Quantum Mechanics

Week 6

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Exercise Material

Webpage

Week 6

Review

Midterm

Exercises

Review of Last Week

- Any questions on last week's topics?
- Feedback on the previous session?

Review

SE in 3D

Considering Cartesian coordinates, the Hamiltonian can be defined as:

$$\hat{H} = \frac{1}{2m}\left(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2\right) + V(\vec{r}),$$

where $\hat{p}_n = -i\hbar\frac{\partial}{\partial n}$ for $n = x, y, z$, and $V(\vec{r})$ represents the potential energy which is a function of the position vector $\vec{r}$. Alternatively, using the Laplacian operator, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, we can express the Time-Dependent Schrödinger Equation (T.D.S.E.) as:

$$\boxed{i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi,}$$

where Ψ is the wave function of the system. For a time-independent potential, $V(\vec{r})$, we obtain stationary states similar to those in one-dimensional systems, but with the position variable x replaced by the position vector $\vec{r}$.

The search for stationary solutions involves the separation of variables for each coordinate and separation of time and space. Solving the Time-Independent Schrödinger Equation (T.I.S.E.) of each variable will give you the final space solution $\psi = X(x)Y(y)Z(z)$.

In spherical coordinates for spherical potentials:

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

Insert into $\hat{H}$ and apply separation of variables:

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

We have to solve $\underbrace{R(r)}_{\text{Radial Solution}}$ and $\underbrace{Y(\theta,\phi)}_{\text{Angular Solution}} = \Theta(\theta)\cdot\Phi(\phi)$

Solution Angular Equation

We solve the following PDE (derivation in the Lecture) assuming θ and ϕ are independent:

$$\boxed{\frac{1}{Y}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right)=-\ell(\ell+1)}$$

The spherical harmonics $Y(\theta,\phi)$ can be separated: $Y(\theta,\phi)=\Theta(\theta)\cdot\Phi(\phi)$

Where:

- $\Theta(\theta)=A\cdot P_\ell^m(\cos\theta)$, Legendre functions.
- $\Phi(\phi)=\exp(i\cdot m_\ell\cdot\phi)$, azimuthal dependency.

Legendre functions

$$P_\ell^m(x) = (1-x^2)^{\frac{|m|}{2}}(\frac{d}{dx})^{|m|}P_\ell(x)$$

$$P_\ell(x) = \frac{1}{2^\ell \ell!}(\frac{d}{dx})^\ell (x^2-1)^\ell$$

where $P_\ell(x)$ are the Legendre polynomials and m and ℓ are integers with $0 \leq m \leq \ell$.

- $\ell =$ azimuthal quantum number
- $m_\ell =$ magnetic quantum number

Spherical Harmonics solutions

$$\begin{aligned} Y_\ell^m(\theta,\phi) &= \Theta(\theta)\Phi(\phi) \\ &= A P_\ell^m(\cos\theta) \times \exp(im\phi) \\ &= (-1)^{\frac{m+|m|}{2}} \sqrt{\frac{(2\ell+1)}{4\pi} \frac{(\ell-|m|)!}{(\ell+|m|)!}} P_\ell^m(\cos\theta) e^{im\phi}, \end{aligned}$$

This is a normalized solution for **any** problem with a spherically symmetric $V(r)$.

Remark: In the UIS you can find the first few Spherical Harmonics

Solution Radial Equation

We solve the following ODE:

$$\boxed{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}\left[V(r)-E\right]=\ell\left(\ell+1\right)}$$

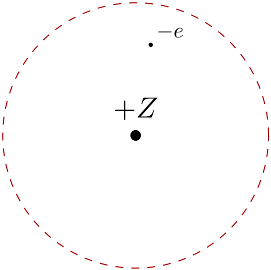
by taking $u(r)=rR(r)$ we can rewrite the equation as:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}+\left[V+\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u(r)=Eu,$$

We can clearly see that our new V_{eff} is equal to the potential energy V and the centrifugal energy $\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$.

Hydrogen Atom

Atom with one proton and a single valence electron:



Potential of the electron in the hydrogenic atom: $V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$

Radial Solutions for the Hydrogen Atom

Solving for the Radial part of the wave function, $R_{n\ell}(r)$, in terms of generalized Laguerre polynomials gives you:

$$\boxed{R_{n\ell}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}} e^{-\frac{\rho}{2}} L_{n-\ell-1}^{2\ell+1}(\rho)}$$

with $\rho = \frac{r}{na_0}$, where: n is the principal quantum number, a_0 is the Bohr radius, $L_{n-\ell-1}^{2\ell+1}(x)$ are the associated Laguerre polynomials. For physically relevant solutions, n must be a positive integer.

The total wave function $\psi_n(r,\theta,\varphi) = R_{n\ell}(r) Y_{\ell m}(\theta,\varphi)$.

Energy Levels of the Hydrogen Atom

$$\boxed{E_n = -\left[\frac{m_e^4 e^4}{2\hbar^2(4\pi\varepsilon_0)^2}\right]\frac{1}{n^2} = \frac{E_1}{n^2}}$$

- $E_1 = -13.6\,$eV is the ground state energy level.
- This formula gives the energies of the orbitals in the hydrogen atom.
- Energy levels depend only on n.
- This is valid for hydrogen and hydrogenic atoms(atoms with multiple protons and one electron).

Quantum Numbers

- **Principal (n):** Energy level and size of electron cloud. $E_n = -\frac{Z^2}{n^2}E_1$
- **Azimuthal (ℓ):** Orbital shape. Values from 0 to $n-1$.
- **Magnetic (m_ℓ):** Orientation of orbital. Values from $-\ell$ to $+\ell$.

Principal (n)	Azimuthal (ℓ)	Magnetic (m_ℓ)
$1, 2, 3, \ldots$	$0, 1, 2, \ldots, n-1$	$-\ell, \ldots, 0, \ldots, +\ell$

Midterm

Exercises

Exercise 1

To practice the commutation calculations.
Remark: Use the properties from the ZF

Exercise 2

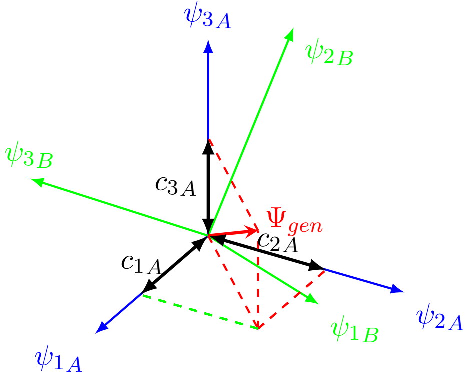
Long but really helpful example. Good exam-like problem

Exercise 3

Really useful to get comfortable with Spherical Harmonics

Exercise 4

Really useful to get comfortable with Spherical Harmonics **and** Radial solutions



ψ_{3A}
ψ_{2B}
ψ_{3B}
c_{3A}
Ψ_{gen}
c_{2A}
c_{1A}
ψ_{1B}
ψ_{2A}
ψ_{1A}