Quadratic Zeeman Effect in ^{3}He and Beyond

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Financial Support: NSERC and SHARCnet

^{3}He Magnetometry Workshop
University of Michigan
Ann Arbor, MI, October 14, 2024

Outline

1. Orders of magnitude
2. The Zeeman effect – review of basic formalism
3. The Foldy-Wouthuysen transformation
4. Quadratic Zeeman effect for ^{3}He
5. Possible wave function corrections
6. Results for $^3\text{He}^+$ for odd powers of B
7. Higher order quadratic perturbations
8. Nonrelativistic wave functions for helium and second-order perturations
9. Relativistic M1 Corrections for $^3\text{He}^+$

Not covered: nuclear polarizability and excitation, recoil, QED corrections to the linear Zeeman effect $\cdots$.

Quadratic Zeeman effect studied by J. Killingbeck, J. Phys. B **12**, 25 (1979) for hydrogen in isolation from other physical effects.

J. Phys. B 12, 25 (1979)

The quadratic Zeeman effect

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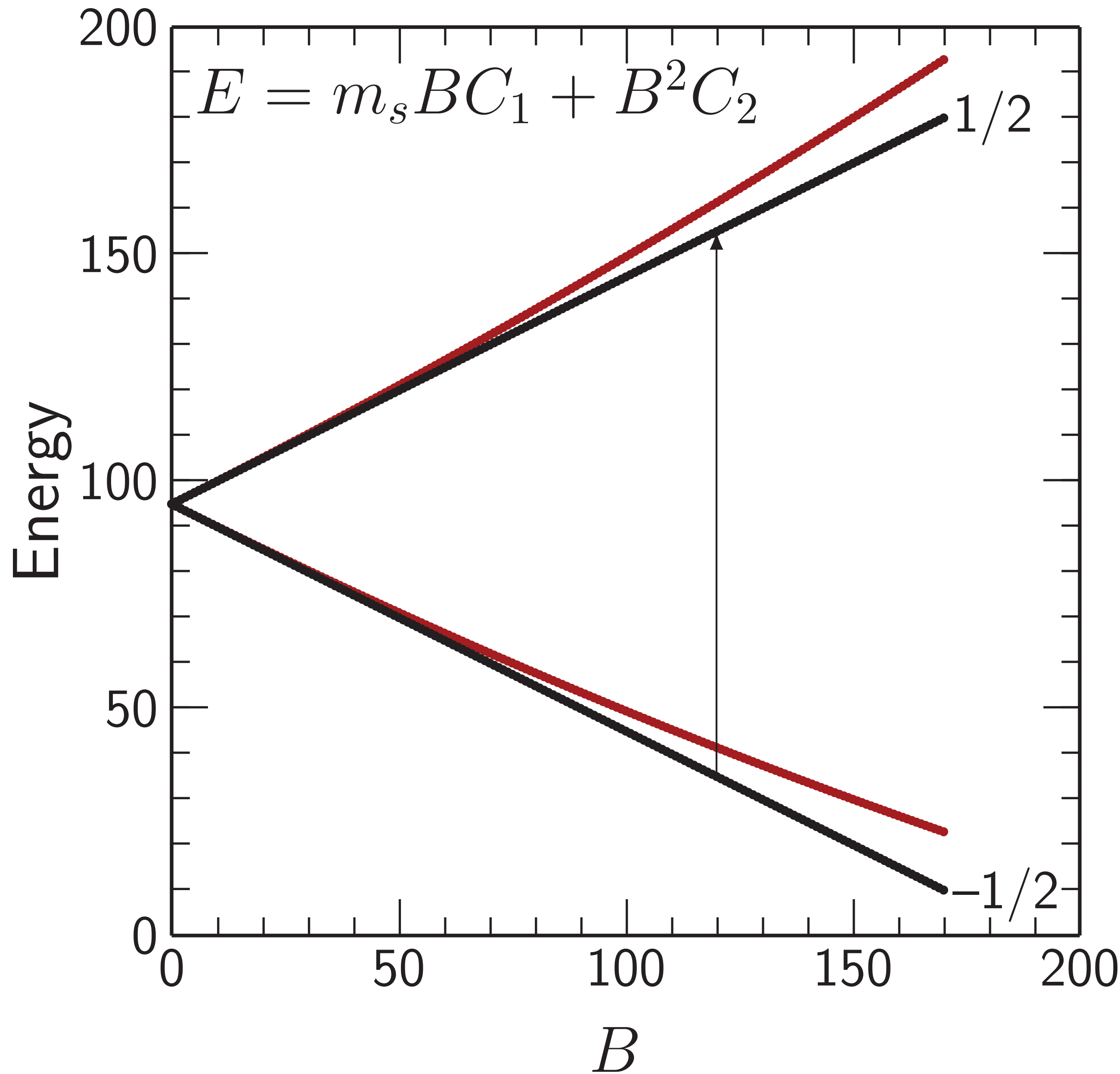
Received 6 March 1978, in final form 25 July 1978

Abstract. The hydrogen-atom quadratic Zeeman effect is treated by several techniques, and a new perturbation approach is suggested which involves numerical solution of a radial equation based on the s part of the potential. The low-field results appear to be more accurate than those of previous workers.

1. Introduction

Many papers have been written on the theory of the quadratic Zeeman effect for the hydrogen atom. Besides being deceptively simple from a theoretical viewpoint, the problem has relevance for astrophysics and also for the theory of simple excitons in solid-state physics. Garstang (1977) gives a good survey of the theory and of its applications. The vast majority of the calculations on the problem use very large matrices which are diagonalised on a computer, and there has been some discussion in the literature about the way in which continuum-type basis functions should be included to give a complete basis set. An alternative approach has been tried by Cizek and Vrscay (1977); they transformed the Hamiltonian and then treated the resulting eigenvalue problem by perturbation theory, forming Padé approximants to their energy series. For the ground-state problem they went up to about 30th order, which presumably involves considerable computation. Some of the most accurate results for the ground-state problem are those of Cabib *et al* (1972), who used a method which involves fairly large matrices as well as numerical integration of the Schrödinger differential equation. We



$E = m_s B C_1 + B^2 C_2$
1/2
−1/2
Energy
B
0
50
100
150
200
0
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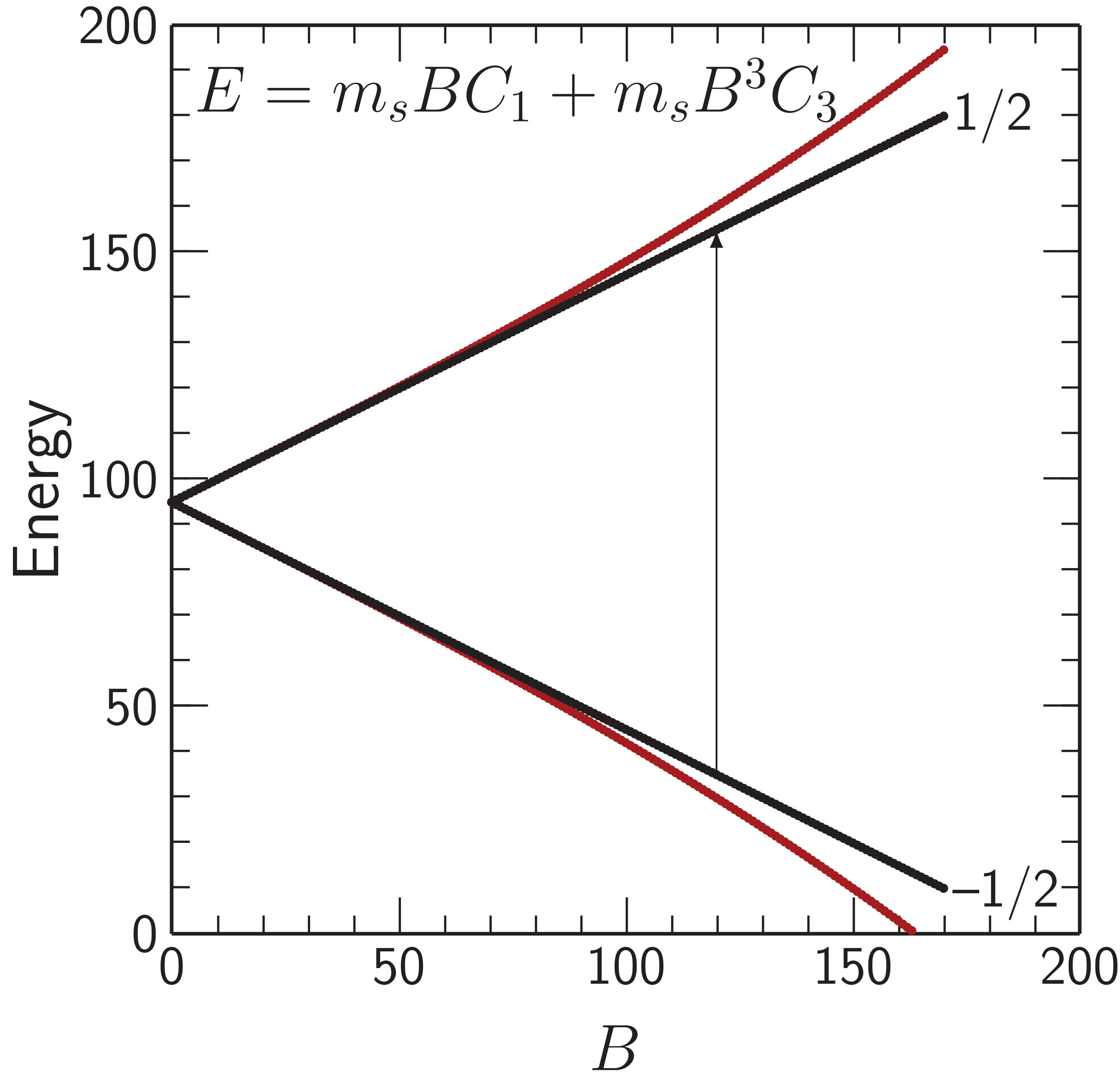
150
200



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A. Schneider et al. Nature **606**, 878 (2022)

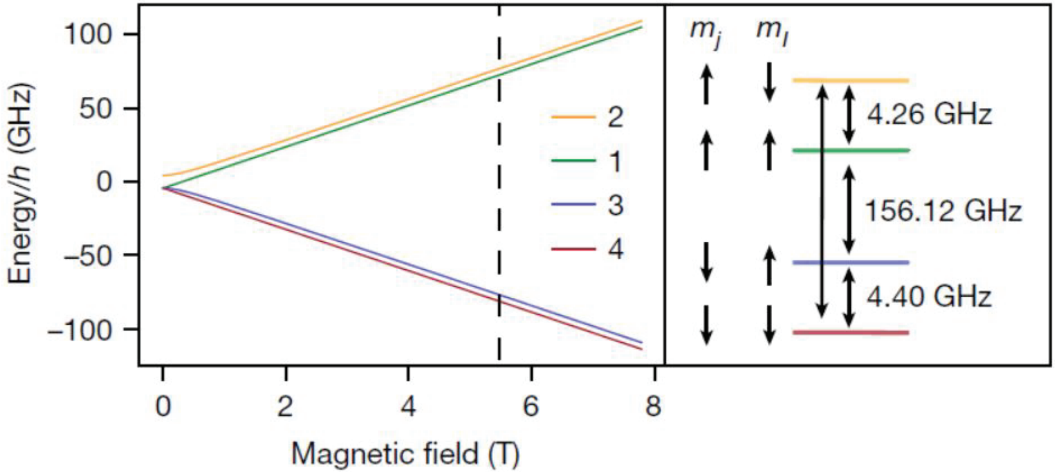


Fig. 1 | Breit–Rabi diagram of $^3He^+$. The energies of the hyperfine states E_1, E_2, E_3 and E_4 are plotted as a function of the magnetic field according to equation (1). The arrows below m_j and m_I indicate the orientation with respect to the magnetic field of the total angular momentum of the electron $j = 1/2$ and the nuclear spin $I = 1/2$, which are antiparallel to the magnetic moments μ_e and μ_I, respectively. The four double-headed arrows indicate the hyperfine transitions measured in this work. The transition frequencies given on the right side refer to the magnetic field in the Penning trap $B = 5.7$ T, which is marked in the plot by the black dashed line.

Orders of Magnitude

The atomic unit of magnetic field strength is

$$\frac{\hbar}{ea_0^2} = 2.35051757077(73) \times 10^5 \text{ T} = \kappa$$

The largest steady magnetic field ever produced is 45.22 T,
which is only 1.9×10^{-4} a.u.

At 1T, $B = 4.25 \times 10^{-6}$ a.u.

The helion to electron mass ratio is $M_{^3\mathrm{He}}/m_e = 5495.9$ and $M_p.m_e = 1836$.

For a quadratic Zeeman effect at 1 T,

$$B\frac{M_p}{m_e} = 0.007811$$

which is not that small, but it is <u>even</u> in the magnetic quantum number M.

The fine structure constant squared $\alpha^2 = 5.325 \times 10^{-5}$.

The Zeeman Effect – Review of Basic Formalism

Start from the Dirac Hamiltonian for an electron

$$H_{\rm D} = c\boldsymbol{\alpha}\cdot\boldsymbol{\pi} - \beta mc^2 + V - \frac{e\hbar}{4M_p} g_I \boldsymbol{\sigma}_{\mathsf{N}}\cdot\mathbf{B}$$

and wave function

$$\psi(\mathbf{r},\sigma_{\mathsf{N}}) = \psi_e(\mathbf{r})\chi(\sigma_{\mathsf{N}}), \quad \text{with } \sigma_{\mathsf{N}} = \uparrow \text{ or } \downarrow$$

where $\boldsymbol{\pi} = \mathbf{p} - e\mathbf{A}$, M_p is the proton mass

and $\mathbf{A}$ is the vector potential $\mathbf{A} = \frac{1}{2}B(y\hat{\mathbf{i}} - x\hat{\mathbf{j}})$

so that $\mathbf{B} = \nabla\times\mathbf{A} = B\hat{\mathbf{k}}$ is a uniform field pointing in the z-direction.

Then for the electron $H_{\rm Zeeman} = -ce\boldsymbol{\alpha}\cdot\mathbf{A} = -\frac{1}{2}ceB(x\alpha_y - y\alpha_x)$

At this level there is no obvious quadratic Zeeman effect!

The Foldy-Wouthuysen Transformation

Objective: transform away the coupling to the small component of the wave functions so that the Dirac $\boldsymbol{\alpha}$ operator gets replaced by the Pauli 2×2 $\boldsymbol{\sigma}$ operator.

i.e., find an operator S such that the unitary transformation

$$H_{\mathrm{FW}} = e^{iS}(H - i\partial_t)e^{-iS}$$

does not couple large with small components. Choose

$$S = -\frac{i}{2mc}\left\{\beta\boldsymbol{\alpha}\cdot\boldsymbol{\pi} - \frac{1}{3m^2c^2}\beta(\boldsymbol{\alpha}\cdot\boldsymbol{\pi})^3 + \frac{1}{2mc^2}[\boldsymbol{\alpha}\cdot\boldsymbol{\pi},\, V - i\partial_t]\right\}$$

References:

K. Pachucki, Phys. Rev. A **69**, 052502 (2004).

L. L. Foldy and S. A. Wouthuysen, Phys. Rev. **78**, 30 (1950).

Expand $H_{\mathrm{FW}} = e^{iS}(H - i\partial_t)e^{-iS}$ in a power series to obtain

$$\begin{aligned} H_{\mathrm{FW}} &= (1 + iS + \frac{1}{2!}(iS)^2 + \cdots)(H_{\mathrm{D}} - i\partial_t)(1 - iS + \frac{1}{2!}(iS)^2 + \cdots) \\ &= H_{\mathrm{D}} + [iS,\, H_{\mathrm{D}} - i\partial_t] + \frac{1}{2!}[iS,\, [iS,\, H_{\mathrm{D}} - i\partial_t]] + \cdots \end{aligned}$$

Finally, substitute for S from the previous slide to obtain

$$\begin{aligned} H_{\mathbf{FW}} &= \frac{\boldsymbol{\pi}^2}{2m} + V - \frac{\boldsymbol{\pi}^4}{8m^3c^2} \\ &\quad - \frac{e\hbar}{4m} g_s \boldsymbol{\sigma}\cdot\mathbf{B} - \frac{e\hbar}{4M_p} g_I \boldsymbol{\sigma}_{\mathsf{N}}\cdot\mathbf{B} \\ &\quad + \frac{e\hbar}{8m^2c^2}[\hbar\nabla\cdot\mathbf{E} + \boldsymbol{\sigma}\cdot(\mathbf{E}\times\boldsymbol{\pi} - \boldsymbol{\pi}\times\mathbf{E})] \\ &\quad + \frac{e\hbar}{4m^3c^2}\boldsymbol{\pi}^2\boldsymbol{\sigma}\cdot\mathbf{B} \end{aligned}$$

with $g_s \simeq -2$ and $g_I \simeq -4.2549955\cdots$. The main linear Zeeman contribution comes from the terms $\frac{e\hbar}{4mc} g_s \boldsymbol{\sigma}\cdot\mathbf{B}$ and $\frac{e\hbar}{4M_pc} g_I \boldsymbol{\sigma}_{\mathsf{N}}\cdot\mathbf{B}$, with $M_p/m \simeq 1836$.

The main quadratic Zeeman contributions come from the first and last terms, with $\boldsymbol{\pi} = \mathbf{p} - e\mathbf{A}$.

$$\boldsymbol{\pi}^2 = \mathbf{p}^2 - \mathbf{A}\cdot\mathbf{p} - \mathbf{p}\cdot\mathbf{A} + \mathbf{A}^2$$

In the Coulomb gauge $\nabla\cdot\mathbf{A} = 0$, $\mathbf{p}\cdot\mathbf{A} = \frac{1}{2}\mathbf{B}\cdot\mathbf{L}$, and $\mathbf{A}^2 = \frac{1}{4}B^2(x^2 + y^2)$.

Calculations for ^{3}He

For two-electron helium, $\boldsymbol{\sigma} \to \boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2$ and $x^2 + y^2 \to \sum_{i=1}^{2}(x_i^2 + y_i^2)$.

For convenience, write the Zeeman Hamiltonian in the form

$$H_{\mathsf{Z}} = \frac{e\hbar}{2M_p} g_I \mathbf{B}\boldsymbol{\cdot}\left\{\boldsymbol{\sigma}_{\mathsf{N}} + \frac{M_p}{m}\left(\frac{g_s}{g_I}(\boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2)\left[1 - \left(\frac{eA}{mc}\right)^2\right] + \mathbf{B}\frac{e}{2g_I\hbar}\sum_{i=1}^{2}(x_i^2 + y_i^2)\right)\right\}$$

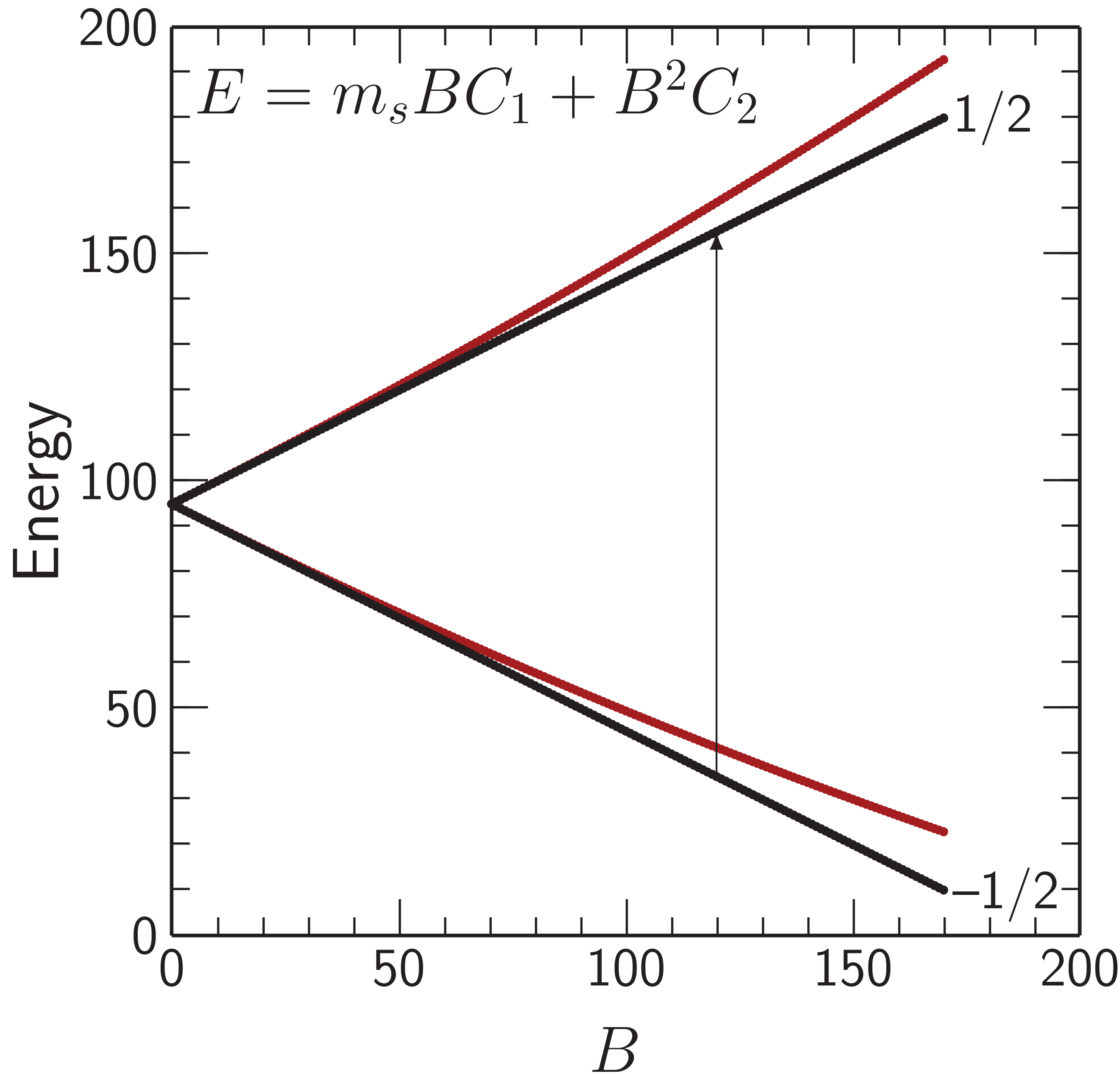
For the $1s^2\ {}^1S_0$ state, $\langle \boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2 \rangle = 0$, and

$$\begin{aligned} \langle \sum_{i=1}^{2}(x_i^2 + y_i^2)\rangle &= \langle \sum_{i=1}^{2}(r_i^2 - z_i^2)\rangle \\ &= \tfrac{2}{3}\langle \sum_{i=1}^{2}\langle r_i^2\rangle = 1.591\,310\cdots\ a_0^2 \end{aligned}$$

With B expressed in Tesla, the fractional correction for the quadratic Zeeman effect is thus

$$\frac{M_p}{m}\frac{B}{2g_I}\langle \sum_{i=1}^{2}(x_i^2 + y_i^2)\rangle = \frac{1836/2}{2.3505 \times 10^5}\cdot\frac{1.5913}{4.255} = 0.001461 \times B$$

This is enhanced by the factor of $M_p/m \simeq 1836$, but it is a common shift for both $\mathcal{M}_{\mathsf{N}} = \pm 1/2$, and so it does not change the transition frequency.



$E = m_s B C_1 + B^2 C_2$
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Wave Function Corrections

Recall that

$$H_{\mathsf{Z}} = \frac{e\hbar}{2M} g_I \mathbf{B}\cdot \left[\boldsymbol{\sigma}_{\mathsf{N}} + \frac{M}{m} \left(\frac{g_s}{g_I} (\boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2) + \mathbf{B} \frac{e}{2 g_I \hbar} \sum_{i=1}^{2} (x_i^2 + y_i^2) \right) \right]$$

In lowest order, the nuclear Zeeman effect depends on the expectation value

$$\begin{aligned} \Delta E(\mathcal{M}) &= \frac{e\hbar}{2M} g_I \frac{\langle \psi | \mathbf{B}\cdot \boldsymbol{\sigma}_{\mathsf{N}} | \psi \rangle}{\langle \psi | \psi \rangle} \\ &= \frac{e\hbar}{2M} g_I B \mathcal{M} \frac{\langle \psi | \psi \rangle}{\langle \psi | \psi \rangle} \qquad \text{with } \mathcal{M} = \pm\tfrac{1}{2}. \end{aligned}$$

In other words, there are no perturbative corrections to the norm.

For the electronic Zeeman term, when relativistic and quadratic terms are included, the operator $\sigma_{1,z} + \sigma_{2,z}$ assumes the more general form

$$\mathcal{O}_1 \sigma_{1,z} + \mathcal{O}_2 \sigma_{2,z} = \tfrac{1}{2}(\mathcal{O}_1 + \mathcal{O}_2)(\sigma_{1,z} + \sigma_{2,z}) + \tfrac{1}{2}(\mathcal{O}_1 - \mathcal{O}_2)(\sigma_{1,z} - \sigma_{2,z})$$

The antisymmetric operator $\sigma_{1,z} - \sigma_{2,z}$ connects ${}^1S_0$ states with ${}^3S_1$ and ${}^3D_1$ states, but still with magnetic quantum number $\mathcal{M} = 0$, and so such terms do not contribute.

Result for He^+

For He^+, the term $\dfrac{e\hbar}{4m^3c^2}\boldsymbol{\pi}^2\boldsymbol{\sigma}\cdot\mathbf{B}$ contributes since $\mathcal{M} = \pm\frac{1}{2}$

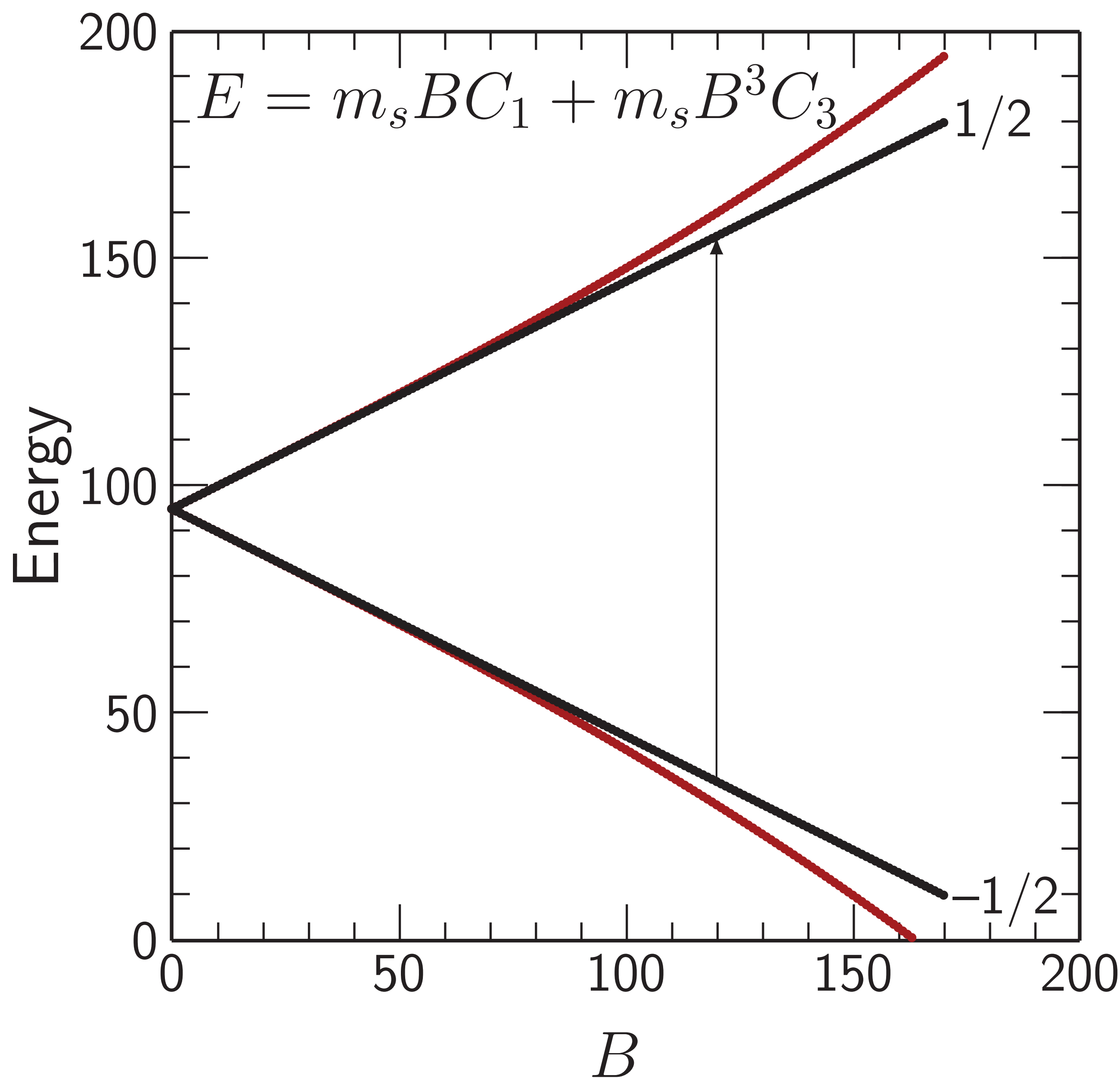
The fractional correction is

$$1 + \frac{g_s}{g_I}\frac{M_p}{m}\left(\frac{eA}{mc}\right)^2$$

$$= 1 + \frac{1}{4}\frac{g_s}{g_I}\frac{M_p}{m}\alpha^2\frac{2}{3}\langle r^2\rangle\frac{B^2}{\kappa^2}$$

$$= 1 + 1.03 \times 10^{-13}\, B^2$$

with B in Tesla, using $\kappa = 2.3506 \times 10^5$ T and $\langle r^2\rangle = 3/4$ for He^+.



$E = m_s B C_1 + m_s B^3 C_3$
1/2
−1/2
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Higher-Order Perturbations

For He^+, the perturbation equation

$$(H^{(0)} - E^{(0)})\psi^{(1)} + (x^2 + y^2)\psi^{(0)} = E^{(1)}\psi^{(0)}$$

can be solved analytically, with the result

$$E = Z^2 \left(-\frac{1}{2} + 2\lambda - \frac{53}{3}\lambda^2 + \frac{5581}{9}\lambda^3 + \cdots \right)$$

for a $1s$ electron with nuclear charge Z, and $\lambda = \dfrac{1}{8Z^4}\left(\dfrac{B}{\kappa}\right)^2$

from J. Killingbeck, J. Phys. B $\mathbf{12}$, 25 (1979).

Second-Order Quadratic Shift for Helium

For brevity, define $V = \sum_{i=1}^{2}(x_i^2 + y_i^2)$

Solve the perturbation equation variationally

$$(H^{(0)} - E^{(0)})\psi^{(1)} + V\psi^{(0)} = E^{(1)}\psi^{(0)}$$

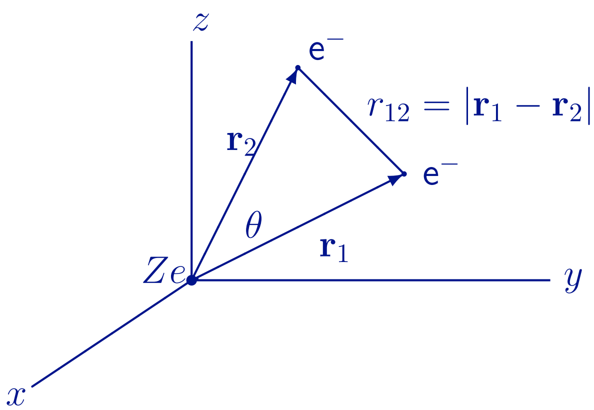
by writing $|\psi^{(1)}\rangle$ in terms of a complete set of pseudostates $|n\rangle$

$$|\psi^{(1)}\rangle = \sum_{n\neq 0} \frac{|n\rangle\langle n|V - E^{(1)}|0\rangle}{E_0 - E_n}$$

Then $E^{(2)} = \langle\psi^{(0)}|V|\psi^{(1)}\rangle/64$

Since $x^2 + y^2 = r^2 - z^2 = \frac{2}{3}[P_0 - P_2(\cos\theta)]$, there are contributions from both intermediate S-states and D-states.

Nonrelativistic Wave functions for Helium



Hylleraas coordinates

(Hylleraas, 1929)

The Hamiltonian in atomic units is

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

Expand

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i,j,k} a_{ijk}\, r_1^i\, r_2^j\, r_{12}^k\, e^{-\alpha r_1 - \beta r_2}\, \mathcal{Y}_{l_1 l_2 L}^M(\hat{\mathbf{r}}_\mathbf{1}, \hat{\mathbf{r}}_\mathbf{2}) \pm \text{exchange}$$

where $i + j + k \leq \Omega$ (Pekeris shell).

Diagonalize H in the

$$\phi_{ijk} = r_1^i\, r_2^j\, r_{12}^k\, e^{-\alpha r_1 - \beta r_2}\, \mathcal{Y}_{l_1 l_2 L}^M(\hat{\mathbf{r}}_\mathbf{1}, \hat{\mathbf{r}}_\mathbf{2}) \pm \text{exchange}$$

basis set.

New Variational Techniques

I. Double the basis set

$$\begin{aligned} \text{If} \quad \phi_{i,j,k}(\alpha,\beta) &= r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2} \\ \text{then} \quad \tilde{\phi}_{i,j,k} &= \underset{\text{asymptotic}}{a_1\phi_{i,j,k}(\alpha_1,\beta_1)} + \underset{\text{inner correlation}}{a_2\phi_{i,j,k}(\alpha_2,\beta_2)} \end{aligned}$$

II. Include the screened hydrogenic function

$$\phi_{\mathsf{SH}} = \psi_{1s}(Z)\psi_{nL}(Z-1)$$

explicitly in the basis set.

III. Optimize the nonlinear parameters

$$\begin{aligned} \frac{\partial E}{\partial \alpha_t} &= -2\langle \Psi_{\mathsf{tr}} \mid H - E \mid r_1\Psi(\mathbf{r}_1,\mathbf{r}_2;\alpha_t) \pm r_2\Psi(\mathbf{r}_2,\mathbf{r}_1;\alpha_t)\rangle \\ \frac{\partial E}{\partial \beta_t} &= -2\langle \Psi_{\mathsf{tr}} \mid H - E \mid r_2\Psi(\mathbf{r}_1,\mathbf{r}_2;\alpha_t) \pm r_1\Psi(\mathbf{r}_2,\mathbf{r}_1;\alpha_t)\rangle \end{aligned}$$

for $t = 1$, 2, with $\langle \Psi_{\mathsf{tr}} \mid \Psi_{\mathsf{tr}}\rangle = 1$.
$\Psi(\mathbf{r}_1,\mathbf{r}_2;\alpha_t) =$ terms in Ψ_{tr} which depend explicitly on α_t.

For all states up to $n = 10$ and $L = 7$, see Drake and Yan, PRA **46**, 2378 (1992) and http://drake.sharcnet.ca for downloadable resources.

Convergence table for ground state energy of helium $1s^2\ {}^1S_0$

N	Eenrgy	Difference	Ratio
44	-2.903 724 131 001 531 809 52		
67	-2.903 724 351 566 477 006 22	0.000 000 220 564 945 196 70	
98	-2.903 724 373 891 109 909 02	0.000 000 022 324 632 902 80	9.88
135	-2.903 724 376 548 959 509 68	0.000 000 002 657 849 600 66	8.40
182	-2.903 724 376 960 412 587 10	0.000 000 000 411 453 077 42	6.46
236	-2.903 724 377 018 168 461 60	0.000 000 000 057 755 874 50	7.12
302	-2.903 724 377 030 786 217 38	0.000 000 000 012 617 755 78	4.58
376	-2.903 724 377 033 426 036 92	0.000 000 000 002 639 819 54	4.78
464	-2.903 724 377 033 966 492 28	0.000 000 000 000 540 455 36	4.88
561	-2.903 724 377 034 076 499 72	0.000 000 000 000 110 007 44	4.91
674	-2.903 724 377 034 107 875 42	0.000 000 000 000 031 375 70	3.51
797	-2.903 724 377 034 116 018 94	0.000 000 000 000 008 143 52	3.85
938	-2.903 724 377 034 118 518 36	0.000 000 000 000 002 499 42	3.26
1090	-2.903 724 377 034 119 239 36	0.000 000 000 000 000 721 00	3.47
1262	-2.903 724 377 034 119 478 92	0.000 000 000 000 000 239 56	3.01
1446	-2.903 724 377 034 119 553 56	0.000 000 000 000 000 074 64	3.21
1652	-2.903 724 377 034 119 582 74	0.000 000 000 000 000 029 18	2.56
1871	-2.903 724 377 034 119 592 06	0.000 000 000 000 000 009 32	3.13
2114	-2.903 724 377 034 119 595 82	0.000 000 000 000 000 003 76	2.48
Extp	-2.903 724 377 034 119 598 13+	-0.000 000 000 000 000 000 23	1.63

Convergence table for $C^{(2)} = \sum_{n\neq 0} \frac{\langle 0|V|n\rangle\langle n|V|0\rangle}{E_0 - E_n}$ with $V = \sum_{i=1}^{2}(x_i^2 + y_i^2)$

N	$C^{(2)}$	Difference
44	–2.256 977 108 97	
67	–2.256 876 425 86	0.000 100 683 12
98	–2.256 839 847 04	0.000 036 578 81
135	–2.256 836 242 96	0.000 003 604 08
182	–2.256 835 064 51	0.000 001 178 46
236	–2.256 834 880 76	0.000 000 183 75
302	–2.256 834 860 98	0.000 000 019 77
376	–2.256 834 846 56	0.000 000 014 42
464	–2.256 834 846 64	–0.000 000 000 08
561	–2.256 834 846 90	–0.000 000 000 26
674	–2.256 834 847 00	–0.000 000 000 10

Second-Order Quadratic Shift for Helium – Results

Define $C^{(2)} = \sum_{n\neq 0} \frac{\langle 0|V|n\rangle\langle n|V|0\rangle}{E_0 - E_n}$ with $V = \sum_{i=1}^{2}(x_i^2 + y_i^2)$

$C^{(2)}$ (S–S part)	–2.256 834 847(1)(674 terms)
$C^{(2)}$ (S–D part)	0.543 351 801(1)
Total	–1.713 483 046(1)(1014 terms)

Compare with –53/192 = –0.2760 for He^+.

Check Sums

$C^{(2)}$(S–D) is the same as two-ninths the quadrupole polarizability

$$2\alpha_q/9 = 0.543\,351\,800(1)$$

[Yan et al. PRA **54**, 2824 (1996)]

By closure

$$\begin{aligned} \sum_n \langle 0|V|n\rangle\langle n|V|0\rangle &= \langle 0|V^2|0\rangle \\ 4.610\,516\,51 &= 4.610\,516\,51 \end{aligned}$$

The total fractional correction to the $\frac{\hbar e}{2M_p}\boldsymbol{\sigma}_{\mathrm{N}}\cdot\mathbf{B}$ term is

$$1 + 0.001461 \times B - 0.445 \times 10^{-15} B^3$$

Relativistic Corrections for $^3\mathrm{He}^+$

For $^3\mathrm{He}^+$, there is also a contribution from terms of the form

$$C_{\mathrm{rel}}^{(2)} = \sum_{n\neq 0} \frac{\langle 0|V|n\rangle\langle n|Q_{\mathrm{M1}}|0\rangle}{E_0 - E_n}$$

with $V = \dfrac{B^2}{8}\sum_{i=1}^{2}(x_i^2 + y_i^2)$

and $Q_{\mathrm{M1}} = \mu_{\mathrm{B}}\left(\dfrac{-2p^2}{3m^2c^2} + \dfrac{Ze^2}{3mc^2 r}\right)\boldsymbol{\sigma}\cdot\mathbf{B}$

The order of magnitude as a fractional correction to $\mu_{\mathrm{N}}\boldsymbol{\sigma}_{\mathrm{N}}\cdot\mathbf{B}$ is

$$\frac{M_p g_s}{m g_I}\kappa^2\alpha^2 B^2 \sim 1.03\times 10^{-13} B^2 \qquad \text{with } B \text{ in Tesla.}$$

Dirac Equation for the Helion Nucleus

Regard the ^{3}He nucleus as a Dirac particle with anomalous magnetic moment $\mathcal{A} = (Mg_I)/(2M_p) + 1$ corresponding to $g_I = -4.5525\cdots$ relative to $g_e = -2$

$$H_{\mathrm{D}} = c\boldsymbol{\alpha}\cdot\boldsymbol{\pi} - \beta Mc^2 + V + \frac{e\mathcal{A}}{2M}(i\beta\boldsymbol{\alpha}\cdot\mathbf{E} - \beta\boldsymbol{\Sigma}\cdot\mathbf{B})$$

(K. Pachucki, Phys. Rev. A **69**, 052502 (2004).)
Apply a Foldy-Wouthuysen transformation as before to obtain (in simplified form)

$$\begin{aligned} H_{\mathbf{FW}} &= \frac{\boldsymbol{\pi}^2}{2M} + V - \frac{\boldsymbol{\pi}^4}{8M^3c^2} \\ &\quad - \frac{e\hbar}{4M_p} g_I \boldsymbol{\sigma}_{\mathsf{N}}\cdot\mathbf{B} \\ &\quad + \frac{e\hbar}{8M^2c^2}(1+2\mathcal{A})(\hbar\nabla\cdot\mathbf{E} + \boldsymbol{\sigma}_{\mathsf{N}}\cdot(\mathbf{E}\times\boldsymbol{\pi} - \boldsymbol{\pi}\times\mathbf{E})) \\ &\quad + \frac{e\hbar}{4M^3c^2}\left[\boldsymbol{\pi}^2\boldsymbol{\sigma}_{\mathsf{N}}\cdot\mathbf{B} + \mathcal{A}\boldsymbol{\pi}\cdot\mathbf{B}\boldsymbol{\pi}\cdot\boldsymbol{\sigma}_{\mathsf{N}}\right] \end{aligned}$$

The fractional correction is now

$$\begin{aligned} & 1 + \frac{1}{g_I}\frac{M_p}{M}\left(\frac{eA}{Mc}\right)^2 \\ &= 1 + \frac{1}{4g_I}\frac{M_p}{M}\left(\frac{m}{M}\right)^2 \alpha^2 \frac{2}{3}\langle r_{\mathsf{N}}^2\rangle \frac{B^2}{\kappa^2} \\ &= 1 + \frac{1}{4g_I}\frac{M_p}{M}\left(\frac{m}{M}\right)^4 \alpha^2 \frac{2}{3}\langle r^2\rangle \frac{B^2}{\kappa^2} \\ &= 1 + 3.10\times 10^{-32}\, B^2 \end{aligned}$$

Summary

1. We have surveyed possible sources of nonlinearity in the Zeeman effect for ^{3}He.
2. The quadratic effect is relatively large, especially for the electronic energy shift in comparison with the nuclear Zeeman effect, but it has no effect on the transition frequency.
3. The cubic Zeeman effect does alter the transition frequency, but it is at the level of parts in 10^{13}.
4. We have presented new results for the quadratic effect in helium beyond lowest order.