
WorkBookQM. 18 The hydrogen atom

- This is the corrected version of the WorkBookQM.18 given on the CD with Physical Chemistry Quantum Mechanics
- **WorkBookQM.18.1. The Coulomb interaction energy**

Define a function that gives Coulomb interaction energy between the proton and the electron in eV, when r is given in Å
Use

$$V(r) = \frac{e^2}{4\pi\epsilon_0 r^2}$$

Use SI units to get V in joule. The conversion from meter to Å is

$$1 \text{ m} = 10^{10} \text{ Å}$$

and

$$1 \text{ joule} = 6.242 * 10^{18} \text{ eV}$$

```
Off[Remove::rmnsm]
Remove["Global`*"]
```

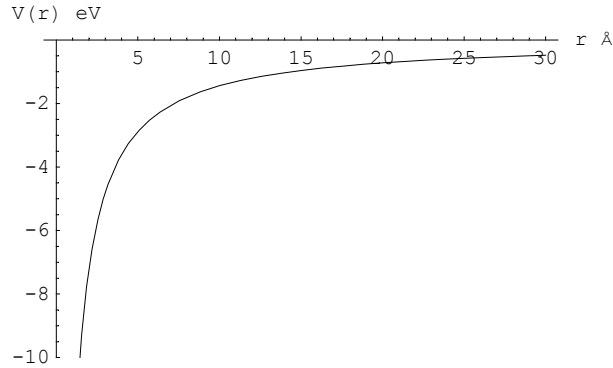
```
V[r_(*in A*)] := With[{e = 1.602177 * 10^-19 (*Coulomb*),
  ε0 = 8.854187 * 10^-12 (*C^2 / (N m^2)*),
  convertJtoeV = 6.242 * 10^18,
  AtoM = 10^-10 (*converts A to meter*)},
  -convertJtoeV * e^2 / (4 Pi ε0 r * AtoM)]
```

Check that the function works:

```
V[1]
```

```
-14.4008
```

```
Plot[V[r], {r, 0, 30}, PlotRange -> {-10, 0}, AxesLabel -> {"r Å", "V(r) eV"}]
```



- Graphics -

Note two things: the interaction energy goes to $-\infty$ when $r \rightarrow 0$ and the interaction is very long ranged. It is not zero even when $r = 30 \text{ \AA}$

■ WorkBookQM.18. 2. The energy of the hydrogen atom

The energy is given by :

$$E_n = \frac{\mu e^4}{2(4\pi\epsilon_0)^2 \hbar^2} \frac{Z}{n^2} \quad n=1, 2, 3, \dots \quad \text{SI units}$$

with the reduced mass

$$\mu = \frac{m_e m_N}{m_e + m_N}$$

The values of the constants are

$$m_e = 9.109389 \times 10^{-31} \text{ kg}$$

$$m_p = 1.672623 \times 10^{-27} \text{ kg}$$

$$e = 1.602177 \times 10^{-19} \text{ Coulomb,}$$

$$\epsilon_0 = 8.854187 \times 10^{-12} \text{ Coulomb Newton}^{-1} \text{ meter}^{-2},$$

$$\hbar = 1.054572 \times 10^{-34} \text{ J sec,}$$

$$1 \text{ joule} = 10^7 * 6.2420 * 10^{11} \text{ eV}$$

Define a function that gives the energy of the hydrogen atom in eV

```
Needs["Utilities`CleanSlate`"]
```

```
CleanSlate[]
```

```
Remove["Global`*"]
```

```
(CleanSlate) Contexts purged: {Global`}
```

```
(CleanSlate) Approximate kernel memory recovered: 13 Kb
```

```
{Utilities`CleanSlate`, Global`, System`}
```

■ Cell 1: Calculate the energy and make an energy level diagram for H

```

Clear[energyH];
energyH[n_] :=
Module[{me = 9.109389 * 10^-31 (*kg*),
        mp = 1.672623 * 10^-27 (*kg*),
        e = 1.602177 * 10^-19 (*Coulomb*),
        ε0 = 8.854187 * 10^-12 (*C Newton^-1 meter^-2*),
        ħ = 1.054572 * 10^-34 (*J sec*),
        JToeV = 10^7 * 6.2420 * 10^11, R, μ},
  μ = me * mp / (me + mp);
  R = JToeV * μ * e^4 / (2 (4 Pi ε0 ħ)^2);
  -R / n^2]

```

Test the function:

```

energyH[n] (*eV*)

```

$$-\frac{13.5994}{n^2}$$

Make a table with the energies for various values of n:

```
Table[{n, energyH[n]}, {n, 1, 30}] // TableForm[#, TableHeadings -> {None, {"n", "En eV"}}] &
```

n	E _n eV
1	-13.5994
2	-3.39984
3	-1.51104
4	-0.849961
5	-0.543975
6	-0.37776
7	-0.277538
8	-0.21249
9	-0.167894
10	-0.135994
11	-0.112392
12	-0.0944401
13	-0.0804697
14	-0.0693846
15	-0.0604417
16	-0.0531226
17	-0.0470567
18	-0.0419734
19	-0.0376714
20	-0.0339984
21	-0.0308376
22	-0.0280979
23	-0.0257077
24	-0.02361
25	-0.021759
26	-0.0201174
27	-0.0186548
28	-0.0173461
29	-0.0161705
30	-0.0151104

Note that as n increases the energies get closer and closer together and closer and closer to zero. The states having high values of n are called Rydberg states and. All atoms and all molecules have Rydberg states.

Make an energy level diagram. Create horizontal lines at coordinates equal to the energy of the atom.

```
energies = Table[ln[n] = Line[{{0, energyH[n]}, {1, energyH[n]}], {n, 1, 10}]
{Line[{{0, -13.5994}, {1, -13.5994}}], Line[{{0, -3.39984}, {1, -3.39984}}],
Line[{{0, -1.51104}, {1, -1.51104}}], Line[{{0, -0.849961}, {1, -0.849961}}],
Line[{{0, -0.543975}, {1, -0.543975}}], Line[{{0, -0.37776}, {1, -0.37776}}],
Line[{{0, -0.277538}, {1, -0.277538}}], Line[{{0, -0.21249}, {1, -0.21249}}],
Line[{{0, -0.167894}, {1, -0.167894}}], Line[{{0, -0.135994}, {1, -0.135994}}]}
```

```
Show[Graphics[#] & /@energies , Axes → True];
```



■ Cell 2: The effect of mass

Calculate the energy in the case when the nuclear mass is infinity (in this case the reduced mass equals the electron mass)

```
Clear[energyHInfNucl];
energyHInfNucl[n_] :=
Module[{me = 9.109389 * 10^-31 (*kg*),
        mp = 1.672623 * 10^-27 (*kg*),
        e = 1.602177 * 10^-19 (*Coulomb*),
        ε0 = 8.854187 * 10^-12 (*C Newton^-1 meter^-2*),
        ħ = 1.054572 * 10^-34 (*J sec*),
        JToeV = 10^7 * 6.2420 * 10^11, R},
  μ = me;
  R = JToeV * μ * e^4 / (2 (4 Pi ε0 ħ)^2);
  -R/n^2] (*gives the energy in eV*)

energyHInfNucl[n]
- 13.6068
  n^2

energyH[n]
- 13.5994
  n^2
```

Calculate the energy of the photon causing the transition

$$\{n=1\} \rightarrow \{n=2\}$$

for infinite nuclear mass and for the real mass. For the real mass:

```
eH = energyH[2] - energyH[1]
10.1995
```

For infinite nuclear mass:

```
eInf = energyHInfNucl[2] - energyHInfNucl[1]
```

```
10.2051
```

The difference is:

```
eInf - eH
```

```
0.00555484
```

This energy difference is detectable in the laboratory.

■ WorkBookQM.18. 3. The radial wave functions $R_{n,\ell}(r)$ and $\Phi_{n,\ell}(r)$: the definitions and expressions for various values of n and ℓ

The definition of the radial wave function is:

$$R_{n,\ell}(r) = \left(\frac{2Z}{na}\right)^{3/2} \Phi_{n,\ell}(\rho) \quad (1)$$

$$\Phi_{n,\ell}(r) = \sqrt{\frac{(n-\ell-1)!}{(n+\ell)! 2^n}} \left(\frac{2Z\rho}{n}\right)^\ell \text{Exp}\left[-\frac{Z\rho}{n}\right] L_{n-\ell-1}^{2\ell+1}\left(\frac{2Z\rho}{n}\right) \quad (2)$$

with

$$\rho = \frac{r}{a} \quad (3)$$

and

$$a = \frac{\hbar^2(4\pi\epsilon_0)}{\mu e^2} \quad (4)$$

In many books the general equations (1)-(3) are erroneous: they do not generate the examples given in the same books (i.e. the expression for $R_{2,1}(r)$ obtained from their general formula do not agree with the function $R_{2,1}(r)$ given in the same book).

Define a function that generates $\Phi_{n,\ell}(\rho)$

```
Unprotect[Φ];
Clear[Φ]; Unprotect[a, Z]; Clear[a, Z]; Protect[a, Z];
Φ[n_Integer, ℓ_Integer][ρ_] := Module[{const},
const = Sqrt[ $\frac{(n - \ell - 1)!}{(n + \ell)! 2^n}$ ];
const (2 Z ρ / n) ^ ℓ LaguerreL[n - ℓ - 1, 2 ℓ + 1,  $\frac{2 Z \rho}{n}$ ] Exp[- $\frac{Z \rho}{n}$ ]]
Protect[Φ];
```

Check that Φ works properly:

```
Φ[3, 2][ρ]
```

$$\frac{e^{-\frac{2\rho}{3}} Z^2 \rho^2}{27 \sqrt{5}}$$

Define a function that generates $R_{n,\ell}(r)$

```
Unprotect[R];
Clear[R];
R[n_, l_][r_] := (2 Z / (n a)) ^ (3 / 2) B[n, l][r / a]
Protect[R];
```

See if $R_{n,\ell}(r)$ works

```
R[1, 0][r]
2 e^{-r Z / a} (Z / a)^{3/2}
```

I made below a table with the radial function $R_{n,\ell}(r)$ and I compared my results with those given by W. H. Flygare, Molecular Structure and Dynamics, Prentice Hall, Inc., Englewood Cliffs, New Jersey, 1978, p.144. My functions agree with Flygare's. They also agree with the functions given by Pauling and Wilson for specific values of n and ℓ . However their general formula Eq. 20-11 (in the Dover edition of Pauling and Wilson) does not agree with the examples given by them.

```
Table[{n, l, (R[n, l][r] // Simplify // Cancel)
}, {n, 1, 4}, {l, 0, n - 1}] // Flatten[#, 1] & //
TableForm[#, TableHeadings -> {None, {"n", "l", "R_{n,l}(r)"}}] &
```

n	l	$R_{n,\ell}(r)$
1	0	$2 e^{-\frac{rZ}{a}} \left(\frac{Z}{a}\right)^{3/2}$
2	0	$\frac{e^{-\frac{rZ}{2a}} Z \sqrt{\frac{Z}{a}} (2a - rZ)}{2\sqrt{2} a^2}$
2	1	$\frac{e^{-\frac{rZ}{2a}} r \left(\frac{Z}{a}\right)^{5/2}}{2\sqrt{6}}$
3	0	$\frac{2 e^{-\frac{rZ}{3a}} Z \sqrt{\frac{Z}{a}} (27 a^2 - 18 a r Z + 2 r^2 Z^2)}{81 \sqrt{3} a^3}$
3	1	$\frac{2 \sqrt{\frac{2}{3}} e^{-\frac{rZ}{3a}} r Z^2 \sqrt{\frac{Z}{a}} (6 a - r Z)}{81 a^3}$
3	2	$\frac{2}{81} \sqrt{\frac{2}{15}} e^{-\frac{rZ}{3a}} r^2 \left(\frac{Z}{a}\right)^{7/2}$
4	0	$\frac{e^{-\frac{rZ}{4a}} Z \sqrt{\frac{Z}{a}} (192 a^3 - 144 a^2 r Z + 24 a r^2 Z^2 - r^3 Z^3)}{768 a^4}$
4	1	$\frac{e^{-\frac{rZ}{4a}} r Z^2 \sqrt{\frac{Z}{a}} (80 a^2 - 20 a r Z + r^2 Z^2)}{256 \sqrt{15} a^4}$
4	2	$\frac{e^{-\frac{rZ}{4a}} r^2 Z^3 \sqrt{\frac{Z}{a}} (12 a - r Z)}{768 \sqrt{5} a^4}$
4	3	$\frac{e^{-\frac{rZ}{4a}} r^3 Z^3 \left(\frac{Z}{a}\right)^{3/2}}{768 \sqrt{35} a^3}$

To compare to Pauling and Wilson I use their variable

$$\rho \equiv \frac{2Zr}{na}$$

Make a table of $R_{n\ell}(\rho)$ with this variable

```
Table[{n, l, (R[n, l][r] /. r -> rho n a / (2 Z)) // Cancel
}, {n, 1, 4}, {l, 0, n - 1}] // Flatten[#, 1] & //
TableForm[#, TableHeadings -> {None, {"n", "l", "R_{n,l}(r)"}}] &
```

n	l	$R_{n,l}(r)$
1	0	$2 e^{-\rho/2} \left(\frac{Z}{a}\right)^{3/2}$
2	0	$-\frac{e^{-\rho/2} Z \sqrt{\frac{Z}{a}} (-2+\rho)}{2\sqrt{2} a}$
2	1	$\frac{e^{-\rho/2} \left(\frac{Z}{a}\right)^{3/2} \rho}{2\sqrt{6}}$
3	0	$\frac{e^{-\rho/2} Z \sqrt{\frac{Z}{a}} (6-6\rho+\rho^2)}{9\sqrt{3} a}$
3	1	$-\frac{e^{-\rho/2} Z \sqrt{\frac{Z}{a}} (-4+\rho) \rho}{9\sqrt{6} a}$
3	2	$\frac{e^{-\rho/2} \left(\frac{Z}{a}\right)^{3/2} \rho^2}{9\sqrt{30}}$
4	0	$-\frac{e^{-\rho/2} Z \sqrt{\frac{Z}{a}} (-24+36\rho-12\rho^2+\rho^3)}{96 a}$
4	1	$\frac{e^{-\rho/2} Z \sqrt{\frac{Z}{a}} \rho (20-10\rho+\rho^2)}{32\sqrt{15} a}$
4	2	$-\frac{e^{-\rho/2} Z \sqrt{\frac{Z}{a}} (-6+\rho) \rho^2}{96\sqrt{5} a}$
4	3	$\frac{e^{-\rho/2} \left(\frac{Z}{a}\right)^{3/2} \rho^3}{96\sqrt{35}}$

The functions in the table are the same as those of Pauling and Wilson, p. 135 (Dover edition)

In the textbook I prefer to use the dimensionless function $\Phi_{n,l}(\rho)$ which I display below (for $Z=1$):


```
radf = Table[{n, ℓ, (Φ[n, ℓ][ρ] /. Z → 1 // Simplify) // Cancel},
  {n, 1, 4}, {ℓ, 0, n - 1}] // Flatten[#, 1] &;
TableForm[radf, TableSpacing → {5, 3}, TableHeadings → {None, {"n", "ℓ", "Φ[n, ℓ][ρ]"}},
  TableSpacing → {3, 5}]
```

n	ℓ	Φ[n, ℓ][ρ]
1	0	$\frac{e^{-\rho}}{\sqrt{2}}$
2	0	$-\frac{e^{-\rho/2}(-2+\rho)}{2\sqrt{2}}$
2	1	$\frac{e^{-\rho/2}\rho}{2\sqrt{6}}$
3	0	$\frac{e^{-\rho/3}(27-18\rho+2\rho^2)}{27\sqrt{2}}$
3	1	$-\frac{1}{27}e^{-\rho/3}(-6+\rho)\rho$
3	2	$\frac{e^{-\rho/3}\rho^2}{27\sqrt{5}}$
4	0	$-\frac{e^{-\rho/4}(-192+144\rho-24\rho^2+\rho^3)}{192\sqrt{2}}$
4	1	$\frac{e^{-\rho/4}\rho(80-20\rho+\rho^2)}{64\sqrt{30}}$
4	2	$-\frac{e^{-\rho/4}(-12+\rho)\rho^2}{192\sqrt{10}}$
4	3	$\frac{e^{-\rho/4}\rho^3}{192\sqrt{70}}$

■ WorkBookQM.18. 4. Test orthonormality

$$\int_0^\infty r^2 R_{n,\ell}(r)^* R_{n',\ell'}(r) dr = \delta_{n,n'}$$

Copy the function R[n,ℓ][r], which defines the radial wave function, from WorkBookQM.18.3 :

```

Off[Remove::rmptc] (*this removes some annoying and irrelevant messages*)
Off[Remove::relex] (*this removes some annoying and irrelevant messages*)
Needs["Utilities`CleanSlate`"]
CleanSlate[]
Remove["Global`*"]
Off[General::spell1]
Off[General::spell]

(CleanSlate) Contexts purged: {Global`}

(CleanSlate) Approximate kernel memory recovered: 37 Kb

{Utilities`CleanSlate`, Global`, System`}

```

Redefine the functions Φ and R:

```

Unprotect[ $\Phi$ ];
Clear[ $\Phi$ ]; Unprotect[a, Z]; Clear[a, Z]; Protect[a, Z];
 $\Phi$ [n_Integer,  $\ell$ _Integer][ $\rho$ _] := Module[{const},
const = Sqrt[ $\frac{(n - \ell - 1)!}{(n + \ell)! 2^n}$ ];
const (2 Z  $\rho$  / n) ^  $\ell$  LaguerreL[n -  $\ell$  - 1, 2  $\ell$  + 1,  $\frac{2 Z \rho}{n}$ ] Exp[- $\frac{Z \rho}{n}$ ]]
Protect[ $\Phi$ ];

```

Define a function that generates $R_{n,\ell}(r)$

```

Unprotect[R];
Clear[R];
R[n_,  $\ell$ _][r_] := (2 Z / (n a)) ^ (3 / 2)  $\Phi$ [n,  $\ell$ ][r / a]
Protect[R];

```

Test that

$$\int_0^\infty r^2 R_{n,\ell}(r) dr = 1$$

meaning that the radial functions are normalized

```

Integrate[Expand[r^2 R[2, 1][r]^2] // Evaluate,
{r, 0, Infinity}, GenerateConditions -> False]
1
Table[Integrate[Expand[r^2 R[n,  $\ell$ ][r]^2], {r, 0, Infinity}, GenerateConditions -> False],
{n, 1, 5}, { $\ell$ , 0, n - 1}]
{{1}, {1, 1}, {1, 1, 1}, {1, 1, 1, 1}, {1, 1, 1, 1, 1}}

```

Now let me check the orthogonality:

$$\int_0^\infty r^2 R_{n,\ell}(r) R_{m,\ell}(r) dr = \delta_{n,m}$$

The integral must be zero if n differs from m and the two functions have the same value for ℓ .

Below I examine the case when n differs from m and $\ell = 0$ in both functions.

```

totable = Table[{n, m, Integrate[Expand[r^2 R[n, 0][r] * R[m, 0][r]],
  {r, 0, Infinity}, GenerateConditions -> False]},
  {n, 1, 3}, {m, n + 1, 4}] // Flatten[#, 1] &
{1, 2, 0}, {1, 3, 0}, {1, 4, 0}, {2, 3, 0}, {2, 4, 0}, {3, 4, 0}}

TableForm[totable, TableHeadings -> {None, {"n", "m", "integral"}}]

```

n	m	integral
1	2	0
1	3	0
1	4	0
2	3	0
2	4	0
3	4	0

Below I calculate the integrals for different principal quantum numbers in the two functions, but with $\ell = 1$ in both functions:

```

totable = Table[{n, m, Integrate[Expand[r^2 R[n, 1][r] * R[m, 1][r]],
  {r, 0, Infinity}, GenerateConditions -> False]},
  {n, 2, 4}, {m, n + 1, 4}] // Flatten[#, 1] &
{2, 3, 0}, {2, 4, 0}, {3, 4, 0}}

TableForm[totable, TableHeadings -> {None, {"n", "m", "integral"}}]

```

n	m	integral
2	3	0
2	4	0
3	4	0

Integrals in which $n \neq n'$ and $\ell \neq \ell'$ do not have to be orthogonal; the orthogonality of the total wave function is ensured by the integral over the spherical harmonics. Below the principal quantum numbers n and m are different from each other and the ℓ values are different (in one function $\ell = 1$ and in the other $\ell = 0$)

```

totable = Table[{n, m, Integrate[Expand[r^2 R[n, 0][r] * R[m, 1][r]],
  {r, 0, Infinity}, GenerateConditions -> False]},
  {n, 2, 4}, {m, n + 1, 4}] // Flatten[#, 1] &
{2, 3,  $\frac{384\sqrt{3}}{3125}$ }, {2, 4,  $\frac{16\sqrt{\frac{10}{3}}}{243}$ }, {3, 4,  $\frac{48960\sqrt{5}}{823543}$ }}

```

```
TableForm[totable, TableHeadings -> {None, {"n", "m", "integral"}}]

n      m      integral
2      3       $\frac{384\sqrt{3}}{3125}$ 
2      4       $\frac{16\sqrt{\frac{10}{3}}}{243}$ 
3      4       $\frac{48960\sqrt{5}}{823543}$ 
```

■ WorkBookQM.18.5. A radial function for numerical calculations for hydrogen.

Define a function RHNum[n,ℓ][x] which gives the radial wave function for the H atom in a form appropriate for numerical calculations

```
Clear[RHNum]
RHNum[n_Integer /; n > 0, ℓ_Integer /; ℓ ≥ 0][r_(*Angstrom*)] :=
Module[{const, ρ, me = 9.109389 * 10^-31 (*kg*),
        mp = 1.672623 * 10^-27 (*kg*),
        e = 1.602177 * 10^-19 (*Coulomb*),
        ε0 = 8.854187 * 10^-12 (*C Newton^-1 meter^-2*),
        ħ = 1.054572 * 10^-34 (*J sec*),
        JToeV = 10^7 * 6.2420 * 10^11, Z = 1, μ, a},
  μ = me * mp / (me + mp);
  a = 10^10 * ħ^2 * (4 Pi ε0) / (μ e^2);
  If[ℓ < n, Null, Print["ℓ must be less than n"]];
  const = Sqrt[ $\frac{(2 Z / (n a))^3 (n - \ell - 1)!}{(n + \ell)! 2 n}$ ];
  ρ =  $\frac{2 Z r}{n a}$ ;
  const ρ^ℓ LaguerreL[n - ℓ - 1, 2 ℓ + 1, ρ] Exp[- $\frac{\rho}{2}$ ]]
```

Check that it works

```
RHNum[2, 1][r]
1.00069 e^-0.944349 r r
```

■ WorkBookQM.18.6. Plots of $R_{n,\ell}(r)$ and of the radial probability $r^2 R_{n,\ell}(r)^2$ as a function of r, for various values of n and ℓ.

Make plots of $R_{n,\ell}(r)$ and of $r^2 R_{n,\ell}(r)^2$ as a function of r, for n = 1, ℓ = 0 and n = 2, ℓ = 0, 1

I plot the two functions for various values on n and ℓ. However, I use dynamic labelling (the values of n and ℓ are automatically updated by the computer in the labels of the axes) and I also changed the fonts because otherwise the labels would be hard to read.

```

Off[Remove::rmptc] (*this removes some annoying and irrelevant messages*)
Off[Remove::relex] (*this removes some annoying and irrelevant messages*)
Needs["Utilities`CleanSlate`"]
CleanSlate[]
Remove["Global`*"]
Off[General::spell1]
Off[General::spell]

(CleanSlate) Contexts purged: {Global`}

(CleanSlate) Approximate kernel memory recovered: 84 Kb

{Utilities`CleanSlate`, Global`, System`}

```

Copy from WorkBookQM.18.5 the function RHNu[m,n,l][r] which gives the radial wave function for the hydrogen atom

```

Unprotect[RHNu];
Clear[RHNu];
RHNu[n_Integer /; n > 0, l_Integer /; l ≥ 0][r_(*Angstrom*)] :=
Module[{const, ρ, me = 9.109389 * 10^-31 (*kg*),
  mp = 1.672623 * 10^-27 (*kg*),
  e = 1.602177 * 10^-19 (*Coulomb*),
  ε0 = 8.854187 * 10^-12 (*C Newton^-1 meter^-2*),
  ħ = 1.054572 * 10^-34 (*J sec*),
  JToeV = 10^7 * 6.2420 * 10^11, Z = 1, μ, a},
  μ = me * mp / (me + mp);
  a = 10^10 * ħ^2 * (4 Pi ε0) / (μ e^2);
  If[l < n, Null, Print[" l must be less than n"]];
  const = Sqrt[ (2 Z / (n a))^3 (n - l - 1)! / ((n + l)! 2^n)];
  ρ = (2 Z r) / (n a);
  const ρ^l LaguerreL[n - l - 1, 2 l + 1, ρ] Exp[-ρ/2];
Protect[RHNu];

```

The function plR[n, l, rmax] plots $R_{n,l}(r)$ versus r. rmax determines the largest value of r in the plot. The function is calculated with RHNu which was defined in WorkBookQM.18.5, and gives the wave function for hydrogen.

```

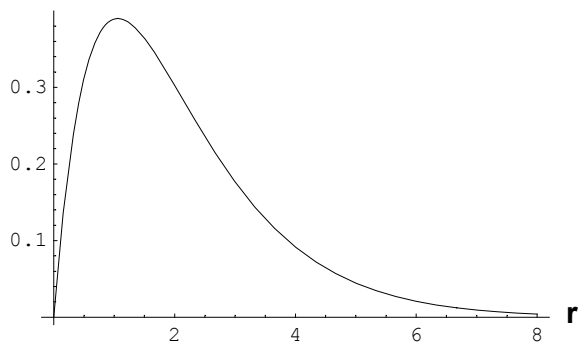
Clear[plR]
plR[n_, l_, rMax_] := Plot[RHNu[n, l][r], {r, 0, rMax},
  PlotRange -> All,
  AxesLabel -> {StyleForm["r", FontSize -> 14, FontWeight -> "Bold", FontFamily -> "Geneva"],
  StyleForm[ToString[StringForm[" R[`, `][r]", n, l]], FontSize -> 14,
  FontWeight -> "Bold", FontFamily -> "Geneva"]}, DisplayFunction -> Identity];

```

Let us look at the graph for n=2 and l=1:

```
Show[p1R[2, 1, 8] , DisplayFunction -> $DisplayFunction]
```

R[2,1][r]



- Graphics -

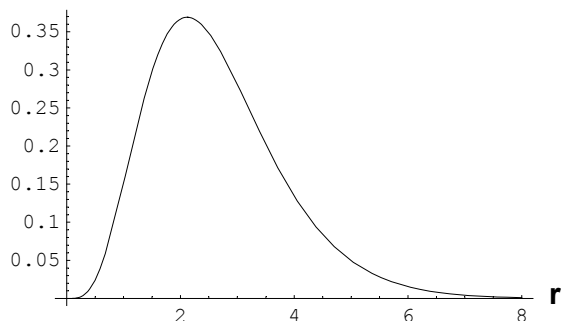
The function `p1P[n, ℓ, rmax]` plots $r^2 R_{n,\ell}(r)^2$ versus r . `rmax` determines the largest value of r in the plot. The function is calculated with the help of `RHNum`, which was defined in `WorkBookQM.18.5`, and gives the probability function for hydrogen.

```
Clear[p1P]
p1P[n_, ℓ_, rMax_] := Plot[r^2 * RHNum[n, ℓ][r]^2, {r, 0, rMax},
  PlotRange -> All,
  AxesLabel -> {StyleForm["r", FontSize -> 14, FontWeight -> "Bold", FontFamily -> "Geneva"],
    StyleForm[ToString[StringForm["r^2 R[`, `"][r]^2", n, ℓ], FontSize -> 14,
      FontWeight -> "Bold", FontFamily -> "Geneva"]]}, DisplayFunction -> Identity]
```

Display the probability for $n=2$ and $\ell=1$:

```
Show[p1P[2, 1, 8] , DisplayFunction -> $DisplayFunction]
```

r^2 R[2,1][r]^2



- Graphics -

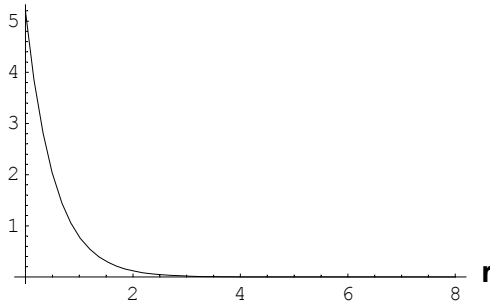
Make a table with the plots of the two functions for $n=1$ and $n=2$ and the corresponding values of ℓ

```
tb12 = Table[{p1R[n, ℓ, 8], p1P[n, ℓ, 8]}, {n, 1, 2}, {ℓ, 0, n - 1}] // Flatten[#, 1] &;
```

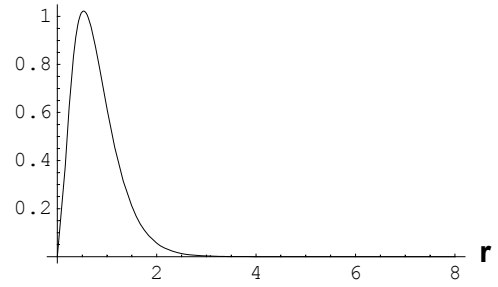
Show the plots. Use `GraphicsArray` to put all the graphs in one plot.

Show[GraphicsArray[**tb12**, DisplayFunction → \$DisplayFunction]]

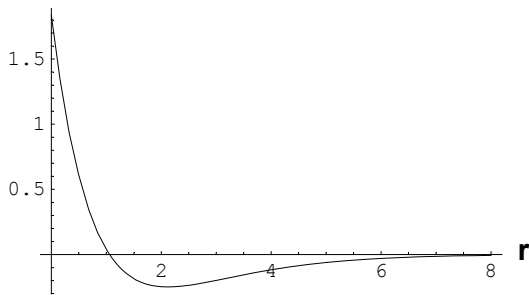
R[1,0][r]



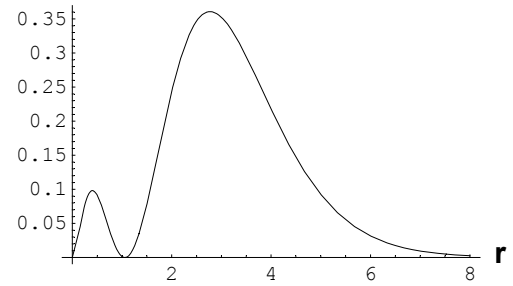
r^2 R[1,0][r]^2



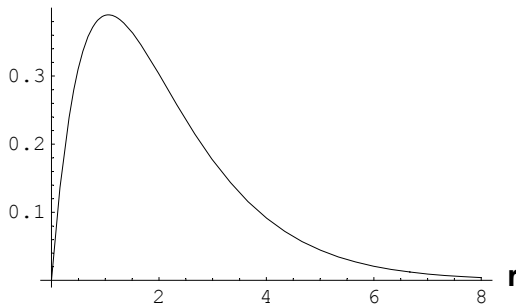
R[2,0][r]



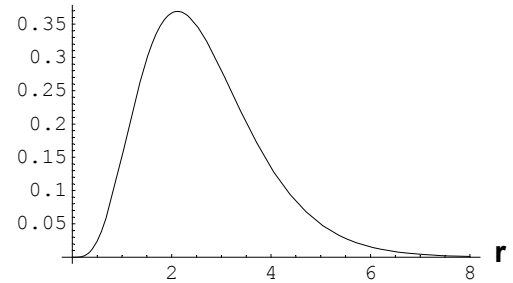
r^2 R[2,0][r]^2



R[2,1][r]



r^2 R[2,1][r]^2



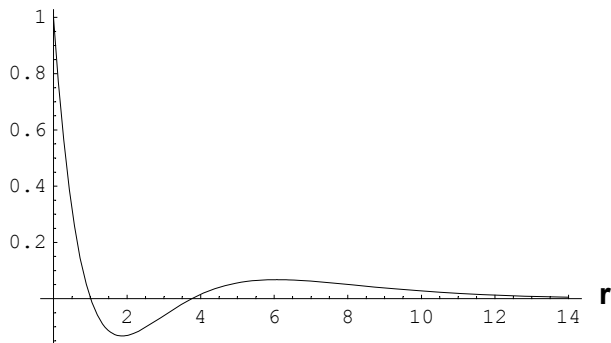
- GraphicsArray -

Make the same plots for n=3 and $\ell=0, 1, 2$

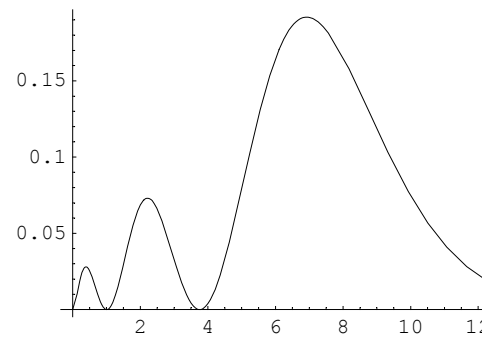
tb3 = Table[{p1R[3, ℓ , 14], p1P[3, ℓ , 14]}, { ℓ , 0, 2}];

```
Show[GraphicsArray[tb3, DisplayFunction -> $DisplayFunction]]
```

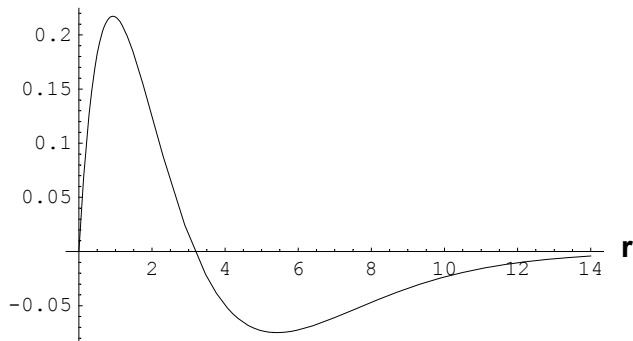
R[3,0][r]



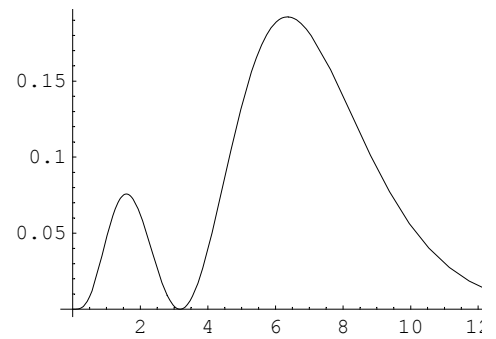
r^2 R[3,0][r]^2



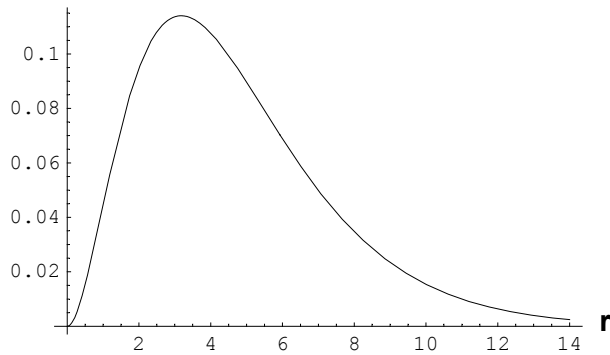
R[3,1][r]



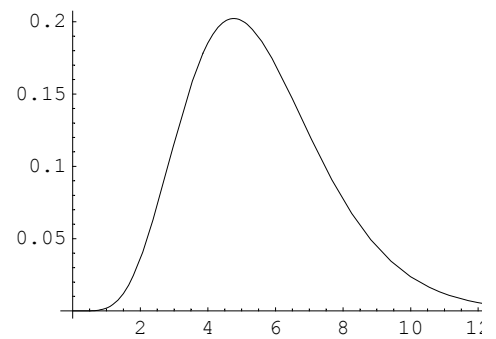
r^2 R[3,1][r]^2



R[3,2][r]



r^2 R[3,2][r]^2



- GraphicsArray -

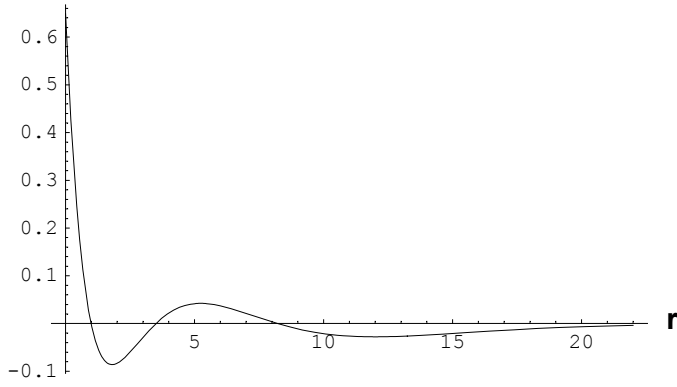
Make the same plots for n=4 and l=0, 1, 2, 3

```
tb4 = Table[{p1R[4, l, 22], p1P[4, l, 22]}, {l, 0, 3}];
```

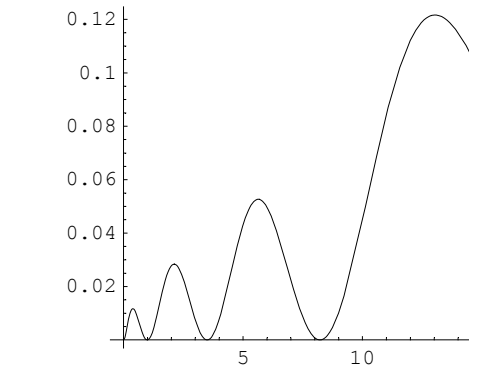
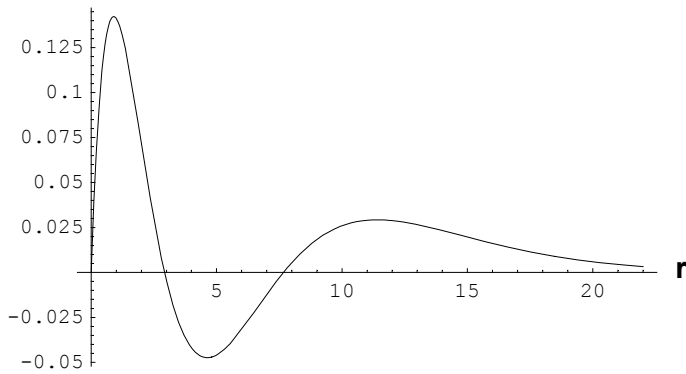
```
Show[GraphicsArray[tb4, DisplayFunction -> $DisplayFunction]]
```

R[4,0][r]

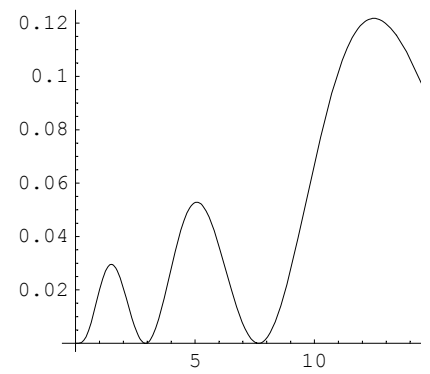
r^2 R[4,0][r]^2



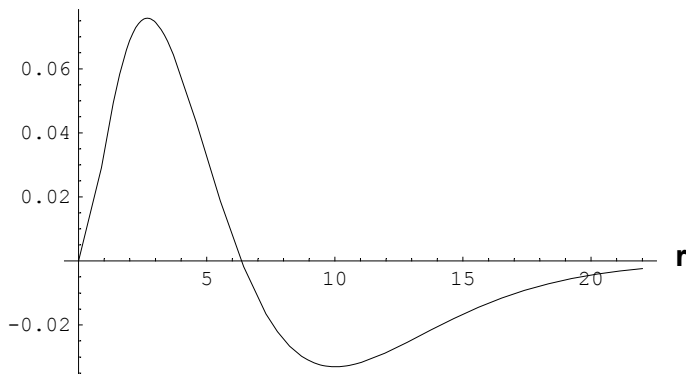
R[4,1][r]



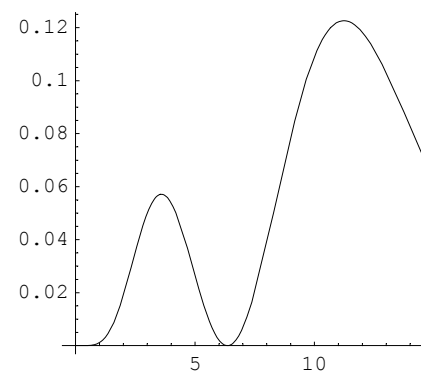
r^2 R[4,1][r]^2



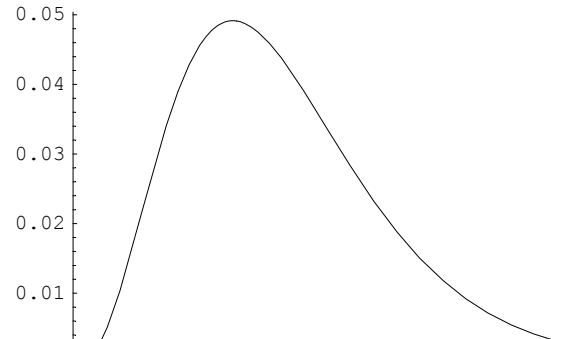
R[4,2][r]



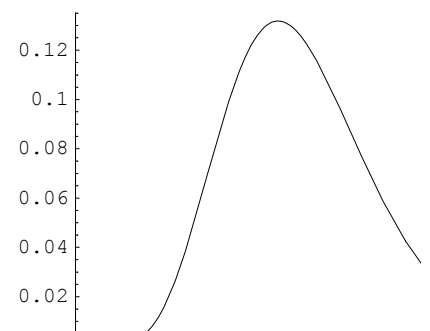
r^2 R[4,2][r]^2

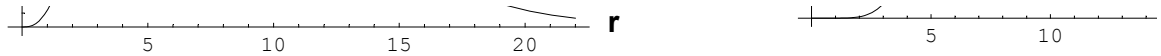


R[4,3][r]



r^2 R[4,3][r]^2





- GraphicsArray -

Note various peaks in the probability that indicate that the electron seems to reside in "shells".

■ **WorkBookQM.18. 7. Mean position, mean position squared, mean Coulomb interaction energy, mean rotational energy and the mean kinetic energy.**

```
Off[Remove::rmptc] (*this removes some annoying and irrelevant messages*)
Off[Remove::relex] (*this removes some annoying and irrelevant messages*)
Needs["Utilities`CleanSlate`"]
CleanSlate[]
Remove["Global`*"]
Off[General::spell1]
Off[General::spell]

(CleanSlate) Contexts purged: {Global`}

(CleanSlate) Approximate kernel memory recovered: 125 Kb

{Utilities`CleanSlate`, Global`, System`}
```

■ **Cell 0: The radial wave function**

```
Unprotect[Φ];
Clear[Φ]; Unprotect[a, Z]; Clear[a, Z]; Protect[a, Z];
Φ[n_Integer, ℓ_Integer][ρ_] := Module[{const},
const = Sqrt[

$$\frac{(n - \ell - 1)!}{(n + \ell)! 2^n}$$

];
const (2 Z ρ / n) ^ ℓ LaguerreL[n - ℓ - 1, 2 ℓ + 1,  $\frac{2 Z \rho}{n}$ ] Exp[- $\frac{Z \rho}{n}$ ]]
Protect[Φ];
```

Define a function that generates $R_{n,\ell}(r)$

```
Unprotect[R];
Clear[R];
R[n_, ℓ_][r_] := (2 Z / (n a)) ^ (3 / 2) Φ[n, ℓ][r / a]
Protect[R];
```

Check that R works

R[3, 2][r]

$$\frac{2 \sqrt{\frac{2}{15}} e^{-\frac{r Z}{3 a}} r^2 Z^2 \left(\frac{Z}{a}\right)^{3/2}}{81 a^2}$$

Φ does not work if n and ℓ are symbols

$$\Phi[n, \ell][r/a]$$

$$\Phi[n, \ell]\left[\frac{r}{a}\right]$$

Φ works if n and ℓ have numerical values.

$$\Phi[3, 2]\left[\frac{r}{a}\right]$$

$$\frac{e^{-\frac{r^2}{3a}} r^2 Z^2}{27 \sqrt{5} a^2}$$

■ Cell 1: Mean position, mean position squared and the dispersion σ of the position

$$\langle n, \ell | r | n, \ell \rangle \equiv \int_0^\infty r R_{n,\ell}(r)^* R_{n,\ell}(r) r^2 dr \quad (1)$$

$$\langle r^2 \rangle \equiv \langle n, \ell | r^2 | n, \ell \rangle = \int_0^\infty r^2 \{r^2 R_{n,\ell}(r)^* R_{n,\ell}(r)\} dr \quad (2)$$

$$\sigma = \sqrt{\frac{\langle r^2 \rangle - \langle r \rangle^2}{\langle r^2 \rangle}} \quad (3)$$

Calculate the mean position $\langle n, \ell | r | n, \ell \rangle$ (see Eq. 1) and $\langle r^2 \rangle$ (see Eq. 2) for various values of n and ℓ ; make a table with the results:

```
tbMeanr = Table[{n, ℓ, rmean[n][ℓ] = Integrate[r^3 R[n, ℓ][r]^2, {r, 0, Infinity},
GenerateConditions → False]}, {n, 1, 4}, {ℓ, 0, n - 1}] // Flatten[#, 1] &
```

```
{{{1, 0, 3 a / (2 Z)}, {2, 0, 6 a / Z}, {2, 1, 5 a / Z}, {3, 0, 27 a / (2 Z)}, {3, 1, 25 a / (2 Z)},
{3, 2, 21 a / (2 Z)}, {4, 0, 24 a / Z}, {4, 1, 23 a / Z}, {4, 2, 21 a / Z}, {4, 3, 18 a / Z}}}
```

```
TableForm[tbMeanr, TableHeadings → {None, {"n", "ℓ", "<r>"}}]
```

n	ℓ	<r>
1	0	$\frac{3a}{2Z}$
2	0	$\frac{6a}{Z}$
2	1	$\frac{5a}{Z}$
3	0	$\frac{27a}{2Z}$
3	1	$\frac{25a}{2Z}$
3	2	$\frac{21a}{2Z}$
4	0	$\frac{24a}{Z}$
4	1	$\frac{23a}{Z}$
4	2	$\frac{21a}{Z}$
4	3	$\frac{18a}{Z}$

```

Clear[rMean2]
tb = Table[{n, l, rMean2[n][l] =
  Integrate[r^4 R[n, l][r]^2, {r, 0, Infinity}, GenerateConditions -> False]},
  {n, 1, 4}, {l, 0, n - 1}] // Flatten[#, 1] &;
TableForm[tb, TableHeadings -> {None, {"n", "l", "<r^2>"}}]

```

n	l	$\langle r^2 \rangle$
1	0	$\frac{3 a^2}{Z^2}$
2	0	$\frac{42 a^2}{Z^2}$
2	1	$\frac{30 a^2}{Z^2}$
3	0	$\frac{207 a^2}{Z^2}$
3	1	$\frac{180 a^2}{Z^2}$
3	2	$\frac{126 a^2}{Z^2}$
4	0	$\frac{648 a^2}{Z^2}$
4	1	$\frac{600 a^2}{Z^2}$
4	2	$\frac{504 a^2}{Z^2}$
4	3	$\frac{360 a^2}{Z^2}$

We see that, as expected, $\langle r \rangle$ and $\langle r^2 \rangle$ are proportional to the length scale a and a^2 respectively and inverse proportional to Z or Z^2 (respectively). Higher the nuclear charge closer is the electron to the nucleus. Since the probability function is rather complicated the magnitude of σ is not meaningful.

Calculate numerical values of the same quantities, for hydrogen. For this I need the wave function of the hydrogen atom, which I copy (see below) from WorkBookQM.18.5

```

tb = Table[
  {n, l, rmean[n][l], rMean2[n][l], Sqrt[rMean2[n][l] - rmean[n][l]^2] / rmean[n][l]} /.
  {Z -> 1, a -> 0.529 (*Å*)}, {n, 1, 4}, {l, 0, n - 1}] // Flatten[#, 1] &
{
  {1, 0, 0.7935, 0.839523, 0.57735}, {2, 0, 3.174, 11.7533, 0.408248},
  {2, 1, 2.645, 8.39523, 0.447214}, {3, 0, 7.1415, 57.9271, 0.368514},
  {3, 1, 6.6125, 50.3714, 0.389872}, {3, 2, 5.5545, 35.26, 0.377964},
  {4, 0, 12.696, 181.337, 0.353553}, {4, 1, 12.167, 167.905, 0.366354},
  {4, 2, 11.109, 141.04, 0.377964}, {4, 3, 9.522, 100.743, 0.333333}
}

```

`TableForm[tb, TableHeadings → {None, {"n", "ℓ", "⟨r⟩", "⟨r2⟩", "√ $\frac{\langle r^2 \rangle - \langle r \rangle^2}{\langle r \rangle^2}$ "}}]`

n	ℓ	⟨r⟩	⟨r ² ⟩	$\sqrt{\frac{\langle r^2 \rangle - \langle r \rangle^2}{\langle r \rangle^2}}$
1	0	0.7935	0.839523	0.57735
2	0	3.174	11.7533	0.408248
2	1	2.645	8.39523	0.447214
3	0	7.1415	57.9271	0.368514
3	1	6.6125	50.3714	0.389872
3	2	5.5545	35.26	0.377964
4	0	12.696	181.337	0.353553
4	1	12.167	167.905	0.366354
4	2	11.109	141.04	0.377964
4	3	9.522	100.743	0.333333

If n increases, at fixed ℓ, the mean radius increases; if ℓ increases, at fixed n, the mean radius decreases. That seems strange: the mean distance between the electron and the nucleus decreases as the rotational energy is increased. This happens because of the manner in which the Coulomb and the centrifugal energies combine to give the total energy.

■ **Cell 2: The average radial kinetic energy ⟨K⟩, rotational energy ⟨E_r⟩ and Coulomb energy ⟨C⟩**

$$\langle K \rangle = \langle n, \ell | -\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} | n, \ell \rangle = \int_0^\infty r^2 R_{n,\ell}(r) \left\{ -\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right\} R_{n,\ell}(r) dr \quad (1)$$

$$\langle E_r \rangle = \langle n, \ell | \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} | n, \ell \rangle = \int_0^\infty r^2 R_{n,\ell}(r) \left\{ -\frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} \right\} R_{n,\ell}(r) dr \quad (2)$$

$$\langle C \rangle = \langle n, \ell | -\frac{e^2}{4\pi\epsilon_0 r} | n, \ell \rangle = \int_0^\infty r^2 R_{n,\ell}(r) \left\{ -\frac{e^2}{4\pi\epsilon_0 r} \right\} R_{n,\ell}(r) dr \quad (3)$$

Calculate the mean kinetic energy: define the function KinR[n, ℓ][r] that gives

$$-\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} R_{n,\ell}(r)$$

`Clear[KinR];`

`KinR[n_, ℓ_][r_] := (-ħ^2 / (2 μ)) * (1 / x^2) * D[x^2 D[R[n, ℓ][x], x], x] /. x → r;`

Calculate ⟨K⟩ from Eq. 1:

`K = .`

`K[n_, ℓ_] :=`

`Integrate[r^2 R[n, ℓ][r] * KinR[n, ℓ][r], {r, 0, Infinity}, GenerateConditions → False]`

Check that it works

K[3, 1]

$$\frac{5 Z^2 \hbar^2}{162 a^2 \mu}$$

Calculate the mean "rotational energy":

Er = .

Er[n_, l_] := Integrate[r^2 R[n, l][r]^2 * \hbar^2 l (l + 1) / (2 \mu r^2),
{r, 0, Infinity}, GenerateConditions -> False]

Check that it works

Er[3, 2]

$$\frac{2 Z^2 \hbar^2}{45 a^2 \mu}$$

Compare the numerical results to the equation

$$\langle E_r \rangle = \frac{\hbar^2}{2\mu} \frac{l(l+1)Z^2}{a^2 n^3 (l + \frac{1}{2})}$$

ErFormula[n_, l_] := \hbar^2 Z^2 l (l + 1) / (2 \mu a^2 n^3 (l + 1 / 2))

ErFormula[3, 2]

$$\frac{2 Z^2 \hbar^2}{45 a^2 \mu}$$

The two calculations give the same result.

Calculate the mean Coulomb energy <C>

c = .

c[n_, l_] := Integrate[r^2 R[n, l][r]^2 * (-1) * Z e^2 / (4 \pi \epsilon_0 r),
{r, 0, Infinity}, GenerateConditions -> False]

Calculate the mean Coulomb energy for n=3 and l=2, to see if it works

c[3, 2]

$$-\frac{e^2 Z^2}{36 a \pi \epsilon_0}$$

Compare to the formula:

$$\langle C \rangle = -\frac{Z e^2}{4 \pi \epsilon_0} \frac{Z}{a n^2}$$

cFormula = .

cFormula[n_] := -Z^2 e^2 / (4 \pi \epsilon_0 a n^2)

cFormula[3]

$$-\frac{e^2 Z^2}{36 a \pi \epsilon_0}$$

Since all other equations are given in terms of a and μ and do not contain ϵ_0 I eliminate ϵ_0 from this equation by using

$$\epsilon_0 = \frac{\mu e^2 a}{4\pi \hbar^2}$$

which is obtained from the definition of a in §5.

rule ϵ_0 = $\epsilon_0 \rightarrow \mu e^2 a / (4 \pi \hbar^2)$

$$\epsilon_0 \rightarrow \frac{a e^2 \mu}{4 \pi \hbar^2}$$

cFormula[n] /. rule ϵ_0

$$-\frac{Z^2 \hbar^2}{a^2 n^2 \mu}$$

Make a function giving the total energy

energy = .

energy[n_] :=

Module[{abc},

- $\mu * Z^2 * e^4 / (2 n^2 (4 \text{Pi} \epsilon_0 \hbar)^2)$]

energy[n]

$$-\frac{e^4 Z^2 \mu}{32 n^2 \pi^2 \hbar^2 \epsilon_0^2}$$

Replace ϵ_0 with its expression:

energy[n] /. rule ϵ_0

$$-\frac{Z^2 \hbar^2}{2 a^2 n^2 \mu}$$

Calculate the mean kinetic energy $\langle K \rangle$, the mean rotational energy $\langle E_r \rangle$, the mean Coulomb energy $\langle C \rangle$ and the total energy E, for various values on n and ℓ and make a table with the results:

```
tb = Table[{n, l, K[n, l], ErFormula[n, l], cFormula[n] /. rulee0, energy[n] /. rulee0},
  {n, 1, 4}, {l, 0, n - 1}] // Flatten[#, 1] &;
TableForm[tb, TableHeadings -> {None, {"n", "l", "<K>", "<Er>", "<C>", "E"}}]
```

n	l	<K>	<Er>	<C>	E
1	0	$\frac{Z^2 \hbar^2}{2 a^2 \mu}$	0	$-\frac{Z^2 \hbar^2}{a^2 \mu}$	$-\frac{Z^2 \hbar^2}{2 a^2 \mu}$
2	0	$\frac{Z^2 \hbar^2}{8 a^2 \mu}$	0	$-\frac{Z^2 \hbar^2}{4 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{8 a^2 \mu}$
2	1	$\frac{Z^2 \hbar^2}{24 a^2 \mu}$	$\frac{Z^2 \hbar^2}{12 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{4 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{8 a^2 \mu}$
3	0	$\frac{Z^2 \hbar^2}{18 a^2 \mu}$	0	$-\frac{Z^2 \hbar^2}{9 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{18 a^2 \mu}$
3	1	$\frac{5 Z^2 \hbar^2}{162 a^2 \mu}$	$\frac{2 Z^2 \hbar^2}{81 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{9 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{18 a^2 \mu}$
3	2	$\frac{Z^2 \hbar^2}{90 a^2 \mu}$	$\frac{2 Z^2 \hbar^2}{45 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{9 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{18 a^2 \mu}$
4	0	$\frac{Z^2 \hbar^2}{32 a^2 \mu}$	0	$-\frac{Z^2 \hbar^2}{16 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{32 a^2 \mu}$
4	1	$\frac{Z^2 \hbar^2}{48 a^2 \mu}$	$\frac{Z^2 \hbar^2}{96 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{16 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{32 a^2 \mu}$
4	2	$\frac{Z^2 \hbar^2}{80 a^2 \mu}$	$\frac{3 Z^2 \hbar^2}{160 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{16 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{32 a^2 \mu}$
4	3	$\frac{Z^2 \hbar^2}{224 a^2 \mu}$	$\frac{3 Z^2 \hbar^2}{112 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{16 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{32 a^2 \mu}$

We can replace a with its expression $\hbar^2 4 \pi \epsilon_0 / (\mu e^2)$ to get results in terms of the fundamental constants.

Note an interesting result: the mean Coulomb energy is equal to the total energy divided by two. Now we know that the total kinetic energy must be equal to the total energy minus the Coulomb energy and it is also equal to the radial kinetic energy plus the rotational energy. You can check that these equality are true, which indicates that our calculations are correct.

As a test let us check that the three mean energies add up to the total energy:

```
tbt =
  Table[{n, l, K[n, l] + (ErFormula[n, l] /. rulee0) + (cFormula[n] /. rulee0), energy[n]} /.
    rulee0, {n, 1, 4}, {l, 0, n - 1}] // Flatten[#, 1] &;
tbt // TableForm[#, TableHeadings -> {None, {"n", "l", "sum", "E"}}] &
```

n	l	sum	E
1	0	$-\frac{Z^2 \hbar^2}{2 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{2 a^2 \mu}$
2	0	$-\frac{Z^2 \hbar^2}{8 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{8 a^2 \mu}$
2	1	$-\frac{Z^2 \hbar^2}{8 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{8 a^2 \mu}$
3	0	$-\frac{Z^2 \hbar^2}{18 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{18 a^2 \mu}$
3	1	$-\frac{Z^2 \hbar^2}{18 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{18 a^2 \mu}$
3	2	$-\frac{Z^2 \hbar^2}{18 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{18 a^2 \mu}$
4	0	$-\frac{Z^2 \hbar^2}{32 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{32 a^2 \mu}$
4	1	$-\frac{Z^2 \hbar^2}{32 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{32 a^2 \mu}$
4	2	$-\frac{Z^2 \hbar^2}{32 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{32 a^2 \mu}$
4	3	$-\frac{Z^2 \hbar^2}{32 a^2 \mu}$	$-\frac{Z^2 \hbar^2}{32 a^2 \mu}$

■ WorkBookQM.18. 9. The total wave function (radial and angular)

The wave function of the one-electron atom is

$$\Psi_{n,\ell,m} = R_{n,\ell}(r) Y_{\ell}^m(\theta, \phi) \quad (1)$$

The radial wave function is:

$$R_{n,\ell}(r) = \left(\frac{2Z}{na}\right)^{3/2} \Phi_{n,\ell}(\rho) \quad (2)$$

with

$$\Phi_{n,\ell}(r) = \sqrt{\frac{(n-\ell-1)!}{2n(n+\ell)!}} \left(\frac{2Z\rho}{n}\right)^{\ell} \text{Exp}\left[-\frac{Z\rho}{n}\right] L_{n-\ell-1}^{2\ell+1}\left(\frac{2Z\rho}{n}\right) \quad (3)$$

You may find that Eq. 2 differs from what some books give. Many books give an erroneous formula for this quantity.

We have

$$\rho = \frac{r}{a} \quad (4)$$

and

$$a = \frac{\hbar^2(4\pi\epsilon_0)}{\mu e^2} \quad (5)$$

Plan:

1. Define the radial wave function $R_{n,\ell}$
2. Define the total wave function $\Psi_{n,\ell,m}$ and display the formulae for various values of n, ℓ and m
3. Define the wave functions $1s, 2s, 3s, 2p_x, 2p_y, 2p_z$, etc. and display the formulae and plot them

```
Needs["Utilities`CleanSlate`"]
```

```
CleanSlate[]
```

```
Unprotect[a, R, Z, \Phi];
```

```
Remove["Global`*"]
```

```
Off[General::spell1]
```

```
Off[General::spell]
```

```
Protect[a, R, Z, \Phi];
```

```
(CleanSlate) Contexts purged: {Global`}
```

```
(CleanSlate) Approximate kernel memory recovered: 19 Kb
```

```
{Utilities`CleanSlate`, Global`, System`}
```

■ Cell 1: The radial wave function. This is copied from WorkBookQM.18.3

The function Φ :

```

Unprotect[Φ];
Clear[Φ]; Unprotect[a, Z]; Clear[a, Z]; Protect[a, Z];
Φ[n_Integer, ℓ_Integer][ρ_] := Module[{const},
const = Sqrt[ $\frac{(n - \ell - 1)!}{(n + \ell)! 2^n}$ ];
const (2 Z ρ / n) ^ ℓ LaguerreL[n - ℓ - 1, 2 ℓ + 1,  $\frac{2 Z \rho}{n}$ ] Exp[- $\frac{Z \rho}{n}$ ]]
Protect[Φ];

```

Define a function that generates $R_{n,\ell}(r)$

```

Unprotect[R];
Clear[R];
R[n_, ℓ_][r_] := (2 Z / (n a)) ^ (3 / 2) Φ[n, ℓ][r / a]
Protect[R];

```

Test that the function works

```

R[3, 2][r]

```

$$\frac{2 \sqrt{\frac{2}{15}} e^{-\frac{r Z}{3 a}} r^2 Z^2 \left(\frac{Z}{a}\right)^{3/2}}{81 a^2}$$

■ Cell 2: Define the total wave function $\Psi_{n,\ell,m}(r, \theta, \phi)$

Use Eq. 1 to define $\psi[n, \ell, m][r, \theta, \phi]$

```

ψ[n_, ℓ_, m_][r_, θ_, φ_] := R[n, ℓ][r] * SphericalHarmonicY[ℓ, m, θ, φ]

```

See if it works:

```

ψ[3, 2, -1][r, θ, φ]

```

$$\frac{e^{-\frac{r Z}{3 a} - i \phi} r^2 Z^2 \left(\frac{Z}{a}\right)^{3/2} \text{Cos}[\theta] \text{Sin}[\theta]}{81 a^2 \sqrt{\pi}}$$

Make a table with $\Psi_{n,\ell,m}(r, \theta, \phi)$ for various values of n, ℓ and m

tb =

Table[{n, ℓ, m, ψ[n, ℓ, m][r, θ, φ]}, {n, 1, 3}, {ℓ, 0, n - 1}, {m, -ℓ, ℓ}] // Flatten[#, 2] &
 TableForm[tb, TableHeadings → {None, {"n", "ℓ", "m", "ψ_{n,ℓ,m}(r,θ,φ)"}]}

n	ℓ	m	ψ _{n,ℓ,m} (r,θ,φ)
1	0	0	$\frac{e^{-\frac{rZ}{a}} \left(\frac{Z}{a}\right)^{3/2}}{\sqrt{\pi}}$
2	0	0	$\frac{e^{-\frac{rZ}{2a}} \left(\frac{Z}{a}\right)^{3/2} \left(2 - \frac{rZ}{a}\right)}{4\sqrt{2}\pi}$
2	1	-1	$\frac{e^{-\frac{rZ}{2a} - i\phi} r Z \left(\frac{Z}{a}\right)^{3/2} \text{Sin}[\theta]}{8a\sqrt{\pi}}$
2	1	0	$\frac{e^{-\frac{rZ}{2a}} r Z \left(\frac{Z}{a}\right)^{3/2} \text{Cos}[\theta]}{4a\sqrt{2}\pi}$
2	1	1	$-\frac{e^{-\frac{rZ}{2a} + i\phi} r Z \left(\frac{Z}{a}\right)^{3/2} \text{Sin}[\theta]}{8a\sqrt{\pi}}$
3	0	0	$\frac{e^{-\frac{rZ}{3a}} \left(\frac{Z}{a}\right)^{3/2} (27a^2 - 18a r Z + 2r^2 Z^2)}{81a^2\sqrt{3}\pi}$
3	1	-1	$\frac{e^{-\frac{rZ}{3a} - i\phi} r Z \left(\frac{Z}{a}\right)^{3/2} \left(4 - \frac{2rZ}{3a}\right) \text{Sin}[\theta]}{54a\sqrt{\pi}}$
3	1	0	$\frac{e^{-\frac{rZ}{3a}} r Z \left(\frac{Z}{a}\right)^{3/2} \left(4 - \frac{2rZ}{3a}\right) \text{Cos}[\theta]}{27a\sqrt{2}\pi}$
3	1	1	$-\frac{e^{-\frac{rZ}{3a} + i\phi} r Z \left(\frac{Z}{a}\right)^{3/2} \left(4 - \frac{2rZ}{3a}\right) \text{Sin}[\theta]}{54a\sqrt{\pi}}$
3	2	-2	$\frac{e^{-\frac{rZ}{3a} - 2i\phi} r^2 Z^2 \left(\frac{Z}{a}\right)^{3/2} \text{Sin}[\theta]^2}{162a^2\sqrt{\pi}}$
3	2	-1	$\frac{e^{-\frac{rZ}{3a} - i\phi} r^2 Z^2 \left(\frac{Z}{a}\right)^{3/2} \text{Cos}[\theta] \text{Sin}[\theta]}{81a^2\sqrt{\pi}}$
3	2	0	$\frac{e^{-\frac{rZ}{3a}} r^2 Z^2 \left(\frac{Z}{a}\right)^{3/2} (-1 + 3\text{Cos}[\theta]^2)}{81a^2\sqrt{6}\pi}$
3	2	1	$-\frac{e^{-\frac{rZ}{3a} + i\phi} r^2 Z^2 \left(\frac{Z}{a}\right)^{3/2} \text{Cos}[\theta] \text{Sin}[\theta]}{81a^2\sqrt{\pi}}$
3	2	2	$\frac{e^{-\frac{rZ}{3a} + 2i\phi} r^2 Z^2 \left(\frac{Z}{a}\right)^{3/2} \text{Sin}[\theta]^2}{162a^2\sqrt{\pi}}$

Note the following:

If $m \neq 0$ the function is complex (this means that its values are complex numbers, not that the function is complicated)

When $m \neq 0$ the dependence on the angle ϕ is given by $\exp[\pm i m \phi]$

When $m = 0$ the wave function is independent of ϕ .

■ Cell 3: The wave functions

$$ns(r, \theta, \phi) = R_{n,0}(r) Y_0^0(\theta, \phi)$$

This generates the functions 1s, 2s, 3s,

The spherical harmonic $Y_0^0(\theta, \phi)$ is:

SphericalHarmonicY[0, 0, θ, φ]

$$\frac{1}{2\sqrt{\pi}}$$

This is independent of angles θ and ϕ

Create the function $s[r, \theta, \phi][n]$ which gives

$$ns[r, \theta, \phi] = R_{n,0}(r) Y_0^0(\theta, \phi)$$

```
Unprotect[s];
s = .
s[r_, \theta_, \phi_][n_] := Module[{} ,
  R[n, 0][r] * SphericalHarmonicY[0, 0, \theta, \phi]
Protect[s];
```

Make a table with the functions 1s, 2s, 3s,

```
tbs = Table[{ToString[StringForm["`s(r, \theta, \phi)", n]], s[r, \theta, \phi][n]}, {n, 1, 5}];
TableForm[tbs]
```

1s(r, \theta, \phi)	$\frac{e^{-\frac{r}{a}} \left(\frac{r}{a}\right)^{3/2}}{\sqrt{\pi}}$
2s(r, \theta, \phi)	$\frac{e^{-\frac{r}{2a}} \left(\frac{r}{a}\right)^{3/2} \left(2 - \frac{r}{a}\right)}{4\sqrt{2}\pi}$
3s(r, \theta, \phi)	$\frac{e^{-\frac{r}{3a}} \left(\frac{r}{a}\right)^{3/2} (27a^2 - 18ar + 2r^2)}{81a^2\sqrt{3}\pi}$
4s(r, \theta, \phi)	$\frac{e^{-\frac{r}{4a}} \left(\frac{r}{a}\right)^{3/2} (192a^3 - 144a^2r + 24a^2r^2 - r^3)}{1536a^3\sqrt{\pi}}$
5s(r, \theta, \phi)	$\frac{e^{-\frac{r}{5a}} \left(\frac{r}{a}\right)^{3/2} (9375a^4 - 7500a^3r + 1500a^2r^2 - 100ar^3 + 2r^4)}{46875a^4\sqrt{5}\pi}$

These s-orbitals are the $R_{n,0}(r)$ functions multiplied with $Y_0^0(\theta, \phi) = 1/(2\sqrt{\pi})$.

All the $ns(r, \theta, \phi)$ functions are real (take real values) and are independent of ϕ or θ . This means that they have spherical symmetry. The probability of finding the electron is the same on any point on a sphere whose center is on the nucleus. The electron has no angular preference.

For making contour plots I want to have the ns function in cartesian coordinates. Use the replacement rule

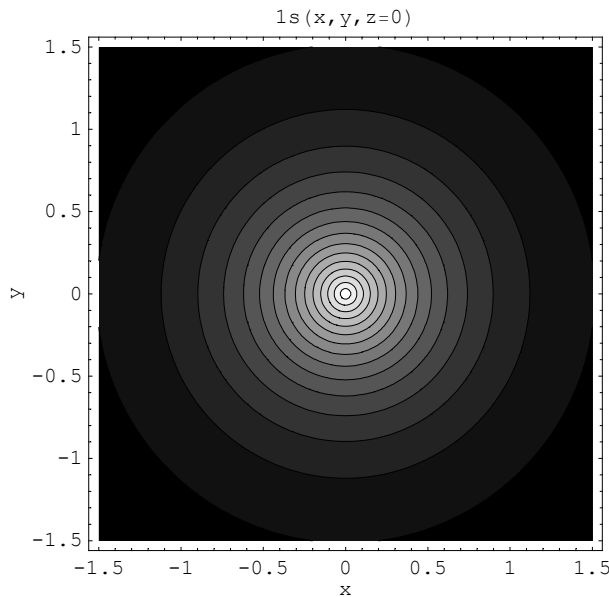
```
convCarts = {r -> Sqrt[x^2 + y^2 + z^2]}
{r -> Sqrt[x^2 + y^2 + z^2]}
```

For the s functions the conversion is easy since they depend on r only.

The clearest way of representing these functions is to make contour plots which show the function in one of the planes of the coordinate system.

Below I plot 1s(x, y, z=0).

```
ContourPlot[Evaluate[(s[r, θ, φ][1] /. convCarts) /. {a → 0.5292, z → 1} /. z → 0],
  {x, -1.5, 1.5}, {y, -1.5, 1.5}, PlotPoints → 200, Contours → 15,
  PlotRange → All, FrameLabel → {"x", "y"}, PlotLabel -> "1s(x,y,z=0)"];
```



The spherical symmetry is evident in the graph. In the regions that are whiter than the background the function takes positive values. The 2s, 3s and 4s functions look the same except that they extend further away from the nucleus.

■ Cell 4: The wave functions

$$np_x(r, \theta, \phi) = \frac{1}{\sqrt{2}} \{Y_1^{-1}(\theta, \phi) - Y_1^1(\theta, \phi)\} R_{n,1}(r)$$

The angular part of all np_x function is the same for all n, and it is given below

```
Clear[pxAng]
pxAng[θ, φ] :=
(SphericalHarmonicY[1, -1, θ, φ] - SphericalHarmonicY[1, 1, θ, φ]) / Sqrt[2] //
ComplexExpand
```

```
pxAng[θ, φ]
```

$$\frac{1}{2} \sqrt{\frac{3}{\pi}} \cos[\phi] \sin[\theta]$$

To convert to cartesian coordinates I use:

$$\begin{aligned} \cos(\theta) &= \frac{z}{r} \\ \sin(\theta) &= \frac{\sqrt{x^2+y^2}}{r} \\ \sin(\phi) &= \frac{y}{\sqrt{x^2+y^2}} \\ \cos(\phi) &= \frac{x}{\sqrt{x^2+y^2}} \end{aligned}$$

These are obtained by simple geometry (see any calculus book).
 For calculations I use also

$$r = \sqrt{x^2 + y^2 + z^2}$$

but when I give the expression of the functions in cartesian coordinate I leave r in the formulae to make them shorter.

```
convCarts = { r -> Sqrt[x^2 + y^2 + z^2] }
convCartp = { Cos[θ] -> z / r, Sin[θ] -> Sqrt[x^2 + y^2] / r,
  Cos[φ] -> x / Sqrt[x^2 + y^2], Sin[φ] -> y / Sqrt[x^2 + y^2] }
{ r -> Sqrt[x^2 + y^2 + z^2] }
{ Cos[θ] -> z / r, Sin[θ] -> Sqrt[x^2 + y^2] / r, Cos[φ] -> x / Sqrt[x^2 + y^2], Sin[φ] -> y / Sqrt[x^2 + y^2] }

pxAng[θ, φ] /. convCartp

Sqrt[3/π] x / (2 r)
```

Define the function

```
px[r, θ, φ][n]
```

which gives $np_x(r, \theta, \phi)$ (these are $2 p_x(r, \theta, \phi)$, $3 p_x(r, \theta, \phi)$, etc.)

```
Unprotect[px];
Clear[px]
px[r_, θ_, φ_][n_] := Module[{ },
  int = (SphericalHarmonicY[1, -1, θ, φ] - SphericalHarmonicY[1, 1, θ, φ]) / Sqrt[2] //
  ComplexExpand ;
  R[n, 1][r] * int]
Protect[px];
```

Check whether the function works

```
px[r, θ, φ][3]

e-x2/3a r z (z/a)3/2 (4 - 2xz/3a) Cos[φ] Sin[θ] / (27 a sqrt(2) π)
```

Convert the trigonometric functions to cartesian coordinates

```
px[r, θ, φ][3] /. convCartp

e-x2/3a x z (z/a)3/2 (4 - 2xz/3a) / (27 a sqrt(2) π)
```

Make a table with the np_x orbitals:

```

tbp = Table[{ToString[StringForm["`px(r, θ, φ)", n]],
  px[r, θ, φ][n], px[r, θ, φ][n] /. convCartp}, {n, 2, 5}];

```

```

TableForm[tbp, TableHeadings → {None, {"", "spherical", "cartesian"}}]

```

	spherical	cartesian
2 $p_x(r, \theta, \phi)$	$\frac{e^{-\frac{r}{2a}} r z (\frac{z}{a})^{3/2} \cos[\phi] \sin[\theta]}{4 a \sqrt{2\pi}}$	$\frac{e^{-\frac{r}{2a}} x z (\frac{z}{a})^{3/2}}{4 a \sqrt{2\pi}}$
3 $p_x(r, \theta, \phi)$	$\frac{e^{-\frac{r}{3a}} r z (\frac{z}{a})^{3/2} (4 - \frac{2rz}{3a}) \cos[\phi] \sin[\theta]}{27 a \sqrt{2\pi}}$	$\frac{e^{-\frac{r}{3a}} x z (\frac{z}{a})^{3/2} (4 - \frac{2rz}{3a})}{27 a \sqrt{2\pi}}$
4 $p_x(r, \theta, \phi)$	$\frac{e^{-\frac{r}{4a}} r z (\frac{z}{a})^{3/2} (80 a^2 - 20 a r z + r^2 z^2) \cos[\phi] \sin[\theta]}{512 a^3 \sqrt{5\pi}}$	$\frac{e^{-\frac{r}{4a}} x z (\frac{z}{a})^{3/2} (80 a^2 - 20 a r z + r^2 z^2)}{512 a^3 \sqrt{5\pi}}$
5 $p_x(r, \theta, \phi)$	$\frac{e^{-\frac{r}{5a}} \sqrt{\frac{2}{5\pi}} r z (\frac{z}{a})^{3/2} (3750 a^3 - 1125 a^2 r z + 90 a r^2 z^2 - 2 r^3 z^3) \cos[\phi] \sin[\theta]}{46875 a^4}$	$\frac{e^{-\frac{r}{5a}} \sqrt{\frac{2}{5\pi}} x z (\frac{z}{a})^{3/2} (3750 a^3 - 1125 a^2 r z + 90 a r^2 z^2 - 2 r^3 z^3)}{46875 a^4}$

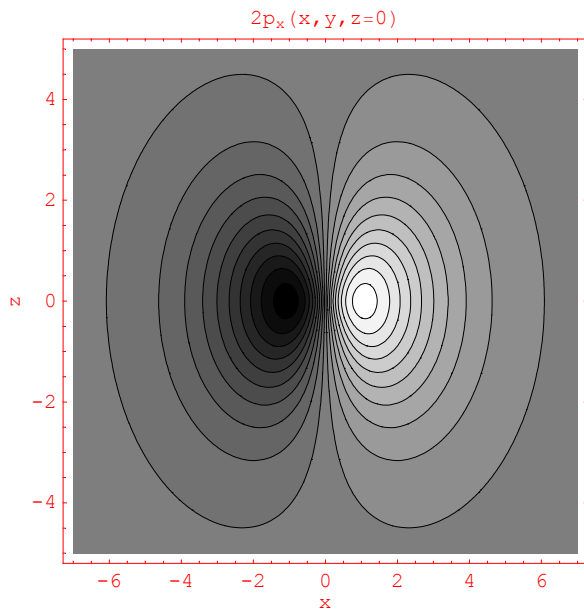
These functions are all proportional to x and decay exponentially with r. These two elements controls their shape.

Make a contour plot of $2 p_x(x, y, z = 0)$

```

pl2C = ContourPlot[
  Evaluate[px[r, θ, φ][2] /. convCartp /. convCarts /. z → 0 /. {a → 0.5292, z → 1}],
  {x, -7, 7}, {y, -5, 5},
  PlotPoints → 200, Contours → 20, PlotRange → All,
  FrameLabel → {"x", "z"}, PlotLabel -> "2px(x, y, z=0)",
  ContourSmoothing → True, DefaultColor → RGBColor[1, 0, 0]]

```

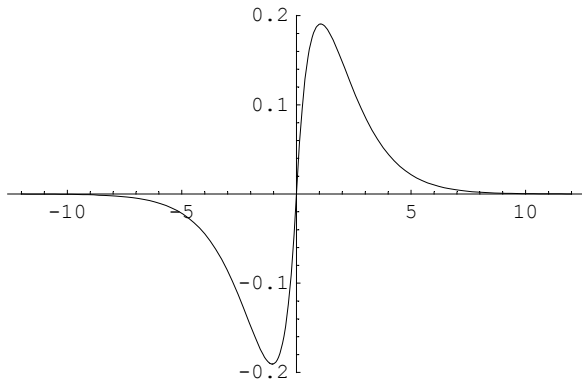


- ContourGraphics -

The function is elongated along the OX axis. The graph is whiter than the background where the function is positive and darker where the function is negative. The darker or the whiter a region, the higher the value of the function at those points.

Look at the function $2 p_x(x, y = 0, z = 0)$

```
p12x = Plot[
  Evaluate[px[r, θ, φ][2] /. convCartp /. convCarts /. {y → 0, z → 0} /. {a → 0.5292, z → 1}],
  {x, -12, 12}, PlotPoints → 100,
  PlotRange → All ]
```



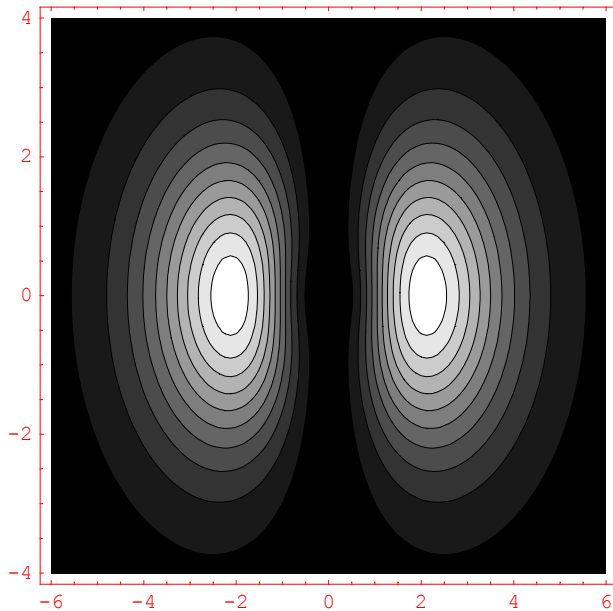
- Graphics -

You see that $2 p_x(x, y = 0, z = 0)$ is negative when $x \leq 0$ and positive otherwise

Look at the probability

$$r^2 \quad 2 p_x(x, y, z)^2 \text{ for } z=0$$

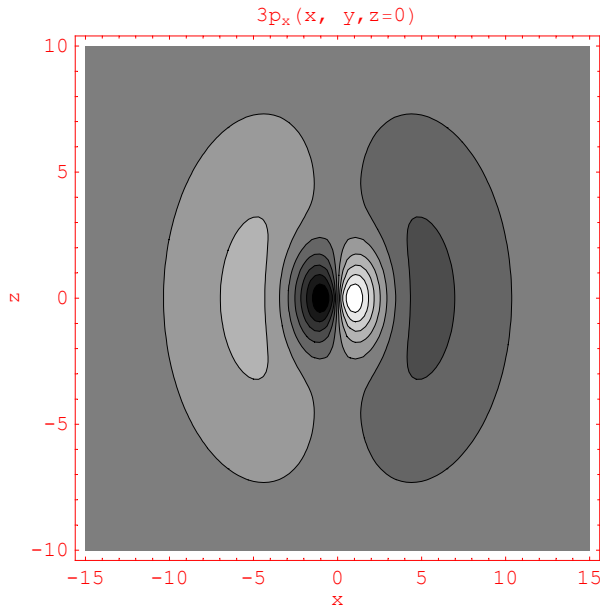
```
p12p = ContourPlot[
  Evaluate[r^2 px[r, θ, φ][2]^2 /. convCartp /. convCarts /. z → 0 /. {a → 0.5292, z → 1}],
  {x, -6, 6}, {y, -4, 4}, PlotPoints → 100, Contours → 10,
  PlotRange → All, AxesLabel → {"x", "z"}, ContourSmoothing → True,
  DefaultColor → RGBColor[1, 0, 0] ]
```



- ContourGraphics -

Plot 3 $p_x(x, y, z = 0)$

```
p13C = ContourPlot[
  Evaluate[px[r, θ, φ][3] /. convCartp /. convCarts /. z → 0 /. {a → 0.5292, z → 1}],
  {x, -15, 15}, {y, -10, 10}, PlotPoints → 100, Contours → 10,
  PlotRange → All, FrameLabel → {"x", "z"}, PlotLabel → "3px(x, y, z=0)",
  DefaultColor → RGBColor[1, 0, 0]]
```

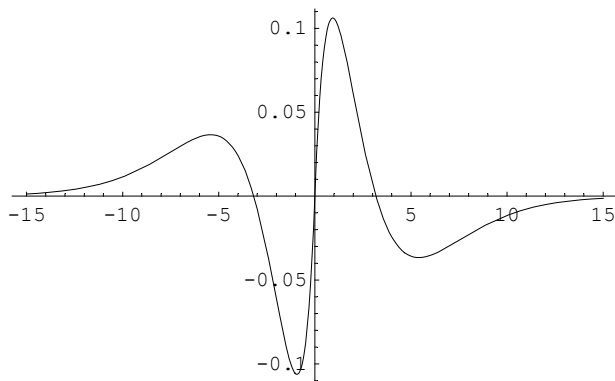


- ContourGraphics -

Plot

$r^2 3 p_x(x, y, z)^2$ as a function of x, for y=z=0

```
p13x = Plot[
  Evaluate[ px[r, θ, φ][3] /. convCartp /. convCarts /. {z → 0, y → 0} /. {a → 0.5292, z → 1}],
  {x, -15, 15}]
```



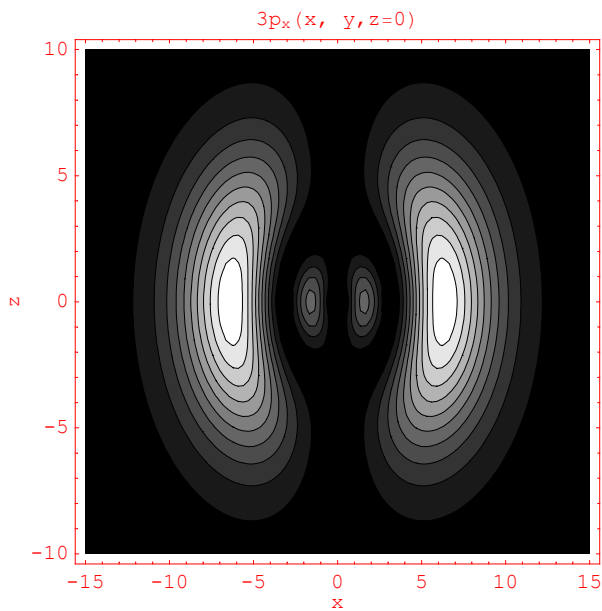
- Graphics -

Plot the probability

$$r^2 \int_0^{2\pi} \int_0^\pi p_x(x, y, z)^2$$

as a function of x, for z=0

```
p13p = ContourPlot[
  Evaluate[r^2 px[r, θ, φ][3]^2 /. convCartp /. convCarts /. z → 0 /. {a → 0.5292, z → 1}],
  {x, -15, 15}, {y, -10, 10}, PlotPoints → 100, Contours → 10,
  PlotRange → All, FrameLabel → {"x", "z"}, PlotLabel → "3px(x, y, z=0)",
  DefaultColor → RGBColor[1, 0, 0]]
```



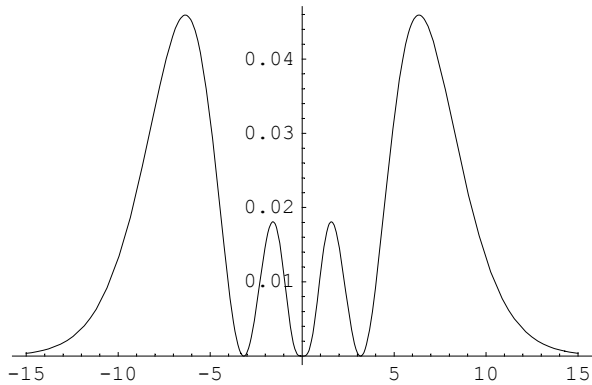
- ContourGraphics -

Plot

$$r^2 \int_0^{2\pi} \int_0^\pi p_x(x, y, z)^2$$

as a function of x, for y=z=0

```
Plot[Evaluate[r^2 px[r,  $\theta$ ,  $\phi$ ][3]^2 /. convCartp /. convCarts /. {z  $\rightarrow$  0, y  $\rightarrow$  0} /.
{a  $\rightarrow$  0.5292, z  $\rightarrow$  1}], {x, -15, 15}]
```

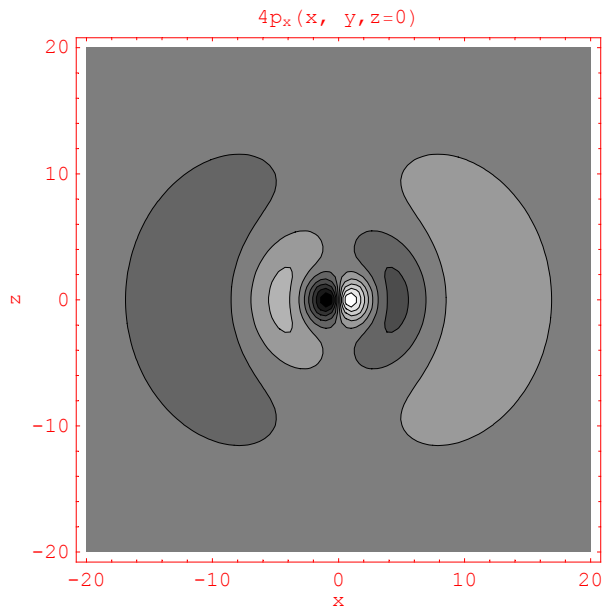


- Graphics -

Plot

4 $p_x(x, y, z = 0)$

```
p14C = ContourPlot[
Evaluate[px[r,  $\theta$ ,  $\phi$ ][4] /. convCartp /. convCarts /. z  $\rightarrow$  0 /. {a  $\rightarrow$  0.5292, z  $\rightarrow$  1}],
{x, -20, 20}, {y, -20, 20}, PlotPoints  $\rightarrow$  100, Contours  $\rightarrow$  10,
PlotRange  $\rightarrow$  All, FrameLabel  $\rightarrow$  {"x", "z"}, PlotLabel  $\rightarrow$  "4px(x, y, z=0)",
DefaultColor  $\rightarrow$  RGBColor[1, 0, 0]]
```

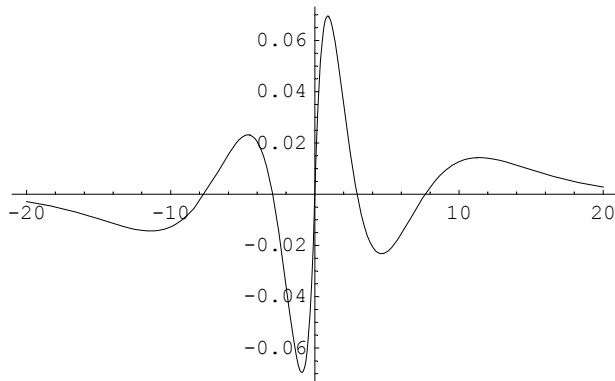


- ContourGraphics -

Plot

3 $p_x(x, y, z)$ versus x, when y=z=0

```
p14x = Plot[
  Evaluate[ px[r, θ, φ][4] /. convCartp /. convCarts /. {z → 0, y → 0} /. {a → 0.5292, z → 1}],
  {x, -20, 20}]
```

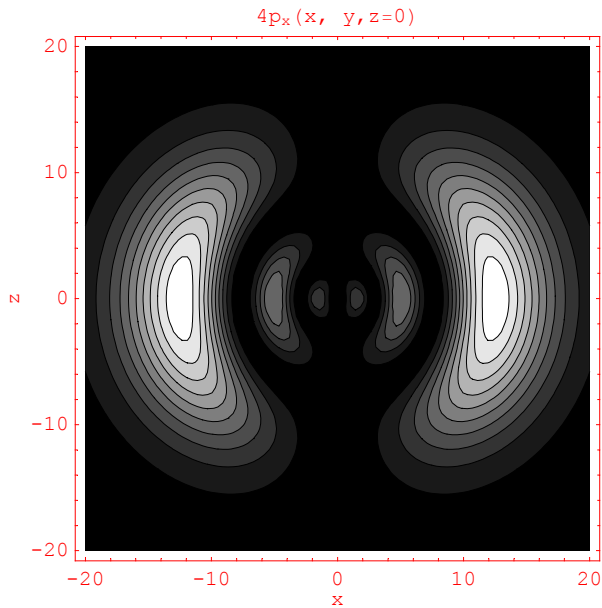


- Graphics -

Plot

$r^2 3 p_x(x, y, z)^2$ as a function of x and y, for z=0

```
p14p = ContourPlot[
  Evaluate[r^2 px[r, θ, φ][4]^2 /. convCartp /. convCarts /. z → 0 /. {a → 0.5292, z → 1}],
  {x, -20, 20}, {y, -20, 20}, PlotPoints → 100, Contours → 10,
  PlotRange → All, FrameLabel → {"x", "z"}, PlotLabel → "4p_x(x, y, z=0)",
  DefaultColor → RGBColor[1, 0, 0]]
```



- ContourGraphics -

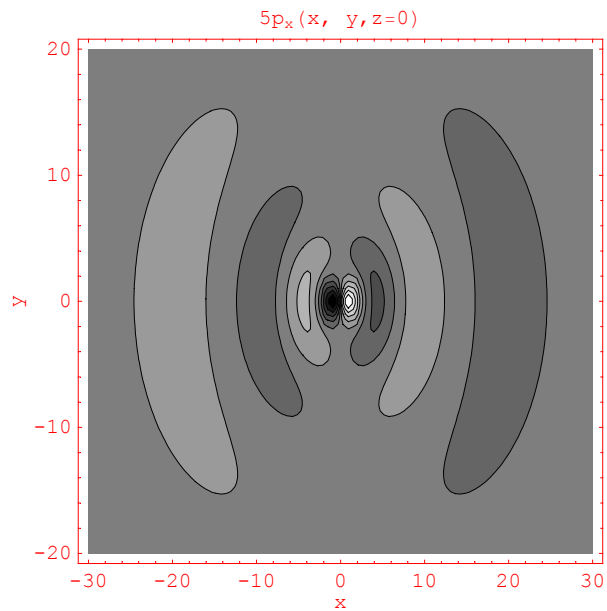
Plot

$5 p_x(x, y, z = 0)$

```

p15C = ContourPlot[
  Evaluate[px[r,  $\theta$ ,  $\phi$ ][5] /. convCartp /. convCarts /. z  $\rightarrow$  0 /. {a  $\rightarrow$  0.5292, z  $\rightarrow$  1}],
  {x, -30, 30}, {y, -20, 20}, PlotPoints  $\rightarrow$  100, Contours  $\rightarrow$  10,
  PlotRange  $\rightarrow$  All, FrameLabel  $\rightarrow$  {"x", "y"}, PlotLabel  $\rightarrow$  "5px(x, y, z=0)",
  DefaultColor  $\rightarrow$  RGBColor[1, 0, 0]]

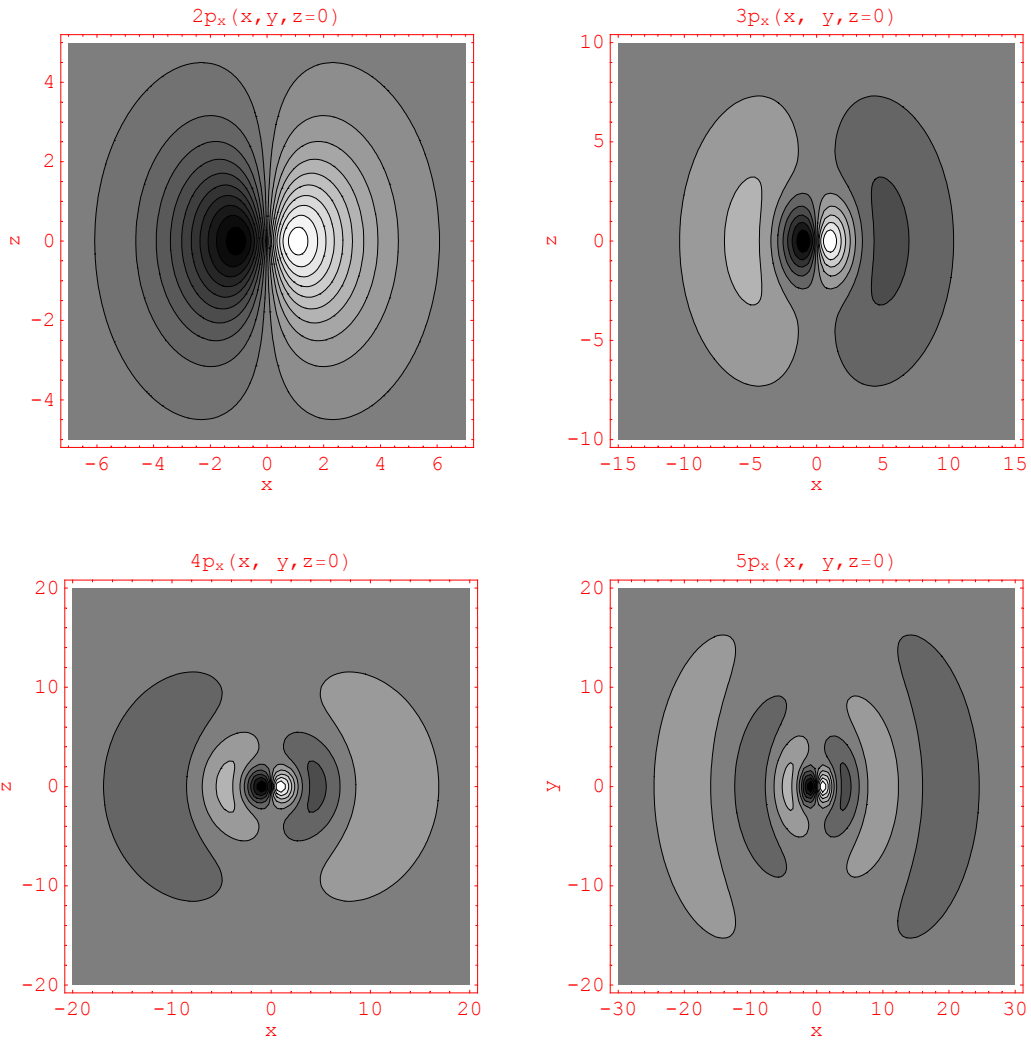
```



- ContourGraphics -

Show 2 p_x , 3 p_x , 4 p_x and 5 p_x on the same graph:

```
Show[GraphicsArray[{{p12C, p13C}, {p14C, p15C}}]]
```



- GraphicsArray -

■ Cell 5: The functions

$$np_y(r, \theta, \phi) = \frac{i}{\sqrt{2}} \{Y_1^1(\theta, \phi) + Y_1^{-1}(\theta, \phi)\} R_{n,1}(r)$$

The angular part of \$np_y\$ is:

```
Clear[pyAng]
pyAng[theta_, phi_] := (I / Sqrt[2]) *
  (SphericalHarmonicY[1, 1, theta, phi] + SphericalHarmonicY[1, -1, theta, phi]) // ComplexExpand
```

pyAng[θ , ϕ]

$$\frac{1}{2} \sqrt{\frac{3}{\pi}} \sin[\theta] \sin[\phi]$$

Unprotect[**py**];

py = .

py[**r**_, **θ** _, **ϕ** _] [**n**_] := **Module**[{**pyang**},

pyang =

(**I** / **Sqrt**[2]) * (**SphericalHarmonicY**[1, 1, **θ** , **ϕ**] + **SphericalHarmonicY**[1, -1, **θ** , **ϕ**]) //

ComplexExpand // **FullSimplify**;

pyang * **R**[**n**, 1] [**r**]

]

py[**r**, **θ** , **ϕ**] [**n**]

$$\sqrt{\frac{6}{\pi}} \left(\frac{z}{an}\right)^{3/2} \sin[\theta] \sin[\phi] \Phi[n, 1] \left[\frac{r}{a}\right]$$

Convert to cartesian:

py[**r**, **θ** , **ϕ**] [**n**] /. **convCartp**

$$\frac{\sqrt{\frac{6}{\pi}} y \left(\frac{z}{an}\right)^{3/2} \Phi[n, 1] \left[\frac{r}{a}\right]}{r}$$

Compare to np_x :

px[**r**, **θ** , **ϕ**] [**n**] /. **convCartp**

$$\frac{\sqrt{\frac{6}{\pi}} x \left(\frac{z}{an}\right)^{3/2} \Phi[n, 1] \left[\frac{r}{a}\right]}{r}$$

Note that you can obtain np_y by interchanging x with y in np_x . All plots on np_y are the same as those of np_x except that we exchange the labels x and y on the axes

Exercise: Check the orthogonality of $2 p_x$ to $2 p_y$

■ **Cell 6: The functions**

$$np_z(\theta, \phi) = Y_1^0(\theta, \phi) R_{n,1}(r)$$

Clear[**pz**]

pzAng[**θ** _, **ϕ** _] := **SphericalHarmonicY**[1, 0, **θ** , **ϕ**]

pzAng[**θ** , **ϕ**]

$$\frac{1}{2} \sqrt{\frac{3}{\pi}} \cos[\theta]$$

```
Unprotect[pz];
pz = .
pz[r_, θ_, φ_] [n_] := Module[{pz},
  pz = SphericalHarmonicY[1, 0, θ, φ];
  pz * R[n, 1][r]]
Protect[pz];
```

Convert to cartesian coordinates:

```
pz[r, θ, φ] [n] /. convCartp
```

$$\frac{\sqrt{\frac{6}{\pi}} z \left(\frac{z}{a n}\right)^{3/2} \Phi[n, 1]\left[\frac{r}{a}\right]}{r}$$

Compare to np_x :

```
px[r, θ, φ] [n] /. convCartp
```

$$\frac{\sqrt{\frac{6}{\pi}} x \left(\frac{z}{a n}\right)^{3/2} \Phi[n, 1]\left[\frac{r}{a}\right]}{r}$$

You can obtain np_z by interchanging x with z in np_x

■ Cell 7: The function

$$nd_{xy}(r, \theta, \phi) = R_{n,2}(r) \frac{1}{i\sqrt{2}} \{Y_2^2(\theta, \phi) - Y_2^{-2}(\theta, \phi)\}$$

The angular part of nd_{xy}

```
Clear[dxyAng]
dxyAng[θ_, φ_] := (1 / (I Sqrt[2])) *
  (SphericalHarmonicY[2, 2, θ, φ] - SphericalHarmonicY[2, -2, θ, φ]) // ComplexExpand
```

Test that it works:

```
dxyAng[θ, φ]
```

$$\frac{1}{4} \sqrt{\frac{15}{\pi}} \sin[\theta]^2 \sin[2\phi]$$

The conversion to cartesian coordinates is delicate, if I want to obtain the form usually given in textbooks, because of the presence of $\sin(2\phi)$ for which we have not defined a conversion rule. However *Mathematica* can be used to write this expression in a convenient form. I'll do this in several steps:

```
temp1 = (dxyAng[θ, φ] // TrigExpand) /. convCartp /. convCarts // FullSimplify
```

$$\frac{\sqrt{\frac{15}{\pi}} x y}{2 (x^2 + y^2 + z^2)}$$

I want to get rid of $x^2 + y^2 + z^2$ and replace it with r^2 . I use `ReplacePart` in combination with `Position`:


```
dxycart = ReplacePart[temp1, r^2, Position[temp1, x^2 + y^2 + z^2] // Flatten]
```

$$\frac{\sqrt{\frac{15}{\pi}} x y}{2 r^2}$$

Define the function $nd_{xy}[r, \theta, \phi][n]$ that gives

$nd_{xy}(r, \theta, \phi)$

```
Clear[dxycart]  
dxycart[r_, \theta_, \phi_][n_] := R[n, 2][r] * dxycart[r, \theta, \phi]
```

Check that it works

```
dxycart[r, \theta, \phi][3]
```

$$\frac{e^{-\frac{r z}{3 a}} r^2 z^2 \left(\frac{z}{a}\right)^{3/2} \sin[\theta]^2 \sin[2 \phi]}{81 a^2 \sqrt{2 \pi}}$$

```
dxycart[r, \theta, \phi][4]
```

$$\frac{e^{-\frac{r z}{4 a}} r^2 z^2 \left(\frac{z}{a}\right)^{3/2} \left(6 - \frac{r z}{2 a}\right) \sin[\theta]^2 \sin[2 \phi]}{512 a^2 \sqrt{3 \pi}}$$

Make a function that uses the coordinates x, y, z, and r (r is redundant, but I want to avoid using $\sqrt{x^2 + y^2 + z^2}$ (which is equal to r) so that the expressions are shorter. When I use the function I convert r to its cartesian expression by using the rule convCarts).

```
dxycartesian[n_] := dxycart * R[n, 2][r]
```

```
dxycartesian[3]
```

$$\frac{e^{-\frac{r z}{3 a}} \sqrt{\frac{2}{\pi}} x y z^2 \left(\frac{z}{a}\right)^{3/2}}{81 a^2}$$

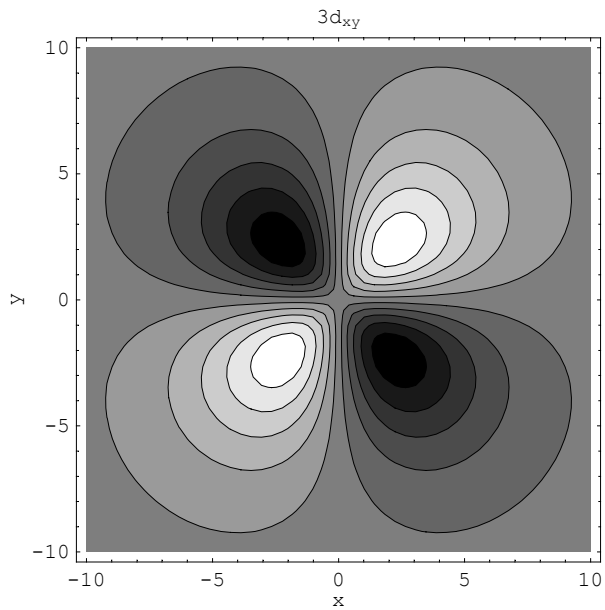
```
dxycartesian[4]
```

$$\frac{e^{-\frac{r z}{4 a}} x y z^2 \left(\frac{z}{a}\right)^{3/2} \left(6 - \frac{r z}{2 a}\right)}{256 a^2 \sqrt{3 \pi}}$$

The nd_{xy} functions are proportional to xy and this makes them large on the diagonals of the quadrants of the XOY plane. They also decay exponentially with r. These two factors control the shape of the functions nd_{xy} .

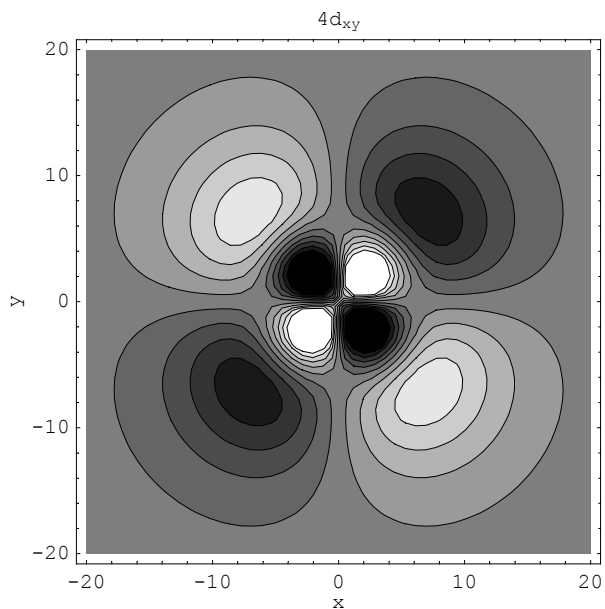
Plot 3 d_{xy} as a function of x and y for z=0.

```
pl3dxy = ContourPlot[Evaluate[ dxyCartesian[3] /. convCarts /. z -> 0 /. {a -> 0.5292, z -> 1}],
  {x, -10, 10}, {y, -10, 10},
  PlotPoints -> 50, FrameLabel -> {"x", "y"}, PlotLabel -> "3dxy"]
```



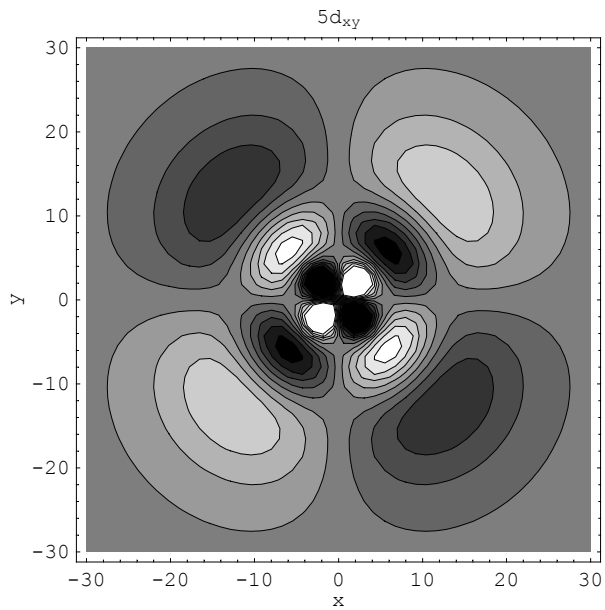
- ContourGraphics -

```
pl4dxy = ContourPlot[Evaluate[ dxyCartesian[4] /. convCarts /. z -> 0 /. {a -> 0.5292, z -> 1}],
  {x, -20, 20}, {y, -20, 20},
  PlotPoints -> 50, FrameLabel -> {"x", "y"}, PlotLabel -> "4dxy"]
```



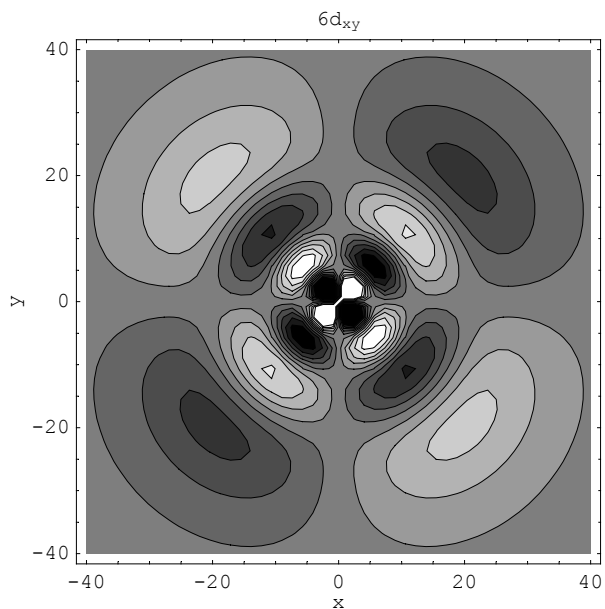
- ContourGraphics -

```
p15dxy = ContourPlot[Evaluate[ dxyCartesian[5] /. convCarts /. z -> 0 /. {a -> 0.5292, z -> 1}],
  {x, -30, 30}, {y, -30, 30},
  PlotPoints -> 50, FrameLabel -> {"x", "y"}, PlotLabel -> "5dxy"]
```



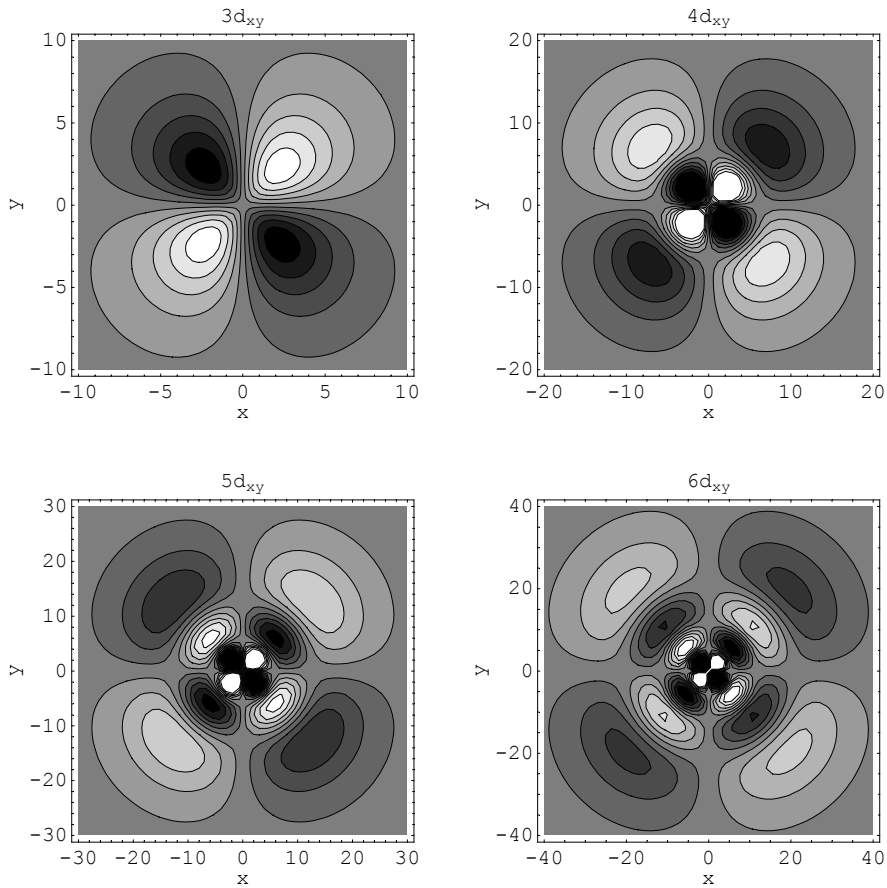
- ContourGraphics -

```
p16dxy = ContourPlot[Evaluate[ dxyCartesian[6] /. convCarts /. z -> 0 /. {a -> 0.5292, z -> 1}],
  {x, -40, 40}, {y, -40, 40},
  PlotPoints -> 50, FrameLabel -> {"x", "y"}, PlotLabel -> "6dxy"]
```



- ContourGraphics -

```
Show[GraphicsArray[{{p13dxy, p14dxy}, {p15dxy, p16dxy}}]]
```



- GraphicsArray -

■ Cell 8: The functions

$$nd_{yz}(\mathbf{r}, \theta, \phi) = R_{n,\ell}(r) \frac{i}{\sqrt{2}} \{Y_2^{-1}(\theta, \phi) + Y_2^1(\theta, \phi)\}$$

Define the angular part of

$$nd_{yz}(\mathbf{r}, \theta, \phi)$$

which is

$$\frac{i}{\sqrt{2}} \{Y_2^{-1}(\theta, \phi) + Y_2^1(\theta, \phi)\}$$

```
Unprotect[dyzAng];
Clear[dyzAng]
dyzAng[theta_, phi_] :=
  (I / (Sqrt[2])) * (SphericalHarmonicY[2, -1, theta, phi] + SphericalHarmonicY[2, 1, theta, phi]) //
  ComplexExpand // FullSimplify
Protect[dyzAng];
```

dyzAng[θ , ϕ]

$$\frac{1}{2} \sqrt{\frac{15}{\pi}} \cos[\theta] \sin[\theta] \sin[\phi]$$

Define the function **dyz**[r , θ , ϕ][n], which gives $nd_{yz}(r, \theta, \phi)$

```
Unprotect[dyz];
Clear[dyz]
dyz[r_,  $\theta$ _,  $\phi$ ][n_] := Module[{ },
  dyzAng[ $\theta$ ,  $\phi$ ] * R[n, 2][r]
Protect[dyz];

dyz[r,  $\theta$ ,  $\phi$ ][3]

$$\frac{e^{-\frac{r^2}{3a}} \sqrt{\frac{2}{\pi}} r^2 z^2 \left(\frac{z}{a}\right)^{3/2} \cos[\theta] \sin[\theta] \sin[\phi]}{81 a^2}$$

```

Write the functions in cartesian coordinates since plotting is easier

```
dyz[r,  $\theta$ ,  $\phi$ ][n] /. convCartp

$$\frac{\sqrt{\frac{30}{\pi}} y z \left(\frac{z}{an}\right)^{3/2} \Phi[n, 2]\left[\frac{r}{a}\right]}{r^2}$$

```

Compare this to d_{xy} given in Cartesian coordinates.

```
dxCartesian[n]

$$\frac{\sqrt{\frac{30}{\pi}} x y \left(\frac{z}{an}\right)^{3/2} \Phi[n, 2]\left[\frac{r}{a}\right]}{r^2}$$

```

nd_{yz} can be obtained from nd_{xy} by exchanging x with z . The plots of d_{yz} in the YOZ plane will look like the plots of nd_{xy} in the XOY plane, with the OZ axis replacing the OX axis.

■ Cell 9: The functions

$$nd_{xz}(\theta, \phi) = R_{n,l}(r) \frac{1}{\sqrt{2}} \{Y_2^{-1}(\theta, \phi) - Y_2^1(\theta, \phi)\}$$

```
Unprotect[dxzAng];
Clear[dxzAng]
dxzAng[ $\theta$ _,  $\phi$ _] :=
  (1 / Sqrt[2]) * (SphericalHarmonicY[2, -1,  $\theta$ ,  $\phi$ ] - SphericalHarmonicY[2, 1,  $\theta$ ,  $\phi$ ]) //
  ComplexExpand // FullSimplify;
Protect[
  dxzAng];
```

dxzAng[θ , ϕ]

$$\frac{1}{2} \sqrt{\frac{15}{\pi}} \cos[\theta] \cos[\phi] \sin[\theta]$$

In cartesian coordinates this is:

dxzAng[θ , ϕ] /. **convCartp**

$$\frac{\sqrt{\frac{15}{\pi}} x z}{2 r^2}$$

Unprotect[**dxz**];

Clear[**dxz**];

dxz[r _, θ _, ϕ _] [n] :=
dxzAng[θ , ϕ] * **R**[n , 2] [r]

Protect[**dxz**];

dxz[r , θ , ϕ] [n]

$$\sqrt{\frac{30}{\pi}} \left(\frac{z}{a n}\right)^{3/2} \cos[\theta] \cos[\phi] \sin[\theta] \Phi[n, 2] \left[\frac{r}{a}\right]$$

dxz[r , θ , ϕ] [n] /. **convCartp**

$$\frac{\sqrt{\frac{30}{\pi}} x z \left(\frac{z}{a n}\right)^{3/2} \Phi[n, 2] \left[\frac{r}{a}\right]}{r^2}$$

This can be obtained from d_{xy} by replacing y with z and keeping r unchanged. The plots of nd_{xz} in the XOZ plane look like those of nd_{xy} in the OXY plane; the OZ axis replaces the OY axis.

■ **Cell 10: The functions**

$$n d_{x^2-y^2}(\theta, \phi) = \frac{1}{\sqrt{2}} \{Y_2^2(\theta, \phi) + Y_2^{-2}(\theta, \phi)\}$$

Define the function

dxSmySAng[θ , ϕ]

which gives the angular dependence of

$$n d_{x^2-y^2}$$

Unprotect[**dxSmySAng**];

Clear[**dxSmySAng**]

dxSmySAng[θ _, ϕ _] := (1 / Sqrt[2]) * (SphericalHarmonicY[2, 2, θ , ϕ]
+ SphericalHarmonicY[2, -2, θ , ϕ]) // **ComplexExpand**

Protect[**dxSmySAng**];

dxSmySAng[θ , ϕ]

$$\frac{1}{4} \sqrt{\frac{15}{\pi}} \cos[2 \phi] \sin[\theta]^2$$

Convert to cartesian coordinates:

temp1 = (dxSmySAng[θ, φ] /. convCartp // TrigExpand) /. convCartp

$$\frac{\sqrt{\frac{15}{\pi}} x^4}{4 r^2 (x^2 + y^2)} - \frac{\sqrt{\frac{15}{\pi}} y^4}{4 r^2 (x^2 + y^2)}$$

temp2 = temp1 // FullSimplify

$$\frac{\sqrt{\frac{15}{\pi}} (x - y) (x + y)}{4 r^2}$$

Give the result the name andx2my2

angdx2my2 = (x^2 - y^2) Sqrt[15 / Pi] / (4 r^2)

$$\frac{\sqrt{\frac{15}{\pi}} (x^2 - y^2)}{4 r^2}$$

Create a function that gives

nd_{x²-y²}

Unprotect[dxSmyS];

Clear[dxSmyS]

dxSmyS[r_, θ_, φ_] [n_] := dxSmySAng[θ, φ] * R[n, 2][r]

Protect[dxSmyS];

dxSmyS[r, θ, φ] [n]

$$\sqrt{\frac{15}{2\pi}} \left(\frac{z}{a n}\right)^{3/2} \cos[2\phi] \sin[\theta]^2 \Phi[n, 2]\left[\frac{r}{a}\right]$$

dxSmyS[r, θ, φ] [3]

$$\frac{e^{-\frac{r z}{3a}} r^2 z^2 \left(\frac{z}{a}\right)^{3/2} \cos[2\phi] \sin[\theta]^2}{81 a^2 \sqrt{2\pi}}$$

dxSmyS[r, θ, φ] [4]

$$\frac{e^{-\frac{r z}{4a}} r^2 z^2 \left(\frac{z}{a}\right)^{3/2} \left(6 - \frac{r z}{2a}\right) \cos[2\phi] \sin[\theta]^2}{512 a^2 \sqrt{3\pi}}$$

Convert to cartesian coordinates x, y, z and r (as variables)

temp1 = ((dxSmyS[r, θ, φ] [n] /. convCartp) // TrigExpand) /. convCartp

$$\frac{\sqrt{\frac{15}{2\pi}} x^4 z \sqrt{\frac{z}{a n}} \Phi[n, 2]\left[\frac{r}{a}\right]}{a n r^2 (x^2 + y^2)} - \frac{\sqrt{\frac{15}{2\pi}} y^4 z \sqrt{\frac{z}{a n}} \Phi[n, 2]\left[\frac{r}{a}\right]}{a n r^2 (x^2 + y^2)}$$

temp2 = temp1 /. convCarts // FullSimplify

$$\frac{\sqrt{\frac{15}{2\pi}} (x - y) (x + y) \left(\frac{z}{a n}\right)^{3/2} \Phi[n, 2]\left[\frac{\sqrt{x^2 + y^2 + z^2}}{a}\right]}{x^2 + y^2 + z^2}$$

Replace $x^2 + y^2 + z^2$ with r^2 :

```
temp3 = ReplacePart[temp2, r^2, Position[temp2, x^2 + y^2 + z^2]]
```

$$\frac{\sqrt{\frac{15}{2\pi}} (x - y) (x + y) \left(\frac{z}{an}\right)^{3/2} \Phi[n, 2] \left[\frac{\sqrt{r^2}}{a}\right]}{r^2}$$

Make a function out of this expression:

```
dxSmySCart[p_] :=
  (1 / r^2) * Sqrt[15 / (2 Pi)] (x^2 - y^2) (z / (a n)) ^ (3 / 2) \Phi[n, 2] [r / a] /. n -> p
```

Look at two examples, for n=3 and n=4

```
dxSmySCart[3]
```

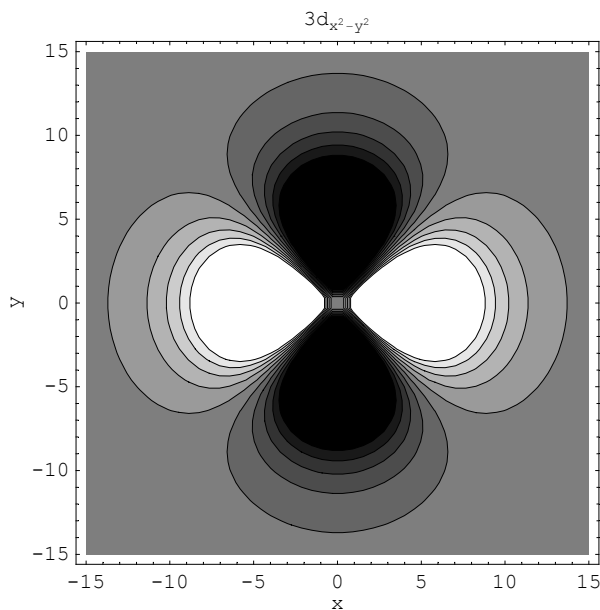
$$\frac{e^{-\frac{r z}{3 a}} (x^2 - y^2) z^2 \left(\frac{z}{a}\right)^{3/2}}{81 a^2 \sqrt{2 \pi}}$$

```
dxSmySCart[4]
```

$$\frac{e^{-\frac{r z}{4 a}} (x^2 - y^2) z^2 \left(\frac{z}{a}\right)^{3/2} \left(6 - \frac{r z}{2 a}\right)}{512 a^2 \sqrt{3 \pi}}$$

Plot the function $3d_{x^2-y^2}$ in the OXY plane (z=0)

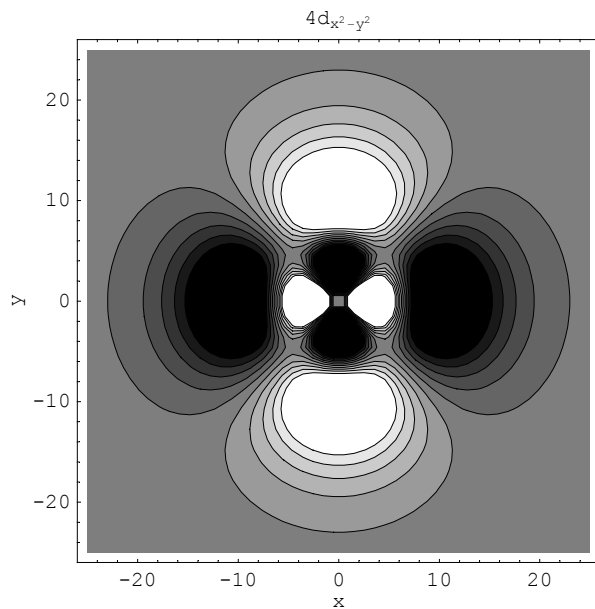
```
pl3dxSmyS = ContourPlot[Evaluate[dxSmySCart[3] /. convCarts /. z -> 0 /. {a -> 0.5292, z -> 1}],
  {x, -15, 15}, {y, -15, 15},
  PlotPoints -> 50, FrameLabel -> {"x", "y"}, PlotLabel -> "3d_{x^2-y^2}"]
```



- ContourGraphics -

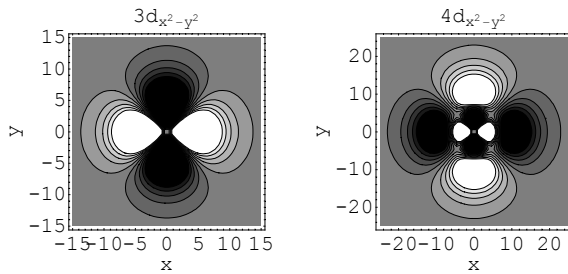
Plot the function $3d_{x^2-y^2}$ in the OXY plane ($z=0$)

```
pl4dxSmyS = ContourPlot[Evaluate[ dxSmySCart[4] /. convCarts /. z -> 0 /. {a -> 0.5292, z -> 1}],
  {x, -25, 25}, {y, -25, 25},
  PlotPoints -> 50, FrameLabel -> {"x", "y"}, PlotLabel -> "4d_{x^2-y^2}"]
```



- ContourGraphics -

```
Show[GraphicsArray[{pl3dxSmyS, pl4dxSmyS}]]
```



- GraphicsArray -

■ Cell 11: The functions

$$nd_{z^2}(\theta, \phi) = R_{n,2}(r) Y_2^0(\theta, \phi)$$

```
Unprotect[dz2Ang];
Clear[dz2Ang]
dz2Ang[theta_, phi_] := SphericalHarmonicY[2, 0, theta, phi]
Protect[dz2Ang];
```

dz2Ang[θ , ϕ]

$$\frac{1}{4} \sqrt{\frac{5}{\pi}} (-1 + 3 \cos[\theta]^2)$$

dz2Ang[θ , ϕ] /. convCartp

$$\frac{1}{4} \sqrt{\frac{5}{\pi}} \left(-1 + \frac{3 z^2}{r^2}\right)$$

Unprotect[dz2**];**

Clear[dz2**]**

dz2 [r_, θ _, ϕ _][n_] :=

SphericalHarmonicY[2, 0, θ , ϕ] *R[n, 2][r]

Protect[dz2**];**

dz2 [r, θ , ϕ][3]

$$\frac{e^{-\frac{r z}{3 a}} r^2 z^2 \left(\frac{z}{a}\right)^{3/2} (-1 + 3 \cos[\theta]^2)}{81 a^2 \sqrt{6 \pi}}$$

dz2 [r, θ , ϕ][4]

$$\frac{e^{-\frac{r z}{4 a}} r^2 z^2 \left(\frac{z}{a}\right)^{3/2} \left(6 - \frac{r z}{2 a}\right) (-1 + 3 \cos[\theta]^2)}{1536 a^2 \sqrt{\pi}}$$

Write the functions in cartesian coordinates since plotting is easy

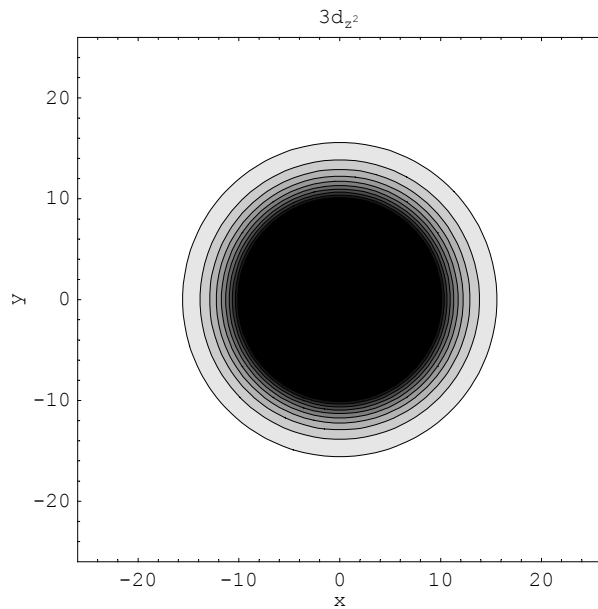
dz2 [r, θ , ϕ][3] /. convCartp

$$\frac{e^{-\frac{r z}{3 a}} r^2 \left(-1 + \frac{3 z^2}{r^2}\right) z^2 \left(\frac{z}{a}\right)^{3/2}}{81 a^2 \sqrt{6 \pi}}$$

dz2 [r, θ , ϕ][4] /. convCartp

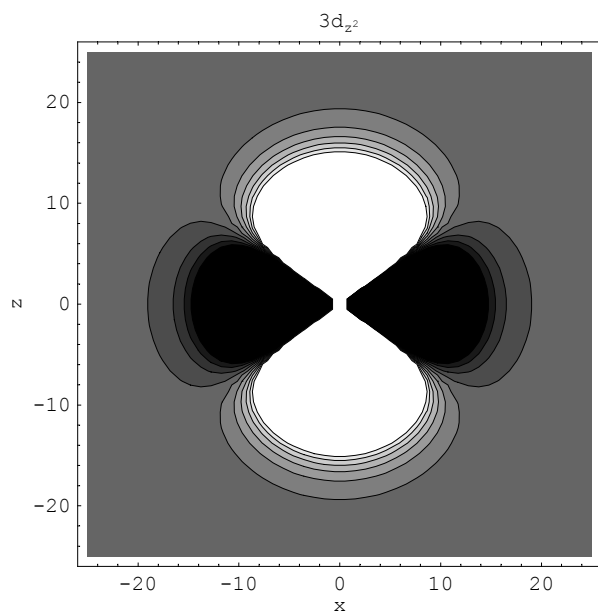
$$\frac{e^{-\frac{r z}{4 a}} r^2 \left(-1 + \frac{3 z^2}{r^2}\right) z^2 \left(\frac{z}{a}\right)^{3/2} \left(6 - \frac{r z}{2 a}\right)}{1536 a^2 \sqrt{\pi}}$$

```
p13dz2 = ContourPlot[
  Evaluate[ dz2[r,  $\theta$ ,  $\phi$ ][3] /. convCartp /. convCarts /. z  $\rightarrow$  0 /. {a  $\rightarrow$  0.5292, z  $\rightarrow$  1}],
  {x, -25, 25}, {y, -25, 25},
  PlotPoints  $\rightarrow$  50, FrameLabel  $\rightarrow$  {"x", "y"}, PlotLabel  $\rightarrow$  "3dz2"]
```



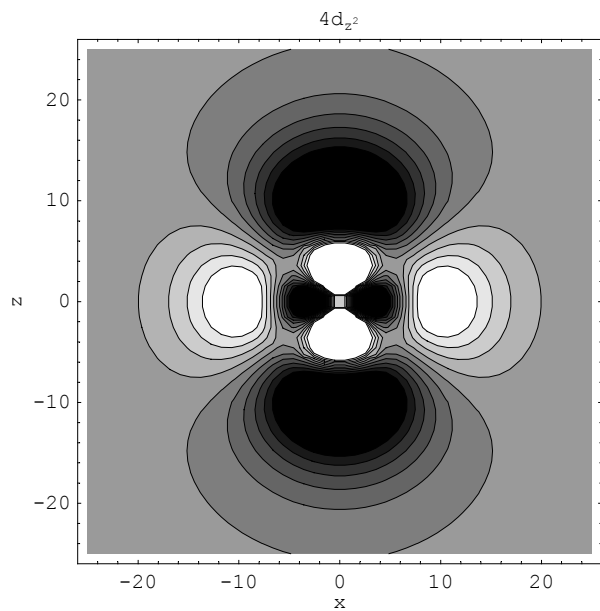
- ContourGraphics -

```
p13dz2 = ContourPlot[
  Evaluate[ dz2[r,  $\theta$ ,  $\phi$ ][3] /. convCartp /. convCarts /. y  $\rightarrow$  0 /. {a  $\rightarrow$  0.5292, z  $\rightarrow$  1}],
  {x, -25, 25}, {z, -25, 25},
  PlotPoints  $\rightarrow$  50, FrameLabel  $\rightarrow$  {"x", "z"}, PlotLabel  $\rightarrow$  "3dz2"]
```



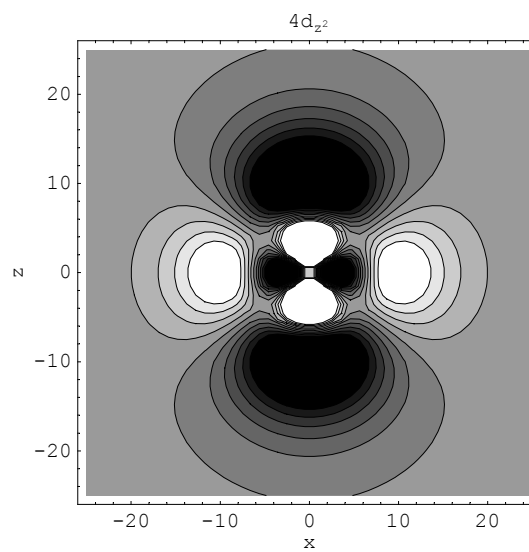
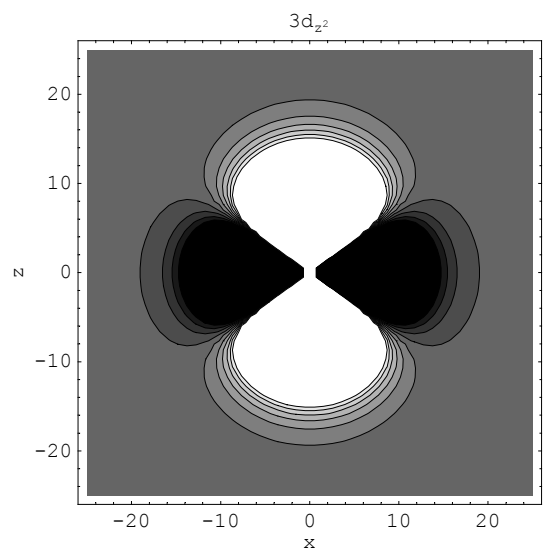
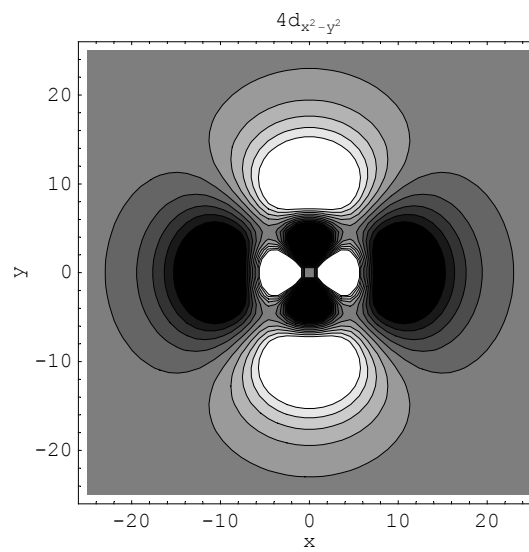
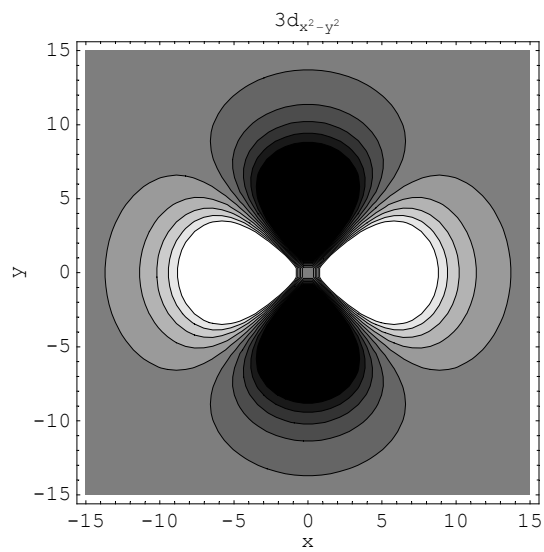
- ContourGraphics -

```
p14dz2 = ContourPlot[
  Evaluate[ dz2[r,  $\theta$ ,  $\phi$ ][4] /. convCartp /. convCarts /. y  $\rightarrow$  0 /. {a  $\rightarrow$  0.5292, z  $\rightarrow$  1}],
  {x, -25, 25}, {z, -25, 25},
  PlotPoints  $\rightarrow$  50, FrameLabel  $\rightarrow$  {"x", "z"}, PlotLabel  $\rightarrow$  "4dz2"]
```



- ContourGraphics -

```
Show[GraphicsArray[{{p13dxSmyS, p14dxSmyS}, {p13dz2, p14dz2}}]]
```



- GraphicsArray -

- Cell 12: Collect the functional forms and make a table. This cell works only after you have run all other cells

```
tb = {{"np_x", pxAng[θ, φ] Rn,1[r], pxAng[θ, φ] Rn,1[r] /. convCartp},
      {"np_y", pyAng[θ, φ] Rn,1[r], pyAng[θ, φ] Rn,1[r] /. convCartp},
      {"np_z", pzAng[θ, φ] Rn,1[r], pzAng[θ, φ] Rn,1[r] /. convCartp},
      {"nd_xy", dxyAng[θ, φ] Rn,2[r], dxyCart * Rn,2[r]},
      {"nd_yz", dyzAng[θ, φ] Rn,2[r], (dyzAng[θ, φ] /. convCartp) Rn,2[r]},
      {"nd_xz", dxzAng[θ, φ] Rn,2[r], (dxzAng[θ, φ] /. convCartp) Rn,2[r]},
      {"nd_x2-y2", dxSmySAng[θ, φ] Rn,2[r], angdx2my2},
      {"nd_z2", dz2Ang[θ, φ] Rn,2[r], (dz2Ang[θ, φ] /. convCartp) Rn,2[r]};
```

```
TableForm[tb]
```

np _x	$\frac{1}{2} \sqrt{\frac{3}{\pi}} \cos[\phi] \sin[\theta] R_{n,1}[r]$	$\frac{\sqrt{\frac{3}{\pi}} x R_{n,1}[r]}{2 r}$
np _y	$\frac{1}{2} \sqrt{\frac{3}{\pi}} \sin[\theta] \sin[\phi] R_{n,1}[r]$	$\frac{\sqrt{\frac{3}{\pi}} y R_{n,1}[r]}{2 r}$
np _z	$\frac{1}{2} \sqrt{\frac{3}{\pi}} \cos[\theta] R_{n,1}[r]$	$\frac{\sqrt{\frac{3}{\pi}} z R_{n,1}[r]}{2 r}$
nd _{xy}	$\frac{1}{4} \sqrt{\frac{15}{\pi}} \sin[\theta]^2 \sin[2\phi] R_{n,2}[r]$	$\frac{\sqrt{\frac{15}{\pi}} x y R_{n,2}[r]}{2 r^2}$
nd _{yz}	$\frac{1}{2} \sqrt{\frac{15}{\pi}} \cos[\theta] \sin[\theta] \sin[\phi] R_{n,2}[r]$	$\frac{\sqrt{\frac{15}{\pi}} y z R_{n,2}[r]}{2 r^2}$
nd _{xz}	$\frac{1}{2} \sqrt{\frac{15}{\pi}} \cos[\theta] \cos[\phi] \sin[\theta] R_{n,2}[r]$	$\frac{\sqrt{\frac{15}{\pi}} x z R_{n,2}[r]}{2 r^2}$
nd _{x²-y²}	$\frac{1}{4} \sqrt{\frac{15}{\pi}} \cos[2\phi] \sin[\theta]^2 R_{n,2}[r]$	$\frac{\sqrt{\frac{15}{\pi}} (x^2 - y^2)}{4 r^2}$
nd _{z²}	$\frac{1}{4} \sqrt{\frac{5}{\pi}} (-1 + 3 \cos[\theta]^2) R_{n,2}[r]$	$\frac{1}{4} \sqrt{\frac{5}{\pi}} \left(-1 + \frac{3 z^2}{r^2}\right) R_{n,2}[r]$

■ WorkBookQM.18. 10. Spectroscopy: the transition moment

I have shown that if the light is linearly polarized, the only allowed transitions from the ground state are those in which

$$\{\ell=0, m=0\} \rightarrow \{\ell=1, m=0\}$$

The transition dipole matrix element, which controls the intensity of these transitions is proportional to

$$\langle n, \ell = 1 | r | n = 1, \ell = 0 \rangle = \int_0^\infty r^2 R_{n,1}(r) r R_{1,1}(r) dr \quad (1)$$

The analytical evaluation of these integrals is complicated and leads to expressions that are hard to evaluate. I prefer to use *Mathematica* to evaluate the individual integrals as needed.

The radial wave function is:

$$R_{n,\ell}(r) = \left(\frac{2Z}{na}\right)^{3/2} \Phi_{n,\ell}(\rho) \quad (2)$$

with

$$\Phi_{n,\ell}(r) = \sqrt{\frac{(n-\ell-1)!}{2n(n+\ell)!}} \left(\frac{2Z\rho}{n}\right)^\ell \text{Exp}\left[-\frac{Z\rho}{n}\right] L_{n-\ell-1}^{2\ell+1}\left(\frac{2Z\rho}{n}\right) \quad (3)$$

with

$$\rho = \frac{r}{a} \quad (4)$$

and

$$a = \frac{\hbar^2(4\pi\epsilon_0)}{\mu e^2} \quad (5)$$

Plan:

1. Define the radial wave function. $R_{n,\ell}$
2. Calculate the integral Eq. (1).

```
Needs["Utilities`CleanSlate`"]
CleanSlate[]
Unprotect[a, R, Z, \[Phi];
Remove["Global`*"]
Off[General::spell1]
Off[General::spell]
Protect[a, R, Z, \[Phi];

(CleanSlate) Contexts purged: {Global`}

(CleanSlate) Approximate kernel memory recovered: 1970 Kb

{Utilities`CleanSlate`, Global`, System`}
```

■ **Cell 1: The radial wave function. This is copied from WorkBookQM.18.3**

The function Φ :

```

Unprotect[Φ];
Clear[Φ]; Unprotect[a, Z]; Clear[a, Z]; Protect[a, Z];
Φ[n_Integer, ℓ_Integer][ρ_] := Module[{const},
const = Sqrt[ $\frac{(n - \ell - 1)!}{(n + \ell)! 2^n}$ ];
const (2 Z ρ / n) ^ ℓ LaguerreL[n - ℓ - 1, 2 ℓ + 1,  $\frac{2 Z \rho}{n}$ ] Exp[- $\frac{Z \rho}{n}$ ]]
Protect[Φ];

```

Define a function that generates $R_{n,\ell}(r)$

```

Unprotect[R];
Clear[R];
R[n_, ℓ_][r_] := (2 Z / (n a)) ^ (3 / 2) Φ[n, ℓ][r / a]
Protect[R];

```

Test that the function works

```

R[3, 2][r]

$$\frac{2 \sqrt{\frac{2}{15}} e^{-\frac{r Z}{3 a}} r^2 Z^2 \left(\frac{Z}{a}\right)^{3/2}}{81 a^2}$$


```

■ **Cell 2. The transition dipole**

To perform the integral defined by Eq. (1) I note that the integrand

$$r^3 R_{n,1}(r) R_{1,0}(r)$$

is a polynomial in r multiplied with an exponential that decays as $r \rightarrow \infty$. This means that I will not have trouble with the limit $r \rightarrow \infty$. Here is what I do to have control of the execution. I denote by F(r) the definite integral

$$F(r) \equiv \int r^3 R_{n,1}(r) R_{1,0}(r) dr$$

Then I recognize that

$$\int_0^\infty r^3 R_{n,1}(r) R_{1,0}(r) dr = F(\infty) - F(0) = - F(0)$$

In this way I do not give *Mathematica* a chance to worry about convergence and mess things up. Here is a function transDip[n] that performs the integral

```

transDip[n_Integer] := -Integrate[r^3 R[n, 1][r] R[1, 0][r], r] /. r -> 0

```


transDip[2]

$$\frac{128 \sqrt{\frac{2}{3}} a}{81 Z}$$

transDip[3]

$$\frac{27 \sqrt{\frac{3}{2}} a}{64 Z}$$

Let us make a table with the results

toTable = Table[transDip[n] // N, {n, 2, 10}]

$$\left\{ \frac{1.29027 a}{Z}, \frac{0.516689 a}{Z}, \frac{0.304584 a}{Z}, \frac{0.208704 a}{Z}, \right. \\ \left. \frac{0.155135 a}{Z}, \frac{0.12142 a}{Z}, \frac{0.0984981 a}{Z}, \frac{0.0820453 a}{Z}, \frac{0.0697478 a}{Z} \right\}$$

Reduce the number of significant figures to four (this is too much but it costs us nothing)

toTb = NumberForm[#, 4] & /@ toTable

$$\left\{ \frac{1.29 a}{Z}, \frac{0.5167 a}{Z}, \frac{0.3046 a}{Z}, \frac{0.2087 a}{Z}, \right. \\ \left. \frac{0.1551 a}{Z}, \frac{0.1214 a}{Z}, \frac{0.0985 a}{Z}, \frac{0.08205 a}{Z}, \frac{0.06975 a}{Z} \right\}$$

Make a table with the results:

**TableForm[Transpose[{Table[n, {n, 2, 10}], toTb}],
TableHeadings → {None, {"n", "<n,1|r|1,0">}}]**

n	<n,1 r 1,0>
2	$\frac{1.29 a}{Z}$
3	$\frac{0.5167 a}{Z}$
4	$\frac{0.3046 a}{Z}$
5	$\frac{0.2087 a}{Z}$
6	$\frac{0.1551 a}{Z}$
7	$\frac{0.1214 a}{Z}$
8	$\frac{0.0985 a}{Z}$
9	$\frac{0.08205 a}{Z}$
10	$\frac{0.06975 a}{Z}$

We can calculate any transition dipole

$$\langle n_f, \ell_f | r | n_i, \ell_i \rangle$$

but we have to make sure that $\ell_f \leq n_f - 1$ and $\ell_i \leq n_i - 1$

The calculation is performed by the function shown below

```
transitionDipole[nf_Integer, lf_Integer][ni_Integer, li_Integer] :=  
  -Integrate[r^3 R[nf, lf][r] R[ni, li][r], r] /. r -> 0
```

For example

$\langle 3, 2 | r | 1, 0 \rangle$ is

```
transitionDipole[3, 2][1, 0]
```

$$\frac{9 \sqrt{\frac{15}{2}} a}{64 Z}$$