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Semiclassical perturbation theory for the hydrogen atom in a uniform magnetic field*

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We study a perturbative semiclassical expansion for the energy levels of the hydrogen atom in a magnetic field. A recursion relation is derived for the calculation of the ground-state energy in each azimuthal subspace. Four terms of the series have been obtained analytically and higher-order corrections have been computed by numerical iteration of the recursion relation. The semiclassical series yields accurate results for field strengths up to the intermediate region, and a simple Shanks extrapolation extends its applicability into the region of very strong fields. A similar calculation for the Stark Hamiltonian is also outlined.

I. INTRODUCTION

The study of perturbations of atomic spectra due to external magnetic fields has been a problem of long-standing interest.[1,2] The anticipated observation of strongly perturbed spectra from astrophysical sources has stimulated a large amount of theoretical work. In the absence of an exact solution, even for the simplest case of a hydrogen atom in a uniform magnetic field, numerical solution of the Schrödinger equation could, in principle, resolve this issue. In fact, numerical calculations have already been performed for the hydrogen atom, for various regions of magnetic field intensities. Nevertheless, reasons of economy as well as theoretical curiosity have motivated the development of approximation techniques. The ordinary perturbation expansion in powers of the magnetic field was recently carried out to large order, using an algebraic method based on the SO(4, 2) group that suppresses contributions from the continuous spectrum, and its asymptotic large-order behavior was studied.[3,4] A semiclassical method in the spirit of the $1/N$ expansion was also suggested.[5] The purpose of the present work is to extend the calculation of Ref. 5 to higher orders, to examine the domain of validity of the semiclassical expansion, and to propose a simple extrapolation that extends its applicability well into the region of strong fields.

The physical basis of the semiclassical expansion is reminiscent of a WKB calculation. The leading approximation to the ground-state energy in each angular momentum sector is given by the energy of an electron on a circular classical trajectory, whereas quantum corrections, as well as radial excitations, are treated as perturbations. The resulting series is organized in inverse powers of the "pseudospin" parameter $k \sim |m| + 1$, where m is the azimuthal angular momentum. A few terms of the $1/k$ series were calculated[5] by an algebraic method based on the SO(2, 1) algebra associated with one-particle Hamiltonians. In the present work, the ground-state energy in each azimuthal subspace is calculated from a recursion relation of the type employed earlier for large-order coupling-constant and $1/N$ expansions for the anharmonic oscillator.[6,7]

In Sec. II, we explain the origin of the semiclassical expansion and present analytic expressions for the first *four* terms of the $1/k$ series. The more technical aspects of the calculation, such as the derivation of the recursion formula, are relegated to an appendix. Higher-order corrections are computed in Sec. III by a numerical iteration of the recursion formula, and the domain of validity of the $1/k$ expansion is discussed in detail. We find that the semiclassical series is directly useful for field strengths up to the intermediate region ($B \sim 10^{10}$ G), but extrapolation becomes necessary for stronger fields. A simple extrapolation (Shanks transformation) improves the series in the intermediate region and continues to work well for fields as strong as 10^{14} G. Section IV outlines application of the semiclassical method to the study of the Stark Hamiltonian. Only the leading approximation to the ground-state energy is examined, but, if desired, higher-order calculations may be performed using the methods of the present work.

This article emphasizes the derivation of explicit results that may be useful in practice, whereas some more rigorous considerations concerning the large-order behavior of semiclassical expansions are reserved for a future publication.

II. ANALYTIC RESULTS

The nonrelativistic Hamiltonian for a hydrogenlike atom in a uniform magnetic field is given by

$$\mathcal{H} = H + \tfrac{1}{2}B(L_z + 2S_z),$$
$$H = \tfrac{1}{2}(p_1^2 + p_z^2 + \tfrac{1}{4}B^2\rho^2) - \frac{Z}{(\rho^2+z^2)^{1/2}}, \tag{2.1}$$

where L_z and S_z are the components of the angular momentum and spin in the direction of the magnetic field $\rho^2 = x^2 + y^2$, and $p_\perp^2 = p_x^2 + p_y^2$. Units have been chosen such that the energy is given in *atomic units*, whereas the magnetic field will be measured in the standard unit $B = 1 \simeq 2.35 \times 10^9$ G. The nuclear charge Z is left arbitrary, but it will eventually be chosen to be an integer $Z = 1, 2, \ldots$, corresponding to a neutral hydrogen atom, an He^+ ion ....

The second term in the Hamiltonian $\mathcal{H}$ of (2.1) is trivially diagonal in each azimuthal eigenspace. Our concern will be the diagonalization of the operator H, which leads to the Schrödinger equation

$$\left[-\frac{1}{2}\left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{\partial^2}{\partial z^2}\right) + \tfrac{1}{8}B^2\rho^2 + \frac{m^2}{2\rho^2} - \frac{Z}{(\rho^2+z^2)^{1/2}}\right]\psi = \mathcal{E}\psi, \tag{2.2}$$

where $m = 0, \pm 1, \pm 2, \ldots$ is the azimuthal angular momentum. Substituting

$$\phi = \rho^{1/2}\psi \tag{2.3}$$

into Eq. (2.2) leads to

$$\left[-\frac{1}{2}\left(\frac{\partial^2}{\partial\rho^2} + \frac{\partial^2}{\partial z^2}\right) + \frac{(k-1)(k-3)}{8\rho^2} + \tfrac{1}{8}B^2\rho^2 - \frac{Z}{(\rho^2+z^2)^{1/2}}\right]\phi = \mathcal{E}\phi, \tag{2.4}$$

$$k = 2(|m| + 1).$$

Notice that our present conventions differ from those of Ref. 5.

For sufficiently large k, the effective potential in (2.4) exhibits a minimum at $z = 0$ and $\rho = \rho_0 \neq 0$, which corresponds roughly to circular classical electron motion with angular momentum $L_z^2 = \frac{1}{4}k^2 (= \frac{1}{4}\hbar^2 k^2)$. The semiclassical expansion amounts to identifying the minimum of the effective potential with a leading approximation to the ground-state energy, and calculating higher-order corrections as fluctuations around the minimum, organized in inverse powers of k.

A convenient way to exhibit explicitly the large-k limit is to define rescaled variables $\bar{Z}$ and u:

$$Z = \bar{Z}k^{3/2}, \quad \rho = uk^{1/2}, \tag{2.5}$$

and stipulate that $\bar{Z}$ be treated as k independent in all intermediate stages of the calculation. Equation (2.4) then reads

$$\left[-\frac{1}{2k^2}\left(\frac{\partial^2}{\partial u^2} + k\frac{\partial^2}{\partial z^2}\right) + V(u, z; k)\right]\phi = \mathcal{E}/k\,\phi,$$
$$V(u, z; k) = \frac{(1-1/k)(1-3/k)}{8u^2} + \tfrac{1}{8}B^2u^2 - \frac{\bar{Z}}{(u^2 + z^2/k)^{1/2}}. \tag{2.6}$$

In introducing the rescaled variables (2.5), we anticipated that the minimum of the potential occurs at $z = 0$. In general (see Sec. IV), z must also be rescaled.

The large-k effective potential is given by

$$V_c(u) \equiv V(u, z; k = \infty) = \frac{1}{8u^2} + \tfrac{1}{8}B^2u^2 - \frac{\bar{Z}}{u}. \tag{2.7}$$

Its minimum occurs at $u = u_0 > 0$, the solution to the algebraic equation $V_c'(u = u_0) = 0$, namely,

$$B^2u_0^4 + 4\bar{Z}u_0 = 1, \tag{2.8}$$

which possesses a unique positive root that is a minimum of $V_c(u)$. The value of the potential at the minimum is identified with the leading approximation for $\mathcal{E}/k$.

Convenient parametrization is achieved by introducing a dimensionless parameter η:

$$\eta = u_0 B^{1/2}, \tag{2.9}$$

so that Eq. (2.8) becomes

$$\eta^4 + \lambda\eta = 1, \quad \lambda = \frac{4\bar{Z}}{B^{1/2}} = \frac{4Z}{B^{1/2}k^{3/2}}. \tag{2.10}$$

λ is an effective coupling constant that depends on the nuclear charge and the magnetic field, as well as the particular sector considered. The unique real positive root of (2.10) lies in the interval

$$0 \leq \eta \leq 1. \tag{2.11}$$

For large magnetic fields η approaches unity, while it vanishes for vanishing B. Its asymptotic behavior is given by

$$\eta \simeq 1 - \frac{\lambda}{4} = 1 - \frac{Z}{B^{1/2}k^{3/2}} \tag{2.12}$$

and

$$\eta \simeq \frac{1}{\lambda} = \frac{B^{1/2} k^{3/2}}{4Z}, \tag{2.13}$$

respectively.

All intermediate expressions may be parametrized in terms of B and η; contact with the original variables can be made through the algebraic equation (2.10), in the end of the calculation. For instance, the value of the potential $V_c(u)$ at its minimum is given by

$$V_c(u = u_0) = \frac{3\eta^4 - 1}{8\eta^2} B, \tag{2.14}$$

and the leading approximation to the ground-state energy reads

$$\mathcal{E} = k V_c(u_0) = \frac{B}{\eta^2} [\tfrac{1}{8}(3\eta^4 - 1)k]. \tag{2.15}$$

Higher-order corrections to the ground-state energy are calculated using the recursion formula derived in the Appendix. We now give a detailed description of the actual results. Including Gaussian fluctuations around the classical minimum, Eq. (2.15) becomes

$$\mathcal{E} = \frac{B}{\eta^2}\{\tfrac{1}{8}(3\eta^4 - 1)k + \tfrac{1}{4}[(1 + 3\eta^4)^{1/2} + (1 - \eta^4)^{1/2} - 2]\},$$

$$k = 2(|m| + 1). \tag{2.16}$$

The Coulomb limit of Eq. (2.16), $B = 0$, is obtained from Eq. (2.13):

$$\mathcal{E} = -\frac{2Z^2}{k^2} = -\frac{Z^2}{2(|m| + 1)^2}. \tag{2.17}$$

It coincides with the exact ground-state energy in each azimuthal eigenspace, as is explicitly verified by writing the exact Coulomb spectrum in parabolic quantum numbers,

$$\mathcal{E} = -\frac{Z^2}{2(|m| + n_1 + n_2 + 1)^2}, \tag{2.18}$$

and setting the quantum numbers n_1 and n_2 equal to zero.[5]

The $B \to \infty$ limit of (2.16) is obtained from Eq. (2.12):

$$\mathcal{E} = \tfrac{1}{4} Bk = \tfrac{1}{2} B(|m| + 1), \tag{2.19}$$

and coincides with the exact Landau spectrum for the ground-state energy in each sector. [Note: In order to compare (2.19) with the standard expression for the Landau spectrum, one should also include the contribution coming from the second term of the Hamiltonian (2.1).]

The Gaussian approximation (2.16) is thus found to correctly interpolate between the Coulomb and the Landau limit. This is, of course, an asymptotic property that should not be taken to imply that (2.16) is exact throughout the region of magnetic field intensities. Rather, it is an encouraging sign for the success of the semiclassical expansion, after higher-order corrections have been included. Such corrections have been calculated using the recursion formula of the Appendix. We have succeeded in obtaining analytic expressions for two additional corrections to (2.16), with algebraic manipulation using the MACSYMA program at M.I.T. In order to express the results in a relatively concise form, we write the (asymptotic) series representation for $\mathcal{E}$ as

$$\mathcal{E} = \frac{B}{\eta^2} \sum_{s=-1}^{\infty} E_s k^{-s}, \tag{2.20}$$

and also introduce the notation

$$f = \tfrac{1}{2}(1 + 3\eta^4)^{1/2}, \quad g = \tfrac{1}{2}(1 - \eta^4)^{1/2}. \tag{2.21}$$

Notice that f and g are constrained by the identity

$$f^2 + 3g^2 = 1. \tag{2.22}$$

The terms E_{-1} and E_0 in Eq. (2.20) are already contained in Eq. (2.16). In the present notation they read

$$E_{-1} = \tfrac{1}{4} - \tfrac{3}{2} g^2, \quad E_0 = \tfrac{1}{2}(f + g - 1). \tag{2.23}$$

E_1 may be written in the form

$$E_1 = -\frac{A(g) + fgB(g)}{32(1 - 7g^2) f^4}, \tag{2.24}$$

where A and B are rational polynomials in g. Explicitly, one finds

$$\begin{aligned} A &= 736g^6 - 504g^5 - 218g^4 \\ &\quad + 240g^3 - 41g^2 - 24g + 9, \\ B &= -144g^4 + 168g^3 + 42g^2 - 24g - 6. \end{aligned} \tag{2.25}$$

Taking into account our notational conventions, the present results for E_{-1}, E_0, and E_1 agree with those of Ref. 5. We have further obtained an analytic expression for E_2, presented here for the first time:

$$E_2 = \frac{C(g) + fgD(g)}{512g(1 - 7g^2)^3 f^{10}}, \tag{2.26}$$

where

$$C = 8\,026\,560g^{16} - 13\,926\,528g^{15} - 3\,895\,812g^{14} + 19\,135\,584g^{13} - 3\,900\,219g^{12} - 9\,855\,776g^{11} + 3\,758\,132g^{10}$$
$$+ 2\,215\,456g^{9} - 1\,190\,083g^{8} - 126144g^{7} + 151\,068g^{6} - 33\,376g^{5} - 113g^{4} + 5984g^{3} - 1676g^{2} - 288g + 111,$$
$$D = -2\,720\,352g^{14} + 6\,314\,112g^{13} - 2\,718\,492g^{12} - 6\,665\,760g^{11} + 5\,358\,953g^{10} + 2\,860\,560g^{9} - 2\,901\,427g^{8}$$
$$-668\,352g^{7} + 790\,305g^{6} + 95\,904g^{5} - 123\,557g^{4} - 8352g^{3} + 10\,930g^{2} + 336g - 432. \quad (2.27)$$

Still higher-order corrections have been computed numerically and are discussed in Sec. III. In the remainder of this section, we analyze various features of the preceding explicit results. Notice that the functions f and g take values in the intervals

$$0 \leq g \leq \tfrac{1}{2} \leq f \leq 1, \quad (2.28)$$

as is evident from their definition (2.21) and Eq. (2.11). The Coulomb limit ($\eta = 0$) corresponds to $f = g = \frac{1}{2}$. Inserting these values in Eqs. (2.24)–(2.27), one finds $E_1 = E_2 = 0$. In fact, all but the leading term in the series (2.20) vanish in that limit, which is equivalent to our earlier remark that the Coulomb limit of the leading term, Eq. (2.17), gives the exact answer for the ground-state energy.

One would expect a similar result for the Landau limit ($\eta = 1$, $g = 0$, $f = 1$), because the leading term, Eq. (2.19), yields the exact answer. However, simple inspection of Eqs. (2.24)–(2.27) reveals that this is not the case. Thus,

$$E_1 \sim -\tfrac{9}{32}, \quad E_2 \sim \frac{111}{512g} \sim \frac{111k^{3/4}}{512Z^{1/2}}B^{1/4}, \quad (2.29)$$

where we have used the asymptotic formula (2.12). The origin of this anomaly is easy to trace. It is a typical example of secular behavior due to the appearance of small denominators in the perturbation expansion: g is the frequency of fluctuations in the z direction, which are suppressed in the large-B limit. One may further observe that the dependence on B of individual terms of the $1/k$ series is algebraic, in contrast to the logarithmic dependence of the exact solution in the $B \to \infty$ limit, as was already mentioned in Ref. 5, where references to work addressing the large-B limit may be found. It should be noted, however, that the large-field behavior of individual terms in the present expansion is milder than that of the ordinary perturbation series. While (2.29) suggests that the semiclassical expansion cannot be directly useful for very strong fields, it also indicates that the domain of its validity is wider than ordinary perturbation theory. In fact, a Shanks extrapolation will be used later in the text that extends the applicability of the present expansion well into the region of strong fields.

The pole at $g^2 = \frac{1}{7}$ occurring in Eqs. (2.24) and (2.26) is artificial; the numerators vanish at the same value of g, and $f = (1 - 3g^2)^{1/2} = (\frac{4}{7})^{1/2}$. In fact, the result may be written in a form that makes the pole disappear at the cost of lengthier expressions. Hence, we find it preferable to maintain relatively simple expressions, and to stipulate that our formulas be applied with care for field values that give $g^2 \simeq \frac{1}{7}$. We should also

TABLE I. Detailed results for field strengths in the intermediate region.

Order of partial sums	$B = 0.1$		$B = 1$	
	$\lvert m\rvert = 0$	$\lvert m\rvert = 1$	$\lvert m\rvert = 0$	$\lvert m\rvert = 1$
−1	−0.498 753 101 8	−0.107 259 699 5	−0.394 304 64	0.464 311 40
0	−0.497 513 118 7	−0.100 143 657 1	−0.315 188 04	0.564 439 07
1	−0.497 523 464 6	−0.100 926 064 9	−0.335 698 39	0.537 900 21
2	−0.497 526 723 9	−0.100 837 722 2	−0.329 786 49	0.544 550 51
3	−0.497 526 508 8	−0.100 845 924 0	−0.331 665 83	0.543 508 05
4	−0.497 526 472 2	−0.100 845 834 2	−0.330 867 30	0.542 930 46
5	−0.497 526 480 2	−0.100 845 639 6	−0.331 525 74	0.543 968 39
6	−0.497 526 480 7	−0.100 845 649 6	−0.330 616 86	0.542 882 65
Numerical (Ref. 8)	−0.497 52(5)	−0.100 84(5)	−0.331 16(5)	0.543 41

mention that, while large coefficients are involved in Eq. (2.27), cancellations occur for a wide range of values of f and g which make the final result very small.

Actual application of Eqs. (2.20)–(2.27) is straightforward. The required input is an explicit value for η, which is the unique positive root of the quartic equation (2.10) and depends on specific values for B, Z, and $k=2(|m|+1)$. Explicit results and the domain of validity of the above approximation will be discussed in Sec. III.

III. NUMERICAL RESULTS AND DISCUSSION

We have calculated energies for several values of the magnetic field and angular momentum, and have compared our results with representative numerical results for intermediate[8] as well as for strong fields.[9] All computations in the following concern the hydrogen atom ($Z=1$). Using the recursion formula derived in the Appendix, we compute partial sums for the energy, defined by

$$\mathcal{E}_n = \frac{B}{\eta^2} \sum_{s=-1}^{n} E_s k^{-s}, \quad n=-1, 0, 1, \ldots \tag{3.1}$$

which is a truncated form of Eq. (2.20).

Table I contains eight partial sums for field strengths in the intermediate region and angular momenta $|m|=0, 1$. It is evident that the semiclassical series converges very well in the region $B<1$, where the accuracy of the current calculation appears to exceed that of the numerical calculation of Praddaude.[8] In fact, Table I suggests that for $B<1$ accurate results are obtained by maintaining only four terms of the series, for which analytic expressions were given in Sec. II. Similar conclusions hold for states with higher angular momenta.

However, the above picture gradually changes for field intensities above the intermediate region. Already at $B=1$, the $1/k$ series does not provide directly more than two significant figures, for it oscillates around the correct value and eventually becomes divergent after yet higher-order corrections have been included. This situation becomes clear at $B=100$ (see Table III), where a direct estimate is not possible because the amplitude of oscillations is very large. Larger oscillations occur for very strong fields, as is illustrated by the examples shown in Tables IV and V.

It is thus evident that the semiclassical expansion may be useful for very strong fields only through a suitable extrapolation. Indeed, we have found that a Shanks transformation extends the applicability of the $1/k$ series well into the region of strong fields. As is usual with extrapolation schemes, we cannot provide a rigorous justification for the use of this particular extrapolation, but we present detailed empirical evidence for its suitability. A description of the Shanks transformation may be found in Ref. 10, where it is explained why this transformation eliminates oscillating transients and where further examples and some stipulations concerning round-off errors are discussed.

In practice, application of the Shanks extrapolation is straightforward. Given the sequence of partial sums $\mathcal{E}_n$, $n=-1, 0, 1, 2, \ldots$ of Eq. (3.1), a sequence of first-order Shanks extrapolants S_n, $n=0, 1, 2, \ldots$ is defined by

$$S_n = \frac{\mathcal{E}_{n+1}\mathcal{E}_{n-1}-\mathcal{E}_n^2}{\mathcal{E}_{n+1}+\mathcal{E}_{n-1}-2\mathcal{E}_n}, \quad n=0, 1, 2, \ldots . \tag{3.2}$$

Similarly, one defines a sequence of second-order extrapolants,

$$S'_n = \frac{S_{n+1}S_{n-1}-S_n^2}{S_{n+1}+S_{n-1}-2S_n}, \quad n=1, 2, \ldots \tag{3.3}$$

third-order extrapolants S''_n, $n=2, 3, \ldots$, and so on.

We have tested the above procedure for $B=1$ and $m=0$, for which the original series directly provides between two and three significant figures. The detailed results of the extrapolation are shown in Table II. It is evident that the Shanks transformation accelerates the convergence of the series, and provides two or three *additional* significant figures, so that Praddaude's num-

TABLE II. Shanks extrapolation for the absolute ground state at $B \simeq 2.35 \times 10^9$ G.

$B=1$, $m=0$; numerical value (Ref. 8): −0.331 16(5)			
$\mathcal{E}_n$	S_n	S'_n	S''_n
−0.394 304 646 894			
−0.315 188 048 702	−0.331 475 899 572		
−0.335 698 394 804	−0.331 109 265 939	−0.331 189 827 514	
−0.329 786 496 239	−0.331 212 514 691	−0.331 159 947 535	−0.331 162 4
−0.331 665 832 340	−0.331 105 424 667	−0.331 162 619 316	
−0.330 867 309 579	−0.331 228 181 061		
−0.331 525 742 687			

TABLE III. Results for $B \simeq 2.35 \times 10^{11}$ G and Shanks extrapolation.

$B=100$, $m=0$; numerical value (Ref. 9): 46.210(7)		
$\mathcal{E}_n$	S_n	S_n'
42.799 352		
49.907 291	46.136 660	
41.876 441	46.320 828	46.258 041
51.828 362	46.225 564	
39.007 705		

TABLE V. Results for $B \simeq 4.7 \times 10^{13}$ G and Shanks extrapolation.

$B=20\,000$, $m=0$; numerical value (Ref. 9): 9983.293(5)		
$\mathcal{E}_n$	S_n	S_n'
9 899.874 68		
10 364.093 24	9 975.288 61	
7 970.764 63	10 050.518 68	9984.666 80
23 844.293 50	9 522.267 46	
−122 685.309 20		

erical result is reached using seven terms of the semiclassical series.

The effect of the extrapolation becomes much more evident for very strong fields, for which the original series fails to provide any direct information. Various examples are presented in Tables III, IV, and V, and the results are compared with the numerical calculation of Simola and Virtamo.[9] Five terms of the original series yield answers for the energy $\mathcal{E}$ that are accurate to within a few parts in 10 000, uniformly throughout a wide range of magnetic field intensities. Of course, it should be kept in mind that this uniformity in the error is somewhat deceptive; the quantity of practical interest is the binding energy, rather than the energy $\mathcal{E}$, for which the error increases with increasing B. Including higher-order corrections should further improve the above estimates.

In order to gain some insight into the details of the Shanks extrapolation, as applied to the present problem, we examine the very first extrapolant

$$S_0 = \frac{\mathcal{E}_1\mathcal{E}_{-1} - \mathcal{E}_0^2}{\mathcal{E}_1 + \mathcal{E}_{-1} - 2\mathcal{E}_0}. \tag{3.4}$$

Expressing the partial sums $\mathcal{E}_{-1}$, $\mathcal{E}_0$, and $\mathcal{E}_1$ in terms of the coefficients E_{-1}, E_0, and E_1 entering the series (3.1), namely,

$$\mathcal{E}_{-1} = \frac{B}{\eta^2}(kE_{-1}), \quad \mathcal{E}_0 = \frac{B}{\eta^2}(kE_{-1} + E_0), \quad \mathcal{E}_1 = \frac{B}{\eta^2}\left(kE_{-1} + E_0 + \frac{1}{k}E_1\right), \tag{3.5}$$

TABLE IV. Results for $B \simeq 4.7 \times 10^{12}$ G and Shanks extrapolation.

$B=2000$, $m=0$; numerical value (Ref. 9): 990.695(3)		
$\mathcal{E}_n$	S_n	S_n'
968.251 22		
1046.209 78	989.174 78	
833.704 49	997.332 45	990.919 47
1545.114 16	967.347 14	
−1530.468 61		

the extrapolant S_0 reads

$$S_0 = \frac{B}{\eta^2}\,\frac{kE_{-1}E_0 + E_0^2 - E_{-1}E_1}{E_0 - E_1/k}. \tag{3.6}$$

Explicit expressions for E_{-1}, E_0, and E_1 can be found in Eqs. (2.23) and (2.24); therefore, S_0 can be easily calculated for any desired value of the magnetic field and the angular momentum, providing approximate results for the energy $\mathcal{E}$. Table VI presents explicit values for S_0 and compares them with accurate numerical results. It is again observed that the relative error is small over a very wide range of magnetic field strengths.

In order to understand the success of the semiempirical formula (3.6), we examine its asymptotic behavior in the Coulomb and Landau limits. Using the results of Sec. II, we find that (3.6) interpolates between the exact Coulomb value (at $B=0$, $\eta=0$) and the exact Landau value (at $B\to\infty$, $\eta\to 1$). It was pointed out in Sec. II that the Gaussian approximation (2.16) possesses a similar behavior, which, nonetheless, is spoiled as soon as the first higher-order correction is included, because of the secular behavior of E_1 shown in Eq. (2.29). Although E_1 is also important for the construction of the Shanks extrapolant (3.6), its secular behavior does *not* affect the extreme Landau limit of S_0.

To summarize, Eq. (3.6) provides a valuable tool for quick and reasonably accurate estimates of the energy, for weak as well as for strong fields. The explicit results of Table VI may be used as a guide for the accuracy of the above approximation; as was noted earlier, the error for the binding energy increases with increasing B. However, (3.6) provides binding-energy estimates to within a few percent in the region $100 \lesssim B \lesssim 200$, and more accurate results for weaker fields. Of course, higher-order extrapolants may be used for more accurate calculations. It should also be noted that Eq. (3.6) may be used for arbitrary values of the angular momentum, as is demonstrated in Table VII.

We conclude this section with some comments

TABLE VI. Predictions of the *first* Shanks extrapolant for the absolute ground state ($m=0$).

B	0.1	1	100	200	2000
S_0	−0.497 523	−0.331 47	46.137	95.101	989.175
Numerical (Refs. 8 and 9)	−0.497 52(5)	−0.331 16	46.210	95.273	990.695

on an important omission of this paper, namely, the calculation of excited states in each azimuthal eigenspace. We do not know whether a recursion relation can be derived for that case, but, at any rate, the algebraic method of Ref. 5 may be used for such purposes. As was shown in that reference, the semiclassical method provides states that are parametrized in a way that naturally interpolates between the parabolic quantum numbers of the pure Coulomb case and the standard Landau quantum numbers in the $B\to\infty$ limit. It should be noted, however, that the accuracy of the semiclassical series diminishes for excited states, and more elaborate extrapolation might become necessary.

IV. THE STARK HAMILTONIAN

We briefly describe the application of the semiclassical expansion to the Stark effect for hydrogen. Although the Stark Hamiltonian is to some extent similar to the Zeeman Hamiltonian analyzed in this paper, its semiclassical limit is qualitatively different.

The analog of Eq. (2.4) for the hydrogen atom in a uniform electric field reads

$$\left[-\frac{1}{2}\left(\frac{\partial^2}{\partial\rho^2}+\frac{\partial^2}{\partial z^2}\right)+\frac{k^2}{8\rho^2}-\frac{1}{(\rho^2+z^2)^{1/2}}+Fz\right]\phi=\mathcal{E}\phi\,, \tag{4.1}$$

where we have suppressed terms that are unimportant for the semiclassical limit, since we will only discuss the leading approximation. Introducing rescaled coordinates u and v, from $\rho=k^2u$ and $z=k^2v$, Eq. (4.1) is written as

TABLE VII. Predictions of the *first* Shanks extrapolant for various angular momenta, and comparison with numerical results of Praddaude (P) (Ref. 8).

	$B=1$		$B=3$	
$\lvert m\rvert$	S_0	P	S_0	P
0	−0.331 47	−0.331 16	0.334 84	0.335 47
1	0.543 46	0.543 41	2.296 09	2.296 48
2	1.146 87	1.146 94	3.941 94	3.942 75
3	1.699 85		5.520 34	

$$\left[-\frac{1}{2k^2}\left(\frac{\partial^2}{\partial u^2}+\frac{\partial^2}{\partial v^2}\right)+V(u,v)\right]\phi=(\mathcal{E}k^2)\phi\,, \tag{4.2}$$

with

$$V(u,v)=\frac{1}{8u^2}-\frac{1}{(u^2+v^2)^{1/2}}+\bar{F}v\,,\qquad \bar{F}\equiv Fk^4\,. \tag{4.3}$$

In the course of the semiclassical expansion, the effective electric field $\bar{F}$ is treated as a k-independent constant; its true value given by Eq. (4.3) is restored at the end of the calculation.

The large-k limit of (4.2) leads to an approximation where the kinetic energy is suppressed and the leading contribution to the ground-state energy is determined by the minimum of the effective potential (4.3). Stationary points of $V=V(u,v)$ are roots of the algebraic equations $\partial V/\partial u=0=\partial V/\partial v$. Explicitly, one finds that

$$v=-4\bar{F}u^4,\quad 4u=(1+16\bar{F}^2u^6)^{3/2}\,. \tag{4.4}$$

For a sufficiently weak electric field, the second equation in (4.4) possesses two distinct positive roots $u=u_1$ and $u=u_2$, ordered such that $u_1<u_2$. v is accordingly determined by the first equation in (4.4). Only the smaller root u_1 is a local minimum of the potential (4.3), so the semiclassical expansion is performed around $u=u_1$ and $v=v_1=-4\bar{F}u_1^4$. u_1 and u_2 approach each other, with increasing values of the electric field, and eventually become equal at some $\bar{F}=\bar{F}_0$ that corresponds to classical quenching of the atom. For $\bar{F}>\bar{F}_0$ the (real) local minimum disappears. A similar discussion within a more conventional approach may be found in Ref. 11.

It is not difficult to explicitly calculate $\bar{F}_0$. One finds that

$$\bar{F}_0=2^{16}/3^9\,. \tag{4.5}$$

In terms of the original electric field $F=F_0$, related to $\bar{F}=\bar{F}_0$ by (4.3), Eq. (4.5) yields

$$F_0=\frac{2^{16}}{3^9k^4}=\frac{2^{12}}{3^9(\lvert m\rvert+1)^4}\,. \tag{4.6}$$

In ordinary units, the last equation reads

$$F_0=\frac{1.07\times10^9}{(\lvert m\rvert+1)^4} \tag{4.7}$$

in units of V/cm. This is a semiclassical ap-

proximation for the quenching value of the electric field for an atom in its ground state in a given azimuthal subspace. As expected, the electric field required for ionization of the atom is smaller for high-angular-momentum states.

Although the finer details of Eq. (4.7) are not to be taken too seriously because quantum fluctuations and barrier penetration have been neglected, the preceding discussion suggests that a semiclassical expansion is possible for $F < F_0$. This entails expanding the potential around its minimum at $u = u_1$ and $v = v_1$, and proceeding essentially as in our previous calculation. There are some differences, however: The Gaussian fluctuations are not automatically diagonal in the present example, a situation that occurred previously in the study of the helium atom.[5] After diagonalizing the quadratic terms with an elementary Bogoliubov rotation, the calculation proceeds along the lines of the Appendix of this paper. It would be interesting to follow the above discussion to higher orders and examine the behavior of the resulting series. Just as in the magnetic field problem, the obtained recursion relation leads to a finite algorithm, in which contributions from continuum eigenstates are not manifestly present. The algebraic method of Ref. 5 is also applicable to the above problem, with suitable modifications to account for the detailed nature of the minimum of the semiclassical Hamiltonian.

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APPENDIX: THE RECURSION FORMULA

The results presented in the main text were obtained with a recursion formula for the coefficients E_s, $s = -1, 0, 1, \ldots$, appearing in the series representation of the ground-state energy (2.20). To derive the recursion relation, we first simplify the notation of Sec. II using dimensional arguments. The position of the minimum ($u = u_0$) is chosen to be the independent scale parameter, and η is taken as the independent dimensionless coupling constant. We also set $u_0 = 1$ in intermediate stages and include a dimensional factor $1/u_0^2 = B/\eta^2$ in the energy, at the end of the calculation. All quantities may then be expressed in terms of η. For instance,

$$\bar{Z} = \frac{1-\eta^4}{4}, \quad B = \eta^2, \tag{A1}$$

which are Eqs. (2.8) and (2.9) for $u_0 = 1$. Accordingly, Eq. (2.20) reads

$$\mathcal{E} = \sum_{s=-1}^{\infty} E_s k^{-s}, \tag{A2}$$

where E_s, $s = -1, 0, \ldots$, are functions of η alone. For notational simplicity, we will continue using the functions $f = f(\eta)$ and $g = g(\eta)$ defined in (2.21), so that (A1) may also be written as

$$\bar{Z} = g^2, \quad B = (1-4g^2)^{1/2}. \tag{A3}$$

To account for small fluctuations around the minimum of the potential, we shall further shift the variable u of Eq. (2.6) according to

$$u = u_0 + \frac{v}{k^{1/2}} = 1 + \frac{v}{k^{1/2}}. \tag{A4}$$

Putting everything together, Eq. (2.6) may be written as

$$-\frac{1}{2}\left(\frac{\partial^2}{\partial v^2} + \frac{\partial^2}{\partial z^2} + W(v, z; k)\right)\phi = (\mathcal{E} - kE_{-1})\phi, \tag{A5}$$

where

$$W = -2\left[\left(\frac{k}{8} - \frac{1}{2} + \frac{3}{8k}\right)(1+vk^{-1/2})^{-2} + \frac{k}{2}(\tfrac{1}{4} - g^2)(1+vk^{-1/2})^2 - kg^2\left[(1+vk^{-1/2})^2 + z^2k^{-1}\right]^{-1/2} - kE_{-1}\right], \tag{A6}$$

$$kE_{-1} = k(\tfrac{1}{4} - \tfrac{3}{2}g^2).$$

In obtaining (A5), the leading approximation to the energy has been subtracted from both sides of (2.6).

We finally introduce the function Ω:

$$\phi = e^{\Omega}, \tag{A7}$$

and rewrite Eq. (A5) in the form

$$\Omega_{vv}+\Omega_v^2+\Omega_{zz}+\Omega_z^2+W=-2\sum_{s=0}^{\infty}E_s k^{-s}, \tag{A8}$$

where we have also inserted the series (A2). Representing W by its Taylor series

$$W=\sum_{l,\alpha,\beta=0}^{\infty}W^l_{\alpha,\beta}v^\alpha z^\beta k^{-l/2}, \tag{A9}$$

the ground-state solution of (A8) is sought in the form

$$\Omega(v,z)=\sum_{l=0}^{\infty}\sum_{\gamma=0}^{l+1}\sum_{\substack{\alpha+\beta=\gamma\\ \alpha,\beta\geq 0}}(D^l_{\alpha,\beta}v^{2\alpha}z^{2\beta}k^{-l}+C^l_{\alpha,\beta}v^{2\alpha+1}z^{2\beta}k^{-l-1/2}). \tag{A10}$$

By convention, all Greek indices in the following take non-negative integer values.

A recursion formula is derived by inserting (A9) and (A10) into Eq. (A8) and equating coefficients. The final recursion relation for $D^l_{\alpha,\beta}$, $C^l_{\alpha,\beta}$, and E_s reads

$$-8(\alpha D^0_{1,0}+\beta D^0_{0,1})D^l_{\alpha,\beta}=W^{2l}_{2\alpha,2\beta}+\sum_{\substack{\sigma+\sigma'=l\\ \sigma,\sigma'<l\\ \lambda+\lambda'=\alpha+1\\ \mu+\mu'=\beta}}4\lambda\lambda' D^\sigma_{\lambda,\mu}D^{\sigma'}_{\lambda',\mu'}$$

$$+\Delta(\beta)\left(\sum_{\substack{\sigma+\sigma'=l\\ \sigma,\sigma'<l\\ \lambda+\lambda'=\alpha\\ \mu+\mu'=\beta+1}}4\mu\mu' D^\sigma_{\lambda,\mu}D^{\sigma'}_{\lambda',\mu'}+\sum_{\substack{\sigma+\sigma'=l-1\\ \lambda+\lambda'=\alpha-1\\ \mu+\mu'=\beta+1}}4\mu\mu' C^\sigma_{\lambda,\mu}C^{\sigma'}_{\lambda',\mu'}\right)$$

$$+\sum_{\substack{\sigma+\sigma'=l-1\\ \lambda+\lambda'=\alpha\\ \mu+\mu'=\beta}}(2\lambda+1)(2\lambda'+1)C^\sigma_{\lambda,\mu}C^{\sigma'}_{\lambda',\mu'}+\Delta(\alpha+\beta-l-1)$$

$$\times[2(\alpha+1)(2\alpha+1)D^l_{\alpha+1,\beta}+2(\beta+1)(2\beta+1)D^l_{\alpha,\beta+1}] \tag{A11a}$$

and

$$-[(8\alpha+4)D^0_{1,0}+8\beta D^0_{0,1}]C^l_{\alpha,\beta}=W^{2l+1}_{2\alpha+1,2\beta}+\sum_{\substack{\sigma+\sigma'=l\\ \sigma<l\\ \lambda+\lambda'=\alpha+1\\ \mu+\mu'=\beta}}4(2\lambda+1)\lambda' C^\sigma_{\lambda,\mu}D^{\sigma'}_{\lambda',\mu'}+8\Delta(\beta)\sum_{\substack{\sigma+\sigma'=l\\ \sigma<l\\ \lambda+\lambda'=\alpha\\ \mu+\mu'=\beta+1}}\mu\mu' C^\sigma_{\lambda,\mu}D^{\sigma'}_{\lambda',\mu'}$$

$$+\Delta(\alpha+\beta-l-1)[2(\alpha+1)(2\alpha+3)C^l_{\alpha+1,\beta}+2(\beta+1)(2\beta+1)C^l_{\alpha,\beta+1}], \tag{A11b}$$

and

$$E_{-1}=\tfrac{1}{4}-\tfrac{3}{2}g^2,$$
$$E_s=-\tfrac{1}{2}\sum_{\sigma+\sigma'=s-1}C^\sigma_{0,0}C^{\sigma'}_{0,0}-D^s_{1,0}-D^s_{0,1}-\tfrac{1}{2}W^{2s}_{0,0},\quad s\geq 0. \tag{A11c}$$

In the preceding formulas we have used some notational abbreviations: First, $\Delta(\alpha)$ is defined as

$$\Delta(\alpha)=1-\delta_{\alpha,0}, \tag{A12}$$

so that $\Delta(0)=0$ and $\Delta(\alpha)=1$, $\alpha\neq 0$. Second, we have introduced auxilliary coefficients $C^l_{\alpha,\beta}$ and $D^l_{\alpha,\beta}$ with $\alpha+\beta>l+1$, even though the expansion (A10) requires only coefficients with $\alpha+\beta\leq l+1$. Hence, the recursion relation (A11) should be supplemented with the stipulation that the C and D coefficients vanish if $\alpha+\beta>l+1$.

The lowest-order terms in (A11) are defined as follows: Terms of the form $D^l_{0,0}$ are clearly irrelevant, for they merely contribute to the normalization of the wave function. The coefficients $D^0_{1,0}$ and $D^0_{0,1}$ appearing in the left side of (A11) are determined by examining the Gaussian fluctuations around the minimum of the potential; namely, terms that are quadratic in v and z. Linear terms do not appear, be-

cause we are expanding around a minimum. This leads to the identifications

$$(D^0_{1,0})^2 = \frac{f^2}{4}, \quad (D^0_{0,1})^2 = \frac{g^2}{4}, \tag{A13}$$

where f and g are the functions of η defined in Eq. (2.21). Taking the square roots, we write

$$D^0_{1,0} = -f/2, \quad D^0_{0,1} = -g/2, \tag{A14}$$

where the choice of the sign has been dictated by the requirement that the wave function vanish at infinity.

All higher coefficients are determined by (A11) using a finite number of operations once the Taylor coefficients for the potential W are computed. They are obtained by writing the potential (A6) in the form (A9). Explicitly, one finds for the nonvanishing $W^l_{\alpha,\beta}$'s:

$$\begin{aligned} &W^l_{l,0} = (-1)^l(l+1), \quad l \geq 0 \\ &W^l_{l+2,0} = \tfrac{1}{4}(-1)^{l+1}(l+3) + 2g^2Q^l_0, \quad l \geq 0 \\ &W^l_{l-2,0} = \tfrac{3}{4}(-1)^{l+1}(l-1), \quad l \geq 2 \\ &W^l_{l+2-2n,2n} = 2g^2Q^l_n, \quad n = 1, 2, \ldots, L(l), \quad l \geq 0 \end{aligned} \tag{A15}$$

where

$$L(l) = \begin{cases} \dfrac{l+2}{2}, & l \text{ even} \\ \dfrac{l+1}{2}, & l \text{ odd} \end{cases} \tag{A16}$$

and

$$Q^l_n = (-2)^{l+2} \sum_{m=n}^{L(l)} (-\tfrac{1}{4})^m \frac{(l+2-m)!(2l+3-2m)!!}{n!(m-n)!(l+2-2m)!(2l+4-2m)!!}. \tag{A17}$$

The recursion formula given by Eqs. (A11)–(A17) was solved using the MACSYMA program at M.I.T. to obtain the results described in the text. The reader who is interested in calculations that go beyond the explicit results of Sec. II, or the numerical examples of Sec. III, may directly use the above recursion or contact the authors for further details. The actual program is very concise, taking less than half of a printed page.

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