

# NEW RELATIVISTIC ZEEMAN SPECTROSCOPY IN ATOMIC HYDROGEN

by

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## ABSTRACT

A novel type of Zeeman spectroscopy is inferred by realizing that the main kinetic energy term in the ECE fermion equation (or chiral Dirac equation), is defined by relativistic momentum. The Lorentz factor is calculated without using the rough Dirac approximation, which effectively reduces the relativistic momentum to the classical momentum. Quantization shows that the Zeeman effect develops an intricate new spectral structure, which is exemplified with the 2p to 3d (visible) and 4p to 5d (infra red) transitions of atomic hydrogen. The former is split into nine lines, and the latter into forty five lines. These can be resolved with double resonance techniques, providing an entirely new spectroscopy.

Keywords: ECE2 theory, ECE fermion equation, new Zeeman spectroscopy.

UFT 331



## 1. INTRODUCTION

In recent papers of this series {1 - 12} the consequences of ECE2 theory have been developed systematically in UFT313 - 321 and UFT322 to 330. The central characteristic of ECE2 is that its field equations have the same structure as the Maxwell Heaviside (MH) field equations, so ECE2 has the property of being Lorentz covariant in a space in which both torsion and curvature are non zero. ECE2 can therefore be developed with the well known equations of special relativity, with the added advantage of being able to define the four potentials of electromagnetism and gravitation to spacetime torsion and curvature. The latter therefore become routinely observable in well known spectral techniques based on special relativity, notably fine structure in atomic and molecular spectra, ESR, NMR and MRI.

In this paper, the well known Zeeman splitting of atomic spectra by a magnetic field is shown to have a hitherto unknown relativistic counterpart that produces entirely new and very rich fine structure. The latter can be resolved with well known double resonance techniques and is of immediate interest in the analytical laboratory. In Section two this fine structure is shown to be the result of correctly developing the main kinetic energy term of the fermion equation with the correctly relativistic linear momentum. The Lorentz factor of the relativistic momentum is worked out by discarding the rough Dirac approximation and replacing it with the correct definition of the Lorentz factor in terms of classical velocity and classical momentum. Upon quantization this leads to a new type of Zeeman effect in which the energetic degeneracy of the non relativistic Zeeman effect theory is lifted, thus resolving many new lines. The theory is illustrated with the 2p to 3d and 4p to 5d transitions of atomic hydrogen (H). In Section three these new spectra are computed and illustrated as energy level diagrams.

This paper is a synopsis of detailed calculations given in the notes accompanying UFT331 on [www.aias.us](http://www.aias.us). In Note 331(1) the term responsible for the Zeeman effect is defined. In Notes 331(2) and 331(4) the first attempt is made to quantize this term, the final version of which is given in Note 331(5) and used in Section 2. Notes 331(3), 331(6) and 331(7) derive the new relativistic Zeeman spectrum in terms of energy levels.

## 2. THE NEW RELATIVISTIC ZEEMAN EFFECT.

The usual theory of the Zeeman effect is based on the classical hamiltonian:

$$H_0 = T + U \quad - (1)$$

where T is the kinetic energy and U the potential energy. The classical kinetic energy is defined by:

$$T = \frac{p_0^2}{2m} \quad - (2)$$

The influence of a magnetic field is defined through the minimal prescription:

$$\underline{p}_0 \rightarrow \underline{p}_0 - e\underline{A} \quad - (3)$$

where  $\underline{A}$  is the vector potential and e the charge on the proton, -e being the charge on the electron. The mass of the electron is denoted by m. Non relativistic quantization uses Schroedinger's rule:

$$\underline{p}_0 \psi = -i\hbar \underline{\nabla} \psi \quad - (4)$$

where  $\psi$  is the non relativistic wave function. As shown in detail in Note 331(1), the non relativistic theory contains a term:

$$H_1 = -\frac{e}{m} \underline{A} \cdot \underline{p}_0 \quad - (5)$$

in which the vector potential of a static magnetic field is defined as:

$$\underline{A} = \frac{1}{2} \underline{B} \times \underline{r} \quad - (6)$$

so the term (5) becomes:

$$\begin{aligned} H_1 &= -\frac{e}{2m} \underline{B} \times \underline{r} \cdot \underline{p}_0 = -\frac{e}{2m} \underline{B} \cdot \underline{r} \times \underline{p}_0 \\ &= -\frac{e}{2m} \underline{B} \cdot \underline{L}_0 \quad - (7) \end{aligned}$$

where:

$$\underline{L}_0 = \underline{r} \times \underline{p}_0 \quad - (8)$$

is the orbital angular momentum. As shown in UFT330, the classical hamiltonian (1)

is the limit of the relativistic hamiltonian:

$$H_0 = H - mc^2 = \frac{p^2}{(1+\gamma)m} + U \sim \frac{p^2}{2m} \left( 1 - \left( \frac{\langle \hat{H}_0 \rangle - \bar{U}}{2mc^2} \right) \right) + U \quad - (9)$$

Therefore the relativistic hamiltonian may be written as:

$$H_0 = H - mc^2 \sim \frac{p^2}{2m} + U - \dots \quad - (10)$$

Note carefully that the  $\underline{p}$  defined in Eq. (10) is the RELATIVISTIC momentum:

$$\underline{p} = \gamma \underline{p}_0 \quad - (11)$$

in which the Lorentz factor is

$$\gamma = \left(1 - \frac{p_0^2}{m^2 c^2}\right)^{-1/2} \quad - (12)$$

Therefore the relativistic hamiltonian governing the Zeeman effect is as defined and developed in Note 331(5):

$$\begin{aligned} H_1 &= -\frac{e}{2m} \left(1 - \frac{p_0^2}{m^2 c^2}\right)^{-1/2} \underline{L}_0 \cdot \underline{B} \quad - (13) \\ &\sim -\frac{e}{2m} \left(1 + \frac{1}{2} \frac{p_0^2}{m^2 c^2}\right) \underline{L}_0 \cdot \underline{B} \end{aligned}$$

when

$$p_0 \ll mc \quad - (14)$$

This hamiltonian is quantized using:

$$\hat{H}_1 \psi = -\frac{e}{2m} \left(1 + \frac{1}{2} \frac{p_0^2}{m^2 c^2}\right) \underline{B} \cdot \hat{\underline{L}}_0 \psi \quad - (15)$$

in which  $\hat{\underline{L}}_0$  is an operator and  $p_0^2$  a function.

Align the magnetic field in the Z axis to obtain:

$$\hat{H}_1 \psi = -\frac{e}{2m} \left(1 + \frac{1}{2} \frac{p_0^2}{m^2 c^2}\right) B_z \hat{L}_{0z} \psi \quad - (16)$$

where

$$\hat{L}_{0z} = m_L \hbar \psi \quad - (17)$$

with

$$m_L = -L, \dots, L \quad - (18)$$

Here  $\hbar$  is the reduced Planck constant,  $L$  is the orbital angular momentum quantum number, and  $m_L$  the azimuthal quantum number. The energy levels are given by the expectation value:

$$H_1 = \langle \hat{H}_1 \rangle = -\frac{e\hbar}{2m} \left( 1 + \frac{1}{2} \frac{P_0^2}{m^2 c^2} \right) m_L \quad (19)$$

in which:

$$\frac{P_0^2}{2m} = \left\langle \frac{\hat{P}_0^2}{2m} \right\rangle \quad (20)$$

Therefore the energy levels are:

$$H_1 = -\frac{e\hbar}{2m} m_L \left( 1 + \frac{1}{m c^2} \left\langle \frac{\hat{P}_0^2}{2m} \right\rangle \right) \quad (20)$$

$$= -\frac{e\hbar}{2m} m_L \left( 1 - \frac{\hbar^2}{4m^2 c^2} \int \psi^* \nabla^2 \psi d\tau \right)$$

In a rigorous development  $\psi$  must be the relativistic wave function of an atom or molecule.

To illustrate the new spectroscopy consider the simplest atom, atomic hydrogen H, and approximate the relativistic wave functions with the non relativistic hydrogenic wavefunctions. In H this is a plausible approximation, because the spin orbit fine structure splitting is small. So for H in this approximation:

$$\left\langle \frac{\hat{P}_0^2}{2m} \right\rangle = \frac{m e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^3} \quad (21)$$

and the hamiltonian of the relativistic Zeeman effect is:

$$H_1 = \frac{e\hbar}{2m} m_L \left( 1 + \frac{e^4}{32\pi^2 \epsilon_0^2 \hbar^2 c^2 n^3} \right) \quad (22)$$

Here  $\epsilon_0$  is the S. I. vacuum permittivity,  $c$  the vacuum speed of light and  $n$  the principal

quantum number. The result (22) can be expressed as:

$$H_1 = -\frac{e\hbar}{2m} m_L \left( 1 + \frac{1}{2} \left( \frac{\lambda_c}{a_0} \right) \frac{\alpha}{n^2} \right) \quad (23)$$

where

$$\lambda_c = \frac{\hbar}{mc} = 3.861591 \times 10^{-13} \text{ m} \quad (24)$$

is the Compton wavelength, where

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2} = 5.29177 \times 10^{-11} \text{ m} \quad (25)$$

is the Bohr radius, and where

$$\alpha = \frac{e^2}{4\pi\hbar c \epsilon_0} = 0.007297351 \quad (26)$$

is the fine structure constant. So the relativistic Zeeman effect hamiltonian is:

$$H_1 = \langle H_1 \rangle = -\frac{e\hbar}{2m} m_L B_z \left( 1 + \frac{2.662567 \times 10^{-5}}{n^2} \right) \quad (27)$$

This is added to the energy levels of the H atom.

In the first approximation, assume that these energy levels are the non relativistic:

$$E_0 = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2 n^2} \quad (28)$$

The usual non relativistic Zeeman effect is therefore:

$$E_1 = E_0 - \frac{e\hbar}{2m} m_L B_z \quad (29)$$

and the new relativistic Zeeman effect is:





$$\begin{array}{l}
 2p \left( \begin{array}{l} n=2, L=1, m_L=0 \\ \\ \\ \end{array} \right) \rightarrow 3d \left( \begin{array}{l} n=3, L=2, m_L=-1 \\ \\ \\ \end{array} \right) \\
 2p \left( \begin{array}{l} " \\ " \\ " \\ \end{array} \right) \rightarrow 3d \left( \begin{array}{l} " \\ " \\ " \\ \end{array} \right) \\
 2p \left( \begin{array}{l} " \\ " \\ " \\ \end{array} \right) \rightarrow 3d \left( \begin{array}{l} " \\ " \\ " \\ \end{array} \right)
 \end{array}$$

Using these rules in the non relativistic Zeeman hamiltonian ( 29 ) produces three absorption lines ( $\Delta m_L = -1, 0, 1$ ), illustrated in Section 3. Each of these lines are made up of triply degenerate transitions occurring with the same energy. So the usual non relativistic Zeeman spectrum consists of three lines, one at the original frequency, one at a higher frequency, and one at a lower frequency. The three lines are symmetrically arranged.

However, the new relativistic hamiltonian ( 30 ) produces a hitherto unknown spectrum of nine lines as illustrated in Section 3, because the triple degeneracy is lifted. There is a symmetric central grouping, and two asymmetric groupings which are mirror images of each other. These groupings are within range of ultra high resolution double resonance spectroscopy.

Finally, Note 313(7) illustrates the new relativistic splittings in the  $n=4$  to  $n=5$  transition of atomic hydrogen at  $2,469.1 \text{ cm}^{-1}$  in the infra red. There are seventeen degenerate transitions as follows ( $\Delta m_L = 1$ ):

$$\begin{array}{l}
 1) 4s \rightarrow 5p \left( \begin{array}{l} n=4, L=0, m_L=0 \rightarrow n=5, L=1, m_L=1 \\ \\ \\ \end{array} \right) \\
 2) 4p \rightarrow 5s \left( \begin{array}{l} n=4, L=1, m_L=-1 \rightarrow n=5, L=0, m_L=0 \\ \\ \\ \end{array} \right) \\
 * 3) 4p \rightarrow 5d \left( \begin{array}{l} n=4, L=1, m_L=-1 \rightarrow n=5, L=2, m_L=0 \\ \\ \\ \end{array} \right) \\
 * 4) \quad \quad \quad \left( \begin{array}{l} " \\ " \\ " \\ \end{array} \right) \\
 * 5) \quad \quad \quad \left( \begin{array}{l} " \\ " \\ " \\ \end{array} \right) \\
 * 6) 4d \rightarrow 5f \left( \begin{array}{l} n=4, L=2, m_L=-2 \rightarrow n=5, L=3, m_L=-1 \\ \\ \\ \end{array} \right) \\
 * 7) \quad \quad \quad \left( \begin{array}{l} " \\ " \\ " \\ \end{array} \right) \\
 * 8) \quad \quad \quad \left( \begin{array}{l} " \\ " \\ " \\ \end{array} \right) \\
 * 9) \quad \quad \quad \left( \begin{array}{l} " \\ " \\ " \\ \end{array} \right) \\
 * 10) \quad \quad \quad \left( \begin{array}{l} " \\ " \\ " \\ \end{array} \right)
 \end{array}$$

* 11)	4f	→	5g	(	n=4, L=3, m <sub>L</sub> = -3	to	n=5, L=4, m <sub>L</sub> = -2	)
* 12)	"		"	(	"		"	)
* 13)	"		"	(	"		"	)
* 14)	"		"	(	"		"	)
* 15)	"		"	(	"		"	)
* 16)	"		"	(	"		"	)
* 17)	"		"	(	"		"	)

For absorption ( $\Delta L = 1$ ) there are fifteen degenerate transitions marked with an asterisk. Therefore the non relativistic hamiltonian (29) produces three Zeeman lines, each of which are fifteen fold degenerate. The relativistic hamiltonian (30) produces forty five lines in three groupings of fifteen lines as illustrated in Section 3, i.e. very rich spectrum that can be used for analytical purposes using ultra high resolution double resonance spectroscopy.

In general for an n to n + 1 absorption of atomic H there are 3 (n squared - 1) absorption lines in the new relativistic Zeeman effect. So for the n = 13 to n = 14 transition that occurs at 81.52 cm<sup>-1</sup> in the far infra red, there are 804 lines, in three groupings of 268 lines each.

Bearing in mind that H is the simplest atom, and that this is a simple first approximation theory, it becomes clear that a new spectroscopy of great utility has been inferred. This is also a severe test of the Dirac approximation and of the fundamentals of relativistic quantum mechanics.

### SECTION 3: ENERGY LEVEL DIAGRAMS

By Dr. Horst Eckardt

# New relativistic Zeeman spectroscopy in atomic Hydrogen

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## 3 Energy level diagrams

The energies of the transitions described in section 2 have been calculated. In Eqs.(29, 30) the non-relativistic energies  $E_1$  and new relativistic energies  $E_2$  of the Zeeman effect were given. The new splitting depends on the magnetic quantum number  $m_L$  as usual and, in addition, on the principal quantum number  $n$ . There is no dependence on the angular quantum number  $l$ . It is therefore sufficient to consider the transitions with highest possible  $l$  for given main quantum numbers  $n_1$  and  $n_2$ . For example the splittings of the transition

$$3p \rightarrow 4d$$

are contained in

$$3d \rightarrow 4f$$

for all possible  $m_L$  values and selection rules  $\Delta m_L = 0, \pm 1$ . For comparability of the results we plotted the relative energy differences related to the non-relativistic case. For an initial state  $i$  and final state  $f$  the spectroscopically observable energy difference is

$$\Delta E = E_f - E_i. \quad (33)$$

This difference, giving the new Zeeman splitting, is first related to the non-relativistic case. Then the splitting is normalized by dividing by  $e\hbar/(2m)$  so that a dimensionless number for the splitting is obtained:

$$\Delta E_{relative} = \frac{2m}{e\hbar} (E_f - E_i - (E_{f,non-rel} - E_{i,non-rel})). \quad (34)$$

Figs. 1-12 show all possible splittings with  $\Delta l = 1$  (absorption) and  $\Delta m_L = 0, \pm 1$  for neighboring principal quantum numbers, i.e.  $n_1 = 1 \rightarrow n_2 = 2$ ,  $n_1 = 2 \rightarrow n_2 = 3$ , etc. The diagrams are separate for each of the three selection

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rules  $\Delta m_L = 0, \pm 1$  which correspond to linear and circularly polarized light as explained in section 2. For comparability, the scale of the y axis has been chosen equal for all diagrams. For the transition  $1s \rightarrow 2p$  there is only a shift for  $\Delta m_L = \pm 1$  and no splitting because there is only one possible transition. The transition for  $\Delta m_L = 0$  is unchanged because of  $m_L = 0$ . In general the splitting is  $2l - 1$  fold where  $l$  is the quantum number of the final state. The terms are graphed in Figs. 3-12. It can be seen that the splitting becomes smaller for higher  $n$  values. This is a consequence of the factor  $1/n^2$  in Eq.(30).

In addition to the transitions between neighbouring principal quantum numbers, we have also investigated two cases with larger differences:

$$2p \rightarrow 4d$$

and

$$2p \rightarrow 5d,$$

see Figs. 13 and 14, plotted only for the selection rule  $\Delta m_L = -1$ . These diagrams should be compared with Fig. 4 which describes the corresponding splitting for  $2p \rightarrow 3d$ . The width of the splitting is somewhat enlarged and the splitting is shifted to the middle for transitions to higher  $n$ . Another general result is that the splitting is always equidistant.

The calculations have been done by a Maxima program which computes transitions between any energy levels of Hydrogen with automatic plot. The program can be obtained from the authors on request.

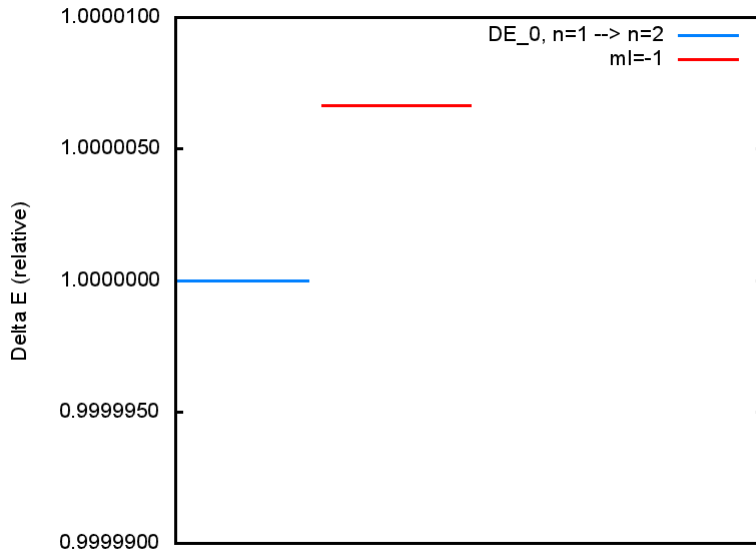


Figure 1: Term schema for  $n = 1 \rightarrow 2$ ,  $\Delta m_L = -1$ .

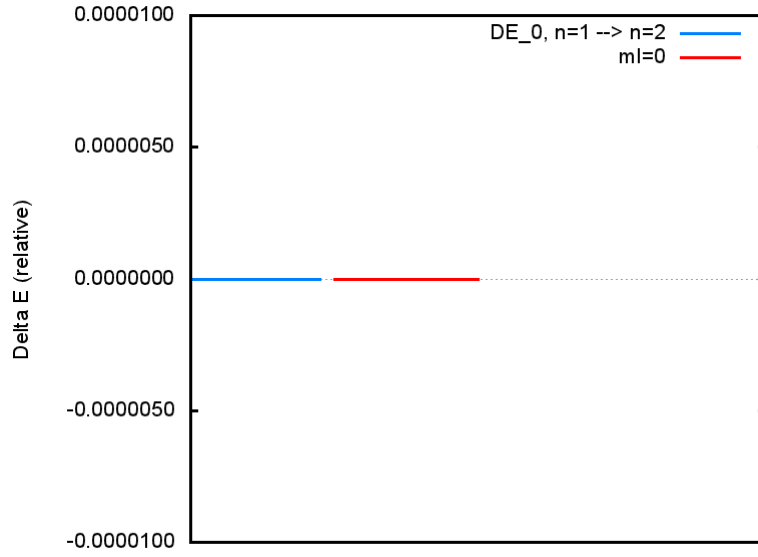


Figure 2: Term schema for  $n = 1 \rightarrow 2$ ,  $\Delta m_L = 0$ .

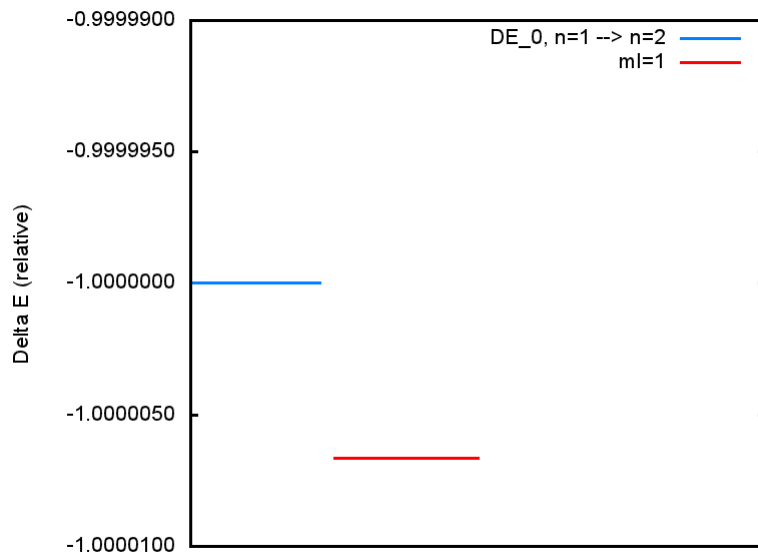


Figure 3: Term schema for  $n = 1 \rightarrow 2$ ,  $\Delta m_L = 1$ .

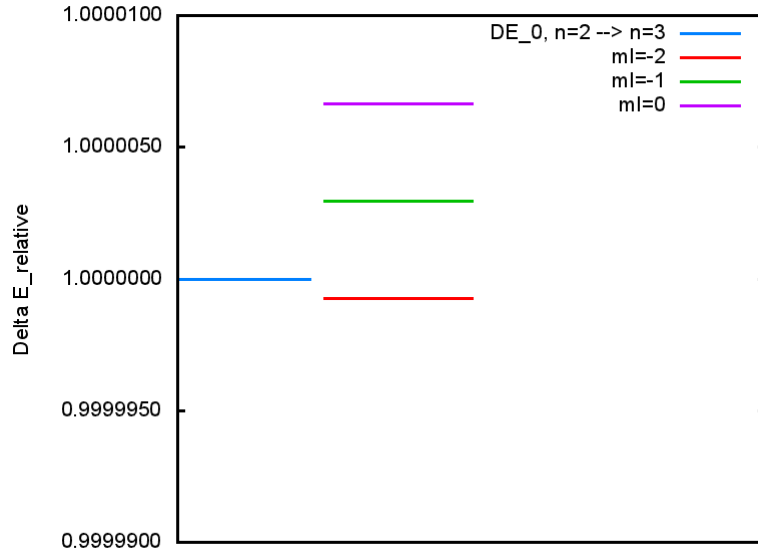


Figure 4: Term schema for  $n = 2 \rightarrow 3$ ,  $\Delta m_L = -1$ .

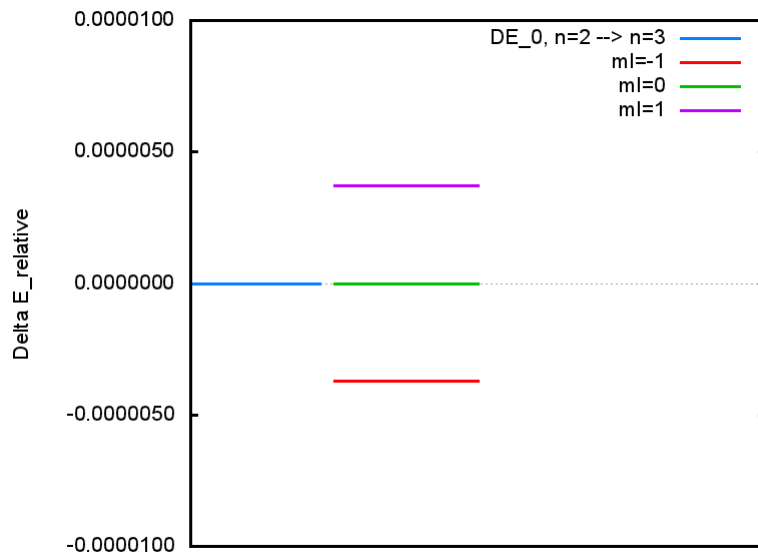


Figure 5: Term schema for  $n = 2 \rightarrow 3$ ,  $\Delta m_L = 0$ .

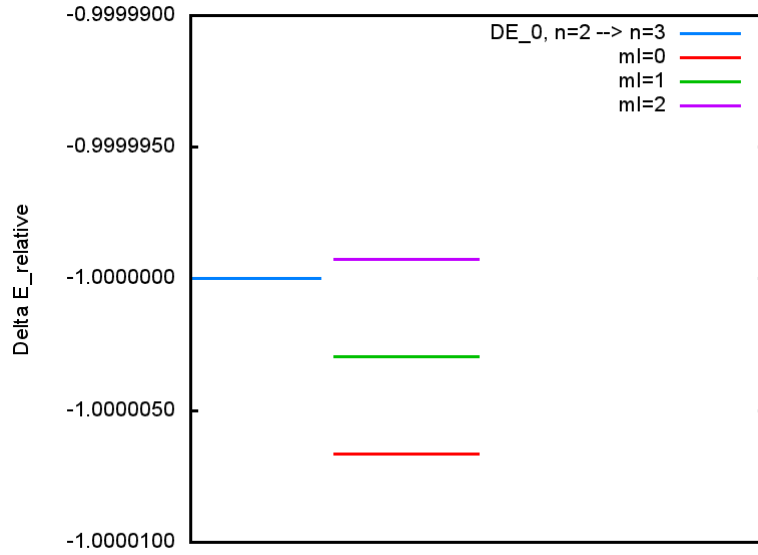


Figure 6: Term schema for  $n = 2 \rightarrow 3$ ,  $\Delta m_L = 1$ .

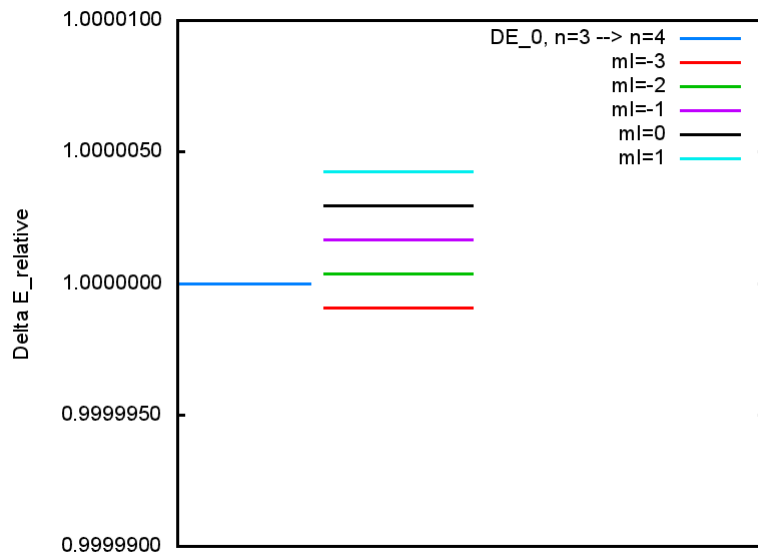


Figure 7: Term schema for  $n = 3 \rightarrow 4$ ,  $\Delta m_L = -1$ .

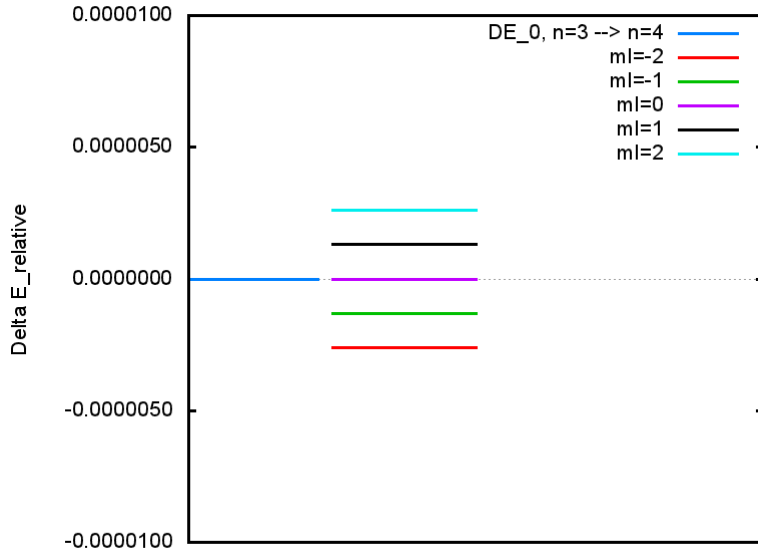


Figure 8: Term schema for  $n = 3 \rightarrow 4$ ,  $\Delta m_L = 0$ .

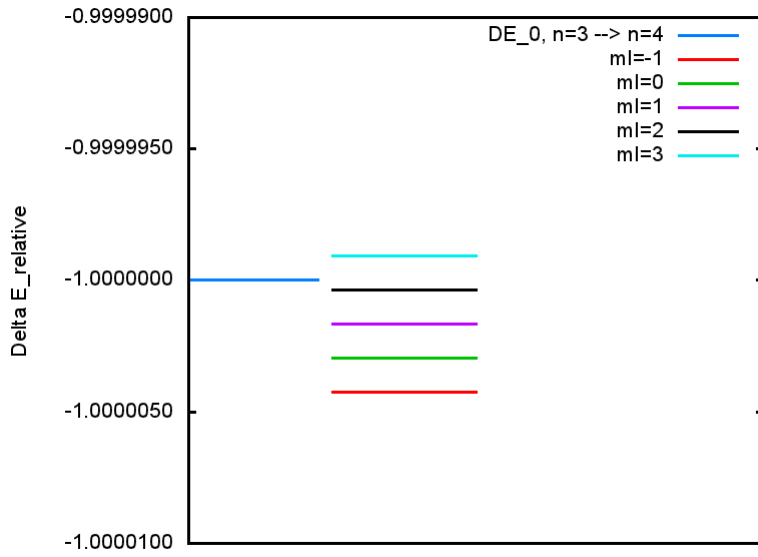


Figure 9: Term schema for  $n = 3 \rightarrow 4$ ,  $\Delta m_L = 1$ .



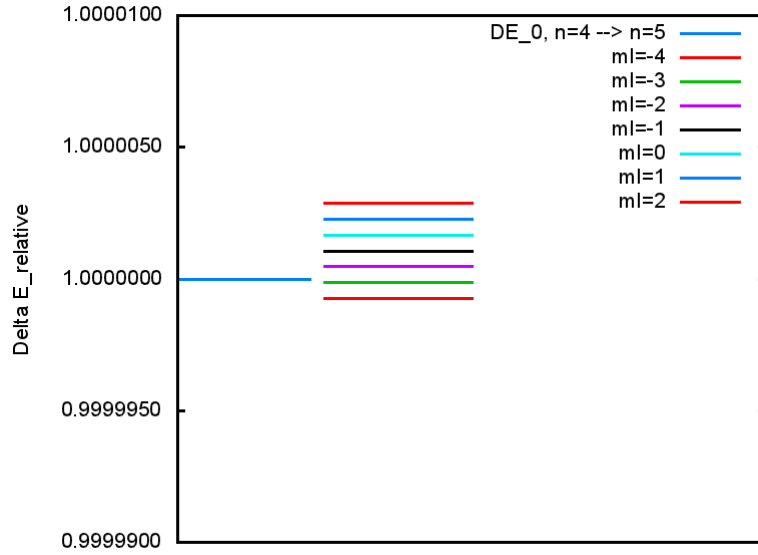


Figure 10: Term schema for  $n = 4 \rightarrow 5$ ,  $\Delta m_L = -1$ .

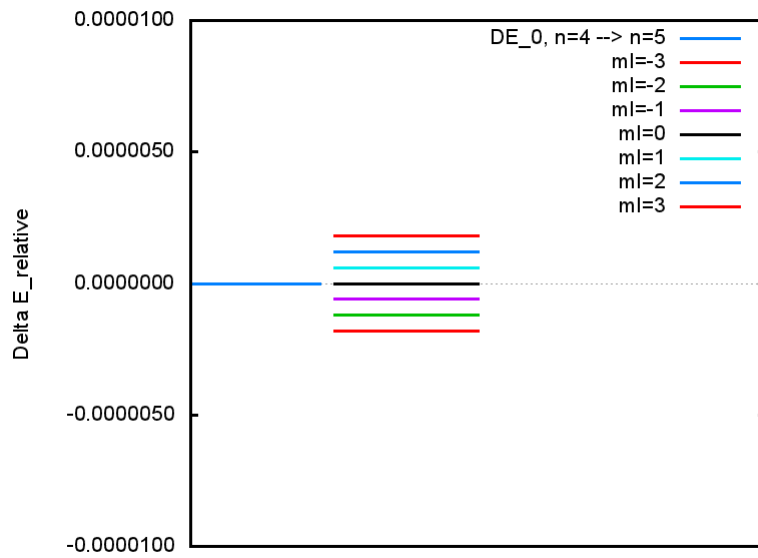


Figure 11: Term schema for  $n = 4 \rightarrow 5$ ,  $\Delta m_L = 0$ .

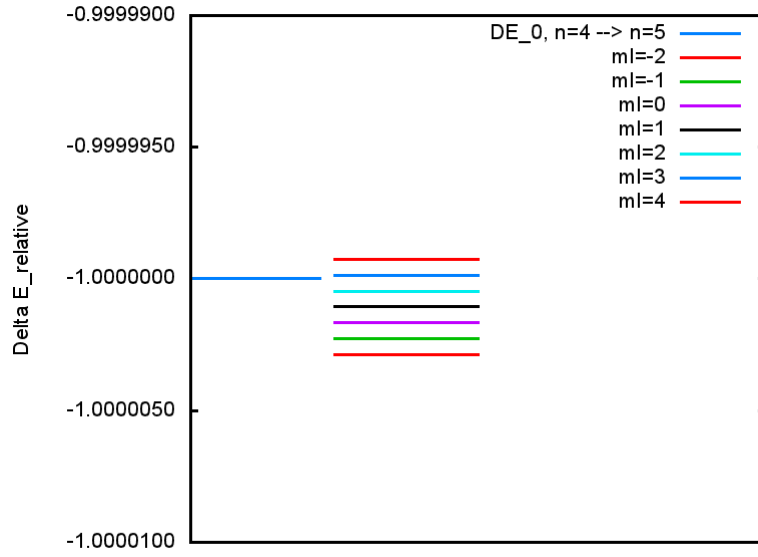


Figure 12: Term schema for  $n = 4 \rightarrow 5$ ,  $\Delta m_L = 1$ .

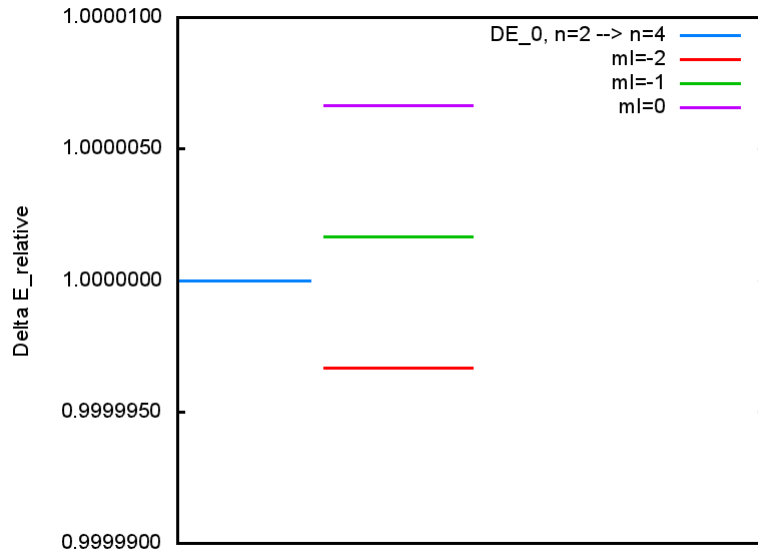


Figure 13: Term schema for  $n = 2 \rightarrow 4$ ,  $\Delta m_L = -1$ .

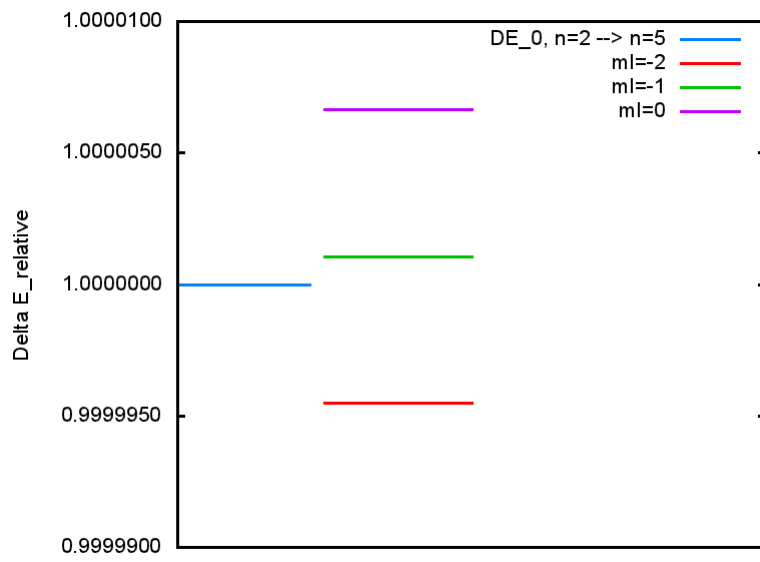


Figure 14: Term schema for  $n = 2 \rightarrow 5$ ,  $\Delta m_L = -1$ .

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