Schrödinger equation - central force problem

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Bohr model
Schrödinger equation
Solution of the second order differential equation
Fine structure constant

Niels Henrik David Bohr (7 October 1885 – 18 November 1962) was a Danish physicist who made fundamental contributions to understanding atomic structure and quantum mechanics, for which he received the Nobel Prize in Physics in 1922. Bohr mentored and collaborated with many of the top physicists of the century at his institute in Copenhagen. He was part of a team of physicists working on the Manhattan Project. Bohr married Margrethe Nørlund in 1912, and one of their sons, Aage Bohr, grew up to be an important physicist who in 1975 also received the Nobel prize. Bohr has been described as one of the most influential scientists of the 20th century.

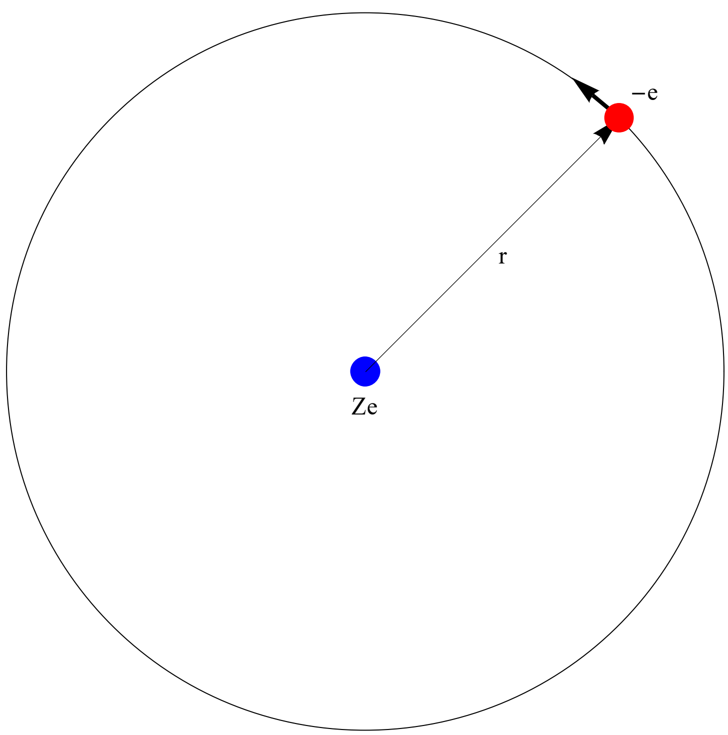
http://en.wikipedia.org/wiki/Niels_Bohr

Erwin Rudolf Josef Alexander Schrödinger (12 August 1887– 4 January 1961) was an Austrian theoretical physicist who was one of the fathers of quantum mechanics, and is famed for a number of important contributions to physics, especially the Schrödinger equation, for which he received the Nobel Prize in Physics in 1933. In 1935, after extensive correspondence with personal friend Albert Einstein, he proposed the Schrödinger's cat thought experiment.

http://en.wikipedia.org/wiki/Erwin_Schr%C3%B6dinger

1 Bohr model for hydrogen-like system

We now consider the Bohr model shown in this figure. The system consists of a charge (*Ze*) at the center and an electron (-*e*) rotating around the center. These two particles are coupled with an attractive Coulomb interaction.



The total energy for the electron with the reduced mass μ and charge ($-e$) orbiting around a nucleus with the charge (Ze) is

$$E = \frac{1}{2}\mu v^2 - \frac{Ze^2}{r} = -\frac{Ze^2}{2r}.$$

The force toward the origin:

$$\mu\frac{v^2}{r} = \frac{Ze^2}{r^2}, \quad \text{or} \qquad \mu r v^2 = Ze^2,$$

Bohr-Sommerfeld condition:

$$\mu v r = n\hbar,$$

where n is a positive integer. Then, we have the velocity v_n and radius r_n as

$$v_n = \frac{Ze^2}{n\hbar} \qquad \text{and} \qquad r_n = \frac{n^2\hbar^2}{\mu Ze^2} = \frac{n^2 a}{Z} = \frac{n}{\kappa},$$

and the energy level

$$E_n = -\frac{Ze^2}{2r_n} = -\frac{Z^2\mu e^4}{2\hbar^2 n^2} = -\frac{Z^2e^2}{2n^2 a} = -\frac{Z^2\Re}{n^2} = -\varepsilon_1,$$

or

$$\frac{Z^2\mu e^4}{2\hbar^2} = -Z^2\left(\frac{\mu}{m}\right)\frac{\alpha^2 mc^2}{2},$$

$$a = \frac{\hbar^2}{\mu e^2} = \frac{m}{\mu}\left(\frac{\hbar^2}{me^2}\right) = \frac{m}{\mu}a_B,$$

$$\Re = \frac{\mu e^4}{2\hbar^2} = \frac{e^2}{2a} = \frac{\mu}{m}\frac{me^4}{2\hbar^2} = \frac{\mu}{m}\Re_0,$$

where α is the structure fine constant (the definition is given below) and m is the mass of electron.

((Note)) **Physical constant for the hydrogen atom (in CGS units)**

(a) Bohr radius

$$a_B = \frac{\hbar^2}{me^2} = 0.52917720859(36)\ \text{Å}.$$ (Bohr radius)

(b) Rydberg constant:

$$\Re_0 = \frac{me^4}{2\hbar^2} = \frac{e^2}{2a_B} = 13.6056923(12)\ \text{eV}.$$

(c) The electron rest mass

$$mc^2 = 0.510997\ \text{MeV}.$$

(d) The fine structure constant

$$\alpha = \frac{e^2}{\hbar c}\ \text{(CGS units)} \qquad \alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c}\ \text{(SI units)}$$

α is equal to

$$\alpha = \frac{1}{137.036}.$$

((**Mathematica**)) Physics constant in cgs units

```
Clear["Global`*"];

rule1 = {c → 2.99792 × 10^10, ℏ → 1.054571628 10^-27,
   me → 9.10938215 10^-28, qe → 4.8032068 × 10^-10,
   eV → 1.602176487 × 10^-12, meV → 1.602176487 × 10^-15,
   keV → 1.602176487 × 10^-9, MeV → 1.602176487 × 10^-6,
   α → 7.2973525376 × 10^-3};
```

Borh radius a0 = 0.529168 Å

$$a0 = \frac{\hbar^2}{me\ qe^2} \ /.\ rule1$$

5.29177×10^{-9}

a0 in the units of 1 Å = 10^{-8} cm

```
a0 / Å /. rule1
```

$$\frac{5.29177 \times 10^{-9}}{\text{Å}}$$

Rydberg constant, R = 13.6061 eV

1 eV = $1.60217642 \times 10^{-12}$ erg

$$\left(\frac{me\ qe^4}{2\ \hbar^2\ eV} \ /.\ rule1\right)$$

13.6057

Fine structure $\alpha = \frac{e^2}{\hbar c}$ (dimensionless)

$$\alpha = \frac{qe^2}{\hbar\ c} \ /.\ rule1$$

0.00729737

```
1 / α // N
```

137.036

Thus the constant α is close to 1/137.

$$\frac{me\ c^2}{MeV} \ /.\ rule1$$

0.510997

((**Mathematica**)) Physics constant in SI units

```
Clear["Global`*"];

rule1 = {me → 9.1093821545 × 10^-31, eV → 1.602176487 × 10^-19,
   qe → 1.602176487 × 10^-19, c → 2.99792458 × 10^8,
   μ0 → 12.566370614 × 10^-7, ϵ0 → 8.854187817 × 10^-12,
   ℏ → 1.05457162853 × 10^-34};

aB = (4 π ϵ0 ℏ^2)/(me qe^2) /. rule1

5.29177 × 10^-11

α = qe^2/(4 π ϵ0 ℏ c) /. rule1

0.00729735

1 / α // N

137.036
```

((**Note-1**)) **Fine structure constant** α ((**Basdevant**))

We notice that $v = e^2/\hbar$ has the dimension of a velocity. Unless the differential equation had pathologies (which is not the case), it must represent the typical velocity v of the electron in the lowest energy levels of the hydrogen atom. This velocity must be compared with the velocity of light *c*, which is the absolute velocity standard in physics. The ratio between these two velocities is a dimensionless constant α, which is a combination of the fundamental constants *e*, $\hbar$, and *c*

$$\alpha = \frac{v}{c} = \frac{e^2}{\hbar c} \approx \frac{1}{137}.$$

The smallness of this constant α guarantees that the nonrelativistic approximation is acceptable up to effects of the order of

$$\frac{v^2}{c^2} \approx 137^{-2} = 5.33 \times 10^{-5}$$

The constant α is called, for (unfortunate) historical reasons, the fine structure constant. A more appropriate terminology would have been: fundamental constant of electromagnetic interactions.

Any charge Q is an integer multiple of the elementary charge $Q = Ze$. Therefore the fundamental form of Coulomb's law between two charges $Q = Ze$ and $Q' = Z'e$ is

$$V(r) = \frac{ZZ'e^2}{r} = \alpha ZZ'(\frac{\hbar c}{r}),$$

with Z and Z' integers, which only involves mechanical quantities. The experimental determination of the fundamental constant α is a key point in physics: $1/\alpha$ = 137.0359779 (32). The fact that this is a dimensionless number stirred minds at the beginning. One cannot change the value of α by changing units. For a long time, after this discovery (i.e., the discovery of the universality of Planck's constant), people have tried to obtain it starting from transcendental numbers e, π, the Euler constant γ, and so on. For instance

$$\exp(-\frac{\pi^2}{2}) = 1/139.046 \text{ or better } \frac{1}{2}\pi^{-e^2/2} = 1/137.33.$$

The great astronomer Eddington, at the end of his life, had made an arithmetic theory of α. This constant is encountered in the hydrogen atom, made of a proton and electron. We live in a four-dimensional space–time, and the proton and electron both have 4 degrees of freedom. Now 4×4 = 16, and if we consider the symmetric real 16×16 matrices, they have 136 different elements, to which we must add spin, hence the number 137. Hans Bethe had replied. The theory of Mr. Eddington is very interesting because it explains features of ideal gases. Indeed, the simplest ideal gas is molecular hydrogen. If each of the two atoms in the molecule H_2 has 137 degrees of freedom, then 2 × 137 = 274, to which we must subtract 1 since the atoms are bound, which gives 273, namely the temperature of the absolute zero."

From J.-L. Basdevant, Lectures on Quantum Mechanics (Springer, 2007). p.187.

((**Note-2**)) **My consideration**

In the Bohr model, the velocity of electron in the state (n) is given by

$$v_n = \frac{Ze^2}{n\hbar}$$

The velocity in the ground state is the largest;

$$v_{n=1} = \frac{Ze^2}{\hbar}$$

We consider the ration of the velocity of electron in the ground state to the velocity of light,

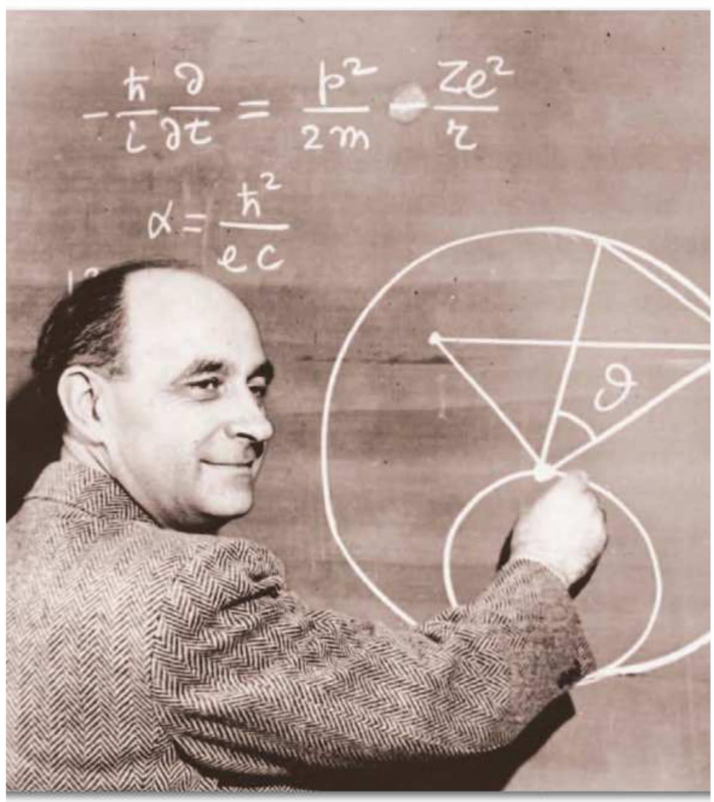
$$\frac{v_{n=1}}{c} = \frac{Ze^2}{c\hbar} = Z\alpha \approx \frac{Z}{137}$$

which is smaller than 1. So, we get the atomic number Z which is always smaller than 137.

((Note)) **Fine structure constant**

Even Enrico Fermi (one of the greatest physicists) made a mistake of writing the fine structure const as $\alpha = \hbar^2 / ec$ (wrong one), instead of $\alpha = e^2 / (\hbar c)$ (correct one)

THE BRITANNICA GUIDE TO RELATIVITY AND QUANTUM MECHANICS



Italian-born physicist Enrico Fermi explaining a problem in physics, c. 1950.
National Archives, Washington, D.C.

REFERENCE

E. Gregersen (editor), The Britanica Guide to Relativity and Quantum Mechanics (Encyclopedia Britannica, 2011).

2 The central-field problem

We consider the infinitesimal rotation

$$|\psi'\rangle = \hat{R}(\varepsilon)|\psi\rangle .$$

If $\hat{H}$ is invariant under the rotation,

$$\langle \psi' | \hat{H} | \psi' \rangle = \langle \psi | \hat{H} | \psi \rangle ,$$

or

$$\langle \psi | \hat{R}^{+}(\varepsilon) \hat{H} \hat{R}(\varepsilon) | \psi \rangle = \langle \psi | \hat{H} | \psi \rangle ,$$

or

$$\hat{R}^{+}(\varepsilon) \hat{H} \hat{R}(\varepsilon) = \hat{H} ,$$

or

$$\hat{H} \hat{R}(\varepsilon) = \hat{R}(\varepsilon) \hat{H} ,$$

or

$$[\hat{R}(\varepsilon), \hat{H}] = 0 .$$

We now consider the time-dependent Schrödinger equation given by

$$|\psi(\Delta t)\rangle = (\hat{1} - \frac{i\Delta t \hat{H}}{\hbar}) |\psi(0)\rangle .$$

Then we have

$$|\psi'(\Delta t)\rangle = (1 - \frac{i\Delta t \hat{H}}{\hbar}) |\psi'(0)\rangle = (1 - \frac{i\Delta t \hat{H}}{\hbar}) \hat{R}(\varepsilon) |\psi(0)\rangle ,$$

and

$$|\psi'(\Delta t)\rangle = \hat{R}(\varepsilon) |\psi(\Delta t)\rangle = \hat{R}(\varepsilon)(1 - \frac{i\Delta t \hat{H}}{\hbar}) |\psi(0)\rangle .$$

This means that

$$[\hat{H}, \hat{R}(\varepsilon)] = 0 .$$

Since $\hat{R}(\varepsilon) = 1 - \frac{i}{\hbar}(\hat{\boldsymbol{J}}.\boldsymbol{n})\varepsilon$, we obtain the following commutation relations.

$$[\hat{H}, \hat{\boldsymbol{J}}.\boldsymbol{n}] = 0 .$$

Since $\boldsymbol{n}$ is any unit vector,

$$[\hat{H}, \hat{J}_x] = \hat{0}, \; [\hat{H}, \hat{J}_y] = \hat{0}, \; [\hat{H}, \hat{J}_z] = \hat{0} .$$

We also get the commutation relations,

$$[\hat{H}, \hat{J}_x{}^2] = \hat{H}\hat{J}_x\hat{J}_x - \hat{J}_x\hat{J}_x\hat{H} = \hat{J}_x[\hat{H}, \hat{J}_x] = \hat{0} .$$

Similarly,

$$[\hat{H}, \hat{J}_y{}^2] = [\hat{H}, \hat{J}_z{}^2] = \hat{0} .$$

In the present case, $\hat{\boldsymbol{J}} = \hat{\boldsymbol{L}}$ (orbital angular momentum).

Since $[\hat{H}, \hat{\boldsymbol{L}}^2] = [\hat{H}, \hat{L}_z{}^2] = [\hat{H}, \hat{L}_z] = [\hat{\boldsymbol{L}}^2, \hat{L}_z] = \hat{0}$, we can find a basis such that $|k,l,m\rangle$ is a simultaneous eigenket of $\hat{H}$, $\hat{\boldsymbol{L}}^2$, and $\hat{L}_z$;

$$\hat{H}|k,l,m\rangle = E_k|k,l,m\rangle .$$

$$\hat{\boldsymbol{L}}^2|k,l,m\rangle = \hbar^2 l(l+1)|k,l,m\rangle .$$

$$\hat{L}_z|k,l,m\rangle = \hbar m|k,l,m\rangle .$$

$$[H_0, L_z]$$

$$[H_0, L^2]$$

$$[L^2, L_z]$$

$$H_0|nlm\rangle = E_n|nlm\rangle$$

$$L_z|nlm\rangle = m\hbar|nlm\rangle$$

$$L^2|nlm\rangle = \hbar^2 l(l+1)|nlm\rangle$$

Fig. Simultaneous eigenket of $\hat{H}_0, \hat{L}_z, \hat{\boldsymbol{L}}^2$. Eigenstate is described by $|nlm\rangle$.

3 Commutation relations (more direct method)

In a central-field potential,

$$\hat{H} = \frac{1}{2\mu}\hat{\boldsymbol{P}}^2 + V(|\hat{\boldsymbol{r}}|).$$

Angular momentum $\hat{\boldsymbol{L}}$:

$$[\hat{L}_z, \hat{p}_x] = i\hbar\hat{p}_y, \qquad [\hat{L}_z, \hat{p}_y] = -i\hbar\hat{p}_x \qquad [\hat{L}_z, \hat{p}_z] = \hat{0}$$

$$\begin{aligned}[\hat{L}_z, \hat{p}_x{}^2] &= \hat{L}_z\hat{p}_x{}^2 - \hat{p}_x{}^2\hat{L}_z \\ &= [\hat{L}_z, \hat{p}_x]\hat{p}_x + \hat{p}_x[\hat{L}_z, \hat{p}_x] \\ &= i\hbar(\hat{p}_y\hat{p}_x + \hat{p}_x\hat{p}_y)\end{aligned}$$

$$\begin{aligned}[\hat{L}_z, \hat{p}_y{}^2] &= \hat{L}_z\hat{p}_y{}^2 - \hat{p}_y{}^2\hat{L}_z \\ &= [\hat{L}_z, \hat{p}_y]\hat{p}_y + \hat{p}_y[\hat{L}_z, \hat{p}_y] \\ &= -i\hbar(\hat{p}_x\hat{p}_y + \hat{p}_y\hat{p}_x)\end{aligned}$$

Therefore,

$$[\hat{L}_z, \hat{\boldsymbol{p}}^2] = \hat{0} \qquad [\hat{L}_x, \hat{\boldsymbol{p}}^2] = \hat{0} \qquad [\hat{L}_y, \hat{\boldsymbol{p}}^2] = \hat{0}$$

Similarly,

$$[\hat{L}_z{}^2, \hat{\boldsymbol{p}}^2] = \hat{0} \qquad [\hat{L}_x{}^2, \hat{\boldsymbol{P}}^2] = \hat{0} \qquad [\hat{L}_y{}^2, \hat{\boldsymbol{P}}^2] = \hat{0}$$

Thus we have

$$[\hat{\boldsymbol{L}}^2, \hat{\boldsymbol{p}}^2] = \hat{0}.$$

On the other hand, $V(|\hat{\boldsymbol{r}}|)$ depends only on $|\hat{\boldsymbol{r}}|$ (central potential).

$$[\hat{L}_z, \hat{x}] = i\hbar\hat{y}, \qquad [\hat{L}_z, \hat{y}] = -i\hbar\hat{x} \qquad [\hat{L}_z, \hat{z}] = \hat{0}.$$

Then

$$[\hat{L}_z, \hat{x}^2 + \hat{y}^2 + \hat{z}^2] = \hat{0},$$

or

$$[\hat{L}_z, \hat{\boldsymbol{r}}^2] = \hat{0}.$$

Thus $\hat{L}_z$ commutes with a potential energy that is s function of the magnitude of the radius vector. Therefore we have a relation

$$[\hat{H}, \hat{\boldsymbol{L}}^2] = [\hat{H}, \hat{L}_z^{\ 2}] = [\hat{H}, \hat{L}_z] = [\hat{\boldsymbol{L}}^2, \hat{L}_z] = \hat{0},$$

for the central potential.

((**Mathematica**))

```
Clear["Global`"];

<< VectorAnalysis`;

SetCoordinates[Cartesian[x, y, z]];

ux = {1, 0, 0}; uy = { 0, 1, 0}; uz = {0, 0, 1}; r = {x, y, z};
rr = x^2 + y^2 + z^2;

Lx := (ux.(-ⅈ ℏ Cross[r, Grad[#]]) &) // Simplify;
Ly := (uy.(-ⅈ ℏ Cross[r, Grad[#]]) &) // Simplify;
Lz := (uz.(-ⅈ ℏ Cross[r, Grad[#]]) &) // Simplify;

px := (ux.(-ⅈ ℏ Grad[#])) &; py := (uy.(-ⅈ ℏ Grad[#])) &;
pz := (uz.(-ⅈ ℏ Grad[#])) &;

Lz[px[ψ[x, y, z]]] - px[Lz[ψ[x, y, z]]] - ⅈ ℏ py[ψ[x, y, z]] // Simplify

0

Lz[py[ψ[x, y, z]]] - py[Lz[ψ[x, y, z]]] + ⅈ ℏ px[ψ[x, y, z]] // Simplify

0

Lz[pz[ψ[x, y, z]]] - pz[Lz[ψ[x, y, z]]] // Simplify

0
```

```
Lz[px[px[ψ[x, y, z]]]] + Lz[py[py[ψ[x, y, z]]]] + Lz[pz[pz[ψ[x, y, z]]]] -
   px[px[Lz[ψ[x, y, z]]]] - py[py[Lz[ψ[x, y, z]]]] -
   pz[pz[Lz[ψ[x, y, z]]]] // Simplify // Simplify
```

0

```
Lx[px[px[ψ[x, y, z]]]] + Lx[py[py[ψ[x, y, z]]]] + Lx[pz[pz[ψ[x, y, z]]]] -
   px[px[Lx[ψ[x, y, z]]]] - py[py[Lx[ψ[x, y, z]]]] -
   pz[pz[Lx[ψ[x, y, z]]]] // Simplify // Simplify
```

0

```
Ly[px[px[ψ[x, y, z]]]] + Ly[py[py[ψ[x, y, z]]]] + Ly[pz[pz[ψ[x, y, z]]]] -
   px[px[Ly[ψ[x, y, z]]]] - py[py[Ly[ψ[x, y, z]]]] -
   pz[pz[Ly[ψ[x, y, z]]]] // Simplify // Simplify
```

0

```
Lz[Lz[px[px[ψ[x, y, z]]]]] + Lz[Lz[py[py[ψ[x, y, z]]]]] +
   Lz[Lz[pz[pz[ψ[x, y, z]]]]] - px[px[Lz[Lz[ψ[x, y, z]]]]] -
   py[py[Lz[Lz[ψ[x, y, z]]]]] - pz[pz[Lz[Lz[ψ[x, y, z]]]]] // Simplify //
 Simplify
```

0

```
Lz[x ψ[x, y, z]] - x Lz[ ψ[x, y, z]] // Simplify
```

ⅈ y ℏ ψ[x, y, z]

```
Lz[y ψ[x, y, z]] - y Lz[ ψ[x, y, z]] // Simplify
```

-ⅈ x ℏ ψ[x, y, z]

```
Lz[z ψ[x, y, z]] - z Lz[ ψ[x, y, z]] // Simplify
```

0

```
Lz[rr ψ[x, y, z]] - rr Lz[ ψ[x, y, z]] // Simplify
```

0

4 Schrödinger equation in a central potential

$$\langle \boldsymbol{r}|\frac{\hat{\boldsymbol{p}}^2}{2\mu}|\psi\rangle + \langle \boldsymbol{r}|V(|\hat{\boldsymbol{r}}|)|\psi\rangle = E\langle \boldsymbol{r}|\psi\rangle,$$

or

$$-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial}{\partial r}(\frac{\partial}{\partial r}r\langle \boldsymbol{r}|\psi\rangle)+\frac{1}{2\mu r^2}\langle \boldsymbol{r}|\hat{\boldsymbol{L}}^2|\psi\rangle+V(r)\langle \boldsymbol{r}|\psi\rangle=E\langle \boldsymbol{r}|\psi\rangle.$$

or

$$[-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial}{\partial r}(\frac{\partial}{\partial r}r)+\frac{\hbar^2 l(l+1)}{2\mu r^2}+V(r)]\langle \boldsymbol{r}|\psi\rangle=E\langle \boldsymbol{r}|\psi\rangle.$$

Here we assume that

$$\langle \boldsymbol{r}|\psi\rangle=\psi(\boldsymbol{r})=R_{E,l}(r)Y_l^m(\theta,\phi),$$

(*separation variable*) with

$$\langle \boldsymbol{n}|l,m\rangle=\langle \theta,\phi|l,m\rangle=Y_l^m(\theta,\phi).$$

$R_{E,l}(r)$ depends only on E and l, but not on m. $Y_l^m(\theta,\phi)$ is the spherical harmonics. The differential equation for $R_{E,l}(r)$,

$$[-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial}{\partial r}(\frac{\partial}{\partial r}r)+\frac{\hbar^2 l(l+1)}{2\mu r^2}+V(r)]R_{E,l}(r)=ER_{E,l}(r).$$

We assume that

$$R_{E,l}(r)=\frac{u(r)}{r}, \qquad E=-\varepsilon_1 \qquad (\varepsilon_1>0)$$

Then, we have

$$u''(r)-[\frac{l(l+1)}{r^2}+\frac{2\mu[\varepsilon_1+V(r)]}{\hbar^2}]u(r)=0.$$

We further assume a Coulomb potential given by

$$V(r)=-\frac{Ze^2}{r}.$$

Then

$$u''(r)-[\frac{l(l+1)}{r^2}+\frac{2\mu(\varepsilon_1-Ze^2/r)}{\hbar^2}]u(r)=0.$$

We now introduce a new variable

$$r = \frac{\hbar}{\sqrt{8\mu\varepsilon_1}}\rho = \frac{\hbar\rho}{\sqrt{8\mu\frac{\mu Z^2 e^4}{2\hbar^2 n^2}}} = \frac{\hbar^2 n\rho}{2\mu Z e^2} = \frac{an\rho}{2Z} = \frac{\rho}{2\kappa},$$

where

$$\varepsilon_1 = \frac{Z^2\mu e^4}{2\hbar^2 n^2} = \frac{Z^2 e^2}{2an^2},$$

$$a = \frac{\hbar^2}{\mu e^2},$$

$$\kappa = \frac{Z}{na}.$$

Since

$$\rho = \frac{2rZ}{na} = 2\kappa r,$$

we have

$$\frac{d}{dr} = \frac{d\rho}{dr}\frac{d}{d\rho} = 2\kappa\frac{d}{d\rho},$$

$$\frac{d^2}{dr^2} = 2\kappa\frac{d}{d\rho}(2\kappa\frac{d}{d\rho}) = 4\kappa^2\frac{d^2}{d\rho^2},$$

and

$$4\kappa^2 u''(\rho) - [4\kappa^2\frac{l(l+1)}{\rho^2} + \kappa^2(1-\frac{4n}{\rho})]u(\rho) = 0,$$

where

$$\frac{2\mu}{\hbar^2}(\varepsilon_1 - Ze^2/r) = \kappa^2(1-\frac{4n}{\rho}).$$

Finally, we get

$$u''(\rho) - [\frac{l(l+1)}{\rho^2} + (\frac{1}{4} - \frac{n}{\rho})]u(\rho) = 0,$$

or

$$[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{n}{\rho} - \frac{1}{4}]u(\rho) = 0. \qquad (1)$$

Using Mathematica, the solution of Eq.(1) can be solved as

$$u(\rho) = C\exp(-\frac{\rho}{2} + l\ln\rho) LaguerreL[-1+n-l, 1+2l, \rho].$$

LaguerreL[n, a, x]: generalized Laguerre polynomials [$= L_n^a(x)$].

((Landau-Lifshitz))

We have the following differential equation for $R(\rho)$ with $\rho = 2\kappa r$.

$$[\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} + (-\frac{1}{4} + \frac{n}{\rho} - \frac{l(l+1)}{\rho^2})]R(\rho) = 0,$$

which is given by Landau and Lifshitz.

5. Comment on the reason for the choice of the number of 1/4 in the differential equation of radial part wave function

The differential equation for the radial part is given by

$$u''(r) - [\frac{l(l+1)}{r^2} + \frac{2\mu(\varepsilon_1 - \frac{Ze^2}{r})}{\hbar^2}]u(r) = 0.$$

Suppose that

$$\rho = \alpha r,$$

where α is constant to be determined (not the fine structure constant). Since

$$\frac{d}{dr} = \frac{d\rho}{dr}\frac{d}{d\rho} = \alpha\frac{d}{d\rho}, \qquad \frac{d^2}{dr^2} = \alpha\frac{d}{d\rho}\alpha\frac{d}{d\rho} = \alpha^2\frac{d^2}{d\rho^2},$$

Then we get

$$\alpha^2\frac{d^2u(\rho)}{d\rho^2} - [\frac{\alpha^2 l(l+1)}{\rho^2} + \frac{2\mu\varepsilon_1}{\hbar^2} - \frac{2\mu Ze^2\alpha}{\hbar^2\rho}]u(\rho) = 0.$$

or

$$\frac{d^2u}{d\rho^2}-\frac{l(l+1)}{\rho^2}u-\frac{2\mu\varepsilon_1}{\alpha^2\hbar^2}u+\frac{2\mu Ze^2}{\alpha\hbar^2\rho}u=0$$

In the above text, we choose the parameter p as

$$p=\frac{2\mu\varepsilon_1}{\alpha^2\hbar^2}=\frac{1}{4}, \qquad \alpha=\sqrt{\frac{2\mu\varepsilon_1}{p\hbar^2}}=\sqrt{\frac{8\mu\varepsilon_1}{\hbar^2}}$$

When the energy ε_1 is given by

$$\varepsilon_1=\frac{\mu Z^2e^4}{2\hbar^2n^2}, \qquad \text{(from the Bohr model)}$$

then the differential equation can be rewritten as the Whittaker differential equation,

$$\frac{d^2u}{d\rho^2}+[-\frac{1}{4}+\frac{n}{\rho}-\frac{l(l+1)}{\rho^2}]u=0,$$

since

$$\left(\frac{2\mu Ze^2}{\alpha\hbar^2}\right)^2=\frac{4\mu^2Z^2e^4}{\alpha^2\hbar^4}=\frac{4\mu^2Z^2e^4}{\hbar^4}\frac{\hbar^2}{8\mu\varepsilon_1}=\frac{\mu Z^2e^4}{2\hbar^2\varepsilon_1}=n^2.$$

((**Note**))

According to Schiff (Quantum Mechanics), "the particular choice of p = 1/4 is arbitrary but convenient for the following development." But I am not convinced about this comment. I will check the validity of the choice of p = 1/4 using the Mathematica here.

We note that using the Mathematica, the solution of the Whittaker differential equation

$$\frac{d^2u}{d\rho^2}-\frac{l(l+1)}{\rho^2}u-\frac{1}{4}u+\frac{n}{\rho}u=0,$$

can be obtained as the linear combination of the two functions

WhittakerM[n, $\frac{1+2l}{2}$, ρ],

$$\text{WhittakerW}[\,n\,,\ \frac{1+2l}{2},\ \rho\,].$$

We now discuss why we need to choose p = 1/4. The solution of

$$\frac{d^2u}{d\rho^2}+[-p+\frac{n}{\rho}-\frac{l(l+1)}{\rho^2}]u=0,$$

is given by the linear combination of

$$\text{WhittakerM}[\frac{n}{2\sqrt{p}},\ \frac{1+2l}{2},\ 2\sqrt{p}\rho\,],$$

$$\text{WhittakerW}[\frac{n}{2\sqrt{p}},\ \frac{1+2l}{2},\ 2\sqrt{p}\rho\,].$$

For convenience, we choose n = 2 and l = 1. We make a plot of the function $\text{WhittakerM}[\frac{n}{2\sqrt{p}},\ \frac{1+2l}{2},\ 2\sqrt{p}\rho\,]$ as a function of p, where p is changed between p = 0.247 and 0.253 around p = 1/4.

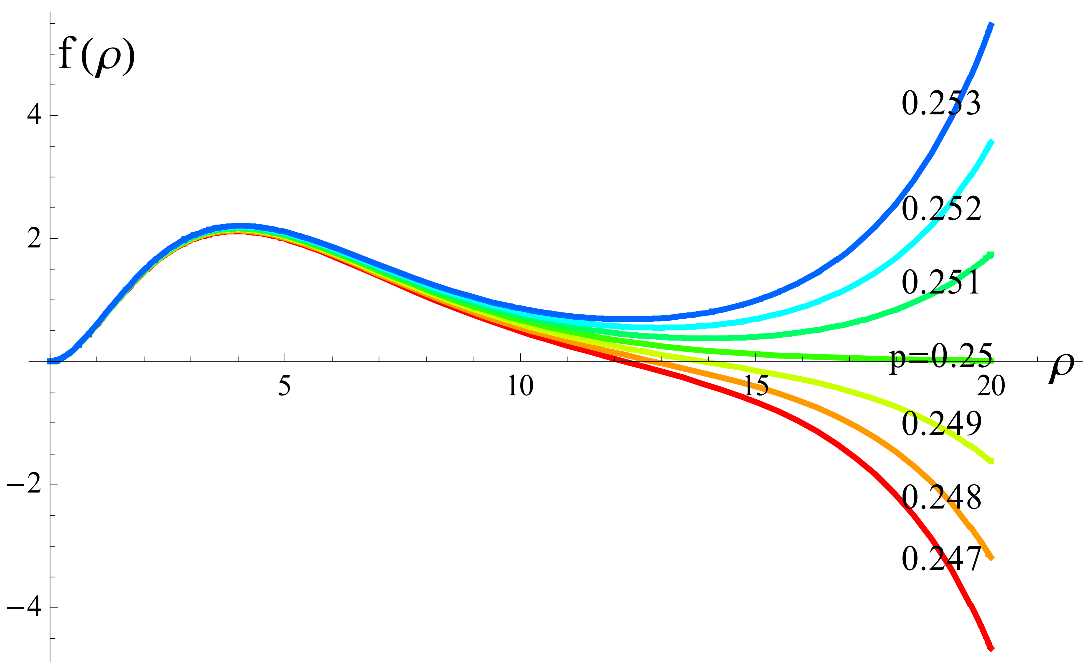


Fig. Plot of $f(\rho)$ vs ρ where p is changed as a parameter. p = 0.247 - 0.253. When p = 0.25, $f(\rho)$ tends to zero in the large value of ρ.

We also make a plot of the function $f(p) = \text{WhittakerM}[\frac{n}{2\sqrt{p}}, \frac{1+2l}{2}, 2\sqrt{p}\rho]$ with fixed ρ (=50), as a function of p between between p = 0.247 and 0.253 around p = 1/4. Here we calculate $f(p)$, where n = 4, l = 3, 2, 1, 0. We find that $f(p)$ becomes zero only for p = 1/4 in the limit of $\rho \to \infty$.

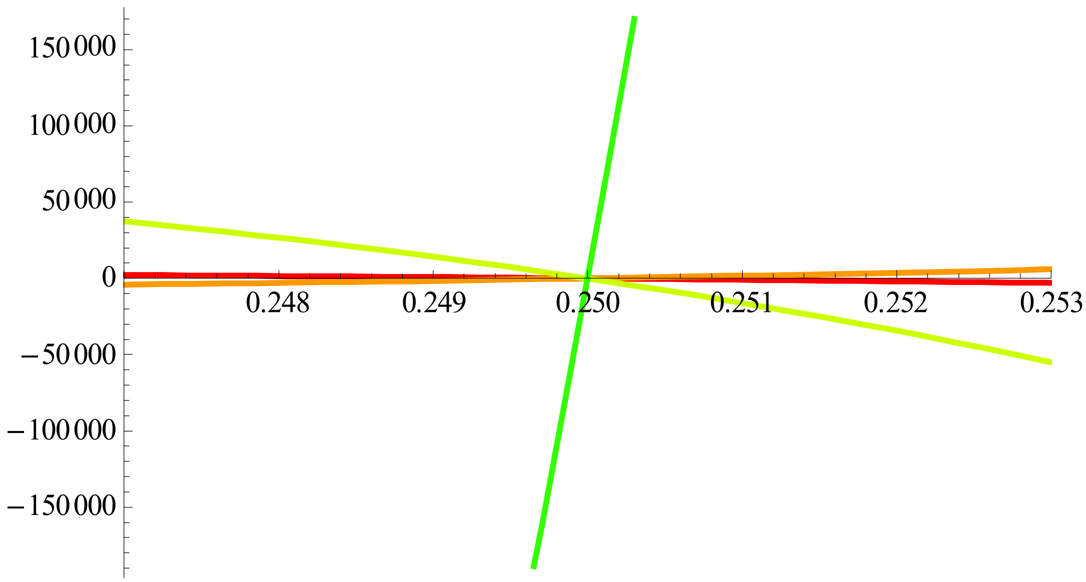


Fig. $f(p)$ vs p where n = 4, l = 0 (red), 1, 2, 3 (green). ρ = 50.

From the above discussion we find that p should be equal to 1/4.

6. Comment on the Radial equation

((**Note**)) **L.I. Schiff, Quantum Mechanics:** solution of the **radial equation** of the Coulomb potential of hydrogen atom.

Here we follow the discussion given by Schiff, on the solving the radial equation of hydrogen atom. To this end, we start with a second-order differential equation for the radial part of hydrogen atom (**Schiff**),

$$\frac{d^2}{dr^2}[rR_{nl}(r)] - \frac{l(l+1)}{r^2}[rR_{nl}(r)] + \frac{2\mu}{\hbar^2}[E - V(r)][rR_{nl}(r)] = 0. \qquad (1)$$

Using the relation.

$$\frac{d^2}{dr^2}[rR_{nl}(r)] = \frac{1}{r}\frac{d}{dr}(r^2\frac{dR_{nl}(r)}{dr})$$

Eq.(1) can be rewritten as

$$\frac{1}{r^2}\frac{d}{dr}[r^2\frac{dR_{nl}(r)}{dr}]-\frac{l(l+1)}{r^2}R_{nl}(r)+\frac{2\mu}{\hbar^2}[E-V(r)]R_{nl}(r)=0\,, \qquad (2)$$

where we use $E=-|E|$ (bound state) and $V(r)=-\frac{Ze^2}{r}$ (Coulomb potential). By introducing variable $\rho=\alpha_0 r$ (dimensionless), we have

$$\frac{1}{\rho^2}\frac{d}{d\rho}(\rho^2\frac{dR_{nl}(\rho)}{d\rho})-\frac{l(l+1)}{\rho^2}R_{nl}(\rho)+\frac{2\mu}{\alpha_0{}^2\hbar^2}(-|E|+\frac{\alpha_0 Ze^2}{\rho})R_{nl}(\rho)=0$$

With the use of new parameters,

$$\frac{2\mu|E|}{\alpha_0{}^2\hbar^2}=\frac{1}{4}, \qquad \lambda=\frac{2\mu Ze^2}{\alpha_0\hbar^2}=\frac{Ze^2}{\hbar}(\frac{\mu}{2|E|})^{1/2}$$

we have the final form

$$\frac{1}{\rho^2}\frac{d}{d\rho}(\rho^2\frac{dR_{nl}(\rho)}{d\rho})-\frac{l(l+1)}{\rho^2}R_{nl}(\rho)+(\frac{\lambda}{\rho}-\frac{1}{4})R_{nl}(\rho)=0\,, \qquad (2)$$

Using the relation

$$\frac{d}{d\rho}(\rho^2\frac{dR_{nl}(\rho)}{d\rho})=\rho\frac{d^2}{d\rho^2}[\rho R_{nl}(\rho)]$$

Eq.(2) can be written as

$$\frac{1}{\rho}\frac{d^2}{d\rho^2}[\rho R_{nl}(\rho)]-\frac{l(l+1)}{\rho^2}R_{nl}(\rho)+(\frac{\lambda}{\rho}-\frac{1}{4})R_{nl}(\rho)=0$$

or

$$\frac{d^2}{d\rho^2}[\rho R_{nl}(\rho)]-\frac{l(l+1)}{\rho^2}\rho R_{nl}(\rho)+(\frac{\lambda}{\rho}-\frac{1}{4})\rho R_{nl}(\rho)=0$$

or

$$\frac{d^2}{d\rho^2}u_{nl}(\rho)-\frac{l(l+1)}{\rho^2}u_{nl}(\rho)+(\frac{\lambda}{\rho}-\frac{1}{4})u_{nl}(\rho)=0\,, \qquad (3)$$

where $u_{nl}(\rho)=\rho R_{nl}(\rho)$.

In his book of Schiff, Schiff gives the following comment. that the particular choice of the number 1/4 for the eigenvalue term is arbitrary but convenient. When I encountered this comment for the first time, I did not understand why Schiff choses the factor ¼ (such a specified factor). I found that Eq.(2) is used as a radial equation in many textbooks (see References)

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7. Revisit: Derivation of the factor 1/4

Here the radial equation is discussed again. I will show that the factor 1/4 comes out automatically. We use

$$rR_{nl}(r)=u(r)\,, \qquad V(r)=-\frac{Ze^2}{r}$$

The radial equation is given by

$$\frac{d^2}{dr^2}u(r)-\frac{l(l+1)}{r^2}u(r)+\frac{2\mu}{\hbar^2}(E+\frac{Ze^2}{r})u(r)=0$$

First, we assume that

$$x = \alpha_0 r \qquad \text{(a dimensionless variable)}$$

$$\frac{d}{dr} = \frac{dx}{dr}\frac{d}{dx} = \alpha_0 \frac{d}{dx}, \qquad \frac{d^2}{dr^2} = \alpha_0 \frac{d}{dx}\alpha_0 \frac{d}{dx} = \alpha_0^2 \frac{d^2}{dx^2}$$

The parameter α_0 will be determined later. We also use $E = -|E|$ (bound state). Thus, we get

$$\alpha_0^2 \frac{d^2}{dx^2}u - \frac{l(l+1)}{x^2}\alpha_0^2 u + \frac{2\mu}{\hbar^2}(-|E| + \frac{Ze^2\alpha_0}{x})u = 0$$

or

$$\frac{d^2}{dx^2}u - \frac{l(l+1)}{x^2}u + (-\frac{2\mu|E|}{\alpha_0^2\hbar^2} + \frac{2\mu Ze^2}{\alpha_0\hbar^2 x})u = 0 .$$

We define a parameter γ and λ_0 as

$$\gamma = \frac{2\mu|E|}{\alpha_0^2\hbar^2} \ (>0) \qquad \text{or} \qquad \alpha_0 = \sqrt{\frac{2\mu|E|}{\gamma\hbar^2}}$$

and

$$\lambda_0 = \frac{2\mu Ze^2}{\alpha_0\hbar^2} = \frac{2\mu Ze^2}{\hbar^2}\sqrt{\frac{\gamma\hbar^2}{2\mu|E|}} = \frac{Ze^2}{\hbar}\sqrt{\frac{2\mu\gamma}{|E|}}$$

Thus, we have

$$\frac{d^2}{dx^2}u - \frac{l(l+1)}{x^2}u + (\frac{\lambda_0}{x} - \gamma)u = 0$$

Here we define $\lambda_0 = 2\sqrt{\gamma}\lambda$ with

$$\lambda = \frac{\lambda_0}{2\sqrt{\gamma}} = \frac{Ze^2}{\hbar}\sqrt{\frac{\mu}{2|E|}}$$

Furthermore, we assume that

$$\rho = 2\sqrt{\gamma}x \qquad \text{(a new variable)}$$

$$\frac{d}{dx} = \frac{d\rho}{dx}\frac{d}{d\rho} = 2\sqrt{\gamma}\frac{d}{d\rho}, \qquad \frac{d}{dx}\frac{d}{dx} = 2\sqrt{\gamma}\frac{d}{d\rho}2\sqrt{\gamma}\frac{d}{d\rho} = 4\gamma\frac{d^2}{d\rho^2}$$

and

$$\frac{l(l+1)}{x^2} = \frac{l(l+1)}{\rho^2}4\gamma,$$

$$\frac{\lambda_0}{x} - \gamma = (\frac{4\lambda}{\rho} - 1)\gamma$$

Thus, we have

$$\frac{d^2u}{d\rho^2} - \frac{l(l+1)}{\rho^2}u + (\frac{\lambda}{\rho} - \frac{1}{4})u = 0$$

with

$$\lambda = \frac{Ze^2}{\hbar}\sqrt{\frac{\mu}{2|E|}} \qquad (E\text{; energy eigenvalue, bound state})$$

The relation between r and ρ is

$$\rho = 2\sqrt{\gamma}\alpha_0 r$$
$$= 2\sqrt{\gamma}\sqrt{\frac{2\mu|E|}{\gamma\hbar^2}}r$$
$$= \sqrt{\frac{8\mu|E|}{\hbar^2}}r$$

In conclusion. the factor 1/4 can come out automatically in the radial equation.

$$\frac{d^2u}{d\rho^2} - \frac{l(l+1)}{\rho^2}u + (\frac{\lambda}{\rho} - \frac{1}{4})u = 0$$

with

$$r = \sqrt{\frac{\hbar^2}{8\mu|E|}}\rho, \qquad \lambda = \frac{Ze^2}{\hbar}\sqrt{\frac{\mu}{2|E|}}$$

((**Solution**))

(a) $\rho \to \infty$

$$\frac{d^2u}{d\rho^2} - \frac{1}{4}u = 0$$

The solution of this equation is

$$u(\rho) = e^{-\rho/2} \qquad \text{(asymptotic form)}$$

(b) $\rho \simeq 0$

We assume that $u = a_0\rho^s$ ($a_0 \neq 0$).

$$a_0[s(s-1)\rho^{s-2} - l(l+1)\rho^{s-2} + (\frac{\lambda}{x}\rho^{s-1} - \frac{1}{4}\rho^s)] + ... = 0$$

The coefficient of ρ^{s-2}:

$$s(s-1) - l(l+1) = 0 \qquad (s+l)(s-l-1) = 0$$

Since s>0, we get $s = l+1$.

From these discussions, we get the form of $u(\rho)$ as

$$u(\rho) = \rho^{l+1} e^{-\rho/2} F(\rho).$$

So, we need to determine the form $F(\rho)$. We use the Mathematica for the radial equation

$$\frac{d^2 u}{d\rho^2} - \frac{l(l+1)}{\rho^2} u + (\frac{\lambda}{\rho} - \frac{1}{4}) u = 0,$$

with

$$u \to Function[\rho, \rho^{l+1} e^{-\rho/2} F(\rho)],$$

leading to

$$\frac{d^2 F(\rho)}{d\rho^2} + \frac{(2l+2-\rho)}{\rho} \frac{dF(\rho)}{d\rho} + \frac{(\lambda - l - 1)}{\rho} F(\rho) = 0.$$

((**Mathematica**))

```
Clear["Global`"];
eq1 = u''[ρ] - (L (L + 1))/ρ^2 u[ρ] +
   (λ/ρ - 1/4) u[ρ];
rule1 =
  {u → Function[ρ, ρ^(L+1) Exp[(-ρ)/2] F[ρ]]};
eq2 = eq1 //. rule1 // Simplify
```

$$-e^{-\rho/2} \rho^{L} \left((1 + L - \lambda) F[\rho] + (-2 - 2L + \rho) F'[\rho] - \rho F''[\rho] \right)$$

The series expansion method can be used to determine the form $F(\rho)$.

8. Form of the wave function

n: the principal quantum number.
l: the azimuthal quantum number.
m: the magnetic quantum number.

For the fixed n (=1, 2, 3, 4, ...),

$l = n$-1, n-2,......., 1, and 0.

$l = 0$ sharp (*s*)
$m = 0$

$l = 1$ principal (*p*)
$m = 1, 0, -1$

$l = 2$ diffuse (*d*)
$m = 2, 1, 0, -1, -2$

$l = 3$ fundamental (*f*)
$m = 3, 2, 1, 0, -1, -2, -3$

$l = 4$ (*g*)
$m = 4, 3, 2, 1, 0, -1, -2, -3, -4$.

There are (2l+1) solutions to the Schrödinger equation corresponding to the same energy eigenvalue E_n.

Degeneracy:

$$E_n = \sum_{l=0}^{n-1}(2l+1) = 2\frac{n(n-1)}{2} + n = n^2.$$

((**Note**)) Including spin degeneracy of states is $2n^2$.

	n	l	m	m_s
1s	1	0	0	$\pm 1/2$
2s	2	0	0	$\pm 1/2$
2p	2	1	0, ±1	$\pm 1/2$
3s	3	0	0	$\pm 1/2$
3p	3	1	0, ±1	$\pm 1/2$
3d	3	2	0, ±1, , ±2	$\pm 1/2$

4s	4	0	0	$\pm 1/2$
4p	4	1	0, ±1	$\pm 1/2$
4d	4	2	0, ±1, ±2	$\pm 1/2$
4f	4	3	0, ±1, ±2, ±3	$\pm 1/2$

The solution of the above differential equation is given by

$$rR_{nl}(r) = u_{nl}(r) = Ae^{-\rho/2}\rho^{l+1}L_{n-l-1}^{2l+1}(\rho),$$

where

$$\rho = 2\kappa r.$$

Then we have

$$R_{nl}(r) = \frac{u_{nl}(r)}{r} = \frac{A}{r}e^{-\rho/2}\rho^{l+1}L_{n-l-1}^{2l+1}(\rho) = 2A\kappa e^{-\rho/2}\rho^{l}L_{n-l-1}^{2l+1}(\rho).$$

A is determined from the condition of normalization.

$$1 = \int_0^\infty [R_{nl}(r)]^2 r^2 dr = \frac{A^2}{2\kappa}\int_0^\infty e^{-\rho}\rho^{2l+2}[L_{n-l-1}^{2l+1}(\rho)]^2 d\rho. \qquad (1)$$

Here we use the formula:

$$\int_0^\infty e^{-\rho}\rho^{q+1}L_p^q(\rho)L_p^q(\rho)d\rho = \frac{(p+q)!}{p!}(2p+q+1).$$

Note that

$p = n-l-1$, $q = 2l+1$, $p+q = n+l$, and $2p+q+1 = 2n$.

Then we have

$$\int_0^\infty e^{-\rho}\rho^{2l+2}[L_{n-l-1}^{2l+1}(\rho)]^2 d\rho = \frac{(n+l)!}{(n-l-1)!}(2n).$$

Using this formula, Eq.(1) can be rewritten as

$$1 = \frac{A^2}{2\kappa}\frac{(n+l)!}{(n-l-1)!}(2n),$$

or

$$A = \frac{Z^{1/2}}{na^{1/2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}} .$$

Thus we get

$$R_{nl}(r) = R_{nl}(\rho)$$
$$= \frac{2Z^{3/2}}{n^2 a^{3/2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) ,$$

or

$$R_{nl}(r) = R_{nl}(\rho) = A_{nl} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho),$$

with

$$A_{nl} = \frac{2Z^{3/2}}{n^2 a^{3/2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}} .$$

This function satisfies the differential equation

$$[\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} + (-\frac{1}{4} + \frac{n}{\rho} - \frac{l(l+1)}{\rho^2})]R_{nl}(\rho) = 0 .$$

We also have

$$u_{nl}(r) = u_{nl}(\rho) = \frac{Z^{1/2}}{na^{1/2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}} e^{-\rho/2} \rho^{l+1} L_{n-l-1}^{2l+1}(\rho) .$$

Here we introduce a new function. We assume that

$$\Phi_p^q(\rho) = e^{-\rho/2} \rho^{(q+1)/2} L_p^q(\rho).$$

Then

$$u_{nl}(\rho) = \frac{Z^{1/2}}{na^{1/2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}} \Phi_{n-l-1}^{2l+1}(\rho) .$$

This function satisfies the differential equation

$$[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{n}{\rho} - \frac{1}{4}]u_{nl}(\rho) = 0,$$

or

$$[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{n}{\rho} - \frac{1}{4}]\Phi_{n-l-1}^{2l+1}(\rho) = 0 .$$

This equation is rewritten as

$$[\frac{d^2}{d\rho^2} - \frac{(q^2-1)}{4\rho^2} + \frac{2p+q+1}{2\rho} - \frac{1}{4}]\Phi_p^q(\rho) = 0 .$$

9. Average values $\langle r^n \rangle$

We consider the average distance for the state $|l, m\rangle$. The wave function is normalized as

$$1 = \int |\psi(\boldsymbol{r})| d\Omega r^2 dr ,$$

where Ω is the solid angle.

$$\psi(\boldsymbol{r}) = R_{nl}(r) Y_l^m(\theta,\phi) ,$$

$$1 = \int dr r^2 |R_{nl}(r)|^2 \int d\Omega |Y_l^m(\theta,\phi)|^2 = \int dr r^2 |R_{nl}(r)|^2 ,$$

We define $P_r dr$ as

$$P_r dr = r^2 \,|\, R(r)\,|^2 \, dr .$$

The average $\langle r^s \rangle$ is defined by

$$< r^s > = \int_0^\infty dr r^2 [R_{nl}(r)]^2 r^s = \int_0^\infty dr r^{s+2} [R_{nl}(r)]^2 .$$

where

$$a = \frac{\hbar^2}{\mu e^2}$$

$$E_n = -\frac{Ze^2}{2n^2 a}$$

The average $\langle r^s \rangle$ is obtained as

$$\langle r^{-4}\rangle = \frac{Z^4[3n^2 - l(l+1)]}{n^5 a^4 l(l+1/2)(l+1)[2l(l+1)-3/2]},$$

$$\langle r^{-3}\rangle = \frac{Z^3}{n^4 a l(l+1/2)(l+1)},$$

$$\langle r^{-2}\rangle = \frac{Z^2}{n^3 a^2 (l+1/2)},$$

$$\langle r^{-1}\rangle = \frac{Z}{n^2 a},$$

$$\langle r^{0}\rangle = 1,$$

$$\langle r\rangle = \frac{a}{2Z}[3n^2 - l(l+1)],$$

$$\langle r^{2}\rangle = \frac{a^2}{2Z^2} n^2[5n^2 + 1 - 3l(l+1)],$$

$$\langle r^{3}\rangle = \frac{a^3}{8Z^3} n^2[35n^4 + 3(l-1)l(l+1)(l+2) - 5n^2(6l(l+1)-5)].$$

10. Form of the wave function

For the plot by using Mathematica, we use the radial wave function as

$$R_{nl}(r) = R_{nl}(\rho) == \frac{2Z^{3/2}}{n^2 a^{3/2}}\sqrt{\frac{(n-l-1)!}{(n+l)!}} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho),$$

where

$$\rho = 2\kappa r == \frac{2Zr}{na}.$$

```
Clear["Global`*"];
```

```
rwave[n_, ℓ_, r_] :=
```

$$\frac{1}{\sqrt{(n+\ell)\,!}}\left(2^{1+\ell}\ a^{-\ell-\frac{3}{2}}\ e^{-\frac{Z\,r}{a\,n}}\ n^{-\ell-2}\ Z^{\ell+\frac{3}{2}}\ r^{\ell}\ \sqrt{(n-\ell-1)\,!}\ \text{LaguerreL}\left[-1+n-\ell,\ 1+2\,\ell,\ \frac{2\,Z\,r}{a\,n}\right]\right)$$

```
list1 = Table[rwave[n, ℓ, r], {n, 1, 3}, {ℓ, 0, n - 1}] //
  TableForm[#, TableHeadings → {{"n=1", "n=2", "n=3"}, {"ℓ=0", "ℓ=1", "ℓ=2"}}] &
```

	ℓ=0	ℓ=1	ℓ=2
n=1	$\frac{2\,e^{-\frac{r\,Z}{a}}\,Z^{3/2}}{a^{3/2}}$		
n=2	$\frac{e^{-\frac{r\,Z}{2\,a}}\,Z^{3/2}\left(2-\frac{r\,Z}{a}\right)}{2\sqrt{2}\,a^{3/2}}$	$\frac{e^{-\frac{r\,Z}{2\,a}}\,r\,Z^{5/2}}{2\sqrt{6}\,a^{5/2}}$	
n=3	$\frac{2\,e^{-\frac{r\,Z}{3\,a}}\,Z^{3/2}\left(27\,a^2-18\,a\,r\,Z+2\,r^2\,Z^2\right)}{81\sqrt{3}\,a^{7/2}}$	$\frac{\sqrt{\frac{2}{3}}\,e^{-\frac{r\,Z}{3\,a}}\,r\,Z^{5/2}\left(4-\frac{2\,r\,Z}{3\,a}\right)}{27\,a^{5/2}}$	$\frac{2\sqrt{\frac{2}{15}}\,e^{-\frac{r\,Z}{3\,a}}\,r^2\,Z^{7/2}}{81\,a^{7/2}}$

Radial wave function interms of ρ : $\rho = \frac{2\,Z\,r}{a\,n}$

```
ρwave[n_, ℓ_, ρ_] := rwave[n, ℓ, r] /. {r → a n ρ/(2 Z)} // PowerExpand
```

```
ρwave[n, ℓ, ρ]
```

$$\frac{2\,e^{-\rho/2}\,Z^{3/2}\,\rho^{\ell}\,\sqrt{(-1+n-\ell)\,!}\ \text{LaguerreL}[-1+n-\ell,\ 1+2\,\ell,\ \rho]}{a^{3/2}\,n^2\,\sqrt{(n+\ell)\,!}}$$

```
list1 = Table[ρwave[n, ℓ, ρ], {n, 1, 3}, {ℓ, 0, n - 1}] // Simplify //
  TableForm[#, TableHeadings → {{"n=1", "n=2", "n=3"}, {"ℓ=0", "ℓ=1", "ℓ=2"}}] &
```

	ℓ=0	ℓ=1	ℓ=2
n=1	$\frac{2\,e^{-\rho/2}\,Z^{3/2}}{a^{3/2}}$		
n=2	$-\frac{e^{-\rho/2}\,Z^{3/2}\,(-2+\rho)}{2\sqrt{2}\,a^{3/2}}$	$\frac{e^{-\rho/2}\,Z^{3/2}\,\rho}{2\sqrt{6}\,a^{3/2}}$	
n=3	$\frac{e^{-\rho/2}\,Z^{3/2}\left(6-6\,\rho+\rho^2\right)}{9\sqrt{3}\,a^{3/2}}$	$-\frac{e^{-\rho/2}\,Z^{3/2}\,(-4+\rho)\,\rho}{9\sqrt{6}\,a^{3/2}}$	$\frac{e^{-\rho/2}\,Z^{3/2}\,\rho^2}{9\sqrt{30}\,a^{3/2}}$

((**Mathematica**))

Plot of the probability of the wave function

(i) $r^2 rwave[n,l,r]^2$ vs r/a, where $a = 1$ and $Z = 1$.

(ii) $< r >= \frac{a}{2Z}[3n^2 - l(l+1)]$, where $a = 1$ and $Z = 1$.

```
average[n_, ℓ_] := a/(2 Z) (3 n^2 - ℓ (ℓ + 1)) /. {a → 1, Z → 1};

h[n_, ℓ_, r_] := Which[0 < r < average[n, ℓ], 1, r > average[n, ℓ], 0]

p11[n_] := Plot[Evaluate[Table[r^2 rwave[n, ℓ, r]^2 /. {a → 1, Z → 1}, {ℓ, 0, n - 1}]],
  {r, 0.01, 7 n}, PlotStyle → Table[{{Thick, Hue[0.2 i]} }, {i, 0, 10}],
  PlotRange → {{0, 7 n}, {0, 0.55 1/n^1.2}}, AxesLabel → {"r/a", "Pr"}];

p12[n_] := Plot[Evaluate[Table[h[n, ℓ, r], {ℓ, 0, n - 1}]], {r, 0.01, 7 n},
  PlotStyle → Table[{{Thick, Hue[0.2 i]} }, {i, 0, 10}], PlotRange → {{0, 7 n}, {0, 1}},
  AxesLabel → {"r/a", "Pr"}];

g1 = Graphics[{Text[Style["n=1", Black, 15], {3, 0.4}], Text[Style["ℓ=0", Black, 15], {2, 0.3}],
   Text[Style["<r>/a", Blue, 15], {1.5, 0.5}]}];
Show[p11[1], p12[1], g1]
```

For the 1s state,

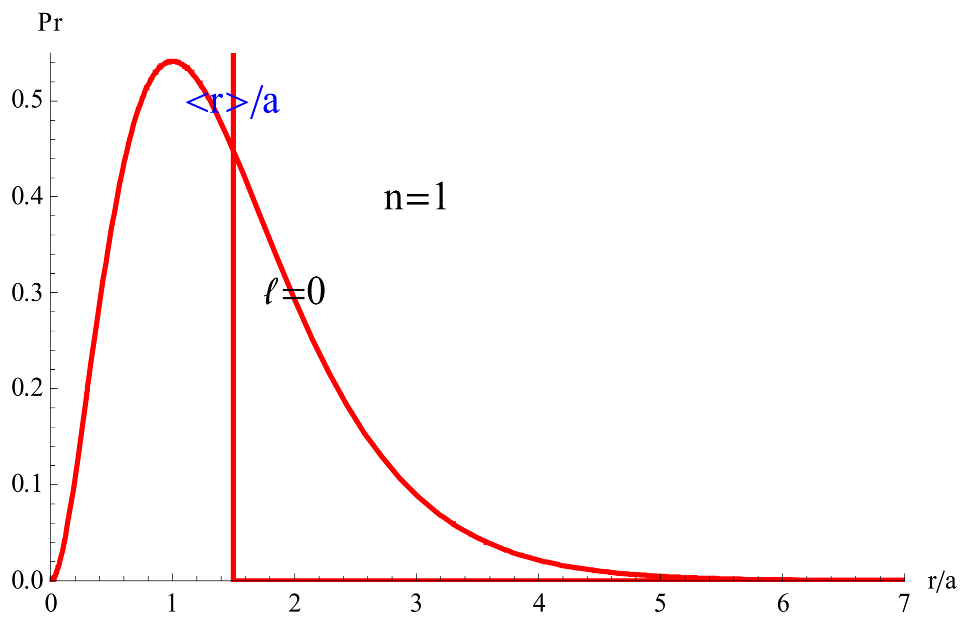


Fig. 1*s* (n = 1, l = 0). The straight line denotes the average value (<r>/a).

For the 2s, 2p states

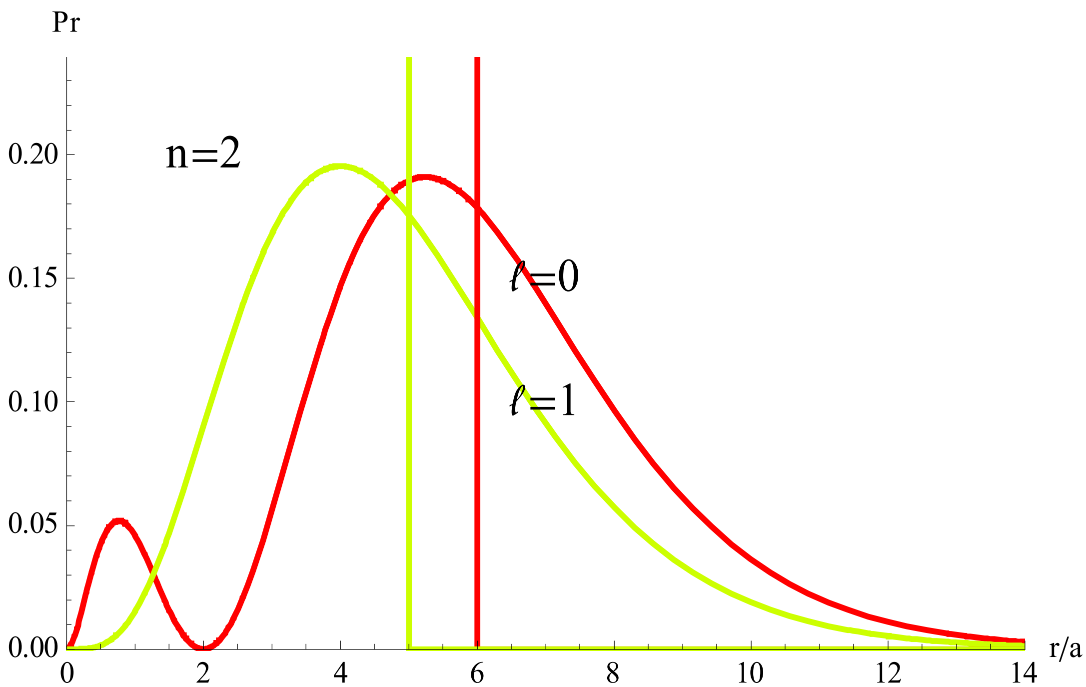


Fig. 2*s* (n = 2, l = 0). 2*p* (n = 2, l = 1). The straight lines denote the average value (<*r*>/a).

For the 3s, sp, and 3d states,

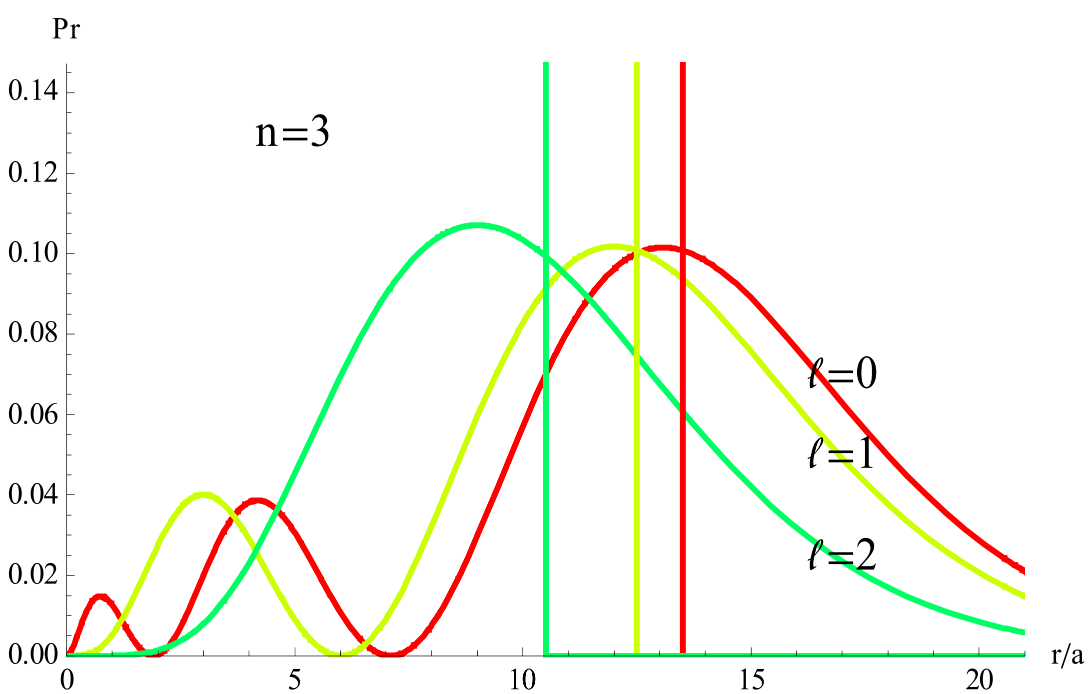


Fig. 3*s* (n = 3, l = 0). 3*p* (n = 3, l = 1). 3*d* (n = 3, l = 2). The straight lines denote the average value (<*r*>/a).

For the 4*s*, 4p, 4d, and 4f states,

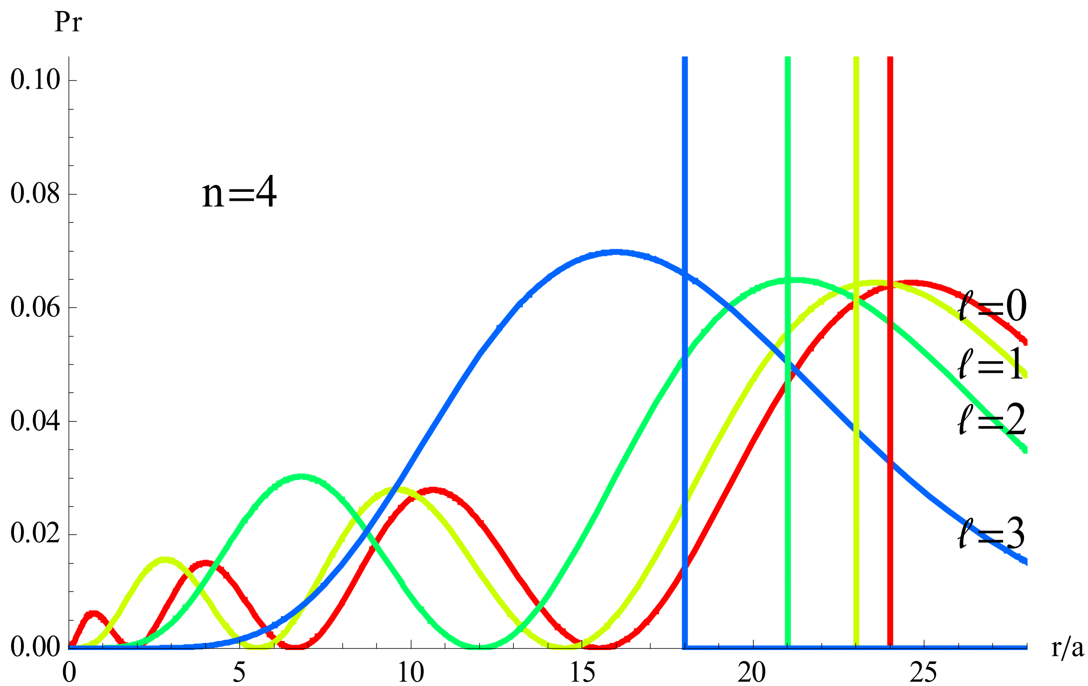


Fig. 4*s* (n = 4, l = 0). 4*p* (n = 4, l = 1). 4*d* (n = 4, l = 2). 4*f* (n = 4, l = 3). The straight lines denote the average value (<*r*>/a).

APPENDIX-A

A1. Derivation of the differential equation

Differential equation for the Radial component

```
Clear["Global`*"]; Op := D[r #, r] &;
```

$$eq1 = -\frac{\hbar^2}{2\mu}\frac{1}{r}D[Op[R[r]], r] + \left(\frac{\hbar^2 \ell (\ell+1)}{2\mu r^2} + V[r]\right) R[r] == \varepsilon R[r] \text{ // Simplify;}$$

```
Rule1 = Solve[eq1, R''[r]] // Simplify // Flatten;

Req1 = R''[r] - (R''[r] /. Rule1) == 0 /. ε → -ε1
```

$$-\frac{R[r]\left(2 r^2 \varepsilon 1 \mu + \ell (1+\ell) \hbar^2 + 2 r^2 \mu V[r]\right) - 2 r \hbar^2 R'[r]}{r^2 \hbar^2} + R''[r] == 0$$

$$R[r] = \frac{u[r]}{r}$$

$$arule1 = \left\{R \to \left(\frac{u[\#]}{\#} \&\right)\right\}; \text{ Req2 = Req1 /. arule1 // Simplify;}$$

```
Req3 = Solve[Req2, u''[r]] // Flatten; Req4 = u''[r] - (u''[r] /. Req3) == 0;
```

$$Replace1 = \left\{V \to \left(-\frac{e^2}{\#} \&\right)\right\};$$

```
Req5 = Req4 /. Replace1
```

$$-\frac{\left(-2 e^2 r \mu + 2 r^2 \varepsilon 1 \mu + \ell \hbar^2 + \ell^2 \hbar^2\right) u[r]}{r^2 \hbar^2} + u''[r] == 0$$

A2. Mathematica

LaguerreL[n,a,x]

gives the generalized Laguerre polynomial $L_n^a(x)$

We use the Laguerre polynomial as $L_{n-l-1}^{2l+1}(\rho)$, for the quantum state |*n*,*l*,*m*>.

When this operator is applied to a differential equation Eq of the function ψ[x], it changes the variable from x to z where x = f[z].

$r = \frac{\hbar}{\sqrt{8\,\mu\,\varepsilon 1}}\,\rho$

```
vchange[Eq_, ψ_, x_, z_, f_] :=
  Eq /. {D[ψ[x], {x, n_}] :→ Nest[(1/D[f, z] D[#, z] &), ψ[z], n], ψ[x] :→ ψ[z], x :→ f}

Ueq1 = vchange[Req5, u, r, ρ, ħ/Sqrt[8 μ ε1] ρ] // PowerExpand // FullSimplify
```

$$\frac{-2\sqrt{2}\,e^2\sqrt{\varepsilon 1}\,\mu\,\rho\,u[\rho] + \varepsilon 1\sqrt{\mu}\,\hbar\left(\left(4\,\ell\,(1+\ell)+\rho^2\right)u[\rho] - 4\,\rho^2\,u''[\rho]\right)}{\rho\,\hbar} == 0$$

```
Ueq2 = Solve[Ueq1, u''[ρ]] // PowerExpand // Flatten;
Ueq3 = u''[ρ] - (u''[ρ] /. Ueq2) == 0; substitution = {μ → ħ^2/(a e^2), ε1 → e^2/(2 n^2) 1/a};
Ueq4 = Ueq3 /. substitution // PowerExpand // Simplify; Ueq41 = Solve[Ueq4, u''[ρ]];
Ueq42 = u''[ρ] - (u''[ρ] /. Ueq41[[1]]) == 0 // Simplify
```

$$u''[\rho] == \frac{\left(4\,\ell + 4\,\ell^2 + \rho\,(-4\,n+\rho)\right)u[\rho]}{4\,\rho^2}$$

```
G[ρ_] := Exp[-ρ/2] ρ^(ℓ+1) F[ρ];

Ueq43 = Ueq42 /. u → G // Simplify
```

$$e^{-\rho/2}\,\rho^{\ell}\,\left((1-n+\ell)\,F[\rho] + (-2-2\,\ell+\rho)\,F'[\rho] - \rho\,F''[\rho]\right) == 0$$

```
Ueq5 = DSolve[Ueq43, F[ρ], ρ] // Flatten
```

{F[ρ] → C[1] HypergeometricU[1 - n + ℓ, 2 + 2 ℓ, ρ] + C[2] LaguerreL[-1 + n - ℓ, 1 + 2 ℓ, ρ]}

```
norm = {C[1] → 0, C[2] → 2^(ℓ+1) (1/(a n))^ℓ Sqrt[(n - ℓ - 1)! / (a^3 n^4 (n + ℓ)!)]};

ρwave[n_, ℓ_, ρ_] := G[ρ] /. Ueq5 /. norm // PowerExpand // Simplify;
ρwave[n, ℓ, ρ]
```

$$\frac{2^{1+\ell}\, a^{-\frac{3}{2}-\ell}\, e^{-\rho/2}\, n^{-2-\ell}\, \rho^{1+\ell} \sqrt{(-1+n-\ell)!}\ \mathrm{LaguerreL}[-1+n-\ell,\ 1+2\ell,\ \rho]}{\sqrt{(n+\ell)!}}$$

$$\frac{\hbar}{\sqrt{8\,\mu\,\varepsilon 1}}\rho = r,\ \ \text{or}\ \rho = \frac{\sqrt{8\,\mu\,\varepsilon 1}}{\hbar} r,\ \ \varepsilon 1 = \frac{e^2 Z^2}{2\,a\,n^2},\ \ \mu = \frac{\hbar^2}{a\,e^2}$$

```
ρ1 = Sqrt[8 μ ε1]/ħ r /. {ε1 → e^2/(2 a n^2), μ → ħ^2/(a e^2)} // PowerExpand // Simplify;
rwave[n_, ℓ_, r_] = ρwave[n, ℓ, ρ]/r /. {ρ → 2 r/(a n)} // PowerExpand
```

$$\frac{2^{2+2\ell}\, a^{-\frac{5}{2}-2\ell}\, e^{-\frac{r}{a\,n}}\, n^{-3-2\ell}\, r^{\ell} \sqrt{(-1+n-\ell)!}\ \mathrm{LaguerreL}\left[-1+n-\ell,\ 1+2\ell,\ \frac{2r}{a\,n}\right]}{\sqrt{(n+\ell)!}}$$

APPENDIX-B Balmer series

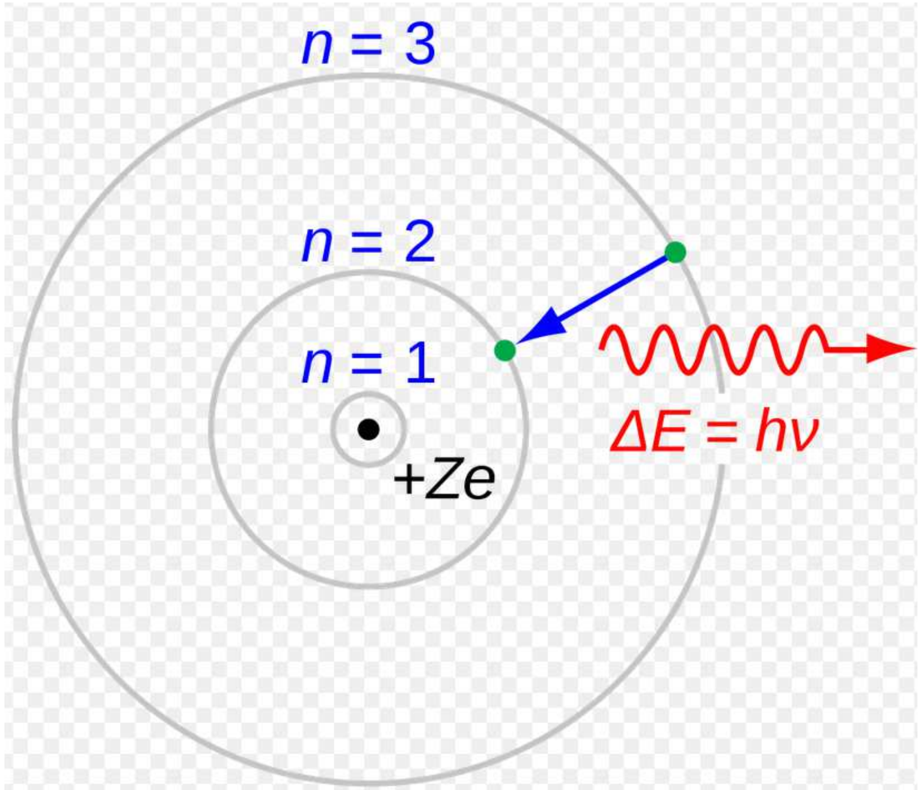
Balmer's formula was purely empirical, with no model of an underlying physical mechanism. This does not dimmish its value, though, for when a phenomenon can be fitted into a simple arithmetic scheme one is justified in having hope that a deeper understanding may not be far off. Balmer's formula was a key clue for Niels Bohr's development of the first really successful theory of atomic structure.

Johann Balmer (1885)

$$E_n = -\frac{13.6}{n^2}\ \text{(eV)}$$

$$h\nu = \frac{hc}{\lambda} = E_n - E_{n-2} = -13.6\left(\frac{1}{n^2} - \frac{1}{4}\right) = 13.6\left(\frac{n^2-4}{4n^2}\right)\ \text{eV}$$

$$\lambda = 364.50682\left(\frac{n^2}{n^2-4}\right)\ \text{nm}$$



https://en.wikipedia.org/wiki/Balmer_series

((**Experimental results**))

Balmer series

$\lambda = 656.279$ nm (H_α)	$n = 3 \to 2$	(red line at the right)
$\lambda = 486.135$ nm (H_β)	$n = 4 \to 2$	(Aqua)
$\lambda = 434.0472$ nm (H_γ)	$n = 5 \to 2$	(blue)
$\lambda = 410.1734$ nm (H_δ)	$n = 6 \to 2$	(violet)

The visible hydrogen emission spectrum lines in the Balmer series.