Laplace's equation in spherical polar coordinates

- In this lecture we will:
  - See how Legendre polynomials arise in the solution of Laplace's equation in spherical polar coordinates.
  - Introduce spherical harmonics.
  - See how spherical harmonics are used in the quantum mechanical description of atoms.
- A comprehension question for this lecture:
  - Prove that the function $G = r^{-l-1}$ is a solution of the equation

$$\frac{1}{G}\frac{d}{dr}\left(r^2\frac{dG}{dr}\right) = l(l+1).$$

Laplace's equation in spherical polar coordinates

- In spherical polar coordinates, the gradient is: $\nabla V = \frac{\partial V}{\partial r}\hat{r} + \frac{1}{r}\frac{\partial V}{\partial \theta}\hat{\theta} + \frac{1}{r\sin\theta}\frac{\partial V}{\partial \phi}\hat{\phi}.$
- The divergence is: $\nabla \cdot \vec{A} = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2 A_r) + \frac{1}{r\sin\theta}\frac{\partial}{\partial \theta}(\sin\theta A_\theta) + \frac{1}{r\sin\theta}\frac{\partial}{\partial \phi}(A_\phi).$
- Putting them together, we get the Laplacian in spherical polar coordinates:

$$\nabla \cdot \nabla V = \nabla^2 V = \frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2 \frac{\partial V}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial V}{\partial \theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 V}{\partial \phi^2}\right].$$

- Setting this expression equal to zero gives us Laplace's equation in spherical polar coordinates:

$$\nabla \cdot \nabla V = \nabla^2 V = 0.$$

- Lots of physical potentials are described by this equation and many of them depend on r and θ, but not on ϕ.
- Look for solutions to Laplace's equation that are independent of ϕ.
- Also assume we can solve by separating variables, i.e. that $V(r,\theta) = G(r)H(\theta)$.

Solving Laplace's equation by separating variables

- We can then rewrite the equation as:
$$\frac{1}{G}\frac{d}{dr}\left(r^2\frac{dG}{dr}\right) = -\frac{1}{H\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dH}{d\theta}\right).$$
- The only way that a function of r and a function of θ can be equal for all values of r and θ is if they are both equal to the same constant.
- Write that constant as $l(l+1)$. (We will see later why this form is chosen!)
- We then have:
$$\frac{1}{G}\frac{d}{dr}\left(r^2\frac{dG}{dr}\right) = l(l+1).$$
- Two solutions of this equation are: $G = r^l$ and $G = r^{-l-1}$.
- Prove that $G = r^l$ is a solution of
$$\frac{1}{G}\frac{d}{dr}\left(r^2\frac{dG}{dr}\right) = l(l+1).$$

Solving Laplace's equation by separating variables

- Also: $-\frac{1}{H\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}H\right)=l(l+1).$ Change variables by setting $w=\cos\theta.$
- This gives: $\frac{d}{d\theta}=\frac{dw}{d\theta}\frac{d}{dw}=-\sin\theta\frac{d}{dw}$ and $-\frac{1}{\sin\theta}\frac{d}{d\theta}=\frac{d}{dw}.$
- We then have: $-\frac{1}{H}\frac{d}{dw}\left(\sin^2\theta\frac{dH}{dw}\right)=l(l+1)$ or $\frac{d}{dw}\left(\sin^2\theta\frac{dH}{dw}\right)=-l(l+1)H$
- Rearranging: $\frac{d}{dw}\left(\sin^2\theta\frac{dH}{dw}\right)+l(l+1)H=0\Rightarrow\frac{d}{dw}\left((1-w^2)\frac{dH}{dw}\right)+l(l+1)H=0.$
- Differentiating w.r.t. w gives: $(1-w^2)\frac{d^2H}{dw^2}-2w\frac{dH}{dw}+l(l+1)H=0.$

- This is Legendre's equation (with l instead of n)!
- The solutions of this equation are the Legendre polynomials $P_l(w)=P_l(\cos\theta).$
- The solutions of the Laplace equation (without ϕ dependence) are therefore:

$$G(r)H(\theta)=r^lP_l(\cos\theta) \text{ and } G(r)H(\theta)=r^{-l-1}P_l(\cos\theta).$$

Spherical harmonics

- If we allow ϕ dependence, the Laplace equation can still be solved by separating variables; the angular part of the solution is given by the *spherical harmonics*:

$$Y_l^m(\theta,\phi) \propto \sin^m\theta \frac{d^m}{d(\cos\theta)^m} P_l(\cos\theta)\exp[im\phi], \text{ with } -l \le m \le l.$$

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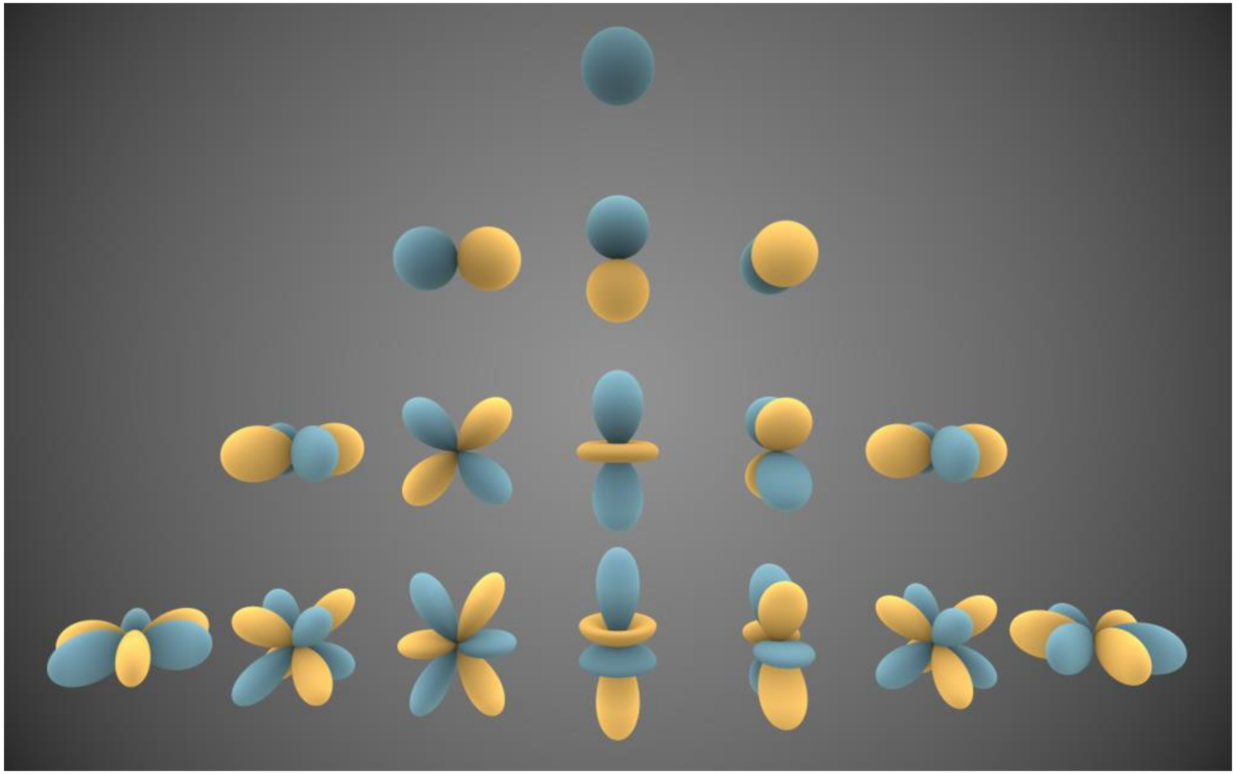


- The picture shows the first few real spherical harmonics ($m = 0 ... 3$).
- The distance from the origin shows the value of $Y_l^m(\theta,\phi)$ in the (θ,ϕ) direction, with blue being positive and yellow negative.

Schrödinger's equation for an H-like atom

- Schrödinger's equation describing an electron moving around a nucleus is:

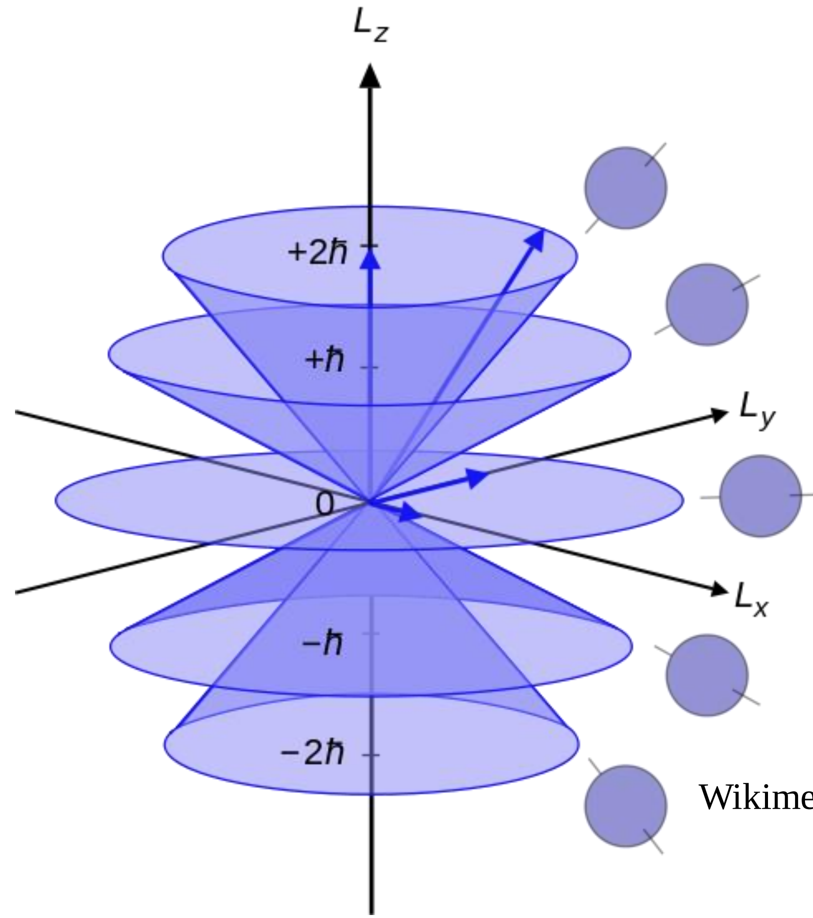
$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E\psi.$$

- The solutions are of the form:

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

- The energy $E_n \propto 1/n^2$, i.e. it can only take on discrete values.
- The value of l is limited by $l \leq n-1$.
- The magnitude of the orbital angular momentum of the electron is given by $L = \sqrt{l(l+1)}\hbar$.
- The z component of the orbital angular momentum is given by $L_z = m\hbar$.

- The *magnetic* quantum number m is restricted to the range $-l \leq m \leq l$.



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Schrödinger's equation for an H-like atom

- The value of *n*, is called the principal quantum number.
- If an electron shifts from an orbit with $n = n_1$ to one with $n = n_2$, it emits (or absorbs) an energy:
  $$E \propto \frac{1}{n_2} - \frac{1}{n_1}.$$
- As $E = hf = hc/\lambda$, this means energy is emitted from atoms at particular frequencies/wavelengths.
- As the nuclear charge of (and the number of electrons in) an atom influence the energy levels, this gives rise to distinctive spectra which allow atoms to be identified.
- Note that, in this solution, the energy is independent of *l* and *m*.
- The independence of the energy on the magnitude of the angular momentum vanishes when relativistic effects are considered.
- These effects introduce *fine structure* to the spectra.
- A further *l* dependence is also introduced if the atom is placed in a magnetic field, the *Zeeman effect*.
- This latter effect is used in nuclear magnetic resonance spectroscopy (NMR) and magnetic resonance imaging (MRI).