Two-dimensional rotor in the presence of an electric field applied in the plane: typical example of perturbation of degenerate case. Masatsugu Sei Suzuki and Itsuko S, Suzuki (Date: March 28, 2022)

Here we discuss the energy eigenvalue and energy eigenstate for the 2D rotor (diatomic molecule) in the presence of an electric field. Without electric field, the ground state of the unperturbed system is a non-degenerate state, while all the excited states are doubly degenerate. In the presence of electric field, we need to apply the perturbation theory (non-degenerate case) for the ground state, and the perturbation theory (degenerate case) for the excited states, respectively, to this system. Here we show our calculations for the possible shift of the energy, taking into account of the selection rule for the transition between these states. Although the model is simple, the solution of this problem is so instructive for both undergraduate and graduate students.

The perturbation for the 2D rotor problem in an electric field is also discussed in books;

- (i) Chapter 5, Problem 5-4) in Sakurai and Napolitano, Modern Quantum Mechanics 3rd edition (Cambridge, 2021).
- (ii) Chapter 7 (problem 7-5) of M. Kotani and H. Umezawa, Quantum Mechanics Problems and Solutions (in Japanese, problem 7-5),
- (iii) Chapter 10 (problem 10-23) of Y. Peleg, R. Pnini, and E. Zaarur, Schaum's Outline of Theory and Problems of Quantum Mechanics (McGraw-Hill, 1998).

((Note)) Here we use a noun of rotor, instead of noun of rotator (see the definition of noun rotor in

https://en.wikipedia.org/wiki/Rotor

((Example))

Helicopter rotor, the rotary wing(s) of a helicopter. The present model (diatomic molecule) looks like a model of helicopter rotor.

1. Model of 2D rotor (diatomic molecule)

We consider the simplest model of two atoms of mass m separated by a distance R rotating as a whole about their midpoint fixed in space, can be thought of as a rigid rotor of moment of inertia

$$I=2m(\frac{R}{2})^2=2mR^2.$$



Fig.1 Two-dimensional (2D) Rigid rotor model. The electric filed is directed along the x axis. The angle between the electric dipole moment p and the electric field ε .

2. ((5-4)) Sakurai and Napolitano (Cambridge, 2021)

A diatomic molecule can be modeled as a rigid rotor with moment of inertia I and an electric dipole moment p along the axis of the rotor. The rotor is constrained to rotate in a plane, and a weak uniform electric field e lies in the plane. Write the classical Hamiltonian for the rotor, and find the unperturbed energy levels by quantizing the angular-momentum operator. Then treat the electric field as a perturbation, and find the first nonvanishing corrections to the energy levels.

((Solution))

The Hamiltonian is given by

$$H = H_0 + V$$

= $\frac{L_z^2}{2I} - \mathbf{p} \cdot \mathbf{\epsilon}$
= $\frac{L_z^2}{2I} - p\varepsilon \cos \phi$
= $-\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2} - p\varepsilon \cos \phi$

with

$$H_0 = \frac{L_z^2}{2I}$$
, (unperturbed Hamiltonian)

and

$$V = -p\varepsilon\cos\phi$$
, (perturbation)

where the electric field is directed along the x axis. p is the electric dipole moment, We use the differential operators

$$L_{z} = \frac{\hbar}{i} \frac{\partial}{\partial \phi}, \qquad \qquad L_{z}^{2} = -\hbar^{2} \frac{\partial^{2}}{\partial \phi^{2}},$$

in the cylindrical coordinates. The Schrödinger equation for the unperturbed Hamiltonian H_0

$$-\frac{\hbar^2}{2I}\frac{\partial^2\psi(\phi)}{\partial\phi^2}=E\psi(\phi)\,,$$

or

$$\frac{\partial^2 \psi(\phi)}{\partial \phi^2} + \frac{2IE}{\hbar^2} \psi(\phi) = 0,$$

or

$$\frac{\partial^2 \psi(\phi)}{\partial \phi^2} + n^2 \psi(\phi) = 0$$

where $\psi(\phi)$ is the wavefunction, and

$$n^2=\frac{2IE}{\hbar^2},$$

For simplicity, we use the periodic boundary condition,

$$\psi(\phi) = \psi(\phi + 2\pi).$$

It is found that the normalized wavefunction of the unperturbed system

$$\psi_n(\phi) = \frac{1}{\sqrt{2\pi}} e^{in\phi},$$
 (*n* = 0, 0, ±1, ±2, ±3,.....)

and the energy eigenvalue

$$E_n^{(0)} = \frac{\hbar^2 n^2}{2I}.$$

Note that

$$\left|\psi_n(\phi)\right| = \frac{1}{\sqrt{2\pi}}.$$

We have a non-degenerate state at n = 0. We have degenerate states (degeneracy 2) at $\pm n$ (n = 1, 2, 3, 4, ...).

We now use the perturbation theory. The matrix element is

$$\begin{split} \left\langle n \left| \hat{V} \right| m \right\rangle &= \int_{0}^{2\pi} d\phi \psi_{n}^{*}(\phi) (-p\varepsilon \cos \phi) \psi_{m}(\phi) \\ &= \frac{1}{2\pi} (-p\varepsilon) \frac{1}{2} \int_{0}^{2\pi} d\phi e^{-in\theta} (e^{i\phi} + e^{-i\phi}) e^{im\theta} \\ &= \frac{1}{4\pi} (-p\varepsilon) \int_{0}^{2\pi} d\phi [e^{i(m-n+)\phi} + e^{i(m-n-1)\phi}] \\ &= -\frac{1}{2} p\varepsilon (\delta_{m,n+1} + \delta_{m,n-1}) \\ &= -\frac{1}{2} p\varepsilon \delta_{m,n\pm 1} \end{split}$$

So that, we have the selection rule for the transition

$$\langle n | \hat{V} | n \pm 1 \rangle = -\frac{1}{2} p \varepsilon$$
 (selection rule)

3. n = 0 (nondegenerate)

The ground state is non-degenerate.

$$E_0^{(0)} = 0$$
.

The energy shit for the first order is

$$E_0^{(1)} = \left\langle 0 \left| \hat{V} \right| 0 \right\rangle = 0.$$

So that, we need to evaluate the energy shift for the second order is

$$\begin{split} E_{0}^{(2)} &= \sum_{n \neq 0} \frac{\left| \left\langle n \left| \hat{V} \right| 0 \right\rangle \right|^{2}}{E_{0}^{(0)} - E_{n}^{(0)}} \\ &= \frac{\left| \left\langle +1 \right| \hat{V} \left| 0 \right\rangle \right|^{2}}{E_{0}^{(0)} - E_{1}^{(0)}} + \frac{\left| \left\langle -1 \right| \hat{V} \left| 0 \right\rangle \right|^{2}}{E_{0}^{(0)} - E_{-1}^{(0)}} \\ &= -\frac{p^{2} \varepsilon^{2} I}{\hbar^{2}} \end{split}$$

or

$$E_0 = E_0^{(0)} + E_1^{(0)} + E_2^{(0)} + \dots$$
$$= -\frac{p^2 \varepsilon^2 I}{\hbar^2}$$

How about the energy eigen state? The first order of $\left|0\right\rangle$ is

$$\begin{split} \left|\psi_{0}^{(1)}\right\rangle &= \left|+1\right\rangle \frac{\left\langle+1\right|\hat{V}\left|0\right\rangle}{E_{0}^{(0)} - E_{1}^{(0)}} + \left|-1\right\rangle \frac{\left\langle-1\right|\hat{V}\left|0\right\rangle}{E_{0}^{(0)} - E_{1}^{(0)}} \\ &= \left|+1\right\rangle \frac{-\frac{1}{2}p\varepsilon}{-\frac{\hbar^{2}}{2I}} + \left|-1\right\rangle \frac{-\frac{1}{2}p\varepsilon}{-\frac{\hbar^{2}}{2I}} \\ &= \frac{p\varepsilon I}{\hbar^{2}}[\left|+1\right\rangle + \left|-1\right\rangle] \\ &= \left|0\right\rangle + \lambda \left|\psi_{0}^{(1)}\right\rangle \\ &= \left|0\right\rangle + \frac{p\varepsilon I}{\hbar^{2}}[\left|+1\right\rangle + \left|-1\right\rangle] \end{split}$$

which is the superposition of the three states $|0\rangle$, $|+1\rangle$, $|-1\rangle$. Note that $\langle \psi_0^{(0)} | \psi_0^{(1)} \rangle = 0$ as is seen from the perturbation theory (non-degenerate case). The wavefunction is expressed by

$$\langle \phi | \psi_0 \rangle = \langle \phi | 0 \rangle + \frac{p \varepsilon I}{\hbar^2} [\langle \phi | +1 \rangle + \langle \phi | -1 \rangle]$$

$$= \frac{1}{\sqrt{2\pi}} [1 + \frac{p \varepsilon I}{\hbar^2} (e^{i\phi} + e^{-i\phi})]$$

$$= \frac{1}{\sqrt{2\pi}} (1 + \frac{2p \varepsilon I}{\hbar^2} \cos \phi)$$

3. n=1 (g=2 degeneracy): the first-order and the second-order contributions

((First-order))

The first order for the doubly degenerate state $|\pm n\rangle$ is zero. The matrix element of \hat{V} for the two states $|n\rangle$ and $|-n\rangle$

$$\langle n | \hat{V} | n \rangle = 0$$
, $\langle n | \hat{V} | -n \rangle = 0$.

((Second-order))

We now consider the second-order contribution.

$$E_1^{(0)} - E_0^{(0)} = \frac{\hbar^2}{2I}, \qquad E_1^{(0)} - E_2^{(0)} = -\frac{3\hbar^2}{2I}.$$

We need to evaluate the four matrix elements,

$$V = \begin{pmatrix} V(+1,+1) & V(+1,-1) \\ V(-1,+1) & V(-1,-1) \end{pmatrix}$$

(a) V(+1,+1)

Both the initial state and the final state are $|+1\rangle$.



Fig.2 The matrix element $V(\pm 1, \pm 1)$ Blue line (not allowed transition from the selection rule). The selection rule: $\Delta n = \pm 1$.

$$V(+1,+1) = \frac{\langle +1|\hat{V}|+2\rangle\langle +2|\hat{V}|+1\rangle}{E_1^{(0)} - E_2^{(0)}} + \frac{\langle +1|\hat{V}|0\rangle\langle 0|\hat{V}|+1\rangle}{E_1^{(0)} - E_0^{(0)}}$$
$$= \frac{\frac{1}{4}(p\varepsilon)^2}{-\frac{3\hbar^2}{2I}} + \frac{\frac{1}{4}(p\varepsilon)^2}{\frac{\hbar^2}{2I}}$$
$$= \frac{p^2\varepsilon^2 I}{3\hbar^2}$$

(b) V(-1,+1)

The initial state is $|+1\rangle$ and the final state is $|-1\rangle$.





We get

$$V(-1,+1) = \frac{\langle -1|\hat{V}|0\rangle\langle 0|\hat{V}|+1\rangle}{E_1^{(0)} - E_0^{(0)}}$$
$$= \frac{p^2 \varepsilon^2 I}{2\hbar^2}$$

(c)
$$V(+1,-1)$$

The initial state is $\left|-1\right\rangle\,$ and the final state is $\left|+1\right\rangle.$



Fig.4 The matrix element V(+1, -1). Blue and red lines (not allowed transition)

$$V(+1,-1) = \frac{\langle +1|\hat{V}|0\rangle\langle 0|\hat{V}|-1\rangle}{E_1^{(0)} - E_0^{(0)}}$$
$$= \frac{\left(\frac{p\varepsilon}{2}\right)^2}{\frac{\hbar^2}{2I}}$$
$$= \frac{p^2\varepsilon^2 I}{2\hbar^2}$$

(d)
$$V(-1,-1)$$

The initial state is $|-1\rangle$ and the final state is $|-1\rangle$.





$$V(-1,-1) = \frac{\langle -1|\hat{V}|-2\rangle\langle -2|\hat{V}|-1\rangle}{E_1^{(0)} - E_2^{(0)}} + \frac{\langle -1|\hat{V}|0\rangle\langle 0|\hat{V}|-1\rangle}{E_1^{(0)} - E_0^{(0)}}$$
$$= \frac{\frac{1}{4}p^2\varepsilon^2}{-\frac{3\hbar^2}{2I}} + \frac{\frac{1}{4}p^2\varepsilon^2}{\frac{\hbar^2}{2I}}$$
$$= \frac{p^2\varepsilon^2 I}{3\hbar^2}$$

So that, we get the matrix element (2x2) as

$$\hat{V} = \begin{pmatrix} \frac{p^2 \varepsilon^2 I}{3\hbar^2} & \frac{p^2 \varepsilon^2 I}{2\hbar^2} \\ \frac{p^2 \varepsilon^2 I}{2\hbar^2} & \frac{p^2 \varepsilon^2 I}{3\hbar^2} \end{pmatrix} = \frac{p^2 \varepsilon^2 I}{\hbar^2} \begin{pmatrix} \frac{1}{3} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{3} \end{pmatrix}$$

or

$$\hat{V}|+1\rangle = \frac{p^2 \varepsilon^2 I}{3\hbar^2} [|+1\rangle + \frac{3}{2}|-1\rangle]$$

and

$$\hat{V}|-1\rangle = \frac{p^2 \varepsilon^2 I}{3\hbar^2} [\frac{3}{2}|+1\rangle + |-1\rangle]$$

We note that

$$\hat{V}(|+1\rangle + |-1\rangle = \frac{5p^2\varepsilon^2 I}{6\hbar^2}[|+1\rangle + |-1\rangle]$$
$$\hat{V}(|+1\rangle - |-1\rangle = -\frac{p^2\varepsilon^2 I}{6\hbar^2}[|+1\rangle - |-1\rangle]$$

Thus we have the energy eigenvalue and eigenkets as follows

$$E_1^{(0)} = \frac{\hbar^2}{2I}$$

Energy eigenvalue Eigenstate $\frac{\hbar^2}{2I} + \frac{5p^2 \varepsilon^2 I}{6\hbar^2} \qquad \qquad \left| \psi_{\pm 1,s}^{(0)} \right\rangle = \frac{1}{\sqrt{2}} [|+1\rangle + |-1\rangle] \qquad (\text{symmetric state})$ $\frac{\hbar^2}{2I} - \frac{p^2 \varepsilon^2 I}{6\hbar^2} \qquad \qquad \left| \psi_{\pm 1,a}^{(0)} \right\rangle = \frac{1}{\sqrt{2}} [|+1\rangle - |-1\rangle] \qquad (\text{antisymmetric state})$

The wavefunctions are given by

$$\left\langle \phi \left| \psi_{\pm 1,s}^{(0)} \right\rangle = \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2\pi}} (e^{i\phi} + e^{-i\phi})$$

$$= \frac{1}{\sqrt{\pi}} \cos \phi$$
(symmetric state)

$$\left\langle \phi \left| \psi_{\pm 1,a}^{(0)} \right\rangle = \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2\pi}} (e^{i\phi} - e^{-i\phi})$$

= $\frac{1}{\sqrt{\pi}} i \sin \phi$ (antisymmetric states)

We note that $|\psi_{\pm 1,s}^{(0)}\rangle$ is the eigenket of the o-th order, even if we use the second-order perturbation for the degenerate case. The new eigenkets $|\psi_{\pm 1,s}^{(0)}\rangle$ and $|\psi_{\pm 1,a}^{(0)}\rangle$ are expressed only by a linear combination of $|\pm 1\rangle$.

4. n = 2 (g = 2 degeneracy): first-order and second order contribution

((First order))

The matrix element of \hat{V} for the two states $|n\rangle$ and $|-n\rangle$

 $\langle n | \hat{V} | n \rangle = 0, \qquad \langle n | \hat{V} | -n \rangle = 0$

So that, there is no first-order contribution.

((Second order))

Next, we calculate the second-order contribution.

$$E_2^{(0)} - E_3^{(0)} = -\frac{5\hbar^2}{2I}, \qquad \qquad E_2^{(0)} - E_1^{(0)} = \frac{3\hbar^2}{2I}$$

(a) V(+2,+2)

Both the initial state and the final state are $|+2\rangle$.



Fig.6 The transition between $|+2\rangle$ to $|+2\rangle$. The blue line and the purple line are not allowed.

$$V(+2,+2) = \frac{\langle +2|\hat{V}|+3\rangle\langle +3|\hat{V}|+2\rangle}{E_2^{(0)} - E_3^{(0)}} + \frac{\langle +2|\hat{V}|+1\rangle\langle +1|\hat{V}|+2\rangle}{E_2^{(0)} - E_1^{(0)}}$$
$$= \frac{\frac{1}{4}(p\varepsilon)^2}{-\frac{5\hbar^2}{2I}} + \frac{\frac{1}{4}(p\varepsilon)^2}{\frac{3\hbar^2}{2I}}$$
$$= \frac{p^2\varepsilon^2 I}{15\hbar^2}$$

(b)

V(-2,+2)The initial state is $|+2\rangle$ and the final state is $|-2\rangle$.

We note that

$$V(-2,+2) = 0$$

since all the transitions are forbidden.



Fig.7 All transitions from $|+2\rangle$ to $|-2\rangle$ are forbidden.

(c) V(+2,-2)

The initial state is $|-2\rangle$ and the final state is $|+2\rangle$.

We note that

V(+2,-2) = 0

since all the transitions are forbidden.





(d) V(-2,-2)

The initial state is $|-2\rangle$ and the final state is $|-2\rangle$.



Fig.9 The transitions from $|-2\rangle$ to $|-2\rangle$. The transitions with red and green lines are forbidden.

$$V(-2,-2) = \frac{\langle -2|\hat{V}|-3\rangle\langle -3|\hat{V}|-2\rangle}{E_2^{(0)} - E_3^{(0)}} + \frac{\langle -2|\hat{V}|-1\rangle\langle -1|\hat{V}|-2\rangle}{E_2^{(0)} - E_1^{(0)}}$$
$$= \frac{\frac{1}{4}(p\varepsilon)^2}{-\frac{5\hbar^2}{2I}} + \frac{\frac{1}{4}(p\varepsilon)^2}{\frac{3\hbar^2}{2I}}$$
$$= \frac{p^2\varepsilon^2 I}{15\hbar^2}$$

So that, we get the matrix element (2x2) as

$$\hat{V} = \begin{pmatrix} \frac{p^2 \varepsilon^2 I}{15\hbar^2} & 0\\ 0 & \frac{p^2 \varepsilon^2 I}{15\hbar^2} \end{pmatrix} = \frac{p^2 \varepsilon^2 I}{15\hbar^2} \begin{pmatrix} 1 & 0\\ 0 & 1 \end{pmatrix}$$

or

$$\hat{V}|+2\rangle = \frac{p^2 \varepsilon^2 I}{15\hbar^2}|+2\rangle$$

and

$$\hat{V}|-2\rangle = \frac{p^2 \varepsilon^2 I}{15\hbar^2}|-2\rangle$$

where

$$E_2^{(0)} = \frac{4\hbar^2}{2I} = \frac{2\hbar^2}{I}$$

Energy eigenvalue

Eigenstate

$$\frac{2\hbar^2}{I} + \frac{p^2 \varepsilon^2 I}{15\hbar^2} \qquad \left| +2 \right\rangle$$

$$\frac{2\hbar^2}{I} + \frac{p^2 \varepsilon^2 I}{15\hbar^2} \qquad |-2\rangle]$$

The new states $(|\pm 2\rangle$ are still degenerate with the same energy shifted from the unperturbed Hamiltonian.

5. The energy eigenstate for the degenerate state; $|\pm n\rangle$ (*n* =2, 3, 4,...)

We use the same discussion for $|\pm 2\rangle$. We use n instead of 2.

$$V(+n,+n) = \frac{\langle +n|\hat{V}|+n+1\rangle\langle +n+1|\hat{V}|+n\rangle}{E_n^{(0)} - E_{n+1}^{(0)}} + \frac{\langle +n|\hat{V}|+n-1\rangle\langle +n-1|\hat{V}|+n\rangle}{E_n^{(0)} - E_{n-1}^{(0)}}$$
$$= \frac{\frac{1}{4}(p\varepsilon)^2}{-\frac{\hbar^2}{2I}(2n+1)} + \frac{\frac{1}{4}(p\varepsilon)^2}{\frac{\hbar^2}{2I}(2n-1)}$$
$$= \frac{p^2\varepsilon^2 I}{\hbar^2} \frac{1}{4n^2 - 1}$$
$$\langle -n|\hat{V}|+n+1\rangle\langle +n+1|\hat{V}|-n\rangle - \langle -n|\hat{V}|-n+1\rangle\langle -n+1|\hat{V}|-n\rangle$$

$$V(-n,-n) = \frac{\langle -n|V|+n+1\rangle\langle +n+1|V|-n\rangle}{E_n^{(0)} - E_{n+1}^{(0)}} + \frac{\langle -n|V|-n+1\rangle\langle -n+1|V|-n\rangle}{E_n^{(0)} - E_{n-1}^{(0)}}$$
$$= \frac{\frac{1}{4}(p\varepsilon)^2}{-\frac{\hbar^2}{2I}(2n+1)} + \frac{\frac{1}{4}(p\varepsilon)^2}{\frac{\hbar^2}{2I}(2n-1)}$$
$$= So that, we get the matrix element (2x2) as or and where Energy eigenvalue$$

Note that the non-diagonal matric elements are zero from the selection rule.

So that, we get the matrix element (2x2) as

$$\hat{V} = \frac{1}{4n^2 - 1} \frac{p^2 \varepsilon^2 I}{\hbar^2} \begin{pmatrix} 1 & 0\\ 0 & 1 \end{pmatrix}$$

or

$$\hat{V}|+n\rangle = \frac{p^2 \varepsilon^2 I}{\hbar^2} \frac{1}{(4n^2 - 1)} |+n\rangle$$

and

$$\hat{V}|-n\rangle = \frac{p^2 \varepsilon^2 I}{\hbar^2} \frac{1}{(4n^2 - 1)} |-n\rangle$$

where

$$E_{\pm n}^{(0)} = \frac{\hbar^2}{2I} n^2$$

Energy eigenvalue

Eigenstate



The new states ($|\pm n\rangle$ (n=2, 3, 4,...) are still degenerate with the same energy shifted from the unperturbed Hamiltonian.

6. Summary

We get the eigenvalues and eigenkets for the 2D rotor in the presence of electric field. We apply the perturbation theory (both for non-degenerate case and



Fig.10 No energy shift occurs in the first order perturbation. The energy shifts occur in the second-order to the perturbation, $\alpha = \frac{\hbar^2}{2I}$. $\beta = \frac{p^2 \varepsilon^2 I}{\hbar^2}$

Energy eigenvalue

Energy eigenstate

$$4\alpha + \frac{1}{15}\beta = \frac{2\hbar^2}{I} + \frac{p^2\varepsilon^2 I}{15\hbar^2} \qquad \qquad \left|\psi_{\pm 2}^{(0)}\right\rangle = \left|\pm 2\right\rangle \text{ (doubly degenerate)}$$

$$4\alpha + \frac{5}{6}\beta = \frac{\hbar^2}{2I} + \frac{5p^2\varepsilon^2 I}{6\hbar^2} \qquad |\psi_{\pm 1,s}^{(0)}\rangle = \frac{1}{\sqrt{2}}[|+1\rangle + |-1\rangle]$$

$$\alpha - \frac{1}{6}\beta = \frac{\hbar^2}{2I} - \frac{p^2\varepsilon^2 I}{6\hbar^2} \qquad |\psi_{\pm 1,a}^{(0)}\rangle = \frac{1}{\sqrt{2}}[|+1\rangle - |-1\rangle]$$

$$-\beta = -\frac{p^2\varepsilon^2 I}{\hbar^2} \qquad |\psi_0^{(1)}\rangle = \frac{1}{\sqrt{2}}[|+1\rangle - |-1\rangle]$$

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