
(2) Second-order sum.
(3) Third-order sum.
† From Cizek and Vrscay (1982) and Silverman (1983).

The form of $\tilde{H}_1$ in (9) implies that the first-order RSPT solution ψ_1 has the functional form

$$\psi_1 = \psi_0[f_0(r) - \tfrac{1}{2}\nu f_2(r) P_2(\cos\theta)] \tag{14}$$

leading to two independent equations for f_0 and f_2. Neither of these admits of a simple analytical solution, and we have therefore used the variational procedure of Hylleraas (1930), adopting for f_i ($i = 0, 2$) simple polynomial forms

$$f_i = \sum_{n=1}^{M} a_{in} r^n \qquad (i = 0, 2). \tag{15}$$

This procedure shows rapid convergence with increasing M.

The resulting second- and third-order energies and the normalisation integral $\langle\psi_1|\psi_1\rangle$ may now be used to compute the following *variational upper bound* (Dalgarno and Stewart 1961):

$$E_{var} = \alpha^2(E_0 + E_1 + rE_2) \tag{16}$$

where r satisfies the equation

$$\langle\psi_1|\psi_1\rangle r^2 + (1 - E_3/E_2)r - 1 = 0. \tag{17}$$

(In our calculations, the parameters α and β were kept fixed at the same values which optimise $\alpha^2(E_0 + E_1)$, and were not recalculated. Thus, our values of E_{var} are not fully optimised.)

Table 1 contains perturbation sums through first, second and third order, which show steady convergence towards the most accurate values available (Cizek and Vrscay 1982, Silverman 1983). In addition, we list variational bounds from (16), as well as results of the *geometric approximation*:

$$E = \alpha^2[E_0 + E_1 + E_2/(1 - E_3/E_2)] \tag{18}$$

which may be expected to be a good approximation to the variational upper bound (16), particularly when $\langle\psi_1|\psi_1\rangle$ is *small* (cf equation (17) above); however, (18) is *not* a rigorous bound.

The accuracy of all these results is high for low field strengths γ, but is clearly deteriorating rapidly with increasing γ. This is a consequence of our choice of ψ_0 (cf equation (4) above), which is spherically symmetric at all field strengths, whereas in the intense-field limit, the system Hamiltonian (6) possesses essentially *cylindrical* symmetry. It would be necessary to calculate several higher-order RSPT corrections in order to overcome this basic defect in ψ_0, and although such calculations are quite feasible, we preferred an alternative procedure, outlined below.

3. Intense-field wavefunctions and energies

An alternative choice of ψ_0 (which is *correct* asymptotically, see below) is

$$\psi_0 = N \exp[-(r + \tfrac{1}{2}\mu r^2 \sin^2\theta)]. \tag{19}$$

This ψ_0 corresponds to a somewhat different choice of $\tilde{H}_0$, $\tilde{H}_1$:

$$\tilde{H}_0 = -\tfrac{1}{2}\nabla^2 - 1/r + (\mu r + \tfrac{1}{2}\mu^2 r^2)\sin^2\theta \tag{20}$$

$$\tilde{H}_1 = \lambda/r - (\mu r + \tfrac{1}{2}\bar{\nu} r^2)\sin^2\theta \tag{21}$$

where λ and μ are as in equation (7) above, and $\bar{\nu}$ is given by

$$\bar{\nu} = \mu^2 - 3\nu/2 = \mu^2 - \gamma^2/4\alpha^4. \tag{22}$$

This choice (19) has the correct cylindrical symmetry in the intense (superstrong)-field limit $\gamma \to \infty$, and is actually a generalisation of the trial function suggested by Rau *et al* (1975). We note here that if taken alone, the high-field portion of (19), $\exp(-\tfrac{1}{2}\mu r^2 \sin^2\theta)$, leads to *divergence* in first-order RSPT, and was therefore discarded in favour of the spherically symmetric function in CH. Inclusion of the low-field exponential in (19) has the additional effect of a *convergence factor* as well as improving the accuracy of the description in the intense-field limit.

Straightforward calculation now yields in scaled (α^2) au

$$E_0 = -\tfrac{1}{2} + \mu \tag{23}$$

and

$$E_1 = \lambda\langle 1/r\rangle_0 - \mu\langle r\sin^2\theta\rangle_0 - \tfrac{1}{2}\nu\langle r^2\sin^2\theta\rangle_0 \tag{24}$$

the calculation of these *two-dimensional* integrals is described in appendix 2. As before, the energy through first order is optimised through variation of α and β, leading to the values given in table 2. It will be seen that for all $\gamma \geq 5$, these energies corrected through *first* order only are lower (and therefore more accurate) than those described above corrected through *third* order; this is a direct consequence of the correct asymptotic behaviour of the present ψ_0.

Table 2. Ground state energies of a hydrogen atom in a uniform magnetic field (in au), $\psi_0 = N\exp(-r - \tfrac{1}{2}\mu r^2 \sin^2\theta)$.

			Perturbation sums			
γ	α	β	(1)	(2)	E_{var}	Accurate†
0.1	0.9892	0.0150	−0.497 47	−0.497 48	−0.497 53	−0.497 53
0.2	0.9895	0.0291	−0.490 27	−0.490 28	−0.490 29	−0.490 38
0.5	1.009	0.0845	−0.446 83	−0.447 11	−0.447 07	−0.447 21
1.0	1.032	0.2322	−0.329 56	−0.330 77	−0.330 52	−0.331 17
2.0	1.084	0.5665	−0.017 63	−0.021 46	−0.020 86	−0.022 23
3.0	1.128	0.9269	0.342 98	0.336 39	0.337 17	0.335 39
4.0	1.131	1.308	0.729 46	0.718 92	0.721 94	0.719 13
5.0	1.196	1.692	1.132 4	1.120 7	1.122 7	1.119 8
10.0	1.310	3.723	3.275 8	3.257 3	3.257 5	3.256 4
20.0	1.450	8.004	7.824 5	7.786 2	7.792 5	7.784 7
100	2.072	41.88	46.361	46.263	46.275	46.211
200	2.180	90.06	95.433	95.297	95.318	95.273
300	2.230	140.0	144.82	144.65	144.67	144.65
1000	2.557	490.0	492.72	492.40	492.44	492.36
2000	2.830	990.0	991.22	990.80	990.85	990.70

(1) First-order sum.
(2) Second-order sum.
† From Cizek and Vrscay (1982) and Silverman (1983).

In principle, these results may also be improved by means of RSPT. However, in this case, the forms of ψ_0, $\tilde{H}_0$ and $\tilde{H}_1$ imply that ψ_1 has the form of an *infinite* sum:

$$\psi_1 = \psi_0 \sum_{n=0}^{\infty} f_{2n}(r) \sin^{2n}\theta. \tag{25}$$

The radial functions $f_{2n}(r)$ are thus unfortunately coupled together, so that a full variational determination of ψ_1 will involve extensive calculation. We have preferred to truncate ψ_1 after its leading term $f_0(r)$, a procedure which still yields an *upper bound* to E_2 (though not to E_3); furthermore the variational upper bound (16) also remains valid, and results based on it are presented in table 2. In view of the approximate nature of ψ_1, we list perturbation sums through first and second order only, as well as the variational bounds (16). In this case, the approximate ψ_1 leads to approximate values of E_3 which are positive, so that the perturbation sums through second order (which are *not* rigorous bounds to the energy) are slightly closer to the most accurate values than our variational bounds (16). Nevertheless, the accuracy of these results is impressive, especially for $\gamma > 10$.

4. Discussion and conclusions

Both zero-order functions include the leading effect of the magnetic field, so that there is no catastrophic loss of accuracy even through first order at any field strength. The variational parameters α and β approach their various limiting values smoothly, but in the case of the ψ_0 of (19), we note that α is not approaching zero as $\gamma \to \infty$. This is presumably a further indication of the divergent energy expansion which stems from $\exp(-\frac{1}{2}\mu r^2 \sin^2 \theta)$. Similar behaviour was observed by Rau *et al* (1975).

The two zero-order functions differ mainly in their *angular* characteristics, (7) being spherically symmetric, while (19) has the formal expansion

$$\psi_0 = \sum_{n=0}^{\infty} R_{2n}(r) P_{2n}(\cos \theta). \tag{26}$$

From the results of Cabib *et al* (1972) it is known that the exact solution has an expansion of this form, and that the weights of the higher angular terms increase with the field strength. Our results at intense fields suggested that a major portion of the exact angular function behaviour is already included in our simple function (19).

Our procedures may be extended to excited states of hydrogen and to many-electron systems without substantial changes to the formalism, and it is anticipated that results of similar quality will be obtained for intense fields.

Appendix 1. One-dimensional integrals

The function ψ_0 of equation (7) leads to the integrals

$$\langle r^n \rangle_0 = 4\pi N^2 I_{n+2} = I_{n+2}/I_2 \tag{A.1}$$

where we write I_n for $I_n(\mu)$ and

$$I_n = \int_0^{\infty} r^n \exp[-(2r + \mu r^2)] \, dr. \tag{A.2}$$

The following recurrence relations are easily derived by partial integration:

$$\mu I_1 + I_0 = \tfrac{1}{2} \tag{A.3}$$

and

$$\mu I_{n+2} + I_{n+1} = \tfrac{1}{2}(n+1) I_n \qquad (n \geqslant 0). \tag{A.4}$$

Furthermore, I_0 is given in terms of the complementary error function (cf Abramowitz and Stegun 1972):

$$I_0 = \tfrac{1}{2}(\pi/\mu)^{1/2} \exp(1/\mu) \operatorname{erfc}(1/\mu^{1/2}). \tag{A.5}$$

Equation (A.4) has been found to be unstable when employed with n increasing, particularly for small μ. However, it is stable when used with n decreasing. In this case, initial values of I_n for large n are obtained numerically using standard Gauss–Laguerre procedures.

We note that I_n may also be expressed in terms of integrals of the complementary error function or of parabolic cylinder functions, but recursive calculation of these has been found to suffer from the same instabilities as equation (A.4).

Appendix 2. Two-dimensional integrals

The function ψ_0 of equation (19) leads to the integrals

$$\langle r^n \sin^{2m} \theta\rangle_0 = 4\pi N^2 J^m_{n+2} = J^m_{n+2}/J^0_2 \tag{A.6}$$

where

$$J^m_n = \int_0^\infty \sin^{2m+1} \theta \, d\theta \int_0^\infty r^n \exp[-(2r+\mu r^2 \sin^2 \theta)] \, dr. \tag{A.7}$$

Partial integrations, with respect to r or θ or both, lead to several recurrence relations; in particular

$$\mu J^0_{n+2} + J^0_{n+1} - \tfrac{1}{2} n J^0_n = n!/2^{n+1} \qquad (n \geqslant 0) \tag{A.8}$$

and

$$\mu J^m_{n+2} + J^m_{n+1} + (m - \tfrac{1}{2}n) J^m_n = m J^{m-1}_n \qquad (n \geqslant 0;\ m \geqslant 1). \tag{A.9}$$

For (A.8) the initial value J^0_1 is required. This is obtained conveniently by use of *parabolic* coordinates, in terms of which

$$J^0_1 = \tfrac{1}{2} \int_0^\infty e^{-x} \, dx \int_0^\infty e^{-y(1+\mu x)} \, dy = \frac{1}{2\mu} \exp\left(\frac{1}{\mu}\right) E_1\left(\frac{1}{\mu}\right) \tag{A.10}$$

where $E_1(x)$ denotes the exponential integral (cf Abramowitz and Stegun 1972).

The use of (A.9) requires additional initial values; however, in the present work, it was more convenient to calculate the required J^m_n for $m = 1$ by means of the differential relationship

$$\mu J^{m+1}_{n+2} = -dJ^m_n/d\mu \qquad (m, n \geqslant 0). \tag{A.11}$$

Equation (A.8) is unstable for small μ and n increasing, but is stable with n decreasing. Initial values of J^0_n with large n were obtained numerically.

Note added in proof. After this work was submitted for publication, a paper by A V Turbiner (1984 *J. Phys. A: Math. Gen.* **17** 859–75) appeared which treats both ground and excited states by methods quite similar to ours. However, Turbiner's ground-state energies are less accurate than those obtained here.

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