Notes on Bohr-Sommerfeld Quantization and the Classical Limit

February 22, 1996

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Physics 8.04 February 22, 1996

The basic idea behind semi-classical, or Bohr-Sommerfeld quantization, is that we may determine the allowed quantized states of a system by performing a classical analysis of the motion and then insisting, that in order to avoid destructive interference, there are exactly an integral number of de Broglie wavelengths around the orbit or one period of the classical motion. Mathematically, if q is the coordinate of the particle (usually written "r" in three dimensions or "x" in one) and p as its momentum, then

$$n = \oint \frac{dq}{\lambda} = \oint \frac{dq}{h/p} = \frac{1}{h}\oint p dq$$

or,

$$nh = \oint p dq, \quad n = 1, 2, \ldots \tag{1}$$

Note that this is an approximate and not an exact condition because by looking at classical trajectories we are ignoring many details of the wave function.

1 Atom

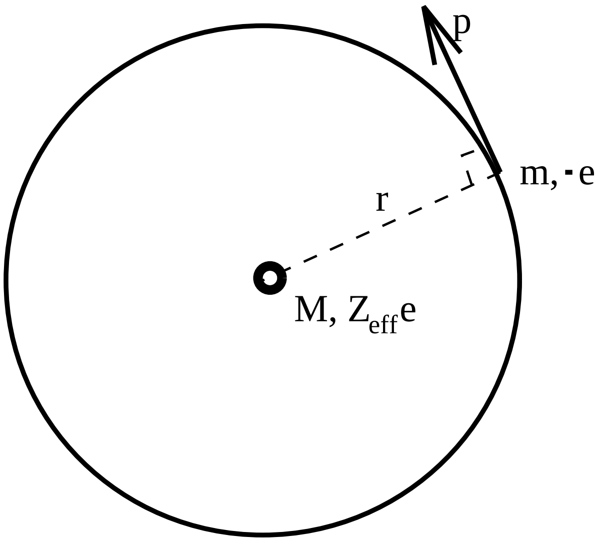
In an atom we have a nucleus with mass M and charge $Z_{\text{eff}}e$ with an orbiting electron of mass m and charge $-e$.

1.1 Classical Analysis

To perform the classical analysis we will restrict ourselves here to considering circular orbits of radius r and will call the momentum of the electron about its orbit p. We leave the central charge an "effective" charge to allow for "shielding" of the nucleus in the case of many-electron atoms.

The first stage in the classical analysis is to replace the concerted motion of the nucleus and electron with the motion of their relative coordinate (the vector from the nucleus to the electron), which then moves as though it had an effective mass

$$\mu = \frac{mM}{m+M}.$$



Note that the effective mass is very close to the mass of the electron (because $m \ll M$), a basic reflection of the fact that the nucleus, being so massive, hardly moves and the motion is almost entirely due to the electron. $\vec{r}$ now becomes the distance between the electron and the nucleus and $p \equiv \mu\dot{\vec{r}}$ is the momentum of the relative coordinate.

Next we balance the centripetal acceleration and the central force (note the use of the effective mass μ throughout),

$$\frac{p^2}{\mu r} = \frac{Z_{\rm eff}e^2}{r^2}.$$

(Note that this is usually written $\frac{\mu v^2}{r} = F$) which gives our first relation

$$\frac{p^2}{\mu} = \frac{Z_{\rm eff}e^2}{r} \tag{2}$$

which may be used to eliminate p in any expression in terms of r,

$$p = \sqrt{Z_{\rm eff}e^2\mu/r} \tag{3}$$

We may use this to find immediately the period of the motion in terms of the orbital distance

$$T = \frac{2\pi r}{v} = \frac{2\pi r}{p/\mu} = 2\pi\mu\frac{r}{p} = 2\pi\sqrt{\frac{\mu}{Z_{\rm eff}e^2}}\, r^{\frac{3}{2}} \tag{4}$$

which we keep for future reference.

The last stage of the classical analysis is to consider the energy of the system. We have both kinetic and potential energies

$$E = T + V = \frac{p^2}{2\mu} - \frac{Z_{\rm eff}e^2}{r} \tag{5}$$

Note that from (2) we have a special case of the the Virial theorem for orbital motion $2T = -V$ and so we may eliminate p from (5) and find the energy in terms of the orbital distance alone,

$$E = T + V = \left(-\frac{V}{2}\right) + V = +\frac{1}{2}V = -\frac{1}{2}\frac{Z_{\rm eff}e^2}{r}. \tag{6}$$

1.2 Quantization

With the classical analysis complete, we now perform the quantization procedure. In this case we have found all quantities in terms of the classical orbital distance r and so all that remains is to find the allowed quantized values of r. The condition (1) gives, because the momentum is constant around an orbit,

$$nh = \oint pdq = p \oint dq = 2\pi rp$$

But because from (3) $p = \sqrt{Z_{\text{eff}} e^2 \mu / r}$, we may eliminate p and solve for r,

$$\begin{aligned} nh &= 2\pi rp = 2\pi r \sqrt{Z_{\text{eff}} e^2 \mu / r} \\ n\hbar &= \sqrt{Z_{\text{eff}} e^2 \mu r} \\ r_n &= \frac{n^2 \hbar^2}{Z_{\text{eff}} \mu e^2} \end{aligned} \tag{7}$$

where we have given r a subscript n indicating its value in the n^{th} quantum state. Now that we have the allowed radii, we also have the allowed energies from (6),

$$E_n = -\frac{1}{2} \frac{Z_{\text{eff}} e^2}{r_n} = -\frac{1}{2} \frac{Z_{\text{eff}}^2 \mu e^4}{\hbar^2} \frac{1}{n^2}, n = 1, 2, \ldots \tag{8}$$

(8) is often also written as

$$\begin{aligned} E_n &= -Z_{\text{eff}}^2 \left(\frac{me^4}{\hbar^2} \right) \frac{\mu}{m} \frac{1}{n^2} \\ E_n &= -Z_{\text{eff}}^2 \cdot \mathcal{R} \left(\frac{M}{M+m} \right)^{-1} \frac{1}{n^2} \simeq -Z_{\text{eff}}^2 R \frac{1}{n^2} \quad n = 1, 2, \ldots \end{aligned} \tag{9}$$

where the special combination of constants

$$R \equiv \frac{1}{2} \frac{me^4}{\hbar^2} \simeq 13.6 \ eV$$

is given a special name, the Rydberg.

The *spectrum* of states may be plotted on an energy-level diagram as in Figure 1.2.

Note that the spacings decrease as infinitely many states $n = 1, , \ldots \infty$, accumulate below $E = 0$.

1.3 Correspondence Principle

If we had not an atom, but an orbiting charged macroscopic system, we know from classical electromagnetism that the system would radiate electromagnetic energy at a frequency given by one divided by the period of the motion

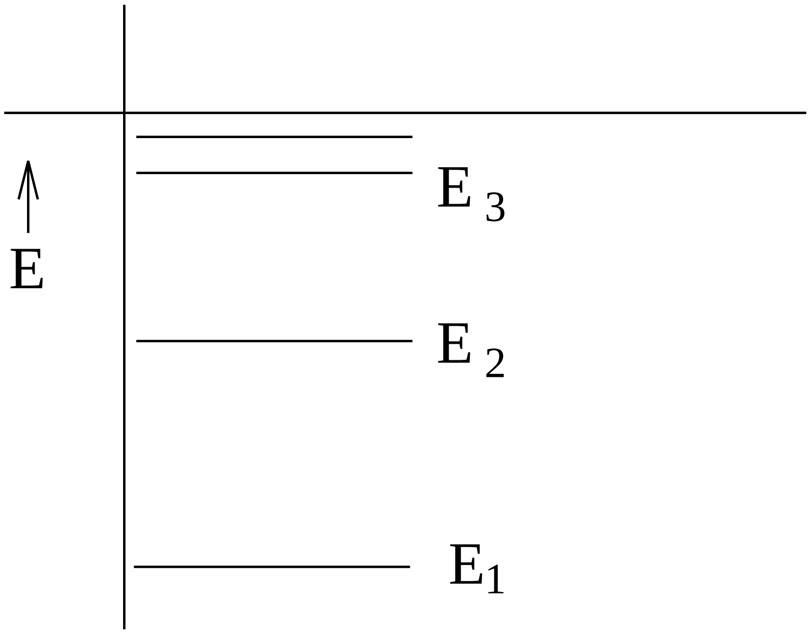
$$\nu_{cl} = \frac{1}{T_{cl}} = \frac{1}{2\pi} \sqrt{\frac{Z_{\text{eff}} e^2}{\mu}} r^{-\frac{3}{2}} \tag{10}$$

where we have used (4) to find the period in terms of r.

On the other hand, in our quantum picture, the system emits photons of energy $h\nu = E_n - E_{n-1} \equiv \Delta E$ when making transitions $E_n \to E_{n-1}$ between neighboring energy levels at spacing ΔE.

In the classical limit ($\hbar \to 0$), we expect these two pictures to correspond so that the frequencies expected in both the classical and equation pictures agree. This gives us a very general result, relating the spacing in the quantum energy spectrum ΔE, to the classical period of the motion T_{cl},

$$\begin{aligned} \Delta E = h\nu_{quant} \to h\nu_{cl} &= \frac{h}{T_{cl}} \\ \Delta E &\to \frac{h}{T_{cl}} \end{aligned} \tag{11}$$



This result is so general because we can imagine placing a small test charge on any system. As the energy increases the classical period gets larger and the quantum spacing ΔE gets less. More precisely,

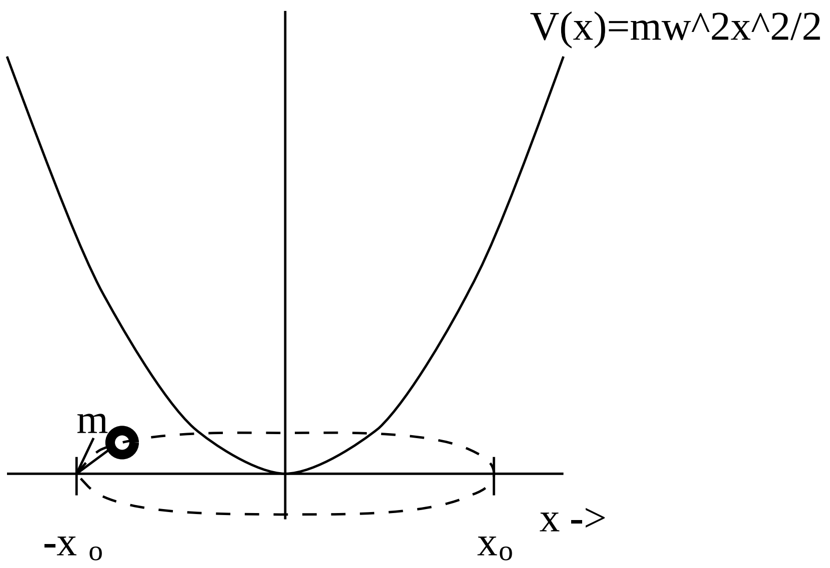
$$n = \frac{\sqrt{Z_{\rm eff}\mu e^2 r}}{\hbar}$$

So as $\hbar \to 0, n \to \infty$ and thus

$$\begin{aligned}
\Delta E = E_n - E_{n-1} &= -Z_{\rm eff}^2\left(\frac{1}{2}\frac{\mu e^4}{\hbar^2}\right)\left(\frac{1}{n^2} - \frac{1}{(n-1)^2}\right) \\
&= -Z_{\rm eff}^2\left(\frac{1}{2}\frac{\mu e^4}{\hbar^2}\right)\frac{(n-1)^2 - n^2}{n^2(n-1)^2} \\
&= Z_{\rm eff}^2\left(\frac{\mu e^4}{\hbar^2}\right)\frac{1}{2}\frac{2n-1}{n^2(n-1)^2} \\
&\to Z_{\rm eff}^2\left(\frac{\mu e^4}{\hbar^2}\right)\frac{1}{n^3} \\
&= Z_{\rm eff}^2\left(\frac{\mu e^4}{\hbar^2}\right)\left(\frac{\hbar}{\sqrt{Z_{\rm eff}\mu e^2 r}}\right)^3 \\
&= \hbar\sqrt{\frac{Z_{\rm eff}e^2}{\mu}}r^{-\frac{3}{2}}
\end{aligned}$$

And, in accordance with (11) and using (10) we find this is the same as

$$\frac{h}{T_{cl}} = h\,\nu_{cl} = h\,\frac{1}{2\pi}\sqrt{\frac{Z_{\rm eff}e^2}{\mu}}r^{-\frac{3}{2}}$$



2 Simple Harmonic Oscillator

Here, a mass m moves under the influence of a classical force $-m\omega^2 x$. The energy of the system is given by

$$E = T + V = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \tag{12}$$

See Figure 2.

2.1 Classical Analysis

The standard classical analysis of this system gives simple harmonic motion:

$$x(t) = x_0 \cos \omega t \tag{13}$$

where ω is the frequency of the oscillator as in (1) and x_0 is the amplitude of the oscillations. The period of the motion in (12) is just constant

$$T_{cl} = \frac{2\pi}{\omega} \tag{14}$$

and so from the arguments in (1.3), we expect the spacings in the quantum spectrum in the classical limit to also be constant

$$\Delta E \to \frac{h}{T_{cl}} = h/\left(\frac{2\pi}{\omega}\right) = \hbar\omega. \tag{15}$$

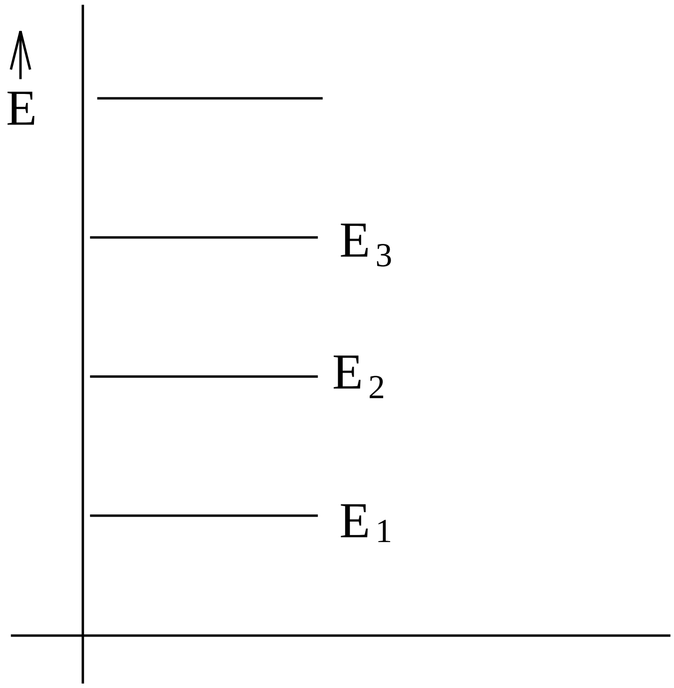
Finally, the energy of the motion is

$$E = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}m\omega^2 x^2 = \frac{1}{2}mx_0^2 \sin^2 \omega t + \frac{1}{2}mx_0^2\omega^2 \cos^2 \omega t = \frac{1}{2}mx_0^2\omega^2 \tag{16}$$

2.2 Semi Classical Quantization

We now impose the Bohr-Sommerfeld quantization condition

$$nh = \oint pdq$$



Here, the motion is along x and so $dq = dx = \frac{dx}{dt}\ dt = \dot{x}(t)dt$. Also, the momentum is just $p = mv = m\dot{x}(t)$, and finally the $\oint$ symbol means we are to integrate over one complete period $T_{cl} = \frac{2\pi}{\omega}$. Putting this together, we have

$$\begin{aligned} nh = \oint pdq &= \int_0^{\frac{2\pi}{\omega}} (m\dot{x}(t))\,(\dot{x}(t)dt) \\ &= \int_0^{\frac{2\pi}{\omega}} m\,(\dot{x}(t))^2\,dt \\ &= \int_0^{\frac{2\pi}{\omega}} m\ x_0^2\omega^2 \sin^2\omega t \\ &= m\ x_0^2\omega^2 \int_0^{\frac{2\pi}{\omega}} \sin^2\omega t\ dt = m\ x_0^2\omega^2\ \frac{2\pi}{\omega}\ \frac{1}{2} \end{aligned}$$

where we have used the fact that the average of $\sin^2\omega t$ over one full period is $\frac{1}{2}$. We now have our condition on E:

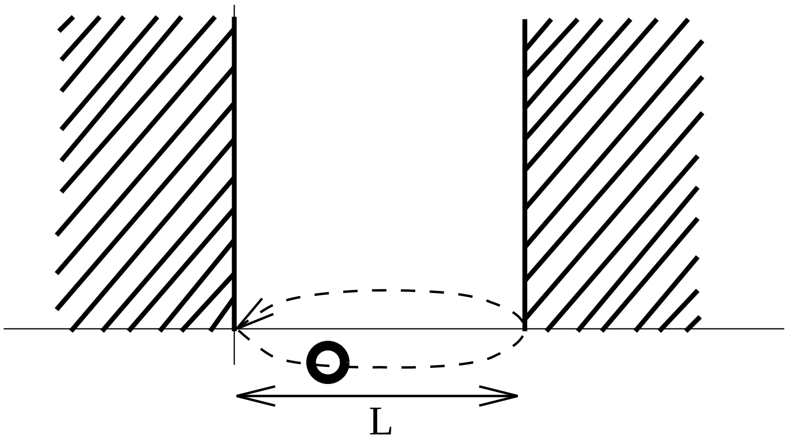
$$\begin{aligned} \frac{nh\omega}{2\pi} &= \frac{1}{2}m\omega^2 x_0^2 \\ n\hbar\omega &= E_n \end{aligned} \tag{17}$$

which is in perfect accord with our expectations in (15)! The spectrum we predict then appears as in Figure 2.2.

As we learned from the uncertainty principle the lowest energy is actually $\frac{1}{2}h\nu = \frac{1}{2}\hbar\omega$. It will turn out that the actual spectrum of the harmonic oscillator is just our prediction (17) with a simple shift to bring our result in accord with the uncertainty principle

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \tag{18}$$

3 Particle in a Box



Here a particle of mass m moves freely with no potential but is constrained to the region $0 \leq x < L$. Its energy is given by

$$E = \frac{p^2}{2m}$$

See Figure 3.

3.1 Classical Analysis

Classically the motion consists of the ball moving along the material $0 \to L$ with momentum $p = \sqrt{2mE}$ and then moving back along $L \to 0$ with momentum $p = -\sqrt{2mE}$. The period of the motion is

$$T_{cl} = \frac{2L}{v} = \frac{2mL}{p} = L\frac{2m}{\sqrt{2mE}} = L\sqrt{\frac{2m}{E}} \tag{19}$$

3.2 Semi Classical Quantization

Now,

$$\begin{aligned} nh &= \oint pdq \\ &= \int_0^L \sqrt{2mE}dx + \int_L^0 -\sqrt{2mE}dx \\ &= L\sqrt{2mE} + (-L)\left(-\sqrt{2mE}\right) \\ &= 2L\sqrt{2mE} \end{aligned}$$

and so,

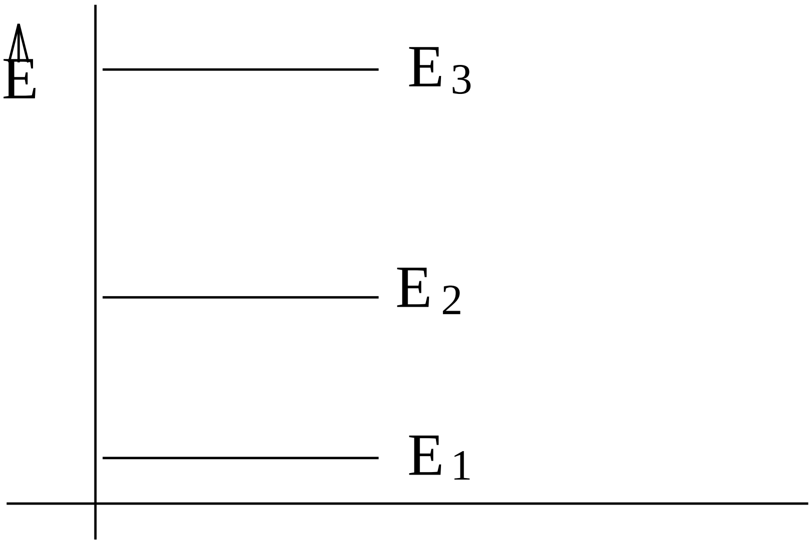
$$E_n = \frac{1}{2m}\left(\frac{nh}{2L}\right)^2 = \frac{1}{2m}\left(\frac{n\pi\hbar}{L}\right)^2 = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 n^2, \quad n = 1, 2 \ldots \tag{20}$$

We shall see later that this result is exact! The spectrum appears as in Figure 3.2.

3.3 Correspondence Principle

From (20) we have

$$n = \sqrt{\frac{2mE}{\hbar^2}\left(\frac{L}{\pi}\right)^2}$$



and so as $\hbar \to 0, n \to \infty$. In this limit,

$$\begin{aligned} \Delta E_{\text{quant}} = E_n - E_{n-1} &= \frac{\hbar}{2m}\left(\frac{\pi}{L}\right)^2 \left(n^2 - (n-1)^2\right) \\ &= \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 (2n-1) \\ &\simeq \frac{\hbar^2}{m}\left(\frac{\pi}{L}\right)^2 n \\ &= \frac{\hbar^2}{m}\left(\frac{\pi}{L}\right)^2 \sqrt{\frac{2mE}{\hbar^2}\left(\frac{L}{\pi}\right)^2} \\ &= \pi\hbar\frac{1}{L}\sqrt{\frac{2E}{m}} \end{aligned}$$

And, using (19)

$$\frac{h}{T_{cl}} = 2\pi\hbar\left(L\sqrt{\frac{2m}{E}}\right) = \pi\hbar\frac{1}{L}\sqrt{\frac{2E}{m}}$$

is in perfect accord with (11)!

Qualitatively, we see that as we increase E, the particle moves faster so that T_{cl} decreases. This decrease in T_{cl} must then correspond to the increase in the spacing ΔE as E increases, as we see in Figure 3.2.