

Chapter 28
Schrödinger equation - central potential problem
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Bohr model
Schrödinger equation

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

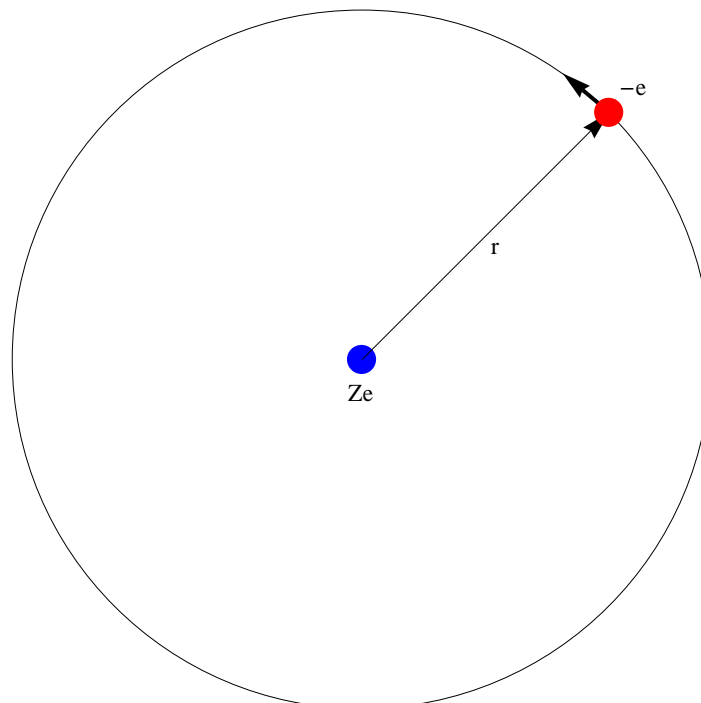
Erwin Rudolf Josef Alexander Schrödinger (12 August 1887– 4 January 1961) was an Austrian theoretical physicist who was one of the fathers of quantum mechanics, and is famed for a number of important contributions to physics, especially the Schrödinger equation, for which he received the Nobel Prize 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

28.1 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:

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

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

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

and the energy level

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

where

$$\varepsilon_1 = \frac{Z^2 e^2}{2n^2 a} = \frac{Z^2 \mathfrak{R}}{n^2} \quad (>0).$$

$$\mu = \frac{\hbar^2}{ae^2} \quad \text{or} \quad a = \frac{\hbar^2}{\mu e^2}.$$

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

$$\mathfrak{R} = \frac{\mu e^4}{2\hbar^2} = \frac{e^2}{2a}.$$

Note that

$$\mathfrak{R}_0 = \frac{me^4}{2\hbar^2} = 13.6056923(12) \text{ eV}.$$

where m is the mass of electron.

28.2 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

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

or

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

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

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

Then we have

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

and

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

This means that

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

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

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

Since \mathbf{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, $\hat{\mathbf{J}} = \hat{\mathbf{L}}$ (orbital angular momentum).

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

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

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

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

28.3 Commutation relations (more direct method)

In a central potential,

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

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

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

Therefore,

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

Similarly,

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

Thus we have

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

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

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

Then

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

or

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

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

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

for the central potential.

28.4 Schrödinger equation in a central potential

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

or

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

or

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

Here we assume that

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

(separation variable) with

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

$R_{E,l}(r)$ depends only on E and l , but not on m .

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

We assume that

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

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

We further assume a Coulomb potential given by

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

Then

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

We now introduce a new variable

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

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

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

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

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

where

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

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

or

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

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

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

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

((Landau-Lifshitz))

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

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

which is given by Landau and Lifshitz.

28.5 Form of the wave function

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

For the fixed n ($=1, 2, 3, 4, \dots$),

$l = n-1, n-2, \dots, 1, \text{ and } 0.$

$l = 0$ 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 Schrodinger equation corresponding to the same energy eigenvalue E_n .

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

((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.

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

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

$$p = n - l - 1, \quad q = 2l + 1, \quad p + q = n + l, \quad \text{and} \quad 2p + q + 1 = 2n$$

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

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

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

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

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

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

or

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

This equation is rewritten as

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

28.6 Average values $\langle r^n \rangle$

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

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

where Ω is the solid angle.

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

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

We define $P_r dr$ as

$$P_r dr = r^2 |R(r)|^2 dr$$

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

$$\langle r^s \rangle = \int_0^\infty dr r^2 [R_{nl}(r)]^2 r^s = \int_0^\infty dr r^{s+2} [R_{nl}(r)]^2$$

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

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

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

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

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

$$\langle r^0 \rangle = 1$$

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

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

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

15.8 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_] :=

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

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

Radial wave function interms of ρ : $\rho = \frac{2Zr}{a}$

$\rho\text{wave}[n_, l_, \rho_] := \text{rwave}[n, l, r] /. \left\{r \rightarrow \frac{a n \rho}{2 Z}\right\} //$ PowerExpand

$\rho\text{wave}[n, l, \rho]$

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

list1 = Table[$\rho\text{wave}[n, l, \rho]$, {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 | $\frac{e^{-\rho/2} Z^{3/2} (6-6\rho+\rho^2)}{9\sqrt{3} a^{3/2}}$ | $-\frac{e^{-\rho/2} Z^{3/2} (-4+\rho) \rho}{9\sqrt{6} a^{3/2}}$ | $\frac{e^{-\rho/2} Z^{3/2} \rho^2}{9\sqrt{30} a^{3/2}}$ |

((Mathematica))

Plot of the probability of the wave function

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

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

```

average[n_, ℓ_] :=  $\frac{a}{2Z} (3n^2 - \ell(\ell+1)) /. \{a \rightarrow 1, Z \rightarrow 1\};$ 

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  $\frac{1}{n^{1.2}}$ }}, 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,

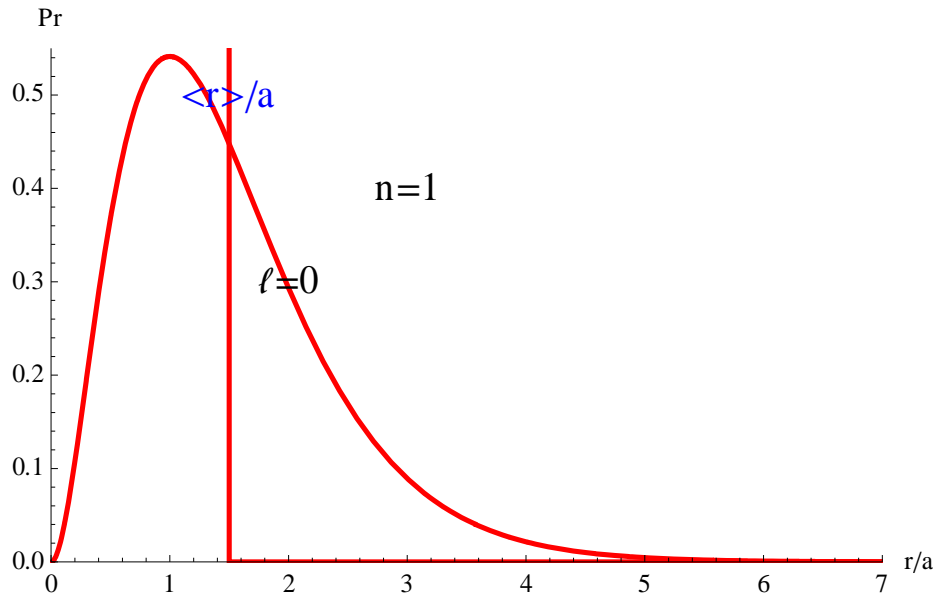


Fig. 1s ($n = 1, l = 0$). The straight line denotes the average value $\langle r \rangle / a$.

For the 2s, 2p states

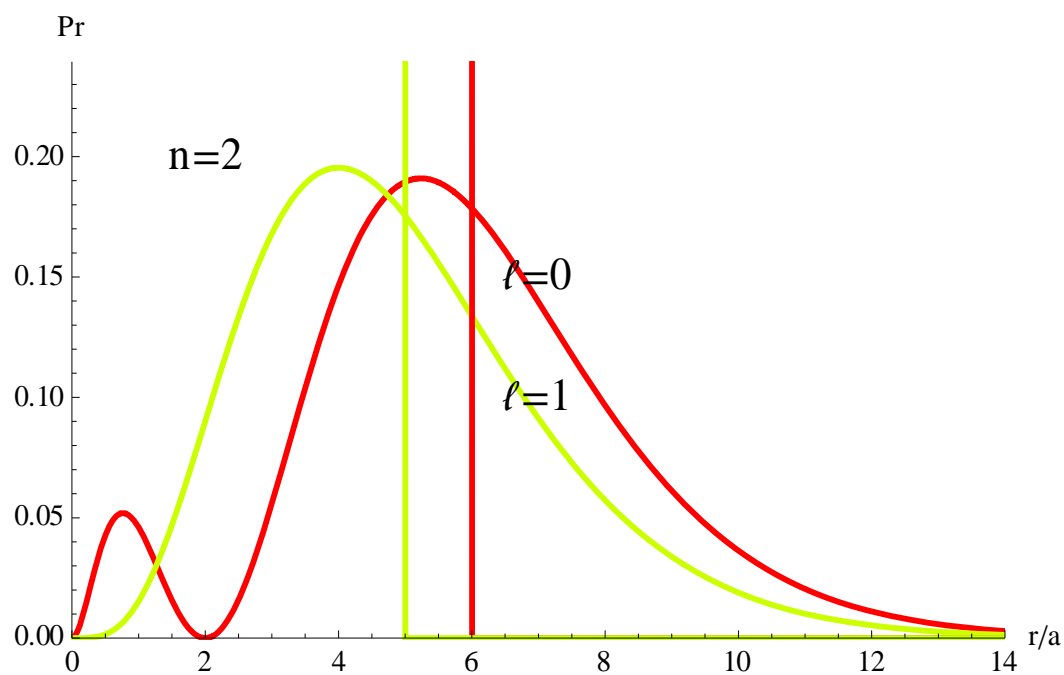


Fig. $2s$ ($n = 2, l = 0$). $2p$ ($n = 2, l = 1$). The straight lines denote the average value $\langle r \rangle/a$.

For the $3s$, $3p$, and $3d$ states,

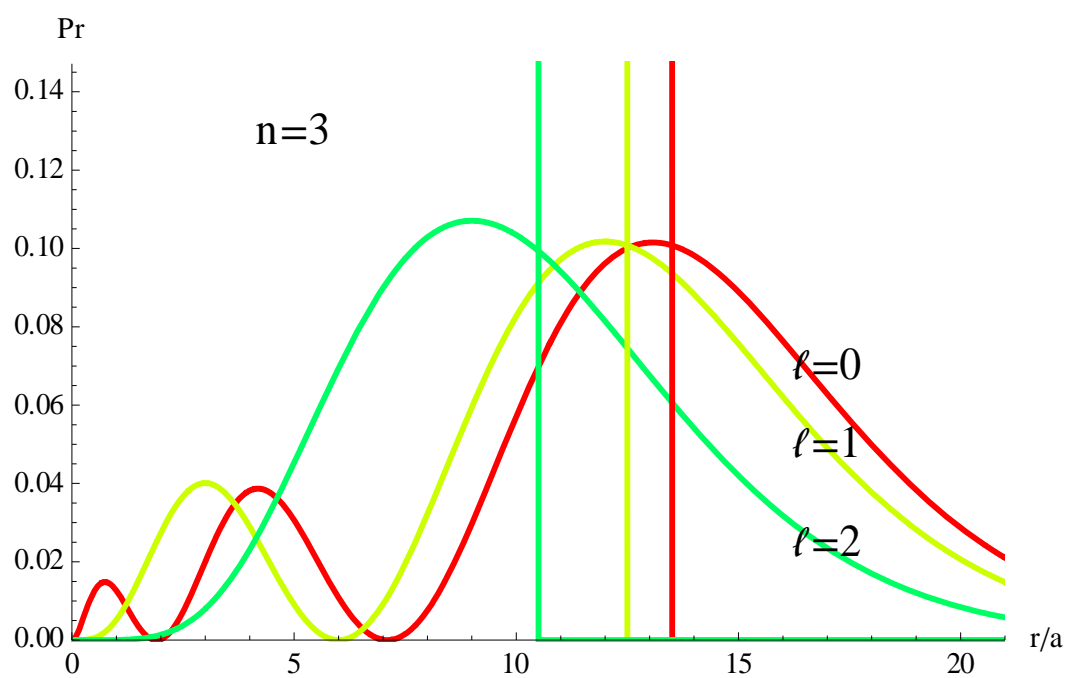


Fig. $3s$ ($n = 3, l = 0$). $3p$ ($n = 3, l = 1$). $3d$ ($n = 3, l = 2$). The straight lines denote the average value $\langle r \rangle/a$.

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

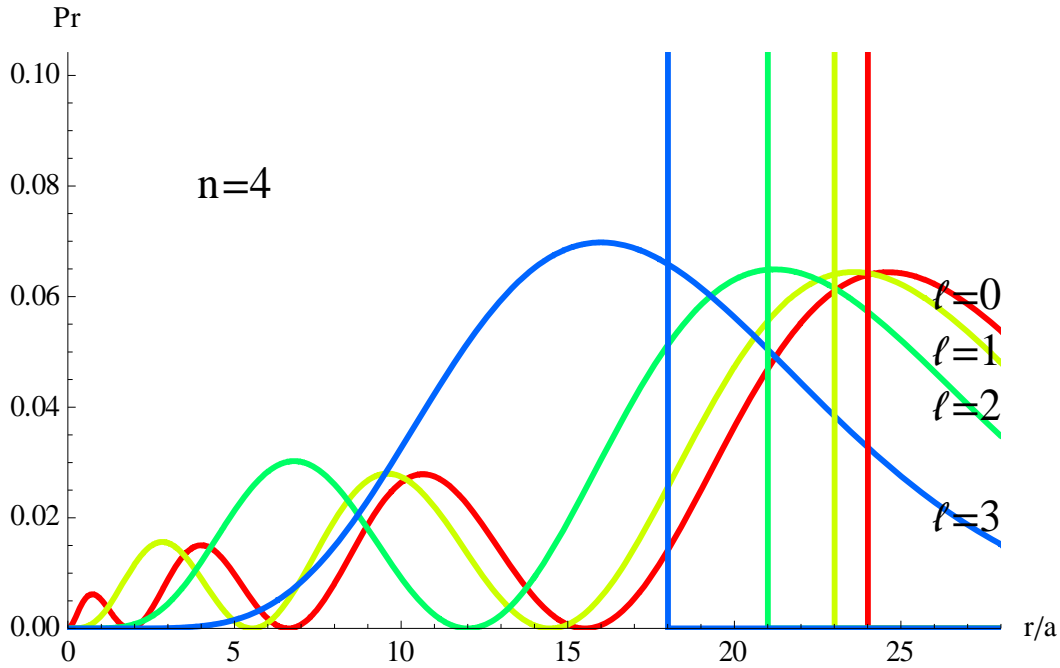


Fig. $4s$ ($n = 4, l = 0$). $4p$ ($n = 4, l = 1$). $4d$ ($n = 4, l = 2$). $4f$ ($n = 4, l = 3$). The straight lines denote the average value $\langle r \rangle/a$.

APPENDIX

A1. Derivation of the differential equation

Differential equation for the Radial component

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

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

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

Req1 = R''[r] - (R''[r] /. Rule1) == 0 /.  $\epsilon \rightarrow -\epsilon_1$ 

-  $\frac{R[r] (2 r^2 \epsilon_1 \mu + \ell (1 + \ell) \hbar^2 + 2 r^2 \mu V[r]) - 2 r \hbar^2 R'[r]}{r^2 \hbar^2} + R''[r] == 0$ 
```

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

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

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

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

Req5 = Req4 /. Replace1

-  $\frac{(-2 e^2 r \mu + 2 r^2 \epsilon_1 \mu + \ell \hbar^2 + \ell^2 \hbar^2) u[r]}{r^2 \hbar^2} + u''[r] == 0$ 
```

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 $|n,l,m\rangle$.

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

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

`vchange[Eq_, ψ _, x_, z_, f_] :=`

`Eq /. {D[ψ [x], {x, n_}] => Nest[$\left(\frac{1}{D[f, z]} D[\#, z] \&\right)$, $\psi[z], n$], $\psi[x] \rightarrow \psi[z], x \rightarrow f$ }`

`Ueq1 = vchange[Req5, u, r, ρ , $\frac{\hbar}{\sqrt{8 \mu \epsilon 1}} \rho$] // PowerExpand // FullSimplify`

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

`Ueq2 = Solve[Ueq1, u''[ρ]] // PowerExpand // Flatten;`

`Ueq3 = u''[ρ] - (u''[ρ] /. Ueq2) == 0; substitution = { $\mu \rightarrow \frac{\hbar^2}{a e^2}, \epsilon 1 \rightarrow \frac{e^2}{2 n^2} \frac{1}{a}$ };`

`Ueq4 = Ueq3 /. substitution // PowerExpand // Simplify; Ueq41 = Solve[Ueq4, u''[ρ]];`

`Ueq42 = u''[ρ] - (u''[ρ] /. Ueq41[[1]]) == 0 // Simplify`

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

`G[ρ _] := Exp[$\frac{-\rho}{2}$] ρ'^{+1} F[ρ];`

`Ueq43 = Ueq42 /. u -> G // Simplify`

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

`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]}`

$$\text{norm} = \left\{ C[1] \rightarrow 0, C[2] \rightarrow 2^{\ell+1} \left(\frac{1}{a n} \right)^{\ell} \sqrt{\frac{(n-\ell-1)!}{a^3 n^4 (n+\ell)!}} \right\};$$

$$\rho\text{wave}[n_, \ell_, \rho_] := G[\rho] /. \text{Ueq5} /. \text{norm} // \text{PowerExpand} // \text{Simplify};$$

$$\rho\text{wave}[n, \ell, \rho]$$

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

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

$$\rho 1 = \frac{\sqrt{8 \mu \epsilon 1}}{\hbar} r /. \left\{ \epsilon 1 \rightarrow \frac{e^2}{2 a n^2}, \mu \rightarrow \frac{\hbar^2}{a e^2} \right\} // \text{PowerExpand} // \text{Simplify};$$

$$r\text{wave}[n_, \ell_, r_] = \frac{\rho\text{wave}[n, \ell, \rho]}{r} /. \left\{ \rho \rightarrow \frac{2 r}{a n} \right\} // \text{PowerExpand}$$

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