Semiclassical atom

Berthold-Georg Englert and Julian Schwinger
Department of Physics, University of California, Los Angeles, California 90024
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Semiclassical quantization is incorporated into the average potential approach to atomic physics. The stationary energy functional is shown to be the sum of the Thomas-Fermi functional and a mainly oscillatory part. The latter turns out to be a small correction for sufficiently large atomic numbers, allowing perturbative treatment. Further, a detailed study of semiclassical spectra, with emphasis on energy degeneracy, is performed.

INTRODUCTION

In theoretical atomic physics two main approaches have been pursued. One is the Hartree-Fock (HF) method and its refinements; it can be viewed as a generalization of Schrödinger's description of the hydrogen atom to many-electron systems. It is, by construction, more reliable the smaller the number of electrons. The other one is the statistical Thomas-Fermi (TF) treatment and its improvements. This one uses the picture of an electronic atmosphere surrounding the nucleus; it is better the larger the number of electrons. Somewhere between the HF and TF treatments is the semiclassical approach that we want to study here. It borrows the idea of a common average potential for all electrons from the TF method while using the concept of angular and radial quantum numbers much as the HF method does.

The present paper is devoted to developing the general scheme of such a semiclassical theory. We demonstrate that it contains the TF approximation as the limit of very large quantum numbers. Then we study general properties of semiclassical spectra. Finally, a qualitative discussion of oscillatory contributions, that supplement the TF approximation, is presented. Subsequent papers will use this information in addressing more detailed problems of particular interest.

ENERGY FUNCTIONAL

The basic approximation replaces the complicated many-particle problem by a one-particle treatment. The electrons are regarded as moving independently in a common local average potential V. The one-particle Hamilton operator (atomic units: $e=m=\hbar=1$)

$$H=\tfrac{1}{2}p^2+V \tag{1}$$

gives rise to the total one-particle energy

$$E_{1\mathrm{p}}=\mathrm{tr}[H\eta(-H-\zeta)]\ , \tag{2}$$

where Heaviside's unit step function η selects those states with eigenvalue H' less than $-\zeta$. The count of those occupied states equals N, the number of electrons,

$$N=\mathrm{tr}[\eta(-H-\zeta)]\ . \tag{3}$$

We combine Eqs. (2) and (3) into

$$E_{1\mathrm{p}}=\mathrm{tr}[(H+\zeta)\eta(-H-\zeta)]-\zeta N\equiv E_1-\zeta N \tag{4}$$

and recognize the relation

$$\frac{\partial}{\partial\zeta}E_1=\mathrm{tr}[\eta(-H-\zeta)]=N\ . \tag{5}$$

Another differential statement expresses the fact that the response of the one-particle energy to infinitesimal variations of the potential exhibits the particle density n:

$$\delta_V E_{1\mathrm{p}}=\delta_V E_1=\int(d\mathbf{r})n\,\delta V\ . \tag{6}$$

Since E_1 of Eq. (4) contains ζ and V only as the sum $V+\zeta$, we conclude from Eqs. (5) and (6) that the total number of electrons is equal to the integrated density

$$N=\int(d\mathbf{r})n\ , \tag{7}$$

as it should.

The one-particle energy $E_{1\mathrm{p}}$ counts the interaction energy of each electron pair twice. In order to obtain the total energy of the system we must therefore subtract this interaction energy once. If we disregard exchange,[1] as we shall do throughout this paper, this is simply accomplished by subtracting the electrostatic energy of the electron cloud, here written in terms of the integrated square of the electric field:

$$E=E_1-\zeta N-\int(d\mathbf{r})\frac{1}{8\pi}\left[\nabla\left[V+\frac{Z}{r}\right]\right]^2\ . \tag{8}$$

This energy functional is particularly advantageous because, for given Z and N, it is stationary under infinitesimal variations of both ζ and V,

$$\delta E=\left[\frac{\partial E_1}{\partial\zeta}-N\right]\delta\zeta+\int(d\mathbf{r})\left[n+\frac{1}{4\pi}\nabla^2\left[V+\frac{Z}{r}\right]\right]\delta V$$
$$=0\ . \tag{9}$$

The latter equality is a consequence of Eq. (5) and Poisson's equation

$$-\frac{1}{4\pi}\nabla^2\left[V+\frac{Z}{r}\right]=n\ . \tag{10}$$

In the extreme semiclassical limit of very large quantum numbers, the trace in E_1 [Eq. (4)] is evaluated as the phase-space integral covering the classical domain (the factor of 2 is the spin multiplicity),

$$E_1=2\int\int\frac{(d\mathbf{r})(d\mathbf{p})}{(2\pi)^3}(\tfrac{1}{2}p^2+V+\zeta)\eta(-\tfrac{1}{2}p^2-V-\zeta)\ . \tag{11}$$

After carrying out the momentum integration, this reproduces the familiar TF expressions for E_1 and n [Eq. (6)]:

$$(E_1)_{\rm TF}=\int(d\mathbf{r})\left[-\frac{1}{15\pi^2}\right][-2(V+\zeta)]^{5/2}\ , \tag{12}$$

$$n_{\rm TF}=\frac{1}{3\pi^2}[-2(V+\zeta)]^{3/2}\ . \tag{13}$$

The combination of Eqs. (10) and (13) is the TF differential equation for the potential V.

A significant improvement over the TF method, and towards the HF method, is achieved by evaluating E_1 as a sum over discrete eigenvalues of the one-particle Hamilton operator H. These eigenvalues E_{l,n_r} are labeled by the angular quantum number l and the radial quantum number n_r, both being integers $0,1,2,\ldots$. We relate the spherically symmetric potential $V(r)$ to these energy values by means of the semiclassical quantization condition (usually derived from the WKB approximation)

$$n_r+\tfrac{1}{2}=\frac{1}{\pi}\int dr\left[2\left[E_{l,n_r}-V-\frac{(l+\frac{1}{2})^2}{2r^2}\right]\right]^{1/2}$$

$$\equiv\frac{1}{\pi}\int dr\,p_{l,n_r}(r)\ . \tag{14}$$

The domain of radial integration covers the classically allowed region, where the argument of the square root is positive.

With E_{l,n_r} given implicitly by Eq. (14), E_1 is now [note the $2(2l+1)$-fold spin and angular momentum multiplicity]

$$E_1=2\sum_{l,n_r=0}^{\infty}(2l+1)(E_{l,n_r}+\zeta)\eta(-E_{l,n_r}-\zeta)\ , \tag{15}$$

and, as expected,

$$N=\frac{\partial E_1}{\partial\zeta}=2\sum_{l,n_r=0}^{\infty}(2l+1)\eta(-E_{l,n_r}-\zeta)\ , \tag{16}$$

where the step function removes E_{l,n_r} values larger than $-\zeta$.

There is ample justification for using the semiclassical quantization rule (14). For large quantum numbers it represents a very good approximation. Small quantum numbers belong to the strongly bound electrons; for these the potential is essentially Coulombic,

$$V\sim-\frac{Z}{r}+\text{const}+O(r^2)\ \text{ as } r\to0\ , \tag{17}$$

and Eq. (14) supplies the exact answer.

For the sake of completeness, we report the semiclassical density associated with (15). First note that an infinitesimal change of the potential causes E_{l,n_r} to be modified according to

$$\delta E_{l,n_r}=\frac{\int dr\,\delta V(p_{l,n_r})^{-1}}{\int dr(p_{l,n_r})^{-1}}\ . \tag{18}$$

Therefore, the contribution of any individual quantum number pair (l,n_r) to the density

$$n=\sum_{l,n_r}n_{l,n_r}\eta(-E_{n_r,l}-\zeta) \tag{19}$$

is given by

$$n_{l,n_r}(r)=\frac{2(2l+1)}{4\pi r^2}\left[p_{l,n_r}(r)\int\frac{dr'}{p_{l,n_r}(r')}\right]^{-1}\ , \tag{20}$$

which accounts for $2(2l+1)$ electrons,

$$\int(d\mathbf{r})n_{l,n_r}=2(2l+1)\ , \tag{21}$$

and the correct total number N [Eqs. (16) and (7)].

At the boundaries of the classically allowed regions, the densities (20) display the typical WKB infinities associated with the vanishing of $p_{l,n_r}(r)$. This deficiency can be removed by introducing quantum corrections that provide a smooth transition into the classically forbidden regions.[2] More about this on another occasion.

FOURIER FORMULATION

The sums over quantum numbers in (15) and (16), which have their range defined implicitly by ζ and, through (14), by V, are not well suited for further use. We therefore rewrite (15), in a few steps. First, instead of summing over l and n_r, we equivalently integrate over λ and ν, given by

$$\lambda\equiv l+\tfrac{1}{2},\quad \nu\equiv n_r+\tfrac{1}{2}\ , \tag{22}$$

and introduce

$$\varepsilon_{\lambda,\nu}\equiv E_{l,n_r}\ , \tag{23}$$

which is related to ν and λ by [Eq. (14)]

$$\nu=\frac{1}{\pi}\int\frac{dr}{r}[2r^2(\varepsilon_{\lambda,\nu}-V)-\lambda^2]^{1/2}\ . \tag{24}$$

Through the introduction of δ functions to select the discrete quantum numbers, Eq. (15) now reads

$$E_1=4\int_0^\infty d\lambda\,\lambda\sum_{l=-\infty}^{\infty}\delta(l+\tfrac{1}{2}-\lambda)\int_0^\infty d\nu\sum_{n_r=-\infty}^{\infty}\delta(n_r+\tfrac{1}{2}-\nu)(\varepsilon_{\lambda,\nu}+\zeta)\eta(-\varepsilon_{\lambda,\nu}-\zeta)\ . \tag{25}$$

Then the twofold application of the Poisson identity

$$\sum_{l=-\infty}^{\infty}\delta(l+\tfrac{1}{2}-\lambda)=\sum_{k=-\infty}^{\infty}(-1)^k e^{2\pi i k\lambda}\,,$$
$$\sum_{n_r=-\infty}^{\infty}\delta(n_r+\tfrac{1}{2}-\nu)=\sum_{j=-\infty}^{\infty}(-1)^j e^{2\pi i j\nu} \tag{26}$$

produces

$$E_1=4\sum_{k,j=-\infty}^{\infty}(-1)^{k+j}\int_0^\infty d\lambda\,\lambda e^{2\pi i k\lambda}\times\int_0^\infty d\nu\, e^{2\pi i j\nu}\times(\varepsilon_{\lambda,\nu}+\zeta)\eta(-\varepsilon_{\lambda,\nu}-\zeta)\,. \tag{27}$$

The count of electrons is similarly expressed by

$$N=\frac{\partial E_1}{\partial\zeta}=4\sum_{k,j=-\infty}^{\infty}(-1)^{k+j}\int_0^\infty d\lambda\,\lambda e^{2\pi i k\lambda}\times\int_0^\infty d\nu\, e^{2\pi i j\nu}\eta(-\varepsilon_{\lambda,\nu}-\zeta)\,. \tag{28}$$

We shall find it easier to concentrate on N rather than on E_1; the relation

$$E_1(\zeta)=-\int_\zeta^\infty d\zeta' N(\zeta') \tag{29}$$

will turn information about N into knowledge of E_1.

So far we have been reading Eq. (24) [and likewise Eq. (14) before] as implicitly defining $\varepsilon_{\lambda,\nu}$ for given λ and ν. However, another view is more useful. It understands ν as a function of λ and ε, $\nu=\nu_\varepsilon(\lambda)$, which for each $\varepsilon\le 0$ defines a "line of degeneracy" in a λ-ν diagram. The term *degeneracy* is appropriate here because such lines connect (λ,ν) values belonging to the same energy ε. If it should happen that several (l,n_r) pairs of (integer) quantum numbers refer to (λ,ν)'s on the same line of degeneracy, then there is more than one state with the corresponding energy; these states are *degenerate*. This is certainly possible among the lines of degeneracy that are straight, but it can also occur for bent ones.

The domain of integration in (28) consists of all λ,ν below the line of degeneracy $\nu_\varepsilon(\lambda)$ with $\varepsilon=-\zeta$. Thus

$$N(\zeta=-\varepsilon)=4\sum_{k,j=-\infty}^{\infty}(-1)^{k+j}\int_0^{\lambda_\varepsilon}d\lambda\,\lambda e^{2\pi i k\lambda}\times\int_0^{\nu_\varepsilon(\lambda)}d\nu\, e^{2\pi i j\nu}\,, \tag{30}$$

where λ_ε denotes the maximal λ, such that $\nu_\varepsilon(\lambda_\varepsilon)=0$; it is given by

$$\lambda_\varepsilon=\max_r\{[2r^2(\varepsilon-V)]^{1/2}\}\,. \tag{31}$$

The ν integration in (30) is immediate and produces

$$N(\zeta=-\varepsilon)=4\sum_{k,j=-\infty}^{\infty}(-1)^{k+j}\int_0^{\lambda_\varepsilon}d\lambda\lambda e^{2\pi i k\lambda}\times\frac{e^{2\pi i j\nu_\varepsilon(\lambda)}-1}{2\pi i j}\,. \tag{32}$$

ISOLATING THE TF PART

The $j=k=0$ term in (30) [and (32)] gives the result of integrating over λ and ν, *without* reference to the δ functions that enforce the integral nature of $\lambda-\frac{1}{2}$ and $\nu-\frac{1}{2}$. We therefore expect it to reproduce the TF version. Indeed, it does, when $\nu_\varepsilon(\lambda)$ [Eq. (24)] is introduced,

$$4\int_0^{\lambda_\varepsilon}d\lambda\,\lambda\nu_\varepsilon(\lambda)=\frac{2}{\pi}\int\frac{dr}{r}\int_0^{\lambda_\varepsilon^2}d(\lambda^2)[2r^2(\varepsilon-V)-\lambda^2]^{1/2}$$
$$=\int(d\mathbf{r})\frac{1}{3\pi^2}[2(\varepsilon-V)]^{3/2}$$
$$=N_{\rm TF}(\zeta=-\varepsilon)\,, \tag{33}$$

and the integration (29) yields (12). This observation implies the decomposition of N [Eq. (32)] into $N_{\rm TF}$ and a supplement that represents quantum corrections,

$$N(\zeta)=N_{\rm TF}(\zeta)+N_{\rm qu}(\zeta)\,, \tag{34}$$

with $N_{\rm qu}$ equal to the right-hand side of Eq. (32) without the $j=k=0$ term. Quite analogously, E_1 is split into the TF expression plus a quantum correction.[3] We shall see that this correction is usually small compared to the TF part, allowing its perturbative evaluation. But first we have to study the semiclassical spectrum.

SEMICLASSICAL SPECTRA

We are going to use the word "spectrum" somewhat loosely, for the entirety of the lines of degeneracy, since knowledge of the latter is tantamount to knowing all E_{l,n_r}.

The distance r_ε, at which the maximum of Eq. (31) is located, obeys

$$V(r_\varepsilon)+\frac{d[r_\varepsilon V(r_\varepsilon)]}{dr_\varepsilon}=2\varepsilon\,; \tag{35}$$

thus

$$\lambda_\varepsilon^2\equiv 2r_\varepsilon^2[\varepsilon-V(r_\varepsilon)]=r_\varepsilon^2\left[\frac{d}{dr_\varepsilon}-\frac{1}{r_\varepsilon}\right][r_\varepsilon V(r_\varepsilon)]\,. \tag{36}$$

The immediate implication of the maximum property of r_ε,

$$\frac{d}{d\varepsilon}\lambda_\varepsilon^2=2r_\varepsilon^2\ , \tag{37}$$

shows that if we were given λ_ε for some range of ε, we could calculate r_ε and then employ the definition of λ_ε^2 in (36) to find $V(r)$ for r in the corresponding range of r_ε. (This can easily be demonstrated for the Coulomb potential for which $\lambda_\varepsilon=Z/\sqrt{-2\varepsilon}$.)

For λ's close to λ_ε, the domain of integration in (24) is a small neighborhood of r_ε. There we can approximate the argument of the square root by a quadratic polynomial in $r-r_\varepsilon$,

$$2r^2(\varepsilon-V)-\lambda^2\cong\lambda_\varepsilon^2-\lambda^2-\tfrac{1}{2}\omega_\varepsilon^2(r-r_\varepsilon)^2\ , \tag{38}$$

with

$$\omega_\varepsilon^2=\frac{d^2}{dr^2}[2r^2(V-\varepsilon)]\bigg|_{r=r_\varepsilon}$$
$$=2\left[r_\varepsilon\frac{d^2}{dr_\varepsilon^2}+\frac{d}{dr_\varepsilon}-\frac{1}{r_\varepsilon}\right][r_\varepsilon V(r_\varepsilon)]\ . \tag{39}$$

Note the relations

$$\omega_\varepsilon^2=\frac{4r_\varepsilon}{dr_\varepsilon/d\varepsilon}=8\frac{d(\lambda_\varepsilon^2)/d\varepsilon}{d^2(\lambda_\epsilon^2)/d\varepsilon^2}\ ; \tag{40}$$

again, knowledge of just λ_ε is sufficient.

Upon inserting Eq. (38) into Eq. (24) we obtain, for $\lambda\lesssim\lambda_\varepsilon$,

$$\nu_\varepsilon(\lambda)\cong\sqrt{2}\frac{\lambda_\varepsilon}{\omega_\varepsilon r_\varepsilon}(\lambda_\varepsilon-\lambda)\ . \tag{41}$$

This is exact in the limit $\lambda\to\lambda_\varepsilon$, implying

$$\frac{\partial\nu_\varepsilon(\lambda)}{\partial\lambda}\bigg|_{\lambda=\lambda_\varepsilon}=-\sqrt{2}\frac{\lambda_\varepsilon}{\omega_\varepsilon r_\varepsilon}\ . \tag{42}$$

Equations (36) and (39) are utilized in writing this in the form

$$\frac{\partial\nu_\varepsilon(\lambda)}{\partial\lambda}\bigg|_{\lambda=\lambda_\varepsilon}=-\left[1+\frac{\nabla^2V}{(\mathbf{r}/r^2)\cdot\nabla V}\bigg|_{r=r_\varepsilon}\right]^{-1/2}\ . \tag{43}$$

Since the force on the electrons is towards the nucleus, $\nabla V(r_\varepsilon)$ points outwards, so that the denominator in (43) is positive. Also, V obeys the Poisson equation (10), causing $\nabla^2V(r_\varepsilon)=-4\pi n(r_\varepsilon)$ to be negative. Consequently, the contents of the large parentheses in (43) are less than 1. This implies

$$\frac{\partial\nu_\varepsilon(\lambda)}{\partial\lambda}\bigg|_{\lambda=\lambda_\varepsilon}<-1\ . \tag{44}$$

The limit of -1 is approached for large binding energies $-\varepsilon$ belonging to strongly bound electrons, where $V\cong-Z/r$.

One can also use the general expression

$$\frac{\partial\nu_\varepsilon(\lambda)}{\partial\lambda}=-\frac{1}{\pi}\int\frac{dr}{r}\frac{\lambda}{[2r^2(\varepsilon-V)-\lambda^2]^{1/2}}\ , \tag{45}$$

together with (38), to derive (42). Let us now employ (45) to find $\partial\nu_\varepsilon/\partial\lambda$ for $\lambda\to0$. No, the answer is not zero, for in this limit the integration reaches down to $r=0$ from which neighborhood a finite contribution arises. We isolate that part of the integral by introducing an upper limit $\bar{r}$, independent of λ and so small that $V\cong-Z/r$ already is a good approximation. At this stage we have

$$\frac{\partial\nu_\varepsilon(\lambda)}{\partial\lambda}\bigg|_{\lambda=0}=-\frac{1}{\pi}\int_{\lambda^2/(2Z)}^{\bar{r}}dr\frac{1}{r}\frac{\lambda}{(2Zr-\lambda^2)^{1/2}}\bigg|_{\lambda\to0}\ . \tag{46}$$

Now the substitution $2Zr=\lambda^2(1+x^2)$ yields

$$\frac{\partial\nu_\varepsilon(\lambda)}{\partial\lambda}\bigg|_{\lambda=0}=-\frac{2}{\pi}\int_0^\infty dx\frac{1}{1+x^2}=-1\ . \tag{47}$$

This statement holds for all ε, except $\varepsilon=0$, where there is the possibility of an additional contribution from the upper limit of the integral. This is the situation if $V\sim-r^{-m}$ for $r\to\infty$, with $m>2$. Potentials with $m\leq2$ are long-range potentials, of which the important example is $-(Z-N)/r$. In such a long-range potential there is no limit to the quantum numbers. Consequently, a finite line of degeneracy does not exist for $\varepsilon=0$. On the other hand, for $m>2$, we have a short-range potential with a limit to the possible quantum numbers.

Again we isolate this upper part of the integral, now by a λ-independent lower limit $\bar{r}$ ($V=-c/r^m$, $m>2$):

$$-\frac{1}{\pi}\int_{\bar{r}}^{(2c/\lambda^2)^{1/(m-2)}}dr\frac{1}{r}\frac{\lambda}{(2cr^{2-m}-\lambda^2)^{1/2}}\bigg|_{\lambda\to0}$$
$$=-\frac{1}{m-2}\frac{2}{\pi}\int_0^\infty dx\frac{1}{1+x^2}=-\frac{1}{m-2}\ , \tag{48}$$

where the substitution $2cr^{2-m}=\lambda^2(1+x^2)$ has been made. Thus, for potentials with $V(r\to\infty)\sim-1/r^m$, $m>2$ we have

$$\frac{\partial\nu_\varepsilon(\lambda)}{\partial\lambda}\bigg|_{\lambda=0}\begin{cases}-1 & \text{for } \varepsilon<0\\ -1-\dfrac{1}{m-2} & \text{for } \varepsilon=0.\end{cases} \tag{49}$$

The sudden increase of the initial slope at $\varepsilon=0$ for short-range potentials is accompanied by a rapid change of $\nu_\varepsilon(\lambda=0)$ as ε approaches zero. An evaluation of

$$\frac{\partial\nu_\varepsilon(\lambda)}{\partial\varepsilon}=\frac{1}{\pi}\int dr\frac{r}{[2r^2(\varepsilon-V)-\lambda^2]^{1/2}} \tag{50}$$

for $\lambda=0$, performed analogously to Eq. (48), produces

$$\frac{\partial\nu_\varepsilon(\lambda=0)}{\partial\varepsilon}=\frac{c^{1/m}}{\sqrt{2\pi}}\frac{\left[\frac{1}{m}-\frac{1}{2}\right]!}{\left[\frac{1}{m}-1\right]!}\frac{1}{(-\epsilon)^{(2+m)/2m}}$$
$$\text{for } \varepsilon\lesssim0\ . \tag{51}$$

A consequence thereof is

$$\nu_\varepsilon(\lambda=0)\cong\nu_0(0)+\frac{c^{1/m}}{\sqrt{2\pi}}\frac{\left[\frac{1}{m}-\frac{3}{2}\right]!}{\left[\frac{1}{m}-1\right]!}(-\varepsilon)^{(m-2)/2m}$$

$$\text{for } \varepsilon\lesssim 0\ . \qquad (52)$$

Please note that, because $m>2$, the numerical coefficient in (51) is positive, whereas it is negative in (52), and that the exponent of $(-\varepsilon)$ in (52) is a positive number less than $\frac{1}{2}$. Indeed, $\nu_\varepsilon(\lambda=0)$ grows rapidly as $\varepsilon\to 0$. Equations (51) and (52) are illustrations of the fact that $\nu_\varepsilon(\lambda=0)$ for $\varepsilon\lesssim 0$ tests the outer reaches of the potential. However, $\nu_\varepsilon(0)$ as a function of ε is not as easily converted into knowledge about V as is λ_ε [recall the remark after Eq. (37)].

Equations (44) and (49) together indicate that, at least for $\varepsilon<0$, the lines of degeneracy are steeper at $\lambda=\lambda_\varepsilon$ than at $\lambda=0$. Since they can be expected to have very little structure for reasonable potentials, one can picture them as gradually getting steeper for increasing λ. In other words, the second derivative $\partial^2\nu_\varepsilon/\partial\lambda^2$ will generally be negative. Unfortunately, a direct investigation of $\partial^2\nu_\varepsilon/\partial\lambda^2$ is hindered by the circumstance that Eq. (45) cannot be formally differentiated due to the λ dependence of the integration limits. It is, however, possible to circumvent this obstacle when higher derivatives of $\nu_\varepsilon(\lambda)$ at $\lambda=\lambda_\varepsilon$ are asked for. A general method for producing explicit expressions for these, such as (42) for the first derivative, is developed in the Appendix.

We now turn to the TF potential for neutral atoms. It satisfies the TF differential equation [Eqs. (10) and (13) for $\zeta=0$]

$$-\frac{1}{4\pi}\nabla^2\left[V_{\rm TF}+\frac{Z}{r}\right]=\frac{1}{3\pi^2}(-2V_{\rm TF})^{3/2} \qquad (53)$$

and is subject to [Eqs. (7) and (13)]

$$N=Z=\int(d\mathbf{r})\frac{1}{3\pi^2}(-2V_{\rm TF})^{3/2}\ . \qquad (54)$$

As usual, we introduce TF variables according to

$$V=-\frac{Z}{r}F(x),\quad x=Z^{1/3}r/a\ ,$$
$$a=\frac{1}{2}\left[\frac{3\pi}{4}\right]^{2/3}=0.8853\ . \qquad (55)$$

The differential equation for $F(x)$ is then

$$\frac{d^2}{dx^2}F(x)=\frac{[F(x)]^{3/2}}{x^{1/2}} \qquad (56)$$

with boundary conditions

$$F(0)=1,\quad F(\infty)=0\ . \qquad (57)$$

The lines of degeneracy are given by

$$\frac{\nu_\varepsilon(\lambda)}{Z^{1/3}}=\frac{1}{\pi}\int\frac{dx}{x}\left[2(ax)^2\left[\frac{F(x)}{ax}+\frac{\varepsilon}{Z^{4/3}}\right]-\left[\frac{\lambda}{Z^{1/3}}\right]^2\right]^{1/2}\ . \qquad (58)$$

This way of writing it makes explicit that $\nu_\varepsilon(\lambda)/Z^{1/3}$ is a Z-independent function of both $\lambda/Z^{1/3}$ and $\varepsilon/Z^{4/3}$. We present a plot of such lines of degeneracy in Fig. 1. It illustrates the remarks made above. Note that $\nu_\varepsilon(\lambda)$ becomes steeper for larger λ, and that for large binding energies $(-\varepsilon/Z^{4/3}\gtrsim 1)$ the degeneracy is the linear Coulombic one,

$$\frac{\nu_\varepsilon(\lambda)}{Z^{1/3}}=\left[\frac{2(\varepsilon_0-\varepsilon)}{Z^{4/3}}\right]^{-1/2}-\frac{\lambda}{Z^{1/3}}=\frac{\lambda_\varepsilon-\lambda}{Z^{1/3}}\ , \qquad (59)$$

where $\varepsilon_0=Z^{4/3}[-F'(0)/a]$ is the constant of Eq. (17). Further, note that for $\varepsilon<0$ the initial slope is always -1; that for $\varepsilon=0$ it is $-\frac{3}{2}$ because $F(x)\sim 144/x^3$ as $x\to\infty$, that is, $m=4$ in Eq. (49); and that $\nu_\varepsilon(\lambda=0)$ changes rapidly as $\varepsilon\to 0$.

SIGNIFICANT NUMBERS

Here are some important numbers referring to $\varepsilon=0$. The function $xF(x)$ has its maximum at $x_0=2.10403$ where

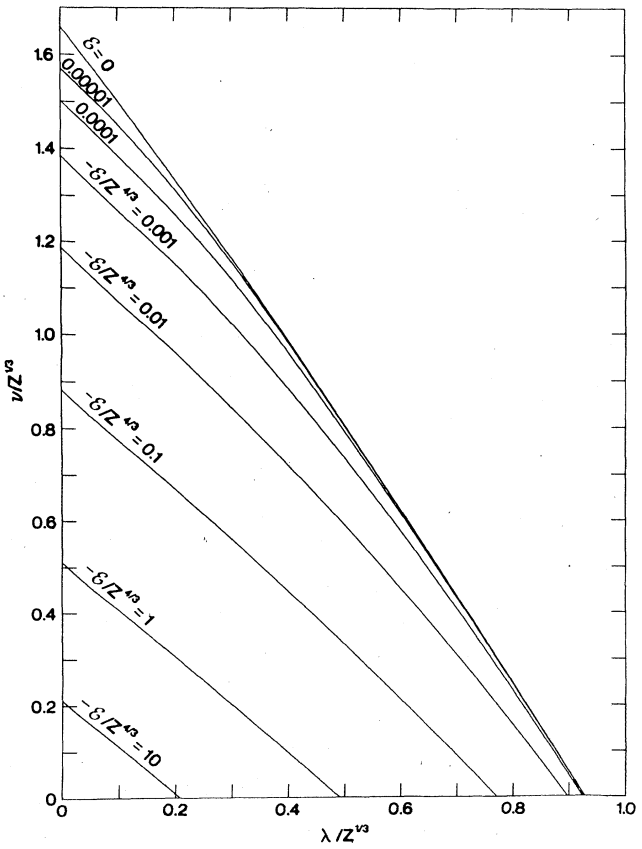

FIG. 1. Lines of degeneracy for the Thomas-Fermi potential.

$$F(x_0)=0.231\,151\ ,$$
$$F'(x_0)=-\frac{F(x_0)}{x_0}=-0.109\,862\ , \tag{60}$$
$$F''(x_0)=\frac{[F(x_0)]^{3/2}}{x^{1/2}}=0.076\,616\,0\ .$$

From that we get

$$r_0=x_0 a/Z^{1/3}=1.862\,78Z^{-1/3}\ ,$$
$$\lambda_0=\sqrt{2ax_0F(x_0)}Z^{1/3}=0.927\,992Z^{1/3}\ , \tag{61}$$
$$\omega_0=\left[\frac{2}{a}F(x_0)\left[-x_0F''(x_0)-F'(x_0)+\frac{F(x_0)}{x_0}\right]\right]^{1/2}Z^{2/3}$$
$$=\left[\frac{2}{a}F(x_0)\left[\frac{2}{x_0}-\sqrt{x_0F(x_0)}\right]\right]^{1/2}Z^{2/3}$$
$$=0.363\,593Z^{2/3}\ ,$$
$$\left.\frac{\partial\nu_0}{\partial\lambda}\right|_{\lambda=0}=-\left[1+\frac{x_0F''(x_0)}{2F'(x_0)}\right]^{-1/2}$$
$$=-[1-\tfrac{1}{2}x_0\sqrt{x_0F(x_0)}]^{-1/2}$$
$$=-1.937\,68\ .$$

Also interesting is the maximum value of ν, namely,

$$\nu_0(\lambda=0)=\frac{1}{\pi}\sqrt{2a}\,Z^{1/3}\int_0^\infty dx[F(x)/x]^{1/2}$$
$$=1.658\,65Z^{1/3} \tag{62}$$

(the numerical value of the integral is 3.915 93).[4] The coefficient in (52) is $-1.705\,28$ ($m=4$, $c=144a^3=81\pi^2/8$), so that, for $\varepsilon\lesssim 0$,

$$\nu_\varepsilon(\lambda=0)\cong 1.658\,65Z^{1/3}-1.705\,28Z^{1/3}\left[\frac{-\varepsilon}{Z^{4/3}}\right]^{1/4}\ . \tag{63}$$

If desired this can be improved by taking into account the next term in the asymptotic form of $F(x)$,

$$F(x)\cong\frac{144}{x^3}\left[1-\frac{\beta}{x^\gamma}+\cdots\right]\quad\text{for } x\to\infty\ , \tag{64}$$

wherein

$$\beta=13.270\,97,\quad \gamma=\tfrac{1}{2}(\sqrt{73}-7)=0.772\,002\ . \tag{65}$$

We do not report the details of this calculation which is analogous to the one that produced Eqs. (51) and (52); it results in an addition to the right-hand side of Eq. (63) given by

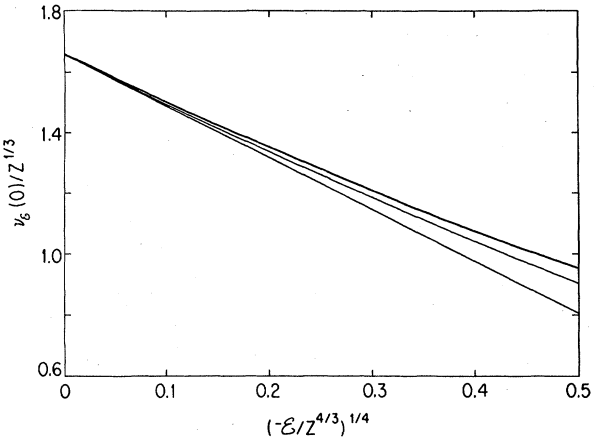

FIG. 2. $\nu_\varepsilon(0)/Z^{1/3}$ as a function of $(-\varepsilon/Z^{4/3})^{1/4}$ for the Thomas-Fermi potential (thicker top curve), approximation (63) (bottom curve), and approximation (63) plus (66) (central curve).

$$-\frac{\beta}{4}\left[\frac{a}{c^{1/4}}\right]^\gamma\frac{c^{1/4}}{\sqrt{2\pi}}\frac{\left[-\frac{5+\gamma}{4}\right]!}{\left[-\frac{3+\gamma}{4}\right]!}Z^{-\gamma/3}(-\varepsilon)^{(1+\gamma)/4}$$
$$=0.331\,72Z^{1/3}\left[-\frac{\varepsilon}{Z^{4/3}}\right]^{0.443\,000}\ . \tag{66}$$

The quality of the successive approximations (63), and (63) plus (66), is illustrated in Fig. 2.

Also for illustrative purposes, we present, in Fig. 3, various quantities as a function of $\varepsilon/Z^{4/3}$. Note that for large binding energies, i.e., $-\varepsilon\gg Z^{4/3}$, $\nu_\varepsilon(0)$ equals λ_ε [cf. Eq. (59)]. This is typical for Coulombic potentials, $V=-Z/r+$ const, for which these relations hold:

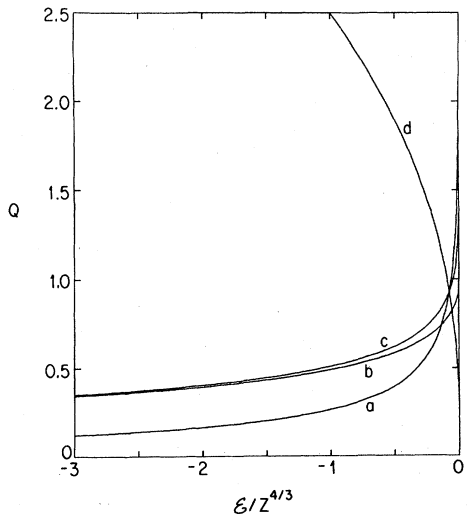

FIG. 3. Various quantities Q as a function of $\varepsilon/Z^{4/3}$ for the Thomas-Fermi potential. a, $Q=r_\varepsilon/Z^{-1/3}$; b, $Q=\lambda_\varepsilon/Z^{1/3}$; c, $Q=\nu_\varepsilon(0)/Z^{1/3}$; d, $Q=\omega_\varepsilon/Z^{2/3}$.

$$\nu_\varepsilon(0)/Z^{1/3}=\lambda_\varepsilon/Z^{1/3}\,,$$
$$r_\varepsilon/Z^{-1/3}=(\lambda_\varepsilon/Z^{1/3})^2\,, \tag{67}$$
$$\omega_\varepsilon/Z^{2/3}=\sqrt{2}/(\lambda_\varepsilon/Z^{1/3})\,.$$

Of course, Coulombic degeneracy for strongly bound electrons was anticipated; see the remarks preceding Eq. (17) and the discussion of Fig. 1, after Eq. (58).

OSCILLATORY TERMS

We are now prepared to examine the quantum corrections added to the TF contribution in Eq. (34). To do so, let us first ask the question, how many states are available in the TF potential for a given Z? In other words, what is $N(\zeta=0)$ for $V=V_{\rm TF}$? Of course, we know already that $N_{\rm TF}(\zeta=0)=Z$. Thus we are now concerned with $N_{\rm qu}$.

A detailed answer is somewhat elaborate, and we decided to present it in a separate publication.[5] However, some general qualitative features of $N_{\rm qu}$ can be demonstrated without great effort. This is our objective here.

Consider the sequence of states $1s,3p,5d,\ldots,$ or $(l,n_r)=(0,0),(1,1),(2,2),\ldots,$ which are characterized by a common value for the ratio ν/λ, namely, one. As Z increases, these states become available at certain values of Z: $Z_{1s},Z_{3p},Z_{5d},\ldots$. Now recall the essential $Z^{1/3}$ dependence of the line of degeneracy $\nu_0(\lambda)$. It implies

$$Z_{1s}^{1/3}=\tfrac{1}{3}Z_{3p}^{1/3}=\tfrac{1}{5}Z_{5d}^{1/3}=\cdots\,, \tag{68}$$

because the respective λ's (or ν's) of these states are in proportions of 1:3:5:.... Consequently, the contribution to the number of available states made by said sequence of states is given by

$$N_{(1s)}(Z)=\begin{cases} 0 & \text{for} \quad (Z/Z_{1s})^{1/3}<1 \\ 2 & \text{for} \quad 1<(Z/Z_{1s})^{1/3}<3 \\ 2+6 & \text{for} \quad 3<(Z/Z_{1s})^{1/3}<5 \\ 2+6+10 & \text{for} \quad 5<(Z/Z_{1s})^{1/3}<7 \\ \vdots & \vdots \quad\quad \vdots \\ 2m^2 & \text{for} \quad 2m-1<(Z/Z_{1s})^{1/3}<2m+1, \end{cases} \tag{69}$$

where m is an integer. The difference between $\frac{1}{2}[(Z/Z_{1s})^{1/3}+1]$ and its integer part m can be expressed by an elementary Fourier series, so that a compact way of writing the staircase-type dependence on $Z^{1/3}$ in Eq. (69) is

$$N_{(1s)}(Z)=2\left\{\frac{1}{2}\left[\frac{Z}{Z_{1s}}\right]^{1/3}+\sum_{j=1}^{\infty}\frac{(-1)^j}{\pi j}\sin\left[\pi j\left[\frac{Z}{Z_{1s}}\right]^{1/3}\right]\right\}^2$$
$$=2\mathcal{N}[(Z/Z_{1s})^{1/3}]\,.$$

The function $\mathcal{N}(z)$ thus defined is universal, which is to say that it is the same for each such sequence of states. This observation is based upon the fact that the successive (λ,ν) values of any sequence consist of all odd multiples of the initial one (recall that the physical values of λ are $l+\frac{1}{2}$), and the analog of (68) holds, therefore, for any sequence of states. There is nothing special about the one starting with the $1s$ state; we just selected it in order to have a concrete example. For any other sequence, characterized by its initial state (l_0,n_{r_0}), Z_{1s} in (70) is replaced by the respective minimal Z value, while the factor in front of $\mathcal{N}$ is the multiplicity of the initial state, i.e., $2(2l_0+1)$. For illustration, Table I lists the essential numbers for the first 15 sequences of states.

It is technically impossible to sum Eq. (70) over all such sequences of states. But we can nevertheless learn an important lesson from the structure of $\mathcal{N}((Z/Z_{\rm min})^{1/3})$. Note that it consists of a smooth part, with a leading term of order $Z^{2/3}$, and an oscillatory one with the periodicity $Z^{1/3}\to Z^{1/3}+2Z_{\rm min}^{1/3}$, which has a leading term of order $Z^{1/3}$. Inasmuch as summing all sequences must produce $N(Z)$ we infer that the sum of all leading smooth terms results in $N_{\rm TF}(Z)=Z$. As far as the Z dependence is concerned, the smooth terms therefore effectively gain a factor of $Z^{1/3}$. This will not be equally true for the oscillatory terms. While they all have a (leading) amplitude of order $Z^{1/3}$ and are periodic functions of $Z^{1/3}$, they have what looks like randomly assigned periods. Consequently, these many oscillations will not interfere constructively. We conclude that $N_{\rm qu}(Z)$ contains somewhat irregular oscillations, reminiscent of a periodic function of $Z^{1/3}$ but with additional structure. Thereby the leading term is expected to possess an amplitude of an order between $Z^{1/3}$ and $Z^{2/3}$. (The random character of the various periodicities suggests that the amplitude is enhanced not by a factor of $Z^{1/3}$ but by its square root. In this case the amplitude of the leading oscillation would be of order $Z^{1/2}$.) These observations are confirmed by the plots of $N(Z)$

TABLE I. Initial state, characterizing ratio ν/λ, multiplicity of initial state, and minimal $Z^{1/3}$ of initial state, for the first 15 sequences of states (ordered by increasing $Z_{\rm min}^{1/3}$).

Initial state	ν/λ	Multiplicity	$Z_{\rm min}^{1/3}$
$1s$	1	2	0.822
$2s$	3	2	1.41
$2p$	$\frac{1}{3}$	6	1.90
$3s$	5	2	2.00
$4s$	7	2	2.60
$3d$	$\frac{1}{5}$	10	2.97
$4p$	$\frac{5}{3}$	6	3.05
$5s$	9	2	3.19
$4d$	$\frac{3}{5}$	10	3.54
$5p$	$\frac{7}{3}$	6	3.63
$6s$	11	2	3.79
$4f$	$\frac{1}{7}$	14	4.05
$7s$	13	2	4.39
$5f$	$\frac{3}{7}$	14	4.61
$6d$	$\frac{7}{5}$	10	4.69

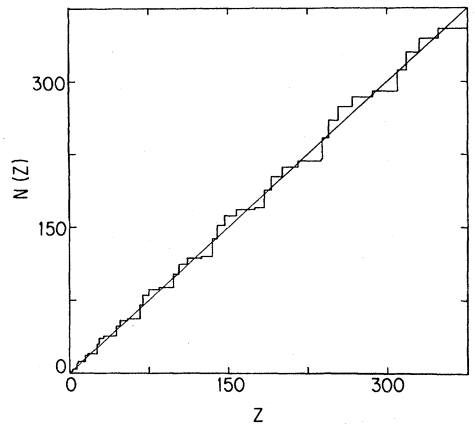

FIG. 4. Number of states $N(Z)$ available in the Thomas-Fermi potential, as a function of Z. The straight line is $N_{\rm TF}(Z)=Z$.

and $N_{\rm qu}(Z)/Z^{1/3}$, presented in Figs. 4 and 5, respectively.

An essential point in this reasoning is the fact that $\nu_0(\lambda)$ is a bent, not a straight, line. This was responsible for the oscillations being somewhat random. The situation is different for linear degeneracy. For illustration, consider Coulombic degeneracy, i.e., $\nu_0(\lambda)=\lambda_0-\lambda$. Here a whole Bohr shell becomes available when one of its states does. If this happens at $Z=Z_0$ for the first shell, the mth one is filled at $Z=m^3Z_0$. Consequently, we have

$$N(Z)=\sum_{m'=1}^{m}2m'^2=\tfrac{2}{3}(m+\tfrac{1}{2})^3-\tfrac{1}{6}(m+\tfrac{1}{2})$$
$$\text{for } m<(Z/Z_0)^{1/3}<m+1\ . \qquad (71)$$

The relation between $(Z/Z_0)^{1/3}$ and the integer m is conveyed by

$$m+\tfrac{1}{2}=\left[\frac{Z}{Z_0}\right]^{1/3}+\sum_{j=1}^{\infty}\frac{1}{\pi j}\sin[2\pi j(Z/Z_0)^{1/3}]\ , \qquad (72)$$

and the leading terms of $N(Z)$ are

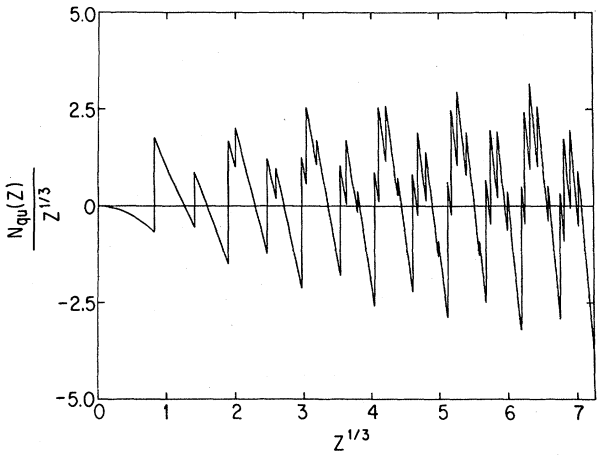

FIG. 5. $N_{\rm qu}(Z)/Z^{1/3}=[N(Z)-Z]/Z^{1/3}$ as a function of $Z^{1/3}$ for the Thomas-Fermi potential.

$$N(Z)\cong\frac{2}{3}\frac{Z}{Z_0}+2\left[\frac{Z}{Z_0}\right]^{2/3}\sum_{j=1}^{\infty}\frac{1}{\pi j}\sin[2\pi j(Z/Z_0)^{1/3}]\ . \qquad (73)$$

Indeed, the leading oscillatory term is here of order $Z^{2/3}$, enhanced by the same $Z^{1/3}$ factor that multiplies the leading smooth term of Eq. (70). Equation (73) also implies $Z_0=\frac{2}{3}$. This is consistent with $\lambda_0=(Z/Z_0)^{1/3}$ and

$$Z=N_{\rm TF}=4\int_0^{\lambda_0}d\lambda\,\lambda\nu_0(\lambda)$$
$$=4\int_0^{\lambda_0}d\lambda\,\lambda(\lambda_0-\lambda)=\tfrac{2}{3}\lambda_0^3\ . \qquad (74)$$

We shall say more about linear degeneracy in a separate paper[6] containing a systematic treatment for arbitrary slope $\partial\nu_0/\partial\lambda$. Not surprisingly, one can demonstrate that the leading oscillatory term in $N_{\rm qu}$ always is of order $Z^{2/3}$ if $\nu_0(\lambda)$ is a straight line.

Armed with all this insight into the number of states, we can now employ Eq. (29) and gain related information about the energy. Since $\zeta=-\varepsilon$ is of the order $Z^{4/3}$ we see immediately that the leading term of E_1 must be of order $Z^{7/3}$. This is, of course, also evident from $(E_1)_{\rm TF}$ [Eq. (12), combined with (55)],

$$[E_1(\zeta=0)]_{\rm TF}=-\frac{2}{5}\frac{Z^{7/3}}{a}\int_0^{\infty}dx\,x^{-1/2}[F(x)]^{5/2}$$
$$=-\frac{2}{7}Z^{7/3}\frac{B}{a}\ , \qquad (75)$$

with

$$B=-\left.\frac{dF}{dx}\right|_{x=0}=1.588\,07\ , \qquad (76)$$

the initial slope of the TF function. [In passing, we note that ε_0 of Eq. (59) has the value $1.793\,74Z^{4/3}$.]

On the other hand, oscillatory terms do not acquire a factor $Z^{4/3}$ when integrated as in Eq. (29). They merely gain by $Z^{3/3}$. This is caused by the Z dependence of the periodicity which is of order $Z^{1/3}$. In order to illustrate this point, let us take the function $\lambda_\varepsilon\sin\lambda_\varepsilon$ as a model for oscillations with both amplitude and period proportional to $Z^{1/3}$. Successive partial integrations are exhibited by

$$\lambda_\varepsilon\sin\lambda_\varepsilon=\frac{d}{d\varepsilon}\left[-\frac{\lambda_\varepsilon}{d\lambda_\varepsilon/d\varepsilon}\cos\lambda_\varepsilon\right.$$
$$\left.+\frac{1}{d\lambda_\varepsilon/d\varepsilon}\frac{d}{d\varepsilon}\left[\frac{\lambda_\varepsilon}{d\lambda_\varepsilon/d\varepsilon}\right]\sin\lambda_\varepsilon+\cdots\right]\ . \qquad (77)$$

The terms in square brackets are, for $\varepsilon=-\zeta$ and after a change of sign, contributions to $E_1(\zeta)$ if $\lambda_\varepsilon\sin\lambda_\varepsilon$ is a term of $N_{\rm qu}(\zeta=-\varepsilon)$. Evidently, these terms are of order $Z^{4/3}$, $Z^{3/3}$, etc. Indeed, through integration only a factor $Z^{3/3}=Z^{4/3}/Z^{1/3}$ is gained.

For the TF potential this means that the leading oscillatory term in E_1 has an amplitude of order between $Z^{4/3}$ and $Z^{5/3}$ (or of order $Z^{3/2}$ if one is willing to accept the square-root argument based on the randomness of the

periodicities). Indeed, as promised, this is small compared to the leading TF energy term ($\sim Z^{7/3}$) if only Z is sufficiently large. A perturbative treatment of these oscillations is fully justified; we report details thereof elsewhere.[5]

Finally, we note that $E_{\rm qu}=E-E_{\rm TF}$ is not entirely oscillatory. It also contains nonoscillatory contributions. For example, since the semiclassical spectral sum (15) handles the strongly bound electrons correctly, whereas they are misrepresented in

$$E_{\rm TF}=-\frac{3}{7}\frac{B}{a}Z^{7/3}\ \text{ for } N=Z\ , \tag{78}$$

the known correction[7] to E (an additive term $\frac{1}{2}Z^2$) must be part of $E_{\rm qu}$. Accordingly, $N_{\rm qu}$ possesses a related smooth term. The slight asymmetry in Fig. 5, somewhat larger negative peaks than positive ones, is consistent with the presence of such a term.

ACKNOWLEDGMENT

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APPENDIX

Here we return to the problem of calculating higher derivatives of $\nu_\varepsilon(\lambda)$ at $\lambda=\lambda_\varepsilon$. While the method to be presented now is quite general, we shall only use it explicitly for deriving the analog of Eq. (42) for the second derivative.

The range of integration in Eq. (45) is given by those values of r about r_ε for which the argument of the square root is positive. Accordingly, as r increases from its lower limit to its upper one, $2r^2(\varepsilon-V)$ changes from λ^2 to the maximum value λ_ε^2, reached at $r=r_\varepsilon$, and then back to λ^2. We exploit this symmetry by introducing a new integration variable θ, related to r by

$$2r^2[\varepsilon-V(r)]-\lambda^2=(\lambda_\varepsilon^2-\lambda^2)\cos^2\theta\ , \tag{79}$$

or

$$1-2r^2[\varepsilon-V(r)]/\lambda_\varepsilon^2=(1-\lambda^2/\lambda_\varepsilon^2)\sin^2\theta\ . \tag{80}$$

If we insist upon θ and $r-r_\varepsilon$ having the same sign, then this relation is unique. In particular, $\theta=0$ corresponds to $r=r_\varepsilon$, while $\theta=-\pi/2$ and $\pi/2$ belong to the lower and upper limits of the r integration, respectively.

When expanding the left-hand side of (80) into powers of $r-r_\varepsilon$, it is fitting to use the dimensionless variable y, defined by

$$y=\left[\frac{\omega_\varepsilon r_\varepsilon}{\sqrt{2}\lambda_\varepsilon}\right]\left[\frac{r-r_\varepsilon}{r_\varepsilon}\right]=\frac{1}{\nu'_\varepsilon}\frac{r-r_\varepsilon}{r_\varepsilon}\ , \tag{81}$$

$$r=r_\varepsilon(1+\nu'_\varepsilon y)\ ,$$

where [cf. Eq. (42)]

$$\nu'_\varepsilon\equiv-\frac{\partial}{\partial\lambda}\nu_\varepsilon(\lambda)\Big|_{\lambda=\lambda_\varepsilon} \tag{82}$$

is the slope of $\nu_\varepsilon(\lambda)$ at $\lambda=\lambda_\varepsilon$. Equation (80) now reads

$$\begin{aligned} &y^2-c_3y^3+c_4y^4-\cdots=t^2\ ,\\ &t\equiv(1-\lambda^2/\lambda_\varepsilon^2)^{1/2}\sin\theta\ . \end{aligned} \tag{83}$$

(For simplicity, we suppress the ε index on y, c_m, and t.) The numerical coefficients c_3, c_4, etc., are simply obtainable as derivatives of the potential at $r=r_\varepsilon$:

$$c_m=\frac{(-1)^m}{m!}\frac{2}{\lambda_\varepsilon^2}(\nu'_\varepsilon r_\varepsilon)^m\left[\frac{d}{dr_\varepsilon}\right]^m[r_\varepsilon^2V(r_\varepsilon)]\ , \tag{84}$$

$$m=3,4,\ldots\ .$$

Equation (83) expresses t as a power series of y. We invert it and write

$$y=t+\tfrac{1}{2}c_3t^2+(\tfrac{5}{8}c_3^2-\tfrac{1}{2}c_4)t^3+\cdots\ . \tag{85}$$

After these preparations we return to Eq. (45) and note that

$$\frac{dr}{r}[2r^2(\varepsilon-V)-\lambda^2]^{-1/2}=\frac{\nu'_\varepsilon}{\lambda_\varepsilon}\frac{d\theta}{1+\nu'_\varepsilon y}\frac{dy}{dt}\ , \tag{86}$$

so that

$$-\frac{\partial\nu_\varepsilon(\lambda)}{\partial\lambda}=\nu'_\varepsilon\frac{\lambda}{\lambda_\varepsilon}\int_{-\pi/2}^{\pi/2}d\theta\frac{1}{\pi}\frac{1}{1+\nu'_\varepsilon y}\frac{dy}{dt}\ . \tag{87}$$

After employing (85) to produce

$$\begin{aligned} \frac{1}{1+\nu'_\varepsilon y}\frac{dy}{dt}&=1+(c_3-\nu'_\varepsilon)t\\ &\quad+[\tfrac{15}{8}c_3^2-\tfrac{3}{2}c_4-\tfrac{3}{2}\nu'_\varepsilon c_3+(\nu'_\varepsilon)^2]t^2+\cdots\ , \end{aligned} \tag{88}$$

the θ integration is immediate, whereby the terms odd in t, i.e., odd in $\sin\theta$, do not contribute. We have now arrived at

$$\begin{aligned} -\frac{\partial\nu_\varepsilon(\lambda)}{\partial\lambda}=\nu'_\varepsilon\frac{\lambda}{\lambda_\varepsilon}\{1+\tfrac{1}{2}[\tfrac{15}{8}c_3^2-\tfrac{3}{2}c_4-\tfrac{3}{2}\nu'_\varepsilon c_3+(\nu'_\varepsilon)^2]\\ \times(1-\lambda^2/\lambda_\varepsilon^2)+\cdots\}\ , \end{aligned} \tag{89}$$

where the ellipsis indicates the presence of higher powers of $1-\lambda^2/\lambda_\varepsilon^2$. Setting λ equal to λ_ε in (89) reproduces (82), as it should. Additionally, we learn

$$\begin{aligned} -\lambda_\varepsilon\frac{\partial^2}{\partial\lambda^2}\nu_\varepsilon(\lambda)\Big|_{\lambda=\lambda_\varepsilon}\\ =\nu'_\varepsilon[1-(\nu'_\varepsilon)^2+\tfrac{3}{2}\nu'_\varepsilon c_3-\tfrac{15}{8}c_3^2+\tfrac{3}{2}c_4]\ , \end{aligned} \tag{90}$$

and higher derivatives of $\nu_\varepsilon(\lambda)$ at $\lambda=\lambda_\varepsilon$ can be calculated by keeping track of the subsequent terms in (89).

For Coulombic potentials, $\nu_\varepsilon(\lambda)$ is a straight line.

Indeed, Eq. (90) gives the correct null result, because $\nu'_\varepsilon = 1$ and all c_m vanish for $V = -Z/r + \text{const}$. Another application concerns the TF potential for $\varepsilon = 0$. Here we have ν'_0 given in (61), whereas

$$c_3 = \tfrac{1}{6}(\nu'_0)^3 \frac{x_0^2}{F(x_0)} \frac{d^3}{dx_0^3}[x_0 F(x_0)]$$

$$= \tfrac{1}{6}(\nu'_0)^3 x_0 \sqrt{x_0 F(x_0)}$$

$$= \tfrac{1}{3}\nu'_0[(\nu'_0)^2 - 1] = 1.779\,17\,, \tag{91}$$

and

$$c_4 = -\tfrac{1}{24}(\nu'_0)^4 \frac{x_0^3}{F(x_0)} \frac{d^4}{dx_0^4}[x_0 F(x_0)]$$

$$= \tfrac{1}{16}(\nu'_0)^4 x_0 \sqrt{x_0 F(x_0)}\,[\tfrac{10}{3} - x_0 \sqrt{x_0 F(x_0)}]$$

$$= \tfrac{1}{12}[(\nu'_0)^2 - 1][2(\nu'_0)^2 + 3] = 2.412\,38\,. \tag{92}$$

Consequently, for the TF potential,[8]

$$-\lambda_0 \frac{\partial^2}{\partial \lambda^2} \nu_0(\lambda)\Big|_{\lambda=\lambda_0}$$

$$= \tfrac{1}{24}\nu'_0[(\nu'_0)^2 - 1][-5(\nu'_0)^4 + 23(\nu'_0)^2 - 15]$$

$$= 0.193\,647\,. \tag{93}$$

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[1]Exchange effects can be included in the manner described in B.-G. Englert and J. Schwinger, Phys. Rev. A **29**, 2339 (1984).

[2]Reference 1 contains the description of a systematic treatment of such quantum corrections, not on the level of the semiclassical theory, though, but for the statistical atom.

[3]N. H. March and J. S. Plaskett, Proc. R. Soc. London, Ser. A **235**, 419 (1956) already noticed that the semiclassical sum contains the TF approximation in the continuum limit. However, their method is very different from ours and they did not develop a systematic way of analyzing the quantum correction to the TF method.

[4]Presumably due to too crude an approximation for $F(x)$, Fermi reported 3.2 for this number in his classical paper on the systematics of the Periodic Table [E. Fermi, Rend. Lincei **7**, 342 (1928)].

[5]B.-G. Englert and J. Schwinger, this issue, Phys. Rev. A **32**, 47 (1985).

[6]B.-G. Englert and J. Schwinger, following paper, Phys. Rev. A **32**, 36 (1985).

[7]B.-G. Englert and J. Schwinger, Phys. Rev. A **29**, 2331 (1984) contains a recent derivation of this term based on the scaling behavior of the TF method. Let us use this occasion for reporting three misprints in this paper: The number in Eq. (63) should be 1.588 071 0..., the right-hand side of Eq. (102) should be $\frac{1}{3}Z^{-4/3}$, and the last number in the first row of Table I should be (-0.04).

[8]In view of the fact that $5(\nu'_0)^4 + 15$ and $23(\nu'_0)^2$ differ only by about 1%, we had to use more than the six decimals, given for ν'_0 in (61), to find six significant figures for the number in (93).