Lecture 25 — The Hydrogen Atom Schrödinger Equation & Quantum Numbers

Reading: Engel 4th ed., Chapter 9 (Sections 9.1–9.3)

Learning Objectives

- Write the Hamiltonian for the hydrogen atom including the Coulomb potential
- Separate the Schrödinger equation into radial and angular parts
- Identify the quantum numbers n, l, and m_l and their ranges
- State the energy eigenvalues and explain the n-fold degeneracy
- Compare hydrogen-like energies for ions with $Z > 1$

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1. The Hydrogen Atom Hamiltonian

A proton (charge $+e$) and electron (charge $-e$) interacting via the Coulomb potential:

$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$

where $\mu \approx m_e$ is the reduced mass of the electron-proton system and r is the electron-proton distance.

> [!NOTE] **Concept Check 25.1** Why is the Coulomb potential term in the Hamiltonian negative ($-\frac{e^2}{4\pi\epsilon_0 r}$)? What would it mean physically if this term were positive?

Spherical Coordinates

Since the potential depends only on r (spherically symmetric), we use spherical coordinates (r, θ, ϕ):

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

The angular part is exactly $\hat{L}^2/(-\hbar^2 r^2)$ — the angular momentum operator we solved with the rigid rotor!

2. Separation of Variables

We write $\psi(r, \theta, \phi) = R(r) \cdot Y_l^{m_l}(\theta, \phi)$

The angular equation is already solved — the solutions are spherical harmonics $Y_l^{m_l}$.

The **radial equation** becomes:

$$-\frac{\hbar^2}{2\mu}\left[\frac{d^2u}{dr^2} - \frac{l(l+1)}{r^2}u\right] - \frac{e^2}{4\pi\epsilon_0 r}u = Eu$$

where $u(r) = rR(r)$.

The term $\frac{\hbar^2 l(l+1)}{2\mu r^2}$ acts as a **centrifugal barrier** — an effective repulsive potential for $l > 0$ that keeps the electron away from the nucleus.

3. The Three Quantum Numbers

Solving the radial equation with the boundary condition $R(r) \to 0$ as $r \to \infty$ introduces a third quantum number n:

Quantum Number	Symbol	Allowed Values	Physical Meaning
Principal	n	$1, 2, 3, \ldots$	Energy level; determines size of orbital
Angular momentum	l	$0, 1, 2, \ldots, n-1$	Orbital shape; $\|L\| = \hbar\sqrt{l(l+1)}$
Magnetic	m_l	$-l, \ldots, 0, \ldots, +l$	Orientation; $L_z = m_l\hbar$

Spectroscopic Notation

l	0	1	2	3	4
Letter	s	p	d	f	g

Orbital label: $n + \text{letter}$ (e.g., $1s$, $2p$, $3d$, $4f$)

How Many Orbitals?

For a given n:

- l ranges from 0 to $n-1$ → n values
- For each l, m_l ranges from $-l$ to $+l$ → $2l+1$ values
- Total orbitals: $\sum_{l=0}^{n-1}(2l+1) = n^2$

n	l values	Orbitals	Total
1	0 (s)	$1s$	1
2	0, 1 (s, p)	$2s, 2p_{x,y,z}$	4
3	0, 1, 2 (s, p, d)	$3s, 3p, 3d$	9
4	0, 1, 2, 3	$4s, 4p, 4d, 4f$	16

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4. Energy Eigenvalues

$$\boxed{E_n = -\frac{\mu e^4}{32\pi^2\epsilon_0^2\hbar^2} \cdot \frac{1}{n^2} = -\frac{13.6 \text{ eV}}{n^2}, \quad n = 1, 2, 3, \ldots}$$

Key Features

1. **Negative energies**: bound states (electron is trapped)
2. $E \propto 1/n^2$: levels converge toward $E = 0$ (ionization threshold)
3. n^2**-fold degeneracy**: energy depends *only* on n, not on l or m_l
   - This is a special feature of the $1/r$ potential (not true for multi-electron atoms!)
   - Including spin: $2n^2$-fold degeneracy
4. **Ground state**: $E_1 = -13.6$ eV

> [!NOTE] **Concept Check 25.2** In the hydrogen atom (neglecting spin), what is the total degeneracy of the $n = 2$ energy level? List the specific orbitals that share this same energy.

Ionization Energy

$$IE = -E_1 = 13.6 \text{ eV} = 1312 \text{ kJ/mol}$$

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5. Hydrogen-Like Ions ($Z > 1$)

For ions with one electron (He^+, Li^{2+}, etc.):

$$E_n = -\frac{Z^2 \times 13.6 \text{ eV}}{n^2}$$

The electron is bound Z^2 times more tightly.

Bohr Radius Scaling

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.529 \text{ Å}$$

For hydrogen-like ions: $\langle r \rangle \propto n^2/Z$ — orbitals shrink with increasing Z.

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6. Connection to Symmetry

The hydrogen atom has full **spherical symmetry** (R_3 group — the group of all rotations in 3D). This is why:

- Energy depends only on n (not on orientation quantum numbers l, m_l)
- Degeneracy is n^2 (or $2n^2$ with spin)
- Orbitals are classified by l, which labels irreducible representations of the rotation group

When the atom is placed in a molecular environment, the symmetry is lowered to a point group, and the degeneracy is (partially) lifted — this is the basis of **crystal field theory**.

Key Equations Summary

Equation	Expression
Energy levels	$E_n = -13.6 \text{ eV}/n^2$
Bohr radius	$a_0 = 0.529 \text{ Å}$
Angular momentum	$\|L\| = \hbar\sqrt{l(l+1)}$
z-component	$L_z = m_l\hbar$
Degeneracy (no spin)	n^2

Equation	Expression
Degeneracy (with spin)	$2n^2$
H-like ions	$E_n = -Z^2(13.6\ \text{eV})/n^2$

Recent Literature Spotlight

"Highly Excited Rydberg Atoms" *T. F. Gallagher*, Reviews of Modern Physics, **2010**, 82, 2313–2363. DOI

This comprehensive review covers the physics of highly excited Rydberg atoms — atoms with one electron promoted to states with very large principal quantum number n. These "giant atoms" have orbital radii scaling as $n^2 a_0$, binding energies scaling as $1/n^2$ (just like the hydrogen atom solutions derived in this lecture), and remarkably long lifetimes. Rydberg atoms serve as a bridge between quantum and classical mechanics and are now used in quantum computing and simulation.

Practice Problems

1. **Quantum numbers.** List all possible quantum number combinations (n, l, m_l) for $n = 4$. How many orbitals is this?

2. **Ionization energy.** Calculate the ionization energy (in eV and kJ/mol) of Li^{2+} from its ground state.

3. **Orbital size.** Calculate $\langle r \rangle$ for the 1s and 2s orbitals of hydrogen. By what factor does the electron cloud grow from $n = 1$ to $n = 2$?

Next lecture: Atomic Orbitals, Radial Distributions & Angular Wavefunctions