Linear degeneracy in the semiclassical atom

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If the angular and radial quantum numbers of states with the same binding energy satisfy a linear relation, as is the situation in the Coulomb potential, the spectrum is said to be linearly degenerate. We present a detailed study of the consequences of such linear degeneracy in atomic potentials. One of the results is a new, and more general, derivation of Scott's correction to the Thomas-Fermi energy.

INTRODUCTION

This paper continues the discussions given in the preceding one,[1] referred to as I. The notation defined there will be used here without further explanation.

Whereas we developed the general formalism of the semiclassical atom in I, we are now addressing the special situation of linear degeneracy. The main example of a physical system displaying linear degeneracy throughout is a highly ionized atom. There, dynamics is dominated by the nucleus-electron interaction, the interelectronic forces being comparatively small. The average potential is therefore very similar to the Coulomb potential of the nucleus, and the degeneracy is the corresponding one.

For the same reason, Coulombic degeneracy is always present in the part of the spectrum that refers to very large binding energies. We show that this causes the appearance of a term in the single-particle energy, known as Scott's correction.

Exact linear degeneracy can also occur at $\varepsilon=0$. In such situations the degeneracy for $\varepsilon \lesssim 0$ is almost linear. A linear approximation for this part of the spectrum can be a useful device. We shall study an example.

COULOMBIC DEGENERACY

The only atomic potential (i.e., one with $V\sim -Z/r$ as $r\to 0$) with exact linear degeneracy for all binding energies $\varepsilon<0$ is, essentially, the Coulomb potential. To see this we first note that the slope of the lines of degeneracy must be -1 because of Eq. (49) of I. If we insert this slope into Eq. (43) of I, we immediately conclude $\nabla^2 V=0$ for $r\le r_{\varepsilon=0}$. Consequently,

$$V(r)=-\frac{Z}{r}+\varepsilon_0 \quad \text{for } r\le \frac{Z}{\varepsilon_0}=2r_0\ , \tag{1}$$

while $V(r)$ for $r>2r_0$ can be any non-negative function that approaches zero at infinity. Obviously, the region $r>2r_0$ is always classically forbidden, and the shape of the potential there does not matter for semiclassical quantization. This is different in wave mechanics. Therefore, the spectrum obtained from Schrödinger's equation for such a potential will not be exactly linearly degenerate. The main deviation can be expected close to $\varepsilon=0$.

Consider now the situation of m full Coulombic shells and the $(m+1)$th shell filled by a fraction μ, $0\le\mu<1$. The total number of electrons then is

$$N=\sum_{m'=1}^{m} 2(m')^2+\mu 2(m+1)^2$$
$$=\tfrac{2}{3}(m+\tfrac{1}{2})^3-\tfrac{1}{6}(m+\tfrac{1}{2})+2\mu(m+1)^2\ . \tag{2}$$

These electrons have a combined single-particle energy given by

$$E_{1\text{p}}=\sum_{m'=1}^{m} 2(m')^2\left[-\frac{Z^2}{2(m')^2}+\varepsilon_0\right]+\mu 2(m+1)^2\left[-\frac{Z^2}{2(m+1)^2}+\varepsilon_0\right]$$
$$=-Z^2(m+\mu)+\varepsilon_0 N\ . \tag{3}$$

If we understand Eq. (2) as defining m and μ as functions of N, then Eq. (3) displays $E_{1\text{p}}(N)$. Towards the objective of making this functional dependence explicit we proceed from noting that

$$(m+\tfrac{1}{2})^3-\tfrac{1}{4}(m+\tfrac{1}{2})\le \tfrac{3}{2}N<(m+\tfrac{3}{2})^3-\tfrac{1}{4}(m+\tfrac{3}{2})\ . \tag{4}$$

Consequently, if y solves

$$y^3-\tfrac{1}{4}y=\tfrac{3}{2}N\ , \tag{5}$$

then m is the integer part of $y-\frac{1}{2}$. (For $N>0$, there is just one solution larger than $\frac{1}{2}$.) We use the standard Gaussian notation,

$$m=[y-\tfrac{1}{2}]\ . \tag{6}$$

For the sequel, the introduction of $\langle y\rangle$, defined by

$$\langle y\rangle=y-[y+\tfrac{1}{2}]\ , \tag{7}$$

i.e.,

$$y-\langle y\rangle=\text{integer}\ ,\qquad -\tfrac{1}{2}\le\langle y\rangle<\tfrac{1}{2}\ , \tag{8}$$

will prove useful. We employ it in writing

$$m=y-1-\langle y-1\rangle=y-1-\langle y\rangle\ . \tag{9}$$

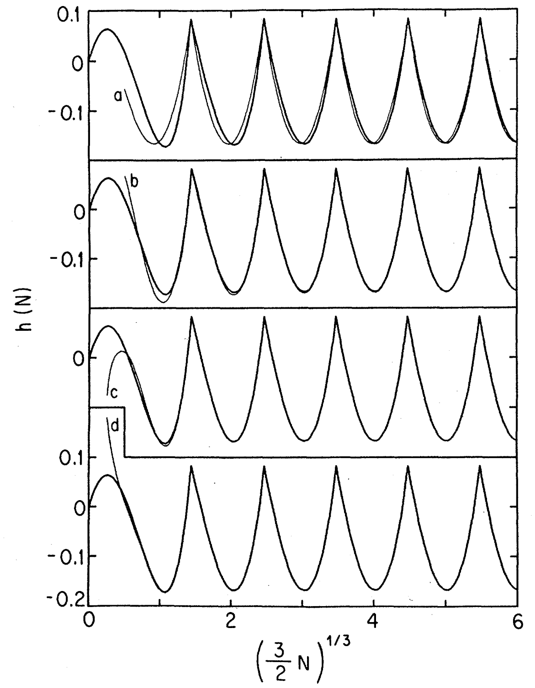

FIG. 1. Oscillation $h(N)$ as a function of $(\frac{3}{2}N)^{1/3}$. Thick curve is exact $h(N)$. Thinner curves are successive approximations of Eq. (17): (a) leading term only, (b) terms up to order $N^{-1/3}$, (c) terms up to order $N^{-2/3}$, (d) terms up to order $N^{-3/3}$.

The latter equality is based upon the obvious periodicity of $\langle y \rangle$,

$$\langle y+1 \rangle = \langle y \rangle \ . \tag{10}$$

Now we insert both Eqs. (5) and (9) into Eq. (2) and solve for μ. The result is

$$\mu = \tfrac{1}{2} + \langle y \rangle + (\langle y \rangle^2 - \tfrac{1}{4}) \frac{y - \frac{2}{3}\langle y \rangle}{(y - \langle y \rangle)^2} \ . \tag{11}$$

Please note that as a consequence of $y > \frac{1}{2}$, the denominator here is nonzero. Also, one easily checks that, as y increases from $m+\frac{1}{2}$ to $m+\frac{3}{2}$, μ grows monotonically from zero to one.

The combination of Eqs. (3), (9), and (11) now produces

$$E_{1\mathrm{p}} = \varepsilon_0 N - Z^2 \left[y - \tfrac{1}{2} + (\langle y \rangle^2 - \tfrac{1}{4}) \frac{y - \frac{2}{3}\langle y \rangle}{(y - \langle y \rangle)^2} \right] , \tag{12}$$

with $y(N)$ from Eq. (5). Obviously, $E_{1\mathrm{p}}$ is a continuous function of y—and therefore of N—although $\langle y \rangle$ occasionally jumps from $+\frac{1}{2}$ to $-\frac{1}{2}$. We shall now turn this exact relation between N and $E_{1\mathrm{p}}$ into a useful approximate one. Equation (5) is solved by

$$y = (\tfrac{3}{2}N)^{1/3} + \tfrac{1}{12}(\tfrac{3}{2}N)^{-1/3} - \tfrac{1}{3}(\tfrac{1}{12})^3 (\tfrac{3}{2}N)^{-5/3} + \cdots \ . \tag{13}$$

This expansion is expected to be good for large N. However, just the first two terms form a practically perfect formula even for small N. For example, for $N=1$, the second term in (13) is less than seven percent of the first, while the third is no more than two-tenths of a percent of the second. We shall therefore be content with the first two terms in Eq. (13).

Another way of demonstrating the high quality of this approximation is to look at the values predicted for N, at which closed shells occur. For $y = \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \ldots,$ we obtain $N = 1.999\,87$, $9.999\,974$, $27.999\,991$, etc.; even for the first shell the agreement is better than one-hundredth of a percent.

Since the two-term approximation for $y(N)$ is exact up to order $N^{-4/3}$, we can, in principle, derive $E_{1\mathrm{p}}(N)$ up to this order. But there is little point in writing out all this detail, and we shall stop at terms of order $N^{-2/3}$. The calculation employs the expansion

$$\frac{y - \frac{2}{3}\langle y \rangle}{(y - \langle y \rangle)^2} = \sum_{k=0}^{\infty} \frac{k+3}{3} \frac{\langle y \rangle^k}{y^{k+1}} \tag{14}$$

and results in

$$E_{1\mathrm{p}} = \varepsilon_0 N - Z^2 [(\tfrac{3}{2}N)^{1/3} - \tfrac{1}{2} + (\tfrac{3}{2}N)^{-1/3} (\langle y \rangle^2 - \tfrac{1}{6}) + (\tfrac{3}{2}N)^{-2/3} \tfrac{4}{3} \langle y \rangle (\langle y \rangle^2 - \tfrac{1}{4}) + \cdots] , \tag{15}$$

with

$$y = (\tfrac{3}{2}N)^{1/3} + \tfrac{1}{12}(\tfrac{3}{2}N)^{-1/3} \ . \tag{16}$$

In Eq. (15) the terms of order $N^{-1/3}$ and beyond are oscillatory functions of N. Observe that in $\langle y \rangle$ we do not neglect the second term of Eq. (16), in order to avoid a wrong phase of the oscillation at smaller values of N. We isolate the oscillations by means of

$$\begin{aligned} (\tfrac{3}{2}N)^{1/3} & \left[-\frac{E_{1\mathrm{p}} - \varepsilon_0 N}{Z^2} - (\tfrac{3}{2}N)^{1/3} + \tfrac{1}{2} \right] \\ & = (\langle y \rangle^2 - \tfrac{1}{6}) + (\tfrac{3}{2}N)^{-1/3} \tfrac{4}{3} \langle y \rangle (\langle y \rangle^2 - \tfrac{1}{4}) + \cdots \\ & \equiv h(N) \ . \end{aligned} \tag{17}$$

Figure 1 compares the exact $h(N)$ to the successive approximations of Eq. (17), with y from Eq. (16). During the filling of the first shell [i.e., $(\frac{3}{2}N)^{1/3} < 3^{1/3} = 1.44$] the exact $h(N)$ naturally does not yet show the shape of the large-N oscillations. Note, in particular, how good already is the leading term of Eq. (17). Three terms are sufficient to make the difference between the two curves indiscernible for $N \gtrsim 1$ [i.e., $(\frac{3}{2}N)^{1/3} \gtrsim 1.14$].

We end the discussion of Coulombic degeneracy here and turn to arbitrary linear degeneracy. The concept of a principal quantum number that labels shells cannot be employed there. Instead, we shall stick to angular and radial quantum numbers and use the tools that have been prepared in I.

NUMBER OF STATES

The number of states with binding energy less than ε is given by [Eq. (32) of I]

$$N(\varepsilon)=4\sum_{k,j=-\infty}^{\infty}(-1)^{k+j}\int_0^{\lambda_\varepsilon}d\lambda\,\lambda e^{2\pi ik\lambda}\times\frac{\exp[2\pi ij\nu_\varepsilon(\lambda)]-1}{2\pi ij}\,. \tag{18}$$

Linear degeneracy means, of course,

$$\nu_\varepsilon(\lambda)=\nu'_\varepsilon(\lambda_\varepsilon-\lambda)\,, \tag{19}$$

where the slope ν'_ε does not depend on λ. For such $\nu_\varepsilon(\lambda)$ the λ integration of Eq. (18) produces

$$N(\varepsilon)=4\sum_{k,j=-\infty}^{\infty}\frac{(-1)^{k+j}}{(2\pi)^3}\nu'_\varepsilon\left\{\frac{2\pi k\lambda_\varepsilon(j\nu'_\varepsilon-k)+i(j\nu'_\varepsilon-2k)}{k^2(k-j\nu'_\varepsilon)^2}\exp(2\pi ik\lambda_\varepsilon)+\frac{1}{j\nu'_\varepsilon(k-j\nu'_\varepsilon)^2}\exp(2\pi ij\lambda_\varepsilon\nu'_\varepsilon)-\frac{i}{k^2j\nu'_\varepsilon}\right\}. \tag{20}$$

This sum contains both oscillatory and nonoscillatory terms. The nonoscillatory ones are (a) the $k=j=0$ contribution; (b) the $k=0$, $j\neq0$ contribution of the first and the last terms in curly brackets; and (c) the $k\neq0$, $j=0$ contribution of the second and the last terms in curly brackets. Together they are

$$4\frac{1}{(2\pi)^3}\nu'_\varepsilon\tfrac{1}{6}(2\pi\lambda_\varepsilon)^3+4\sum_{j\,(\neq0)}\frac{(-1)^j}{(2\pi)^3}\nu'_\varepsilon\frac{-i}{(j\nu'_\varepsilon)^3}[1+2\pi ij\lambda_\varepsilon\nu'_\varepsilon-\tfrac{1}{2}(2\pi j\lambda_\varepsilon\nu'_\varepsilon)^2]$$
$$+4\sum_{k\,(\neq0)}\frac{(-1)^k}{(2\pi)^3}\nu'_\varepsilon\frac{i}{k^3}(2+2\pi ik\lambda_\varepsilon)=\tfrac{2}{3}\lambda_\varepsilon^3\nu'_\varepsilon-\tfrac{1}{6}\frac{\lambda_\varepsilon}{\nu'_\varepsilon}+\tfrac{1}{6}\lambda_\varepsilon\nu'_\varepsilon\,. \tag{21}$$

The oscillatory terms in (20) are (a) λ oscillations, $k\neq0$ contribution of the first term in curly brackets; and (b) ν oscillations, $j\neq0$ contribution of the second term in curly brackets. The λ oscillations are exhibited in

$$4\sum_{k\,(\neq0)}\frac{(-1)^k}{(2\pi)^3}\frac{1}{k}\exp(2\pi ik\lambda_\varepsilon)\nu'_\varepsilon\sum_{j=-\infty}^{\infty}(-1)^j\left[-\frac{2\pi k\lambda_\varepsilon+i}{k(k-j\nu'_\varepsilon)}-\frac{i}{(k-j\nu'_\varepsilon)^2}\right]$$
$$=-2\lambda_\varepsilon\sum_{k=1}^{\infty}\frac{(-1)^k}{\pi k}\frac{\cos(2\pi k\lambda_\varepsilon)}{\sin(\pi k/\nu'_\varepsilon)}+\sum_{k=1}^{\infty}\frac{(-1)^k}{(\pi k)^2}\frac{\sin(2\pi k\lambda_\varepsilon)}{\sin(\pi k/\nu'_\varepsilon)}+\frac{1}{\nu'_\varepsilon}\sum_{k=1}^{\infty}\frac{(-1)^k}{\pi k}\sin(2\pi k\lambda_\varepsilon)\frac{\cos(\pi k/\nu'_\varepsilon)}{\sin^2(\pi k/\nu'_\varepsilon)}\,, \tag{22}$$

while the ν oscillations consist in

$$4\sum_{j\,(\neq0)}\frac{(-1)^j}{(2\pi)^3}\frac{1}{j\nu'_\varepsilon}\exp(2\pi ij\lambda_\varepsilon\nu'_\varepsilon)\nu'_\varepsilon\sum_{k=-\infty}^{\infty}(-1)^k\frac{i}{(j\nu'_\varepsilon-k)^2}=-\sum_{j=1}^{\infty}\frac{(-1)^j}{\pi j}\sin(2\pi j\lambda_\varepsilon\nu'_\varepsilon)\frac{\cos(\pi j\nu'_\varepsilon)}{\sin^2(\pi j\nu'_\varepsilon)}\,. \tag{23}$$

In arriving at Eqs. (22) and (23) we have made use of the identities

$$\sum_{j=-\infty}^{\infty}\frac{(-1)^j}{z-\pi j}=\frac{1}{\sin z}\,,$$
$$\sum_{j=-\infty}^{\infty}\frac{(-1)^j}{(z-\pi j)^2}=\frac{\cos z}{\sin^2 z}\,. \tag{24}$$

We now add up the various contributions to $N(\varepsilon)$ and obtain

$$N(\varepsilon)=\frac{2}{3}\lambda_\varepsilon^3\nu'_\varepsilon-\frac{1}{6}\frac{\lambda_\varepsilon}{\nu'_\varepsilon}+\frac{1}{6}\lambda_\varepsilon\nu'_\varepsilon-2\lambda_\varepsilon\sum_{k=1}^{\infty}\frac{(-1)^k}{\pi k}\frac{\cos(2\pi k\lambda_\varepsilon)}{\sin(\pi k/\nu'_\varepsilon)}+\sum_{k=1}^{\infty}\frac{(-1)^k}{(\pi k)^2}\frac{\sin(2\pi k\lambda_\varepsilon)}{\sin(\pi k/\nu'_\varepsilon)}$$
$$+\frac{1}{\nu'_\varepsilon}\sum_{k=1}^{\infty}\frac{(-1)^k}{\pi k}\sin(2\pi k\lambda_\varepsilon)\frac{\cos(\pi k/\nu'_\varepsilon)}{\sin^2(\pi k/\nu'_\varepsilon)}-\sum_{j=1}^{\infty}\frac{(-1)^j}{\pi j}\sin(2\pi j\lambda_\varepsilon\nu'_\varepsilon)\frac{\cos(\pi j\nu'_\varepsilon)}{\sin^2(\pi j\nu'_\varepsilon)}\,. \tag{25}$$

Of course, the terms with vanishing denominator, which occur whenever either k/ν'_ε or $j\nu'_\varepsilon$ is an integer, need special consideration. We postpone that for a moment in order to first make contact with some results of I.

In I we learned that for the Thomas-Fermi (TF) potential [Eqs. (53)–(55) of I] $\nu_\varepsilon(\lambda)/Z^{1/3}$ is a universal (i.e., Z independent) function of $\lambda/Z^{1/3}$ and $\varepsilon/Z^{4/3}$. Consequently, if we keep the ratio $\varepsilon/Z^{4/3}$ fixed, λ_ε and $\nu_\varepsilon(\lambda=0)$ are proportional to $Z^{1/3}$, $\nu'_\varepsilon\equiv-(\partial\nu_\varepsilon/\partial\lambda)|_{\lambda=\lambda_\varepsilon}$ is Z independent, etc. However, these particular Z dependences are in no way confined to the TF potential. In fact, only one property of the TF potential is used in arriving at these conclusions. This property is the circumstance that $(r/Z)V_{\rm TF}(r)$ is a function of the product $Z^{1/3}r$ and does not depend on Z and r separately. Accordingly, all such potentials will lead to the Z dependences of λ_ε, $\nu_\varepsilon(0)$, etc., stated above. To this class of potentials belong, e.g., the TF potentials of ions with variable Z but fixed degree of ionization, $1-N/Z$. Another example is the Coulombic potential of Eq. (1) if ε_0 is proportional to $Z^{4/3}$.

From now on we shall consider only potentials with this TF-type dependence on Z. Then, with the ratio $\varepsilon/Z^{4/3}$ kept fixed, of the three nonoscillatory terms in Eq. (25), the first is proportional to Z, and the other two are proportional to $Z^{1/3}$. For the λ oscillations the period of $Z^{1/3}$ is the constant $Z^{1/3}/\lambda_\varepsilon$, while the ν oscillations have the period $Z^{1/3}/\lambda_\varepsilon \nu'_\varepsilon$. In other words, the periodicity of the λ and the ν oscillations is determined by the maximal values of λ and ν, respectively, for the given $\varepsilon/Z^{4/3}$. These oscillations have amplitudes that are either Z independent or proportional to $Z^{1/3}$—at least this is what Eq. (25) tells us on first sight. However, a closer look at the terms with vanishing denominators will show that the leading oscillatory term is of order $Z^{2/3}$, in general.

Consider the situation when ν'_ε is the ratio of two relatively prime integers, $\nu'_\varepsilon = u/v$ (we suppress the subscript ε on u and v). Then the denominators in Eq. (25) are zero whenever $k = mu$ or $j = mv$, with $m = 1,2,3,\ldots$. The sum of all these terms is, of course, finite because we proceeded from the well-defined expression in Eq. (18). The various infinities are exhibited by writing $\nu'_\varepsilon = (u/v)(1+\epsilon)$ and examining the limit $\epsilon \to 0$. For example,

$$\frac{1}{\nu'_\varepsilon}\frac{\cos(\pi k/\nu'_\varepsilon)}{\sin^2(\pi k/\nu'_\varepsilon)} = (-1)^{mv}\frac{v}{u}\left[\frac{1}{(\pi m v)^2}\frac{1}{\epsilon^2} + \frac{1}{\pi m v}\frac{1}{\epsilon} - \frac{1}{6} + O(\epsilon)\right], \tag{26}$$

and

$$\sin(2\pi j\lambda_\varepsilon \nu'_\varepsilon)\frac{\cos(\pi j \nu'_\varepsilon)}{\sin^2(\pi j\nu'_\varepsilon)} = (-1)^{mu}\left[\frac{\sin(2\pi m\lambda_\varepsilon u)}{(\pi m u)^2}\frac{1}{\epsilon^2} + 2\lambda_\varepsilon\frac{\cos(2\pi m\lambda_\varepsilon u)}{\pi m u}\frac{1}{\epsilon} - (\tfrac{1}{6} + 2\lambda_\varepsilon^2)\sin(2\pi m \lambda_\varepsilon u) + O(\epsilon)\right]. \tag{27}$$

All these individually divergent terms combine to

$$\left[2\lambda_\varepsilon^2 + \frac{1}{6} - \frac{1}{6}\frac{v^2}{u^2}\right]\frac{1}{v}\sum_{m=1}^{\infty}\frac{(-1)^{m(u+v)}}{\pi m}\sin(2\pi m\lambda_\varepsilon u) + \frac{2\lambda_\varepsilon}{uv}\sum_{m=1}^{\infty}\frac{(-1)^{m(u+v)}}{(\pi m)^2}\cos(2\pi m \lambda_\varepsilon u) - \frac{1}{u^2 v}\sum_{m=1}^{\infty}\frac{(-1)^{m(u+v)}}{(\pi m)^3}\sin(2\pi m\lambda_\varepsilon u). \tag{28}$$

Such sums can be evaluated in terms of the periodic function $\langle y\rangle$ of Eq. (7):

$$\begin{aligned}\sum_{m=1}^{\infty}\frac{(-1)^m}{\pi m}\sin(2\pi m y) &= -\langle y\rangle,\\ \sum_{m=1}^{\infty}\frac{(-1)^m}{(\pi m)^2}\cos(2\pi m y) &= \langle y\rangle^2 - \tfrac{1}{12},\\ \sum_{m=1}^{\infty}\frac{(-1)^m}{(\pi m)^3}\sin(2\pi m y) &= \tfrac{2}{3}\langle y\rangle(\langle y\rangle^2 - \tfrac{1}{4}).\end{aligned} \tag{29}$$

They are obviously related to each other through integration with respect to y. In order to use them in (28), we define w by $(-1)^{m(u+v)}\cos/\sin(2\pi m y) = (-1)^m \cos/\sin \times[2\pi m(y+w)]$, i.e., $w \equiv (u+v+1)/2$, or in view of the periodicity of the circular functions,

$$w = \begin{cases} 0 & \text{for } u+v \text{ odd} \\ \frac{1}{2} & \text{for } u+v \text{ even}.\end{cases} \tag{30}$$

Then the combination of the resulting form of (28) with the nonoscillatory terms of Eq. (25) is

$$N(\varepsilon) = \tfrac{2}{3}\nu'_\varepsilon\left[\frac{\lambda_\varepsilon u - \langle\lambda_\varepsilon u + w\rangle}{u}\right]^3 - \left[\frac{1}{6\nu'_\varepsilon} - \frac{\nu'_\varepsilon}{6}\frac{1}{6uv}\right]\frac{\lambda_\varepsilon u - \langle \lambda_\varepsilon u + w\rangle}{u} + \cdots . \tag{31}$$

The ellipsis in Eq. (31) represents the sums of Eq. (25) with $k \neq mu$ and $j \neq mv$. The leading terms of $N(\varepsilon)$ are

$$N(\varepsilon) \cong \tfrac{2}{3}\lambda_\varepsilon^3\nu'_\varepsilon - 2\lambda_\varepsilon^2\nu'_\varepsilon\langle\lambda_\varepsilon u + w\rangle/u . \tag{32}$$

Indeed, the oscillations are dominated by a term with amplitude of order $Z^{2/3}$.

In the case of Coulombic degeneracy (i.e., $\nu'_\varepsilon = 1$, $u = v = 1$, $w = \frac{1}{2}$) Eq. (31) is the whole answer. It is

$$\begin{aligned}N(\varepsilon) &= \tfrac{2}{3}(\lambda_\varepsilon - \langle\lambda_\varepsilon + \tfrac{1}{2}\rangle)^3 - \tfrac{1}{6}(\lambda_\varepsilon - \langle\lambda_\varepsilon + \tfrac{1}{2}\rangle)\\ &= \tfrac{2}{3}([\lambda_\varepsilon] + \tfrac{1}{2})^3 - \tfrac{1}{6}([\lambda_\varepsilon] + \tfrac{1}{2}) .\end{aligned} \tag{33}$$

The comparison with Eq. (2) indicates that $[\lambda_\varepsilon]$ equals the number of full shells m, whereas it may seem that partly filled shells are not described by Eq. (33). Now, as λ_ε increases from $m-0$ to $m+0$, the whole mth shell is added. Equation (33) tells us that it contains $2m^2$ electrons. The gradual filling of the mth shell is therefore contained in Eq. (33) if we assign the whole range of values between $m-1$ and m to $[\lambda_\varepsilon]$, when $\lambda_\varepsilon = m$. Then Eqs. (33) and (2) are equivalent. The specific values of ε for which λ_ε is an integer are the single-particle energies of the respective shells. Therefore, Eq. (33) not only implies Eq. (2) but also Eq. (3). Incidentally, in solving [cf. Eq. (3)]

$$\varepsilon_m = -\frac{Z^2}{2m^2} + \varepsilon_0 \tag{34}$$

for $m = \lambda_{\varepsilon_m}$, we find, after dropping the subscript m,

$$\lambda_\varepsilon = \frac{Z}{[2(\varepsilon_0 - \varepsilon)]^{1/2}} . \tag{35}$$

This is, of course, identical with [Eq. (31) of I for the V of Eq. (1)]

$$\lambda_\varepsilon = \max_r\{[2r^2(\varepsilon + Z/r - \varepsilon_0)]^{1/2}\} . \tag{36}$$

To sum up, we state that Eqs. (33) and (35) together contain as much information as do Eqs. (2) and (3). It was easier, though, to start with Eqs. (2) and (3) right away, but this was possible only because of the simple Coulombic degeneracy, which allows the use of a single principal quantum number. For arbitrary ν'_ε, one must sum over the angular and radial quantum numbers individually [or over j and k, as in Eq. (18)].

Another example of some particular interest (see below) is the circumstance $\nu'_\varepsilon=2$. Here we have $u=2$, $v=1$, and $w=0$, and to Eq. (31) one must add the terms of Eq. (25) that have odd k. Thus

$$\begin{aligned} N(\varepsilon)&=\tfrac{1}{6}(2\lambda_\varepsilon-\langle 2\lambda_\varepsilon\rangle)^3+\tfrac{1}{12}(2\lambda_\varepsilon-\langle 2\lambda_\varepsilon\rangle)\\ &\quad-2\lambda_\varepsilon\sum_{m=0}^{\infty}\frac{(-1)^{2m+1}}{\pi(2m+1)}\frac{\cos[2\pi(2m+1)\lambda_\varepsilon]}{\sin[\pi(m+\frac{1}{2})]}+\sum_{m=0}^{\infty}\frac{(-1)^{2m+1}}{[\pi(2m+1)]^2}\frac{\sin[2\pi(2m+1)\lambda_\varepsilon]}{\sin[\pi(m+\frac{1}{2})]}\\ &=\tfrac{1}{6}[2\lambda_\varepsilon+\tfrac{1}{2}]^3+\tfrac{1}{12}[2\lambda_\varepsilon+\tfrac{1}{2}]+\left[\lambda_\varepsilon\frac{\partial}{\partial\lambda_\varepsilon}-1\right]\sum_{m=0}^{\infty}\frac{(-1)^m}{[\pi(2m+1)]^2}\sin[2\pi(2m+1)\lambda_\varepsilon]\ . \end{aligned} \tag{37}$$

Upon using

$$\sum_{m=0}^{\infty}\frac{(-1)^m}{[\pi(2m+1)]^2}\sin[\pi(2m+1)y]=\pm\tfrac{1}{4}\langle y\rangle \quad \text{for } [y+\tfrac{1}{2}]=\begin{cases}\text{even}\\ \text{odd}\end{cases} \tag{38}$$

(note that this is a continuous function of y), as well as

$$\begin{aligned}\left[y\frac{d}{dy}-1\right](-1)^{[y+1/2]}\langle y\rangle&=(-1)^{[y+1/2]}(y-\langle y\rangle)\\ &=(-1)^{[y+1/2]}[y+\tfrac{1}{2}]\ ,\end{aligned} \tag{39}$$

we arrive at

$$N(\varepsilon)=\tfrac{1}{6}[2\lambda_\varepsilon+\tfrac{1}{2}]^3+\begin{Bmatrix}\frac{1}{3}\\ -\frac{1}{6}\end{Bmatrix}\times[2\lambda_\varepsilon+\tfrac{1}{2}] \quad \text{for } [2\lambda_\varepsilon+\tfrac{1}{2}]=\begin{cases}\text{even}\\ \text{odd}\end{cases}\ . \tag{40}$$

This $N(\varepsilon)$ has discontinuities whenever $\lambda_\varepsilon=\frac{1}{2}m-\frac{1}{4}$, $m=1,2,\ldots$, where the jump of $N(\varepsilon)$ is

$$\Delta N=\begin{Bmatrix}\frac{1}{2}m^2 \text{ for } m \text{ even}\\ \frac{1}{2}(m-1)^2 \text{ for } m \text{ odd}\end{Bmatrix}=2[m/2]^2\ . \tag{41}$$

Equation (41) is easily interpreted: for $m=1$, $\lambda_\varepsilon=\frac{1}{4}$, no states become available, $\Delta N=0$; for $m=2$, $\lambda_\varepsilon=\frac{3}{4}$, the $1s$ state is added, $\Delta N=2$; for $m=3$, $\lambda_\varepsilon=\frac{5}{4}$, the $2s$ state is added, again $\Delta N=2$; for $m=4$, $\lambda_\varepsilon=\frac{7}{4}$, the $3s$ and the $2p$ states are added, $\Delta N=2+6=8$; etc. Please observe that, unlike Coulombic degeneracy, there are pairs of subsequent shells that contain the same number of electrons. Also note that $N(\varepsilon)$ has a part with periodicity $\lambda_\varepsilon\to\lambda_\varepsilon+\frac{1}{2}$, i.e., $Z^{1/3}\to Z^{1/3}+Z^{1/3}/2\lambda_\varepsilon$, and a second one with periodicity $\lambda_\varepsilon\to\lambda_\varepsilon+1$, i.e., $Z^{1/3}\to Z^{1/3}+Z^{1/3}/\lambda_\varepsilon$. These are, of course, the ν and λ oscillations, respectively.

Let us now return to Eq. (32) for some additional comments. The first term is the $j=k=0$ contribution of Eq. (18), so its significance is the TF limit, here for linear degeneracy,

$$\begin{aligned}N_{\mathrm{TF}}(\varepsilon)&=4\int_0^{\lambda_\varepsilon}d\lambda\,\lambda\nu_\varepsilon(\lambda)\\ &=4\int_0^{\lambda_\varepsilon}d\lambda\,\lambda\nu'_\varepsilon(\lambda_\varepsilon-\lambda)=\tfrac{2}{3}\lambda_\varepsilon^3\nu'_\varepsilon\ .\end{aligned} \tag{42}$$

Since both $\lambda_\varepsilon/Z^{1/3}$ and ν'_ε are functions of $\varepsilon/Z^{4/3}$, $N_{\mathrm{TF}}(\varepsilon)/Z$ is also one. This is a consequence of the TF-type Z dependence of the potential [$(r/Z)V$ being a function of $Z^{1/3}r$] and has nothing to do with the linear degeneracy. Accordingly, for potentials with a finite number of bound states (i.e., for short-range potentials), $N_{\mathrm{TF}}(\varepsilon=0)$ is a numerical multiple of Z. In other words, in the TF limit the maximum number of electrons that can be bound by the potential is proportional to Z. One can make it equal to Z by choosing the parameters of the potential appropriately. For example, this "normalization,"

$$N_{\mathrm{TF}}(\varepsilon=0)=Z=\int(d\mathbf{r})\frac{1}{3\pi^2}(-2V)^{3/2}\ , \tag{43}$$

applied to the Coulombic potential of Eq. (1), requires $\varepsilon_0=Z^{4/3}/(18)^{1/3}$.

This reasoning can be reversed. The statement $N_{\mathrm{TF}}(0)=\mathrm{const}\times Z$ is differentially expressed by

$$\left[Z\frac{\partial}{\partial Z}-1\right]N_{\mathrm{TF}}(0)=0\ . \tag{44}$$

The integral of (43) obeys this equation if the integrand resulting from this operation is a divergence. For dimensional reasons, the only possibility is

$$\left[Z\frac{\partial}{\partial Z}-1\right](-2V)^{3/2}=c\nabla\cdot[\mathbf{r}(-2V)^{3/2}]\ , \tag{45}$$

where the numerical constant c is determined by inserting the Coulomb potential $-Z/r$, which represents the $r=0$ behavior of any atomic potential V. This gives $c=\frac{1}{3}$, and then

$$3Z\frac{\partial}{\partial Z}V=(4+\mathbf{r}\cdot\nabla)V\ , \tag{46}$$

which is, indeed, equivalent to stating that $(r/Z)V$ is a function of $Z^{1/3}r$.

Now to the second term of Eq. (32), the leading oscillatory term. Since a small change of ν'_ε can cause an enormous difference in u and v, slightly different slopes ν'_ε may have very different leading oscillations. How can that be? Certainly, $N(\varepsilon)$ does not change a lot if, e.g., $\nu'_\varepsilon=1$ is replaced by $\nu'_\varepsilon=1.000\,001$. True, but the point is that the leading oscillation is only visible for very large values of λ_ε (i.e., large $Z^{1/3}$) when it actually dominates all but the TF term. And at those large λ_ε, the small change in ν'_ε does cause a big difference in $N(\varepsilon)$. As long as we stay with modest values of λ_ε, $N(\varepsilon)$ is not sensitive to tiny changes in ν'_ε. For example, consider $\lambda_\varepsilon=\frac{5}{2}$. All ν'_ε in the range $\frac{3}{4}<\nu'_\varepsilon<\frac{5}{4}$ are such that the first two Coulomb shells are filled, thus $N(\varepsilon)=10$ for all these ν'_ε. But for a λ_ε five times larger, ν'_ε has to be within $\frac{23}{24}<\nu'_\varepsilon<\frac{25}{24}$ in order to not change $N(\varepsilon)=1300$. The lesson learned here is twofold. First, as long as we do not consider an enormous number of occupied states, small errors in ν'_ε do not matter. Second, the leading oscillatory term may be utterly unimportant in the physically relevant domain of rather modest values of $Z^{1/3}$, unless ν'_ε is the ratio of two small integers.

ENERGY

According to Eq. (29) of I (with $\zeta=-\varepsilon$, etc.), the single-particle energy $E_{1\mathrm{p}}$ is obtained from $N(\varepsilon)$ by integration,

$$E_1(\varepsilon)=E_{1\mathrm{p}}(\varepsilon)-\varepsilon N(\varepsilon)=-\int_{-\infty}^{\varepsilon} d\varepsilon' N(\varepsilon')\ . \tag{47}$$

Again, we first consider the Coulombic potential of (1) for illustration. There, $N(\varepsilon)$ is given by Eq. (33), and because [an implication of Eq. (35)]

$$d\varepsilon'=\frac{Z^2}{\lambda_{\varepsilon'}^3}d\lambda_{\varepsilon'}\ , \tag{48}$$

we write ($\lambda_{\varepsilon'}\equiv\lambda$)

$$E_1(\varepsilon)=-Z^2\int_0^{\lambda_\varepsilon} d\lambda\left[\frac{2}{3}-\frac{2}{\lambda}\langle\lambda+\tfrac{1}{2}\rangle+\frac{2}{\lambda^2}(\langle\lambda+\tfrac{1}{2}\rangle^2-\tfrac{1}{12})-\frac{2}{3\lambda^3}\langle\lambda+\tfrac{1}{2}\rangle(\langle\lambda+\tfrac{1}{2}\rangle^2-\tfrac{1}{4})\right]. \tag{49}$$

The multipliers of the various powers of $1/\lambda$ are functions of the forms displayed in (29), with $y=\lambda+\frac{1}{2}$, so that their integration is straightforward. We obtain

$$E_1(\varepsilon)=-Z^2\left[\frac{2}{3}\lambda_\varepsilon-\frac{1}{2}-\frac{1}{\lambda_\varepsilon}(\langle\lambda_\varepsilon+\tfrac{1}{2}\rangle^2-\tfrac{1}{12})+\frac{1}{3\lambda_\varepsilon^2}\langle\lambda_\varepsilon+\tfrac{1}{2}\rangle(\langle\lambda_\varepsilon+\tfrac{1}{2}\rangle^2-\tfrac{1}{4})\right]. \tag{50}$$

Observe that for $\lambda_\varepsilon<1$, i.e., $\langle\lambda_\varepsilon+\frac{1}{2}\rangle=\lambda_\varepsilon-\frac{1}{2}$, $E_1(\varepsilon)$ is zero, so that $E_1(\varepsilon\to-\infty)=0$, as it should be. Equation (50) can be rewritten as

$$E_1(\varepsilon)=-Z^2[\lambda_\varepsilon]+\frac{Z^2}{2\lambda_\varepsilon^2}N(\varepsilon)=-Z^2[\lambda_\varepsilon]+(\varepsilon_0-\varepsilon)N(\varepsilon)\ , \tag{51}$$

the last step employing Eq. (35). Thus,

$$E_{1\mathrm{p}}(\varepsilon)=-Z^2[\lambda_\varepsilon]+\varepsilon_0 N(\varepsilon)\ ,$$

which is, of course, identical with Eq. (12) when $y=[\lambda_\varepsilon]+\frac{1}{2}$.

Coulombic degeneracy is of practical interest because it is realized in all atomic potentials at large binding energies. We isolate these strongly bound electrons by introducing an ε_s that selects the part of the spectrum with Coulombic degeneracy,

$$E_1(\varepsilon)=E_1(\varepsilon_s)+[E_1(\varepsilon)-E_1(\varepsilon_s)]=-\int_{-\infty}^{\varepsilon_s}d\varepsilon' N(\varepsilon')-\int_{\varepsilon_s}^{\varepsilon}d\varepsilon' N(\varepsilon')\ . \tag{52}$$

The first integral, which is the contribution of the strongly bound electrons, results in an expression analogous to Eq. (50). The constant ε_0, hidden in λ_{ε_s} via Eq. (35), has the physical significance of the (electrostatic) potential produced by the electronic cloud at the location of the nucleus. The leading term of $E_1(\varepsilon_s)$ is, as always, the TF contribution,

$$-\frac{2}{3}Z^2\lambda_{\varepsilon_s}=-\frac{2}{3}\frac{Z^3}{[2(\varepsilon_0-\varepsilon_s)]^{1/2}}=\int(d\mathbf{r})\left[-\frac{1}{15\pi^2}\right]\left[2\left[\varepsilon_s+\frac{Z}{r}-\varepsilon_0\right]\right]^{5/2}=[E_1(\varepsilon_s)]_{\mathrm{TF}}\ , \tag{53}$$

when we insert Eq. (1) into Eq. (12) of I with $\zeta=-\varepsilon_s$. Together with the TF part of the second integral in Eq. (52) this just produces $[E_1(\varepsilon)]_{\mathrm{TF}}$. More interesting is the next-to-leading term of $E_1(\varepsilon_s)$. It equals [cf. Eq. (50)] $\frac{1}{2}Z^2$ and does not depend on ε_s. Actually, being the only part of $E_1(\varepsilon_s)$ independent of ε_s, this term is the only explicitly visible contribution of the strongly bound electrons to $E_1(\varepsilon)$. All the other terms in Eq. (50) cannot themselves be present in $E_1(\varepsilon)$ since $E_1(\varepsilon)$ does not depend on ε_s.

We have thus identified the two leading contributions to E_1,

$$E_1(\varepsilon)=[E_1(\varepsilon)]_{\mathrm{TF}}+\tfrac{1}{2}Z^2+\cdots\ . \tag{54}$$

The term supplementing the TF energy was first surmised by Scott.[2] It has been derived repeatedly—with increasing clarity—most recently by us in the context of a general discussion of the handling of strongly bound electrons in TF theory.[3] While these previous derivations did not employ semiclassical quantization they did make use of the Coulombic degeneracy associated with very large binding energies. The most remarkable feature of Scott's term is that it is the same for all atomic potentials and all numbers of electrons, a circumstance that has remained implicit in earlier derivations.

For the majority of potentials, including the TF potential, linear degeneracy occurs only for large binding energies, where the degeneracy is of Coulomb type. There is, however, the possibility of linear degeneracy at $\varepsilon=0$. How potentials with this property can be constructed systematically is discussed in the Appendix. A particular example is provided by the Tietz potential[4]

$$V=-\frac{Z}{r}\frac{1}{(1+r/R)^2}\ , \tag{55}$$

which represents a rough approximation to the TF potential in the range $1\lesssim Z^{1/3}r\lesssim 5$. For that purpose, normalization in the sense of Eq. (43) is required, yielding

$$R=\left[\frac{9}{2Z}\right]^{1/3}=1.65Z^{-1/3}\ . \tag{56}$$

Please note that then $(r/Z)V$ is, indeed, a function of $Z^{1/3}r$.

At large distances, the Tietz potential is proportional to $1/r^3$, so that Eq. (49) of I implies

$$\left.\frac{\partial\nu_0(\lambda)}{\partial\lambda}\right|_{\lambda=0}=-2\ . \tag{57}$$

On the other hand, insertion of

$$\lambda_0=(\tfrac{1}{2}ZR)^{1/2}\ ,\quad r_0=R\ ,\quad \omega_0=\tfrac{1}{2}(Z/R)^{1/2} \tag{58}$$

into Eq. (42) of I gives

$$\left.\frac{\partial\nu_0(\lambda)}{\partial\lambda}\right|_{\lambda=\lambda_0}=-2\ . \tag{59}$$

Of course, identical slopes at both ends of the line of degeneracy $\nu_0(\lambda)$ do not necessarily imply that $\nu_0(\lambda)$ is a straight line.[5] Also, the vanishing of $\partial^2\nu_0(\lambda)/\partial\lambda^2$ at $\lambda=\lambda_0$, as told by Eq. (90) of I ($c_3=2$, $c_4=3$ here), is strong, yet insufficient, evidence for linear degeneracy. So we make use of Eq. (45) of I and find, after inserting the Tietz potential and slightly rearranging the expression,

$$\frac{\partial\nu_0(\lambda)}{\partial\lambda}=-\frac{1}{\pi}\int_{r_1}^{r_2}dr\frac{1}{r}\frac{r+\sqrt{r_1r_2}}{\sqrt{(r-r_1)(r_2-r)}}\ , \tag{60}$$

wherein the limits of integration obey

$$r_1r_2=R^2\ ,\quad r_1+r_2=2R\left[\frac{ZR}{\lambda^2}-1\right]=2R\,[2(\lambda_0/\lambda)^2-1]\geq 2R\ . \tag{61}$$

The value of the integral in Eq. (60) happens to be independent of r_1 and r_2,

$$\begin{aligned}\int_{r_1}^{r_2}dr\frac{1}{r}\frac{r+\sqrt{r_1r_2}}{\sqrt{(r-r_1)(r_2-r)}}&=\int_{r_1}^{r_2}dr\frac{d}{dr}\left[\arcsin\left[\frac{(r-r_1)-(r_2-r)}{r_2-r_1}\right]+\arcsin\left[\frac{r_2(r-r_1)-r_1(r_2-r)}{r(r_2-r_1)}\right]\right]\\&=2\pi\ .\end{aligned} \tag{62}$$

Therefore, for the Tietz potential, we have

$$\nu_0(\lambda)=\nu_0'(\lambda_0-\lambda),\quad \nu_0'=2\ , \tag{63}$$

i.e., exact linear degeneracy at $\varepsilon=0$, indeed. Consequently, the total number of states in the Tietz potential is given by $N(\varepsilon=0)$ of Eq. (40) with λ_0 from (58).

For values of ε close to zero, the lines of degeneracy for the Tietz potential are not straight lines. However, the main deviation from a straight line occurs for small values of λ [recall the rapid change of $\nu_\varepsilon(\lambda=0)$ for $\varepsilon\lesssim 0$; Eq. (52) of I]. If we use a linear approximation, as in Eq. (19), with

$$\nu_\varepsilon'\equiv-\left.\frac{\partial\nu_\varepsilon(\lambda)}{\partial\lambda}\right|_{\lambda=\lambda_\varepsilon}\ , \tag{64}$$

an error will be made mainly for $\lambda\gtrsim 0$. Thus the states affected by such a linearization have small angular momentum and therefore little multiplicity. This is visible, e.g., in Eq. (18) where the factor λ gives little weight to these states. In short, Eqs. (19) and (64) represent a very reliable approximation to $\nu_\varepsilon(\lambda)$ if $\varepsilon\lesssim 0$. We are now going to use it for finding the leading oscillatory term of $E_1(\varepsilon=0)=E_{1p}(\varepsilon=0)$ for the Tietz potential.

For this purpose, we write

$$\nu_\varepsilon'=2(1-\sigma_\varepsilon),\quad \sigma_0=0\ , \tag{65}$$

which is inserted into Eq. (25). Obviously, σ_ε will play the role of $-\varepsilon$ that appeared in Eqs. (26) and (27). For example, the ν oscillations in $N(\varepsilon)$ have the structure

$$[N_{\rm osc}(\varepsilon)]_\nu=\mathrm{Re}\sum_{j=1}^{\infty}\exp(4\pi ij\lambda_\varepsilon)\sum_{m,m'}c_{jmm'}\lambda_\varepsilon^m\sigma_\varepsilon^{m'}\ , \tag{66}$$

where the numerical coefficients $c_{jmm'}$ do not depend on ε. Equation (66) is directly obtained from Eq. (27) after making $O(\epsilon)$ explicit. Individual terms of the triple sum in (66) are integrated through repeated partial integration, as in Eq. (77) of I, whereby the leading contribution to the energy oscillations stems from the terms with $m'=m-2$. It is given by

$$[E_1(\varepsilon=0)]_\nu=\frac{\lambda_0^2}{\dot\lambda_0}\sum_{m=2}^{\infty}\frac{1}{m(m-1)}\left[\frac{\lambda_0\dot\sigma_0}{\dot\lambda_0}\right]^{m-2}\times\sum_{j=1}^{\infty}\frac{(-1)^j}{(\pi j)^2}\cos(4\pi j\lambda_0)+\cdots\ , \tag{67}$$

which has an amplitude of order $Z^{5/3}$. The dots symbolize differentiation with respect to ε, as is illustrated by

$$\dot{\lambda}_\varepsilon \equiv \frac{d}{d\varepsilon}\lambda_\varepsilon \,. \tag{68}$$

Since it turns out that the leading λ oscillation is of lower order in $Z^{1/3}$, the leading ν oscillation of Eq. (67) is already the leading energy oscillation.

The sum over m in (67) is elementary,[6]

$$\sum_{m=2}^{\infty} \frac{1}{m(m-1)} y^{m-2} = \frac{1}{y} + \frac{1-y}{y^2}\ln(1-y) \,, \tag{69}$$

while the sum over j is given by the second equation of (29), so that Eqs. (54) and (67) together produce the following result for the single-particle energy of the filled Tietz potential ($y=\lambda_0\dot{\sigma}_0/\dot{\lambda}_0$):

$$\begin{aligned} E_1(\varepsilon=0) = {} & [E_1(\varepsilon=0)]_{\mathrm{TF}} + \tfrac{1}{2}Z^2 \\ & + \frac{\lambda_0^2}{\dot{\lambda}_0}\left[\frac{1}{y} + \frac{1-y}{y^2}\ln(1-y)\right] \\ & \times(\langle 2\lambda_0\rangle^2 - \tfrac{1}{12}) + \cdots \,. \end{aligned} \tag{70}$$

The ellipsis indicates the oscillatory terms of order $Z^{4/3}$ and smaller and also nonoscillatory terms which can even be of order $Z^{5/3}$. For, on this level, all we identified are the oscillatory terms; our calculations cannot indicate if there is a nonoscillatory term of order $Z^{5/3}$. [Incidentally, for this reason the additive term $-\frac{1}{12}$ in the last pair of parentheses of (70) is insignificant. We write it, though, because it makes the average of the oscillation, over one period, vanish.]

The leading term in Eq. (70) is

$$\begin{aligned} [E_1(\varepsilon=0)]_{\mathrm{TF}} &= \int (d\mathbf{r}) \left[-\frac{1}{15\pi^2}\right]\left[\frac{2Z}{r}\frac{1}{(1+r/R)^2}\right]^{5/2} \\ &= -\tfrac{7}{96}(2Z)^{5/2}R^{1/2} \\ &= -\tfrac{7}{4}(\tfrac{1}{6})^{2/3}Z^{7/3} = -0.5300Z^{7/3} \,, \end{aligned} \tag{71}$$

where Eq. (56) has been inserted. According to Eq. (37) of I, we have

$$\dot{\lambda}_\varepsilon = \frac{r_\varepsilon^2}{\lambda_\varepsilon} \,, \tag{72}$$

so that for the Tietz potential

$$\dot{\lambda}_0 = \left[\frac{2R^3}{Z}\right]^{1/2} , \tag{73}$$

and then

$$\frac{\lambda_0^2}{\dot{\lambda}_0} = \frac{\lambda_0^3}{r_0^2} = \left[\frac{Z^3}{8R}\right]^{1/2} = \tfrac{1}{2}(\tfrac{1}{6})^{1/3}Z^{5/3} = 0.2752Z^{5/3} \,. \tag{74}$$

Further, we need $\dot{\sigma}_0 = (d/d\varepsilon)(1-\frac{1}{2}\nu'_\varepsilon)\,|_{\varepsilon=0} = -\frac{1}{2}\dot{\nu}'_0$. We proceed from [Eq. (64), and Eq. (42) of I]

$$\begin{aligned} \dot{\nu}'_\varepsilon &= \frac{d}{d\varepsilon}\nu'_\varepsilon = \frac{d}{d\varepsilon}\left[\sqrt{2}\frac{\lambda_\varepsilon}{r_\varepsilon\omega_\varepsilon}\right] \\ &= \nu'_\varepsilon\left[\frac{\dot{\lambda}_\varepsilon}{\lambda_\varepsilon} - \frac{\dot{r}_\varepsilon}{r_\varepsilon} - \frac{\dot{\omega}_\varepsilon}{\omega_\varepsilon}\right] \\ &= \nu'_\varepsilon\left[\left[\frac{r_\varepsilon}{\lambda_\varepsilon}\right]^2 - \left[\frac{2}{\omega_\varepsilon}\right]^2 - \frac{\dot{\omega}_\varepsilon}{\omega_\varepsilon}\right] ; \end{aligned} \tag{75}$$

the last step used Eqs. (37) and (40) of I. We now differentiate Eq. (39) of I to produce $\dot{\omega}_\varepsilon$,

$$\begin{aligned} \dot{\omega}_\varepsilon &= \frac{1}{2\omega_\varepsilon}\frac{d}{d\varepsilon}\omega_\varepsilon^2 = \frac{1}{2\omega_\varepsilon}\frac{dr_\varepsilon}{d\varepsilon}\frac{d}{dr_\varepsilon}\omega_\varepsilon^2 \\ &= \frac{4}{\omega_\varepsilon^3}\left[r_\varepsilon^2\frac{d^3}{dr_\varepsilon^3} + 2r_\varepsilon\frac{d^2}{dr_\varepsilon^2} - \frac{d}{dr_\varepsilon} + \frac{1}{r_\varepsilon}\right][r_\varepsilon V(r_\varepsilon)] \,. \end{aligned} \tag{76}$$

Applied to the Tietz potential, this gives

$$\dot{\omega}_0 = -16\left[\frac{R}{Z}\right]^{1/2} , \tag{77}$$

leading to

$$\begin{aligned} &\dot{\nu}'_0 = 36\frac{R}{Z}, \quad \dot{\sigma}_0 = -18\frac{R}{Z} \,, \\ &y = \frac{\lambda_0\dot{\sigma}_0}{\dot{\lambda}_0} = -9 \,, \\ &\frac{1}{y} + \frac{1-y}{y^2}\ln(1-y) = 0.1732 \,. \end{aligned} \tag{78}$$

Consequently, the single-particle energy of the filled Tietz potential is

$$\begin{aligned} E_1(\varepsilon=0) = {} & -0.5300Z^{7/3} + \tfrac{1}{2}Z^2 \\ & + 0.0476Z^{5/3}(\langle 1.817Z^{1/3}\rangle^2 - \tfrac{1}{12}) + \cdots \,. \end{aligned} \tag{79}$$

The comparison with the filled Coulombic potential (1) [normalized in the sense of (43), so that $\lambda_0=(3Z/2)^{1/3}$], for which, according to Eq. (50),

$$\begin{aligned} E_1(\varepsilon=0) = {} & -0.7631Z^{7/3} + \tfrac{1}{2}Z^2 \\ & + 0.8736Z^{5/3}(\langle 1.145Z^{1/3} + \tfrac{1}{2}\rangle^2 - \tfrac{1}{12}) + \cdots \\ \equiv {} & -0.7631Z^{7/3} + \tfrac{1}{2}Z^2 + E_{\mathrm{osc}} \,, \end{aligned} \tag{80}$$

shows that the Tietz potential leads to a much smaller amplitude of the leading oscillation. This is mainly caused by the factor of Eq. (69) which reduces the amplitude to almost one-sixth. The origin of this factor is the deviation of ν'_ε from $\nu'_0=2$ for $\varepsilon<0$.

In order to avoid a possible misunderstanding, we stress that Eq. (80) should not be confused with Eq. (15) for $N=Z$. These two equations represent answers to two different questions. Equation (80) is the result for a Coulom-

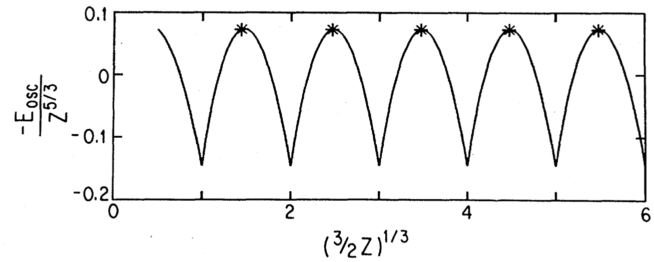

FIG. 2. Energy oscillation of Eq. (80), in units of $Z^{5/3}$, as a function of $(\frac{3}{2}Z)^{1/3}$. Stars mark the Z values of closed Bohr shells.

bic potential filled to the brim with electrons, the total number of which equals Z in the TF limit. As this limit is approached, $N(\varepsilon=0)$ oscillates around Z with an amplitude proportional to $Z^{2/3}$, as expressed by Eq. (73) of I. In contrast, Eq. (15) describes the situation in which the number of electrons is prescribed. For $N=Z$, it means electrically neutral atoms containing noninteracting electrons. [Incidentally, the additive constant ε_0 in (1) must be less than $Z^{4/3}/(18)^{1/3}$, the value used in (80), in order to guarantee the existence of at least Z bound states.] The comparison of Eqs. (15) and (80) shows in particular that the leading oscillatory terms differ in sign and phase. On the curve of $h(N=Z)$ in Fig. 1, which refers to Eq. (15), the closed-shell values of Z $[(\frac{3}{2}Z)^{1/3}=1.44$, 2.47, 3.48, 4.48, and 5.48] mark the *sharp* maxima, whereas they sit close to the tops of *broad* maxima on the analogous plot for Eq. (80), presented in Fig. 2.

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APPENDIX

Here we address the (more mathematical) problem of finding potentials which lead to exact linear degeneracy for $\varepsilon=0$.

We start with Eq. (89) of I. In order to result in a λ-independent $\partial\nu_0/\partial\lambda$, the terms within the curly brackets must be equal to

$$\frac{\lambda_0}{\lambda}=[1-(1-\lambda^2/\lambda_0^2)]^{-1/2}$$
$$=\sum_{l=0}^{\infty}\begin{bmatrix}-\frac{1}{2}\\ l\end{bmatrix}(-1)^l(1-\lambda^2/\lambda_0^2)^l\ , \tag{81}$$

which tells us the required values of the coefficients in (89) of I. Since

$$(-1)^l\begin{bmatrix}-\frac{1}{2}\\ l\end{bmatrix}=\int_{-\pi/2}^{\pi/2}d\theta\frac{1}{\pi}(\sin\theta)^{2l}\ , \tag{82}$$

this implies that all coefficients of even powers of t in (88) of I are unity. Consequently,

$$\frac{1}{1+\nu_0'y}\frac{dy}{dt}=\frac{1}{1-t^2}+\mathscr{F}\ , \tag{83}$$

where $\mathscr{F}$ is some as yet unspecified odd function of t; it is not totally arbitrary, but subject to restrictions which represent the physical boundary conditions on the underlying potential that we are looking for. In particular, $V(r)$ must obey

$$\frac{\partial}{\partial r}(-r^2V)\bigg|_{r=0}=Z \tag{84}$$

and

$$-r^mV(r)\,|_{r\to\infty}=c\equiv ZR^{m-1}\ , \tag{85}$$

where c is the constant that appeared, e.g., in (51) of I, while $m>2$ is related to ν_0' by Eq. (49) of I:

$$\nu_0'=1+\frac{1}{m-2}\ . \tag{86}$$

Note that this definition of R is consistent with its meaning in the case of the Tietz potential of Eq. (55).

It is easier to incorporate these conditions after solving (83) for y. This is done by writing $\mathscr{F}$ as the logarithmic derivative of an arbitrary function of t^2. Then (83) is immediately converted into

$$\frac{r}{r_0}=1+\nu_0'y=(1+t)^{\nu_0'}g(t^2)\ , \tag{87}$$

with $g(t^2)$ waiting to be specified. Since $r=r_0$ means $y=0$ and $t=0$, a first restriction on g is

$$g(0)=1\ . \tag{88}$$

To make use of (84), we note that, according to Eq. (80) of I,

$$-r^2V(r)=\tfrac{1}{2}\lambda_0^2(1-t^2)\ , \tag{89}$$

which implies

$$Z=\frac{d}{dr}[-r^2V(r)]\bigg|_{r=0}=-\lambda_0^2t\frac{dt}{dr}\bigg|_{r=0}$$
$$=-\lambda_0^2\frac{dy}{dr}t\frac{dt}{dy}\bigg|_{r=0}\ . \tag{90}$$

Now, since $r=0$ corresponds to $t=-1$ and since $dy/dr=1/\nu_0'r_0$, this means that

$$\frac{dy}{dt}\bigg|_{t=-1}=\frac{1}{Z}\frac{\lambda_0^2}{\nu_0'r_0}\ . \tag{91}$$

Thus,

$$\frac{d}{dt}[(1+t)^{\nu_0'}g(t^2)]\bigg|_{t=-1}=\frac{\lambda_0^2}{Zr_0}\ . \tag{92}$$

If we combine this with

$$0=\frac{r}{r_0}\bigg|_{t=-1}=(1+t)^{\nu_0'}g(t^2)\bigg|_{t=-1}\ , \tag{93}$$

we learn that

$$g(t^2) \sim \frac{\lambda_0^2}{Zr_0}\left[\frac{2}{1-t^2}\right]^{\nu_0'-1} \quad \text{as } t^2 \to 1 \; . \tag{94}$$

Similarly, the observation that $r \to \infty$ corresponds to $t \to 1$ translates (85) into

$$g(t^2) \sim \frac{R}{2r_0}\left[\frac{ZR/\lambda_0^2}{1-t^2}\right]^{\nu_0'-1} \quad \text{as } t^2 \to 1 \; . \tag{95}$$

The coexistence of (94) and (95) requires the relation

$$ZR = 2\lambda_0^2 \tag{96}$$

to hold. Thus,

$$g(t^2) \sim \frac{R}{2r_0}\left[\frac{2}{1-t^2}\right]^{\nu_0'-1} \quad \text{as } t^2 \to 1 \; . \tag{97}$$

Further, since r is an intrinsically positive quantity, Eq. (87) implies

$$g(t^2) > 0 \; . \tag{98}$$

Finally, for an atomic potential V, $-r^2V(r)$ $[=\lambda_0^2(1-t^2)/2]$ increases monotonically from zero to its global maximum at r_0 and then decreases monotonically to zero again. Therefore, r must monotonically increase with growing t. Consequently, $g(t^2)$ must be such that $dr/dt > 0$, or [Eq. (87)]

$$\frac{d}{dt}\ln[g(t^2)] > -\frac{\nu_0'}{1+t} \; . \tag{99}$$

All $g(t^2)$ that obey Eqs. (88) and (97)—(99) are acceptable and lead to an atomic potential which possesses linear degeneracy with slope ν_0' for $\varepsilon=0$. The simplest way of satisfying all these conditions is exhibited by

$$g(t^2) = \left[\frac{1}{1-t^2}\right]^{\nu_0'-1} , \tag{100}$$

which means that R and r_0 are related to each other through

$$R/r_0 = 2^{2-\nu_0'} \; . \tag{101}$$

If the potential is supposed to be normalized in the sense of Eq. (43) (that is, $Z=\frac{2}{3}\nu_0'\lambda_0^3$), then we have the Z dependences of λ_0 and R expressed by

$$\lambda_0/Z^{1/3} = \left[\frac{3}{2\nu_0'}\right]^{1/3} , \qquad R/Z^{-1/3} = \left[\frac{18}{(\nu_0'^{\,2}}\right]^{1/3} . \tag{102}$$

Now we insert first (96), and then (87), (100), and (101), into (89) and obtain

$$V(r) = -\frac{Z}{r}\frac{R}{4r}(1-t^2) = -\frac{Z}{r}\left[\frac{1-t}{2}\right]^{\nu_0'} . \tag{103}$$

This implies that $f(r/R) \equiv -(r/Z)V(r)$ obeys the algebraic equation

$$[f(r/R)]^{1/\nu_0'-1} - [f(r/R)]^{2/\nu_0'-1} = \frac{r}{R} , \tag{104}$$

which is easily checked to be consistent with both (84) and (85). Consequently, if f satisfies this equation, then the corresponding potential leads to linear degeneracy, for $\varepsilon=0$, with slope ν_0', and Eqs. (96) and (101) hold. For special values of ν_0', Eq. (104) can be solved in an elementary way. For example, $\nu_0'=1$ produces the Coulombic potential of Eq. (1) with $R=2r_0$, as it should be. Also, $\nu_0'=2$ gives the Tietz potential (55) for which $R=r_0$. Thus the class of potentials belonging to the simplest realization of $g(t^2)$, as given in Eq. (100), or equivalently by (104), contains both the Coulombic and the Tietz potentials. Further, we find

$$V(r) = -\frac{Z}{r}\left\{\frac{r}{2R} + \left[1 + \left[\frac{r}{2R}\right]^2\right]^{1/2}\right\}^{-3} \quad \text{for } \nu_0' = \tfrac{3}{2} , \tag{105}$$

and

$$V(r) = -\frac{Z}{r}\left[\frac{1}{2} + \left[\frac{1}{4} + \frac{r}{R}\right]^{1/2}\right]^{-3} \quad \text{for } \nu_0' = 3 \; . \tag{106}$$

The maximum property of $-r^2V(r)$ at $r=r_0$ can be used in (104) in the form

$$\left.\frac{d}{d(r/R)}f(r/R)\right|_{r=r_0} = -\frac{f(r_0/R)}{r_0/R} , \tag{107}$$

in order to evaluate $f(r_0/R)$. The outcome

$$f(r_0/R) = 2^{-\nu_0'} \tag{108}$$

is, of course, consistent with (101) when inserted into (104). Another consequence of (104) is

$$\left.\frac{d}{d(r/R)}f(r/R)\right|_{r=0} = -\nu_0' , \tag{109}$$

so that

$$V(r) \cong -\frac{Z}{r} + \frac{Z\nu_0'}{R} \quad \text{for } r \gtrsim 0 \; . \tag{110}$$

When the potential is normalized according to (43), i.e., when Eqs. (102) hold, this additive constant is proportional to $Z^{4/3}$, as it should be.

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[3]B.-G. Englert and J. Schwinger, Phys. Rev. A **29**, 2331 (1984).

[4]T. Tietz, Acta Phys. Hung. **9**, 73 (1958).

[5]A simple counterexample is $V(r)=-(Z/r)[1+(r/R)^a]^{-b}$ for which the slope of $\nu_0(\lambda)$ at both ends equals $-2/a$, provided that $b=2/[a(2-a)]$. However, $N_{\rm TF}(\varepsilon=0)=\int(d\mathbf{r})(3\pi^2)^{-1}\times(-2V)^{3/2}$ does not agree with the straight-line result $(4/3a)\lambda_0^3$, unless $a=1$, $b=2$. Consequently, for $a\neq 1$, $\nu_0(\lambda)$ cannot be a straight line, although it has identical slopes at both ends. The case $a=1$ is, of course, the Tietz potential.

[6]For $y<-1$, as is the actual situation [cf. Eq. (78)], the right-hand side gives meaning to the left-hand one.