Symmetries

Midterm review sheets for Quantum Mechanics II (Physics 7502, SP16)

(1) Translations

The generator for infinitesimal translations in d dimensions is the total momentum operator:

$$\hat{T}(\vec{\varepsilon}) = \hat{\mathbb{1}} - i\hbar\,\vec{\varepsilon}\cdot\hat{\vec{P}}_{tot} = \hat{\mathbb{1}} - i\hbar\sum_{i=1}^{N_{part}}\vec{\varepsilon}\cdot\vec{P}_i \quad \text{for } N_{part} \text{ particles}$$

in d dimensions, $\vec{P}_i = (\hat{P}_{1i}, \hat{P}_{2i}, \ldots, \hat{P}_{di})$

$\vec{\varepsilon} = (\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_d)$

The operator for finite translations is

$$\hat{T}(\vec{a}) = \lim_{\tilde{N}\to\infty}\left(\mathbb{1} - i\hbar\frac{\vec{a}}{\tilde{N}}\cdot\hat{\vec{P}}_{tot}\right)^{\tilde{N}} = e^{-\frac{i}{\hbar}\vec{a}\cdot\hat{\vec{P}}_{tot}}$$

In x-representation $\hat{T}(\vec{a}) \rightarrow e^{-\vec{a}\cdot\vec{\nabla}} = e^{-\sum_{i=1}^{d} a_i\frac{\partial}{\partial x_i}}$

generates the Taylor expansion of $\psi(\vec{r}-\vec{a})$:

$$\psi(\vec{r}-\vec{a}) = \langle\vec{r}|\underbrace{\hat{T}(\vec{a})|\psi\rangle}_{|\psi_a\rangle} = \psi(\vec{r}) - \vec{a}\cdot\vec{\nabla}\psi(r) + \frac{1}{2!}\sum_{i,j=1}^{d} a_i a_j \frac{\partial^2\psi}{\partial x_i\partial x_j}(\vec{r}) \pm \cdots$$

(finite) translations in different directions commute:

$$\hat{T}(\vec{a})\hat{T}(\vec{b}) = \hat{T}(\vec{a}+\vec{b}) = \hat{T}(\vec{b})\hat{T}(\vec{a})$$

For a translationally invariant system

$$\hat{T}^+(\vec{a})\hat{H}(\hat{\vec{X}},\hat{\vec{P}})\hat{T}(\vec{a}) = \hat{H}(\hat{\vec{X}},\hat{\vec{P}}) \iff \langle\psi_a|\hat{H}|\psi_a\rangle = \langle\psi|\hat{H}|\psi\rangle \quad \forall|\psi\rangle$$

$\hat{\vec{X}} = (\hat{\vec{X}}_1, \hat{\vec{X}}_2, \ldots, \hat{\vec{X}}_{N_{part}})$ $\qquad$ $\hat{\vec{P}} = (\hat{\vec{P}}_1, \hat{\vec{P}}_2, \ldots, \hat{\vec{P}}_{N_{part}})$

$$\Rightarrow \hat{H}\left(\hat{T}^+(\vec{a})\hat{\vec{X}}\hat{T}(\vec{a}), \hat{T}^+(\vec{a})\hat{\vec{P}}\hat{T}(\vec{a})\right) = \hat{H}(\hat{\vec{X}}+\vec{a}\hat{\mathbb{1}}, \hat{\vec{P}}) = \hat{H}(\hat{\vec{X}},\hat{\vec{P}})$$

where we used

$$\hat{T}^+(\vec{a})\hat{X}_{ki}\hat{T}(\vec{a}) = \hat{X}_{ki} + a_i\hat{\mathbb{1}} \iff \langle\psi_a|\hat{\vec{X}}_k|\psi_a\rangle = \langle\psi|\hat{\vec{X}}_k|\psi\rangle + \vec{a}\hat{\mathbb{1}}$$

(k: particle k; i: direction i in $\mathbb{R}^d$) for all particles $k = 1, 2, \ldots N_{part}$

$i = 1, \ldots, d$; $k = 1, \ldots, N_{part}$

$$\hat{T}^+(\vec{a})\hat{P}_{ki}\hat{T}(\vec{a}) = \hat{P}_{ki} \iff \langle\psi_a|\hat{\vec{P}}_k|\psi_a\rangle = \langle\psi|\hat{\vec{P}}_k|\psi\rangle$$

So a translationally invariant Hamiltonian can only depend on coordinate differences $\vec{R}_{ij} \equiv \hat{\vec{X}}_i - \hat{\vec{X}}_j$ but not on the C.M. coordinate. From $\hat{T}^+ \hat{H} \hat{T} = \hat{H}$ it follows that the Hamiltonian must commute with $\hat{T}$ and hence with the total momentum $\hat{\vec{P}}_{CM} = \vec{P}_{tot} = \sum_{i=1}^{N_{part}} \vec{P}_i$:

$$[\hat{H}, \hat{P}_{tot}] = 0 \quad \overset{\text{Ehrenfest}}{\Longleftrightarrow} \quad \boxed{\frac{d}{dt}\langle \hat{\vec{P}}_{tot} \rangle = 0}$$

<u>total momentum conservation</u>

(2) <u>Time translations</u>

To have invariance under time translations, $\hat{H}$ can not depend on time explicitly:

$$\hat{H}(t_1) = \hat{H}(t_2) \quad (t_1, t_2 \text{ arbitrary})$$

$$\Rightarrow \frac{\partial \hat{H}}{\partial t} = 0 \quad \Rightarrow \quad \frac{d}{dt}\langle \hat{H} \rangle = \frac{i}{\hbar} \underbrace{\langle [\hat{H}, \hat{H}] \rangle}_{=0} + \underbrace{\left\langle \frac{\partial \hat{H}}{\partial t} \right\rangle}_{=0} = 0$$

<u>energy conservation</u>

For time-translationally invariant problems, the S.Eq.

$$i\hbar \frac{d}{dt} |\psi\rangle = \hat{H} |\psi\rangle$$

is solved by stationary states

$$|\psi(t)\rangle = |E\rangle \, e^{-i\hat{H}t/\hbar}$$

where $|E\rangle$ is an energy eigenstate: $\hat{H}|E\rangle = E|E\rangle$.

(3) Parity invariance

$$\hat{\pi}|\vec{x}\rangle = |-\vec{x}\rangle \qquad \text{where } \vec{x} = (\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_{N_{part}})$$

$$\hat{\pi}|\vec{p}\rangle = |-\vec{p}\rangle \qquad \text{and } \vec{x}_i = (x_{1i}, x_{2i}, \ldots, x_{di})$$

$(i = 1, 2, \ldots, N_{part})$

Similarly for $\vec{p}$.

Wave function

$$\psi_\pi(\vec{r}) = \langle \vec{r}|\hat{\pi}|\psi\rangle = \psi(-\vec{r})$$

$\hat{\pi}$ is a discrete symmetry transformation with eigenvalues ± 1. Parity eigenstates:

$$\psi_\pi(\vec{r}) = \psi(-\vec{r}) = (+1)\,\psi(\vec{r}) : \text{ even wavefunction, positive parity}$$

$$\psi_\pi(\vec{r}) = \psi(-\vec{r}) = (-1)\,\psi(\vec{r}) : \text{ odd wavefunction, negative parity}$$

$$\hat{\pi}^+ \hat{\vec{X}} \hat{\pi} = -\hat{\vec{X}} \quad , \quad \hat{\pi}^+ \hat{\vec{P}} \hat{\pi} = -\hat{\vec{P}}$$

$$\hat{\pi}^+ = \hat{\pi}^{-1}$$

Parity invariance:

$$\hat{\pi}^+ \hat{H}(\hat{\vec{X}}, \hat{\vec{P}})\,\hat{\pi} = \hat{H}(-\hat{\vec{X}}, -\hat{\vec{P}}) = \hat{H}(\hat{\vec{X}}, \hat{\vec{P}})$$

or $[\hat{H}, \hat{\pi}] = 0$

($\hat{H}$ must be a function of $\hat{\vec{X}}^2$, $\hat{\vec{P}}^2$ and $\hat{\vec{X}} \cdot \hat{\vec{P}}$ only.)

(4) Time reversal symmetry ($t \to -t$): $\hat{\Theta}$:

$$\psi(\vec{r}) \xrightarrow{\hat{\Theta}} \psi^*(\vec{r}) \; ; \; \langle \hat{\vec{X}} \rangle \xrightarrow{\hat{\Theta}} \langle \hat{\vec{X}} \rangle \; ; \; \langle \hat{\vec{P}} \rangle \xrightarrow{\hat{\Theta}} -\langle \hat{\vec{P}} \rangle$$

Rotations in 3 dimensions:

$$\hat{U}[\hat{R}(\vec{\vartheta})] = \lim_{N\to\infty} \underbrace{\left(\hat{1} - \frac{i}{\hbar}\frac{\vartheta}{N}\hat{\theta}\cdot\hat{\vec{L}}\right)}_{\text{infinitesimal rotation}}{}^N = e^{-i/\hbar\, \vec{\vartheta}\cdot\hat{\vec{L}}}$$

ϑ = rotation angle

$\hat{\theta} = \frac{\vec{\vartheta}}{\vartheta}$ = rotation axis (unit vector)

$\hat{\vec{L}} = \hat{\vec{R}} \times \hat{\vec{P}}$ orbital angular momentum operator

example: rotations in x-y-plane are generated by $\hat{L}_z$.

$$\hat{L}_x = \hat{Y}\hat{P}_z - \hat{Z}\hat{P}_y, \quad \hat{L}_y = \hat{Z}\hat{P}_x - \hat{X}\hat{P}_z, \quad \hat{L}_z = \hat{X}\hat{P}_y - \hat{Y}\hat{P}_x$$

$$[\hat{L}_i, \hat{L}_j] = i\hbar\, \varepsilon_{ijk}\hat{L}_k \quad \text{or} \quad \hat{\vec{L}}\times\hat{\vec{L}} = i\hbar\hat{\vec{L}}$$

Eigenvalue problem of $\hat{L}^2$ and $\hat{L}_z$: $\quad (\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2)$

$[\hat{L}^2, \hat{L}_i] = 0 \; (i=1,2,3)$ so $\hat{L}_z$ and $\hat{L}^2$ commute and have common eigenstates.

First $\hat{L}_z$:

$\hat{L}_z|m\rangle = m\hbar|m\rangle$ where in positions space

$$|m\rangle \leftrightarrow \langle\varphi|m\rangle = \psi_m(\varphi) = \frac{e^{im\varphi}}{\sqrt{2\pi}}$$

$$\hat{L}_z \leftrightarrow -i\hbar\frac{\partial}{\partial\varphi}$$

Now $\hat{L}^2, \hat{L}_z$ together:

$\hat{L}^2|lm\rangle = l(l+1)\hbar^2|lm\rangle$

$\hat{L}_z|lm\rangle = m\hbar|lm\rangle$

where in position space

$|lm\rangle \leftrightarrow \langle\vartheta,\varphi|lm\rangle = Y_{lm}(\vartheta,\varphi)$ spherical harmonics

$\hat{L}_x \leftrightarrow i\hbar(\sin\varphi\,\partial_\vartheta + \cos\varphi\cot\vartheta\,\partial_\varphi)$

$\hat{L}^2 \leftrightarrow -\hbar^2\left(\frac{1}{\sin\vartheta}\partial_\vartheta \sin\vartheta\,\partial_\vartheta + \frac{1}{\sin^2\vartheta}\partial_\varphi^2\right)$; $\hat{L}_y \leftrightarrow i\hbar(-\cos\varphi\,\partial_\vartheta + \sin\varphi\cot\vartheta\,\partial_\varphi)$

A few $Y_{\ell m}$'s: $Y_{00} = \frac{1}{\sqrt{4\pi}}$, $Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\vartheta$, $Y_{1,\pm1} = \mp\sqrt{\frac{3}{8\pi}} \sin\vartheta\, e^{\pm i\varphi}$

$Y_{20} = \sqrt{\frac{5}{16\pi}} (3\cos^2\vartheta - 1)$, $Y_{2,\pm1} = \mp\sqrt{\frac{15}{8\pi}} \sin\vartheta \cos\vartheta\, e^{\pm i\varphi}$

$Y_{2,\pm2} = \sqrt{\frac{15}{32\pi}} \sin^2\vartheta\, e^{\pm 2i\varphi}$

generally: $Y_{\ell m}(\vartheta,\varphi) = (-1)^m \sqrt{\frac{2\ell+1}{4\pi}} \sqrt{\frac{(\ell-m)!}{(\ell+m)!}}\, P_\ell^m(\cos\vartheta)\, e^{im\varphi}$

↑ associated Legendre polynomials
$P_\ell^0(\cos\vartheta) = P_\ell(\cos\vartheta)$ Legendre poly.

symmetry: $Y_{\ell,-m} = (-1)^m Y_{\ell m}^*$

orthogonality: $\int d\Omega\, Y_{\ell m}^*(\vartheta,\varphi) Y_{\ell' m'}(\vartheta,\varphi) = \delta_{\ell\ell'}\delta_{mm'}$

$\left(\langle \ell m | \ell' m' \rangle = \delta_{\ell\ell'}\delta_{mm'} \right)$

Raising and lowering operators:

$\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y \xleftrightarrow{\text{coord. repr.}} \pm\hbar e^{\pm i\varphi}(\partial_\vartheta \pm i\cot\vartheta\, \partial_\varphi)$

$[\hat{L}_z, \hat{L}_\pm] = \pm\hbar L_\pm$, $[\hat{L}^2, \hat{L}_\pm] = 0$

$\hat{L}_\pm |\ell m\rangle = \hbar\sqrt{(\ell\mp m)(\ell\pm m+1)}\, |\ell, m\pm1\rangle$

Total angular momentum:

$\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$ $\hat{\vec{S}}$ = spin operator

$[\hat{\vec{L}}, \hat{\vec{S}}] = 0$ $\hat{\vec{S}}$ does not operate on the states describing the orbital motion.

Eigenstates of $\vec{S}$ do not "live" in position space, i.e. they can not be represented in the $\hat{\vec{R}}$-basis. They live in a separate "Spin space"

$\mathbb{V} = \mathbb{V}_0 \otimes \mathbb{V}_S$

($\mathbb{V}_0$: states for orbital motion; $\mathbb{V}_S$: spin states)

$$[\hat{J}_i, \hat{J}_j] = i\hbar\, \varepsilon_{ijk} \hat{J}_k \qquad [\hat{J}^2, \hat{\vec{J}}] = 0$$

$$[\hat{L}_i, \hat{L}_j] = i\hbar\, \varepsilon_{ijk} \hat{L}_k \qquad [\hat{L}^2, \hat{\vec{L}}] = 0$$

$$[\hat{S}_i, \hat{S}_j] = i\hbar\, \varepsilon_{ijk} \hat{S}_k \qquad [\hat{S}^2, \hat{\vec{S}}] = 0$$

Spin, orbital and total angular momentum operators all satisfy the angular momentum algebra.

Allowed eigenvalues:

$j = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots \qquad m_j = j, j-1, \ldots, -j \quad (2j+1 \text{ values})$

$l = 0, 1, 2, \ldots \text{ (integer)} \qquad m_l = l, l-1, \ldots, -l \quad (2l+1 \text{ "})$

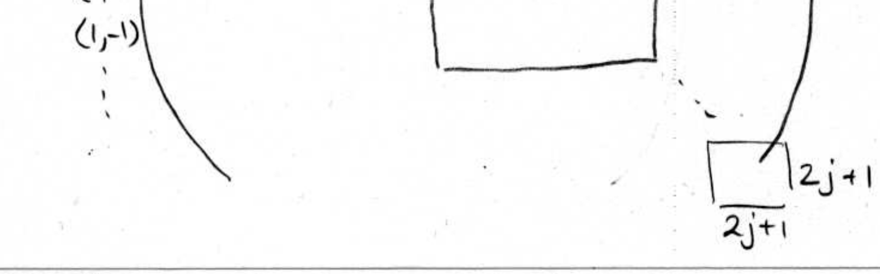
$s = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots \qquad m_s = s, s-1, \ldots, -s \quad (2s+1 \text{ "})$

$$\hat{J}^2 |jm\rangle = j(j+1)\hbar^2 |jm\rangle \qquad \hat{J}_z |jm\rangle = m\hbar |jm\rangle$$

$$\hat{L}^2 |lm\rangle = l(l+1)\hbar^2 |lm\rangle \qquad \hat{L}_z |lm\rangle = m\hbar |lm\rangle$$

$$\hat{S}^2 |sm\rangle = s(s+1)\hbar^2 |sm\rangle \qquad \hat{S}_z |sm\rangle = m\hbar |sm\rangle$$

The matrices $\langle j'm' | \hat{J}^2 | jm \rangle$, $\langle j'm' | \hat{J}_{x,y,z} | jm \rangle$ (and similarly for $\hat{\vec{L}}, \hat{\vec{S}}$) are blockdiagonal:



Spin-1/2:

$$\hat{\vec{S}} = \frac{\hbar}{2}\hat{\vec{\sigma}} \qquad [\hat{\sigma}_i, \hat{\sigma}_j] = 2i\,\varepsilon_{ijk}\hat{\sigma}_k \qquad \text{Pauli operators}$$

In S_z-eigenbasis:

$$\hat{\sigma}_x \longleftrightarrow \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \hat{\sigma}_y \longleftrightarrow \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \hat{\sigma}_z \longleftrightarrow \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\underbrace{|m=\tfrac{1}{2}\rangle}_{=|\frac{1}{2}\frac{1}{2}\rangle\ (|sm\rangle)} \longleftrightarrow \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \underbrace{|m=-\tfrac{1}{2}\rangle}_{=|\frac{1}{2},-\frac{1}{2}\rangle\ (|sm\rangle)} \longleftrightarrow \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

properties:

$$[\hat{\sigma}_i, \hat{\sigma}_j]_+ = 2\delta_{ij}\hat{\mathbb{1}}$$

$$(\vec{n}\cdot\hat{\vec{\sigma}})^2 = \hat{\mathbb{1}} \qquad (\vec{n} = \text{unit vector})$$

$$\mathrm{Tr}\,\sigma_i = 0 \qquad (\text{Pauli matrices are traceless})$$

$$\mathrm{Tr}(\sigma_\alpha\sigma_\beta) = 2\delta_{\alpha\beta} \qquad \left(\alpha,\beta = 0,1,2,3\ ;\ \sigma_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \mathbb{1}_{2\times 2}\right)$$

$$M_{2\times 2} = m_\alpha\sigma_\alpha \quad \text{with} \quad m_\alpha = \frac{1}{2}\mathrm{Tr}(M\sigma_\alpha)$$

$$(\vec{A}\cdot\hat{\vec{\sigma}})(\vec{B}\cdot\hat{\vec{\sigma}}) = (\vec{A}\cdot\vec{B})\hat{\mathbb{1}} + i(\vec{A}\times\vec{B})\cdot\hat{\vec{\sigma}} \qquad (\vec{A},\vec{B}\ \text{3-dim. (complex) vectors})$$

$$e^{-\frac{i}{2}\vec{\theta}\cdot\hat{\vec{\sigma}}} = \cos\left(\frac{\theta}{2}\right)\hat{\mathbb{1}} - i\sin\left(\frac{\theta}{2}\right)\hat{\theta}\cdot\hat{\vec{\sigma}} \qquad \left(\hat{\theta} = \frac{\vec{\theta}}{\theta},\ \theta = |\vec{\theta}|,\ \vec{\theta} = \text{3-d (real) vector}\right)$$

Solving the Schrödinger equation for spherically symmetric problems without spin:

$\hat{H}|E\rangle = E|E\rangle$ ($E > V(\infty)$, continuum states)

$\hat{H}|nlm\rangle = E_n|nlm\rangle$ ($E < V(\infty)$, boundstates)

$\hat{H} = \frac{\hat{\vec{P}}^2}{2\mu} + \hat{V}(\hat{R})$

$\hat{R} = \sqrt{\hat{X}^2 + \hat{Y}^2 + \hat{Z}^2}$

> n = main quantum number (counts nodes of spatial wave-function)
> l = orbital ang. momentum quantum number
> m = magnetic quantum number

In $\vec{r}$-basis $\hat{\vec{R}}|\vec{r}\rangle = \vec{r}|\vec{r}\rangle$, $\vec{r} = (r, \vartheta, \varphi)$ polar coords:

$$\left\{-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2}\underbrace{\left(\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\sin\vartheta\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right)}_{= -\hat{L}^2/\hbar^2}\right] + V(r)\right\}\psi_E(r,\vartheta,\varphi) = E\psi_E(r,\vartheta,\varphi)$$

For rotationally invariant systems $\hat{H}$ commutes with $\hat{L}^2$, $\hat{L}_z$

$\longrightarrow$ common eigenstates

$$\Longrightarrow \psi_{Elm}(r,\vartheta,\varphi) = R_{El}(r)\, Y_{lm}(\vartheta,\varphi) = \frac{u_{El}(r)}{r} Y_{lm}(\vartheta,\varphi)$$

where R_{El}, u_{El} satisfy the ordinary diff. eq.

$$\left[\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{l(l+1)}{r^2} + \frac{2\mu}{\hbar^2}\big(E - V(r)\big)\right] R_{El}(r) = 0$$

$$\left[\frac{d^2}{dr^2} + \frac{2\mu}{\hbar^2}\left(E - V(r) - \frac{l(l+1)\hbar^2}{2\mu r^2}\right)\right] u_{El}(r) = 0$$

$$(0 \le r < \infty)$$

Asymptotic behavior:

$$u_{E\ell}(r) \xrightarrow[r\to\infty]{} \begin{cases} 0 & \text{for bound states (normalized to 1)} \\ e^{ikr} & \text{for continuum states (normalized to } \delta\text{-fct.)} \end{cases}$$

$$u_{E\ell}(r) \xrightarrow[r\to 0]{} 0 \qquad u_\ell(r) \sim r^{\ell+1}$$

For potentials that vanish at $r\to\infty$ faster than $1/r$ $\left(rV(r) \xrightarrow[r\to\infty]{} 0\right)$:

$$u_E(r) \xrightarrow[r\to\infty]{} A e^{-\kappa r} \quad \left(\kappa = \sqrt{\frac{2\mu|E|}{\hbar^2}}\right) \quad (E<0)$$

$$\xrightarrow[r\to\infty]{} A' e^{\pm ikr} \quad \left(k = \sqrt{\frac{2\mu E}{\hbar^2}}\right) \quad (E>0)$$

For the Coulomb potential

Coulomb phase ↓

$$u_E(r) \xrightarrow[r\to\infty]{} \sim e^{\pm i\left(kr + \frac{\mu e^2}{k\hbar^2}\ln r\right)} \quad (E>0)$$

$$\xrightarrow[r\to\infty]{} \sim r^{\frac{\mu e^2}{\kappa\hbar^2}} e^{-\kappa r} \quad (E<0)$$

Orthonormality

$$\int d^3r\, \psi^*_{E\ell m}(r,\vartheta,\varphi)\, \psi_{E'\ell'm'}(r,\vartheta,\varphi) = \delta_{EE'}\,\delta_{\ell\ell'}\,\delta_{mm'} \quad (E,E'<0)$$

Free particle in polar coordinates

$$\psi(r,\vartheta,\varphi) = \int_0^\infty dk \sum_{l=0}^{\infty} \sum_{m=-l}^{l} c_{lm}(k)\, j_l(kr)\, Y_{lm}(\vartheta,\varphi) \quad \left(k = \sqrt{\frac{2\mu E}{\hbar^2}},\ E \geq 0 \right)$$

(general wave function) ↑ spherical Bessel fcts.

$$\int d^3r\ j_l(kr)\, Y^*_{lm}(\vartheta,\varphi)\, j_{l'}(k'r)\, Y_{l'm'}(\vartheta,\varphi) = \frac{\pi}{2k^2}\,\delta(k-k')\,\delta_{ll'}\,\delta_{mm'}$$

$$\int_0^\infty r^2 dr\ j_l(kr)\, j_l(k'r) = \frac{\pi}{2k^2}\,\delta(k-k')$$

- In finite regions where $V = 0$:

$$\psi(r,\vartheta,\varphi) = \int_0^\infty dk \sum_{lm} \left(c_{lm}(k)\, j_l(kr) + d_{lm}(k)\, n_l(kr) \right) Y_{lm}(\vartheta,\varphi)$$

↑ regular. ↑ irregular solution

must be matched to solutions to non-zero V where the potential is no longer zero.

$$j_0(\rho) = \frac{\sin\rho}{\rho},\quad j_1(\rho) = \frac{\sin\rho}{\rho^2} - \frac{\cos\rho}{\rho},\quad j_2(\rho) = \left(\frac{3}{\rho^3} - \frac{1}{\rho}\right)\sin\rho - \frac{3}{\rho^2}\cos\rho, \ldots$$

$$n_0(\rho) = -\frac{\cos\rho}{\rho},\quad n_1(\rho) = -\frac{\cos\rho}{\rho^2} - \frac{\sin\rho}{\rho},\quad n_2(\rho) = -\left(\frac{3}{\rho^3} - \frac{1}{\rho}\right)\cos\rho - \frac{3}{\rho^2}\sin\rho, \ldots$$

- plane wave in polar coordinates:

$$e^{ikz} = e^{ikr\cos\vartheta} = \sum_{l=0}^{\infty} i^l (2l+1)\, j_l(kr)\, P_l(\cos\vartheta)$$

Isotropic oscillator in 3d:

$$E_n = \left(n + \frac{3}{2}\right)\hbar\omega \qquad n = 2k+l \quad (k = 0,1,2,\ldots) \quad \Rightarrow l = n - 2k = n, n-2, \ldots, 1 \text{ or } 0$$

eigenvalues E_n are degenerate (fixed n allows different l values)

$$\psi(r,\vartheta,\varphi) = \sum_{n=0}^{\infty}\sum_{lm} R_{nl}(r)\, Y_{lm}(\vartheta,\varphi)$$

$$R_{nl}(r) = N_{nl}\, e^{-\xi^2/2}\, \xi^{l+1}\, F(-n, l+\tfrac{3}{2}, \xi^2), \quad \xi = \frac{r}{x_0}, \quad x_0 = \sqrt{\frac{\hbar}{\mu\omega}}$$

N_{nl} ↑ normalization

F ↑ confluent hypergeometric function

Hydrogen atom, bound states ($E<0$):

$$\psi(r,\vartheta,\varphi) = \sum_{n=0}^{\infty}\sum_{lm} R_{nl}(r)\, Y_{lm}(\vartheta,\varphi)$$

$$R_{nl}(r) = \tilde{N}_{nl}\, e^{-r/na_0}\left(\frac{r}{na_0}\right)^{l} L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right)$$

L ↑ associated Laguerre polynomials

$$E_n = -R_y \frac{1}{n^2}$$

$$R_y = \frac{me^4}{2\hbar^2} = \frac{1}{2}(mc^2)\alpha^2 = 13.6\,\text{eV}$$

$mc^2 = 511\,\text{keV}$ electron mass

$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137}$ fine structure constant

energies E_n are n^2 degenerate:

for each n, $l = n-k-1 = n-1, n-2, \ldots, 1, 0$ are allowed ($k = 0,1,2,\ldots$)

$$\left\langle \frac{1}{r}\right\rangle_n = \frac{1}{a_0}\frac{1}{n^2} \qquad a_0 = \frac{\hbar^2}{me^2} = \frac{\hbar^2c^2}{mc^2e^2} = \frac{\hbar c}{(mc^2)\alpha} = 53{,}000\,\text{fm} = 0.53\,\text{Å}$$

$$\hbar c = 197.33\,\text{MeV fm}$$

$$\frac{m_e}{m_p} = \frac{1}{1836} \qquad m_pc^2 = 938.3\,\text{MeV}$$

$$\lambda\!\!\!^{-}_e = \frac{\hbar}{mc} = \alpha a_0 = 386\,\text{fm}$$

Compton wavelength of electron (lower limit for how well an electron can be localized)

$$r_e = \frac{e^2}{mc^2} = \alpha \lambda\!\!\!^{-}_e = \alpha^2 a_0 \approx 2.8\,\text{fm}$$

classical electron radius

= radius of sphere with total charge e whose electrostatic potential energy $= mc^2$

- Virial theorem:

$$\langle \hat{T} \rangle = \left\langle \frac{\hat{P}^2}{2\mu} \right\rangle = -\frac{1}{2}\langle \hat{V} \rangle = -\left\langle \frac{e^2}{2r} \right\rangle$$

- Bohr quantization: $mvr = l = n\hbar$
- In hydrogen ground state

$$\beta = \alpha \qquad \left(\left\langle \frac{v}{c} \right\rangle = \frac{e^2}{\hbar c} = \frac{1}{137} \right)$$

- Degeneracy of E_n with different eigenvalues l due to conservation of Runge-Lenz vector:

$$[\hat{H}, \hat{\vec{N}}] = 0 \qquad \hat{\vec{N}} = \frac{1}{2m}\left(\hat{\vec{P}} \times \hat{\vec{L}} - \hat{\vec{L}} \times \hat{\vec{P}}\right) - \frac{e^2 \hat{\vec{R}}}{\hat{R}}$$

$$\left(\hat{R} = \sqrt{\hat{X}^2 + \hat{Y}^2 + \hat{Z}^2} \right)$$

$\hat{N}_+ = \hat{N}_x + i\hat{N}_y$ raises l by one, keeping n fixed:

$$N_+ |n, l, m=l\rangle \sim |n, l+1, m=l+1\rangle$$

Since it commutes with $\hat{H}$, these states have same energy.

Spin

Spin is an intrinsic property of a particle.

The eigenvalue of $\hat{S}^2$, $s(s+1)\hbar^2$, is a property of the particle and never changes.

The eigenvalue $m\hbar$ of $\hat{S}_z$ can change as a function of time.

States of particles with spin can be expanded into direct products of orbital and spin eigenstates:

$$|\psi\rangle = \sum_{nlmm_s} C_{nlmm_s} |nlm\rangle_o \otimes |sm_s\rangle_s$$

↑ orbital motion ↑ spin state

For electrons $s=\frac{1}{2}$:

$$\hat{S}_z |\tfrac{1}{2} m_s\rangle = m_s\hbar |\tfrac{1}{2} m_s\rangle \qquad (m_s = \pm\tfrac{1}{2})$$

$$\hat{S}^2 |\tfrac{1}{2} m_s\rangle = \tfrac{1}{2}(\tfrac{1}{2}+1)\hbar^2 |\tfrac{1}{2} m_s\rangle = \tfrac{3}{4}\hbar^2 |\tfrac{1}{2} m_s\rangle$$

$$\langle \tfrac{1}{2} m_s | \hat{\vec{S}} | \tfrac{1}{2} m_s\rangle = m_s\hbar\,\vec{e}_z = \pm\frac{\hbar}{2}\vec{e}_z$$

- Spin magnetic moment:

$$\hat{\vec{\mu}}_s = -\frac{e}{mc}\hat{\vec{S}} = g\left(-\frac{e}{2mc}\right)\hat{\vec{S}}, \quad \text{for electrons } g\approx 2$$

- orbital magnetic moment:

$$\hat{\vec{\mu}}_o = \frac{q}{2mc}\hat{\vec{L}} \qquad \frac{e\hbar}{2mc} = \text{Bohr magneton} = \begin{cases} 0.6\times10^{-8}\frac{eV}{G} & (e) \\ 0.3\times10^{-11}\frac{eV}{G} & (p)\end{cases}$$

- interaction with external magnetic field:

$$\hat{H}_{int} = -\hat{\vec{\mu}}\cdot\vec{B} = -(\hat{\vec{\mu}}_o + \hat{\vec{\mu}}_s)\cdot\vec{B} = -\left(\frac{-e}{2mc}\hat{\vec{L}} + \frac{-e}{mc}\hat{\vec{S}}\right)\cdot\vec{B}$$

for electrons

$\hat{H}_{int}$ is diagonal in $|nlm\rangle\otimes|sm_s\rangle$ basis.

$\hat{H}_{int}$ splits the degeneracy of the hydrogen eigenenergies (Zeeman effect): $\hat{H}|nlmm_s\rangle = \left(-\frac{R_y}{n^2} + \frac{eB\hbar}{2mc}(m+2m_s)\right)|nlmm_s\rangle$

For $g=2$, some smaller degeneracy remains

For $g = 2\cdot 1.00115965 \neq 2$, degeneracy is completely broken.

- Stern-Gerlach experiment: proved quantization of $\hat{J}_z$.

- Spin dynamics in external $\vec{B}$ field (NMR):

$$|\chi(t)\rangle_s = e^{-i/\hbar\, \hat{H}^{spin}_{int} t}|\chi_0\rangle = e^{i\gamma t\,\hat{\vec{S}}\cdot\vec{B}/\hbar}|\chi_0\rangle \quad \text{if } \vec{B} \text{ constant} \qquad \left(\gamma = -\frac{e}{mc}\right)$$

$\longrightarrow$ spin precession, $\vec{\theta}(t) = -\gamma\vec{B}t$

if $\vec{B} = B_0 \vec{e}_z$: $\hat{U}(t) = e^{i\gamma t B \hat{S}_z/\hbar} = e^{i\omega_0 t \frac{\sigma_z}{2}}$ $\quad (\omega_0 = \gamma B)$

$$\longleftrightarrow \begin{pmatrix} e^{i\omega_0 t/2} & 0 \\ 0 & e^{-i\omega_0 t/2} \end{pmatrix}$$

If $|\chi_0\rangle \leftrightarrow \begin{pmatrix} \cos\vartheta/2 \; e^{-i\varphi/2} \\ \sin\vartheta/2 \; e^{i\varphi/2} \end{pmatrix}$

then $|\chi(t)\rangle = \hat{U}(t)|\chi_0\rangle \leftrightarrow \begin{pmatrix} \cos\vartheta/2 \; e^{-i(\phi - \omega_0 t)/2} \\ \sin\vartheta/2 \; e^{i(\phi - \omega_0 t)/2} \end{pmatrix}$

$\phi(t) = \phi_0 - \omega_0 t$ spin precession

Variational methods

Estimate ground state energy by minimizing $E(\psi) = \langle\psi|\hat{H}|\psi\rangle$ over a set of (normalized) trial states that depend on parameters $\alpha, \beta, \ldots$:

Trial state $|\psi(\alpha,\beta,\ldots)\rangle$ $\quad (\alpha,\beta,\ldots \in \mathbb{R})$

$$E_0 \leq \min_{\alpha,\beta,\ldots} \frac{\langle\psi(\alpha,\beta,\ldots)|\hat{H}|\psi(\alpha,\beta,\ldots)\rangle}{\langle\psi(\alpha,\beta,\ldots)|\psi(\alpha,\beta,\ldots)\rangle} \equiv \min E[\alpha,\beta,\ldots]$$

To derive variational estimates for energies of excited states, must use trial functions that are, for all choices of the parameters $\alpha,\beta,\ldots$, orthogonal on the optimized trial function for the ground state.

Accuracy of variational estimate:

$$E[\psi_n] = E_n + O\left((\delta\psi_n)^2\right)$$ (second order in error of variational wavefunction)

Eigenkets of $\hat{H}$ are stationary points of $E[\psi]$.

Need at least one shape parameter (normalization constant is NOT a variational parameter!)

WKB method

Write $\psi(x) = e^{i/\hbar\,\phi(x)}$, expand $\phi = \phi_0 + \hbar\phi_1 + \ldots$, keep up to order $\hbar$.

Solve S. Eq. with this ansatz to order $\hbar$ and find

$$\psi^{WKB}(x) = \psi(x_0)\sqrt{\left|\frac{p(x_0)}{p(x)}\right|}\; e^{\pm\frac{i}{\hbar}\int_{x_0}^{x} p(x')\,dx'}$$

where $p(x') = \sqrt{2m(E - V(x))}$ is "local momentum" of particle

Works in both classically allowed and classically forbidden regions as long as

$$\frac{1}{2\pi}\left|\frac{d\lambda(x)}{dx}\right| \ll 1 \quad \text{where} \quad \lambda(x) = \frac{2\pi\hbar}{p(x)}$$

or $$\frac{\lambda(x)}{2\pi}\left|\frac{dV}{dx}\right| \ll |T(x)| = \left|\frac{p^2(x)}{2m}\right|$$

or $$\hbar\left|\frac{dp(x)}{dx}\right| \ll |p(x)|^2$$

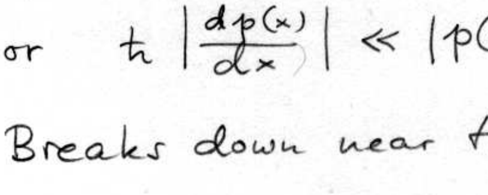
Breaks down near the classical turning points.

Connect WKB solutions in classically allowed and classically forbidden regions by Airy function interpolation. (Airy function = exact solution of S.Eq. for linear potential:

$$Ai(z) \xrightarrow[z\gg 1]{} \frac{1}{2\sqrt{\pi}}\frac{e^{-\frac{2}{3}z^{3/2}}}{z^{1/4}} \qquad Bi(z) \xrightarrow[z\gg 1]{} \frac{1}{\sqrt{\pi}}\frac{e^{\frac{2}{3}z^{3/2}}}{z^{1/4}}$$

$$\left.\begin{matrix} Ai(z) \\ Bi(z) \end{matrix}\right\} \xrightarrow[z\ll -1]{} \pm\frac{1}{\sqrt{\pi}}\frac{1}{|z|^{1/4}}\left\{\begin{matrix}\cos\\ \sin\end{matrix}\right\}\left(\frac{2}{3}|z|^{3/2}-\frac{\pi}{4}\right) \qquad z = \left(\frac{2mg}{\hbar^2}\right)(x-x_{cl})$$

where $g = \left|\frac{dV}{dx}\right|_{x_{cl}}$)



Connection formulae:

$$\text{(II)} \quad \frac{2A}{\sqrt{k(x)}}\cos\left(\int_x^b k(x')dx' - \frac{\pi}{4}\right) - \frac{B}{\sqrt{k(x)}}\sin\left(\int_x^b k(x')dx' - \frac{\pi}{4}\right) \longleftrightarrow \frac{A}{\sqrt{\kappa(x)}}e^{-\int_b^x \kappa(x')dx'} + \frac{B}{\sqrt{\kappa(x)}}e^{\int_b^x \kappa(x')dx'} \quad \text{(III)}$$

$$\text{(I)} \quad \frac{\tilde{A}}{\sqrt{\kappa(x)}}e^{-\int_x^a \kappa(x')dx'} + \frac{\tilde{B}}{\sqrt{\kappa(x)}}e^{\int_x^a \kappa(x')dx'} \longleftrightarrow \frac{2\tilde{A}}{\sqrt{k(x)}}\cos\left(\int_a^x k(x')dx' - \frac{\pi}{4}\right) - \frac{\tilde{B}}{\sqrt{k(x)}}\sin\left(\int_a^x k(x')dx' - \frac{\pi}{4}\right) \quad \text{(II)}$$

$$k(x) = \frac{1}{\hbar}\sqrt{2m(E-V(x))} \quad \text{where } E>V\,; \quad \kappa(x) = \frac{1}{\hbar}\sqrt{2m(V(x)-E)} \quad \text{where } E<V.$$

Energy eigenvalues follow from quantization condition

$$\int_a^b k(x')dx' = \left(n+\tfrac{1}{2}\right)\pi$$

Contrary to the variational method, the WKB estimate for the ground state energy does <u>not always</u> lie <u>above</u> the exact eigenvalue E_0.

- Variational method works best for ground state energy; less accurate for excited states (due to accumulating errors from orthogonalizing w.r.t. only approximate lower trial eigenfunctions.)
- WKB works best for higher-lying states (where semiclassical approximation is more accurate).