Lecture Notes of Quantum Mechanics

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November 24, 2019

Chapter 5

Central potential

In the following, we investigate stationary states in the central potential $V(\vec{r}) = V(r)$, that is, in problems with rotationally symmetric potentials. The Hamiltonian is

$$H = \frac{p^2}{2m} + V(r) \tag{5.1}$$

and we examine the eigenvalue problem

$$H\Psi(\vec{r}) = E\Psi(\vec{r}) \tag{5.2}$$

It is $V = V(r)$ but $\Psi = \Psi(\vec{r})$, which means that the wave function Ψ also has structure in the angle coordinates. The rotational symmetry $[H, U_{\vec{w}}] = 0, U_{\vec{w}} \in \mathcal{SO}(3)$, allows us to diagonalize H, L^2 and L_z at the same time, simplifying the solution of the problem.

The situation is similar to that in mechanics: each symmetry corresponds to a size obtained, in the present problem this is the invariance under translations in time and under rotations; the associated conserved quantities are the energy E and the angular momentum $\vec{L}$. These conservation laws are very helpful in solving the mechanical problem.

The same symmetries in quantum mechanics give us a sharp (received) energy and an obtained angular momentum because $[H, \vec{L}] = 0$. However, a difference occurs due to the non-commutability of the three angular momentum components; although we can set $\vec{L}$ in any direction (we call it the z-direction), it follows that $[L_i, L_j] = i\hbar\varepsilon_{ijk}L_k \neq 0$ that we can not set all three components simultaneously. Thus, the four obtained sizes in mechanics correspond to only three quantum numbers E (to the Hamiltonian H, l (to the angular momentum L^2), and m (to the angular momentum component L_z) in quantum mechanics.)

Technically, the solution of the problem is simplified by just Solving the angular problem by reducing the rotation group in the Hilbert space, we can solve the remaining radial problem in each sector in a fixed way. We go to spherical coordinates so that we can directly exploit the rotational symmetry.

5.1 Eigenvalue problem in spherical coordinates

It is

$$
\begin{aligned}
L^2 &= \varepsilon_{ijk} x_j p_k \varepsilon_{ilm} x_l p_m \\
&= (\delta_{jl}\delta_{km} - \delta_{jm}\delta_{kl})\, x_j p_k x_l p_m \\
&= x_{jl}\delta_{km} - \delta_{jm}\delta_{kl})\, x_j p_k x_l p_m \\
&= x_j p_k x_j p_k - x_j p_k x_k p_j \\
&= x_j\left(x_j p_k - i\hbar\delta_{jk}\right) p_k - x_j\left(x_k p_k - 3i\hbar\right) p_j \\
&= x_j x_j p_k p_k - i\hbar x_j p_j - x_j x_k p_k p_j + 3i\hbar x_j p_j \\
&= r^2 p^2 - i\hbar \vec{r}\cdot\vec{p} - \underbrace{x_j\left(p_j x_k + i\hbar\delta_{jk}\right) p_k}_{(\vec{r}\cdot\vec{p})^2 + th\vec{r}\cdot\vec{p}} \\
&= r^2 p^2 - (\vec{r}\cdot\vec{p})^2 + i\hbar\vec{r}\cdot\vec{p}
\end{aligned}
\tag{5.3}
$$

Classically, $L^2 = r^2 p^2 - (\vec{r}\cdot\vec{p})^2$ for the proof, calculate directly or use the $\lim \hbar \to 0$ of (5.3). It is

$$
\vec{\nabla} = (\partial_x, \partial_y, \partial_z) \to \left(\partial_r, \frac{1}{r\sin\theta}\partial_\varphi, \frac{1}{r}\partial_\theta\right)
$$

and

$$
\vec{r}\cdot\vec{p} = -i\hbar\vec{r}\cdot\vec{\nabla}^{\vec{r}=r\hat{e}_r} - i\hbar r\partial_r
\tag{5.4}
$$

the projection from $\vec{p}$ to $\vec{r}$. With (5.3) we get the kinetic energy (or the Laplace operator Δ) in spherical coordinates,

$$
\begin{aligned}
p^2 = -\hbar^2\nabla^2 = -\hbar^2\Delta &= \frac{1}{r^2}\left(\vec{L}^2 + (\vec{r}\cdot\vec{p})^2 - i\hbar\vec{r}\cdot\vec{p}\right) \\
&= -\frac{\hbar^2}{r^2}\left[(r\partial_r)^2 + r\partial_r\right] + \frac{L^2}{r^2} \\
&= p_r^2 + \frac{L^2}{r^2}
\end{aligned}
\tag{5.5}
$$

p_r is asymptotically the radial component of the momentum and has the forms

$$
p_r = -i\hbar r^{-1}\left(\partial_r r\right) = -i\hbar\left(\partial_r + \frac{1}{r}\right)
\tag{5.6}
$$

The operator p_r^2 can then be written as follows,

$$p_r^2 = -\hbar^2\left(\partial_r^2 + \frac{2}{r}\partial_r\right) = -\hbar^2\left(\partial_r^2 + \frac{\dim -1}{r}\partial_r\right)$$

$$= -\hbar^2\left(\frac{1}{r}\partial_r r \partial_r + \frac{1}{r}\partial_r\right) \tag{5.7}$$

$$= -\hbar^2\left(\frac{1}{r}\partial_r r\right)^2 = -\hbar^2\left(\frac{1}{r}\partial_r^2 r\right) = -\hbar^2\left(\frac{1}{r^2}\partial_r r^2 \partial_r\right)$$

It is $[r, p_r] = i\hbar$, that is, p_r is canonically conjugate to r. The eigenvalue problem takes the following form in spherical coordinates,

$$\left[-\frac{\hbar^2}{2m}\left(\partial_r^2 + \frac{2}{r}\partial_r\right) + \frac{L^2}{2mr^2} + V(r)\right]\Psi(\vec{r}) = E\Psi(\vec{r}) \tag{5.8}$$

The angular coordinates are in L^2, see (4.40) and for the Laplace operator Δ is given

$$\Delta = \partial_r^2 + \frac{2}{r}\partial_r + \underbrace{\frac{1}{r^2\sin^2\theta}\partial_\varphi^2 + \frac{1}{r^2\sin\theta}\partial_\theta\left(\sin\theta\partial_\theta\right)}_{-L^2/\hbar^2 r^2} \tag{5.9}$$

But since we have already solved the angle problem $L^2 Y_{l,m} = \hbar^2 l(l+1)Y_{l,m}$, it makes no sense to go to (5.9). The rotational symmetry $V = V(r)$ separates the angular and radial coordinates

$$\Psi(r,\theta,\varphi) = R(r)Y_{l,m}(\theta,\varphi)$$
$$L^2 Y_{l,m} = \hbar^2 l(l+1)Y_{l,m}$$

and we can immediately go over to the radial problem,

$$\left[-\frac{\hbar^2}{2m}\left(\partial_r^2 + \frac{2}{r}\partial_r\right) + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right]R(r) = ER(r) \tag{5.10}$$

To obtain the form of a 1-D Schrodinger equation we write the radial function $R(r)$ in the form

$$R(r) = \frac{u(r)}{r} \tag{5.11}$$

and get the equation

$$\left[-\frac{\hbar^2}{2m}\partial_r^2 + \underbrace{\frac{\hbar^2 l(l+1)}{2mr^2} + V(r)}_{V_{\text{eff}}(r)}\right]u(r) = Eu(r) \tag{5.12}$$

Only for $l = 0$, angular momentum zero, is $V_{\text{eff}}(r) = V(r)$. Otherwise, in addition to $V(r)$, the repulsive potential $V_l(r) = \hbar^2 l(l+1)/2mr^2$ acts on the particle, the well-known centrifugal barrier, see figure 5.1. We will see that, because of this term, $\Psi(r) \propto r^l$ is suppressed for $r \to 0$ and the particle is displaced from $r = 0$. The equation (5.12) corresponds to a 1-D Schrodinger
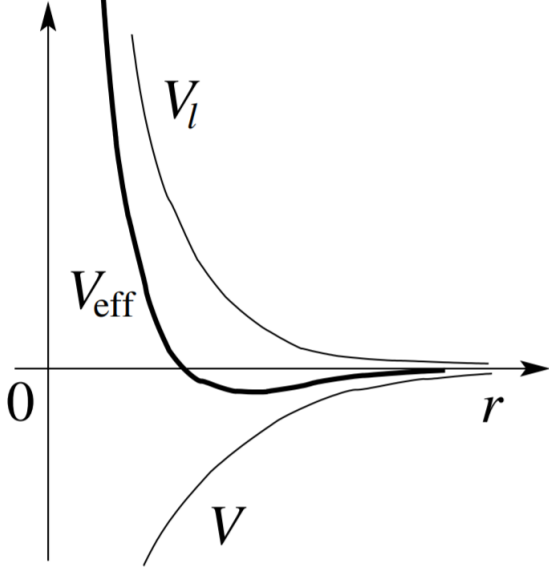

Figure 5.1: The angular momentum generates the potential barrier $V_l = \hbar^2 l(l+1)/2mr^2$ and displaces the wave function from the environment of origin. The potential $V(r)$ combines with $V_l(r)$ to be effective potential $V_{\text{eff}}(r)$.

problem with $V(x < 0) = \infty, V(x > 0) = V(x = r)$; for an attractive potential, the typical situation in Figure 5.2 is sketched. Conversely, the symmetric extension $V(x < 0) = V(|x| = r)$ gives us a typical 1-D problem. In 1-D, every attractive potential (with $V(|x| \to \infty) \to 0, V(0) < 0$) binds at least one (in x direction, $V(x) = V(|x|)$ is invariant under $x \to -x$) state. Now consider the dim $= 3$, $l = 0$ problem. Then $u(0) = 0$, and thus u odd. It follows that the attractive potential in dim $= 3$ must have a minimum strength so that it can bind a state, cf. the discussion in section 3.3 (particles in the pot).

A dimensional estimate gives the condition $V_0 > \hbar^2/2mr_0^2$ for a bound state in the $l = 0$ sector. In addition, the centrifugal barrier counteracts the formation of bound states for $l > 0$. Next we investigate the behavior of $u(r)$ and thus of the wave function $\Psi(\vec{r})$ in the limits $r \to 0$ and $r \to \infty$. Limit case $r \to 0$ For $V(r) \propto 1/r^{2-\varepsilon}, \varepsilon > 0$, the leading terms ($l > 0$) of the differential equation (5.12) are given

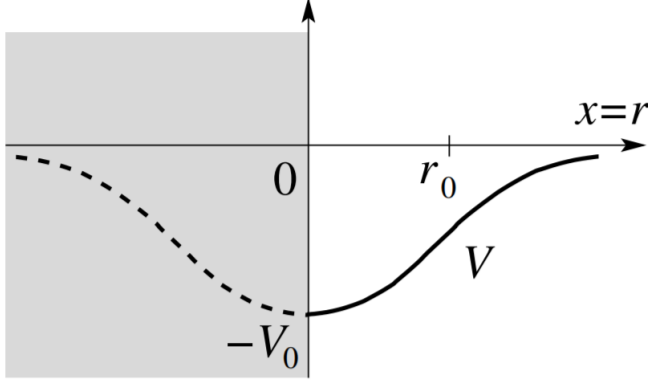$$\left[-\frac{\hbar^2}{2m}\partial_r^2 + \frac{\hbar^2 l(l+1)}{2mr^2}\right] u(r) = 0 \tag{5.13}$$

Figure 5.2: The centrally symmetric potential problem leaves to a equivalent half-sided 1D problem (with $r = x \geq 0$), here for illustrates an attractive potential.

This results in the following solutions for u (r),

$$u(r) \propto \begin{cases} r^{l+1} & \leftarrow \text{ regulre Lsung} \\ r^{-l} & \leftarrow \text{ nicht normierbar} \end{cases} \tag{5.14}$$

For $l = 0, u$ has to disappear at $r = 0$ (proof to absurdity): Let $u(0) = u_0 \neq 0$, then $\Psi(\vec{r}) \propto u_0/r$ at 0 and ∇^2 generates a -function at 0 (the function $1/r$ is just the Green function for the Laplace problem, $\nabla^2(1/r) = -4\delta(\vec{r})$, to be checked using the theorem of Gauss). This δ-function remains uncompensated in the Schrodinger equation and hence $u_0 = 0$. Limit case $r \to \infty$, we assume that $V(r \to \infty) \to 0$ at least as $1/r$; the surviving terms are then

$$\left[-\frac{\hbar^2}{2m}\partial_r^2 - E \right] u = 0 \tag{5.15}$$

and for bound states (with E ¡0) we find the asymptotic

$$u(r) \propto e^{-\alpha r}, \quad \alpha = \sqrt{2m|E|}/\hbar \tag{5.16}$$

Fuchsian approach

After separating the asymptotic for $r \to 0$ and $r \to \infty$, we solve the remaining problem with a Fuchsian approach,

$$u(r) = r^{l+1}e^{-\alpha r}\chi(r); \quad l > 0; \alpha = \sqrt{2m|E|}/\hbar, \quad E < 0$$
$$\chi(r) = r^s \sum_k a_k r^k \text{ Fuchsscher Ansatz.} \tag{5.17}$$

For $V(r) \propto -1/r^{2+\varepsilon}, \varepsilon > 0$, the particle falls into the singularity at 0, see Landau Lifschitz; the case $\varepsilon = 0$ is marginal (pre-factor V_0 of $V(r)$ V_0/r^2 is relevant (check)). In the following we examine in detail two examples, the 3D

well and the attractive Coulomb potential. We concentrate mainly on bound states, $E < 0$. We will deal with the scattering states with positive energies $E > 0$ later.

5.2 The particle in the 3D well

We define as usual $E < 0, k = \sqrt{2m(E + v_0)}/\hbar, \alpha = \sqrt{2m|E|}/\hbar$ solution theorems differ for $l = 0$ and $l > 0$, so we will treat the two cases separately.
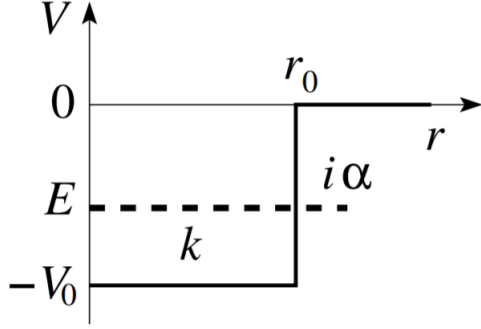

Figure 5.3: Well potential of depth V_0 and width r_0.

5.2.1 For $l = 0$

we get the differential equation

$$\begin{aligned}
\left[\partial_r^2 + k^2\right] u_0(r) = 0, \quad r \leq r_0 \\
\left[\partial_r^2 - \alpha^2\right] u_0(r) = 0, \quad r \geq r_0
\end{aligned} \tag{5.18}$$

with the solution

$$\begin{aligned}
u_0\left(r \leq r_0\right) = Ae^{ikr} + Be^{-ikr} \\
u_0\left(r \geq r_0\right) = Ce^{-\alpha r}
\end{aligned} \tag{5.19}$$

The solution (5.19) must satisfy the boundary conditions at $r = 0, u_0(0) = 0 \Rightarrow A + B = 0$, and at r_0,

$$\begin{aligned}
u_0\left(r_0^-\right) =& u_0\left(r_0^+\right) \\
& \Rightarrow 2iA\sin kr_0 = Ce^{-\alpha r_0} \\
u_0'\left(r_0^-\right) =& u_0'\left(r_0^+\right) \\
& \Rightarrow 2ikA\cos kr_0 = -\alpha Ce^{-\alpha r_0}
\end{aligned} \tag{5.20}$$

We get an (3.29) equivalent implicit equation for E,

$$\cot kr_0 = -\frac{\alpha}{k} \tag{5.21}$$

We find bound states if $V0 > \hbar^2\pi^2/8mr_0^2$, noting that $r_0 \longleftrightarrow w/2$.

5.2.2   For $l = 0$

we define $\rho = kr$ and get the differential equation for $r < r_0$

$$\left[\partial_\rho^2 + \frac{2}{\rho}\partial_\rho + \left(1 - \frac{l(l+1)}{\rho^2}\right)\right] R_l(\rho) = 0 \tag{5.22}$$

This equation also holds for $r > r_0$ if we redefine the variable ρ to $\rho \equiv i\alpha r$. The solutions of (5.22) are the verbal Bessel and Neumann functions,

$$\text{Bessel } \to j_l(\rho) = \sqrt{\frac{\pi}{2\rho}}\mathcal{J}_{l+\frac{1}{2}}(\rho) \tag{5.23}$$

$$\text{Neumann } \to n_l(\rho) = (-1)^{l+1}\sqrt{\frac{\pi}{2\rho}}\mathcal{J}_{-l-\frac{1}{2}}(\rho) \tag{5.24}$$

The Bessel functions $\mathcal{J}n$ are the solutions of the differential equation

$$\left[\partial_\varrho^2 = \frac{1}{\rho}\partial_\varrho \pm \left(1 - \frac{n^2}{\rho^2}\right)\right] \mathcal{J}_n(\rho) = 0 \tag{5.25}$$

Note that (5.22) is less than $l + \frac{1}{2} \to -l - \frac{1}{2}$ symmetric, and thus bypasses the Neumann solutions into the Bessel solutions. Examples of the verbal Bessel and Neumann functions are (see also figure 5.4 and 5.5).

$$
\begin{aligned}
j_0 &= \frac{\sin \rho}{\rho}, & n_0 &= -\frac{\cos \rho}{\rho} \\
j_1 &= \frac{\sin \rho}{\rho^2} - \frac{\cos \rho}{\rho}, & n_1 &= -\frac{\cos \rho}{\rho^2} - \frac{\sin \rho}{\rho} \\
j_2 &= \left(\frac{3}{\rho^3} - \frac{1}{\rho}\right)\sin \rho - \frac{3}{\rho^2}\cos \rho, & n_2 &= -\left(\frac{3}{\rho^3} - \frac{1}{\rho}\right)\cos \rho - \frac{3}{\rho^2}\sin \rho
\end{aligned} \tag{5.26}
$$

The spherical Bessel functions show the following behavior for small (series expansion for $\rho \to 0$) and large (asymptotic for $\rho \to \infty$) arguments:

$$
\begin{aligned}
\rho \to 0: \qquad & \rho \to \infty \\
j_l \sim \frac{\rho^l}{(2l+1)!!}, \quad & j_l \sim \frac{1}{\rho}\cos[\rho - (l+1)\pi/2] \\
n_l \sim -\frac{(2l-1)!!}{\rho^{l+1}}, \quad & n_l \sim \frac{1}{\rho}\sin[\rho - (l+1)\pi/2]
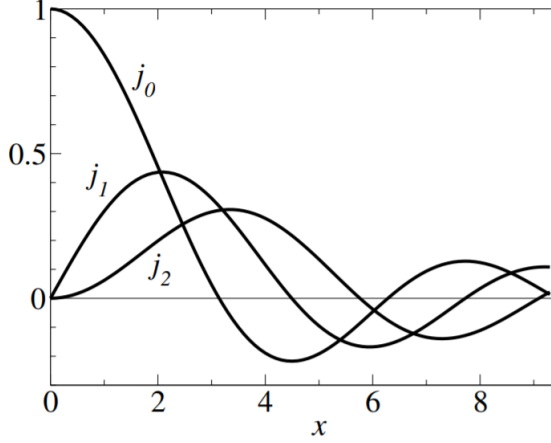\end{aligned} \tag{5.27}
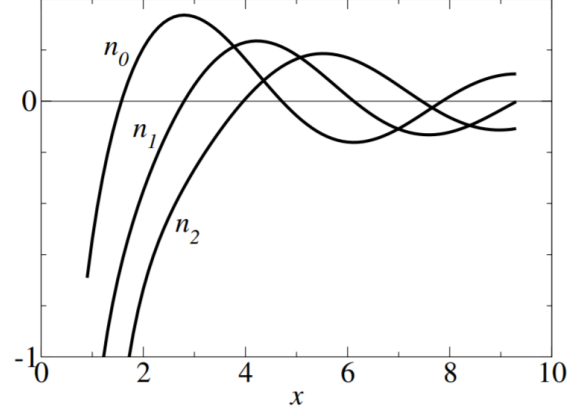$$

Figure 5.5: Bessel functions $j_0(x), j_1(x), j_2(x)$.

Figure 5.6: Neumann functions $n_0(x), n_1(x), n_2(x)$.

For the spherical Bessel functions $z_l = j_l, n_l$ the recursion formulas ($l > 0$) apply

$$z_{l-1} + z_{l+1} = \frac{2l+1}{\rho} z_l$$

$$\partial_\rho z_l = z_{l-1} - \frac{l+1}{\rho} z_l$$

(5.28)

For $\rho \to 0$, n_l is always singular, and thus it is a solution; $R_l(r > r_0)$ can then be represented as

$$R_l\left(r \leq r_0\right) = A j_l(kr)$$

(5.29)

In the outer space $r \geq r_0$ we choose the combinations

$$h_l^{(1)}(\rho) = j_l(\rho) + i n_l(\rho)$$

$$h_l^{(2)}(\rho) = j_l(\rho) - i n_l(\rho)$$

(5.30)

the Hankel functions with the asymptotic behavior

$$h_l^{(1,2)} \sim \frac{1}{\rho} e^{\pm i[\rho - (l+1)\pi/2]}$$

(5.31)

With $\rho \equiv i\alpha r$ we obtain an exponentially decaying function for $R_l(r \geq r_0)$ outside r_0,

$$R_l\left(r \geq r_0\right) = B\left[j_l(i\alpha r) + i n_l(i\alpha r)\right]$$

$$= B h_l^{(1)}(i\alpha r)$$

$$\sim \frac{B}{\rho}(-i)^{l+1} e^{-\alpha r}$$

(5.32)

the component $h_l^{(2)}(kr) \propto exp[-ikr]$ was describing an incident wave, $h_l^{(2)}(i\alpha r) \propto exp[\alpha r]$ describing a non-normative solution. The energy levels are again obtained from the boundary conditions at $r = r_0$: with $\xi = kr_0$ and $\eta = \alpha r_0$, $\hbar k = \sqrt{2m(E + V_0)}$ and $\hbar\alpha = \sqrt{2m|E|}$ we find the relations

$$\xi^2 + \eta^2 = 2mV_0 r_0^2/\hbar^2, \quad E = -\frac{\hbar^2}{2mr_0^2}\eta^2 \tag{5.33}$$

The boundary conditions

$$R_l\left(r_0^-\right) = R_l\left(r_0^+\right), \quad R_l'\left(r_0^-\right) = R_l'\left(r_0^+\right) \tag{5.34}$$

result in the implicit transcendental equations for ξ and η which lead to the energies E,

$$
\begin{aligned}
l = 0: \quad & \xi \cot \xi = -\eta \\
l = 1: \quad & \frac{\cot \xi}{\xi} - \frac{1}{\xi^2} = \frac{1}{\eta} + \frac{1}{\eta^2} \\
& \vdots
\end{aligned}
\tag{5.35}
$$

For every angular momentum sector l, a new transcendental equation $\eta(\xi)$ results. In each equation, a $\cot \xi$ function with an infinite number of branches appears. We number these with n, with the new branches appearing at $\xi = (n + 1/2)\pi$, respectively. These branches define the quantum number n in the angular momentum sector l, thus the eigenvalues depend on 2 quantum numbers, E_{nl}. The levels are degenerate in m, since the magnetic quantum number m does not appear in the differential equation, but for each $l(2l + 1)$ functions Y_{lm} occur, which is why each eigenvalue E_{nl} is just $(2l + 1)$-fold degenerate. This is the normal degeneracy in a SO3 invariant system. The hydrogen atom will turn out to be a special case, with levels only dependent on n, $E_n \propto -1/n^2$, and a higher degeneracy $\propto n^2$. The deeper reason for this higher degeneracy is the greater symmetry in the hydrogen problem, SO4 instead of SO3.

New bound states appear in the $l = 0$ sector if $\cot \xi \to 0$, ie ξ passes through the value $n\pi + \pi/2$; the first bound state (at $E = 0^-$) appears at $\eta = 0$ and $\xi = \pi/2$, ie $V_0 = \hbar^2\pi^2/8mr_0^2$. For $l = 1$, new states appear when $\cot\xi$ becomes finite from $+\infty$, that is, at $\xi = n$, where $n = 0$ does not produce a solution; the first bound state (at $E = 0$-) then appears for $\eta \to 0, \xi \to \pi$ if $V_0 = \hbar^2\pi^2/2mr_0^2$, compare with $l = 0$ where the first state appears at $V_0 = \hbar^2\pi^2/8mr_0^2$; the repulsive centrifugal force counteracts the formation of bonded states.

5.3 Hydrogen atom

5.3.1 2-body problems

First we repeat the classical problem: Let the Hamiltonian be given for two interacting (potential $V(r = |\vec{r}|)$) massive (mass $m_{1,2}$) particles,

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V\left(|\vec{r}_1 - \vec{r}_2|\right) \tag{5.36}$$

We go to center of gravity and relative coordinates $\vec{R}$ and $\vec{r}$ about[1].

$$\vec{r} = \vec{r}_1 - \vec{r}_2, \quad \vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2} \tag{5.37}$$

also for the (conjugate) impulses

$$\vec{p} = \frac{m_2\vec{p}_1 - m_1\vec{p}_2}{m_1 + m_2}, \quad \vec{P} = \vec{p}_1 + \vec{p}_2 \tag{5.38}$$

We define the reduced and the total mass

$$m = \mu = \frac{m_1 m_2}{m_1 + m_2}, \quad M = m_1 + m_2 \tag{5.39}$$

We quantize with the help of the commutation relations: From $[x_{\nu i}, p_{\mu j}] = i\hbar\delta_{ij}\delta_{\nu\mu}$ for $\nu, \mu \in 1, 2; i, j \in 1, 2, 3$ follow the commutation relations for $\vec{r}$ and $\vec{p}$ and $\vec{R}$ and $\vec{P}$,

$$[x_i, p_j] = i\hbar\delta_{ij}, \quad [X_i, P_j] = i\hbar\delta_{ij} \tag{5.40}$$

and we get the following representations for $\vec{p}$ and $\vec{P}$,

$$\vec{p} = \frac{\hbar}{i}\vec{\nabla}_{\vec{r}}, \quad \vec{P} = \frac{\hbar}{i}\vec{\nabla}_{\vec{R}} \tag{5.41}$$

The Hamiltonian in relative and center of gravity coordinates has the shape

$$H = \frac{P^2}{2M} + \frac{p^2}{2\mu} + V(r) \tag{5.42}$$

and allows the separation of center of gravity and relative movement through the approach

$$\Psi_{\vec{K}}(\vec{r}, \vec{R}) = e^{i\vec{K}\cdot\vec{R}} e^{-i\hbar K^2 t/2M} e^{-iEt/\hbar} \psi(\vec{r}) \tag{5.43}$$

---

[1]For a multiple-body problem with n particles in positions $x_i, i = 1, \cdots, n$, defined one the center of gravity coordinate (COM) $nX = \Sigma_1^n x_i$ and the relative COM coordinates $\tilde{x}_i = x_i - X$, then $\Sigma_1^n \tilde{x}_i = 0$. The kinetic energy $T = \Sigma_1^n \dot{x}_i^2$ then lets go to print out the relative coordinates $\delta x_{ij} = x_j - x_i = \delta\tilde{x}_{ij}, T = n\dot{X}^2 + n^{-1}\Sigma_{i<j}\delta\dot{x}_{ij}^2$. To the proof write $T = x\dot{X}^2 + \Sigma_1^n \tilde{x}_i^2$ then print the equation $(\Sigma_1^n \tilde{x}_i)^2 = 0$ by $\Sigma_1^n \tilde{x}_i^2 + R = 0$ and eliminate the remainder R via the relation $\Sigma_{i<j}\delta\dot{x}_{ij}^2 = (n-1)\Sigma_1^n \tilde{x}_i^2 - R$

with the remaining relative problem

$$\left[\frac{p^2}{2\mu} + V(r) \right] \psi(\vec{r}) = E\psi(\vec{r}) \tag{5.44}$$

The total energy is then the combination E + ℏ2K2 / 2M

5.3.2 Coulomb potential, H atom

We solve the relative problem

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(r) \right] \psi(\vec{r}) = E\psi(\vec{r}) \tag{5.45}$$

with the Coulomb potential $V(r) = -Ze^2/r$. After the separation of the angle coordinates $[\psi(\vec{r}) = \psi(r,\theta,\varphi) = Y_{l,m}(\theta,\varphi)R_{\alpha l}(r)]$ and using the approach $R_{\alpha l} = u_{\alpha l}/r$, we obtain the radial problem

$$\left[\partial_\rho^2 - \frac{l(l+1)}{\rho^2} + \frac{2}{\rho} - \alpha^2 \right] u_{\alpha l}(\rho) = 0 \tag{5.46}$$

Here we have the length scale

$$a_B = \hbar^2/m_e e^2 = 0.529\text{A} \tag{5.47}$$

We introduce ($\rho = Zr/a_B$, we approximate $m \approx m_e$ because $M \gg m_e$ of the hydrogen problem) and rewrite the energy E according to the scaling

$$\alpha^2 = \frac{-E}{Z^2 E_R}, \quad E_R = \frac{\hbar^2}{2m_e a_B^2} = 13.605\text{eV} \tag{5.48}$$

a_B is called Bohr radius, E_R is the Rydbergen energy; they are the relevant length and energy scales in the problem. After the usual splitting off of the asymptotic (for $\rho \to 0, \infty$) we use the Fuchsian approach (see (5.13) and (5.16))

$$u_{\alpha l}(\rho) = \rho^{l+1} e^{-\alpha\rho} f_{\alpha l}(\rho) \quad \text{with}$$
$$f_{\alpha l}(\rho) = \sum_\nu a_\nu \rho^\nu \tag{5.49}$$

and get the differential equation

$$\partial_\rho^2 f_{\alpha l} + 2\left(\frac{l+1}{\rho} - \alpha \right) \partial_\rho f_{\alpha l} + \frac{2}{\rho}[1 - \alpha(l+1)]f_{\alpha l}(\rho) = 0 \tag{5.50}$$

The coefficient comparison in the powers ρ^ν gives the recursion

$$a_{\nu+1} = 2\frac{\alpha(l+\nu+1)-1}{(\nu+1)(\nu+2l+2)}a_\nu, \quad \nu = 0,1,2,\ldots \tag{5.51}$$

End level	Name	Energy
n=1	Lyman	UV
n=2	Balmer	Visible
n=3	Paschen	IR
n=4	Bracket	IR
n=5	Pfund	IR

Table 5.1: Transition between levels

The coefficient a_0 is determined by normalization. Since $a_{\nu+1}/a_\nu \sim 2\alpha/\nu, \nu \to \infty$, the series must break off and we get the spectrum

$$\alpha = \frac{1}{l+1+\nu} \tag{5.52}$$

The eigenvalues

$$E_n = -\frac{Z^2 E_R}{n^2}, \quad n = 1, 2, 3, \ldots = \text{ Principal quantum number} \tag{5.53}$$

occur with the degrees of degeneration D_n

$$D_n = \sum_{m,l,\nu} \delta_{l+1+\nu,n} = \sum_{l=0}^{n-1} \underbrace{(2l+1)}_{\Sigma_m} = n^2 \tag{5.54}$$

The quantum numbers n, l, m are called the main quantum number n, the minor or orbital angular momentum quantum number l, and the magnetic quantum number m. The additional degeneracy in l is a consequence of the dynamic symmetry in the Coulomb potential. If the spin is taken into account (see later) the degeneration doubles, $D_n = 2n^2$. The transitions between the levels involve $\Delta l = 1$ (see later) and belong to one of the sequences in table 5.1; see also figure 5.6 for a graphical representation of the states involved.

5.3.3 Radial wave functions

The radial wave functions of the Coulomb potential result from the differential equation (5.50), which we use via the manipulations

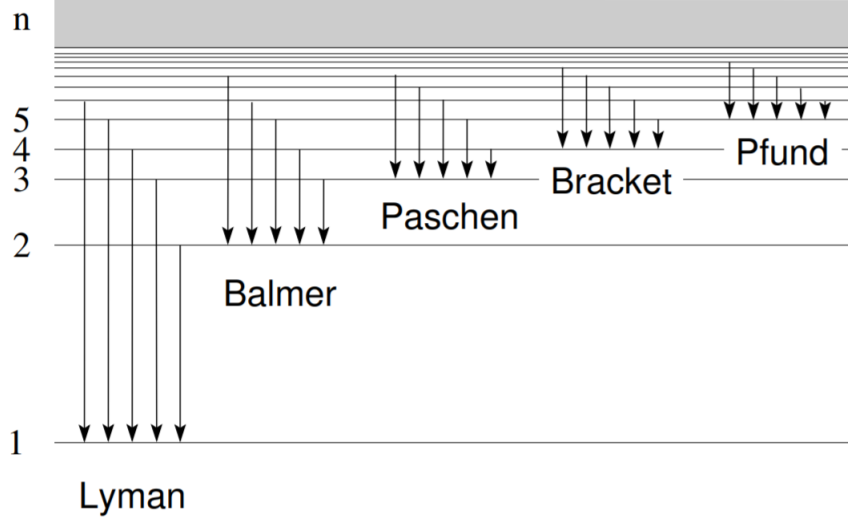$$\partial_\rho^2 + 2[(l+1)/\rho - \alpha]\partial_\rho + (2/\rho)[1 - \alpha(l+1)] \tag{5.55}$$

Figure 5.6: U-tops in the H-atom: Lyman, Balmer, Paschen, Bracket and Pound series. The Lyman series is in the UV range with energies greater than 10 eV; the Balmer series is in the visible range with energies in the range of greater 1.9 eV (red, cyan, violet); the Paschen series is in the IR range with energies greater than 0.65 eV.

$$\downarrow z = 2\alpha\rho$$

$$4\alpha^2 \partial_z^2 + 4\alpha[2\alpha(l+1)/z - \alpha]\partial_z + (4\alpha/z)[1 - \alpha(l+1)] \tag{5.56}$$

$$\downarrow \cdot z/4\alpha^2$$

$$z\partial_z^2 + [\underbrace{2(l+1)}_{b} - z]\partial_z + [\underbrace{1/\alpha - (l+1)}_{-a}] \tag{5.57}$$

into the following form $(n = 1/\alpha)$

$$\left\{ z\partial_z^2 + [2(l+1) - z]\partial_z + [n - (l+1)] \right\} f_{nl}(z) = 0 \tag{5.58}$$

The comparison with the differential equation

$$z\partial_z^2 F + (b-z)\partial_z F - aF = 0 \tag{5.59}$$

with the solutions (confluent hypergeometric functions)

$$F(a, b; z) = 1 + \frac{a}{b1!}z + \frac{a(a+1)}{b(b+1)2!}z^2 + \cdots \tag{5.60}$$

gives us the radial functions in the form

$$R_{nl}\left(r = \rho a_B/Z\right) = \rho^l e^{-\alpha\rho} f_{nl}(z = 2\rho/n)$$
$$\propto (\kappa r)^l e^{-\kappa r} F(-n + l + 1, 2l + 2; 2\kappa r) \tag{5.61}$$

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with $z = 2\alpha\rho = 2Zr/na_B = 2\kappa r, \kappa = Z/a_B n$ the effective wavenumber. The boundary condition (for $r \to \infty$) requires that $n - l - 1 = \geq 0$ is an integer, resulting in the spectrum $E = -\hbar^2/2m_e a_B^2 n^2 = -m_e e^4/2\hbar^2 n^2, n \in \mathbb{N}$. The confluent hypergeometric function with integer parameters is (except for one factor) identical to the associated Laguerre polynomial [2]

$$L_p^k(z) = \frac{p!}{(p-k)!}e^z\partial_z^p\left(z^{p-k}e^{-z}\right) \tag{5.67}$$

$$F(-p + k, k + 1; z) \propto L_p^k(z) \tag{5.68}$$

and the identification $p = n + 1, k = 2l + 1$ gives us the following final results for the generalized hydrogen atom,

$$\Psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{lm}(\theta, \varphi) \tag{5.69}$$

$$R_{nl}(r) = -N_{nl}(2\kappa r)^l e^{-\kappa r} L_{n+l}^{2l+1}(2\kappa r) \tag{5.70}$$

$$N_{nl} = \left(\frac{Z}{a_B}\right)^{\frac{3}{2}} \frac{2}{n^2(n+l)!}\sqrt{\frac{(n-l-1)!}{(n+l)!}}$$

The radial function is normalized to 1,

$$\int_0^\infty dr r^2 \left|R_{nl}(r)\right|^2 = 1 \tag{5.71}$$

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[2]The Laguerre differential equation

$$\left[z\partial_z^2 + (1 - z)\partial_z + p\right] L_p(z) = 0, \quad p > 0 \tag{5.62}$$

is solved by the Laguerre polynomials

$$L_p(z) = e^z\partial_z^p\left(z^p e^{-z}\right), \quad p = 0, 1, \ldots \tag{5.63}$$

The following recursion formulas apply to $L_p(z)$

$$\begin{aligned} L_{p+1} &= (2p + 1 - z)L_p - p^2 L_{p-1} \\ \partial_z L_p &= p\left(\partial_z L_{p-1} - L_{p-1}\right) \end{aligned} \tag{5.64}$$

The assigned Laguerre polynomial

$$L_p^k(z) = \partial_z^k L_p(z) = \frac{p!}{(p-k)!}e^z\partial_z^p\left(z^{p-k}e^{-z}\right) \tag{5.65}$$

solve the differential equation

$$\left[z\partial_z^2 + (k + 1 - z)\partial_z + (p - k)\right] L_p^k(z) = 0, \quad k \leq p \tag{5.66}$$

which is via the integral

$$\int_0^\infty dz\, z^{k+1} \mathrm{e}^{-z} \left[L_p^k(z) \right]^2 = \frac{(p!)^3}{(p-k)!}(2p - k + 1) \tag{5.72}$$

the normalization constant N_{nl} yields. Explicit examples of radial functions with $n \le 3$ are (see also figure 5.7)

$$\begin{aligned}
R_{10} &= 2\kappa^{3/2} \exp[-\kappa r] \\
R_{20} &= 2\kappa^{3/2}(1 - \kappa r) \exp[-\kappa r] \\
R_{21} &= \frac{2\kappa^{3/2}}{\sqrt{3}} \kappa r \exp[-\kappa r] \\
R_{30} &= 2\kappa^{3/2} \left[1 - 2\kappa r + 2(\kappa r)^2/3 \right] \exp[-\kappa r] \\
R_{31} &= \frac{4\sqrt{2}\kappa^{3/2}}{3} \kappa r(1 - \kappa r/2) \exp[-\kappa r] \\
R_{32} &= \frac{2\sqrt{2}\kappa^{3/2}}{3\sqrt{5}}(\kappa r)^2 \exp[-\kappa r]
\end{aligned} \tag{5.73}$$

With increasing principal quantum number n, the orbit $\langle r \rangle_{nl}$ shift outwards

$$\langle r \rangle_{nl} = \frac{a_B}{2Z} \left(3n^2 - l(l+1) \right) \tag{5.74}$$

and the fluctuations $\Delta r = [\langle r^2 \rangle_{nl} - \langle r \rangle_{nl}^2]^{1/2}$ grow according to

$$\Delta r = \frac{a_B}{2Z} \sqrt{n^2 \left(n^2 + 2 \right) - l^2(l+1)^2} \tag{5.75}$$

where we used that

$$\langle r^2 \rangle_{nl} = \frac{n^2 a_B^2}{2Z^2} \left[5n^2 - 3l(l+1) + 1 \right] \tag{5.76}$$

Finally, we consider the characteristics of two particularly simple cases, $l = n - 1$ and $l = 0$. For $l = n - 1$, the radial function $R_{n,n-1}$ has no zeros and their characteristics are

$$\begin{aligned}
\langle r \rangle_{n,n-1} &= \frac{a_B}{2Z} n(2n + 1) \\
\Delta r_{n,n-1} &= \frac{a_B}{2Z} n\sqrt{2n + 1} \\
\Delta r / \langle r \rangle|_{n,n-1} &\sim 1/\sqrt{2n + 1} \to 0 \text{ fr } n \to \infty
\end{aligned} \tag{5.77}$$

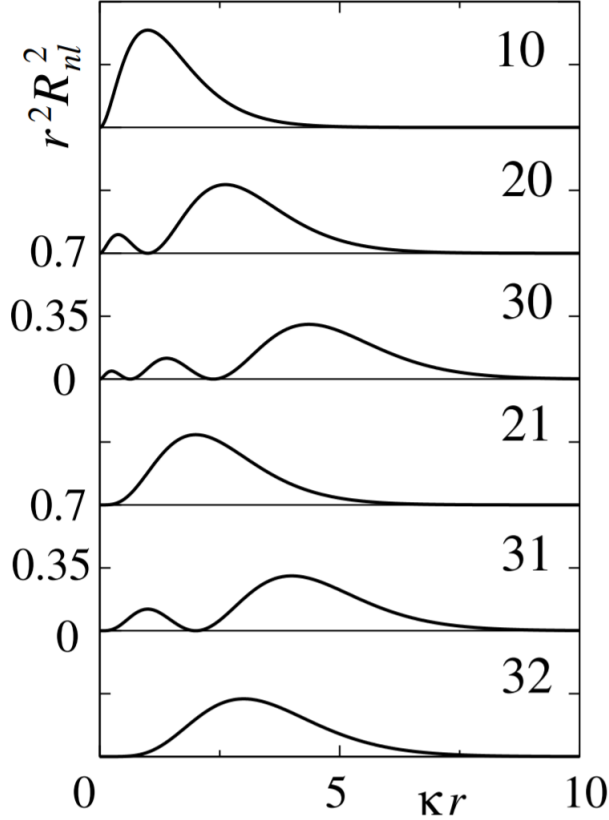For $l = 0$, R_{n0} has the maximum number of $n-1$ zeros and their characteristics are

Figure 5.7: Radial probability densities $r^2 R_{nl}^2$. Note the increasing displacement of the wave function from the environment of $r = 0$ with l ($\leftarrow$ centrifugal barrier) and the increase of zeros with n; the number zero is by $n - l - 1$ given. The radial function $R_{nn-1} = [(2\kappa)^{3/2}/\sqrt{(2n)!}](2\kappa r)^{n-1}e^{-\kappa r}$ with the highest l does not have any zero and defines for $n \to \infty$ sharp tracks (i.e. $\Delta r/r \to 0$) at $r \sim a_B n^2/Z$.

$$R_{n0}(0) \neq 0$$
$$\langle r \rangle_{n,0} = \frac{3a_B}{2Z}n^2 \tag{5.78}$$
$$\Delta r/\left.\langle r \rangle\right|_{n,0} = \sqrt{1 + (2/n^2)/3} \sim 1/3$$

5.3.4 Dynamic Symmetry

The dynamic symmetry is based on a special form of the law of force (the potential), here $V(r) \propto 1/r$. A potential $1/r^{1+\varepsilon}, \varepsilon \neq 0$ has the geometric rotational symmetry, but not an additional dynamic symmetry. In the case of the H atom, dynamic symmetry has a classical analogue, the (obtained) lenz vector. This is not always the case: quantum-mechanically dynamic symmetry does not necessarily have to be a classical analogue. We investigate the Kepler problem $H = p^2/2\mu - \kappa/r$, where μ denotes the reduced mass and κ for the generalized hydrogen atom is chosen to $\kappa = Ze^2$. Classical orbits are closed ellipses (see figure 5.8) with semiaxes a and b and eccentricity $e = (1-b^2/a^2)^{1/2}$ conservation laws are the energy $E = -\kappa/2a$ and the angular momentum $\vec{L}$, the direction $\hat{L}$ lays the orbital plane, the amount L determines the eccentricity

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via $L^2 = \mu\kappa a(1-e^2)$. The trajectory is thus defined by the conserved quantities E and $\vec{L}$ In addition to H and $\vec{L}$ the lenticular Get Runge Vector $\vec{M}$,

$$\vec{M} = \frac{1}{\mu}\vec{p} \wedge \vec{L} - \frac{\kappa}{r}\vec{r}, \quad M = \kappa e, \quad \vec{L} \cdot \vec{M} = 0$$
$$M^2 = \frac{2H}{\mu}L^2 + \kappa^2$$

(5.79)

$\vec{M} = $ const. implies the absence of perihelion rotation, a peculiarity of the $1/r$-potential. Fur $V \propto 1/r^{1+\varepsilon}$ results in a perihelion rotation; a famous example
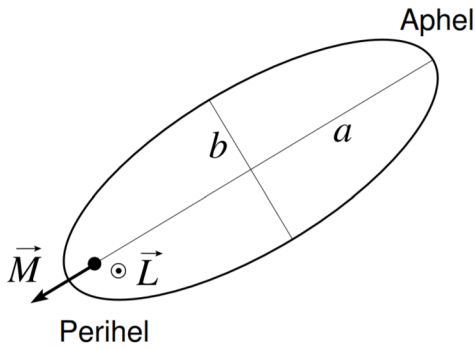

Figure 5.8: The Runge-Lenz vector $\vec{M}$ shows from the focal point to the perihelion and is a preserved size in the Kepler problem. Perturbations of the $1/r$-potential cause a rotation of $\vec{M}$; the observation of the peri-turn of Mercury was one of the first experimental confirmations of ART.

is the corrections to the Kepler problem as a result of the General Relativity Theory (ART); Mercury's peri-rotation was one of the first experimental confirmations of ART. The isotropic harmonic oscillator with r^2 potential also has a dynamic symmetry: In the isotropic harmonic oscillator, the obtained size is not a vector but a quadrupole, because center of attraction is not a focal point but the center of the elliptical orbit. In quantum mechanics we define the Pauli-Lenz vector

$$\vec{M} = \frac{1}{2\mu}(\vec{p} \wedge \vec{L} - \vec{L} \wedge \vec{p}) - \kappa\frac{\vec{r}}{r}$$

(5.80)

It is still $\vec{M} \cdot \vec{L} = 0 = \vec{L} \cdot \vec{M}$ as well

$$M^2 = 2H\left(L^2 + \hbar^2\right)/\mu + \kappa^2$$

(5.81)

with the additional term $\propto \hbar^2$. $\vec{M}$ is a vector, so the exchange relationships apply

$$[L_i, M_j] = i\hbar\varepsilon_{ijk}M_k$$

(5.82)

The permutation of the components M_i among each other

$$[M_i, M_j] = -(2H/\mu)i\hbar\varepsilon_{ijk}L_k$$

(5.83)

We define $\vec{K} = \sqrt{-\mu/2H}\vec{M}$ and constrain $\vec{M}$ to $\mathrm{Eig}_{E<0} H$, $\vec{K} = \sqrt{\mu/2|E|}\vec{M}$; for $E < 0, \vec{K}$ is a Hermitian operator. The six operators $\vec{K}, \vec{L}$ satisfy the commutation relations

$$[K_i, K_j] = i\hbar\varepsilon_{ijk}L_k$$
$$[L_i, K_j] = i\hbar\varepsilon_{ijk}K_k \tag{5.84}$$
$$[L_i, L_j] = i\hbar\varepsilon_{ijk}L_k$$

Extend the variables $x_i, p_i, i \in 1, 2, 3$ to x_4, p_4 by asking for it

$$L_{ij} = r_i p_j - r_j p_i, \quad i \in \{1, 2, 3, 4\}$$
$$L_{14} = K_x, \quad L_{24} = K_y, \quad L_{34} = K_z \quad (\leftrightarrow x_4 \& p_4) \tag{5.85}$$

thus the $L_{ij}, i \in 1, 2, 3, 4$ form the Lie algebra of O(4). We find that the symmetry group of H is not SO(3) but the larger group SO(4). For $E > 0$ we get the Poincare (or Lorentz) group over $\mathbb{M}^4 = (t, \vec{r})$, the Minkowski space, instead of SO(4).

Finally we compute the spectrum to H: using (5.81) we can write H as

$$H = -\frac{\mu\kappa^2}{2\left(K^2 + L^2 + \hbar^2\right)} \tag{5.86}$$

The two vector operators

$$\vec{S} = \frac{1}{2}(\vec{L} + \vec{K}) \quad \text{and} \quad \vec{D} = \frac{1}{2}(\vec{L} - \vec{K}) \tag{5.87}$$

define the two Casimir operators[3] S^2 and D^2 to SO(4):

$$[S_i, S_j] = i\hbar\varepsilon_{ijk}S_k, \quad [D_i, D_j] = i\hbar\varepsilon_{ijk}D_k$$
$$[\vec{S}, \vec{D}] = 0 \longrightarrow \quad \left[S^2, \vec{S}\right] = \left[S^2, \vec{D}\right] = 0 \tag{5.88}$$
$$\left[D^2, \vec{S}\right] = \left[D^2, \vec{D}\right] = 0$$

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[3]The Casimir operator is a bilinear combination of the generators of a LieAlgebra that commutes with these generators. The number of independent Casimir Operators equals the rank of the group, i.e., the maximum number of commuting generatrix. As an example consider the group SO(3) with $[L_i, L_j] = i\hbar\varepsilon_{ijk}L_k$. your Rank is 1, the Casimir operator is L^2, Another example is SO(4), where S_i, D_j stands for i and j form a maximum commuting set. The rank is 2, the Casimir operators are D^2 and S^2,

$\vec{D}$ and $\vec{S}$ each define an SO(3) or SU(2) algebra. Allowed eigenvalues are

$$\text{Eig } D^2 = \hbar^2 d(d+1)$$
$$\text{Eig } S^2 = \hbar^2 s(s+1)$$
$$d, s \in \left\{ 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \cdots \right\} \tag{5.89}$$

Since neither $\vec{S}$ nor $\vec{D}$ are orbital angular momenta, half-integer values for d and s are allowed. It is

$$H = -\frac{\mu\kappa^2}{2\left[(\vec{S}-\vec{D})^2 + (\vec{S}+\vec{D})^2 + \hbar^2\right]}$$
$$= -\frac{\mu\kappa^2}{2\left(2S^2 + 2D^2 + \hbar^2\right)} \tag{5.90}$$

Since $\vec{K} \cdot \vec{L} = 0, (\vec{S}-\vec{D})(\vec{S}+\vec{D}) = S^2 - D^2 = 0$, so $d = s$ and we get the energy eigenvalues

$$E_n = -\frac{\mu\kappa^2}{2\hbar^2[4s(s+1)+1]}$$
$$= -\frac{\mu\kappa^2}{2\hbar^2(2s+1)^2} \tag{5.91}$$
$$= -\frac{\mu\kappa^2}{2\hbar^2 n^2}$$

with $n = (2s+1)$ completely; the dimension of the energy eigenspace is dim $\text{Eig}_{E_n} H = (2s+1)(2d+1) = n^2$.