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Quantum statistics of hydrogen in strong magnetic fields

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Abstract

By an extension of the Feynman–Kleinert variational approach, we calculate the temperature-dependent effective classical potential governing the quantum statistical properties of a hydrogen atom in a uniform magnetic field. In the zero-temperature limit, we obtain ground state energies which are accurate for all magnetic field strengths from weak to strong fields. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The recent discovery of magnetars has renewed interest in the behavior of charged particle systems in the presence of extremely strong external magnetic fields [1]. In this new type of neutron stars, electrons and protons from decaying neutrons produce magnetic fields B reaching up to 10^{15} G, much larger than those in neutron stars and white dwarfs, where B is of order 10^{10} – 10^{12} and 10^6 – 10^8 G, respectively.

Analytic treatments of the strong-field properties of an atomic system are difficult, even in the zero-temperature limit. The reason is the logarithmic asymptotic behavior of the ground state energy [2,3]. In the weak-field limit, perturbative approaches [4] yield well-known series expansions in powers of B^2 . These are useful, however, only for $B \ll B_0$, where B_0

is the atomic magnetic field strength $B_0 = e^3 M^2 / \hbar^3 \approx 2.35 \times 10^5$ T = 2.35×10^9 G.

So far, the most reliable values for strong uniform fields were obtained by numerical calculations [5]. An analytic mapping procedure was introduced in Ref. [3] to interpolate between the weak- and strong-field behavior, and a variational approximation was given in Ref. [6], both with quite good results.

In this Letter, we use an extension of the Feynman–Kleinert variational approach [7] to find a *single approximation* to the effective classical potential of the system for *all* temperatures and magnetic field strengths. From this, the quantum statistical partition function can be obtained by a simple configuration space integral over a classical-looking Boltzmann factor. In the zero-temperature limit, the effective classical potential is the ground state energy of the system.

2. Effective classical potential

The Hamiltonian of the electron in a hydrogen atom in the presence of a uniform external magnetic field

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pointing along the positive z -axis is

$$H(\mathbf{p}, \mathbf{x}) = \frac{1}{2M} \mathbf{p}^2 - \omega_B l_z(\mathbf{p}, \mathbf{x}) + \frac{1}{2} \omega_B^2 \mathbf{x}^2 - \frac{e^2}{|\mathbf{x}|}, \quad (2.1)$$

where $\omega_B = eB/2Mc$ is half the Landau frequency, $\omega_B = \omega_c/2$. Here we have used the symmetric gauge $\mathbf{A}(\mathbf{x}) = (B/2)(-y, x, 0)$, and denoted the z -component of the orbital angular momentum by $l_z(\mathbf{p}, \mathbf{x}) = (\mathbf{x} \times \mathbf{p})_z$. The quantum statistical partition function can always be expressed as a classical-looking configuration space integral [7]

$$Z = \int \frac{d^3 x_0}{\lambda_{\text{th}}^3} \exp[-\beta V_{\text{eff}}(\mathbf{x}_0)], \quad (2.2)$$

where $\lambda_{\text{th}} = \sqrt{2\pi\hbar^2\beta/M}$ is the thermal wavelength, $\beta = 1/k_B T$ is the inverse temperature, and $V_{\text{eff}}(\mathbf{x}_0)$ is the effective classical potential $V_{\text{eff}}(\mathbf{x}_0)$. Generalizing the development in Ref. [7], this is defined by the phase space path integral

$$\begin{aligned} & \exp[-\beta V_{\text{eff}}(\mathbf{x}_0)] \\ & \equiv \lambda_{\text{th}}^3 \int d^3 p_0 \oint \mathcal{D}^3 x \mathcal{D}^3 p \delta(\mathbf{x}_0 - \overline{\mathbf{x}(\tau)}) \\ & \quad \times \delta(\mathbf{p}_0 - \overline{\mathbf{p}(\tau)}) e^{-\mathcal{A}[\mathbf{p}, \mathbf{x}]/\hbar}, \end{aligned} \quad (2.3)$$

where $\mathcal{A}[\mathbf{p}, \mathbf{x}]$ is the Euclidean action

$$\mathcal{A}[\mathbf{p}, \mathbf{x}] = \int_0^{\hbar\beta} d\tau [-i\mathbf{p}(\tau)\dot{\mathbf{x}}(\tau) + H(\mathbf{p}(\tau), \mathbf{x}(\tau))], \quad (2.4)$$

and $\overline{\mathbf{x}(\tau)} = \int_0^{\hbar\beta} d\tau \mathbf{x}(\tau)/\hbar\beta$ and $\overline{\mathbf{p}(\tau)} = \int_0^{\hbar\beta} d\tau \mathbf{p}(\tau)/\hbar\beta$ are the temporal averages of position and momentum. The special treatment of \mathbf{x}_0 and \mathbf{p}_0 is necessary, since the classical harmonic fluctuation widths $\langle \mathbf{x}^2 \rangle^{\text{cl}}$ and $\langle \mathbf{p}^2 \rangle^{\text{cl}}$ are proportional to the temperature T (Dulong–Petit law). Thus they diverge for $T \rightarrow \infty$ and their fluctuations cannot be treated perturbatively. In contrast, the fluctuation widths $\langle (\mathbf{x} - \mathbf{x}_0)^2 \rangle$, $\langle (\mathbf{p} - \mathbf{p}_0)^2 \rangle$ around \mathbf{x}_0 and \mathbf{p}_0 go to zero for large T and are limited down to $T = 0$, thus allowing for a treatment by variational perturbation theory [8]. For this we rewrite action (2.4) as

$$\mathcal{A}[\mathbf{p}, \mathbf{x}] = \mathcal{A}_{\Omega}^{\mathbf{p}_0, \mathbf{x}_0}[\mathbf{p}, \mathbf{x}] + \mathcal{A}_{\text{int}}[\mathbf{p}, \mathbf{x}], \quad (2.5)$$

with a harmonic trial action

$$\begin{aligned} \mathcal{A}_{\Omega}^{\mathbf{p}_0, \mathbf{x}_0}[\mathbf{p}, \mathbf{x}] = & \int_0^{\hbar\beta} d\tau \left\{ -i[\mathbf{p}(\tau) - \mathbf{p}_0] \cdot \dot{\mathbf{x}}(\tau) \right. \\ & + \frac{1}{2M} [\mathbf{p}(\tau) - \mathbf{p}_0]^2 \\ & - \Omega_B l_z(\mathbf{p}(\tau) - \mathbf{p}_0, \mathbf{x}(\tau) - \mathbf{x}_0) \\ & + \frac{1}{2} M \Omega_{\perp}^2 [\mathbf{x}^{\perp}(\tau) - \mathbf{x}_0^{\perp}]^2 \\ & \left. + \frac{1}{2} M \Omega_{\parallel}^2 [z(\tau) - z_0]^2 \right\}, \end{aligned} \quad (2.6)$$

in which $\mathbf{x}^{\perp} = (x, y)$ denotes the transverse part of \mathbf{x} and $\Omega_{\perp} > \Omega_B$, for stability. The frequencies $\Omega = (\Omega_B, \Omega_{\perp}, \Omega_{\parallel})$ are arbitrary for the moment. Inserting decomposition (2.5) into (2.3), we expand the exponential of the interaction, $\exp\{-\mathcal{A}_{\text{int}}[\mathbf{p}, \mathbf{x}]/\hbar\}$, yielding a series of expectation values of powers of the interaction

$$\begin{aligned} \langle \mathcal{A}_{\text{int}}^n[\mathbf{p}, \mathbf{x}] \rangle_{\Omega}^{\mathbf{p}_0, \mathbf{x}_0} = & \frac{(2\pi\hbar)^3}{Z_{\Omega}^{\mathbf{p}_0, \mathbf{x}_0}} \oint \mathcal{D}^3 x \mathcal{D}^3 p \mathcal{A}_{\text{int}}^n[\mathbf{p}, \mathbf{x}] \\ & \times \delta(\mathbf{x}_0 - \overline{\mathbf{x}(\tau)}) \delta(\mathbf{p}_0 - \overline{\mathbf{p}(\tau)}) \\ & \times e^{-\mathcal{A}_{\Omega}^{\mathbf{p}_0, \mathbf{x}_0}[\mathbf{p}, \mathbf{x}]/\hbar}. \end{aligned} \quad (2.7)$$

The path integral over the Boltzmann factor involving the harmonic action (2.6) is exactly solvable and yields the restricted partition function

$$\begin{aligned} Z_{\Omega}^{\mathbf{p}_0, \mathbf{x}_0} = & \frac{\hbar\beta\Omega_{+}/2}{\sinh \hbar\beta\Omega_{+}/2} \frac{\hbar\beta\Omega_{-}/2}{\sinh \hbar\beta\Omega_{-}/2} \frac{\hbar\beta\Omega_{\parallel}/2}{\sinh \hbar\beta\Omega_{\parallel}/2} \\ \equiv & e^{-\beta F_{\Omega}^{\mathbf{p}_0, \mathbf{x}_0}}, \end{aligned} \quad (2.8)$$

where $\Omega_{\pm} \equiv \Omega_{\perp} \pm \Omega_B$. Rewriting the perturbation series as a cumulant expansion, evaluating the expectation values, and integrating out the momenta on the right-hand side of Eq. (2.3) leads to a series representation for the effective classical potential $V_{\text{eff}}(\mathbf{x}_0)$. Since it is impossible to sum up the series, the perturbation expansion must be truncated, leading to an N th-order approximation $W_{\Omega}^{(N)}(\mathbf{x}_0)$ for the effective classical potential. Since the parameters Ω are arbitrary, $W_{\Omega}^{(N)}(\mathbf{x}_0)$ should depend *minimally* on Ω . This determines the optimal values $\Omega^{(N)}(\mathbf{x}_0) = (\Omega_B^{(N)}(\mathbf{x}_0), \Omega_{\perp}^{(N)}(\mathbf{x}_0), \Omega_{\parallel}^{(N)}(\mathbf{x}_0))$ of N th order. Reinserting these into $W_{\Omega}^{(N)}(\mathbf{x}_0)$ yields the optimal approximation $W^{(N)}(\mathbf{x}_0) \equiv W_{\Omega^{(N)}}^{(N)}(\mathbf{x}_0)$.

The first-order approximation to the effective classical potential is

$$W_{\Omega}^{(1)}(\mathbf{x}_0) = F_{\Omega}^{\mathbf{p}_0, \mathbf{x}_0} - M\Omega_B(\omega_B - \Omega_B)b_{\perp}^2(\mathbf{x}_0) + M(\omega_B^2 - \Omega_{\perp}^2)a_{\perp}^2(\mathbf{x}_0) - \frac{1}{2}M\Omega_{\parallel}^2a_{\parallel}^2(\mathbf{x}_0) - \left\langle \frac{e^2}{|\mathbf{x}|} \right\rangle_{\Omega}^{\mathbf{p}_0, \mathbf{x}_0}, \quad (2.9)$$

where the quantities $a_{\perp}^2(\mathbf{x}_0)$, $b_{\perp}^2(\mathbf{x}_0)$, and $a_{\parallel}^2(\mathbf{x}_0)$ are the transverse and longitudinal fluctuation widths

$$a_{\perp}^2(\mathbf{x}_0) = \langle x^2(\tau) \rangle_{\Omega}^{\mathbf{p}_0, \mathbf{x}_0}, \quad a_{\parallel}^2(\mathbf{x}_0) = \langle z^2(\tau) \rangle_{\Omega}^{\mathbf{p}_0, \mathbf{x}_0}, \\ b_{\perp}^2(\mathbf{x}_0) = \frac{2}{M\Omega_B} \langle x(\tau)p_y(\tau) \rangle_{\Omega}^{\mathbf{p}_0, \mathbf{x}_0}. \quad (2.10)$$

The expectation value of the Coulomb potential on the right-hand side of Eq. (2.9) has the integral representation

$$-\left\langle \frac{e^2}{|\mathbf{x}|} \right\rangle_{\Omega}^{\mathbf{p}_0, \mathbf{x}_0} = -e^2 \sqrt{\frac{2}{\pi}} a_{\parallel}^2(\mathbf{x}_0) \int_0^1 \frac{d\xi}{f(\xi, \mathbf{x}_0)} \\ \times \exp\left\{ -\frac{\xi^2}{2} \left(\frac{x_0^2 + y_0^2}{f(\xi, \mathbf{x}_0)} + \frac{z_0^2}{a_{\parallel}^2(\mathbf{x}_0)} \right) \right\} \quad (2.11)$$

with

$$f(\xi, \mathbf{x}_0) = a_{\parallel}^2(\mathbf{x}_0) + \xi^2 [a_{\perp}^2(\mathbf{x}_0) - a_{\parallel}^2(\mathbf{x}_0)]. \quad (2.12)$$

From now on we set $\hbar = e^2 = k_B = c = M = 1$. Thus, energies are measured in units of $\epsilon_0 = Me^4/\hbar^2 \equiv 2 \text{ Ryd} \approx 27.21 \text{ eV}$, temperatures in $\epsilon_0/k_B \approx 3.16 \times 10^5 \text{ K}$, distances in Bohr radii $a_B = \hbar^2/Me^2 \approx 0.53 \times 10^{-8} \text{ cm}$, and magnetic field strengths in $B_0 = e^3M^2/\hbar^3 \approx 2.35 \times 10^5 \text{ T} = 2.35 \times 10^9 \text{ G}$. The variational energy (2.9) is minimized at each \mathbf{x}_0 , and the resulting $W^{(N)}(\mathbf{x}_0)$ is displayed for a low temperature and different magnetic fields in Fig. 1. The curves $W^{(1)}(\mathbf{x}_0)$ are plotted to show their anisotropy with respect to the magnetic field direction. The anisotropy grows when lowering the temperature and increasing the field strength. Far away from the proton at the origin, the potential becomes isotropic, due to the increasing influence of the thermal fluctuations. Analytically, this is seen by going to the limits $\rho_0 \rightarrow \infty$ or $z_0 \rightarrow \infty$, where the expectation value of the Coulomb potential (2.11) tends to zero, leaving an effective clas-

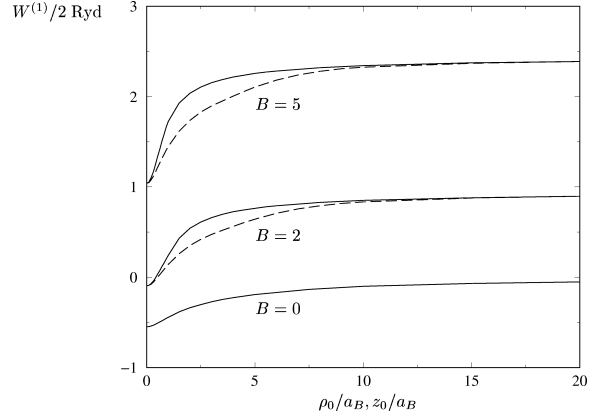


Fig. 1. Effective classical potential plotted along two directions: once as a function of the coordinate $\rho_0 = \sqrt{x_0^2 + y_0^2}$ perpendicular to the field lines at $z_0 = 0$ (solid curves), and once parallel to the magnetic field as a function of z_0 at $\rho_0 = 0$ (dashed curves). The inverse temperature is fixed at $\beta = 100$, and the strengths of the magnetic field B are varied (all in natural units).

sical potential

$$W_{\Omega}^{(1)}(\mathbf{x}_0) \rightarrow F_{\Omega}^{\mathbf{p}_0, \mathbf{x}_0} - \Omega_B(\omega_B - \Omega_B)b_{\perp}^2 + (\omega_B^2 - \Omega_{\perp}^2)a_{\perp}^2 - \frac{1}{2}\Omega_{\parallel}^2a_{\parallel}^2. \quad (2.13)$$

This is \mathbf{x}_0 -independent, and optimization yields the constants $\Omega_B^{(1)} = \Omega_{\perp}^{(1)} = \omega_B$ and $\Omega_{\parallel}^{(1)} = 0$, with the asymptotic energy $W^{(1)}(\mathbf{x}_0) \rightarrow -(1/\beta) \ln(\beta\omega_B/\sinh \beta\omega_B)$. The $B = 0$ curves are, of course, identical with those obtained from variational perturbation theory for the hydrogen atom [9].

For large temperatures, the anisotropy decreases since the violent thermal fluctuations have a smaller preference of the z -direction.

3. Zero-temperature limit

At zero-temperature, the first-order effective classical potential (2.9) at the origin yields an approximation for the ground state energy of the hydrogen atom in a uniform magnetic field — $E_{\Omega}^{(1)} = \lim_{\beta \rightarrow \infty} W_{\Omega}^{(1)}(\mathbf{0})$:

$$E_{\Omega}^{(1)}(B) = \frac{1}{2\Omega_{\perp}}(\Omega_{\perp}^2 + \omega_B^2) + \frac{\Omega_{\parallel}}{4} - \left\langle \frac{1}{|\mathbf{x}|} \right\rangle_{\Omega}^{\mathbf{0}}, \quad (3.1)$$

with the expectation value for the Coulomb potential

$$\left\langle \frac{1}{|\mathbf{x}|} \right\rangle_{\Omega}^0 = \sqrt{\frac{\Omega_{\parallel}}{\pi}} \frac{1}{\sqrt{1 - \Omega_{\parallel}/\Omega_{\perp}}} \times \ln \frac{1 - \sqrt{1 - \Omega_{\parallel}/\Omega_{\perp}}}{1 + \sqrt{1 - \Omega_{\parallel}/\Omega_{\perp}}}. \quad (3.2)$$

Eqs. (3.1) and (3.2) are independent of the frequency parameter Ω_B , such that optimization of the ground state energy (3.1) is ensured by minimizing Ω_{\perp} and Ω_{\parallel} only. Reinserting the extremal $\Omega_{\perp}^{(1)}$ and $\Omega_{\parallel}^{(1)}$ into Eq. (3.1) yields the first-order approximation to the ground state energy $E^{(1)}(B)$. In the absence of the Coulomb interaction the optimization with respect to Ω_{\perp} yields $\Omega_{\perp}^{(1)} = \omega_B$, rendering the ground state energy $E^{(1)}(B) = \omega_B = \omega_c/2$, which is the zeroth Landau level in this special case. The trial frequency Ω_{\parallel} must be set equal to zero to preserve translational symmetry along the z -axis.

In the opposite limit of a vanishing magnetic field, Eq. (3.1) coincides with the first-order variational result for the ground state energy of the hydrogen atom, whose optimization gave $E^{(1)}(B=0) = -4/3\pi \approx -0.4244$ [2 Ryd] obtained in Refs. [7,8]. In Ref. [9], the $B=0$ system was treated up to third order leading to the much more accurate result $E^{(3)}(B=0) \approx -0.490$ [2 Ryd], very near the exact value $E^{\text{ex}}(B=0) = -0.5$ [2 Ryd].

Let us investigate the asymptotics in the strong-field limit $B \rightarrow \infty$. The B -dependence of the binding energy $\varepsilon(B) = B/2 - E$ is plotted in Fig. 2, where it is compared with the results of Ref. [3], with satisfactory agreement. Our results are of similar accuracy as those of other first-order calculations, for example, those from the operator optimization method in first order of Ref. [6]. The advantage of variational perturbation theory is that it yields good results for all magnetic field strengths. From our experience with the fast convergence of the method ([8], Chapters 5 and 9), higher orders of variational perturbation theory will push the approximations rapidly towards the exact value.

3.1. Weak-field behavior

The calculations of the binding energy for weak magnetic fields show that the ratio $\eta \equiv \Omega_{\parallel}/\Omega_{\perp}$ is

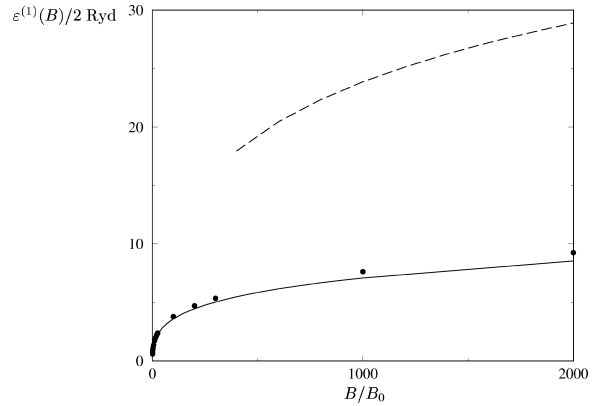


Fig. 2. First-order variational result for the binding energy as a function of the strength of the magnetic field. The dots indicate the values of Ref. [3]. The dashed curve shows the simple estimate $0.5 \ln^2 B$ of Landau–Lifschitz [2].

always smaller than one if $B \neq 0$. Setting $\Omega \equiv \Omega_{\perp}$, we rewrite the binding energy as a function of Ω and η :

$$\varepsilon_{\eta, \Omega}^{(1)}(B) \approx \frac{B}{2} - \frac{\Omega}{2} \left(1 + \frac{\eta}{2}\right) - \frac{B^2}{8\Omega} - \sqrt{\frac{\eta\Omega}{\pi}} \frac{1}{\sqrt{1-\eta}} \ln \frac{1 - \sqrt{1-\eta}}{1 + \sqrt{1-\eta}}. \quad (3.3)$$

This is minimized with respect to the new variational parameters η and Ω by expanding $\eta(B)$ and $\Omega(B)$ in powers of B^2 with unknown coefficients, and inserting these expansions into extremality equations. The expansion coefficients are then determined order by order. The optimal expansions are inserted into (3.3), yielding the optimized binding energy $\varepsilon^{(1)}(B)$ as a power series $\varepsilon^{(1)}(B) = B/2 - \sum_{n=0}^{\infty} \varepsilon_n B^{2n}$. The coefficients ε_n are listed in Table 1 and compared with the exact ones of Ref. [4]. Of course, the higher-order coefficients of this first-order variational approximation become rapidly inaccurate, but the results can be improved, if desired, by going to higher orders in variational perturbation theory as in Ref. [8], Chapters 5 and 9.

3.2. Strong-field behavior

In the discussion of the pure magnetic field we have mentioned that the variational calculation for the ground state energy, which is associated with the

Table 1

Perturbation coefficients up to order B^6 for the weak-field expansion of the binding energy in comparison to the exact ones of Ref. [4]

n	0	1	2	3
ε_n	-0.4244	0.2209	-0.1355	0.2435
ε_n [4]	-0.5	0.25	-0.2760	1.2112

zeroth Landau level, yields a frequency $\Omega_{\perp} \propto B$, while $\Omega_{\parallel} = 0$. We therefore use the assumptions $\Omega_{\perp} \gg \Omega_{\parallel}$ and $\Omega_{\parallel} \ll B$ for an analytic study of the strong-field behavior of the ground state energy (3.1). We expand the last expression of the expectation value (3.2) in terms of $\Omega_{\parallel}/\Omega_{\perp}$, and reinsert this expansion into (3.1). Then we omit all terms proportional to C/Ω_{\perp} , where C stands for any expression with a value much smaller than the field strength B . We thus obtain the strong-field approximation for the first-order binding energy

$$\varepsilon_{\Omega_{\perp}, \Omega_{\parallel}}^{(1)} = \frac{B}{2} - \left(\frac{\Omega_{\perp}}{2} + \frac{B^2}{8\Omega_{\perp}} + \frac{\Omega_{\parallel}}{4} + \sqrt{\frac{\Omega_{\parallel}}{\pi}} \ln \frac{\Omega_{\parallel}}{4\Omega_{\perp}} \right). \quad (3.4)$$

Determining Ω_{\perp} , Ω_{\parallel} by minimization, we obtain the optimized binding energy up to the order $\ln^{-2} B$:

$$\varepsilon^{(1)}(B) = \frac{1}{\pi} \left\{ \ln^2 B - 4 \ln B \ln \ln B + 4 \ln^2 \ln B - 4b \ln \ln B + 2(b+2) \ln B + b^2 - \frac{1}{\ln B} [8 \ln^2 \ln B - 8b \ln \ln B + 2b^2] \right\} + \mathcal{O}(\ln^{-2} B), \quad (3.5)$$

with the abbreviations $a = 2 - \ln 2 \approx 1.307$ and $b = \ln(\pi/2) - 2 \approx -1.548$. Note that the prefactor $1/\pi$ of the leading $\ln^2 B$ term differs from a value $1/2$ obtained by Landau and Lifschitz [2]. Our value is a consequence of the harmonic trial system. The calculation of higher orders in variational perturbation theory should drive our value towards $1/2$.

The convergence of expansion (3.5) is quite slow. At a magnetic field strength $B = 10^5 B_0$, which corresponds to $2.35 \times 10^{10} \text{ T} = 2.35 \times 10^{14} \text{ G}$, the contribution from the first six terms is $(42.19 - 35.82 + 7.60 + 4.82 + 3.31 + 0.76) [2 \text{ Ryd}] = 22.86 [2 \text{ Ryd}]$.

Note the important negative contribution of the next-to-leading term. The next three terms suppressed by a factor $\ln^{-1} B$ contribute $-2.29 [2 \text{ Ryd}]$, while an estimate for the $\ln^{-2} B$ terms yields nearly $-0.3 [2 \text{ Ryd}]$. Thus we find $\varepsilon^{(1)}(10^5) = 20.57 \pm 0.3 [2 \text{ Ryd}]$. This is in very good agreement with the value $20.60 [2 \text{ Ryd}]$ obtained from the full treatment.

In Fig. 2, we have plotted the expression $\varepsilon_L(B) = (1/2) \ln^2 B$ of Landau and Lifschitz [2] to illustrate that it gives far too large binding energies even at very large magnetic fields, e.g., at $2000 B_0 \propto 10^{12} \text{ G}$. Obviously, the nonleading terms in Eq. (3.5) give important contributions to the asymptotic behavior even at such large magnetic fields. As an peculiar property of the asymptotic behavior, the absolute value of the difference between the Landau expression $\varepsilon_L(B)$ and our approximation (3.5) diverges with increasing magnetic field strengths B . Only the relative difference decreases.

4. Summary

We have calculated the effective classical potential for the hydrogen atom in constant magnetic field, which governs the statistical mechanics of the system at all temperatures. At zero temperature, we find a rather accurate ground state energy which interpolates very well between weak and strong fields. More details are published in Ref. [10].

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