Lesson 8

Solid rotor

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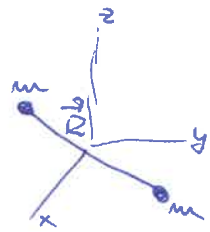
Motivation

- Quantum rotation of ~~an~~ a diatomic molecule in approximation of the solid rotor
- Two-body problem is solved in the difference vector
- Virtual particle with the reduced mass μ



- Quantum Hamiltonian $\hat{H} = -\frac{1}{2\mu}\nabla^2_{\vec{R}}$
- Identity $-\frac{1}{2\mu}\nabla^2\psi = \frac{1}{2\mu}\cdot\frac{1}{R}\left(-\frac{d^2}{dR^2}+\frac{\hat{L}^2}{R^2}\right)R\psi(R,\vartheta,\varphi)$

- Solid rotor : $R =$ constant
- Rotational part of the Hamiltonian , 2-degrees of freedom ϑ, φ

$$\hat{H}_r = \frac{\hat{L}^2}{2\mu R^2} = \frac{\hat{L}^2}{2I} = a\hat{L}^2$$

$I =$ moment of inertia

$a =$ rotational constant (given in meV, cm^{-1})

$$I = \mu R^2 = m\left(\frac{R}{2}\right)^2 + m\left(\frac{R}{2}\right)^2 = \frac{mR^2}{2} \quad ; \mu = \frac{m}{2}$$

- Eigenstates $|jm\rangle$

  Eigenvalues $E_j = a\, j(j+1)$

  $(2j+1)$-fold degeneracy

- Maxwell distribution

$$P(j) = (2j+1)\frac{e^{-\frac{aj(j+1)}{kT}}}{\sum_j (2j+1)\, e^{-\frac{aj(j+1)}{kT}}}$$

General polyatomic molecule :

3 degrees of freedom :

Euler ~~ag~~ angles : α, β, γ

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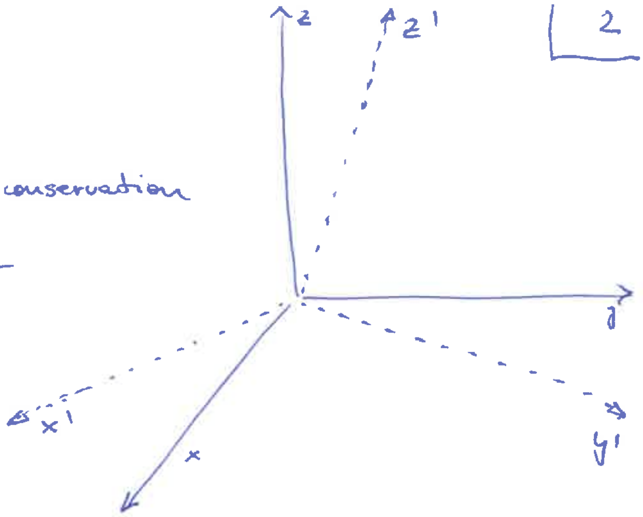


- Invariance of physics in time leads to energy conservation and therefore $\hat{H}$ is a "good" quantum operator
- Space homogenity leads to the momentum $\vec{P}$ conservation (total momentum). Operator of the total translation is $\hat{T} = e^{-i\vec{P}\cdot\vec{A}}$ (translation by $\vec{A}$)
- Isotropy of the space leads to conservation of the total angular momentum $\vec{L}$ of the system. Operator of the rotation around $\vec{n}$ is: $\hat{R}^{\vec{n}}_{\alpha} = e^{-i\alpha\vec{L}\cdot\vec{n}}$

So-called active rotation of the system.

Transformation of the angular-momentum eigenstates upon coordinates frame rotation (passive rotation)

$$\psi(\vec{r}) \xrightarrow{\text{rotation}} \psi'(\vec{r}\,')$$
$$\psi'(\vec{r}\,') = \psi(\vec{r})$$

Operator of the rotation

$$\hat{R}(\alpha,\beta,\gamma) = \hat{R}^{z}_{\gamma}\,\hat{R}^{y}_{\beta}\,\hat{R}^{z}_{\alpha}$$

Three consecutive rotations by the Euler angles α,β,γ.

$$\hat{R}^{z}_{\gamma} = e^{i\gamma\hat{J}_z}\,;\quad \hat{R}^{y}_{\beta} = e^{i\beta\hat{J}_y}\,;\quad \hat{R}^{z}_{\alpha} = e^{i\alpha\hat{J}_z}$$

← passive rotations, positive angles in the exponent

each of them commutes with $\hat{J}^2$

Eigenstates of $\hat{J}^2$ are $|jm\rangle$

$$R(\alpha,\beta,\gamma)\,|jm\rangle = \sum_k |jk\rangle\langle jk|\,R(\alpha,\beta,\gamma)\,|jm\rangle$$

$$\boxed{D^{j}_{mk} \equiv \langle jk|\,R(\alpha,\beta,\gamma)\,|jm\rangle}$$

Wigner functions
generalized spherical harmonics
Wigner D-functions

Because $\underbrace{\langle \vartheta'\varphi' | R(\alpha,\beta,\gamma) | jm \rangle}_{\psi'(\vec{r}\,')} = \boxed{\underbrace{\langle \vartheta\varphi | jm \rangle}_{\psi(\vec{r})} = \sum_k D^j_{mk} \langle \vartheta'\varphi' | jk \rangle}$

$\hat{R}(\alpha,\beta,\gamma)$ is unitary operator. It's matrix representation in the orthonormal basis $|jk\rangle$ must form an unitary matrix

$$(\underline{D}^j)^+ = (\underline{D}^j)^{-1} \Rightarrow \sum_m D^j_{mk} D^{*j}_{mk'} = \sum_m D^{j*}_{km} D^j_{k'm} = \delta_{kk'}$$

$$\Rightarrow \quad \langle \vartheta'\varphi' | jk \rangle = \sum_m \langle \vartheta\varphi | jm \rangle D^{j*}_{mk}$$

$$D^j_{mk}(\alpha,\beta,\gamma) = \langle jk | e^{i\gamma \hat{J}_z} e^{i\beta \hat{J}_y} e^{i\alpha \hat{J}_z} | jm \rangle = e^{im\alpha} d^j_{mk}(\beta) e^{-ik\gamma}$$

where $d^j_{mk}(\beta) = D^j_{mk}(0,\beta,0) = \langle jk | e^{i\hat{J}_y\beta} | jm \rangle$

Several properties without the proof:

$$D^l_{m0}(\alpha,\beta,\gamma) = \sqrt{\frac{4\pi}{2l+1}} Y_{lm}(\beta,\alpha) \quad ; \quad D^l_{0k}(\alpha,\beta,\gamma) = (-1)^k \sqrt{\frac{4\pi}{2l+1}} Y_{lk}(\beta,\gamma)$$

- $D^j_{mk}(\alpha,\beta,\gamma)$ forms a complete and ortho~~normal~~gonal set on space of the 3-dimensional rotations SO_3

$$\sum_k D^j_{mk}(\vartheta_2) \, D^j_{km'}(\vartheta_1) = D^j_{mm'} \; (\vartheta \equiv \vartheta_2 . \vartheta_1)$$

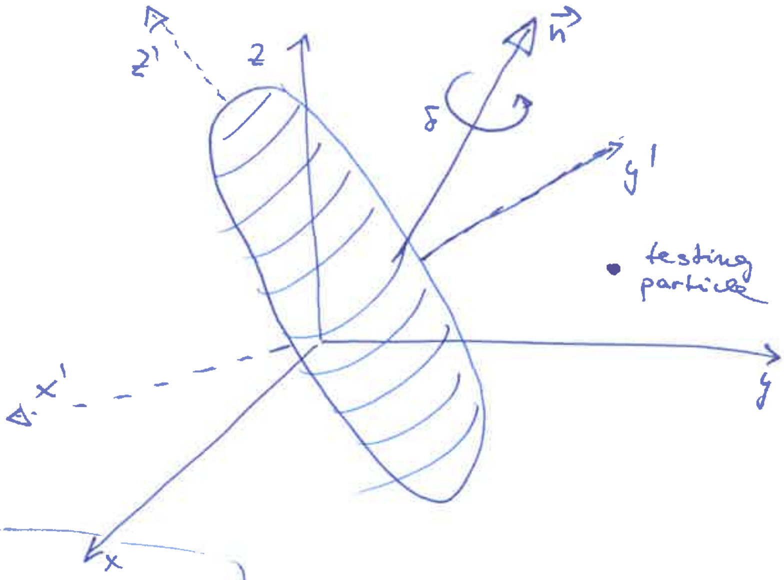
$$\int d\alpha\, d\gamma\, d\beta \sin\beta \; D^{*j}_{mk}(\alpha\beta\gamma) D^{j'}_{m'k'}(\alpha\beta\gamma) = \frac{8\pi^2}{2j+1} \delta_{jj'} \delta_{mm'} \delta_{kk'}$$

Eigenfunctions of the rigid-body angular momentum $\vec{L}$

$\hat{\vec{L}}$ ... angular momentum of the rigid body. Acts on space of the Euler angles α, β, γ

$[\hat{L}_x, \hat{L}_y] = i\hat{L}_z$

- testing particle with $\vec{J}^2, J_z$



$$\boxed{\langle \vartheta\varphi | jm\rangle = \sum_k D^j_{mk}(\alpha,\beta,\gamma)\langle \vartheta'\varphi' | jk\rangle} \qquad (A)$$

Active rotation of the function $D^j_{mk}(\alpha,\beta,\gamma)$

$$[D^j_{mk}(\alpha,\beta,\gamma)]' = e^{-i\delta\hat{\vec{L}}\cdot\vec{n}} D^j_{mk}(\alpha,\beta,\gamma) \overset{\text{small rotation}}{\sim} (1-\delta\hat{\vec{L}}\cdot\vec{n})\, D^j_{mk}(\alpha,\beta,\gamma)$$

- eigenstates of the testing particle does not change in the lab frame

i.e. $\langle \vartheta\varphi | jm\rangle' \overset{\text{after rotation by } \delta}{=} \langle \vartheta\varphi | jm\rangle$

- eigenstates $\langle \vartheta'\varphi' | jm\rangle'_{\underset{\delta \text{ rotation}}{R}} = e^{i\delta\vec{J}\cdot\vec{n}}\langle \vartheta'\varphi' | jm\rangle$

$$\langle \vartheta\varphi | jm\rangle \overset{\text{after } \delta \text{ rotation}}{=} \langle \vartheta\varphi | jm\rangle' = \sum_k [D^j_{mk}(\alpha,\beta,\gamma)]'\langle \vartheta'\varphi' | jk\rangle' =$$

$$= \underline{\sum_k (1-i\delta\hat{\vec{L}}\cdot\vec{n})\, D^j_{mk}\,(1+i\delta\vec{J}\cdot\vec{n})\langle \vartheta'\varphi' | j\cancel{m}k\rangle} \qquad (B)$$

(A)+(B) gives: $\underline{\sum_k (\vec{n}\cdot\hat{\vec{L}}\, D^j_{mk} - D^j_{mk}\,\vec{n}\cdot\hat{\vec{J}})\,|jk\rangle = 0}$

1.) $\vec{n} \parallel z'$ $\quad \boxed{\sum_k |jk\rangle(\hat{L}_{z'}D^j_{mk} - k D^j_{mk}) = 0} \Rightarrow \boxed{\hat{L}_{z'}D^j_{mk} = k D^j_{mk}}$

$$\boxed{\hat{L}_{z'}\, D^j_{mk} = k D^j_{mk}}$$

Acting of the operator $\hat{\vec{L}}.\vec{n}$ on the functions D^j_{mk} copies the action of the operator $\hat{\vec{J}}.\vec{n}$ on $|jk\rangle$ ... angular eigenstates of the testing particle.

Therefore, when we choose the other directions for $\vec{n}$:

2) $\vec{n} \parallel x'$

3) $\vec{n} \parallel y'$

following identities will be valid for $\vec{L}$, because they are valid for $\hat{\vec{J}}$ - inside the primed coordinate system

$$L_{x'} = (L_+ + L_-)\frac{1}{2}$$
$$L_{y'} = (L_+ - L_-)\frac{1}{2i}$$
$$L^2 = \frac{1}{2}(L_+L_- + L_-L_+) + L_{z'}^2$$
$$L_+ D^j_{mk} = \sqrt{j(j+1) - k(k+1)}\, D^j_{mk+1}$$
$$L_- D^j_{mk} = \sqrt{j(j+1) - k(k-1)}\, D^j_{mk-1}$$

$$L^2 = \frac{1}{2}(L_+L_- + L_-L_+) + L_{z'}^2$$

$$\boxed{L^2 D^j_{mk} = j(j+1) D^j_{mk}}$$

The theoretical experiment with the solid rotor and the testing particle is repeated

This time the testing particle is attached to the primed coordinate system. The relation (A) is still valid before the $\vec{n}.\delta$ rotation:

$$\boxed{\langle \vartheta\varphi | jm\rangle = \sum_k D^j_{mk}(\alpha,\beta,\gamma)\,\langle \vartheta'\varphi' | jk\rangle} \quad (A)$$

After the $\delta\vec{n}$ rotation we have:

$$(1 - i\delta\,\hat{\vec{J}}.\vec{n})\langle \vartheta\varphi | jm\rangle = \sum_k (1 - i\delta\,\hat{\vec{L}}.\vec{n})\, D^j_{mk}(\alpha,\beta,\gamma)\langle \vartheta'\varphi' | jk\rangle$$

$$\hat{\vec{J}}.\vec{n}\,\langle \vartheta\varphi | jm\rangle = \sum_k (\hat{\vec{L}}.\vec{n}\, D^j_{mk})\langle \vartheta'\varphi' | jk\rangle$$

We choose $\vec{n} \parallel z$

$$m\langle \vartheta\varphi | jm\rangle = \sum_k (\hat{L}_z D^j_{mk})\langle \vartheta'\varphi' | jk\rangle$$

Then we move the left side to the primed coordinate system:

$$\sum_k m\, D^j_{mk}(\alpha,\beta,\gamma) \langle \vartheta'\varphi' | jk \rangle = \sum_k \left(\hat{L}_z D^j_{mk} \right) \langle \vartheta'\varphi' | jk \rangle$$

$$\sum_k | jk \rangle \left(\hat{L}_z D^j_{mk} - m D^j_{mk} \right) = 0$$

linear combination of an orthonormal basis set elements

$$\Downarrow$$

$$\boxed{\hat{L}_z D^j_{mk} = m D^j_{mk}}$$

$\hat{L}^2 D^j_{mk} = j(j+1) D^j_{mk}$	$\hat{L}_{z'} D^j_{mk} = k D^j_{mk}$	$\hat{L}_z D^j_{mk} = m D^j_{mk}$

$\hat{L}^2, \hat{L}_z, \hat{L}_{z'}$ form a complete set of the independent Hermitian operators on the space spanned by the angles α, β, γ.