Radial wave function of hydrogen-like atom

Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton
(Date February, 21, 2013)

1. The radial wave function for a hydrogen-like atom.

$$R_{nl}(r) = \sqrt{\frac{4Z^3(n-l-1)!}{a^3 n^4 (n+l)!}} e^{-\frac{Zr}{na}} \left(\frac{2Zr}{na}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na}\right)$$

where

$$\int_0^\infty dr r^2 [R_{nl}(r)]^2 = 1 \qquad \text{(the normalization condition)}$$

and

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

For the hydrogen atom, we have $Z = 1$ and $\mu = m$. $a = a_B$ (Bohr radius).

((Note))

(i)

$$r = \frac{\rho}{2\kappa}$$

(ii)

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

(iii)

$$R_{nl}(r) = \sqrt{\frac{4Z^3(n-l-1)!}{a^3 n^4 (n+l)!}} e^{-\frac{Zr}{na}} \left(\frac{2Zr}{na}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na}\right)$$

$$= A_{nl} e^{-\frac{\rho}{2}} \rho^l L_{n-l-1}^{2l+1}(\rho)$$

where

$$A_{nl} = \sqrt{\frac{4Z^3(n-l-1)!}{a^3 n^4 (n+l)!}} .$$

((**Mathematica**))

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

((**Laguerre polynomials**))

$L_{n-l-1}^{2l+1}(x)$ is the associated Laguerre polynomial.

n	$l=0$	$l=1$	$l=2$	$l=3$
1	1			
2	2-x	1		
3	$\frac{1}{2}(6-6x+x^2)$	$4-x$	1	
4	$\frac{1}{6}(24-36x+12x^2-x^3)$	$\frac{1}{2}(20-10x+x^2)$	$6-x$	1

((**Mathematica**))

	$\ell=0$	$\ell=1$	$\ell=2$	$\ell=3$	$\ell=4$
n=1	1				
n=2	$2-x$	1			
n=3	$\frac{1}{2}\left(6-6x+x^2\right)$	$4-x$	1		
n=4	$\frac{1}{6}\left(24-36x+12x^2-x^3\right)$	$\frac{1}{2}\left(20-10x+x^2\right)$	$6-x$	1	
n=5	$\frac{1}{24}\left(120-240x+120x^2-20x^3+x^4\right)$	$\frac{1}{6}\left(120-90x+18x^2-x^3\right)$	$\frac{1}{2}\left(42-14x+x^2\right)$	$8-x$	1

2. (n = 1 and l = 0) 1s state

The radial wave function is given by

$$R_{1,0} = \frac{2Z^{3/2}}{a^{3/2}} e^{-\frac{rZ}{a}} .$$

The probability density distribution $P(r)$ is defined by

$$P(r) = r^2 R_{1,0}{}^2 = \frac{4Z^3}{a^3} r^2 e^{-\frac{2rZ}{a}} ,$$

where $R_{1,0}{}^2$ is called the probability density and

$$P(r)dr = drr^2 R_{1,0}{}^2$$

is the probability for finding the electron in this state between r and r+dr. Note that

$$\int_0^\infty drP(r) = 1 .$$

Since

$$\frac{d}{dr} P(r) = \frac{8Z^3}{a^4} re^{-\frac{2rZ}{a}} (a - rZ) ,$$

$P(r)$ shows a peak at $r = \frac{a}{Z}$. The average of r is given by

$$\langle r \rangle = \int_0^\infty drrP(r) = \int_0^\infty drr^3 R_{1,0}{}^2 = \frac{3a}{2Z} .$$

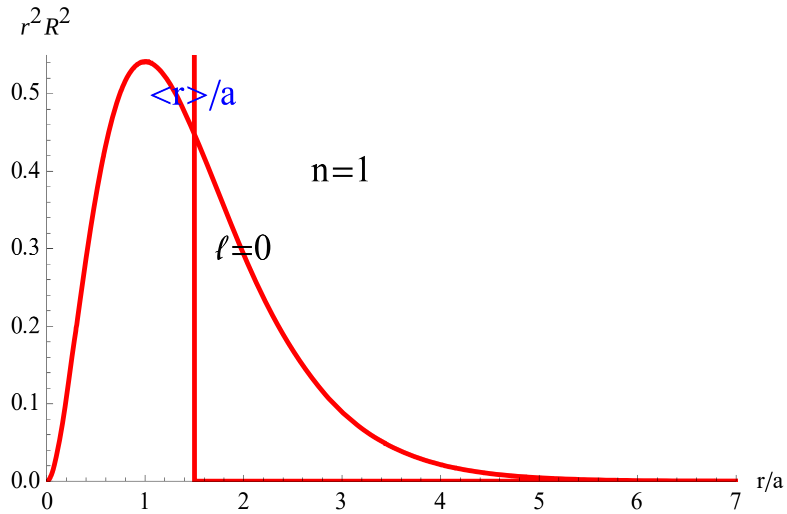


Fig. Radial probability distribution $P(r)$ for the ground state of hydrogen. $a = a_B$. $Z = 1$. $\mu = m$.

The cumulative probability density:

$$\int_0^r P(r)dr = 1 - e^{-\frac{2rZ}{a}}[1 + 2Z(\frac{r}{a}) + 2Z^2(\frac{r}{a})^2].$$

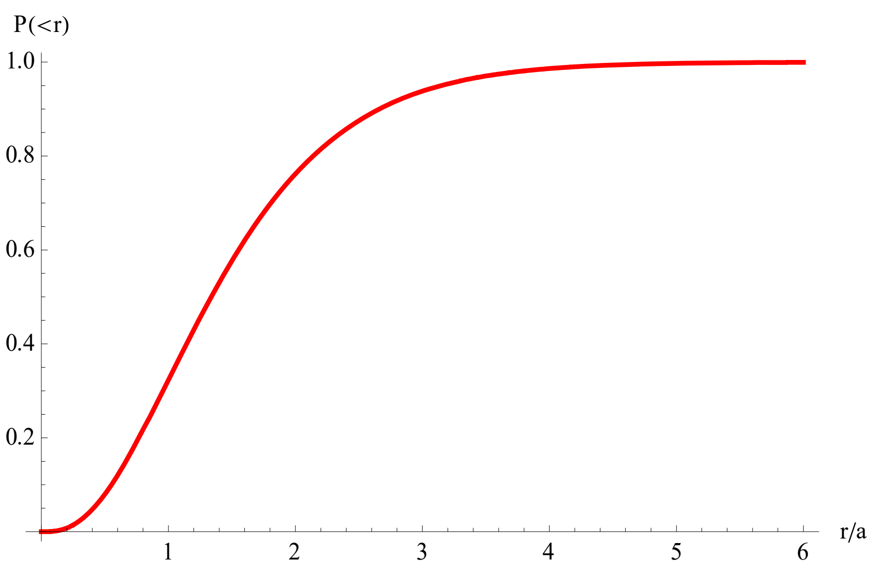


Fig. Cumulative probability density for the 2s state of hydrogen atom. $a = a_B$. $Z = 1$. $\mu = m$.

Average and uncertainty:

$$\left\langle r^p \right\rangle = \int_0^\infty dr r^p P(r) = \frac{1}{2^{p+1}}(\frac{a}{Z})^p (p+2)!,$$

where p is integer;

$$\langle r^2 \rangle = \frac{1}{2^3}(\frac{a}{Z})^2 4! = 3(\frac{a}{Z})^2 .$$

The standard deviation:

$$\frac{\sqrt{\langle r^2 \rangle - \langle r \rangle^2}}{\langle r \rangle} = \frac{1}{\sqrt{3}} .$$

((**Mathematica**))

Hydrogenic atom: Radial wave function

1s state (ground s tate)

```
Clear["Global`*"];
rwave[n_, ℓ_, r_] :=
 1/(√(n + ℓ)!)
  (2^(1+ℓ) a^(-ℓ-3/2) e^(-Z r/(a n)) n^(-ℓ-2) Z^(ℓ+3/2) r^ℓ √(n - ℓ - 1)!
    LaguerreL[-1 + n - ℓ, 1 + 2 ℓ, (2 Z r) / (a n)]);
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", "r²R²"}];
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}]}];
```

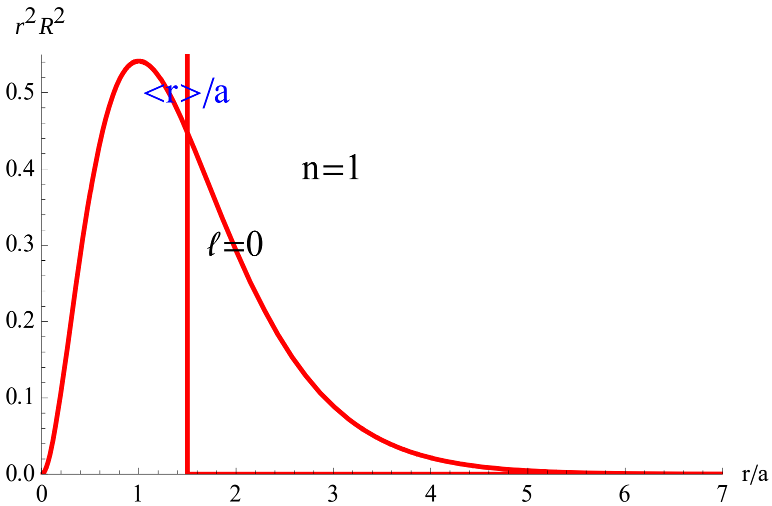
```
rwave[n, ℓ, r] /. {n → 1, ℓ → 0}
```

$$\frac{2\, e^{-\frac{r Z}{a}}\, Z^{3/2}}{a^{3/2}}$$

```
P1 = r^2 rwave[n, ℓ, r]^2 /. {n → 1, ℓ → 0}
```

$$\frac{4\, e^{-\frac{2 r Z}{a}}\, r^2\, Z^3}{a^3}$$

```
Show[p11[1], p12[1], g1]
```



```
D[P1, r] // Simplify
```

$$\frac{8\, e^{-\frac{2 r Z}{a}}\, r\, Z^3\, (a - r Z)}{a^4}$$

Average and standard deviation (uncertainty)

```
K[p_] = Integrate[r^p P1, {r, 0, ∞}] // Simplify[#, {p > -3, Re[Z/a] > 0}] &;

Table[K[p], {p, -2, 3}] // TableForm[#,
   TableHeadings → {{"p=-2", "p=-1", "p=0", "p=1", "p=2", "p=3"}}] &
```

p=-2	$\frac{2 Z^2}{a^2}$
p=-1	$\frac{Z}{a}$
p=0	1
p=1	$\frac{3 a}{2 Z}$
p=2	$\frac{3 a^2}{Z^2}$
p=3	$\frac{15 a^3}{2 Z^3}$

```
k12 = Sqrt[K[2] - K[1]^2] // Simplify
```

$$\frac{1}{2} \sqrt{3} \sqrt{\frac{a^2}{Z^2}}$$

```
k12/K[1] // Simplify[#, {Z > 0, a > 0}] &
```

$$\frac{1}{\sqrt{3}}$$

```
K[p]
```

$$2^{-1-p} \left(\frac{Z}{a}\right)^{-p} \text{Gamma}[3 + p]$$

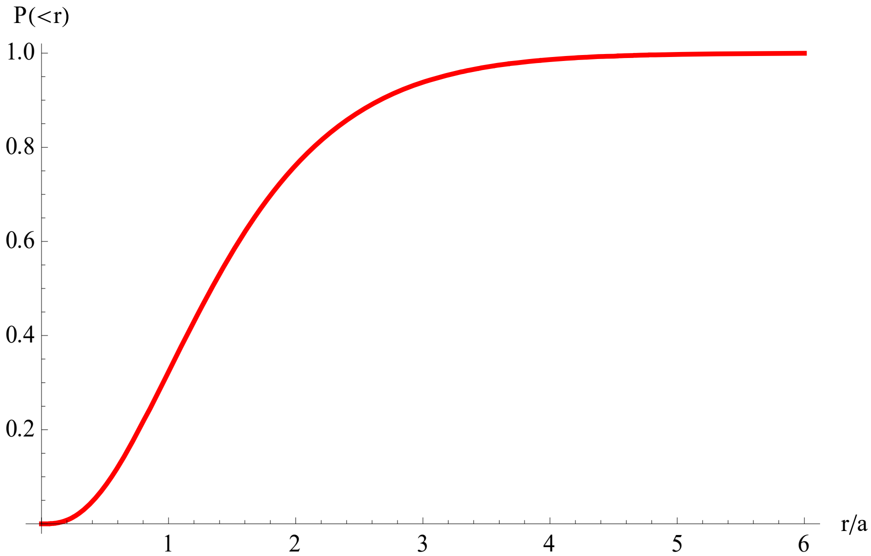
Cumulative probability

```
g1 = Integrate[P1, {r, 0, r}] // Simplify
```

$$1 - \frac{e^{-\frac{2 r Z}{a}} \left(a^2 + 2 a r Z + 2 r^2 Z^2\right)}{a^2}$$

```
g11 = g1 /. {Z → 1, a → 1};

Plot[g11, {r, 0, 6}, PlotStyle → {Red, Thick}, AxesLabel → {"r/a", "P(<r)"}]
```



---

3. ($n = 2$ and $l = 0$) 2s state

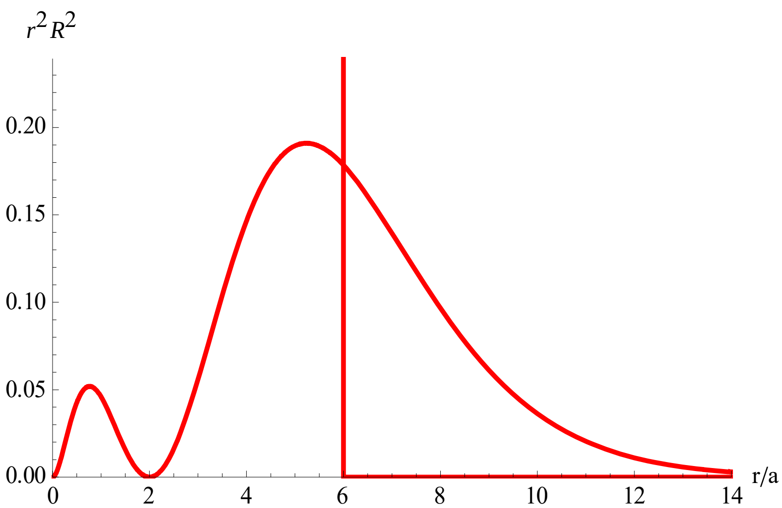


Fig. Radial probability distribution $P(r)$ for the 2s state of hydrogen. $a = a_B$. $Z = 1$. $\mu = m$. The local maxima are at $r/a = 0.7639$, and 5.236. The local minimum is at $r/a = 0$, and 2.

The radial wave function:

$$R_{2,0} = \frac{Z^{3/2}}{2\sqrt{2}a^{3/2}} e^{-\frac{rZ}{2a}} (2 - \frac{rZ}{a}).$$

The probability:

$$P(r) = r^2 R_{2,0}{}^2 = \frac{Z^3}{8a^3} e^{-\frac{rZ}{a}} r^2 (2 - \frac{rZ}{a})^2.$$

Since

$$\frac{d}{dr} P(r) = \frac{Z^3}{8a^6} e^{-\frac{rZ}{a}} r(2a - rZ)(4a^2 - 6arZ + r^2 Z^2),$$

$P(r)$ shows local maxima at

$$r = \frac{(3-\sqrt{5})a}{Z}, \qquad r = \frac{(3+\sqrt{5})a}{Z}$$

and a local minimum at

$$r = \frac{2a}{Z}$$

The average of r^{p} is given by

$$\langle r^p \rangle = \int_0^\infty dr r^p P(r) = \left(\frac{4 + 3p + p^2}{8} \right) \left(\frac{a}{Z} \right)^p (p+2)!$$

For $p = 1$, we have

$$\langle r \rangle = 6\left(\frac{a}{Z} \right).$$

For $p = 2$, we have

$$\langle r^2 \rangle = 42\left(\frac{a}{Z} \right)^2$$

The uncertainty for r is

$$\frac{\sqrt{\langle r^2\rangle - \langle r\rangle^2}}{\langle r\rangle} = \frac{1}{\sqrt{6}}$$

The cumulative probability is

$$\int_0^r P(r)dr = 1 - e^{-\frac{Zr}{a}}[1 + \left(\frac{Zr}{a}\right) + \frac{1}{2}\left(\frac{Zr}{a}\right)^2 + \frac{1}{8}\left(\frac{Zr}{a}\right)^4]$$

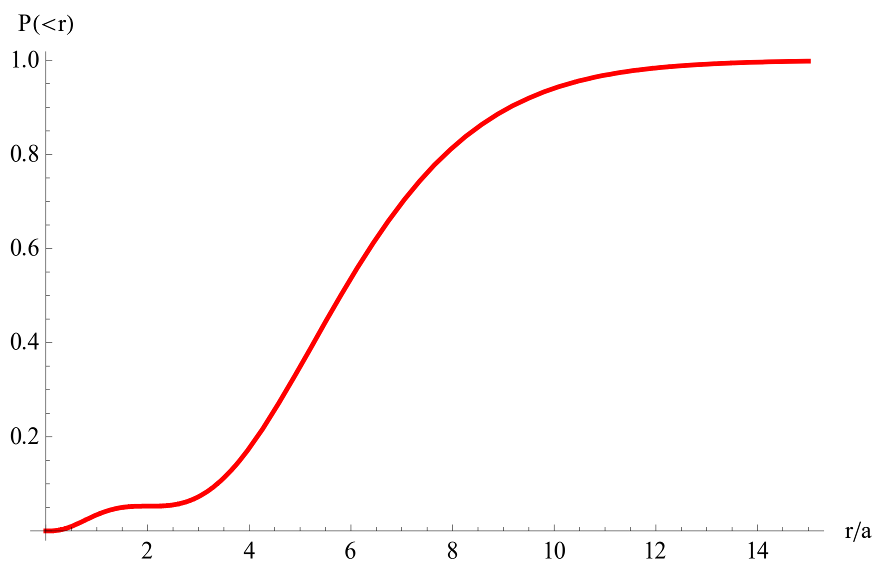


Fig. Cumulative probability density for the 2s state of hydrogen atom. $a = a_B$. $Z = 1$. $\mu = m$.

3. (n = 3 and l = 0) 3s state

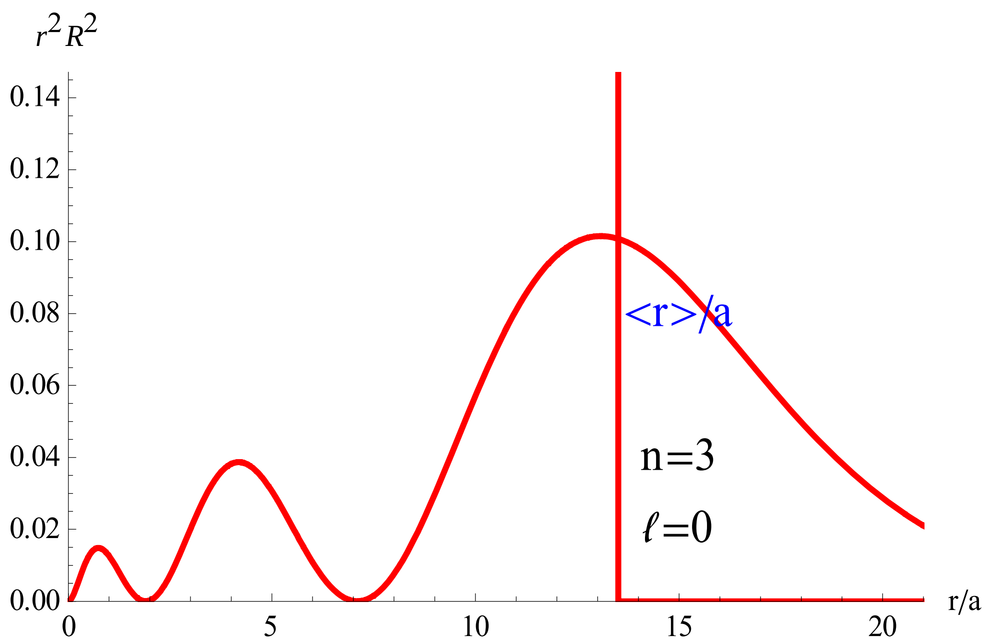


Fig. Radial probability distribution $P(r)$ for the 3s state of hydrogen. $a = a_B$. $Z = 1$. $\mu = m$. The local maxima are at $r/a = 0.740$, 4.186, and 13.07. The local minimum is at $r/a = 0$, 1.9019, 7.098.

The radial wave function:

$$R_{3,0} = \frac{2Z^{3/2}}{81\sqrt{3}a^{7/2}} e^{-\frac{rZ}{3a}} [27 - 18\left(\frac{rZ}{a}\right) + 2\left(\frac{rZ}{a}\right)^2].$$

The probability:

$$P(r) = r^2 R_{3,0}{}^2.$$

Since

$$\frac{d}{dr} P(r) = 0,$$

$P(r)$ shows local maxima at

$$r = 13.074\frac{a}{Z}, \qquad r = 4.18593\frac{a}{Z}, \qquad r = 0.740037\frac{a}{Z}$$

The average of r^p is given by

$$\langle r^p \rangle = \int_0^\infty dr r^p P(r)$$

For $p = 1$, we have

$$\langle r \rangle = \frac{27}{2}\left(\frac{a}{Z}\right).$$

For $p = 2$, we have

$$\langle r^2 \rangle = 207\left(\frac{a}{Z}\right)^2$$

The uncertainty for r is

$$\frac{\sqrt{\langle r^2 \rangle - \langle r \rangle^2}}{\langle r \rangle} = \frac{\sqrt{11}}{9}$$

The cumulative probability is

$$P(< r) = \int_0^r P(r) dr$$

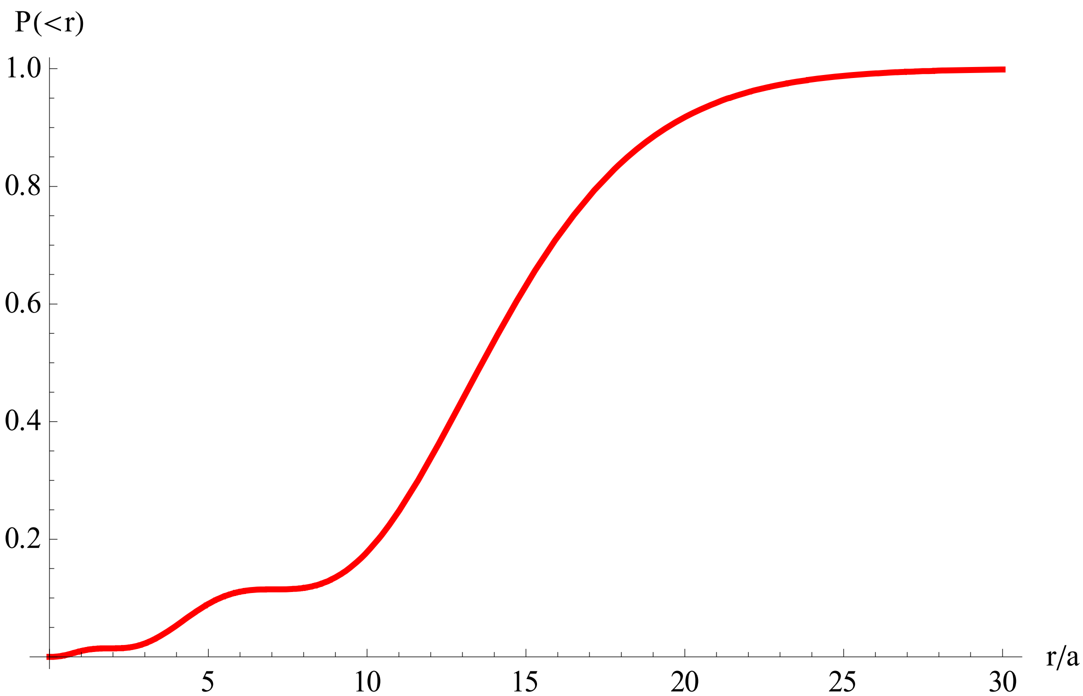


Fig. Cumulative probability density for the 3s state of hydrogen atom. $a = a_B$. $Z = 1$. $\mu = m$.

4. Radial probability distribution

The following figures show radial probability distribution $P(r) = r^2[R(r)]^2 P(r)$ for a number of (n, l) states. For given (n, l), there are number of radii where the value of $P(r)$ is zero (nodes). In general the number of such nodes is given by

$$n - l - 1 .$$

The number of peaks is then given by

$$n - l .$$

If one looks carefully, at the figures, it appears that the electron will on average reside closest to the nucleus when $l = n - 1$

(a) $n = 1$ (ground state)

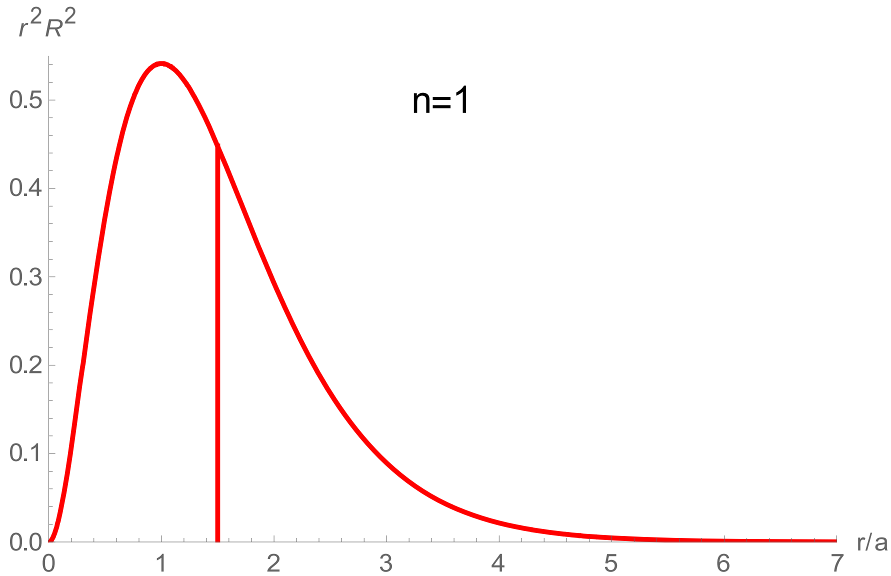


Fig. n = 1. l = 0 (red). The red straight line: average distance.

(b) n = 2

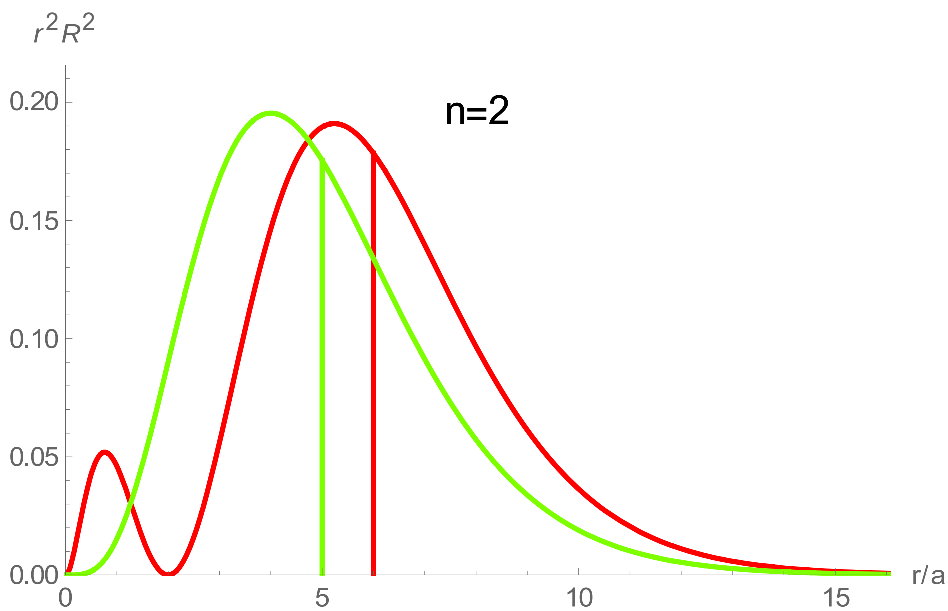


Fig. n = 2. l = 0 (red) and l = 1 (green).

(c) n = 3

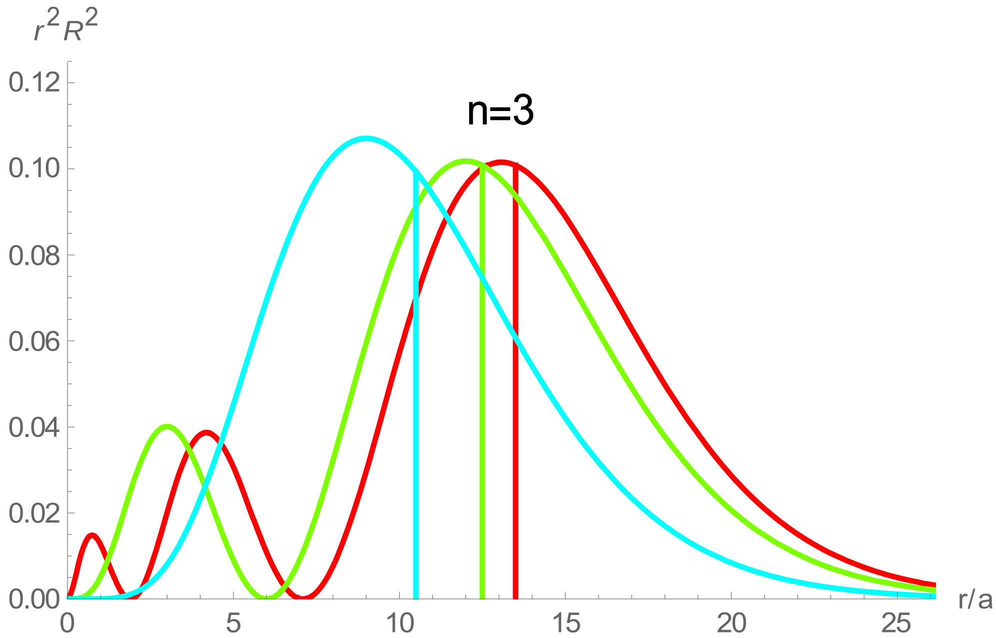


Fig. $n = 3$. $l = 0$ (red), $l = 1$ (green), and $l = 2$ (blue).

(d) $n = 4$

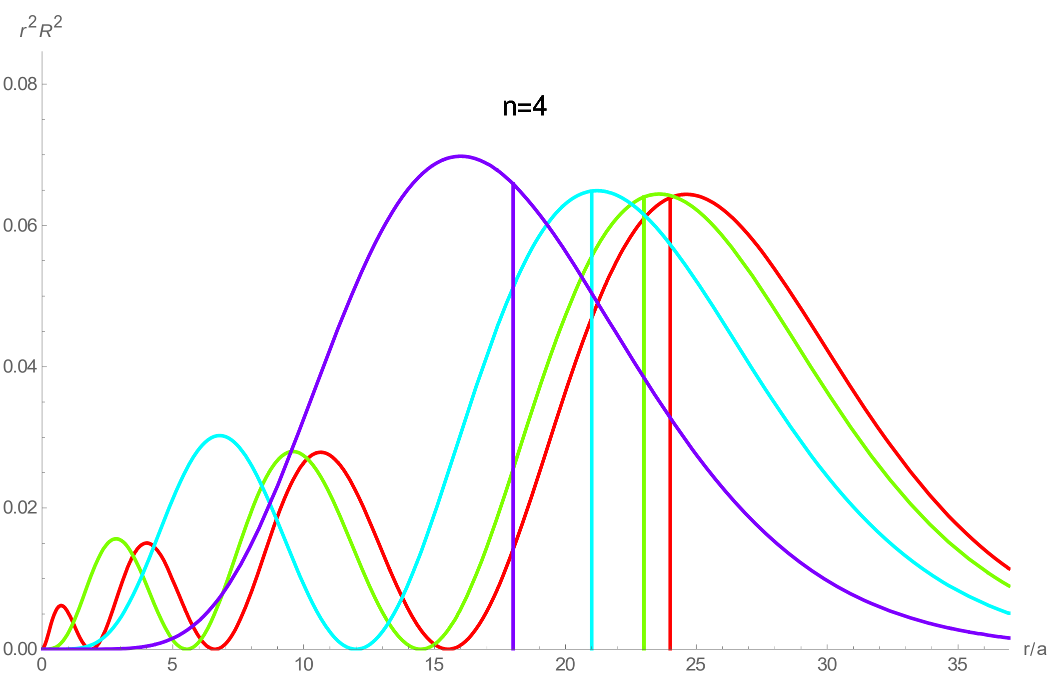


Fig. $n = 4$. $l = 0$ (red), $l = 1$ (green), $l = 2$ (blue) and $l = 3$ (purple).

REFERENCES

B.C. Reed, Quantum Mechanics (Jones and Bartlett Publishers, Sandbury MA, 2008).