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

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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 $V(r,\theta) = G(r)H(\theta)$.

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

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

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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*:

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

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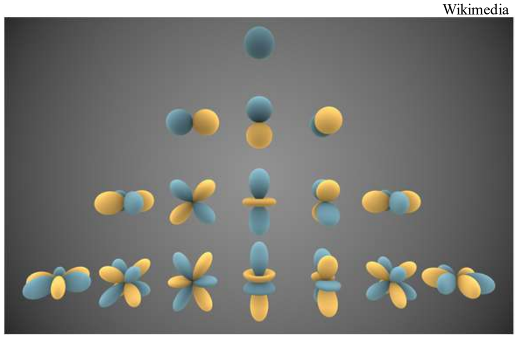

- The picture shows the first few real spherical harmonics ($m = 0 \ldots 3$).
- The distance from the origin shows the value of $Y_l^m(\theta,\phi)$ in the (θ,ϕ) direction, with blue being positive and yellow negative.

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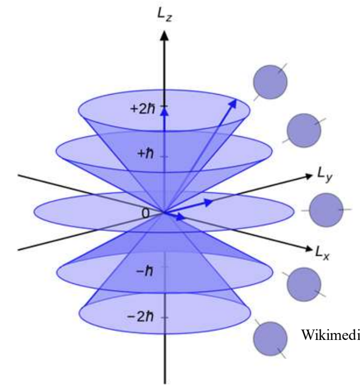
Schrödinger's equation for an H-like atom

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

  $-\dfrac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E\psi.$
- 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 $l \le n-1$.
- 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 $-l \le m \le l$.



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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:

  $E \propto \dfrac{1}{n_2} - \dfrac{1}{n_1}.$
- 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).

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