Notes for Lectures on Quantum Mechanics *

Energy Levels in Spherically Symmetric Potentials
Accidental Degeneracy

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1 General Properties of Bound State Spectra

A potential is spherically symmetric if in polar variables it depends only on r and not on θ and ϕ coordinates . We shall now discuss general properties of solution of 3-dimensional Schrödinger equation $H\psi = E\psi$ where

$$H = \frac{\vec{p}^2}{2m} + V(r)$$

and the potential $V(r)$ is spherically symmetric.

Conserved quantities
We note that all the three components of $\vec{L}$ commute with Hamiltonian

$$[\vec{L}, H] = 0$$

hence

$$[\vec{L}^2, H] = 0 \ .$$

The parity operator $\mathscr{P}$

$$\mathscr{P}\psi(\vec{r}) = \psi(-\vec{r})$$

also commutes with $L^2 L_z$ and H, operators. Therefore, the eigen functions of H will also be eigen functions of L^2, L_z and parity and each level can be assigned a definite value of l, m and parity. For a state with definite value of l, the value of parity is $\equiv (-1)^l$. In this case L^2, L_z and H form a complete commuting set.

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$(2\ell+1)$ degeneracy
We use the notation $|El,m\rangle$ to denote the simultaneous eigenvector of H, L^2 and L_z

$$
\begin{aligned}
H|E,lm\rangle &= E|E,lm\rangle & (1)\\
L^2|E,lm\rangle &= l(l+1)\hbar^2|E,lm\rangle & (2)\\
\text{and}\quad L_z|E,lm\rangle &= m\hbar|E,lm\rangle & (3)\\
\mathscr{P}|E,lm\rangle &= (-1)^l|E,lm\rangle & (4)
\end{aligned}
$$

Applying L_- on $|El,m\rangle$ several times leads successively to

$$|El,m-1>\rangle\ ,\ |E,l,m-2\rangle \quad \cdots \quad |El,-l\rangle \tag{5}$$
$$\tag{6}$$

and the action of L_+ on $|E,lm\rangle$ leads to the states

$$|El,m+1\rangle\ ,\ |E,l,m+2\rangle \quad \cdots \quad |El,l\rangle \tag{7}$$

All these states will have the same value of energy. This statement can be proved by making use of the fact that H commutes with $L_\pm$ and that action of L_+ (or L_-) on $|Elm>$ leads to states $|El,m+1>$ (or $|El,m-1>$). Thus we see that the bound state energy eigenvalues of a spherically symmetric potential problem with have $(2l+1)$ fold degeneracy. (What about the continuous energy eigenvalues?)

Radial wave function
The Schrödinger equation for a spherically symmetric potential can be solved by separation of variables in polar coordinates. The angular part of the wave functions turns out to be a spherical harmonic $Y_{lm}(\theta,\phi)$ and the wave function has the form

$$\psi(r,\theta,\phi) = R(r)Y_{lm}(\theta,\phi)$$

where $R(r)$ is radial wave function satisfying the Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}R(r) + \left(V(r) + \frac{l(l+1)\hbar^2}{2mr^2}\right)R(r) = ER(r)\ .$$

If we define $\chi(r) = rR(r)$, the function χ satisfies the equation

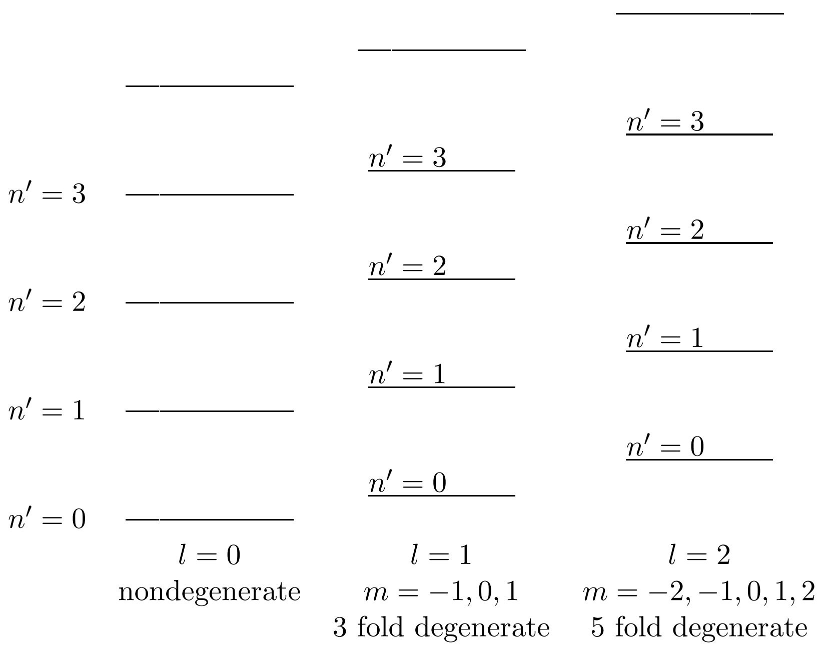
$$-\frac{\hbar^2}{2m}\frac{d^2\chi}{dr^2} + \left(V(r) + \frac{l(l+1)\hbar^2}{2mr^2} - E\right)\chi = 0\ .$$

with boundary condition $\chi(r)|_{r=o} = 0$, otherwise $R(r)$, the radial wave function will tend to ∞ as $r \to \infty$.

2 Bound state spectrum

The equation for χ has the form of one dimensional Schrödinger equation. Let n' denote the number of zeros of the radial wave function, excluding $r = 0$ and at $r = \infty$. Then for a fixed value of l, the energy will increase with n', $n' = 0, 1, 2, \cdots$ will correspond to, for a fixed l, the 'ground' state, first excited state, the second excited state etc. Because of the l dependence of the term $\frac{l(l+1)\hbar^2}{2mr^2}$ in the potential appearing in equation for $\chi(r)$, we expect that as l is changed, keeping the number of nodes to be the same, E would also change. Increasing l would lead to increase in E, when n' is kept fixed.

Thus the spectrum would appear as follows



3 Coulomb problem spectrum

For hydrogen atom the energy levels are given by

$$E = -\frac{Z^2 e^4 m}{2\hbar^2 (n' + l + 1)^2}$$

The energy does not depend on n' and l separately but only on the combination $n = (n' + l + 1)$. For a fixed n, l can have values $0, 1, \cdots, n-1$ (because $n' \geq 0$) and all these solutions correspond to the same energy eigenvalue. The energy level diagram of H-atom, therefore, appears as shown below.

	$l=0$	$l=1$	$l=2$	$l=3$	$l=4$
$n=7$					
$n=6$					
$n=5$					
$n=4$	$n=4$	$n=4$	$n=4$	$n=4$ 7 fold degenerate	$n=4$ 9 fold degenerate
$n=3$	$n=3$	$n=3$	$n=3$ 5 fold degenerate		
$n=2$	$n=2$	$n=2$ 3 fold degenerate			
$n=1$	$n=1$ non-degenerate				

Putting all the levels which have the same energy together we get the following schematic representation of energy levels of H atom. This table also shows that the allowed values of l for each n, and number of m values for each level. The number of total m values, with the same energy, is n^2 and the degeneracy, after taking spin into account, becomes $2n^2$.

		l values	number of m values	degeneracy
		$0, 1, ..n-1$	n^2	$2n^2$
$n = 4$	32	$l = 0, 1, 2, 3$	$\sum(2l+1) = 16$	$2 \times 16 = 32$
$n = 3$	18	$l = 0, 1, 2$	$\sum 2(l+1) = 9$	$2 \times 9 = 18$
$n = 2$	8	$l = 0, 1$	$\sum(2l+1) = 4$	$2 \times 4 = 8$
$n = 1$	degen=2	$l = 0$	$\sum(2l+1) = 1$	$2 \times 1 = 2$

4 Accidental degeneracy

Comparing the hydrogen atom levels with those of a general spherically symmetric potential, we find that energies for states with several different values of l $(= 0, 1, 2 \ldots n-1)$ are the same. For a general spherically symmetric potential different combinations of n, l values correspond to different bound state energies, and are $(2l+1)$ fold degenerate. Thus there is an extra degeneracy is present for H atom beyond the expected $(2l+1)$ fold degeneracy this phenomenon present in the case of hydrogen atom is known as *accidental degeneracy.* Another well known case of accidental degeneracy is that of isotropic harmonic oscillator ($V(r) = \frac{1}{2}kr^2$) in three dimensions.

Remarks

[1] It must be emphasized that the accidental degeneracy is due to the special symmetry of the Coulomb problem.

[2] Any slight deviation of the potential from $\frac{1}{r}$ will result in splitting of energy levels with different values of l.

[3] It is known that the accidental degeneracy is present whenever the Schrödinger equation $H\psi = E\psi$ can be separated into ordinary differential equations in more than one set of coordinate system.

H atom — Separation of variables for the Coulomb problem is possible in

(a) spherical polar coordinates r, θ, ϕ

(b) parabolic coordinates ξ, η, ϕ defined by

$$\xi = r - z = r(1 - \cos\theta) \quad \eta = r + z = r(1 + \cos\theta) \quad \phi = \phi \tag{8}$$

[4] The isotropic oscillator also exhibits accidental degeneracy. For isotropic harmonic oscillator,$V(r) = \frac{1}{2}kr^2$, the Schrodinger equation can be separated in two set of variables, Cartesian and spherical polar coordinates.