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Nonrelativistic Wentzel-Kramers-Brillouin eigenvalues of the Thomas-Fermi neutral-atom potential in the large-atomic-number limit

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The Wentzel-Kramers-Brillouin eigenvalue condition is developed in an expansion in $Z^{-1/3}$ to lowest order in the limit in which the atomic number Z becomes very large. The energy levels are studied explicitly for finite orbital angular momentum l quantum numbers. The nature of the resulting level spectrum is illustrated and its connection with the solutions of Schrödinger's equation by Latter, for a closely related potential, is briefly discussed. It is pointed out that to get the complete level spectrum near the continuum, for large Z, the case of l of order $Z^{1/3}$ will eventually require consideration. Finally, a few general results are established, one of which predicts the maximum value of l for which a bound state can occur for a given value of Z.

I. INTRODUCTION

The Thomas-Fermi theory of heavy atoms was the forerunner of modern density-functional theory.[1] It remains of considerable interest for first-principles theory and, in particular, its connection with the important $1/Z$ expansion[2,3] was established by March and White.[4]

The total energy of atoms is usefully approximated by the semiclassical Thomas-Fermi method, provided suitable corrections are applied.[5,6] In the present work, we have been encouraged by the utility of the above-mentioned formula for total binding energies to attempt a more detailed study of the level spectrum in the self-consistent Thomas-Fermi potential for neutral atoms. This, as is well known, can be written in the form

$$V(r)=-\frac{Ze^2}{r}\phi(x)\ , \tag{1.1}$$

where the dimensionless measure of length x is related to r by

$$r=bx,\quad b\equiv\alpha Z^{-1/3}a_0,\quad \alpha=\tfrac{1}{4}(9\pi^2/2)^{1/3}=0.885\,34\ , \tag{1.2}$$

with a_0, the Bohr radius, equal to $\hbar^2/me^2$. The "screening" function $\phi(x)$, again dimensionless, satisfies the dimensionless Thomas-Fermi equation[3]

$$\frac{d^2\phi}{dx^2}=\frac{\phi^{3/2}}{x^{1/2}}\ , \tag{1.3}$$

with boundary conditions appropriate for the neutral atom

$$\phi(x)=1+O(x)\ \text{ as } x\to 0\ ,$$
$$\phi(x)\to 144/x^3+O(x^{-3-\lambda})\ \text{ as } x\to\infty\ , \tag{1.4}$$

where

$$\lambda=\tfrac{1}{2}[(73)^{1/2}-7]\ . \tag{1.5}$$

The potential energy $V(r)$ defined by Eqs. (1.1)—(1.5) will be used in the present work to study the level spectrum of neutral atoms in the statistical limit in which the atomic number Z becomes very large. In this limit, it seems clear that the asymptotic distribution of eigenvalues will be correctly given by the semiclassical Wentzel-Kramers-Brillouin (WKB) method. In particular, for the orbital angular momentum quantum number l, the WKB condition from which to determine the one-electron nonrelativistic eigenvalues ϵ_{sl} say, is[6,7]

$$\pi(s+\tfrac{1}{2})=Z^{1/3}\int_{x_1}^{x_2}dx\left[2\alpha\frac{\phi(x)}{x}-\frac{(l+\frac{1}{2})^2}{x^2}Z^{-2/3}+\epsilon_{sl}\alpha^2Z^{-4/3}\right]^{1/2}$$
$$=Z^{1/3}I(Z,l,\epsilon_{sl})\ , \tag{1.6}$$

where x_1 and x_2 denote the classical turning points of the motion in dimensionless units and the energy is in Rydbergs.

In the work described below, all attention is focused on the development of this condition (1.6) by expansion to lowest order in $Z^{-1/3}$ for large Z, in order to explicitly determine the eigenvalues ϵ_{sl} for the Thomas-Fermi potential in terms of the pair of quantum numbers s and l. Specifically, we shall study here finite, and usually small, values of the orbital angular momentum quantum number l, even when s is a very large integer; in an example we study below, $s\sim 10^3$.

The outline of the paper is as follows. In Sec. II we obtain a functional relation for $\epsilon_{sl}/(2l+1)^4$ in terms of Z, s, and l which is a valid representation of the WKB condition (1.6) in the limit of large Z and with l and ϵ_{sl} finite, of order Z^0. In Sec. III examples are given to illustrate the use of this relation when varying Z. Section IV describes the relation of the present work to the numerical solution by Latter[8] of Schrödinger's equation for Z in the range of the Periodic Table, for a potential closely related to that of Eq. (1.1). In Sec. V, finally, a relation is obtained for the maximum value of l for which a bound state can occur for a given Z.

II. ASYMPTOTIC FORM FOR LARGE Z OF WKB EIGENVALUES FOR THOMAS-FERMI POTENTIAL

In this section we shall utilize the scaling properties with the atomic number Z of the self-consistent Thomas-Fermi potential for neutral atoms, as summarized in Sec. I, to develop analytically the WKB condition (1.6) by expansion in $Z^{-1/3}$, as Z becomes very large. In order to do so, we need first of all to determine the behavior of the turning points of the classical motion x_1 and x_2 in the limit $Z\to\infty$ and with ϵ_{sl} and l finite, of order Z^0. The turning points are determined by requiring that the WKB integrand in (1.6) vanish, which in terms of the screening function $\phi(x)$ reads

$$x\phi(x)=[(l+\tfrac{1}{2})^2Z^{-2/3}-x^2\epsilon_{sl}\alpha^2Z^{-4/3}]/2\alpha \ . \qquad (2.1)$$

It is found that the two roots x_1 and x_2 tend to infinity and zero, respectively, as Z goes to infinity. By using the asymptotic form of $\phi(x)$ for small and large x given in Eqs. (1.4), one readily obtains for large Z,

$$x_1=(l+\tfrac{1}{2})^2Z^{-2/3}/2\alpha+O(Z^{-4/3}) \ , \qquad (2.2)$$

and

$$x_2=\frac{(l+\frac{1}{2})}{\alpha}\times\left\{\left[1-\left[1-\frac{(36\pi)^2}{(2l+1)^4}\right]^{1/2}\right]\Big/2\epsilon\right\}^{1/2}Z^{1/3}+O(Z^{-1/3-\lambda}) \ . \qquad (2.3)$$

Above, we have now dropped the subscripts of ϵ. We shall do the same in the following when there is no danger of confusion.

Our task now is to evaluate the asymptotic form of the integral on the right-hand side of Eq. (1.6) when $Z\to\infty$ and when x_1 and x_2 are given by Eqs. (2.2) and (2.3), respectively. It can easily be verified that $I(Z,l,\epsilon)$ goes to a finite limit when $Z\to\infty$. Moreover, one can prove (see Appendix) that, for large Z,

$$I(Z,l,\epsilon)=\pi K+\pi i(l,\epsilon)Z^{-1/3}+\cdots \qquad (2.4)$$

where the ellipsis represents higher-order terms. Here

$$K=\pi^{-1}\int_0^\infty dx\left[2\alpha\frac{\phi(x)}{x}\right]^{1/2}=1.6566 \ , \qquad (2.5)$$

$$i(l,\epsilon)=-(l+\tfrac{1}{2})\left[1+2f\left[\frac{\epsilon}{(2l+1)^4}\right]\right] \ . \qquad (2.6)$$

The function $f(y)$ above, which is explicitly evaluated in the Appendix, has a simple expression in terms of complete elliptic integrals of the first and second kinds[9] as follows:

$$f(y)=(1-2t)^{-1/2}[2E(t)-K(t)]/2\pi \ , \qquad (2.7)$$

with

$$t=\tfrac{1}{2}\{1-[1-(36\pi)^2y]^{-1/2}\} \ . \qquad (2.8)$$

By utilizing Eqs. (2.4)—(2.6) in the WKB condition (1.6), one gets the asymptotic form of this as

$$f\left[\frac{\epsilon}{(2l+1)^4}\right]=(KZ^{1/3}-n)/(2l+1) \ , \qquad (2.9)$$

having defined a new quantum number $n=s+l+1$ by analogy with the hydrogenic problem. Relation (2.9) can be formally inverted to give, finally, the energy spectrum in the scaled form

$$\epsilon/(2l+1)^4=f^{-1}[(KZ^{1/3}-n)/(2l+1)] \ . \qquad (2.10)$$

As we anticipated, the relation above gives $\epsilon/(2l+1)^4$ as a unique function of Z, l, and n (or s). Moreover, such a function depends only on a particular combination of Z, l, and n. We discuss the main features of the energy spectrum embodied in Eq. (2.9) in Sec. III. However, we stress here that while the present method of calculation of the WKB levels is certainly valid for finite l and ϵ and sufficiently large Z, caution is of course needed in that the WKB levels only become precise in Bohr's correspondence principle limit of large quantum numbers. Some check of this latter point is possible by comparison with numerical solutions of the Schrödinger equation for a potential closely related to the Thomas-Fermi potential utilized in the present paper.

III. EXPLICIT WKB ENERGIES FROM THE ASYMPTOTIC FORMULA

The asymptotic spectrum of energy levels in the Thomas-Fermi effective potential is easily obtained, for given large Z, by solving numerically[10] Eq. (2.9). The energy levels depend on the two quantum numbers l and n (or s). It is apparent from Eq. (2.9) that, for given Z and l, there is a maximum allowed value for n, that we denote here by n^*. This is a consequence of the properties of the function f in Eq. (2.9), which is positive and which decreases with increasing energy. By using the fact that $f(0)=0.25$ one finds

$$KZ^{1/3}-n^*-l/2\geq 0.25 \ . \qquad (3.1)$$

The existence of a maximum n tells us that, for each finite l, there is a finite number (of order $Z^{1/3}$) of bound states. This is consistent with what one would expect on the basis of the fast decay, at large distances, r^{-4} of the Thomas-Fermi potential. Besides, the particular functional relation (2.10) between ϵ, l, Z, and n implies another great simplification in classifying the levels as a function of Z. Since the energy depends only on the difference $KZ^{1/3}-n$, for given l, it turns out that a change of $KZ^{1/3}$ by an integer is just equivalent to relabeling the levels with quantum numbers n shifted by the same integer. Thus it is sufficient to plot the energy levels as a function of the fractional part of $KZ^{1/3}$ defined as

$$\zeta=KZ^{1/3}-[KZ^{1/3}] \ , \qquad (3.2)$$

with the square brackets [ ] indicating the integer part. This is done in Fig. 1, where energy levels are shown for a

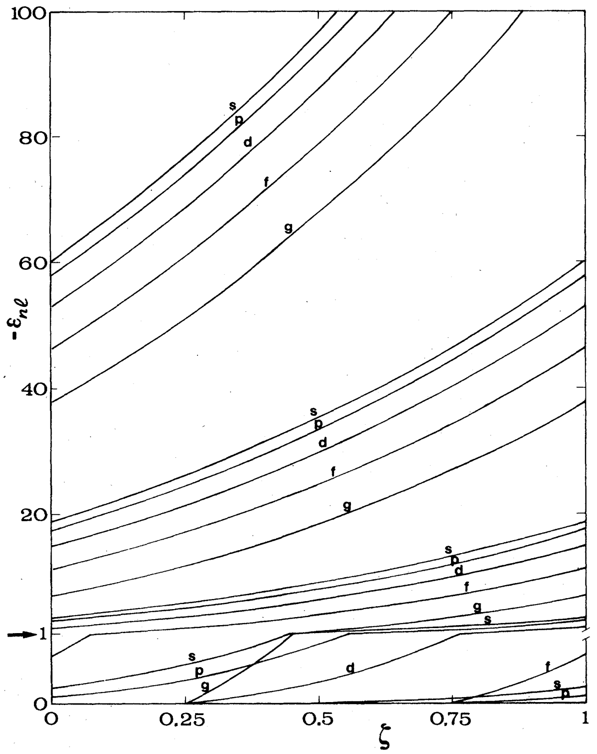

FIG. 1. Energy levels in the Thomas-Fermi potential, from the asymptotic WKB formula (2.10) as function of the fractional part ζ of $KZ^{1/3}$ [defined in Eq. (3.2) of the text] and for a few values of l. The value of l is indicated for each level. The value of n can be obtained as explained in the text, by using Eq. (3.3), when a particular value of Z has been chosen. Notice the change of scale indicated by the arrow.

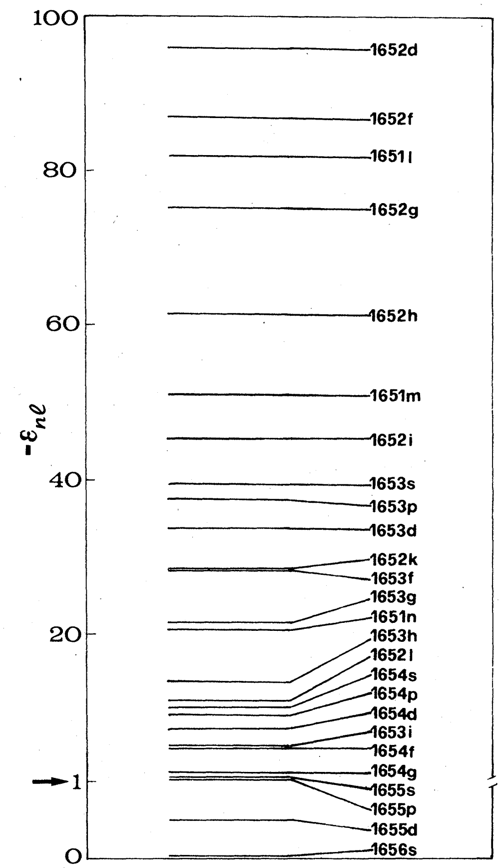

FIG. 2. Energy levels in the Thomas-Fermi potential, from the asymptotic WKB formula (2.10) for $Z^{1/3}=1000$ and $l \leq 10$. The values of n and l are indicated for each level. Notice the change of scale indicated by the arrow.

few values of the angular momentum quantum number l. The quantum number n, for the ith level with a given l counted from the continuum, is

$$n=[KZ^{1/3}]+(\zeta-l/2-0.25)-i+1 \tag{3.3}$$

for atomic number Z.

It is worth noticing the following two qualitative features of the spectrum shown in Fig. 1: (i) New discrete levels emerge from the continuum at two particular values of ζ, at $\zeta=0.25$ for even l, and at $\zeta=0.75$ for odd l. (ii) The first level crossed as one moves from the continuum is always either an s state, if $0.25<\zeta<0.75$; or a p state if $0<\zeta<0.25$ or $0.75<\zeta<1$. An example of the actual spectrum with the appropriate n quantum numbers is given for $Z^{1/3}=1000$ in Fig. 2. Angular momenta up to $l=10$ ($l \ll Z^{1/3}$) are shown.

IV. COMPARISON OF NUMERICAL SOLUTIONS OF SCHRÖDINGER'S EQUATION WITH THE ASYMPTOTIC FORMULA

We have not found precise numerical solutions of the Schrödinger equation for the Thomas-Fermi potential (1.1). Latter has given such solutions for a closely related potential in which $\phi(x)$ is fitted by the approximate formula

$$\phi(x)=(1+0.0274x^{1/2}+1.243x-0.1486x^{3/2}+0.2302x^2+0.007\,298x^{5/2}+0.006\,944x^3)^{-1}, \tag{4.1}$$

which certainly satisfies the conditions (1.4) to leading order.

However, using the form (4.1) for the screening function $\phi(x)$ in Eq. (1.1), Latter then modified the potential, following the work of Fermi and Amaldi,[11] by changing the potential energy to read

$$V(r)=\begin{cases} -\dfrac{Ze^2}{r}\phi(x) & \text{if } V(r)\leq -\dfrac{e^2}{r} \\ -\dfrac{e^2}{r} & \text{otherwise}. \end{cases} \tag{4.2}$$

In Fig. 3 we have compared Latter's results with the WKB asymptotic prediction. The energy levels for three values of Z (25, 65, and 92) taken from Latter's tables are plotted in the scaled form suggested by Eq. (2.10) together with the asymptotic WKB relation. We are well aware of the fact the Z values considered by Latter, being in the range of the Periodic Table, are not large in the sense of

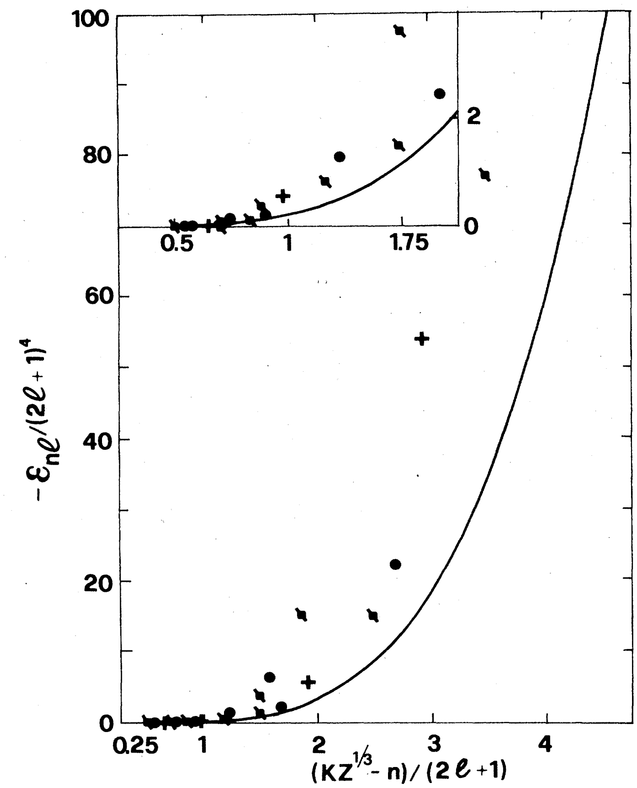

FIG. 3. Comparison of the asymptotic WKB energy formula (2.10) for the Thomas-Fermi potential and numerical solutions of the Schrödinger equation by Latter (Ref. 8) for three values of Z in the range of the Periodic Table. The full curve gives Eq. (2.10) of the text while Latter's results are given by $+$, $Z=26$; ◣, $Z=65$; and ●, $Z=92$.

this paper. Nonetheless, they are seen to follow the asymptotic relation (2.10), at least qualitatively.

Because of the difference between Latter's potential and a true Thomas-Fermi potential, we have studied under what conditions the WKB levels could be changed by the Coulomb tail in Latter's potential (4.2). This is readily achieved by studying the turning points of the classical motion in such a modified potential, in a similar manner to that used in Sec. II. One finds that the levels are changed, with respect to the true Thomas-Fermi potential, if the energy violates the following conditions:

$$-\epsilon > 2[1-(2l+1)^2/8\alpha(144)^{1/3}]/(144)^{1/3}\alpha \quad \text{if } l<2\ ,$$
$$-\epsilon > 4/(2l+1)^2 \quad \text{if } l \geq 2\ . \tag{4.3}$$

This means that the Coulomb tail is seen, within the WKB approximation, only if the energy level is very close to the continuum, the closeness being accentuated as the angular momentum quantum number l increases. Only Latter's levels satisfying Eq. (4.3) have been plotted in Fig. 3.

V. BOUNDS ON ORBITAL ANGULAR MOMENTUM QUANTUM NUMBERS l FOR BOUND STATES OF GIVEN Z

Starting with the work of Fermi, numerous authors have considered the level schemes in Thomas-Fermi-like

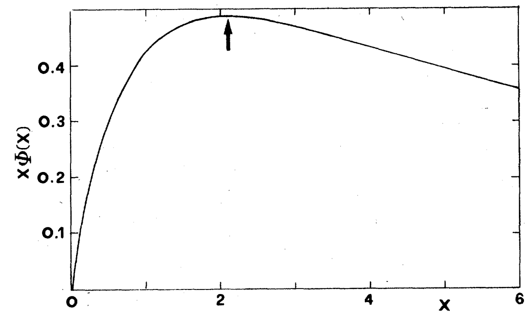

FIG. 4. Thomas-Fermi screening function. The arrow indicates the maximum of $x\phi(x)$ as function of x.

potentials. For example, reference can be made to the table in the paper by Abrahamson.[12]

Our aim here is to give the maximum of l for which the WKB condition (1.6) has two turning points x_1 and x_2. It is clear from Eq. (2.1) that the WKB integrand becomes zero, in terms of the screening function $\phi(x)$, when $x\phi(x)$ intersects a parabola which is increasing with x from the value $(l+\frac{1}{2})^2/2\alpha Z^{2/3}$ at $x=0$. Figure 4 shows a plot to scale of $x\phi(x)$, and it can be seen that when $(l+\frac{1}{2})^2/2\alpha Z^{2/3}$ exceeds the maximum value of $x\phi(x)$, there are no real turning points, even for vanishingly small energy. In fact $[x\phi(x)]_{\max}=0.48635$ and thus one must satisfy, for bound states calculated from the WKB criterion

$$l+\tfrac{1}{2} < (0.9727\alpha)^{1/2}Z^{1/3}\ . \tag{5.1}$$

This condition, while derived somewhat differently, is of the same form as that proposed by Abrahamson.[12] Numerically the inequality (5.1) yields

$$Z > 0.15641(2l+1)^3\ , \tag{5.2}$$

whereas Abrahamson gave the approximate value $\frac{1}{6}$ for the factor multiplying $(2l+1)$.[3]

VI. SUMMARY AND CONCLUSION

For the Thomas-Fermi potential for neutral atoms, it has proved possible to express the WKB nonrelativistic eigenvalues in the universal form of Eq. (2.10), which is valid for sufficiently large Z and for finite energy and orbital angular momentum quantum number l.

This condition, used in conjunction with Fig. 3, turns out to contain within itself a rich variety of level spectra for large Z. Examples, showing the level ordering coming down from the continuum level, are depicted in Figs. 1 and 2. They must be fully quantitative reflections of the WKB eigenvalues.

Should further work on the eigenvalue spectrum be needed subsequently, it would be of obvious interest to complete the level spectra in Figs. 1 and 2 by adding results for l becoming large as $Z^{1/3}$ for large Z. Again, the WKB condition should be the appropriate tool in the limit of large Z, provided the quantum numbers are also large enough to lie in the region where Bohr's correspondence principle holds. We are currently attempting the generalization of the present considerations to molecules, using the known scaling properties of the self-consistent Thomas-Fermi potentials.[13,14]

ACKNOWLEDGMENTS

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APPENDIX

Here, our object is to determine the asymptotic behavior of the integral

$$I(Z,l,\epsilon)=\int_{x_1}^{x_2} dx\left[2\alpha\frac{\phi(x)}{x}-\frac{(l+\frac{1}{2})}{x^2}Z^{-2/3}-\alpha^2\epsilon Z^{4/3}\right]^{1/2} \tag{A1}$$

when Z tends to infinity and the turning points x_1 and x_2 are given asymptotically by Eqs. (2.2) and (2.3).

It is clear that

$$\lim_{Z\to\infty} I(Z,l,\epsilon)=\pi K\equiv\int_0^\infty dx\left[2\alpha\frac{\phi(x)}{x}\right]^{1/2}. \tag{A2}$$

We shall show that the correction term to K, for large Z, goes as $Z^{-1/3}$ and we want to explicitly calculate the coefficient of such a correction term. To this end, we consider the limit

$$\lim_{z\to\infty} -Z^{2/3}\frac{\partial}{\partial Z^{1/3}}I(Z,l,\epsilon)=\lim_{Z\to\infty} -\int_{x_1}^{x_2} dx\frac{(l+\frac{1}{2})^2Z^{-1/3}/x^2+2\epsilon Z^{-1}\alpha^2}{\left[2\alpha\frac{\phi(x)}{x}-\frac{(l+\frac{1}{2})^2}{x^2}Z^{-2/3}-\alpha^2\epsilon Z^{-4/3}\right]^{1/2}}. \tag{A3}$$

If the above limit exists and is finite and we denote it then by $\pi i(l,\epsilon)$, then we can write for large Z

$$I(Z,l,\epsilon)=\pi K+\pi i(l,\epsilon)Z^{-1/3}+\cdots , \tag{A4}$$

where the ellipsis represents higher-order terms. In order to calculate the integral in Eq. (A3), we divide the integration range into three regions $x_1\le x\le\bar{x}_1$, $\bar{x}_1\le x\le\bar{x}_2$, and $\bar{x}_2\le x\le x_2$ where $\bar{x}_1$ and $\bar{x}_2$ are a very small and a very large number, respectively. This is always possible since in the limit $Z\to\infty$, $x_2\sim Z^{1/3}$, and $x_1\sim Z^{-2/3}$. We denote the three integrals by I_1, I_2, and I_3, respectively. By direct inspection it becomes clear that

$$I_2=-\int_{\bar{x}_1}^{\bar{x}_2} dx\frac{(l+\frac{1}{2})^2Z^{-1/3}/x^2+2\epsilon Z^{-1}\alpha^2}{\left[2\alpha\frac{\phi x}{x}-\frac{(l+\frac{1}{2})^2}{x^2}Z^{-2/3}-\alpha^2\epsilon Z^{-4/3}\right]^{1/2}}, \tag{A5}$$

and therefore vanishes as Z tends to infinity. I_1 can be calculated by substituting for $\phi(x)$ the form valid for small x, $\phi(x)=1+\phi' x$ where ϕ' evidently denotes the slope at the origin. Thus

$$I_1=-\int_{x_1}^{\bar{x}_1} dx\frac{(l+\frac{1}{2})^2Z^{-1/3}/x^2+2\epsilon Z^{-1}\alpha^2}{\left[\frac{2\alpha}{x}+2\phi'\alpha-\frac{(l+\frac{1}{2})^2}{x^2}Z^{-2/3}-\alpha^2\epsilon Z^{-4/3}\right]^{1/2}}. \tag{A6}$$

I_1 can be expressed in terms of elementary functions. One finds for Z tending to infinity

$$\lim_{Z\to\infty} I_1=-\pi(l+\tfrac{1}{2}). \tag{A7}$$

Similarly, we calculate I_3 utilizing the fact that $\bar{x}_2\gg 1$ and we approximate $\phi(x)$ with the asymptotic form $144/x^3$. We then obtain

$$I_3\equiv-\int_{\bar{x}_2}^{x_2} dx\frac{(l+\frac{1}{2})^2Z^{-1/3}/x^2+2\epsilon Z^{-1}\alpha^2}{\left[\frac{288\alpha}{x^4}-\frac{(l+\frac{1}{2})^2}{x^2}Z^{-2/3}-\alpha^2\epsilon Z^{-4/3}\right]^{1/2}}. \tag{A8}$$

It is found that I_3 can be expressed simply in terms of elliptic integrals[9] which become complete elliptic integrals as Z tends to infinity. The result is

$$\lim_{Z\to\infty} I_3 = -(l+\tfrac{1}{2})[2E(t)-K(t)](1-2t)^{-1/2}, \quad \text{(A9)}$$

and

$$t=\frac{1}{2}\left[1-\left[1-\frac{(36\pi)^2}{(2l+1)^4}\right]^{-1/2}\right]. \quad \text{(A10)}$$

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