Lecture 2
Elementary Quantum Chemistry

Multidimensional particle in a box; hydrogen-like atoms

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PiaB wavefunctions are orthogonal and normalized (orthonormal)

$$\int \psi_m^*(\tau)\psi_n(\tau)d\tau = \delta_{mn} \equiv \begin{cases} 0 & m \neq n \\ 1 & m = n \end{cases}$$

Kronecker delta function

- Integral is analogous to dot product, in an infinite-dimensional space

$$x^{\mathrm{T}}y = \sum_i x_i y_i$$

  - Each τ value in integral is a different "index"

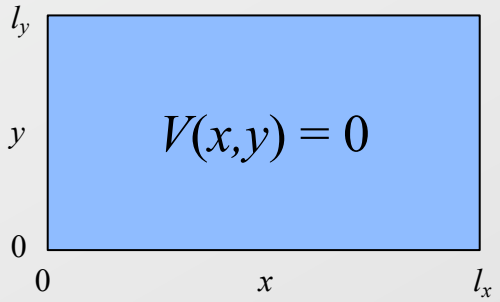
Mathematica evaluation of integral

```
In[3593]:= psi[x_, n_, l_] := Sqrt[2/l] Sin[n Pi x/l]

In[3594]:= Integrate[psi[x, m, l] psi[x, n, l], {x, 0, l}]
           Simplify[%, Assumptions → {n ∈ Integers, m ∈ Integers}]
           Integrate[psi[x, n, l] psi[x, n, l], {x, 0, l}]
           Simplify[%, Assumptions → {n ∈ Integers}]

Out[3594]=
           (2 n Cos[n π] Sin[m π] - 2 m Cos[m π] Sin[n π]) / (m^2 π - n^2 π)

Out[3595]=
           0

Out[3596]=
           1 - Sin[2 n π] / (2 n π)

Out[3597]=
           1
```

Two-dimensional PiaB is a simple extension of the 1D case

$$\hat{H}(\tau)\psi(\tau) = \psi(\tau)E \qquad \tau \equiv (x, y)$$

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi(x,y)}{\partial x^2} + \frac{\partial^2\psi(x,y)}{\partial y^2}\right) = \psi(x,y)E$$



- No coupling of x, y in Hamiltonian, so we can again apply separation of variables: $\psi(x,y) = \psi_x(x)\psi_y(y)$

$$-\frac{\hbar^2}{2m}\left(\frac{1}{\psi_x(x)}\frac{\partial^2\psi_x(x)}{\partial x^2} + \frac{1}{\psi_y(y)}\frac{\partial^2\psi_y(y)}{\partial y^2}\right) = E$$

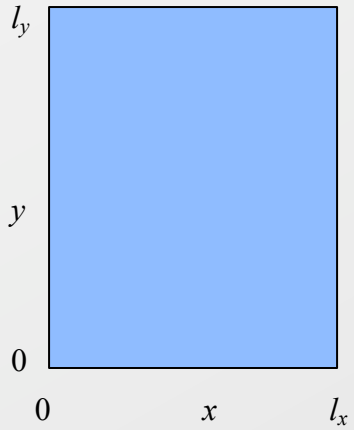
- Solution depends on two quantum numbers, n_x, n_y

$$E_{n_x,n_y} = \frac{h^2}{8m}\left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2}\right), \qquad n_x, n_y = 1, 2, 3, \ldots$$

Symmetry in the system produces degeneracies in the energy levels (different states of same energy)

$$l_y = \frac{5}{4} l_x$$

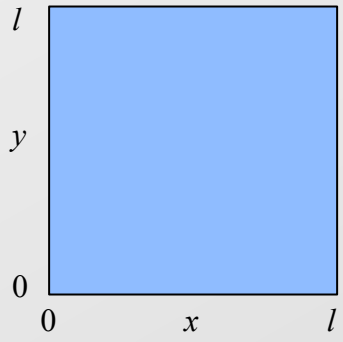
$$E_{n_x,n_y} = \frac{h^2}{8m}\left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2}\right)$$



n_x	n_y	$E/(h^2/8ml_x^2)$	
1	1	1.64	
1	2	3.56	No degeneracy
2	1	4.64	
2	2	6.56	
1	3	6.76	
3	1	9.64	
2	3	9.76	
3	2	11.56	
3	3	14.76	
4	1	16.64	
4	2	18.56	
3	4	19.24	
4	3	21.76	
4	4	26.24	

$$l_y = l_x \equiv l$$

$$E_{n_x,n_y} = \frac{h^2}{8ml^2}\left(n_x^2 + n_y^2\right)$$



n_x	n_y	$E/(h^2/8ml^2)$	
1	1	2.0	
2	1	5.0	degenerate
1	2	5.0	
2	2	8.0	
3	1	10.	
1	3	10.	
3	2	13.	
2	3	13.	
3	3	18.	
4	2	20.	
2	4	20.	
4	3	25.	
3	4	25.	
4	4	32.	

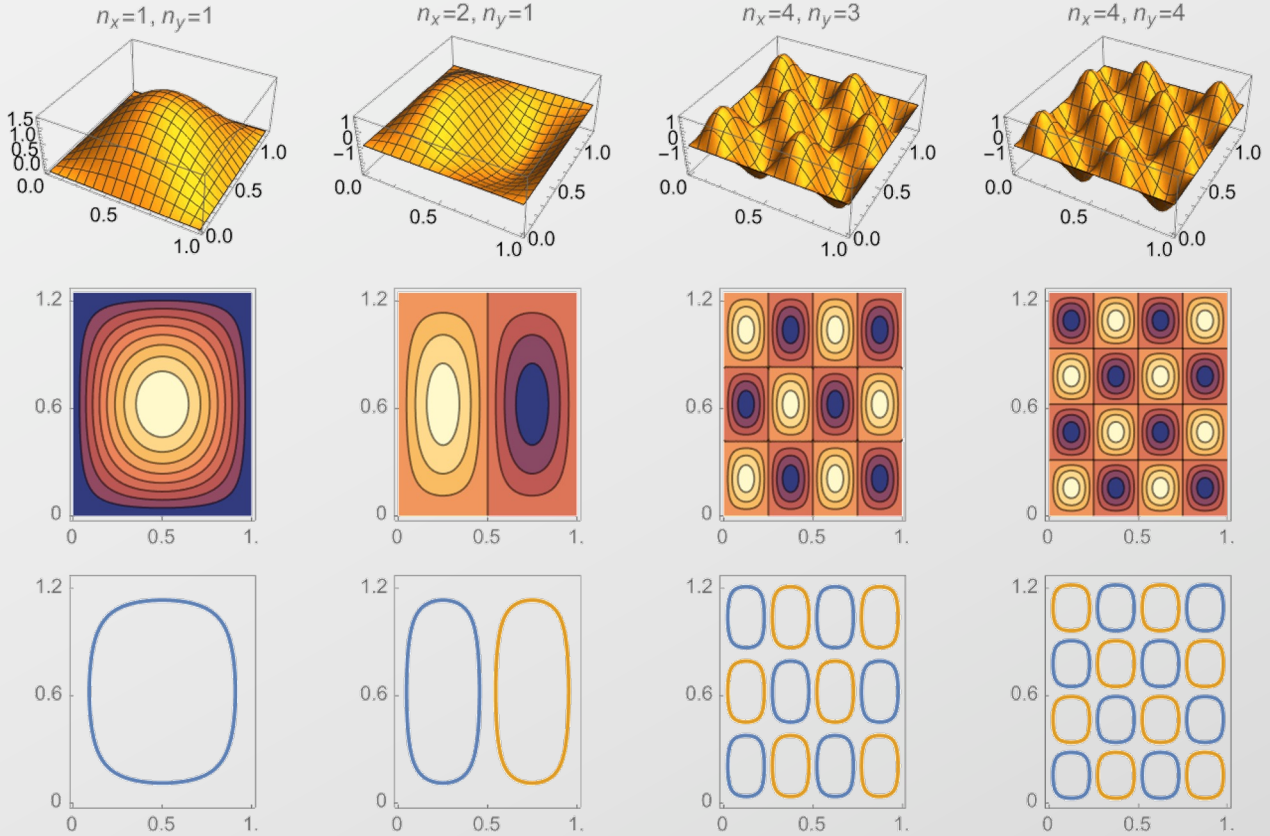
Several ways to view 2D wavefunction

$$\psi_{n_x,n_y}(x,y) = \frac{2}{(l_x l_y)^{1/2}} \sin\left(\frac{n_x \pi}{l_x} x\right) \sin\left(\frac{n_y \pi}{l_y} y\right)$$

Surface

Full contour

Single contour $\psi = \pm 0.5$



3D PiaB wavefunction contours give an example of how electron orbitals will be presented

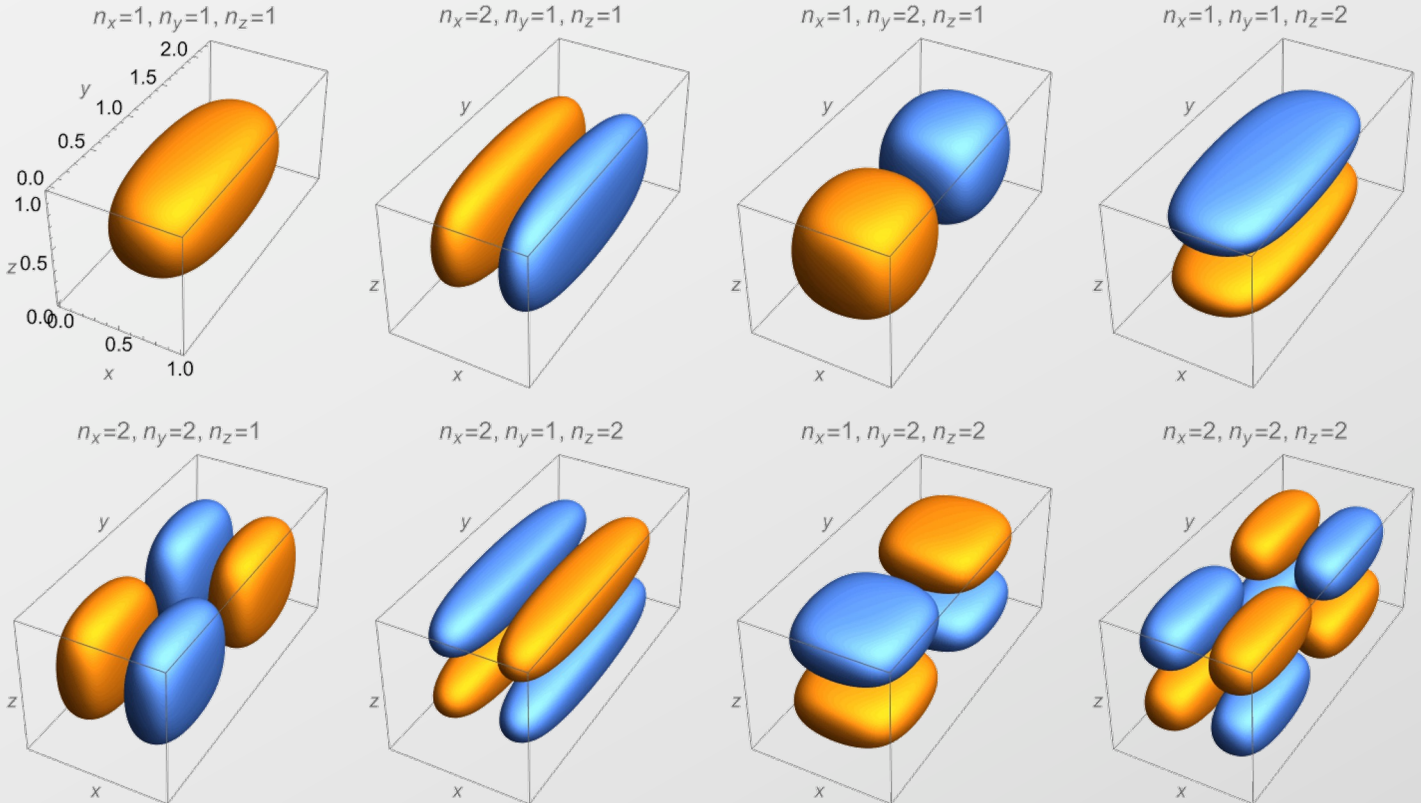
$$\psi_{n_x,n_y,n_z}(x,y,z) = \frac{2^{3/2}}{(l_x l_y l_z)^{1/2}} \sin\left(\frac{n_x \pi}{l_x} x\right) \sin\left(\frac{n_y \pi}{l_y} y\right) \sin\left(\frac{n_z \pi}{l_z} z\right)$$

$l_x = 1$

$l_y = 2.25$

$l_z = 1$

Single contours $\psi = \pm 0.5$



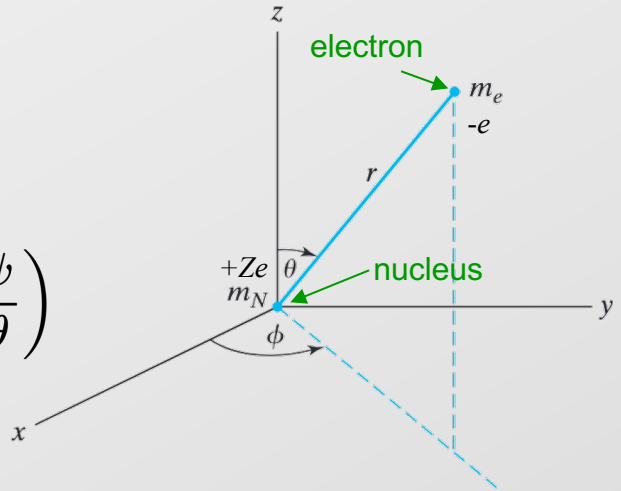
Study of PiaB teaches that confinement leads to energy-level quantization

- In chemistry, electrons are effectively confined by their strong electrostatic attraction to the nucleus
- Uncertainty principle, $\Delta x \Delta p \geq \hbar/2$, (not discussed here) says that kinetic energy must exceed some minimum value, in response to cap on position uncertainty accompanying confinement
  - Kinetic energy cannot be zero, instead there is a "zero-point" energy
  - This prevents electron from collapsing into nucleus

A “hydrogen-like” atom is formed from one nucleus of charge +Ze, and one electron (-e)

- Potential energy given as Coulomb’s law: $V(r) = -\dfrac{Ze^2}{4\pi\epsilon_0 r}$
  - Spherically symmetric, independent of direction
- Suggests use of spherical coordinates
  - Hamiltonian $\hat{H} = -\dfrac{\hbar^2}{2m_e}\nabla^2 + V(r)$

$$\hat{H}\psi(r,\theta,\phi) \equiv -\frac{\hbar^2}{2m_e}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] - \frac{Ze^2}{4\pi\epsilon_0 r}\psi = E\psi$$



- Solution introduces 3 quantum numbers: n, ℓ, m_ℓ

$$\psi_{n,\ell,m_\ell}(r,\theta,\phi) = R_{n,\ell}(r)Y_\ell^{m_\ell}(\theta,\phi)$$

Wavefunction of hydrogen-like atom describes electron's radial and angular motion

$$\psi_{n,\ell,m_\ell}(r,\theta,\phi) = R_{n,\ell}(r)Y_\ell^{m_\ell}(\theta,\phi)$$

- Radial component

$$R_{n,\ell}(r) = r^\ell P_{n,\ell}(r)e^{-(Z/na)r}$$

exponential decay

Associated Laguerre polynomial of degree n-ℓ-1

$a = 4\pi\epsilon_0\hbar^2/\mu e^2$

$\mu \approx m_e$

  - $n = 1,2,3,\ldots$ (defined $n_r+\ell$)
    - principal quantum number
  - $\ell = 0,1,2,\ldots,n$-1
    - orbital angular momentum quantum number
    - ℓ = 0,1,2,3 → s,p,d,f

- Spherical harmonics $Y_\ell^{m_\ell}(\theta,\phi)$

$$Y_\ell^{m_\ell}(\theta,\phi) \propto e^{im_\ell\phi}P_\ell^{m_\ell}(\cos\theta)$$

Associated Legendre polynomial

  - $m_\ell = -\ell, -\ell+1,\ldots,0,\ldots,\ell-1,\ell$
    - magnetic quantum number
    - quantizes direction of angular motion
    - degenerate states, $2\ell+1$
    - combine to express complex part in terms of sin, cos

Wavefunction of hydrogen-like atom describes radial and angular motion

$$\psi_{n,\ell,m_\ell}(r,\theta,\phi) = R_{n,\ell}(r)Y_\ell^{m_\ell}(\theta,\phi)$$

- Radial component
- Spherical harmonics $Y_\ell^{m_\ell}(\theta,\phi)$

TABLE 6.1 Radial Factors in the Hydrogenlike-Atom Wave Functions

$$R_{1s} = 2\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$

$$R_{2s} = \frac{1}{\sqrt{2}}\left(\frac{Z}{a}\right)^{3/2}\left(1 - \frac{Zr}{2a}\right)e^{-Zr/2a}$$

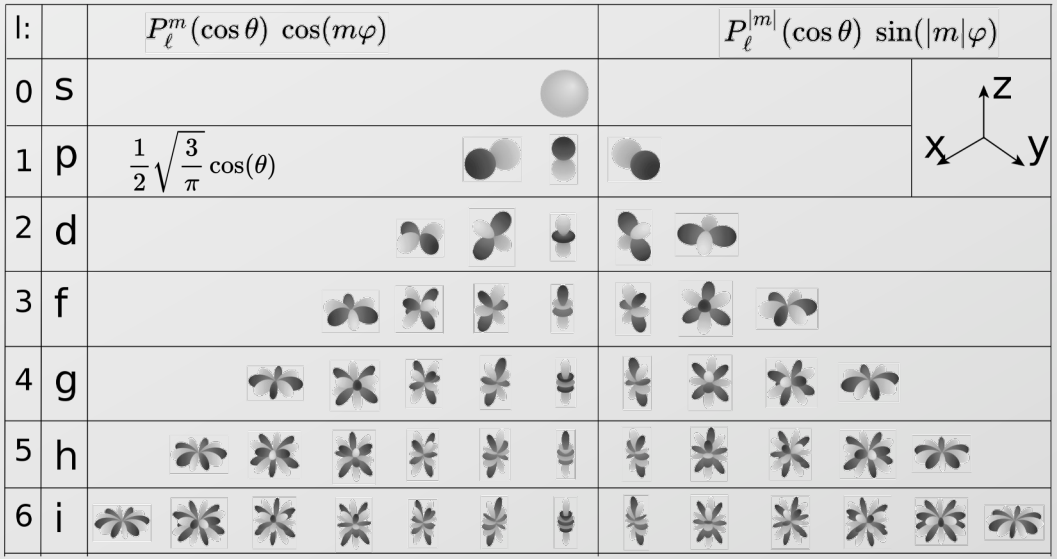
$$R_{2p} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}$$

$$R_{3s} = \frac{2}{3\sqrt{3}}\left(\frac{Z}{a}\right)^{3/2}\left(1 - \frac{2Zr}{3a} + \frac{2Z^2r^2}{27a^2}\right)e^{-Zr/3a}$$

$$R_{3p} = \frac{8}{27\sqrt{6}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a} - \frac{Z^2r^2}{6a^2}\right)e^{-Zr/3a}$$

$$R_{3d} = \frac{4}{81\sqrt{30}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}$$

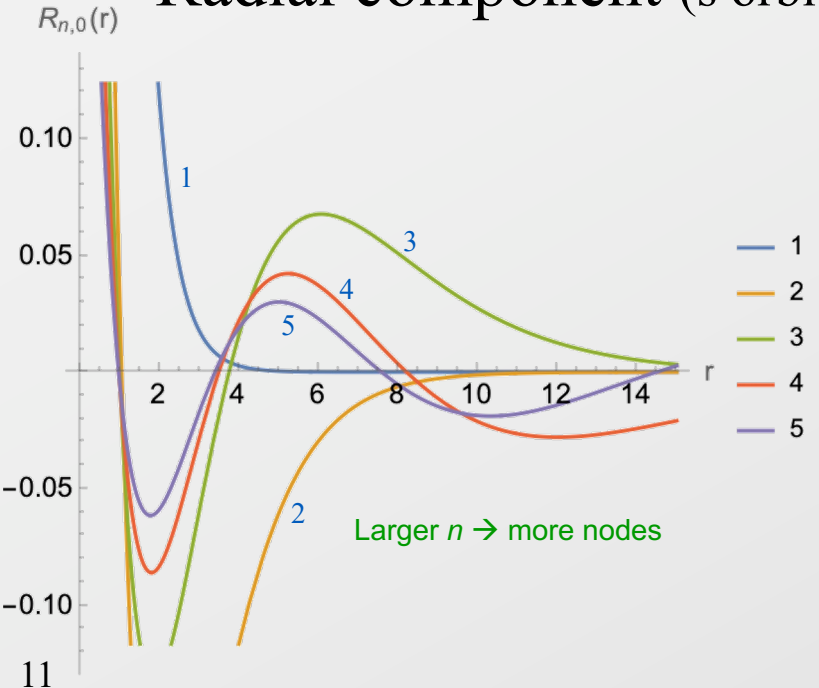
Credit: Levine, 7th ed.



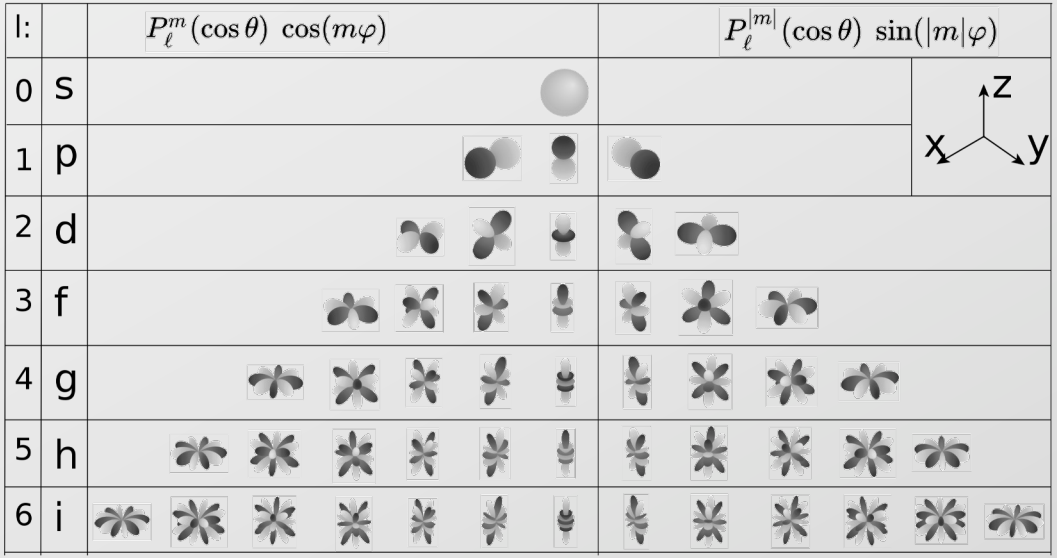
Wavefunction of hydrogen-like atom describes radial and angular motion

$$\psi_{n,\ell,m_\ell}(r,\theta,\phi) = R_{n,\ell}(r)Y_\ell^{m_\ell}(\theta,\phi)$$

- Radial component (s orbitals)



- Spherical harmonics $Y_\ell^{m_\ell}(\theta,\phi)$



Here is an implementation of the hydrogen wavefunctions in Mathematica

Hydrogen-like atom

Define functions

In[1261]:=
```
a0 = Quantity["BohrRadius"] / Quantity["Angstroms"]
(* ψ is <esc>y<esc> *)
ψR[n_, l_, r_, Z_] := With[{b = 2 Z / (n a0)}, Sqrt[b^3 (n - l - 1)! / (2 n (n + l)!)] Exp[-b r / 2] (b r)^l LaguerreL[n - l - 1, 2 l + 1, b r]]
ψ[{n_, l_, m_}, {r_, θ_, ϕ_}, Z_] := ψR[n, l, r, Z] SphericalHarmonicY[l, m, θ, ϕ]
```

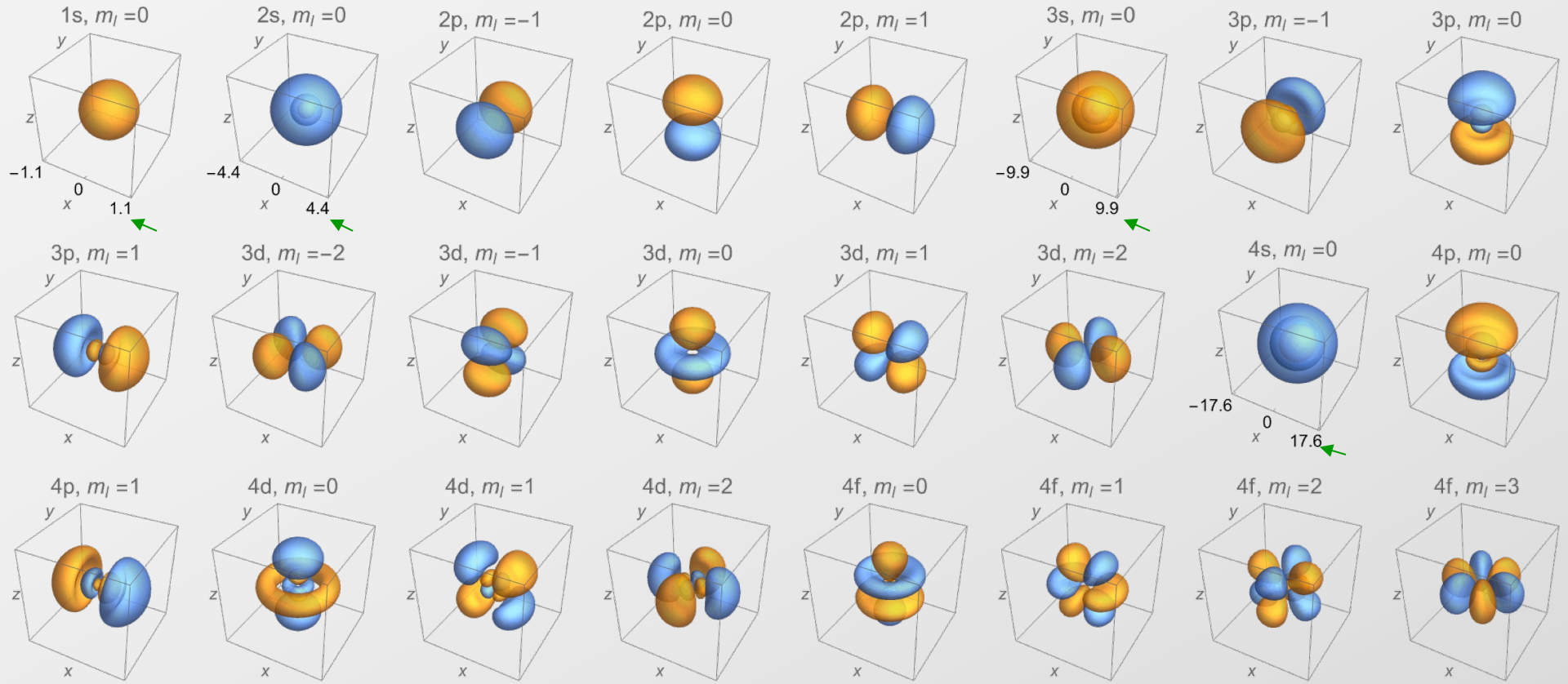
Test normalization

```
(* Function to demonstrate that ψ is normalized *)
(*Use <esc> conj <esc> to complex-conjugate expressions*)
psiNorm[n_, l_, m_, Z_] :=
 If[n > 0 && 0 ≤ l < n && Abs[m] ≤ l, Integrate[ψ[{n, l, m}, {r, θ, ϕ}, Z]* ψ[{n, l, m}, {r, θ, ϕ}, Z] Sin[θ] r^2,
   {ϕ, 0, 2 Pi}, {θ, 0, Pi}, {r, 0, Infinity}],
  Print["Illegal choice of quantum numbers"]
 ]
```

In[650]:=
```
a0 = Quantity["BohrRadius"] / Quantity["Angstroms"];
psiNorm[3, 2, 2, 1]
```

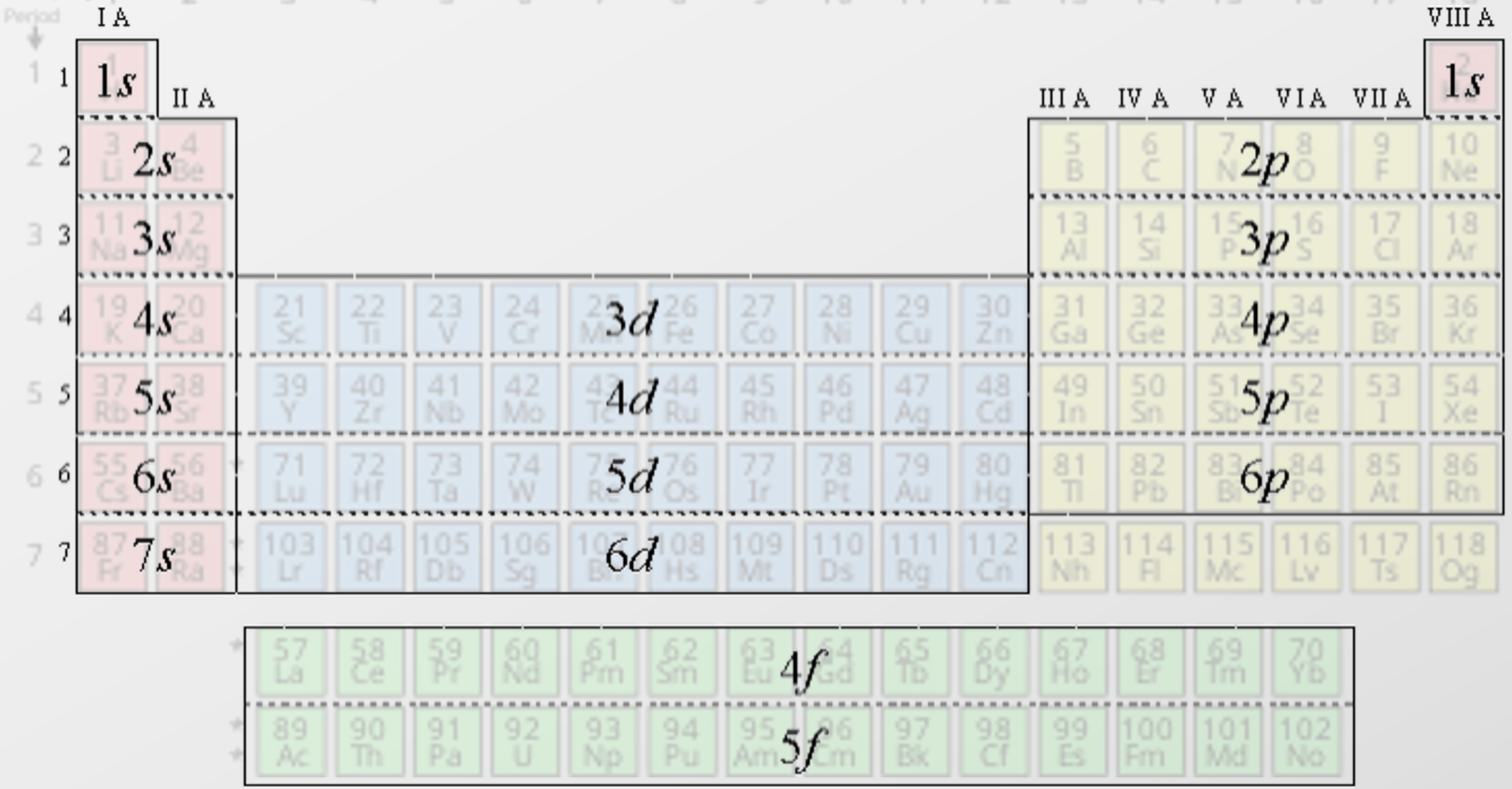
Out[650]= 1.00000000

Orbitals are typically visualized via a contour plot



Note that scale changes with each increment of *n*

The periodic table can be understood in terms of highest occupied (valence) orbitals



Energy levels depend only on principal quantum number

$$E_n = -\frac{Z^2}{2n^2}\frac{\hbar^2}{ma_0^2}, \qquad n = 1, 2, 3, \ldots$$

$a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2$

- n is defined to combine radial and angular motion
- Levels asymptote to $E_\infty = 0$, the unbound electron
  - Ground state (lowest energy) is $n = 1$
  - Negative value indicates binding
- $n > 1$ energies are degenerate, $\nu = n^2$ ($2n^2$ considering spin)
  - n values for ℓ, and $2\ell+1$ values for m_ℓ

Use Mathematica to demonstrate that wavefunction satisfies Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{Ze^2}{4\pi\epsilon_0 r}\psi = E\psi$$

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2}$$

$$-\frac{1}{2}\nabla^2\psi - \frac{m}{\hbar^2}\frac{Ze^2}{4\pi\epsilon_0 r}\psi = \frac{m}{\hbar^2}E\psi$$

$$-\frac{1}{2}\nabla^2\psi - \frac{Z}{a_0 r}\psi = \frac{m}{\hbar^2}E\psi$$

$$\frac{m}{\hbar^2}E = -\frac{Z^2}{2n^2a_0^2}$$

$$E_n = -\frac{Z^2}{2n^2}\frac{\hbar^2}{ma_0^2}$$

```
SEtest[n_, l_, m_, Z_] := -1/2 Laplacian[ψ[{n, l, m}, {r, θ, ϕ}, Z], {r, θ, ϕ}, "Spherical"]/ψ[{n, l, m}, {r, θ, ϕ}, Z] - Z/(a0 r) // FullSimplify

Clear[a0];
SEtest[3, 2, 1, 1] // Simplify
```

$$= -\frac{1}{18\,a0^2}$$

← This should equal $\frac{-Z^2}{2n^2a_0^2}$

Hydrogen-like atomic wavefunctions are the foundation of computational quantum chemistry

- ”Hydrogen-like” = One nucleus of charge +Z, one electron
  - One-electron spatial wavefunction is an *orbital*
  - When spin is added as a parameter, this is termed a *spin-orbital*
- Multi-electron atomic wavefunctions approximated by product of 1-electron wavefunctions
- Orbitals for multi-atomic systems (i.e., molecules) are also computed using atomic orbitals as a starting point

Suggested Reading/Viewing

- Autschbach Chs. 5,6
- Levine Ch. 6