J.J. Sakurai and Jim Napolitano, Modern Quantum Mechanics, 3rd edition (Cambridge, 2021).
Problems and Solutions of Chapter 5
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((5-1))

5.1 A simple harmonic oscillator (in one dimension) is subjected to a perturbation

$$H_1 = bx$$

where b is a real constant.

a. Calculate the energy shift of the ground state to *lowest nonvanishing order*.

b. Solve this problem *exactly* and compare with your result obtained in (a).

((**Solution**))

$$\hat{H}_1 = b\hat{x}$$

Ground state is not degenerate.

$$\hat{\pi}|0\rangle = |0\rangle, \qquad \text{(even parity)}$$

$$E_0 = E_0^{(0)} + E_0^{(1)} + E_0^{(2)} + ...$$

where

$$E_n^{(0)} = (n+\frac{1}{2})\hbar\omega$$

$$E_0^{(1)} = \langle 0|\hat{H}_1|0\rangle = 0$$

since $\hat{\pi}|0\rangle = |0\rangle$ (even parity) and $\hat{H}_1 = b\hat{x}$ is odd-parity operator.

$$E_0^{(2)} = \sum_{n\neq 0} \frac{\left|\langle n|\hat{H}_1|0\rangle\right|^2}{E_0^{(0)} - E_n^{(0)}} = \frac{\left|\langle 1|\hat{H}_1|0\rangle\right|^2}{E_0^{(0)} - E_1^{(0)}} = \frac{b^2 \dfrac{\hbar}{2m\omega}}{-\hbar\omega} = -\frac{b^2}{2m^2}$$

where

$$\langle n'|\hat{x}|n\rangle = \sqrt{\frac{\hbar}{2m\omega}}(\sqrt{n+1}\delta_{n',n+1} + \sqrt{n}\delta_{n',n-1})$$

$$\langle 1|\hat{H}_1|0\rangle = b\langle 1|\hat{x}|0\rangle = b\sqrt{\frac{\hbar}{2m\omega}}$$

Then we have

$$E_0 = \frac{1}{2}\hbar\omega_0 - \frac{b^2}{2m^2}$$

(b)

$$\begin{aligned}\hat{H} &= \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 + b\hat{x} \\ &= \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2(\hat{x} + \frac{b}{m\omega^2}\hat{1})^2 - \frac{b^2}{2m\omega^2}\hat{1}\end{aligned}$$

When

$$\hat{x}' = \hat{x} + \frac{b}{m\omega^2}\hat{1}$$

$$\begin{aligned}\hat{H} &= \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 + b\hat{x} \\ &= \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}'^2 - \frac{b^2}{2m\omega^2}\hat{1}\end{aligned}$$

Thus, the Hamiltonian consists of the simple harmonics and the additional constant value

$$E_n = \hbar\omega(n + \frac{1}{2}) - \frac{b^2}{2m\omega^2}$$

((5-2))

5.2 A one-dimensional potential well has infinite walls at $x = 0$ and $x = L$. The bottom of the well is *not* flat, but rather increases linearly from 0 at $x = 0$ to V at $x = L$. Find the first-order shift in the energy levels as a function of principal quantum number n.

((**Solution**))
The wave function of the unperturbed Hamiltonian is

$$\psi_n^{(0)} = \sqrt{\frac{2}{L}}\sin(k_n x)$$

with

$$k_n = \frac{2\pi n}{L} \qquad (\text{n} = 1, 2, 3, 4, \ \ )$$

The perturbed Hamiltonian is given by

$$\hat{H}' = \frac{V}{L}\hat{x}$$

We use the theory of time independent perturbation with nondegenerate states.

$$\begin{aligned}\left\langle \psi_n^{(0)} \middle| \hat{H}' \middle| \psi_n^{(0)} \right\rangle &= \int dx \psi_n^{(0)}(x)^* \frac{V}{L} x \psi_n^{(0)}(x) \\ &= \frac{2}{L}\frac{V}{L}\int_0^L dx x \sin^2(k_n x) \\ &= \frac{2V}{L^2}\frac{L^2 8n^2\pi^2}{32n^2\pi^2} \\ &= \frac{V}{2}\end{aligned}$$

which is the first-order energy shift, independent of n.

((5-3))

5.3 A particle of mass m moves in a potential well $V(x) = m\omega^2 x^2/2$. Treating relativistic effects to order $\beta^2 = (p/mc)^2$, find the ground-state energy shift.

((Solution))

$$\hat{H} = \hat{H}_0 + \hat{H}_1 = \frac{1}{2m}\hat{p}^2 + \frac{1}{2}m\omega^2\hat{x}^2 - \frac{1}{8m^3c^2}\hat{p}^4$$

where

$$\begin{aligned} c\sqrt{m^2c^2 + p^2} &= mc^2\sqrt{1 + \frac{p^2}{m^2c^2}} \\ &= mc^2(1 + \frac{1}{2}\frac{p^2}{m^2c^2} - \frac{1}{8}\frac{p^4}{m^4c^4} + \ldots) \\ &= mc^2 + \frac{p^2}{2m} - \frac{1}{8}\frac{p^4}{m^3c^2} \end{aligned}$$

We know the eigen values and eigenstates for the unperturbed simple harmonics.

$$H_0|n\rangle = (n + \frac{1}{2})\hbar\omega|n\rangle$$

Each eigenstate is non-degenerate. We now consider the effect of the perturbed Hamiltonian on the energy level of the original simple harmonics.

$$\langle n|H'|n\rangle = -\frac{1}{8m^3c^2}\langle n|\hat{p}^4|n\rangle$$

In order to calculate the matrix element, we use

$$\hat{p} = \frac{m\omega}{i\sqrt{2}\beta}(\hat{a} - \hat{a}^+)$$

where

$$\beta = \sqrt{\frac{m\omega}{\hbar}}$$

So that, we have

$$\langle n|H'|n\rangle = -\frac{1}{8m^3c^2}\left(\frac{m\omega}{i\sqrt{2}\beta}\right)^4 \langle n|(\hat{a}-\hat{a}^+)^4|n\rangle$$

We define

$$\begin{aligned}|\chi\rangle &= (\hat{a}-\hat{a}^+)^2|n\rangle \\ &= (\hat{a}\hat{a}+\hat{a}^+\hat{a}^+ - 2\hat{n}-1)|n\rangle \\ &= \sqrt{n(n-1)}|n-2\rangle + \sqrt{(n+1)(n+2)}|n-2\rangle - (2n+1)|n\rangle\end{aligned}$$

where

$$\hat{a}|n\rangle = \sqrt{n}|n-1\rangle, \qquad \hat{a}^+|n\rangle = \sqrt{n+1}|n+1\rangle$$

The bra vector

$$\begin{aligned}\langle\chi| &= \langle n|(\hat{a}-\hat{a}^+)^2 \\ &= \langle n-2|\sqrt{n(n-1)} + \langle n-2|\sqrt{(n+1)(n+2)} - (2n+1)\langle n|\end{aligned}$$

Thus, we get

$$\begin{aligned}\langle\chi|\chi\rangle &= n(n-1)+(n+1)(n+2)+(2n+1)^2 \\ &= \frac{1}{6}(n^2+n+\frac{1}{2})\end{aligned}$$

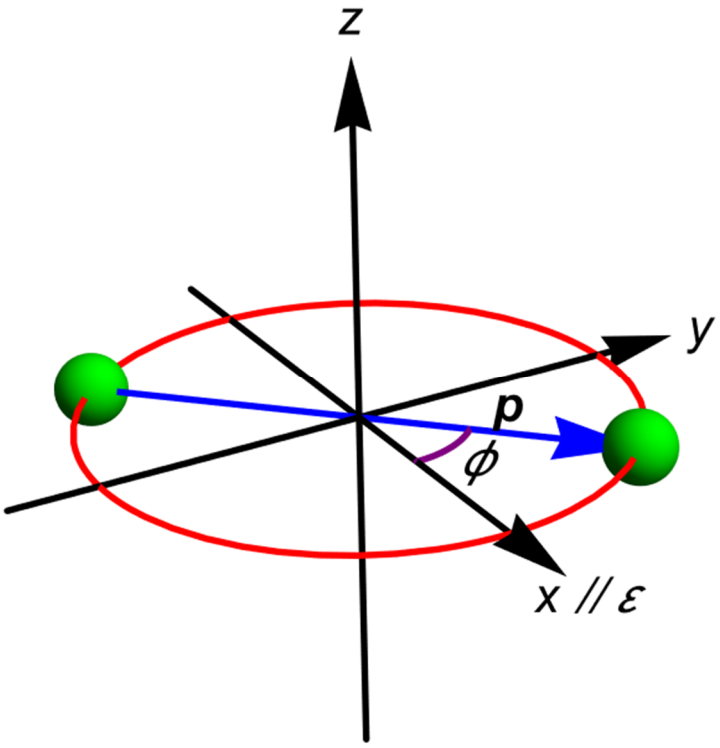
In summary, we get

$$\begin{aligned}E_n &= E_n^{(0)} + E_n^{(1)} + ... \\ &= (n+\frac{1}{2})\hbar\omega - \frac{\hbar^2\omega^2}{192mc^2}(n^2+n+\frac{1}{2}) \\ &= [n+\frac{1}{2} - \frac{1}{192}\frac{\hbar\omega}{mc^2}(n^2+n+\frac{1}{2})]\hbar\omega\end{aligned}$$

((5-4))

((5-4))

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

$$
\begin{aligned}
H &= H_0 + V \\
&= \frac{L_z^{\,2}}{2I} - \mathbf{p}\cdot\boldsymbol{\varepsilon} \\
&= \frac{L_z^{\,2}}{2I} - p\varepsilon\cos\phi \\
&= -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi^2} - p\varepsilon\cos\phi
\end{aligned}
$$

with

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

and

$$V = -p\varepsilon\cos\phi, \qquad \text{(perturbation)}$$

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

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

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

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

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

$$\begin{aligned}
\left\langle n\left|\hat{V}\right|m\right\rangle &= \int_0^{2\pi} d\phi \psi_n^{*}(\phi)(-p\varepsilon\cos\phi)\psi_m(\phi) \\
&= \frac{1}{2\pi}(-p\varepsilon)\frac{1}{2}\int_0^{2\pi} d\phi e^{-in\theta}(e^{i\phi} + e^{-i\phi})e^{im\theta} \\
&= \frac{1}{4\pi}(-p\varepsilon)\int_0^{2\pi} d\phi[e^{i(m-n+)\phi} + e^{i(m-n-1)\phi}] \\
&= -\frac{1}{2} p\varepsilon(\delta_{m,n+1} + \delta_{m,n-1}) \\
&= -\frac{1}{2} p\varepsilon\delta_{m,n\pm 1}
\end{aligned}$$

So that, we have the selection rule for the transition

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

3. $n = 0$ (nondegenerate)

The ground state is non-degenerate.

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

The energy shit for the first order is

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

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

$$\begin{aligned} E_0^{(2)} &= \sum_{n \neq 0} \frac{\left| \langle n | \hat{V} | 0 \rangle \right|^2}{E_0^{(0)} - E_n^{(0)}} \\ &= \frac{\left| \langle +1 | \hat{V} | 0 \rangle \right|^2}{E_0^{(0)} - E_1^{(0)}} + \frac{\left| \langle -1 | \hat{V} | 0 \rangle \right|^2}{E_0^{(0)} - E_{-1}^{(0)}} \\ &= -\frac{p^2 \varepsilon^2 I}{\hbar^2} \end{aligned}$$

or

$$\begin{aligned} E_0 &= E_0^{(0)} + E_1^{(0)} + E_2^{(0)} + ... \\ &= -\frac{p^2 \varepsilon^2 I}{\hbar^2} \end{aligned}$$

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

$$\begin{aligned} |\psi_0^{(1)}\rangle &= |+1\rangle \frac{\langle +1 | \hat{V} | 0 \rangle}{E_0^{(0)} - E_1^{(0)}} + |-1\rangle \frac{\langle -1 | \hat{V} | 0 \rangle}{E_0^{(0)} - E_1^{(0)}} \\ &= |+1\rangle \frac{-\frac{1}{2} p\varepsilon}{-\frac{\hbar^2}{2I}} + |-1\rangle \frac{-\frac{1}{2} p\varepsilon}{-\frac{\hbar^2}{2I}} \\ &= \frac{p\varepsilon I}{\hbar^2} [|+1\rangle + |-1\rangle] \end{aligned}$$

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

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 $|-n\rangle$

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

((**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 $|+1\rangle$.

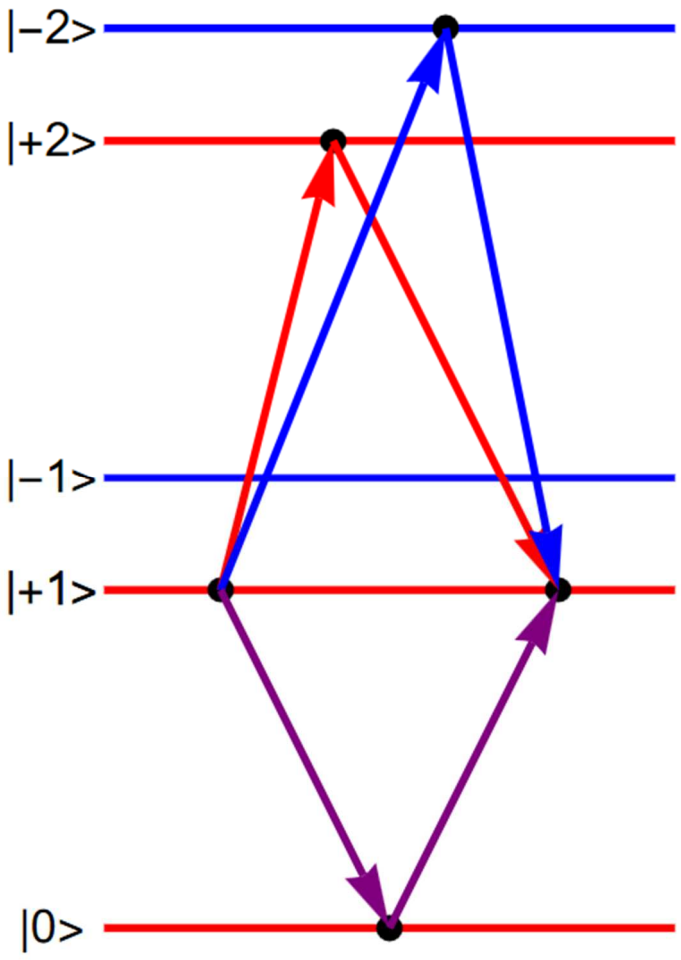


Fig.2 The matrix element . $V(+1,+1)$ Blue line (not allowed transition from the selection rule). The selection rule: $\Delta n = \pm 1$.

We get

$$V(+1,+1) = \frac{\langle +1|\hat{V}|+2\rangle\langle +2|\hat{V}|+1\rangle}{E_1^{(0)} - E_2^{(0)}} + \frac{\langle +1|\hat{V}|0\rangle\langle 0|\hat{V}|+1\rangle}{E_1^{(0)} - E_0^{(0)}}$$

$$= \frac{\frac{1}{4}(p\varepsilon)^2}{-\frac{3\hbar^2}{2I}} + \frac{\frac{1}{4}(p\varepsilon)^2}{\frac{\hbar^2}{2I}}$$

$$= \frac{p^2\varepsilon^2 I}{3\hbar^2}$$

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

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

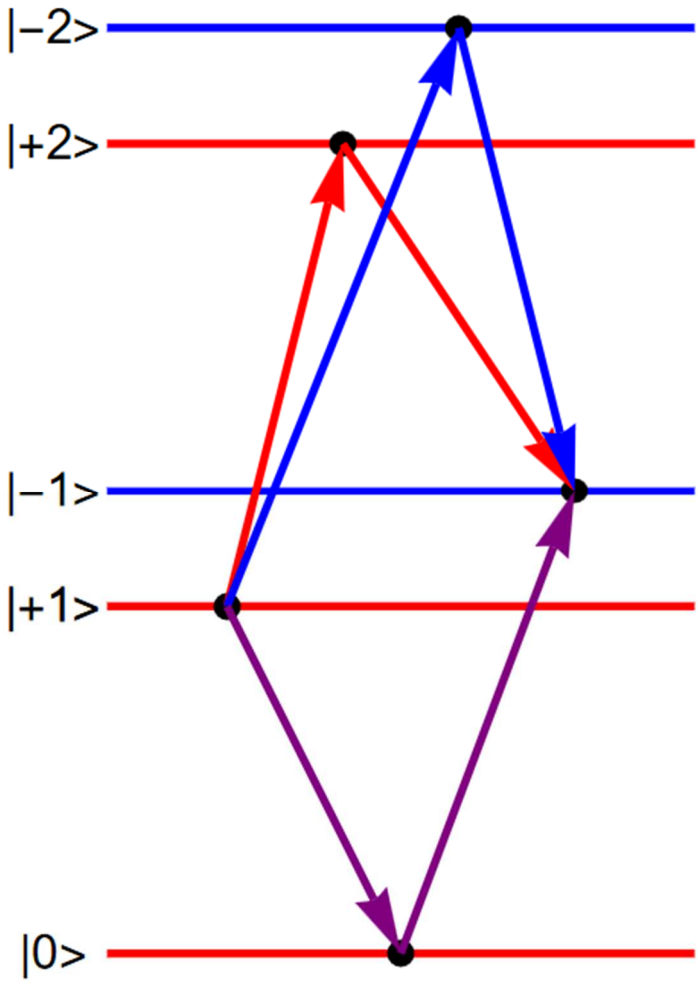


Fig.3 The matrix element $V(-1,+1)$. Red and blue lines (not allowed transition).

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

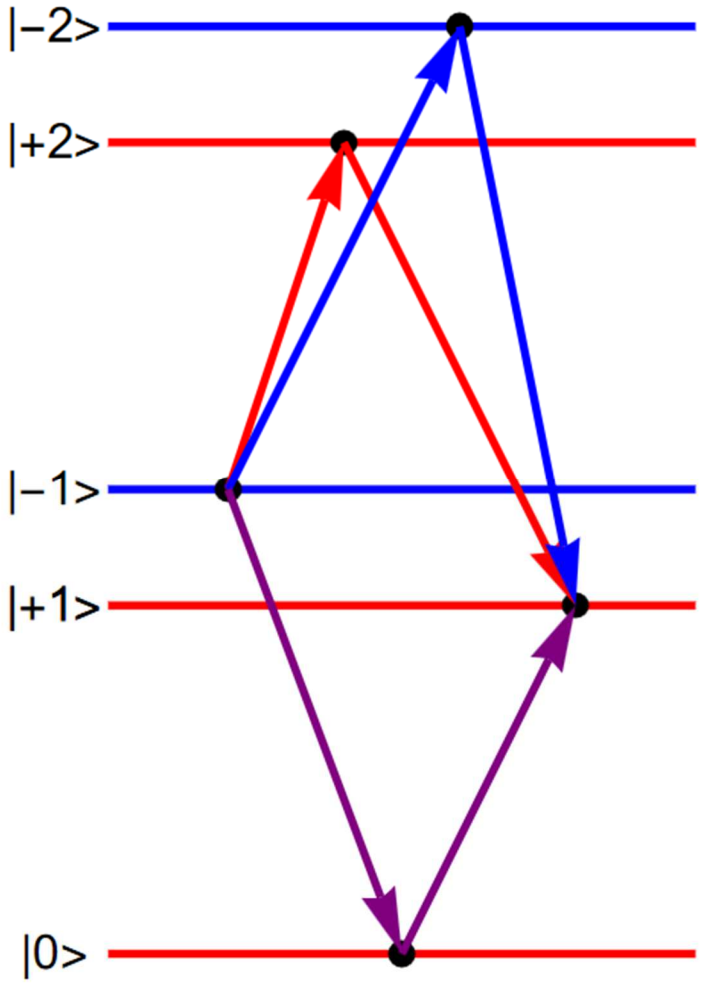


Fig.4 The matrix element $V(+1,-1)$. Blue and red lines (not allowed transition)

We get

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

$$= \frac{\left(\frac{p\varepsilon}{2}\right)^2}{\frac{\hbar^2}{2I}}$$

$$= \frac{p^2\varepsilon^2 I}{2\hbar^2}$$

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

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

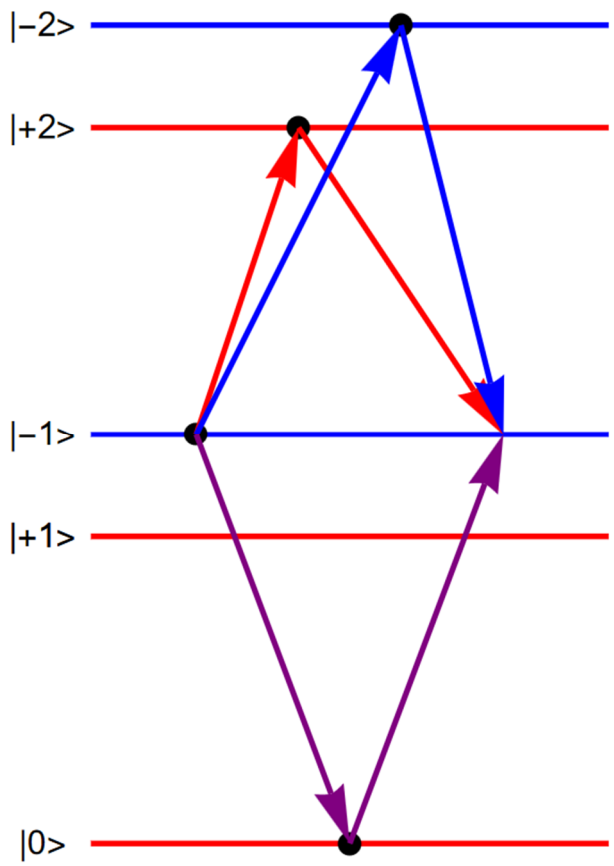


Fig.5 The matrix element $V(-1,-1)$. Red line (not allowed transition)

We get

$$V(-1,-1)=\frac{\langle -1|\hat{V}|-2\rangle\langle -2|\hat{V}|-1\rangle}{E_1^{(0)}-E_2^{(0)}}+\frac{\langle -1|\hat{V}|0\rangle\langle 0|\hat{V}|-1\rangle}{E_1^{(0)}-E_0^{(0)}}$$

$$=\frac{\frac{1}{4}p^2\varepsilon^2}{-\frac{3\hbar^2}{2I}}+\frac{\frac{1}{4}p^2\varepsilon^2}{\frac{\hbar^2}{2I}}$$

$$=\frac{p^2\varepsilon^2 I}{3\hbar^2}$$

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

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

and

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

We note that

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

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

Thus we have the energy eigenvalue and eigenkets as follows

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

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

The wavefunctions are given by

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

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

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

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

((**First order**))

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

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

So that, there is no first-order contribution.

((**Second order**))

Next, we calculate the second-order contribution.

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

(a) $V(+2,+2)$

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

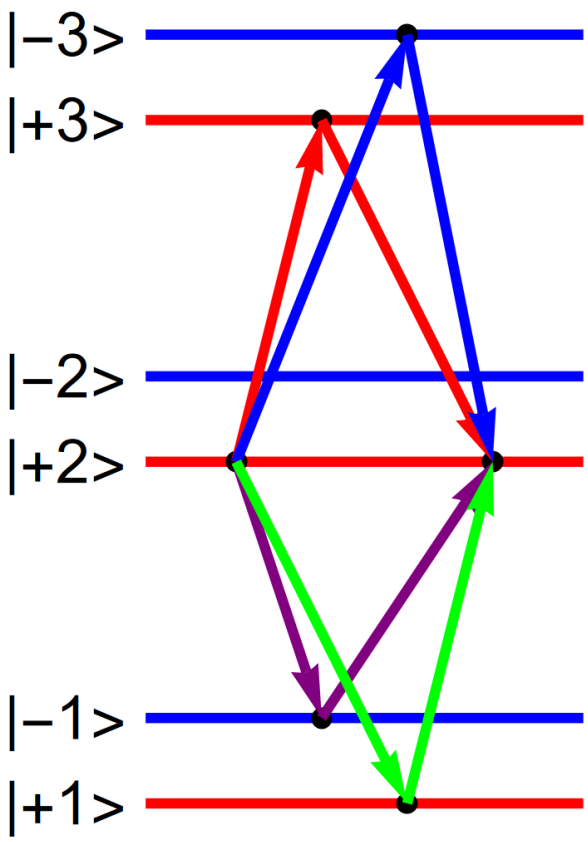


Fig.6 The transition between $|+2\rangle$ to $|+2\rangle$. The blue line and the purple line are not allowed.

We get

$$V(+2,+2)=\frac{\langle+2|\hat{V}|+3\rangle\langle+3|\hat{V}|+2\rangle}{E_2^{(0)}-E_3^{(0)}}+\frac{\langle+2|\hat{V}|+1\rangle\langle+1|\hat{V}|+2\rangle}{E_2^{(0)}-E_1^{(0)}}$$

$$=\frac{\frac{1}{4}(p\varepsilon)^2}{-\frac{5\hbar^2}{2I}}+\frac{\frac{1}{4}(p\varepsilon)^2}{\frac{3\hbar^2}{2I}}$$

$$=\frac{p^2\varepsilon^2 I}{15\hbar^2}$$

(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.

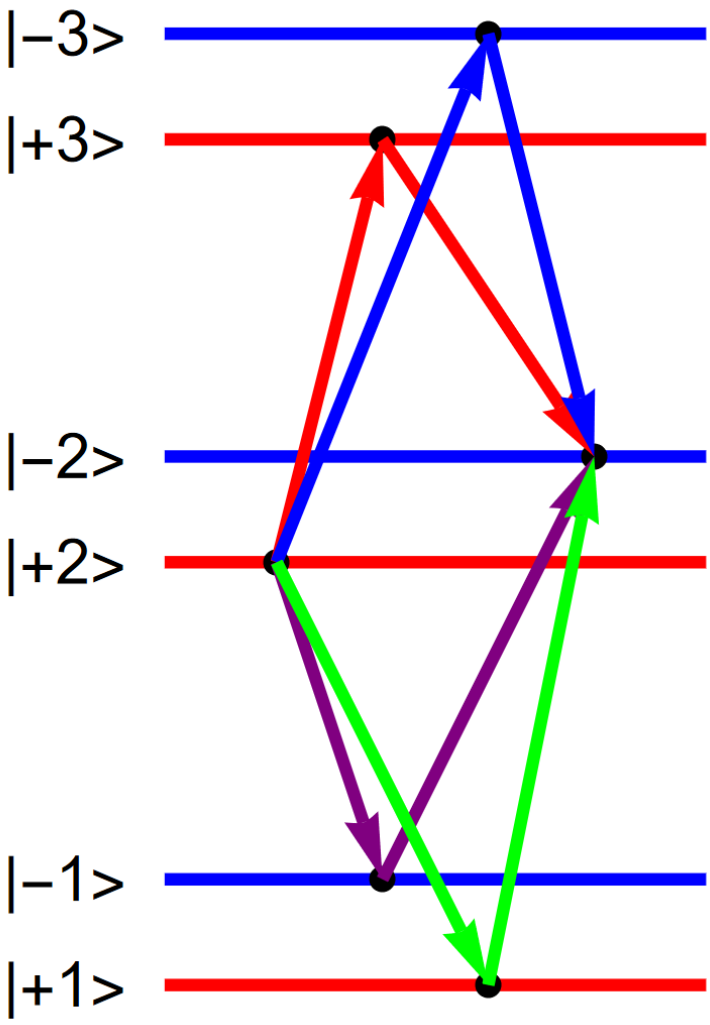


Fig.7 All transitions from $|+2\rangle$ to $|-2\rangle$ are forbidden.

(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.

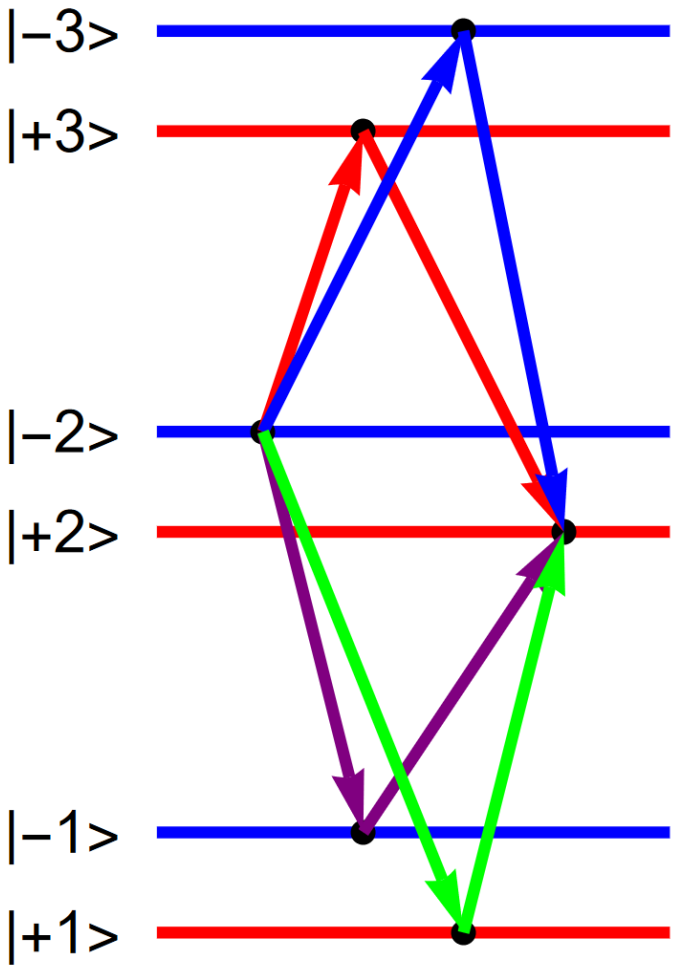


Fig.8 All the transitions from $|-2\rangle$ to $|+2\rangle$ are forbidden.

(d) $V(-2,-2)$

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

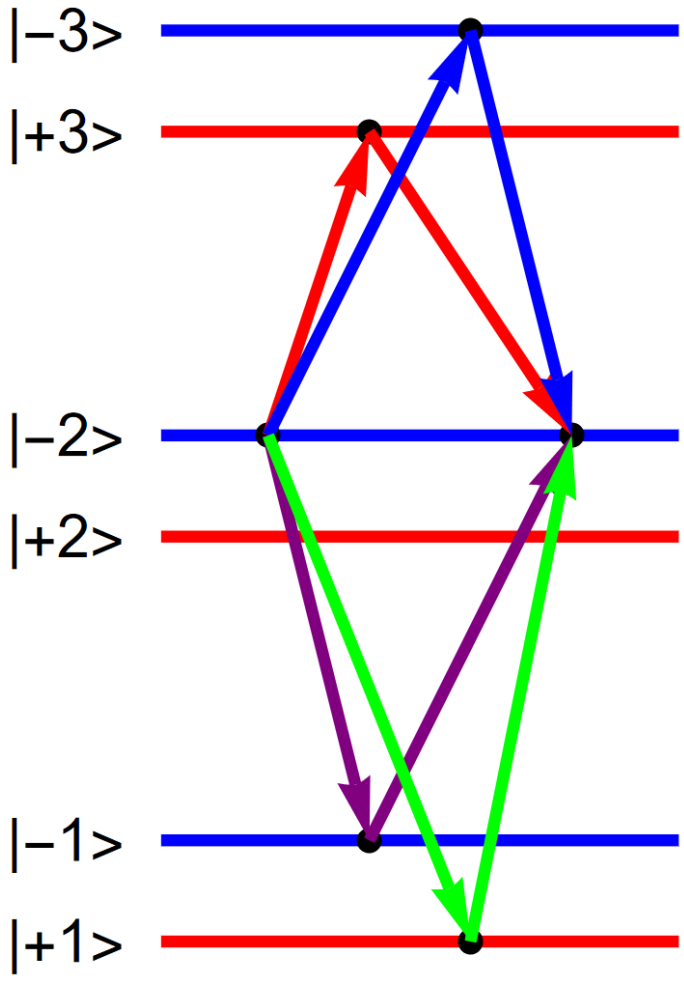


Fig.9 The transitions from $|-2\rangle$ to $|-2\rangle$. The transitions with red and green lines are forbidden.

We get

$$V(-2,-2)=\frac{\langle -2|\hat{V}|-3\rangle\langle -3|\hat{V}|-2\rangle}{E_2^{(0)}-E_3^{(0)}}+\frac{\langle -2|\hat{V}|-1\rangle\langle -1|\hat{V}|-2\rangle}{E_2^{(0)}-E_1^{(0)}}$$

$$=\frac{\frac{1}{4}(p\varepsilon)^2}{-\frac{5\hbar^2}{2I}}+\frac{\frac{1}{4}(p\varepsilon)^2}{\frac{3\hbar^2}{2I}}$$

$$=\frac{p^2\varepsilon^2 I}{15\hbar^2}$$

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

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

and

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

where

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

Energy eigenvalue	Eigenstate
$\frac{2\hbar^2}{I} + \frac{p^2\varepsilon^2 I}{15\hbar^2}$	$\left\|+2\right\rangle$
$\frac{2\hbar^2}{I} + \frac{p^2\varepsilon^2 I}{15\hbar^2}$	$\left\|-2\right\rangle]$

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

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

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

$$V(+n,+n)=\frac{\langle +n|\hat{V}|+n+1\rangle\langle +n+1|\hat{V}|+n\rangle}{E_n^{(0)}-E_{n+1}^{(0)}}+\frac{\langle +n|\hat{V}|+n-1\rangle\langle +n-1|\hat{V}|+n\rangle}{E_n^{(0)}-E_{n-1}^{(0)}}$$

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

$$=\frac{p^2\varepsilon^2 I}{\hbar^2}\frac{1}{4n^2-1}$$

$$V(-n,-n)=\frac{\langle -n|\hat{V}|+n+1\rangle\langle +n+1|\hat{V}|-n\rangle}{E_n^{(0)}-E_{n+1}^{(0)}}+\frac{\langle -n|\hat{V}|-n+1\rangle\langle -n+1|\hat{V}|-n\rangle}{E_n^{(0)}-E_{n-1}^{(0)}}$$

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

$$=\textit{So that, we get the matrix element } (2x2) \textit{ as or and where Energy eigenvalue}$$

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
$\frac{\hbar^2}{2I}n^2+\frac{p^2\varepsilon^2 I}{\hbar^2}\frac{1}{4n^2-1}=\alpha n^2+\frac{\beta}{4n^2-1}$	$\lvert+n\rangle$
$\frac{\hbar^2}{2I}n^2+\frac{p^2\varepsilon^2 I}{\hbar^2}\frac{1}{4n^2-1}=\alpha n^2+\frac{\beta}{4n^2-1}$	$\lvert-n\rangle]$

The new states ($\lvert\pm n\rangle$ (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

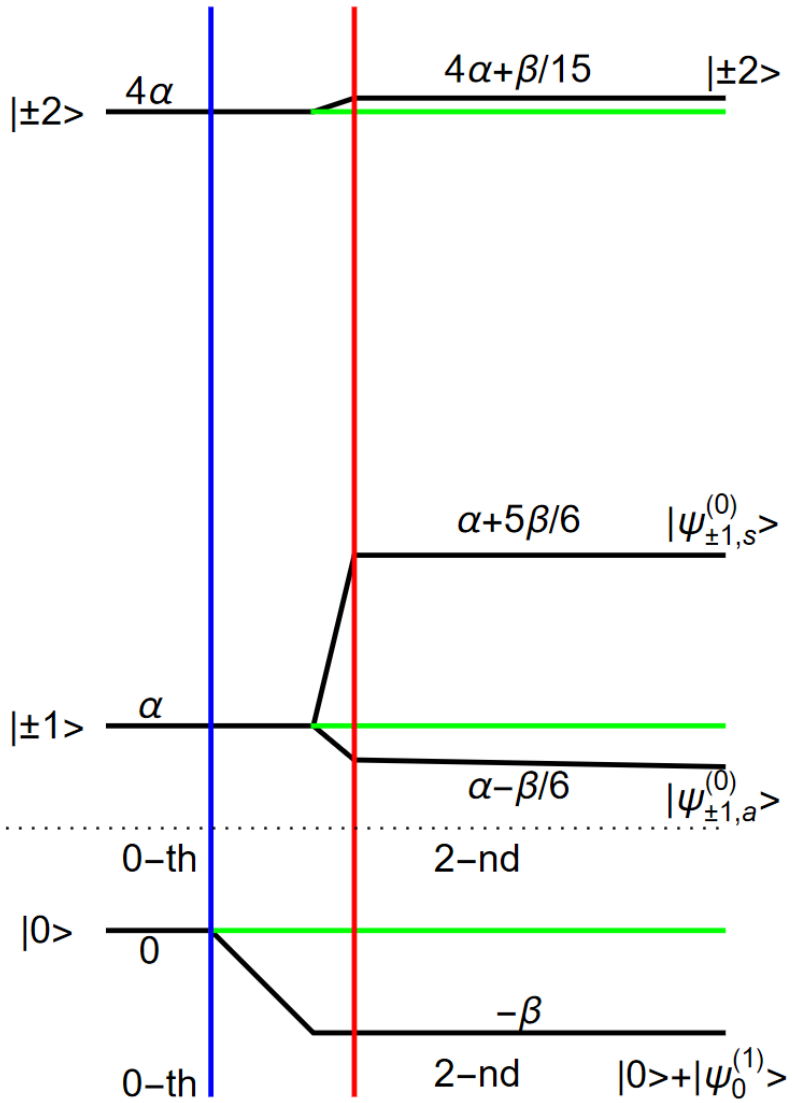


Fig.10 No energy shift occurs in the first order perturbation. The energy shifts occur in the second-order to the perturbation, $\alpha = \frac{\hbar^2}{2I}$. $\beta = \frac{p^2\varepsilon^2 I}{\hbar^2}$

Energy eigenvalue	Energy eigenstate
$4\alpha + \frac{1}{15}\beta = \frac{2\hbar^2}{I} + \frac{p^2\varepsilon^2 I}{15\hbar^2}$	$\left\|\psi^{(0)}_{\pm 2}\right\rangle = \left\|\pm 2\right\rangle$ (doubly degenerate)

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

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

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

((5-5))

5.5 In nondegenerate time-independent perturbation theory, what is the probability of finding in a perturbed energy eigenstate ($|k\rangle$) the corresponding unperturbed eigenstate ($|k^{(0)}\rangle$)? Solve this up to terms of order λ^2.

((**Solution**))

$$|\psi_n\rangle = |\psi_n{}^{(0)}\rangle + \lambda|\psi_n{}^{(1)}\rangle + \lambda^2|\psi_n{}^{(2)}\rangle + \lambda^3|\psi_n{}^{(3)}\rangle + \ldots.$$

Here we need to specify how the states $|\psi_n{}^{(0)}\rangle$ and $|\psi_n\rangle$ overlap. Since $|\psi_n\rangle$ is considered not to be very different from $|\psi_n{}^{(0)}\rangle$, we have

$$\langle\psi_n{}^{(0)}|\psi_n\rangle \approx 1.$$

It is convenient to depart from the usual normalization condition that

$$\langle\psi_n|\psi_n\rangle = 1.$$

Rather we set

$$\langle\psi_n{}^{(0)}|\psi_n\rangle = 1 \qquad \text{(this is the definition we use here)}$$

even for $\lambda \neq 0$. Then we get

$$\langle\psi_n{}^{(0)}|\psi_n\rangle = \langle\psi_n{}^{(0)}|\psi_n{}^{(0)}\rangle + \lambda\langle\psi_n{}^{(0)}|\psi_n{}^{(1)}\rangle + \lambda^2\langle\psi_n{}^{(0)}|\psi_n{}^{(2)}\rangle + \lambda^3\langle\psi_n{}^{(0)}|\psi_n{}^{(3)}\rangle + \ldots.,$$

with

$$\langle\psi_n{}^{(0)}|\psi_n{}^{(0)}\rangle = 1, \qquad \langle\psi_n{}^{(0)}|\psi_n{}^{(1)}\rangle = 0, \qquad \langle\psi_n{}^{(0)}|\psi_n{}^{(2)}\rangle = 0, \ldots.$$

In other words, $|\psi_n{}^{(k)}\rangle$ (k = 1, 2, 3, 4, ...) is orthogonal to $|\psi_n{}^{(0)}\rangle$

In such conditions, we have

$$\begin{aligned}\langle\psi_n|\psi_n\rangle &= (\langle\psi_n^{(0)}| + \lambda\langle\psi_n^{(1)}| + \lambda^2\langle\psi_n^{(2)}| + \lambda^3\langle\psi_n^{(3)}| + ...) \\ &\times(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \lambda^3|\psi_n^{(3)}\rangle + ...) \\ &= \langle\psi_n^{(0)}|\psi_n^{(0)}\rangle + \lambda[\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle + \langle\psi_n^{(0)}|\psi_n^{(1)}\rangle^*] \\ &+ \lambda^2[\langle\psi_n^{(0)}|\psi_n^{(2)}\rangle + \langle\psi_n^{(2)}|\psi_n^{(0)}\rangle^* + \langle\psi_n^{(1)}|\psi_n^{(1)}\rangle] + ... \\ &= 1 + \lambda^2\langle\psi_n^{(1)}|\psi_n^{(1)}\rangle + O(\lambda^2) \\ &= 1 + \lambda^2\sum_{k\neq n}\frac{|\langle\psi_k^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle|^2}{(E_n^{(0)} - E_k^{(0)})^2} + O(\lambda^2)\end{aligned}$$

since

$$|\psi_n^{(1)}\rangle = \sum_{k\neq n}|\psi_k^{(0)}\rangle\langle\psi_k^{(0)}|\psi_n^{(1)}\rangle = \sum_{k\neq n}|\psi_k^{(0)}\rangle\frac{\langle\psi_k^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}}$$

In other words, $|\psi_n\rangle$ is, to the first order, normalized to 1, with the first correction occurring in the second order.

Here we define $|\psi_n\rangle_N$ which satisfies the usual normalization.

$$|\psi_n\rangle_N = \sqrt{Z_n}|\psi_n\rangle$$

Z_n is called as the wave function normalization constant.

$${}_N\langle\psi_n|\psi_n\rangle_N = 1 = Z_n\langle\psi_n|\psi_n\rangle$$

or

$$Z_n = \frac{1}{\langle\psi_n|\psi_n\rangle} = 1 - \lambda^2\sum_{k\neq n}\frac{|\langle\psi_k^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle|^2}{(E_n^{(0)} - E_k^{(0)})^2} + O(\lambda^2)$$

Then we have

$$\langle\psi_n^{(0)}|\psi_n\rangle_N = \sqrt{Z_n}\langle\psi_n^{(0)}|\psi_n\rangle = \sqrt{Z_n}$$

P is the probability of observing $|\psi_n\rangle_N$ in the unperturbed state $|\psi_n^{(0)}\rangle$,

$$\left|\left\langle \psi_n{}^{(0)} \middle| \psi_n \right\rangle_N\right|^2 = Z_n = P = 1 - \lambda^2 \sum_{k \neq n} \frac{\left|\left\langle \psi_k{}^{(0)} \middle| \hat{H}_1 \middle| \psi_n{}^{(0)} \right\rangle\right|^2}{(E_n{}^{(0)} - E_k{}^{(0)})^2}.$$

The second term is to be understood as the probability for leakage to state other than $\left|\psi_n{}^{(0)}\right\rangle$. Note that Z_n is less than 1.

Note that the energy E_n is given by

$$E_n = E_n{}^{(0)} + \lambda \left\langle \psi_n{}^{(0)} \middle| \hat{H}_1 \middle| \psi_n{}^{(0)} \right\rangle + \lambda^2 \sum_{k \neq n} \frac{\left|\left\langle \psi_k{}^{(0)} \middle| \hat{H}_1 \middle| \psi_n{}^{(0)} \right\rangle\right|^2}{E_n{}^{(0)} - E_k{}^{(0)}}.$$

The derivative of E_n with respect to $E_n{}^{(0)}$ is given by

$$\frac{\partial E_n}{\partial E_n{}^{(0)}} = 1 - \lambda^2 \sum_{k \neq n} \frac{\left|\left\langle \psi_k{}^{(0)} \middle| \hat{H}_1 \middle| \psi_n{}^{(0)} \right\rangle\right|^2}{(E_n{}^{(0)} - E_k{}^{(0)})^2} = Z_n,$$

where the matrix element of $\hat{H}_1$ is assumed to be independent of $E_n{}^{(0)}$.

((**5-6**))

5.6 Consider a particle in a two-dimensional potential

$$V_0 = \begin{cases} 0 & \text{for } 0 \le x \le L,\ 0 \le y \le L \\ \infty & \text{otherwise.} \end{cases}$$

Write the energy eigenfunctions for the ground and first excited states. We now add a time-independent perturbation of the form

$$V_1 = \begin{cases} \lambda xy & \text{for } 0 \le x \le L,\ 0 \le y \le L \\ 0 & \text{otherwise.} \end{cases}$$

Obtain the zeroth-order energy eigenfunctions and the first-order energy shifts for the ground and first excited states.

((**Solution**))

Schrödinger equation of particle in a 2D well potential,

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\psi(x,y) = E(k_x,k_y)\psi(x,y)$$

where the energy eigenvalue

$$E(k_x,k_y) = \frac{\hbar^2}{2m}(k_x^2+k_y^2)$$

We us the method of separation variable as

$$\psi(x,y) = X(x)Y(y).$$

Then, we have

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\psi(x,y)+(k_x{}^2+k_y{}^2)\psi(x,y) = 0$$

leading to

$$X''(x)Y(y)+X(x)Y''(y)+(k_x{}^2+k_y{}^2)X(x)Y(y) = 0$$

or

$$\frac{X''(x)}{X(x)}+\frac{Y''(y)}{Y(y)}+({k_x}^2+{k_y}^2)=0$$

From this equation, we get

$$X''(x)=-{k_x}^2X(x),\qquad Y''(y)=-{k_y}^2Y(y)$$

Using the boundary conditions that $X(0)=X(L)=0$, and $Y(0)=Y(L)=0$, we have

$$X(x)=\sqrt{\frac{2}{L}}\sin(k_x x)=\sqrt{\frac{2}{L}}\sin(\frac{\pi n_x x}{L}),\qquad Y(y)=\sqrt{\frac{2}{L}}\sin(k_y y)=\sqrt{\frac{2}{L}}\sin(\frac{\pi n_y y}{L})$$

$$\left\langle x,y\middle|n_x,n_y\right\rangle=\frac{2}{L}\sin(\frac{\pi n_x x}{L})\sin(\frac{\pi n_y y}{L})$$

The energy eigenvalue:

$$E(k_x,k_y)=\frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2(n_x^2+n_y^2)$$

where

$$k_x=\frac{\pi n_x}{L},\qquad k_y=\frac{\pi n_y}{L}$$

The energy levels

(a) The ground state:

$$\left|n_x,n_y\right\rangle=\left|1,1\right\rangle\qquad E_1^{(0)}=E(1,1)=\frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 2\qquad \text{(non-degenerate)}$$

(b) The first excited state:

$$\left|n_x, n_y\right\rangle = \left|1,2\right\rangle, \left|2,1\right\rangle \qquad E_2^{(0)} = E(1,2) = E(2,1) = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 5$$

(degeneracy:2)

(c) The second excited state

$$\left|n_x, n_y\right\rangle = \left|2,2\right\rangle \qquad E_3^{(0)} = E(2,2) = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 8$$

(non-degenerate)

(d) The third excited state

$$\left|n_x, n_y\right\rangle = \left|1,3\right\rangle, \left|3,1\right\rangle \qquad E_3^{(0)} = E(1,3) = E(3,1) = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 10$$

(degeneracy: 2)

The perturbation $V_1 = \lambda xy$

$$\left\langle n_{11}, n_{12}\left|\hat{V}_1\right|n_{21}, n_{22}\right\rangle = \lambda \frac{2}{L}\int_0^L dx x \sin\left(\frac{\pi n_{11} x}{L}\right)\sin\left(\frac{\pi n_{21} x}{L}\right)$$
$$\times \int_0^L dy y \sin\left(\frac{\pi n_{12} y}{L}\right)\sin\left(\frac{\pi n_{22} y}{L}\right)$$

Using the Mathematica, we calculate the matrix element as

$$\left\langle 1,1\left|\hat{V}_1\right|1,1\right\rangle = \frac{1}{4}\lambda L^2$$

$$\left\langle 1,2\left|\hat{V}_1\right|1,2\right\rangle = \left\langle 2,1\left|\hat{V}_1\right|2,1\right\rangle = \frac{1}{4}\lambda L^2$$

$$\left\langle 1,2\left|\hat{V}_1\right|2,1\right\rangle = \left\langle 2,1\left|\hat{V}_1\right|1,2\right\rangle = \frac{256}{81\pi^4}\lambda L^2$$

$$\left\langle 1,2\left|V\right|1,1\right\rangle = \left\langle 2,1\left|V\right|1,1\right\rangle = -\frac{8}{9\pi^2}\lambda L^2$$

(i) The energy shift of the ground state (non-degenerate)

$$E_1 = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2) + \langle 1,1|\hat{V}_1|1,1\rangle$$
$$= \frac{\hbar^2}{m}\left(\frac{\pi}{L}\right)^2 + \frac{1}{4}\lambda L^2$$

eigenstate of ground state = $|1,1\rangle + \frac{|1,2\rangle\langle 1,2|V|1,1\rangle}{E_1^{(0)} - E_2{}^{(0)}} + \frac{|2,1\rangle\langle 2,1|V|1,1\rangle}{E_1^{(0)} - E_2{}^{(0)}}$

$$E_1^{(0)} - E_2{}^{(0)} = -\frac{3\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2, \qquad \langle 1,2|V|1,1\rangle = \langle 2,1|V|1,1\rangle = -\frac{8}{9\pi^2}\lambda L^2$$

(ii) The energy shift of the first excited state (degenerate)

$$V|\psi_1\rangle = E_1|\psi_1\rangle$$

with the matrix,

$$V = \begin{pmatrix} \langle 1,2|V|1,2\rangle & \langle 1,2|V|2,1\rangle \\ \langle 2,1|V|1,2\rangle & \langle 2,1|V|2,1\rangle \end{pmatrix}$$
$$= \lambda L^2 \begin{pmatrix} \frac{1}{4} & \frac{256}{81\pi^4} \\ \frac{256}{81\pi^4} & \frac{1}{4} \end{pmatrix}$$
$$= \frac{\lambda L^2}{4\pi^4} \begin{pmatrix} \pi^4 & \frac{1024}{81} \\ \frac{1024}{81} & \pi^4 \end{pmatrix}$$

$$E_2{}^{(0)} = E(1,2) = E(2,1) = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 5$$

We solve the eigenvalue problem by using the Mathematica.

(i)

$$E_{21} = E_2^{(0)} + (\frac{1024 + 81\pi^4}{324\pi^4})\lambda L^2$$
$$= E_2^{(0)} + 0.282446\lambda L^2$$

Eigenstate: $\frac{1}{\sqrt{2}}[|1,2\rangle + |2,1\rangle]$

(ii)
$$E_{22} = E_2^{(0)} + (\frac{-1024 + 81\pi^4}{324\pi^4})\lambda L^2$$
$$= E_2^{(0)} + 0.217544\lambda L^2$$

Eigenstate: $\frac{1}{\sqrt{2}}[|1,2\rangle - |2,1\rangle]$

((**Mathematica**))

$$\mathbf{V1 = \frac{\lambda L^2}{4\pi^4}\begin{pmatrix} \pi^4 & \frac{1024}{81} \\ \frac{1024}{81} & \pi^4 \end{pmatrix}; Eigensystem[V1]}$$

$$\left\{\left\{\frac{L^2\left(1024 + 81\,\pi^4\right)\,\lambda}{324\,\pi^4}, \frac{L^2\left(-1024 + 81\,\pi^4\right)\,\lambda}{324\,\pi^4}\right\}, \{\{1, 1\}, \{-1, 1\}\}\right\}$$

((5-7))

5.7 Consider an isotropic harmonic oscillator in *two* dimensions. The Hamiltonian is

$$H_0 = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{m\omega^2}{2}(x^2 + y^2).$$

a. What are the energies of the three lowest-lying states? Is there any degeneracy?
b. We now apply a perturbation

$$V = \delta m\omega^2 xy,$$

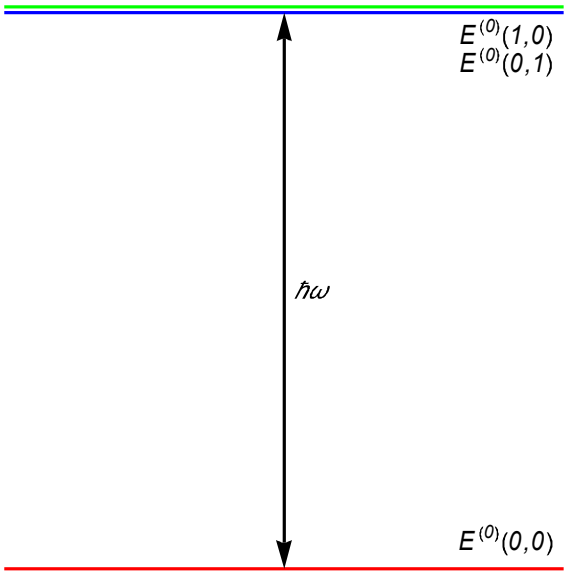
where δ is a dimensionless real number much smaller than unity. Find the zeroth-order energy eigenket and the corresponding energy to first order [that is, the unperturbed energy obtained in (a) plus the first-order energy shift] for each of the three lowest-lying states.
c. Solve the $H_0 + V$ problem *exactly*. Compare with the perturbation results obtained in (b).

((**Solution**))
(a)

$$\hat{H}_0 = (\frac{1}{2m}\hat{p}_x{}^2 + \frac{1}{2}m\omega^2\hat{x}^2) + (\frac{1}{2m}\hat{p}_y{}^2 + \frac{1}{2}m\omega^2\hat{y}^2)$$

$$\hat{H}_0|n_x, n_x\rangle = \{\hbar\omega(n_x + \frac{1}{2}) + \hbar\omega(n_y + \frac{1}{2})\}|n_x, n_x\rangle$$

Ground state:	$\|0,0\rangle$	(non-degenerate state)	$E^{(0)}(0,0) = \hbar\omega$
First excited state:	$\|1,0\rangle$	(degenerate state)	$E^{(0)}(1,0) = 2\hbar\omega$
	$\|0,1\rangle$	(degenerate state)	$E^{(0)}(0,1) = 2\hbar\omega$
Second excited state	$\|2,0\rangle$	(degenerate state)	$E^{(0)}(2,0) = 3\hbar\omega$
	$\|1,1\rangle$	(degenerate state)	$E^{(0)}(1,1) = 3\hbar\omega$
	$\|0,2\rangle$	(degenerate state)	$E^{(0)}(0,2) = 3\hbar\omega$



(b)

$$\hat{V} = \delta m\omega^2 \hat{x}\hat{y}$$

$$\hat{V}|0,0\rangle = \delta m\omega^2 \hat{x}\hat{y}|0,0\rangle$$

$$\hat{x}|0\rangle = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}+\hat{a}^+)|0\rangle = \sqrt{\frac{\hbar}{2m\omega}}\hat{a}^+|0\rangle = \sqrt{\frac{\hbar}{2m\omega}}|1\rangle$$

Then we have

$$\hat{V}|0,0\rangle = \delta m\omega^2 \frac{\hbar}{2m\omega}|1,1\rangle = \frac{\delta}{2}\hbar\omega|1,1\rangle$$

$$\hat{V}|1,0\rangle = \delta m\omega^2 \hat{x}\hat{y}|1,0\rangle = \frac{\delta}{2}\hbar\omega(|0,1\rangle + \sqrt{2}|2,1\rangle$$

$$\hat{V}|0,1\rangle = \delta m\omega^2 \hat{x}\hat{y}|0,1\rangle = \frac{\delta}{2}\hbar\omega(|1,0\rangle + \sqrt{2}|1,2\rangle$$

since

$$\hat{x}|1\rangle = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}+\hat{a}^+)|1\rangle = \sqrt{\frac{\hbar}{2m\omega}}(|0\rangle + \sqrt{2}|2\rangle$$

$$\hat{y}|0\rangle = \sqrt{\frac{\hbar}{2m\omega}}|1\rangle$$

The ground state is non-degenerate.

$$\begin{aligned}
|\Phi_0\rangle &= |0,0\rangle + \sum_{k\neq 0} \frac{|k\rangle\langle k|\hat{V}|0,0\rangle}{E^{(0)}(0,0) - E_k^{(0)}} \\
&= |0,0\rangle + \frac{|1,1\rangle\langle 1,1|\hat{V}|0,0\rangle}{E^{(0)}(0,0) - E^{(0)}(1,1)} \\
&= |0,0\rangle + \frac{\frac{\delta}{2}\hbar\omega}{\hbar\omega - 3\hbar\omega}|1,1\rangle \\
&= |0,0\rangle - \frac{\delta}{4}|1,1\rangle
\end{aligned}$$

$$\begin{aligned}
E(00) &= E^{(0)}(0,0) + \langle 0,0|\hat{V}|0,0\rangle + \frac{|\langle 1,1|V|0,0\rangle|^2}{E^{(0)}(0,0) - E^{(0)}(1,1)} \\
&= \hbar\omega + \frac{\left(\frac{\delta}{2}\hbar\omega\right)^2}{\hbar\omega - 3\hbar\omega} \\
&= \hbar\omega - \frac{\delta^2}{8}\hbar\omega
\end{aligned}$$

(i) First excited state

The matrix element of $\hat{V}$ under the basis of $\{|1,0\rangle$, and $|0,1\rangle\}$

$$\hat{V} = \begin{pmatrix} 0 & \frac{\delta}{2}\hbar\omega \\ \frac{\delta}{2}\hbar\omega & 0 \end{pmatrix} = \frac{\delta}{2}\hbar\omega\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{\delta}{2}\hbar\omega\hat{\sigma}_x$$

Eigenvalue $\frac{\delta}{2}\hbar\omega$ $\qquad |\psi_1\rangle = \frac{1}{\sqrt{2}}[|1,0\rangle + |0,1\rangle]$

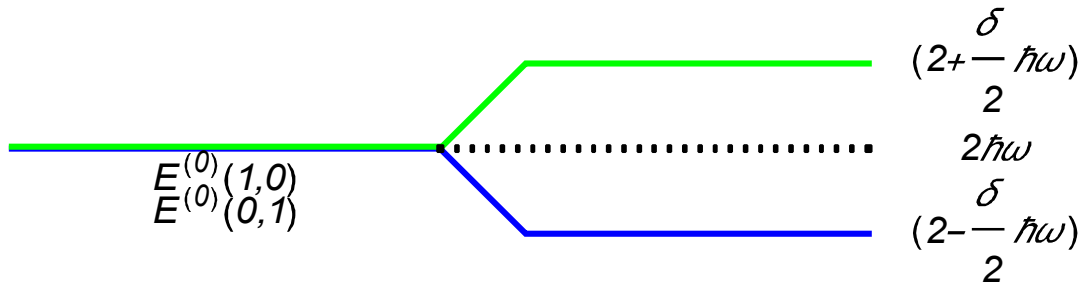
The energy is

$$2\hbar\omega+\frac{\delta}{2}\hbar\omega=\hbar\omega(2+\frac{\delta}{2})$$

Eigenvalue $-\frac{\delta}{2}\hbar\omega$ $\qquad |\psi_2\rangle=\frac{1}{\sqrt{2}}[|1,0\rangle-|0,1\rangle]$

The total energy is

$$2\hbar\omega-\frac{\delta}{2}\hbar\omega=\hbar\omega(2-\frac{\delta}{2})$$



(ii) Exact solution

Suppose that

$|\psi'\rangle=\hat{U}|\psi\rangle$, $\qquad \langle\psi_1|\hat{A}|\psi_2\rangle$

$\hat{U}$ is the unitary operator. Under that basis of $|\psi'\rangle$, the operator $\hat{A}$ can be changed into

$$\langle\psi_1|\hat{A}|\psi_2\rangle=\langle\psi_1'|\hat{U}\hat{A}\hat{U}^+|\psi_2\rangle$$

Suppose that $\hat{U}=\hat{R}$ (rotation operator)

$$\hat{U}\hat{A}\hat{U}^+=\hat{R}\hat{A}\hat{R}^+$$

When $\hat{H}=\hat{H}_0+\hat{V}$, $\quad \hat{R}\hat{H}_0\hat{R}^+=\hat{H}_0$ ($\hat{H}_0$ is invariant under the rotation around the z axis),

$$\hat{R}\hat{H}\hat{R}^+=\hat{R}\hat{H}_0\hat{R}^++\hat{R}\hat{V}\hat{R}^+=\hat{H}_0+\hat{R}\hat{V}\hat{R}^+$$

When $\hat{V} = \delta m\omega^2 \hat{x}\hat{y}$

$$\begin{aligned}\hat{R}\hat{V}\hat{R}^+ &= \delta m\omega^2(\hat{R}\hat{x}\hat{R}^+)(\hat{R}\hat{y}\hat{R}^+) \\ &= \delta m\omega^2(\cos\phi\,\hat{x} + \sin\phi\,\hat{y})(-\sin\phi\,\hat{x} + \cos\phi\,\hat{y}) \\ &= \delta m\omega^2[-\frac{1}{2}\sin(2\phi)(\hat{x}^2 - \hat{y}^2) + \cos(2\phi)\hat{x}\hat{y}]\end{aligned}$$

when $\phi = \pi/4$,

$$\hat{R}\hat{V}\hat{R}^+ = -\frac{1}{2}\delta m\omega^2(\hat{x}^2 - \hat{y}^2)$$

$$\begin{aligned}\hat{H}' &= \hat{R}\hat{H}\hat{R}^+ = \hat{H}_0 + \hat{R}\hat{V}\hat{R}^+ \\ &= \frac{1}{2m}\hat{p}_x{}^2 + \frac{1}{2}m\omega^2(1-\delta)\hat{x}^2 + \frac{1}{2m}\hat{p}_y{}^2 + \frac{1}{2}m\omega^2(1+\delta)\hat{y}^2\end{aligned}$$

Energy eigenvalue of this Hamiltonian is

$$\begin{aligned}E'(n_x, n_y) &= (n_x + \frac{1}{2})\hbar\omega\sqrt{1-\delta} + (n_y + \frac{1}{2})\hbar\omega\sqrt{1+\delta} \\ &= (n_x + \frac{1}{2})\hbar\omega(1 - \frac{\delta}{2} - \frac{\delta^2}{8} + ...) + (n_y + \frac{1}{2})\hbar\omega(1 + \frac{\delta}{2} - \frac{\delta^2}{8} + ...) + \\ &= (n_x + n_y + 1)\hbar\omega - \frac{\delta}{2}\hbar\omega(n_x - n_y) + ...\end{aligned}$$

$$\hat{H}'\left|n_x, n_y\right\rangle = \hat{R}\hat{H}\hat{R}^+\left|n_x, n_y\right\rangle = E'(n_x, n_y)\left|n_x, n_y\right\rangle$$

or

$$\hat{H}\hat{R}^+\left|n_x, n_y\right\rangle = E'(n_x, n_y)\hat{R}^+\left|n_x, n_y\right\rangle$$

$\hat{R}^+\left|n_x, n_y\right\rangle$ is the eigenstate of the Hamiltonian $\hat{H}$ with $E'(n_x, n_y)$.

((5-8))

5.8 Establish (5.54) for the one-dimensional harmonic oscillator given by (5.50) with an additional perturbation $V = \frac{1}{2}\varepsilon m\omega^2 x^2$. Show that all other matrix elements V_{k0} vanish.

((**Solution**))

$$\hat{x} = \frac{1}{\sqrt{2}\beta}(\hat{a} + \hat{a}^+),$$

$$\hat{a}|n\rangle = \sqrt{n}\,|n-1\rangle, \qquad \hat{a}^+|n\rangle = \sqrt{n+1}\,|n+1\rangle$$

$$\beta = \sqrt{\frac{m\omega}{\hbar}}$$

$$\begin{aligned}
\langle n|\hat{V}|0\rangle &= \frac{1}{2}\varepsilon m\omega^2 \langle n|\hat{x}^2|0\rangle \\
&= \frac{1}{2}\varepsilon m\omega^2 \frac{1}{2\beta^2}\langle n|(\hat{a}+\hat{a}^+)^2|0\rangle \\
&= \frac{1}{4}\varepsilon\hbar\omega\langle n|\hat{a}^2 + (\hat{a}^+)^2 + \hat{a}\hat{a}^+ + \hat{a}^+\hat{a}|0\rangle \\
&= \frac{1}{4}\varepsilon\hbar\omega\langle n|(\hat{a}^+)^2 + \hat{a}^+\hat{a} + \hat{1}|0\rangle \\
&= \frac{1}{4}\varepsilon\hbar\omega[\sqrt{2}\langle n|2\rangle + \langle n|0\rangle] \\
&= \frac{1}{4}\varepsilon\hbar\omega[\sqrt{2}\delta_{n,2} + \delta_{n,0}]
\end{aligned}$$

So we have

$$\langle 2|\hat{V}|0\rangle = \frac{\sqrt{2}}{4}\varepsilon\hbar\omega, \qquad \langle 0|\hat{V}|0\rangle = \frac{1}{4}\varepsilon\hbar\omega$$

((5-9))

5.9 A slightly anisotropic three-dimensional harmonic oscillator has $\omega_x = \omega_y \equiv \omega$ and $\omega_z = (1+\varepsilon)\omega$ where $\varepsilon \ll 1$. (See Section 3.7.3 for nomenclature and wave functions.) A charged particle moves in the field of this oscillator and is at the same time exposed to a uniform magnetic field in the x-direction. Assuming that the Zeeman splitting is comparable to the splitting produced by the anisotropy, but small compared to $\hbar\omega$, calculate to first order the energies of the components of the first excited state. Discuss various limiting cases. (This is taken from Problem 17.7 in Merzbacher (1970). You might find it useful to consult Problem 2.16 in Chapter 2 and Problem 3.29 in Chapter 3.)

((Note))

Before solving this problem, I present a brief review on the 3D isotropic simple harmonics.

3D isotropic simple harmonics

Schrödinger equation:

$$\langle \boldsymbol{r}|\frac{\hat{\boldsymbol{p}}^2}{2\mu}|\psi\rangle + \langle \boldsymbol{r}|V(|\hat{\boldsymbol{r}}|)|\psi\rangle = E\langle \boldsymbol{r}|\psi\rangle,$$

or

$$-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial}{\partial r}\left(\frac{\partial}{\partial r}r\langle \boldsymbol{r}|\psi\rangle\right) + \frac{1}{2\mu r^2}\langle \boldsymbol{r}|\hat{\boldsymbol{L}}^2|\psi\rangle + V(r)\langle \boldsymbol{r}|\psi\rangle = E\langle \boldsymbol{r}|\psi\rangle,$$

or

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial}{\partial r}\left(\frac{\partial}{\partial r}r\right) + \frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r)\right]\langle \mathbf{r}|\psi\rangle = E\langle \mathbf{r}|\psi\rangle,$$

where the potential energy is

$$V(r) = \frac{1}{2}\mu\omega^2 r^2$$

Here we assume that

$$\langle \boldsymbol{r}|\psi\rangle = \psi(\boldsymbol{r}) = R_{E,l}(r)Y_l^m(\theta,\varphi)$$

where $Y_l^m(\theta,\varphi)$ is the spherical harmonics.

$$Y_0^0(\theta,\phi)=\frac{1}{2\sqrt{\pi}}$$

$$Y_1^1(\theta,\phi)=-\frac{1}{2}\sqrt{\frac{3}{2\pi}}e^{i\phi}\sin\theta=-\frac{1}{2}\sqrt{\frac{3}{2\pi}}\frac{(x+iy)}{r},$$

$$Y_1^0(\theta,\phi)=\sqrt{\frac{3}{4\pi}}\cos\theta=\sqrt{\frac{3}{4\pi}}\frac{z}{r},$$

$$Y_1^{-1}(\theta,\phi)=\frac{1}{2}\sqrt{\frac{3}{2\pi}}e^{-i\phi}\sin\theta=\frac{1}{2}\sqrt{\frac{3}{2\pi}}\frac{(x-iy)}{r}.$$

$R_{E,l}(r)$ depends only on *E* and *l*, but not on *m*.

$$[-\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial}{\partial r}(\frac{\partial}{\partial r}r)+\frac{\hbar^2 l(l+1)}{2mr^2}+\frac{1}{2}m\omega^2 r^2]R_{E,l}(r)=ER_{E,l}(r)$$

We assume that

$$R_{E,l}(r)=\frac{u(r)}{r},$$

$$u"(r)-[\frac{l(l+1)}{r^2}+\frac{2\mu(-E+V(r)}{\hbar^2}]u(r)=0,$$

or

$$u"(r)-\frac{l(l+1)}{r^2}u-\frac{\mu^2\omega^2}{\hbar^2}r^2u(r)=-\frac{2\mu E}{\hbar^2}u(r).$$

We now introduce a new variable

$$\rho=\sqrt{\frac{m\omega}{\hbar}}r,\qquad\qquad\lambda=\frac{2E}{\hbar\omega}.$$

Then we get the differential equation

$$u''(\rho) - \frac{l(l+1)}{\rho^2} u(\rho) - \rho^2 u(\rho) = -\lambda u(\rho).$$

In the limit of $\rho \to 0$, u is assumed to have the power form $u(\rho) \approx \rho^s$. The substitution of this form into the above differential equation gives rise to

$$\rho^{s-2}[s(s-1) - l(l+1)] - \rho^{s+2} = -\lambda \rho^s,$$

or

$$\rho^{s-2}[s(s-1) - l(l+1)] = 0.$$

So we get $s = l+1$.

In the limit of $\rho \to \infty$, the differential equation can be approximated as

$$u''(\rho) - \rho^2 u(\rho) = 0.$$

We assume that $u(\rho) \approx \exp(-\rho^2/2)$.

$$u''(\rho) - \rho^2 u(\rho) = (\rho^2 - 1)u(\rho) - \rho^2 u(\rho) = -u(\rho),$$

This is almost the same as the original differential equation; $u''(\rho) - \rho^2 u(\rho) = 0$. These suggests that our solution $u(\rho)$ can be expressed by the form

$$u(\rho) = \rho^{l+1} e^{-\rho^2/2} f(\rho).$$

Then we have the differential equation for $f(\rho)$ as

$$\rho f''(\rho) + 2(l+1-\rho^2) f'(\rho) + (\lambda - 2l - 3)\rho f(\rho) = 0.$$

We solve this problem by using the series expansion

$$f(\rho) = \sum_{k=0}^{\infty} C(k) \rho^k .$$

Using the Mathematica, we get

$$2(1+l)C(1)=0\,,$$

$$(-3-2l+\lambda)C(0)+2(3+2l)C(2)=0\,,$$

$$(-5-2l+\lambda)C(1)+6(2+l)C(3)=0\,,$$

$$(-7-2l+\lambda)C(2)+4(5+2l)C(4)=0\,.$$

Then we have

$$C(1)=C(3)=C(5)=...=0\,.$$

In other words, $f(\rho)$ is an even function of ρ. So we assume that

$$f(\rho)=\sum_{k=0}^{\infty}C(2k)\rho^{2k}\,,$$

Then we have

$$\sum_{k=1}(2k)(2k-1)C(2k)\rho^{2k-1}+2(l+1-\rho^2)\sum_{k=1}(2k)C(2k)\rho^{2k-1}$$
$$+(\lambda-2l-3)\sum_{k=0}C(2k))\rho^{2k+1}=0$$

or

$$\sum_{k=1}2k[2k-1+2(l+1)]C(2k)\rho^{2k-1}$$
$$-\sum_{k=1}C(2k)(4k)\rho^{2k+1}+(\lambda-2l-3)\sum_{k=0}C(2k))\rho^{2k+1}=0$$

Using the relation

$$\sum_{k=1}2k[2k-1+2(l+1)]C(2k)\rho^{2k-1}=\sum_{k=0}(2k+2)[2k+1+2(l+1)]C(2k+1)\rho^{2k+1}$$

(conventional mathematical procedure)

$$\sum_{k=1} C(2k)(4k)\rho^{2k+1} = \sum_{k=0} C(2k)(4k)\rho^{2k+1} \qquad \text{(no change with the addition of } k = 0 \text{ term)}$$

this can be rewritten as

$$\sum_{k=0} \{2(k+1)(2k+2l+3)C(2k+2) - (4k+2l+3-\lambda)C(2k)\}\rho^{2k+1} 0$$

From this we get the recursion relation,

$$C(2k+2) = \frac{(4k+2l+3-\lambda)}{2(k+1)(2k+3+2l)} C(2k),$$

When

$$3 + 4n_r + 2l = \lambda \qquad (n_r = 0, 1, 2, 3, ...),$$

the co-efficient $C(2+2n_r)$ should be equal to zero, corresponding to the termination of the power series. Then, from the recursion relation, we have

$$C(2+2n_r) = C(4+2n_r) = ... = 0.$$

So the energy quantization condition is that

$$3 + 4n_r + 2l = \lambda = \frac{2E}{\hbar\omega_0},$$

or

$$E(n_r, l) = (\frac{3}{2} + 2n_r + l)\hbar\omega_0.$$

We define the principal quantum number n as

$$E_n = (n + \frac{3}{2})\hbar\omega_0,$$

with $n = 2n_r + l$.

n	l	n_r	Degeneracy
0	0	0	1 $m = 0$
1	1	0	3 m = -1, 0, 1
2	0	1	1 $m = 0$
2	2	0	5 m =-2, -1, 0, 1, 2

$$\langle r,\theta\psi \,|\, n,l,m\rangle = \frac{1}{\rho} u_{n,l}(\rho) Y_l^m(\theta,\phi)$$

with

$$u_{n,l}(\rho) = (-1)^n \sqrt{2\frac{n!}{(n+l+1/2)!}}\rho^{l+1} e^{-\rho^2/2} L_n^{l+1/2}(\rho)$$

and

$$\rho = \sqrt{\frac{m\omega}{\hbar}} r = \beta r\,.$$

$$\int_0^\infty d\rho\; u_{n.l}(\rho) u_{n'.l}(\rho) = \delta_{n,n'}$$

We note that the wave functions can be derived from the wave functions of simple harmonics as follows.

$$\langle x,y,z|n_x=0,n_y=0,n_z=0\rangle=\langle x|n_x=0\rangle\langle y|n_x=0\rangle\langle z|n_x=0\rangle$$
$$=\left(\frac{m\omega}{\pi\hbar}\right)^{3/4}\exp(-\frac{m\omega x^2}{2\hbar})\exp(-\frac{m\omega y^2}{2\hbar})\exp(-\frac{m\omega z^2}{2\hbar})$$
$$=\left(\frac{m\omega}{\pi\hbar}\right)^{3/4}\exp(-\frac{m\omega r^2}{2\hbar})$$

which corresponds to

$$|l=0,m=0\rangle\rightarrow|n_x=,n_y=0,n_z=0\rangle$$

$$\langle x,y,z|n_x=1,n_y=0,n_z=0\rangle=\langle x|n_x=1\rangle\langle y|n_x=0\rangle\langle z|n_x=0\rangle$$
$$=\left(\frac{4}{\pi}\right)^{1/4}\left(\frac{m\omega}{\pi\hbar}\right)^{3/4}x\exp(-\frac{m\omega y^2}{2\hbar})\left(\frac{m\omega}{\pi\hbar}\right)^{1/2}\exp(-\frac{m\omega y^2}{2\hbar})\exp(-\frac{m\omega z^2}{2\hbar})$$
$$=\left(\frac{4}{\pi}\right)^{1/4}\left(\frac{m\omega}{\pi\hbar}\right)^{3/4}\left(\frac{m\omega}{\pi\hbar}\right)^{1/2}x\exp(-\frac{m\omega r^2}{2\hbar})$$

which corresponds to

$$\frac{|l=1,m=-1\rangle-|l=1,m=1\rangle}{\sqrt{2}}\rightarrow|n_x=1,n_y=0,n_z=0\rangle$$

$$\langle x,y,z|n_x=0,n_y=1,n_z=0\rangle=\langle x|n_x=0\rangle\langle y|n_x=1\rangle\langle z|n_x=0\rangle$$
$$=\left(\frac{4}{\pi}\right)^{1/4}\left(\frac{m\omega}{\pi\hbar}\right)^{3/4}\left(\frac{m\omega}{\pi\hbar}\right)^{1/2}y\exp(-\frac{m\omega r^2}{2\hbar})$$

which corresponds to

$$\frac{|l=1,m=-1\rangle+|l=1,m=1\rangle}{\sqrt{2}(-i)}\rightarrow|n_x=0,n_y=1,n_z=0\rangle$$

$$\langle x,y,z|n_x=1,n_y=0,n_z=0\rangle=\langle x|n_x=0\rangle\langle y|n_x=0\rangle\langle z|n_x=0\rangle$$
$$=\left(\frac{4}{\pi}\right)^{1/4}\left(\frac{m\omega}{\pi\hbar}\right)^{3/4}\left(\frac{m\omega}{\pi\hbar}\right)^{1/2}z\exp(-\frac{m\omega r^2}{2\hbar})$$

which corresponds to

$$|l=1,m=0\rangle \to |n_x=0,n_y=0,n_z=1\rangle$$

Note that

$$\sqrt{\frac{3}{4\pi}}\frac{z}{r}=Y_1^0, \qquad \sqrt{\frac{3}{4\pi}}\frac{x}{r}=-\frac{1}{\sqrt{2}}(Y_1^1-Y_1^{-1}), \qquad \sqrt{\frac{3}{4\pi}}\frac{y}{r}=\frac{i}{\sqrt{2}}(Y_1^1+Y_1^{-1})$$

Thus, we get the relation. For convenience, we use $|+\rangle$, $|0\rangle$, and $|-\rangle$

$$|+\rangle=|l=1,m=1\rangle=-\frac{1}{\sqrt{2}}(|1,0,0\rangle+i|0,1,0\rangle)$$

$$|-\rangle=|l=1,m=-1\rangle=\frac{1}{\sqrt{2}}(|1,0,0\rangle-i|0,1,0\rangle)$$

$$|0\rangle=|l=1,m=0\rangle=|0,0,1\rangle$$

((**Solution**))
The Hamiltonian of charged particle with mass m and charge q is given by

$$\begin{aligned}H&=\frac{1}{2m}(\boldsymbol{p}-\frac{q}{c}\boldsymbol{A})^2+\frac{1}{2}m\omega^2(x^2+y^2)+\frac{1}{2}m\omega^2(1+\varepsilon)^2z^2\\&=\frac{1}{2m}\boldsymbol{p}^2+\frac{q^2}{2mc}\boldsymbol{A}^2-\frac{q}{2mc}(\boldsymbol{p}\cdot\boldsymbol{A}+\boldsymbol{A}\cdot\boldsymbol{p})\\&+\frac{1}{2}m\omega^2(x^2+y^2)+\frac{1}{2}m\omega^2(1+\varepsilon)^2z^2\\&=\frac{1}{2m}\boldsymbol{p}^2+\frac{1}{2}m\omega^2(x^2+y^2+z^2)+\frac{q^2}{2mc}\boldsymbol{A}^2-\frac{q}{2mc}(\boldsymbol{p}\cdot\boldsymbol{A}+\boldsymbol{A}\cdot\boldsymbol{p})\\&+\varepsilon m\omega^2z^2\end{aligned}$$

where q is the charge of particle. Note that

$$\boldsymbol{p}\cdot\boldsymbol{A}-\boldsymbol{A}\cdot\boldsymbol{p}=-i\hbar((\boldsymbol{p}\cdot\boldsymbol{A}+\boldsymbol{A}\cdot\boldsymbol{p}))$$

We use the gauge, where a constant magnetic field $\boldsymbol{B}$ is directed along the x-axis. We use the gauge such that

$$\nabla \cdot \boldsymbol{A} = 0\,, \qquad \boldsymbol{A} = \frac{1}{2}\boldsymbol{B} \times \boldsymbol{r} = \frac{1}{2}(0, -Bz, By)$$

The Hamiltonian is obtained as

$$\begin{aligned} H &= H_0 + H_1 \\ &= \frac{1}{2m}\boldsymbol{p}^2 + \frac{1}{2}m\omega^2(x^2 + y^2 + z^2) \\ &\quad + \frac{q^2}{2mc^2}\boldsymbol{A}^2 - \frac{q}{mc}\boldsymbol{A} \cdot \boldsymbol{p} + \varepsilon m\omega^2 z^2 \end{aligned}$$

where H_0 is the non-perturbed Hamiltonian for the 3D isotropic simple harmonics, and H_1 is the perturbation.

$$H_0 = \frac{1}{2m}\boldsymbol{p}^2 + \frac{1}{2}m\omega^2(x^2 + y^2 + z^2) = \frac{1}{2m}\boldsymbol{p}^2 + \frac{1}{2}m\omega^2 r^2$$

$$\begin{aligned} H_1 &= \frac{q^2}{2mc^2}\boldsymbol{A}^2 - \frac{q}{mc}(A_y p_y + A_z p_z) + \varepsilon m\omega^2 z^2 \\ &= \frac{q^2}{2mc^2}\boldsymbol{A}^2 - \frac{qB}{2mc}(yp_z - zp_y) + \varepsilon m\omega^2 z^2 \\ &= -\frac{qB}{2mc}L_x + \varepsilon m\omega^2 z^2 + \frac{q^2B^2}{8mc^2}(y^2 + z^2) \end{aligned}$$

where L_x is the orbital angular momentum along the x axis.

$$L_x = yp_z - zp_y$$

Here we use the Virial theorem; $m\omega^2\left\langle z^2 \right\rangle \simeq \hbar\omega$.

$$\varepsilon m\omega^2\left\langle z^2 \right\rangle = \varepsilon\hbar\omega$$

and define the cyclotron angular frequency (in cgs units) as

$$\omega_c = \frac{qB}{mc}$$

We assume that the first term and the second term of H_1 are on the same order,

$$\varepsilon\hbar\omega \simeq \frac{q\hbar B}{mc} = \hbar\omega_c , \qquad \text{or} \qquad \varepsilon = \varepsilon = \frac{\omega_c}{\omega}$$

The third term of H_1 is

$$\frac{q^2B^2}{mc^2} < y^2 + z^2 > \approx \frac{q^2B^2}{mc^2}\frac{\hbar}{m\omega} = \frac{q^2B^2}{m^2c^2}\frac{\hbar}{\omega} = \hbar\omega\frac{\omega_c^{\,2}}{\omega^2} = \hbar\omega\ \varepsilon^2$$

which is smaller than the other interaction energies. So we neglect the third term of H_1. Thus we have

$$H_0 = \frac{1}{2m}\boldsymbol{p}^2 + \frac{1}{2}m\omega^2 r^2$$

$$H_1 = -\frac{qB}{2mc}L_x + \varepsilon m\omega^2 z^2$$

In order to simplify the discussion, we change the coordinates such that $x \to z$ and $z \to -x$. Then we have

$$H_1 = -\frac{qB}{2mc}L_z + \varepsilon m\omega^2 x^2$$

Now we solve the problem. The first excited states are degenerate. There are three states, $|+\rangle$, $|0\rangle$, and $|-\rangle$ states with the same energy $\frac{5}{2}\hbar\omega$. We need to calculate the matrix element of $H_1 = -\frac{qB}{2mc}L_z + \varepsilon m\omega^2 x^2$.

$$H_1 = \begin{pmatrix} \langle +|H_1|+\rangle & \langle +|H_1|0\rangle & \langle +|H_1|-\rangle \\ \langle 0|H_1|+\rangle & \langle 0|H_1|0\rangle & \langle 0|H_1|-\rangle \\ \langle -|H_1|+\rangle & \langle -|H_1|0\rangle & \langle -|H_1|-\rangle \end{pmatrix}$$

We note that

$$\langle l,m|L_z|l,m'\rangle = m\hbar\delta_{m,m'}$$

We also note that

$$\langle +|\hat{x}^2|+\rangle = \frac{1}{2}[\langle 1,0,0|\hat{x}^2|1,0,0\rangle + \langle 0,1,0|\hat{x}^2|0,1,0\rangle]$$

$$\langle +|\hat{x}^2|0\rangle = 0$$

$$\langle +|\hat{x}^2|-\rangle = -\frac{1}{2}[\langle 1,0,0|\hat{x}^2|1,0,0\rangle - \langle 0,1,0|\hat{x}^2|0,1,0\rangle]$$

$$\langle -|\hat{x}^2|-\rangle = \frac{1}{2}[\langle 1,0,0|\hat{x}^2|1,0,0\rangle + \langle 0,1,0|\hat{x}^2|0,1,0\rangle]$$

where

$$\begin{aligned}\langle 1,0,0|\hat{x}^2|1,0,0\rangle &= \langle 1|\hat{x}^2|1\rangle \\ &= \frac{1}{2\beta^2}\langle 1|\hat{a}^2 + \hat{a}^{+2} + 2\hat{n} + 1|1\rangle \\ &= \frac{3}{2\beta^2}\end{aligned}$$

$$\begin{aligned}\langle 0,1,0|\hat{x}^2|0,1,0\rangle &= \langle 0|\hat{x}^2|0\rangle \\ &== \frac{1}{2\beta^2}\langle 0|\hat{a}^2 + \hat{a}^{+2} + 2\hat{n} + 1|0\rangle \\ &= \frac{1}{2\beta^2}\end{aligned}$$

$$\langle 0|\hat{x}^2|0\rangle = \langle 0,0,1|\hat{x}^2|0,0,1\rangle = \frac{1}{2\beta^2}$$

where $\beta = \sqrt{\frac{m\omega}{\hbar}}$. Then the matrix based on the degenerated first excited states is

$$H_1 = \begin{pmatrix} \frac{q\hbar B}{2mc} + \varepsilon\hbar\omega & 0 & \frac{1}{2}\varepsilon\hbar\omega \\ 0 & \frac{1}{2}\varepsilon\hbar\omega & 0 \\ \frac{1}{2}\varepsilon\hbar\omega & 0 & -\frac{q\hbar B}{2mc} + \varepsilon\hbar\omega \end{pmatrix}$$

$$= \hbar \begin{pmatrix} \frac{1}{2}\omega_c + \varepsilon\omega & 0 & \frac{1}{2}\varepsilon\omega \\ 0 & \frac{1}{2}\varepsilon\omega & 0 \\ \frac{1}{2}\varepsilon\omega & 0 & -\frac{1}{2}\omega_c + \varepsilon\omega \end{pmatrix}$$

The eigenvalue problem can be solved by the two methods.

(i) Method-1

$$\hat{H}_1 |+\rangle = (\frac{1}{2}\hbar\omega_c + \hbar\varepsilon\omega)|+\rangle + \frac{1}{2}\hbar\varepsilon\omega|-\rangle$$

$$\hat{H}_1 |0\rangle = \frac{1}{2}\hbar\varepsilon\omega|0\rangle$$

$$\hat{H}_1 |-\rangle = \frac{1}{2}\hbar\varepsilon\omega|-\rangle + (-\frac{1}{2}\hbar\omega_c + \hbar\varepsilon\omega)|+\rangle$$

So $|0\rangle$ is the eigenket of H_1 with the eigenvalue $\frac{1}{2}\hbar\varepsilon\omega$. We now introduce a new matrix under the sub-basis of $\{|+\rangle, |-\rangle\}$

$$(H_1)_{sub} = \hbar \begin{pmatrix} \frac{1}{2}\omega_c + \varepsilon\omega & \frac{1}{2}\varepsilon\omega \\ \frac{1}{2}\varepsilon\omega & -\frac{1}{2}\omega_c + \varepsilon\omega \end{pmatrix}$$

$$= \frac{1}{2}\hbar\varepsilon\omega\hat{\sigma}_x + \hbar\varepsilon\omega\hat{1} + \frac{1}{2}\hbar\omega_c\hat{\sigma}_z$$

This can be rewritten as

$$
\begin{aligned}
\left(H_1\right)_{sub} &= \frac{1}{2}\hbar(\omega_c\hat{\sigma}_z + \varepsilon\omega\hat{\sigma}_x) + \hbar\varepsilon\omega\hat{1} \\
&= \frac{1}{2}\hbar\sqrt{\omega_c{}^2 + (\varepsilon\omega)^2}\,(\frac{\omega_c}{\sqrt{\omega_c{}^2 + (\varepsilon\omega)^2}}\hat{\sigma}_z + \frac{\varepsilon\omega}{\sqrt{\omega_c{}^2 + (\varepsilon\omega)^2}}\hat{\sigma}_x) + \hbar\varepsilon\omega\hat{1} \\
&= \frac{1}{2}\hbar\sqrt{\omega_c{}^2 + (\varepsilon\omega)^2}\,\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{n} + \hbar\varepsilon\omega\hat{1}
\end{aligned}
$$

Then we have the eigenstates and eigen eigenvalues as

$$
\left|+\boldsymbol{n}\right\rangle = \begin{pmatrix} \cos\dfrac{\theta}{2} \\ \sin\dfrac{\theta}{2} \end{pmatrix} \qquad \frac{1}{2}\hbar\sqrt{\omega_c{}^2 + (\varepsilon\omega)^2} + \hbar\varepsilon\omega
$$

$$
\left|+\boldsymbol{n}\right\rangle = \begin{pmatrix} -\sin\dfrac{\theta}{2} \\ \cos\dfrac{\theta}{2} \end{pmatrix} \qquad -\frac{1}{2}\hbar\sqrt{\omega_c{}^2 + (\varepsilon\omega)^2} + \hbar\varepsilon\omega
$$

where θ is the angle from the z axis in the z-x plane ($y = 0$).

$$
\cos\theta = \frac{\omega_c}{\sqrt{\omega_c{}^2 + (\varepsilon\omega)^2}}, \qquad \sin\theta = \frac{\varepsilon\omega}{\sqrt{\omega_c{}^2 + (\varepsilon\omega)^2}}
$$

(ii) Method-2.

We use the Mathematica (Eigensystem). The result is as follows.
Energy eigenvalues and eigenkets:

$$
\frac{5}{2}\hbar\omega + \begin{cases} \dfrac{1}{2}\varepsilon\hbar\omega & \left|0\right\rangle \\ \varepsilon\hbar\omega - \dfrac{\hbar}{2}\sqrt{\varepsilon^2\omega^2 + \omega_c{}^2} & (-\omega_c - \sqrt{\varepsilon^2\omega^2 + \omega_c{}^2})\left|+\right\rangle + \varepsilon\omega\left|-\right\rangle \\ \varepsilon\hbar\omega + \dfrac{\hbar}{2}\sqrt{\varepsilon^2\omega^2 + \omega_c{}^2} & \left(-\omega_c + \sqrt{\varepsilon^2\omega^2 + \omega_c{}^2}\right)\left|+\right\rangle + \varepsilon\omega\left|-\right\rangle \end{cases}
$$

When $B = 0$

$$\frac{5}{2}\hbar\omega+\begin{cases}\frac{1}{2}\varepsilon\hbar\omega & |0\rangle \\ \frac{1}{2}\varepsilon\hbar\omega & \frac{-|+\rangle+|-\rangle}{\sqrt{2}} \\ \frac{3}{2}\varepsilon\hbar\omega & \frac{|+\rangle+|-\rangle}{\sqrt{2}}\end{cases}$$

In the limit of $\varepsilon \to 0$

$$\frac{5}{2}\hbar\omega+\begin{cases}0 & |0\rangle \\ -\frac{\hbar}{2}\omega_c & |+\rangle \\ \frac{\hbar}{2}\omega_c & |-\rangle\end{cases}$$

((**Mathematica**))

```
Clear["Global`"];
```

$$\text{H1} = \begin{pmatrix} -\frac{1}{2}\,\omega c + \varepsilon\,\omega & 0 & \frac{1}{2}\,\varepsilon\,\omega \\ 0 & \frac{1}{2}\,\varepsilon\,\omega & 0 \\ \frac{1}{2}\,\varepsilon\,\omega & 0 & \frac{1}{2}\,\omega c + \varepsilon\,\omega \end{pmatrix};$$

```
Eigensystem[H1] // Simplify
```

$$\left\{\left\{\frac{\varepsilon\,\omega}{2},\ \varepsilon\,\omega - \frac{1}{2}\sqrt{\varepsilon^2\,\omega^2 + \omega c^2},\ \varepsilon\,\omega + \frac{1}{2}\sqrt{\varepsilon^2\,\omega^2 + \omega c^2}\right\},\right.$$

$$\left\{\{0, 1, 0\},\ \left\{-\frac{\omega c + \sqrt{\varepsilon^2\,\omega^2 + \omega c^2}}{\varepsilon\,\omega}, 0, 1\right\},\right.$$

$$\left.\left.\left\{\frac{-\omega c + \sqrt{\varepsilon^2\,\omega^2 + \omega c^2}}{\varepsilon\,\omega}, 0, 1\right\}\right\}\right\}$$

((5-10))

5.10 A one-electron atom whose ground state is nondegenerate is placed in a uniform electric field in the z-direction. Obtain an approximate expression for the induced electric dipole moment of the ground state by considering the expectation value of ez with respect to the perturbed state vector computed to first order. Show that the same expression can also be obtained from the energy shift $\Delta = -\alpha|\mathbf{E}|^2/2$ of the ground state computed to second order. (*Note*: α stands for the polarizability.) Ignore spin.

((**Solution**))

The ground state is non-degenerate.

$$|\psi_0\rangle = |n=1, l=0, m=0\rangle$$

Suppose that the charge of electron is $q\ (=-e)$ Under the perturbation ($\hat{H}_1 = -q\varepsilon\hat{z}$), we have the average value of electric dipole moment ($q\hat{z}$),

$$\langle\psi_{1s}|q\hat{z}|\psi_{1s}\rangle = (\langle 1,0,0| - q\varepsilon\sum_{\substack{n\neq 1\\ l,m}}\langle n,l,m|\frac{\langle n,l,m|\hat{z}|1,0,0\rangle^*}{(E_1^{(0)} - E_n^{(0)})} + ...)(q\hat{z})$$

$$(|1,0,0\rangle - q\varepsilon\sum_{\substack{n\neq 1\\ l,m}}|n,l,m\rangle\frac{\langle n,l,m|\hat{z}|1,0,0\rangle}{(E_1^{(0)} - E_n^{(0)})} + ...)$$

or

$$\langle\psi_{1s}|q\hat{z}|\psi_{1s}\rangle = -2q^2\varepsilon\sum_{\substack{n\neq 1\\ l,m}}\frac{|\langle n,l,m|\hat{z}|1,0,0\rangle|^2}{E_1^{(0)} - E_n^{(0)}} = \alpha\varepsilon$$

The polarizability α is given by

$$\alpha = -2q^2\sum_{\substack{n\neq 1\\ l,m}}\frac{|\langle n,l,m|\hat{z}|1,0,0\rangle|^2}{E_1^{(0)} - E_n^{(0)}}$$

Under the perturbation, the energy to the second order:

$$E_1^{(0)} = -R$$

$$E_1^{(1)} = \langle \psi_0 | \hat{H}_1 | \psi_0 \rangle = \langle 1,0,0 | \hat{H}_1 | 1,0,0 \rangle = 0$$

$$E_1^{(2)} = q^2 \varepsilon^2 \sum_{n \neq 1, l, m} \frac{\left| \langle n,l,m | \hat{z} | 1,0,0 \rangle \right|^2}{E_1^{(0)} - E_n^{(0)}}$$

where

$$E_n^{(0)} = -\frac{R}{n^2}$$

$$\Delta E_n = E_n^{(2)} = -\frac{1}{2} \alpha \varepsilon^2 = q^2 \varepsilon^2 \sum_{n \neq 1, l, m} \frac{\left| \langle n,l,m | \hat{z} | 1,0,0 \rangle \right|^2}{E_1^{(0)} - E_n^{(0)}}$$

or

$$\alpha = -2q^2 \sum_{\substack{n \neq 1 \\ l,m}} \frac{\langle n,1,m | \hat{z} | 1,0,0 \rangle^2}{E_1^{(0)} - E_n^{(0)}}$$

This value of α is the same as that derived above.

((5-11))

5.11 Evaluate the matrix elements (or expectation values) given below. If any vanishes, explain why it vanishes using simple symmetry (or other) arguments.

a. $\langle n=2,l=1,m=0|x|n=2,l=0,m=0\rangle$.

b. $\langle n=2,l=1,m=0|p_z|n=2,l=0,m=0\rangle$.

[In (a) and (b), $|nlm\rangle$ stands for the energy eigenket of a nonrelativistic hydrogen atom with spin ignored.]

c. $\langle L_z\rangle$ for an electron in a central field with $j=\frac{9}{2}$, $m=\frac{7}{2}$, $l=4$.

d. $\langle \text{singlet}, m_s=0|S_z^{(e-)}-S_z^{(e+)}|\text{triplet}, m_s=0\rangle$ for an s-state positronium.

e. $\langle \mathbf{S}^{(1)}\cdot\mathbf{S}^{(2)}\rangle$ for the ground state of a hydrogen *molecule*.

((**Solution**))

(a)

$$\langle n'=2,l'=1.m'=0|\hat{x}|n=2,l=0,m=0\rangle$$

Spherical tensor of rank 1

$$\hat{T}_1^{(1)}=-\frac{1}{\sqrt{2}}(\hat{x}+i\hat{y}),\qquad \hat{T}_{-1}^{(1)}=\frac{1}{\sqrt{2}}(\hat{x}-i\hat{y}),\qquad \hat{T}_0^{(1)}=\hat{z}$$

or

$$\hat{x}=\frac{1}{\sqrt{2}}(\hat{T}_{-1}^{(1)}-\hat{T}_{+1}^{(1)})$$

Then we have

$$\langle n'=2,l'=1.m'=0|\hat{x}|n=2,l=0,m=0\rangle=\frac{1}{\sqrt{2}}\langle n'=2,l'=1.m'=0|\hat{T}_{-1}^{(1)}-\hat{T}_{+1}^{(1)}|n=2,l=0,m=0\rangle$$

The Wigner-Eckart theorem:

$$\langle n',l',m'|\hat{T}_q^{(k)}|n,l,m\rangle=0\qquad \text{unless } m'=m+q,\ l'=k+l,\ k+l-1,\ \ldots.,\ |k-l|$$

Using this theorem, we have

$$\langle n'=2,l'=1.m'=0|\hat{T}^{(1)}_{\pm 1}|n=2,l=0,m=0\rangle = 0$$

leading to

$$\langle n'=2,l'=1.m'=0|\hat{x}|n=2,l=0,m=0\rangle = 0$$

(b)

The Hamiltonian of the hydrogen atom is given by

$$\hat{H} = \frac{1}{2\mu}\hat{\boldsymbol{p}}^2 + V(|\hat{\boldsymbol{r}}|)$$

The commutation relation:

$$\begin{aligned}[\hat{H},\hat{z}] &= \frac{1}{2\mu}[\hat{p}_z{}^2,\hat{z}] \\ &= \frac{1}{2\mu}\{\hat{p}_z[\hat{p}_z,\hat{z}]+[\hat{p}_z,\hat{z}]\hat{p}_z\} \\ &= \frac{\hbar}{\mu i}\hat{p}_z\end{aligned}$$

or

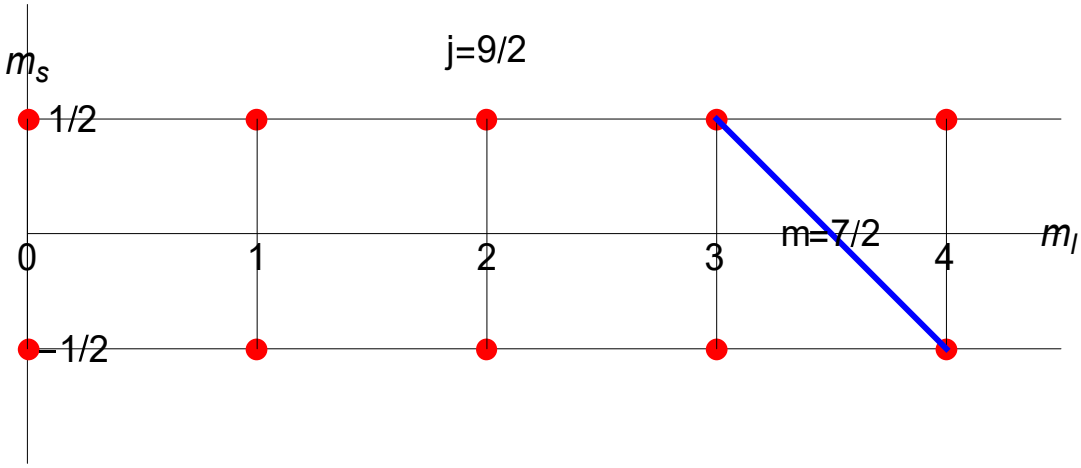
$$\hat{p}_z = \frac{i\mu}{\hbar}[\hat{H},\hat{z}]$$

$$\begin{aligned}\langle n',l',m'|\hat{p}_z|n,l,m\rangle &= \frac{i\mu}{\hbar}\langle n',l',m'|[\hat{H},\hat{z}]|n,l,m\rangle \\ &= \frac{i\mu}{\hbar}(E_{n'}-E_n)\langle n',l',m'|\hat{z}|n,l,m\rangle\end{aligned}$$

When $n'=n$

$$\langle n',l',m'|\hat{p}_z|n,l,m\rangle = 0$$

(c)



$l = 4\,,\qquad s = \frac{1}{2}$

Addition of the angular momentum:

$$j = 4 + \frac{1}{2} = \frac{9}{2},\qquad j = 4 - \frac{1}{2} = \frac{7}{2}$$

Clebsch-Gordan co-efficient:

$$\left| j = \frac{9}{2}, m = \frac{7}{2} \right\rangle = \sqrt{\frac{l + m + \frac{1}{2}}{2l+1}} \left| m_l = 3, m_s = \frac{1}{2} \right\rangle + \sqrt{\frac{l - m + \frac{1}{2}}{2l+1}} \left| m_l = 4, m_s = -\frac{1}{2} \right\rangle$$

$$= \sqrt{\frac{4 + \frac{7}{2} + \frac{1}{2}}{9}} \left| m_l = 3, m_s = \frac{1}{2} \right\rangle + \sqrt{\frac{4 - \frac{7}{2} + \frac{1}{2}}{9}} \left| m_l = 4, m_s = -\frac{1}{2} \right\rangle$$

$$= \frac{2\sqrt{2}}{3} \left| m_l = 3, m_s = \frac{1}{2} \right\rangle + \frac{1}{3} \left| m_l = 4, m_s = -\frac{1}{2} \right\rangle$$

$$\hat{L}_z \left| j = \frac{9}{2}, m = \frac{7}{2} \right\rangle = \frac{2\sqrt{2}}{3} \hat{L}_z \left| m_l = 3, m_s = \frac{1}{2} \right\rangle + \frac{1}{3} \hat{L}_z \left| m_l = 4, m_s = -\frac{1}{2} \right\rangle$$

$$= 2\sqrt{2}\hbar \left| m_l = 3, m_s = \frac{1}{2} \right\rangle + \frac{1}{3} 4\hbar \left| m_l = 4, m_s = -\frac{1}{2} \right\rangle$$

$$\left\langle j=\frac{9}{2},m=\frac{7}{2}\middle|\hat{L}_z\middle|j=\frac{9}{2},m=\frac{7}{2}\right\rangle=\begin{pmatrix}\frac{2\sqrt{2}}{3} & \frac{1}{3}\end{pmatrix}\begin{pmatrix}2\sqrt{2}\hbar \\ \frac{4}{3}\hbar\end{pmatrix}=\frac{28}{9}\hbar$$

(d)

$$\left|\text{singlet } (m=0)\right\rangle=\frac{1}{\sqrt{2}}[\left|+-\right\rangle-\left|-+\right\rangle]$$

$$\left|\text{triplet } (m=0)\right\rangle=\frac{1}{\sqrt{2}}[\left|+-\right\rangle+\left|-+\right\rangle]$$

$$(\hat{S}_z^{(e-)}-\hat{S}_z^{(e+)})\left|\text{triplet } (m=0)\right\rangle=\frac{1}{\sqrt{2}}(\hat{S}_z^{(e-)}-\hat{S}_z^{(e+)})[\left|+-\right\rangle+\left|-+\right\rangle]$$
$$=\frac{\hbar}{\sqrt{2}}(\left|+-\right\rangle-\left|-+\right\rangle=\frac{\hbar}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}$$

$$\left\langle\text{singlet } (m=0)\middle|(\hat{S}_z^{(e-)}-\hat{S}_z^{(e+)})\middle|\text{triplet } (m=0)\right\rangle=\frac{1}{\sqrt{2}}\frac{\hbar}{\sqrt{2}}\begin{pmatrix}1 & -1\end{pmatrix}\begin{pmatrix}1\\-1\end{pmatrix}=\hbar$$

(e)

$$\hat{\boldsymbol{S}}_1\cdot\hat{\boldsymbol{S}}_2=\frac{\hbar^2}{4}(\hat{\boldsymbol{\sigma}}_1\cdot\hat{\boldsymbol{\sigma}}_2)=\frac{\hbar^2}{4}(2\hat{P}_{12}-\hat{1})$$

where $\hat{P}_{12}$ is the Dirac exchange operator.

The ground state is expressed by $\left|\psi_G\right\rangle=\frac{1}{\sqrt{2}}[\left|+-\right\rangle-\left|-+\right\rangle]$

$$(\hat{\boldsymbol{S}}_1\cdot\hat{\boldsymbol{S}}_2)\left|\psi_G\right\rangle=\frac{\hbar^2}{4}(2\hat{P}_{12}-\hat{1})\left|\psi_G\right\rangle$$
$$=\frac{\hbar^2}{4}(2\hat{P}_{12}-\hat{1})\frac{1}{\sqrt{2}}[\left|+-\right\rangle-\left|-+\right\rangle]$$
$$=-\frac{\hbar^2}{4}\frac{3}{\sqrt{2}}[\left|+-\right\rangle-\left|-+\right\rangle]$$

$$\langle \psi_G | (\hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2) | \psi_G \rangle = -\frac{\hbar^2}{4}\frac{3}{2}\begin{pmatrix}1 & -1\end{pmatrix}\begin{pmatrix}1\\-1\end{pmatrix} = -\hbar^2\frac{3}{4}$$

((5-12))

5.12 A p-orbital electron characterized by $|n,l=1,m=\pm1,0\rangle$ (ignore spin) is subjected to a potential

$$V=\lambda(x^2-y^2) \quad (\lambda=\text{constant}).$$

a. Obtain the "correct" zeroth-order energy eigenstates that diagonalize the perturbation. You need not evaluate the energy shifts in detail, but show that the original threefold degeneracy is now completely removed.
b. Because V is invariant under time reversal and because there is no longer any degeneracy, we expect each of the energy eigenstates obtained in (a) to go into itself (up to a phase factor or sign) under time reversal. Check this point explicitly.

((**Solution**))

$|n,l=1,m=\pm1\rangle$ (ignore spin); p-orbital electron

(a)

$\hat{V}=\lambda(\hat{x}^2-\hat{y}^2)$ (λ: real)

$\hat{x}^2-\hat{y}^2=\hat{T}_2^{(2)}+\hat{T}_{-2}^{(2)}$

where the spherical tensor of rank 2,

$$\hat{T}_2^{(2)}=\frac{1}{2}(\hat{x}+i\hat{y})(\hat{x}+i\hat{y}), \qquad \hat{T}_{-2}^{(2)}=\frac{1}{2}(\hat{x}-i\hat{y})(\hat{x}-i\hat{y})$$

The matrix element

$$\langle n,l=1,m'|\hat{V}|n,l=1,m\rangle=\lambda\langle n,l=1,m'|\hat{T}_2^{(2)}+\hat{T}_{-2}^{(2)}|n,l=1,m\rangle$$

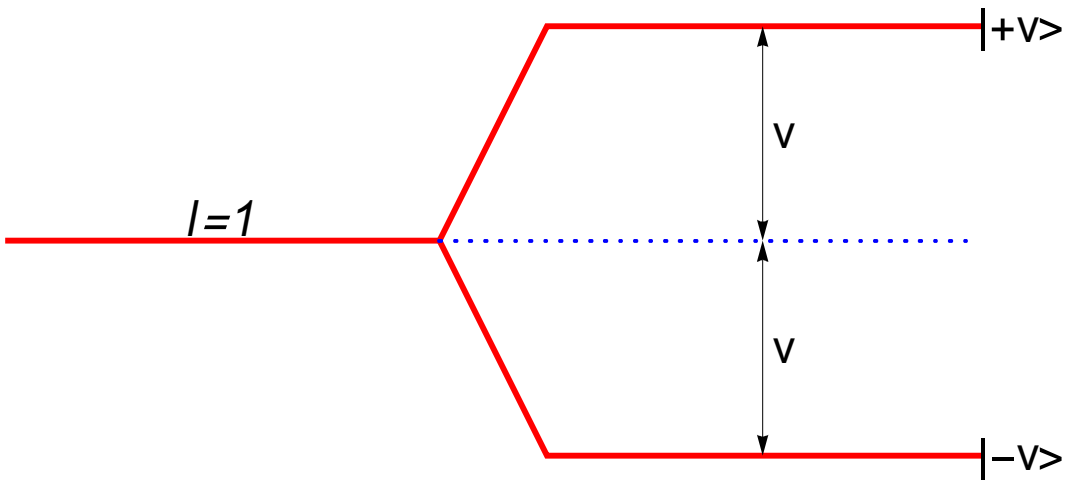
According to the Wigner-Eckart theorem,

$\langle n,l=1,m'|\hat{T}_{\pm2}^{(2)}|n,l=1,m\rangle$ is equal to zero unless $m'=m\pm2$

We denote $|n,l=1,m=\pm1,0\rangle$ as $|+1\rangle$, $|0\rangle$, and $|-1\rangle$. The matrix of $\hat{V}$ is as follows.

$$\langle +1|\hat{V}|-1\rangle = \langle -1|\hat{V}|+1\rangle = v$$

since $\hat{V}$ is Hermitian.



$$\hat{V}|0\rangle = 0\,, \qquad \hat{V}|+1\rangle = v|-1\rangle\,, \qquad \hat{V}|-1\rangle = v|+1\rangle$$

Since $\hat{V} = v\hat{\sigma}_x = v\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$, we have the eigenkets and eignevlaues as

(i) Eigenvalue $+v$, eigenket $|\psi_{+v}\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}}[|+1\rangle + |-1\rangle]$

(ii) Eigenvalue $-v$, eigenket $|\psi_{-v}\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} = \frac{1}{\sqrt{2}}[|+1\rangle - |-1\rangle]$

(b) Θ (time reversal operator)
Since $\Theta|j,m\rangle = (-1)^m|j,-m\rangle$

$$\Theta|+1\rangle = -|-1\rangle$$

$$\Theta|0\rangle = |0\rangle$$

$$\Theta|-1\rangle = -|+1\rangle$$

Thus we have

$$\hat{\Theta}\left|\psi_{+v}\right\rangle = \frac{1}{\sqrt{2}}[\Theta\left|+1\right\rangle + \Theta\left|-1\right\rangle] = \frac{1}{\sqrt{2}}[-\left|-1\right\rangle - \left|+1\right\rangle] = -\left|\psi_{+v}\right\rangle$$

$$\hat{\Theta}\left|0\right\rangle = \left|0\right\rangle$$

$$\hat{\Theta}\left|\psi_{-v}\right\rangle = \frac{1}{\sqrt{2}}[\Theta\left|+1\right\rangle - \Theta\left|-1\right\rangle] = \frac{1}{\sqrt{2}}[-\left|-1\right\rangle + \left|+1\right\rangle] = \left|\psi_{-v}\right\rangle$$

((5-13))

5.13 Consider a spinless particle in a two-dimensional infinite square well:

$$V = \begin{cases} 0 & \text{for } 0 \le x \le a,\ 0 \le y \le a \\ \infty & \text{otherwise.} \end{cases}$$

a. What are the energy eigenvalues for the three lowest states? Is there any degeneracy?

b. We now add a potential

$$V_1 = \lambda xy,\ 0 \le x \le a,\ 0 \le y \le a.$$

Taking this as a weak perturbation, answer the following.

(i) Is the energy shift due to the perturbation linear or quadratic in λ for each of the three states?

(ii) Obtain expressions for the energy shifts of the three lowest states accurate to order λ. (You need not evaluate integrals that may appear.)

(iii) Draw an energy diagram with and without the perturbation for the three energy states. Make sure to specify which unperturbed state is connected to which perturbed state.

((**Solution**))

$V = 0$ for $0 \le x \le a$ and $0 \le y \le a$.

$V = \infty$ otherwise.

Schrödinger equation

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\psi(x,y) = E\psi(x,y)$$

$$\psi(x,y) = X(x)Y(y)$$

$$E = \frac{\hbar^2}{2m}(k_x{}^2 + k_y{}^2)$$

$$-\frac{\hbar^2}{2m}(X''Y + XY'') = \frac{\hbar^2}{2m}(k_x{}^2 + k_y{}^2)XY$$

$$\frac{X''}{X} + \frac{Y''}{Y} = -(k_x{}^2 + k_y{}^2)$$

We assume

$$X'' = -k_x^2 X$$

$$X = A\sin(k_x a) + B\cos(k_x a)$$

with the boundary condition

$X = 0$ at $x = 0$ and a.

$B = 0$, and

$\sin(k_x a) = 0$ or $k_x a = n_x \pi$ ($n_x = 1, 2, 3, \ldots..$)

Similarly for Y, we have

$$Y'' = -k_y^2 Y$$

$$Y = C\sin(k_y a) + D\cos(k_y a)$$

with a boundary condition

$Y = 0$ at $y = 0$ and $y = a$.

$D = 0$, and

$\sin(k_y a) = 0$ or $k_y a = n_y \pi$ ($n_y = 1, 2, 3, \ldots..$)

Then we have

$$E^{(0)}(n_x, n_y) = \frac{\hbar^2}{2m}(\frac{\pi}{a})^2(n_x^2 + n_y^2) = E_a(n_x^2 + n_y^2)$$

$$\psi_{n_x, n_y}(x, y) = \frac{2}{a}\sin\left(\frac{n_x \pi}{a}x\right)\sin\left(\frac{n_y \pi}{a}y\right)$$

where $n_x = 1, 2, 3, 4, \ldots..$ and $n_y = 1, 2, 3, 4, \ldots.$

$$E_a = \frac{\hbar^2}{2m}(\frac{\pi}{a})^2$$

(a)

Ground state ($n_x = 1$, $n_y = 1$)

$g_1 = 1$ (non-degeneracy)

$$E^{(0)}(n_x = 1, n_y = 1) = E^{(0)}(1,1) = 2E_a$$

First excited state ($n_x = 1$, $n_y = 2$, and $n_x = 2$, $n_y = 1$)

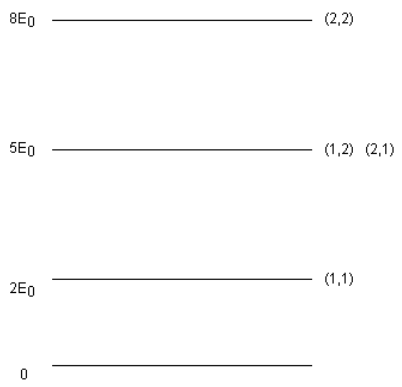
$g_2 = 2$ (doubly degeneracy)

$$E^{(0)}(n_x = 1, n_y = 2) = E^{(0)}(n_x = 2, n_y = 1) = 5E_a$$

Second excited state ($n_x = 2$, $n_y = 2$)

$g_1 = 1$ (non-degeneracy)

$$E^{(0)}(n_x = 2, n_y = 2) = E^{(0)}(2,2) = 8E_a$$



(b)
The perturbation

$$\hat{V}_1 = \lambda \hat{x}\hat{y}$$

The matrix element

$$\left\langle n_x', n_y' \middle| \hat{V}_1 \middle| n_x, n_y \right\rangle = \lambda \left(\frac{2}{a}\right)^2 \int_0^a dx x \sin\left(\frac{n_x'\pi}{a}x\right) in\left(\frac{n_x\pi}{a}x\right) \int_0^a dy y \sin\left(\frac{n_y'\pi}{a}y\right) \sin\left(\frac{n_y\pi}{a}y\right)$$

We calculate the matrix element using Mathematica.

Ground state is non-degenerate

$$E_1 = E^{(0)}(1,1) + E^{(1)}(1,1) + E^{(2)}(1,1) + ... = 2E_a + \lambda\frac{a^2}{4} - 0.00558305\frac{\lambda^2}{E_a}a^4$$

with

$$E^{(0)}(1,1) = 2E_a$$

$$E^{(1)}(1,1) = \langle 1,1|\lambda\hat{V}_1|1,1\rangle = \lambda\frac{a^2}{4}$$

$$E^{(2)}(1,1) = \sum_{(n_x,n_y)\neq(1,1)} \frac{\left|\langle 1,1|\lambda\hat{V}_1|n_x,n_y\rangle\right|^2}{E^{(0)}(1,1) - E^{(0)}(n_x,n_y)}$$

$$= \frac{\left|\langle 1,1|\lambda\hat{V}_1|1,2\rangle\right|^2}{E^{(0)}(1,1) - E^{(0)}(1,2)} + \frac{\left|\langle 1,1|\lambda\hat{V}_1|2,1\rangle\right|^2}{E^{(0)}(1,1) - E^{(0)}(2,1)} + \frac{\left|\langle 1,1|\lambda\hat{V}_1|2,2\rangle\right|^2}{E^{(0)}(1,1) - E^{(0)}(2,2)}$$

$$== -\frac{\lambda^2}{E_a}a^4\left(2\frac{\left(\frac{8}{9\pi^2}\right)^2}{3} + \frac{\left(\frac{256}{81\pi^4}\right)^2}{6}\right)$$

$$= -0.00558305\frac{\lambda^2}{E_a}a^4$$

where

$$\langle 1,1|\hat{V}_1|1,2\rangle = -\frac{8a^2}{9\pi^2}, \quad \langle 1,1|\hat{V}_1|2,1\rangle = -\frac{8a^2}{9\pi^2}, \quad \langle 1,1|\hat{V}_1|2,2\rangle = \frac{256a^2}{81\pi^4}$$

Second excited state is non-degenerate

$$E_2 = E^{(0)}(2,2) + E^{(1)}(2,2) + E^{(2)}(2,2) + ...$$
$$= 8E_a + \lambda\frac{a^2}{4} + 0.005583\frac{\lambda^2 a^4}{E_a}$$

with

$$E^{(0)}(2,2) = 8E_a$$

$$E^{(1)}(2,2) = \langle 2,2|\hat{V}_1|2,2\rangle = \lambda\frac{a^2}{4}$$

$$E^{(2)}(2,2) = \sum_{(n_x,n_y)\neq(1,1)} \frac{\left|\left\langle 2,2\left|\lambda\hat{V}_1\right|n_x,n_y\right\rangle\right|^2}{E^{(0)}(1,1)-E^{(0)}(n_x,n_y)}$$

$$= \frac{\left|\left\langle 2,2\left|\lambda\hat{V}_1\right|1,1\right\rangle\right|^2}{E^{(0)}(2,2)-E^{(0)}(1,1)} + \frac{\left|\left\langle 2,2\left|\lambda\hat{V}_1\right|2,1\right\rangle\right|^2}{E^{(0)}(2,2)-E^{(0)}(2,1)} + \frac{\left|\left\langle 2,2\left|\lambda\hat{V}_1\right|1,2\right\rangle\right|^2}{E^{(0)}(2,2)-E^{(0)}(1,2)}$$

$$== \frac{\lambda^2 a^4}{E_a}\left(\frac{\left(\frac{256}{81\pi^4}\right)^2}{6} + \frac{2\left(\frac{8}{9\pi^2}\right)^2}{3}\right)$$

$$= 0.005583\frac{\lambda^2 a^4}{E_a}$$

where

$$\left\langle 2,2\left|\hat{V}_1\right|1,1\right\rangle = \frac{256a^2}{81\pi^4}, \qquad \left\langle 2,2\left|\hat{V}_1\right|2,1\right\rangle = -\frac{8a^2}{9\pi^2}, \qquad \left\langle 2,2\left|\hat{V}_1\right|1,2\right\rangle = -\frac{8a^2}{9\pi^2}$$

<u>First excited state (doubly degenerate)</u>

$$E^{(0)}(n_x=1,n_y=2) = E^{(0)}(n_x=2,n_y=1) = 5E_a$$

$$\left\langle 1,2\left|\hat{V}_1\right|1,2\right\rangle = \frac{a^2}{4}, \qquad \left\langle 1,2\left|\hat{V}_1\right|2,1\right\rangle = \frac{256a^2}{81\pi^4},$$

$$\left\langle 2,1\left|\hat{V}_1\right|1,2\right\rangle = \frac{256a^2}{81\pi^4}, \qquad \left\langle 2,1\left|\hat{V}_1\right|2,1\right\rangle = \frac{a^2}{4}$$

$$M = \begin{pmatrix} \frac{1}{4} & \frac{256}{81\pi^4} \\ \frac{256}{81\pi^4} & \frac{1}{4} \end{pmatrix} = \frac{1}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{256}{81\pi^4}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

in the unit of λa^2

Eigensystem[M]

$$\left\{\left\{\frac{1}{4} + \frac{256}{81\ \pi^4}, \frac{1}{4} - \frac{256}{81\ \pi^4}\right\}, \{\{1, 1\}, \{-1, 1\}\}\right\}$$

Then we have

(i)

$$E_3^{\,1} = 5E_a + \lambda a^2\left(\frac{1}{4} + \frac{256}{81\pi^4}\right) = 5E_a + \lambda a^2 0.282446$$

$$\left|\psi_3^1\right\rangle = \frac{1}{\sqrt{2}}\left[\left|n_x = 1, n_y = 2\right\rangle + \left|n_x = 1, n_y = 1\right\rangle\right]$$

(ii)

$$E_3^{\,2} = 5E_a + \lambda a^2\left(\frac{1}{4} - \frac{256}{81\pi^4}\right) = 5E_a + \lambda a^2 0.217554$$

$$\left|\psi_3^2\right\rangle = \frac{1}{\sqrt{2}}\left[\left|n_x = 1, n_y = 2\right\rangle - \left|n_x = 1, n_y = 1\right\rangle\right]$$

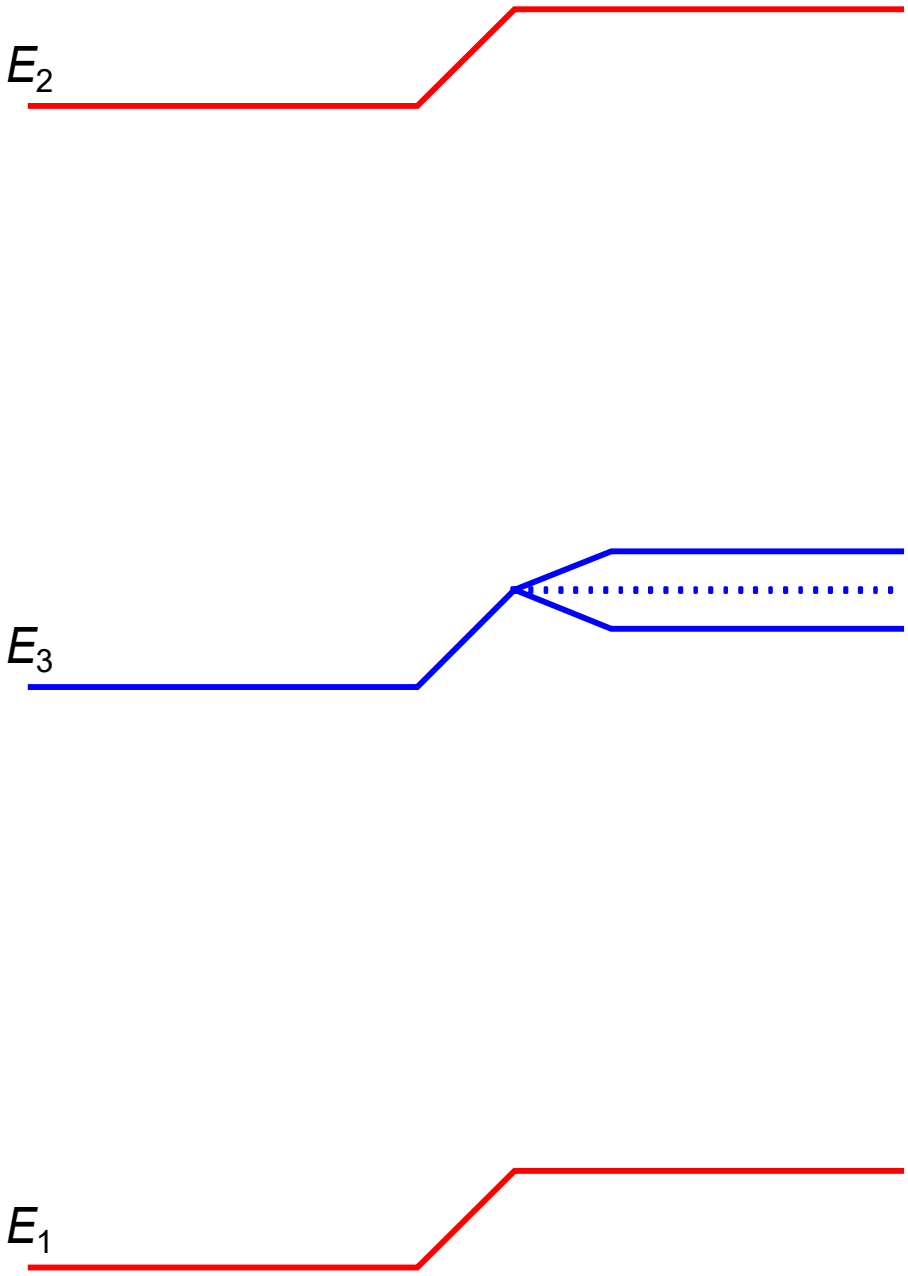


Fig. Energy level splitting due to the perturbation.

$$E_1 = 2E_a + \lambda\frac{a^2}{4} - 0.00558305\frac{\lambda^2}{E_a}a^4$$

$$E_3^{\,1} = 5E_a + \lambda a^2 0.282446\,.$$

$$E_3^{\,2} = 5E_a + \lambda a^2 0.217554$$

$$E_2 == 8E_a + \lambda\frac{a^2}{4} + 0.005583\frac{\lambda^2 a^4}{E_a}$$

((**Mathematica**))

```
Clear["Global`*"];
G[n1_, m1_, n2_, m2_] :=
  (2/a)^2
    (Integrate[x Sin[(n1 π)/a x] Sin[(n2 π)/a x], {x, 0, a}]
    Integrate[y Sin[(m1 π)/a y] Sin[(m2 π)/a y],
      {y, 0, a}]) // Simplify;

G[1, 1, 1, 1]
```

$$\frac{a^2}{4}$$

```
G[1, 1, 1, 2]
```

$$-\frac{8\,a^2}{9\,\pi^2}$$

```
G[1, 1, 2, 1]
```

$$-\frac{8\,a^2}{9\,\pi^2}$$

G[1, 1, 2, 2]

$$\frac{256\,a^2}{81\,\pi^4}$$

G[2, 2, 2, 2]

$$\frac{a^2}{4}$$

G[2, 2, 1, 1]

$$\frac{256\,a^2}{81\,\pi^4}$$

G[2, 2, 2, 1]

$$-\frac{8\,a^2}{9\,\pi^2}$$

G[2, 1, 1, 2]

$$\frac{256\,a^2}{81\,\pi^4}$$

((**5.14**))

5.14 The Hamiltonian matrix for a two-state system can be written as

$$\mathscr{H} = \begin{pmatrix} E_1^0 & \lambda\Delta \\ \lambda\Delta & E_2^0 \end{pmatrix}.$$

Clearly the energy eigenfunctions for the unperturbed problems ($\lambda = 0$) are given by

$$\phi_1^{(0)} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \phi_2^{(0)} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

a. Solve this problem *exactly* to find the energy eigenfunctions ψ_1 and ψ_2 and the energy eigenvalues E_1 and E_2.

b. Assuming that $\lambda|\Delta| \ll |E_1^0 - E_2^0|$, solve the same problem using time-independent perturbation theory up to first order in the energy eigenfunctions and up to second order in the energy eigenvalues. Compare with the exact results obtained in (a).

c. Suppose the two unperturbed energies are "almost degenerate," that is,

$$|E_1^0 - E_2^0| \ll \lambda|\Delta|.$$

Show that the exact results obtained in (a) closely resemble what you would expect by applying *degenerate* perturbation theory to this problem with E_1^0 set exactly equal to E_2^0.

((**Solution**))

$$\boldsymbol{S}_n = \frac{1}{2}\hbar\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}}, \qquad \boldsymbol{S}_n|\pm\rangle_n = \pm\frac{1}{2}\hbar|\pm\rangle_n.$$

(a)

$$H = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}$$
$$= \frac{1}{2}(H_{11}+H_{22})I + \frac{1}{2}(H_{11}-H_{22})\sigma_z$$
$$+ \frac{1}{2}(H_{12}+H_{21})\sigma_x + \frac{1}{2i}(H_{12}-H_{21})\sigma_y$$

Since $H_{12} = H_{21} = \lambda\Delta$, $H_{11} = E_1^0$, $H_{22} = E_2^0$

$$\hat{H} = \frac{1}{2}(E_1^0 + E_2^0)\hat{1} + \lambda\Delta\hat{\sigma}_x + \frac{1}{2}(E_1^0 - E_2^0)\hat{\sigma}_z +$$

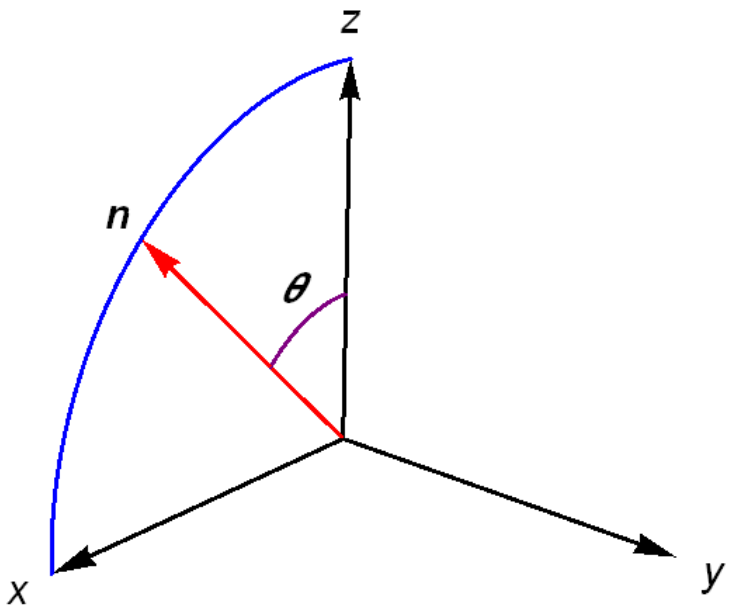
$$= \frac{1}{2}(E_1^0 + E_2^0)\hat{1}$$

$$+ \sqrt{(\lambda\Delta)^2 + \frac{1}{4}(E_1^0 - E_2^0)^2}\left[\frac{\frac{1}{2}(E_1^0 - E_2^0)\hat{\sigma}_z}{\sqrt{(\lambda\Delta)^2 + \frac{1}{4}(E_1^0 - E_2^0)^2}} + \frac{\lambda\Delta\hat{\sigma}_x}{\sqrt{(\lambda\Delta)^2 + \frac{1}{4}(E_1^0 - E_2^0)^2}}\right]$$

$$= \frac{1}{2}(E_1^0 + E_2^0)\hat{1} + \sqrt{(\lambda\Delta)^2 + \frac{1}{4}(E_1^0 - E_2^0)^2}\,(\hat{\boldsymbol{\sigma}} \cdot \boldsymbol{n})$$

where

$$n_x = \frac{\lambda\Delta}{\sqrt{(\lambda\Delta)^2 + \frac{1}{4}(E_1^0 - E_2^0)^2}}, \qquad n_z = \frac{\frac{1}{2}(E_1^0 - E_2^0)}{\sqrt{(\lambda\Delta)^2 + \frac{1}{4}(E_1^0 - E_2^0)^2}}$$



We introduce the angle θ which is defined by

$$\tan\theta = \frac{n_x}{n_z} = \frac{\lambda\Delta}{\frac{1}{2}(E_1^0 - E_2^0)} = \frac{2\lambda\Delta}{E_1^0 - E_2^0}$$

Note that

$$(\boldsymbol{\sigma}\cdot\boldsymbol{n})\left|\pm\boldsymbol{n}\right\rangle = \pm\left|\pm\boldsymbol{n}\right\rangle$$

$$\begin{aligned}
\left|\varphi_1\right\rangle &= \left|+\boldsymbol{n}\right\rangle & \left|\varphi_2\right\rangle &= \left|-\boldsymbol{n}\right\rangle \\
&= \cos\frac{\theta}{2}\left|+z\right\rangle + \sin\frac{\theta}{2}\left|-z\right\rangle \quad , & &= -\sin\frac{\theta}{2}\left|+z\right\rangle + \cos\frac{\theta}{2}\left|-z\right\rangle \\
&= \cos\frac{\theta}{2}\left|\varphi_1^{(0)}\right\rangle + \sin\frac{\theta}{2}\left|\varphi_2^{(0)}\right\rangle & &= -\sin\frac{\theta}{2}\left|\varphi_1^{(0)}\right\rangle + \cos\frac{\theta}{2}\left|\varphi_2^{(0)}\right\rangle
\end{aligned}$$

$$\begin{aligned}
H\left|+\right\rangle_{\boldsymbol{n}} &= [\frac{1}{2}(E_1^0+E_2^0)\hat{1} + \sqrt{(\lambda\Delta)^2+\frac{1}{4}(E_1^0-E_2^0)^2}\,(\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{n})]\left|+\boldsymbol{n}\right\rangle \\
&= [\frac{1}{2}(E_1^0+E_2^0) + \sqrt{(\lambda\Delta)^2+\frac{1}{4}(E_1^0-E_2^0)^2}\,]\left|+\boldsymbol{n}\right\rangle \\
&= E_1\left|+\boldsymbol{n}\right\rangle
\end{aligned}$$

$$\begin{aligned}
H\left|-\right\rangle_{\boldsymbol{n}} &= [\frac{1}{2}(E_1^0+E_2^0)\hat{1} + \sqrt{(\lambda\Delta)^2+\frac{1}{4}(E_1^0-E_2^0)^2}\,(\boldsymbol{\sigma}\cdot\boldsymbol{n})]\left|-\boldsymbol{n}\right\rangle \\
&= [\frac{1}{2}(E_1^0+E_2^0) - \sqrt{(\lambda\Delta)^2+\frac{1}{4}(E_1^0-E_2^0)^2}\,]\left|-\boldsymbol{n}\right\rangle \\
&= E_2\left|-\boldsymbol{n}\right\rangle
\end{aligned}$$

Thus, we have the eigenvalues of the Hamiltonian *H*,

$$E_1 = \frac{1}{2}(E_1^0+E_2^0) + \sqrt{(\lambda\Delta)^2+\frac{1}{4}(E_1^0-E_2^0)^2}\,]$$

and

$$E_1 = [\frac{1}{2}(E_1^0+E_2^0) + \sqrt{(\lambda\Delta)^2+\frac{1}{4}(E_1^0-E_2^0)^2}\,]$$

$$E_2 = [\frac{1}{2}(E_1^0+E_2^0) - \sqrt{(\lambda\Delta)^2+\frac{1}{4}(E_1^0-E_2^0)^2}\,]$$

(b) Perturbation

$$H = H_0 + H'$$

with $\lambda|\Delta| << |E_1^0 - E_2^0|$

$$H_0 = \begin{pmatrix} E_1^0 & 0 \\ 0 & E_2^0 \end{pmatrix}$$

$$H' = \begin{pmatrix} 0 & \lambda\Delta \\ \lambda\Delta & 0 \end{pmatrix}$$

$$H_0|\phi_1^{(0)}\rangle = E_1^{(0)}|\phi_1^{(0)}\rangle, \qquad H_0|\phi_2^{(0)}\rangle = E_2^{(0)}|\phi_2^{(0)}\rangle$$

We assume that $\Delta > 0$. We apply the perturbation theory (non-degenerate case) to this problem,

$$|\phi_1^{(1)}\rangle = |\phi_1^{(0)}\rangle + \frac{\lambda\Delta}{E_1^0 - E_2^0}|\phi_2^{(0)}\rangle$$

$$|\phi_2^{(1)}\rangle = |\phi_2^{(0)}\rangle + \frac{\lambda\Delta}{E_2^0 - E_1^0}|\phi_1^{(0)}\rangle$$

with

$$E_1 = E_1^0 + \frac{(\lambda\Delta)^2}{E_1^0 - E_2^0},$$

$$E_2 = E_2^0 + \frac{(\lambda\Delta)^2}{E_2^0 - E_1^0}$$

These results are compared with the exact results obtained in (a). (We assume $E_1^0 > E_2^0$).

$$\sqrt{(\lambda\Delta)^2 + \frac{1}{4}(E_1^0 - E_2^0)^2}] = \frac{1}{2}(E_1^0 - E_2^0)\sqrt{1 + \frac{4(\lambda\Delta)^2}{(E_1^0 - E_2^0)^2}}$$

$$= \frac{1}{2}(E_1^0 - E_2^0)[1 + \frac{2(\lambda\Delta)^2}{(E_1^0 - E_2^0)^2}]$$

$$\tan\theta \approx \sin\theta \approx \theta \approx \frac{2\lambda\Delta}{E_1^0 - E_2^0},$$

$$\cos\frac{\theta}{2} \approx 1, \qquad \sin\frac{\theta}{2} \approx \frac{\theta}{2} = \frac{\lambda\Delta}{E_1^0 - E_2^0}$$

Then we have

$$\left|\phi_1^{(1)}\right\rangle = \left|\phi_1^{(0)}\right\rangle + \frac{\lambda\Delta}{E_1^0 - E_2^0}\left|\phi_2^{(0)}\right\rangle$$

$$\left|\phi_2^{(1)}\right\rangle = \left|\phi_2^{(0)}\right\rangle + \frac{\lambda\Delta}{E_2^0 - E_1^0}\left|\phi_1^{(0)}\right\rangle$$

with

$$E_1 = E_1^0 + \frac{(\lambda\Delta)^2}{E_1^0 - E_2^0},$$

$$E_2 = E_2^0 - \frac{(\lambda\Delta)^2}{E_1^0 - E_2^0}$$

(c) Suppose that

$$E_1^0 = E_2^0$$

We apply the perturbation theory for the degenerate case.

$$H_1\left|\phi_1^0\right\rangle = \lambda\Delta\left|\phi_2^0\right\rangle$$

$$H_1\left|\phi_2^0\right\rangle = \lambda\Delta\left|\phi_1^0\right\rangle$$

We assume that

$$\left|\psi\right\rangle = C_1\left|\phi_1^0\right\rangle + C_2\left|\phi_2^0\right\rangle$$

$$\begin{pmatrix} 0 & \lambda\Delta \\ \lambda\Delta & 0 \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = E_1\begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

which has non-trivial solutions if

$$\begin{vmatrix} -E_1 & \lambda\Delta \\ \lambda\Delta & -E_1 \end{vmatrix} = 0$$

or

$$E_1^{\,2} - \lambda^2\Delta^2 = 0\,,$$

or

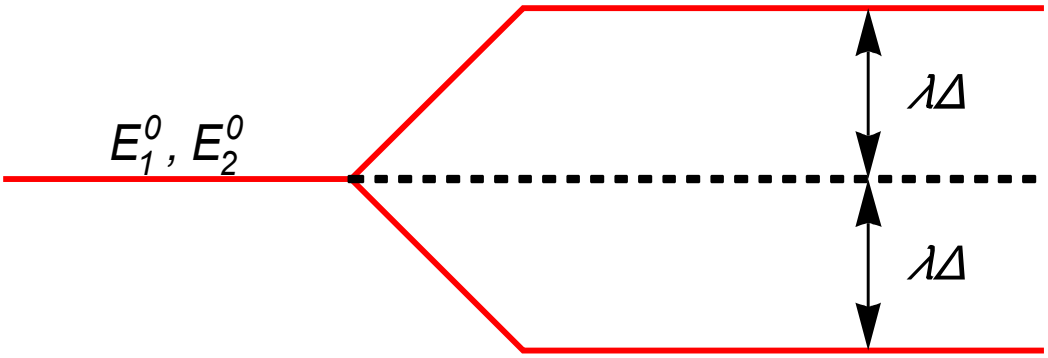
$$E_1 = \pm\lambda\Delta$$

For $E_1 = \lambda\Delta$, or total energy is $E_1^0 + \lambda\Delta$,

$$|\phi_1\rangle = \frac{1}{\sqrt{2}}(|\phi_1^0\rangle + |\phi_2^0\rangle)$$

For $E_1 = -\lambda\Delta$, or total energy is $E_1^0 - \lambda\Delta$,

$$|\phi_2\rangle = \frac{1}{\sqrt{2}}(-|\phi_1^0\rangle + |\phi_2^0\rangle)$$



Now these results are compared with those obtained in (a).

$$\tan\theta \approx \infty\,, \qquad \theta = \frac{\pi}{2}\,.$$

$$|\phi_1\rangle = \frac{1}{\sqrt{2}}(|\phi_1^0\rangle + |\phi_2^0\rangle)$$

$$|\phi_2\rangle = \frac{1}{\sqrt{2}}(-|\phi_1^0\rangle + |\phi_2^0\rangle)$$

with

$$E_1 = \frac{1}{2}(E_1^0 + E_2^0) + \lambda\Delta$$

$$E_2 = \frac{1}{2}(E_1^0 + E_2^0) - \lambda\Delta$$

These results are the same as those obtained above when $E_1^0 = E_2^0$

((**5-15**))

5.15 (This is a tricky problem because the degeneracy between the first and the second state is not removed in first order. See also Gottfried (1966), p. 397, Problem 1.) This problem is from Schiff (1968), p. 295, Problem 4. A system that has three unperturbed states can be represented by the perturbed Hamiltonian matrix

$$\begin{pmatrix} E_1 & 0 & a \\ 0 & E_1 & b \\ a^* & b^* & E_2 \end{pmatrix}$$

where $E_2 > E_1$. The quantities a and b are to be regarded as perturbations that are of the same order and are small compared with $E_2 - E_1$. Use the second-order nondegenerate perturbation theory to calculate the perturbed eigenvalues. (Is this procedure correct?) Then diagonalize the matrix to find the exact eigenvalues. Finally, use the second-order degenerate perturbation theory. Compare the three results obtained.

((**Solution**))

$$H = \begin{pmatrix} E_1 & 0 & a \\ 0 & E_1 & b \\ a^* & b^* & E_2 \end{pmatrix}$$

Det[H - λI] = 0

$$\lambda = E_1,$$

$$\lambda = \frac{E_1 + E_2}{2} \pm \frac{1}{2}\sqrt{(E_2 - E_1)^2 + 4(|a|^2 + |b|^2)}$$

$$= \frac{E_1 + E_2}{2} \pm \frac{1}{2}(E_2 - E_1)[1 + \frac{4(|a|^2 + |b|^2)}{(E_2 - E_1)^2}]^{1/2}$$

When $|a| << E_2 - E_1, |b| << E_2 - E_1$,

$$\lambda = \frac{E_1 + E_2}{2} \pm [\frac{E_2 - E_1}{2} + \frac{(|a|^2 + |b|^2)}{(E_2 - E_1)}]$$

or

$$\lambda = E_1 - \left(\frac{|a|^2 + |b|^2}{E_2 - E_1} \right)$$

$$\lambda = E_2 + \frac{|a|^2 + |b|^2}{E_2 - E_1}$$

((**Perturbation theory**))

$$H_0 = \begin{pmatrix} E_1 & 0 & 0 \\ 0 & E_1 & 0 \\ 0 & 0 & E_2 \end{pmatrix}, \quad H_1 = \begin{pmatrix} 0 & 0 & a \\ 0 & 0 & b \\ a^* & b^* & 0 \end{pmatrix}$$

$$\hat{H}_0 |\phi_\alpha\rangle = E_1 |\phi_\alpha\rangle$$

$$\hat{H}_0 |\phi_\beta\rangle = E_1 |\phi_\beta\rangle$$

$$\hat{H}_0 |\phi_\gamma\rangle = E_2 |\phi_\gamma\rangle$$

$|\phi_\gamma\rangle$ is the eigenket of $\hat{H}_0$ with the energy E_2. Since this state is nondegenerate, we can apply the perturbation theory (non-degenerate case) to calculate the energy

The resulting energy is

$$E_\gamma = E_2 + \langle\phi_3|\hat{H}_1|\phi_3\rangle + \frac{|\langle\phi_1|\hat{H}_1|\phi_3\rangle|^2}{E_2 - E_1} + \frac{|\langle\phi_2|\hat{H}_1|\phi_3\rangle|^2}{E_2 - E_1}$$

$$= E_2 + \frac{|a|^2 + |b|^2}{E_2 - E_1}$$

$$\hat{H}_1 |\phi_\alpha\rangle = a^* |\phi_\gamma\rangle$$

$$\hat{H}_1 |\phi_\beta\rangle = b^* |\phi_\gamma\rangle$$

$$\hat{H}_1 |\phi_\gamma\rangle = a|\phi_\alpha\rangle + b|\phi_\beta\rangle$$

$|\phi_\alpha\rangle$ and $|\phi_\alpha\rangle$ are degenerate.

This is the degenerate case.

First order:

The matrix element of H1 in the basis of $|\phi_\alpha\rangle$ and $|\phi_\alpha\rangle$ is equal to zero. So we need to calculate the second order

$$\sum_{\nu=1}^{g}\langle\varphi_{n,\mu}{}^{(0)}|\hat{\Lambda}|\varphi_{n,\nu}{}^{(0)}\rangle\langle\varphi_{n,\nu}{}^{(0)}|\psi_n{}^{(0)}\rangle = E_n{}^{(2)}\langle\varphi_{n,\mu}{}^{(0)}|\psi_n{}^{(0)}\rangle$$

$$\hat{\Lambda} = \sum_{k\neq n}\frac{\hat{H}_1|\psi_k{}^{(0)}\rangle\langle\psi_k{}^{(0)}|\hat{H}_1}{E_n{}^{(0)} - E_k{}^{(0)}} = \frac{\hat{H}_1|\phi_\gamma\rangle\langle\phi_\gamma|\hat{H}_1}{E_1 - E_2}$$

The matrix element

$$\Lambda = \begin{pmatrix} \frac{\langle\phi_\alpha|\hat{H}_1|\phi_\gamma\rangle\langle\phi_\gamma|\hat{H}_1|\phi_\alpha\rangle}{E_1-E_2} & \frac{\langle\phi_\alpha|\hat{H}_1|\phi_\gamma\rangle\langle\phi_\gamma|\hat{H}_1|\phi_\beta\rangle}{E_1-E_2} \\ \frac{\langle\phi_\beta|\hat{H}_1|\phi_\gamma\rangle\langle\phi_\gamma|\hat{H}_1|\phi_\alpha\rangle}{E_1-E_2} & \frac{\langle\phi_\beta|\hat{H}_1|\phi_\gamma\rangle\langle\phi_\gamma|\hat{H}_1|\phi_\alpha\rangle}{E_1-E_2} \end{pmatrix} = \begin{pmatrix} \frac{|a|^2}{E_1-E_2} & \frac{ab^*}{E_1-E_2} \\ \frac{a^*b}{E_1-E_2} & \frac{|b|^2}{E_1-E_2} \end{pmatrix}$$

Det[Λ-λI] = 0.

$$\begin{vmatrix} \frac{|a|^2}{E_1-E_2}-\lambda & \frac{ab^*}{E_1-E_2} \\ \frac{a^*b}{E_1-E_2} & \frac{|b|^2}{E_1-E_2}-\lambda \end{vmatrix} = 0$$

$$(\frac{|a|^2}{E_2-E_1}+\lambda)(\frac{|b|^2}{E_2-E_1}+\lambda) - \frac{|a|^2|b|^2}{(E_1-E_2)^2} = 0$$

or

$$\lambda[\lambda + \frac{|a|^2+|b|^2}{E_2-E_1}] = 0$$

Then we have

$$\lambda = 0 \text{ and } \lambda = -\frac{|a|^2 + |b|^2}{E_2 - E_1}$$

The final result is

$$\tilde{E}_a = E_1$$

$$\tilde{E}_\beta = E_1 - \frac{|a|^2 + |b|^2}{E_2 - E_1}$$

$$\tilde{E}_\gamma = E_2 + \frac{|a|^2 + |b|^2}{E_2 - E_1}$$

((5-19))

5.19 Compute the Stark effect for the $2s_{1/2}$ and $2p_{1/2}$ levels of hydrogen for a field $\mathscr{E}$ sufficiently weak so that $e\mathscr{E}a_0$ is small compared to the fine structure, but take the Lamb shift δ ($\delta = 1057$ MHz) into account (that is, ignore $2p_{3/2}$ in this calculation). Show that for $e\mathscr{E}a_0 \ll \delta$, the energy shifts are quadratic in $\mathscr{E}$, whereas for $e\mathscr{E}a_0 \gg \delta$ they are linear in $\mathscr{E}$. Briefly discuss the consequences (if any) of time reversal for this problem. This problem is from Gottfried (1966), Problem 7-3.

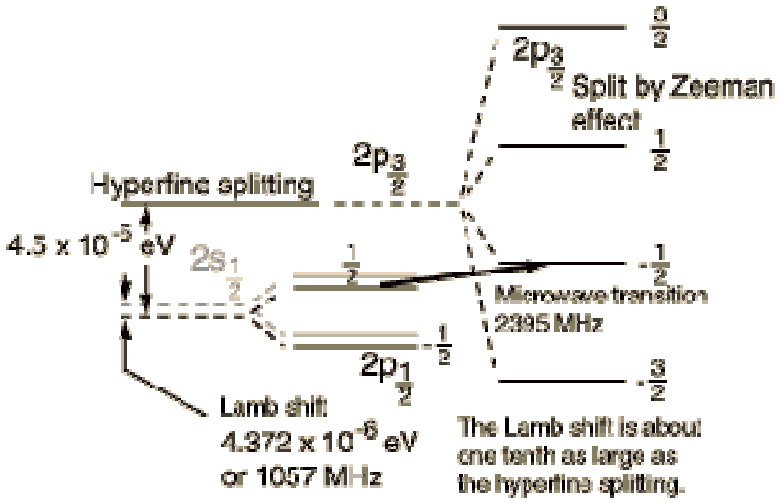


Fig. Lamb shift: the energy level of $2S_{1/2}$ (doubly degenerate states) is higher than that of $2P_{1/2}$ (doubly degenerate) by δ (= 4.372 x 10^{-6} eV = 1057 MHz).

The perturbation (Stark effect)

$$\hat{H}_1 = e\mathscr{E}\hat{z}$$

This Hamiltonian is invariant under the time reversal.

We now consider the state with $n = 2$.

$n = 2$ state (4 states degenerate)
$l = 1$ ($m = \pm 1, 0$): p-state
$l = 0$ ($m = 0$): s-state.

Addition of spin and orbital angular momentum

(i)

$l = 1, s = 1/2$

$$D_1 \times D_{1/2} = D_{3/2} + D_{1/2}$$

$2P_{3/2}$

$j = 3/2$

$m = 3/2, 1/2, -1/2,$ and $-3/2$

$2P_{1/2}$

$j = 1/2$

$m = 1/2, -1/2$

We define spin angular function in two component form as follows.

$$y_{l=1}^{j=1/2,m} = -\sqrt{\frac{-m+3/2}{3}} Y_{l=1}^{m-1/2}(\theta,\phi)\chi_+ + \sqrt{\frac{m+3/2}{3}} Y_{l=1}^{m+1/2}(\theta,\phi)\chi_-$$

or

$$\left|2P_{1/2}; m = 1/2\right\rangle = R_{21} y_{l=1}^{j=1/2,m=1/2} = R_{21}[-\sqrt{\frac{1}{3}} Y_1^0(\theta,\phi)\chi_+ + \sqrt{\frac{2}{3}} Y_1^1(\theta,\phi)\chi_-]$$

or

$$\left|2P_{1/2}; m = 1/2\right\rangle = \begin{pmatrix} -\sqrt{\frac{1}{3}} R_{21} Y_1^0(\theta,\phi) \\ \sqrt{\frac{2}{3}} R_{21} Y_1^1(\theta,\phi) \end{pmatrix} = \begin{pmatrix} -\sqrt{\frac{1}{3}} \left|n = 2, l = 1, m = 0\right\rangle \\ \sqrt{\frac{2}{3}} \left|n = 2, l = 1, m = 1\right\rangle \end{pmatrix}$$

$$\left|2P_{1/2}, m = -1/2\right\rangle = R_{21} y_{l=1}^{j=1/2,m=-1/2} = R_{21}[-\sqrt{\frac{2}{3}} Y_l^{-1}(\theta,\phi)\chi_+ + \sqrt{\frac{1}{3}} Y_1^0(\theta,\phi)\chi_-]$$

$$\left|2P_{1/2}, m = -1/2\right\rangle = \begin{pmatrix} -\sqrt{\frac{2}{3}} \left|n = 2, l = 1, m = -1\right\rangle \\ \sqrt{\frac{1}{3}} \left|n = 2, l = 1, m = 0\right\rangle \end{pmatrix}$$

(ii)

$l = 0, s = 1/2$

$$D_0 \times D_{1/2} = D_{1/2}$$

$2S_{1/2}$

$j = 1/2$
$m = 1/2, -1/2$

$$\left|j=1/2,m\right\rangle = y_0^{j=1/2,m} = \sqrt{m+1/2}Y_{l=0}^{m-1/2}(\theta,\phi)\chi_+ + \sqrt{-m+1/2}Y_{l=0}^{m+1/2}(\theta,\phi)\chi_-$$

$$\left|2S_{1/2},m=1/2\right\rangle = y_0^{j=1/2,m=1/2} = R_{20}Y_0^0(\theta,\phi)\chi_+ = \begin{pmatrix} R_{20}Y_0^0(\theta,\phi) \\ 0 \end{pmatrix} = \begin{pmatrix} \left|n=2,l=0,m=0\right\rangle \\ 0 \end{pmatrix}$$

$$\left|2S_{1/2},m=-1/2\right\rangle = y_0^{j=1/2,m=-1/2} = R_{20}Y_0^0(\theta,\phi)\chi_- = \begin{pmatrix} 0 \\ R_{20}Y_0^0(\theta,\phi) \end{pmatrix} = \begin{pmatrix} \\ \left|n=2,l=0,m=0\right\rangle \end{pmatrix}$$

We calculate the matrix elements of the perturbation.

$$\left\langle 2S_{1/2},m=-1/2\left|\hat{z}\right|2S_{1/2},m=-1/2\right\rangle = \begin{pmatrix} 0 & \left\langle n=2,l=0,m=0\right| \end{pmatrix}\begin{pmatrix} 0 \\ \hat{z}\left|n=2,l=0,m=0\right\rangle \end{pmatrix} = 0$$

$$\left\langle 2S_{1/2},m=1/2\left|\hat{z}\right|2S_{1/2},m=-1/2\right\rangle = \begin{pmatrix} \left\langle n=2,l=0,m=0\right| & 0 \end{pmatrix}\begin{pmatrix} 0 \\ \hat{z}\left|n=2,l=0,m=0\right\rangle \end{pmatrix} = 0$$

$$\left\langle 2P_{1/2},m=-1/2\left|\hat{z}\right|2S_{1/2},m=-1/2\right\rangle$$

$$= \begin{pmatrix} -\sqrt{\frac{2}{3}}\left\langle n=2,l=1,m=-1\right| & \sqrt{\frac{1}{3}}\left\langle n=2,l=1,m=0\right| \end{pmatrix}\begin{pmatrix} 0 \\ \hat{z}\left|n=2,l=0,m=0\right\rangle \end{pmatrix}$$

$$= \sqrt{\frac{1}{3}}\left\langle n=2,l=1,m=0\left|\hat{z}\right|n=2,l=0,m=0\right\rangle = \alpha$$

$$\left\langle 2P_{1/2},m=1/2\left|\hat{z}\right|2S_{1/2},m=-1/2\right\rangle$$

$$= \begin{pmatrix} -\sqrt{\frac{1}{3}}\left\langle n=2,l=1,m=0\right| & \sqrt{\frac{2}{3}}\left\langle n=2,l=1,m=1\right| \end{pmatrix}\begin{pmatrix} 0 \\ \hat{z}\left|n=2,l=0,m=0\right\rangle \end{pmatrix}$$

$$= \sqrt{\frac{2}{3}}\left\langle n=2,l=1,m=1\left|\hat{z}\right|n=2,l=0,m=0\right\rangle = 0$$

$$\left\langle 2S_{1/2},m=-1/2\left|\hat{z}\right|2S_{1/2},m=1/2\right\rangle = \begin{pmatrix} 0 & \left\langle n=2,l=0,m=0\right| \end{pmatrix}\begin{pmatrix} \hat{z}\left|n=2,l=0,m=0\right\rangle \\ 0 \end{pmatrix} = 0$$

$$\left\langle 2S_{1/2},m=1/2\left|\hat{z}\right|2S_{1/2},m=1/2\right\rangle = \begin{pmatrix} \left\langle n=2,l=0,m=0\right| & 0 \end{pmatrix}\begin{pmatrix} \hat{z}\left|n=2,l=0,m=0\right\rangle \\ 0 \end{pmatrix} = 0$$

$$\langle 2P_{1/2}, m=-1/2|\hat{z}|2S_{1/2}, m=1/2\rangle$$

$$=\left(-\sqrt{\frac{2}{3}}\langle n=2,l=1,m=-1| \quad \sqrt{\frac{1}{3}}\langle n=2,l=1,m=0|\right)\begin{pmatrix}\hat{z}|n=2,l=0,m=0\rangle\\ 0\end{pmatrix}$$

$$=-\sqrt{\frac{2}{3}}\langle n=2,l=1,m=-1|\hat{z}|n=2,l=0,m=0\rangle=0$$

$$\langle 2P_{1/2}, m=1/2|\hat{z}|2S_{1/2}, m=1/2\rangle$$

$$=\left(-\sqrt{\frac{1}{3}}\langle n=2,l=1,m=0| \quad \sqrt{\frac{2}{3}}\langle n=2,l=1,m=1|\right)\begin{pmatrix}\hat{z}|n=2,l=0,m=0\rangle\\ 0\end{pmatrix}$$

$$=-\sqrt{\frac{1}{3}}\langle n=2,l=1,m=0|\hat{z}|n=2,l=0,m=0\rangle=\beta$$

Note that the operator $\hat{z}$ is Hermitian, Then we have the matrix of $\hat{H}_1(=e\varepsilon\hat{z})$ and Lamb shift ($\hat{H}_\delta$).

	$\lvert 2P_{1/2}, m=1/2\rangle$	$\lvert 2P_{1/2}, m=-1/2\rangle$	$\lvert 2S_{1/2}, m=1/2\rangle$	$\lvert 2S_{1/2}, m=-1/2\rangle$
$\langle 2P_{1/2}, m=1/2\rvert$	0	0	$e\varepsilon\beta=\sqrt{3}e\varepsilon a_0$	0
$\langle 2P_{1/2}, m=-1/2\rvert$	0	0	0	$e\varepsilon\alpha=-\sqrt{3}e\varepsilon a_0$
$\langle 2S_{1/2}, m=1/2\rvert$	$e\varepsilon\beta=\sqrt{3}e\varepsilon a_0$	0	δ	0
$\langle 2S_{1/2}, m=-1/2\rvert$	0	$e\varepsilon\alpha=-\sqrt{3}e\varepsilon a_0$	0	δ

where δ is the Lamb-shift energy

$$\langle n=2,l=1,m=0|\hat{z}|n=2,l=0,m=0\rangle=-3a_0$$

$$\alpha=\sqrt{\frac{1}{3}}\langle n=2,l=1,m=0|\hat{z}|n=2,l=0,m=0\rangle=-\sqrt{3}a_0$$

$$\beta=-\sqrt{\frac{1}{3}}\langle n=2,l=1,m=0|\hat{z}|n=2,l=0,m=0\rangle=\sqrt{3}a_0$$

The eigenvalue problem

We use the Mathematica 5.2.

Energy eigenvalue and eigenket with $p = \sqrt{3}e\mathcal{E}a_0$

$$E_1 = \frac{\delta}{2} - \frac{\sqrt{4p^2 + \delta^2}}{2}$$

$$|\psi_1\rangle = \frac{1}{\sqrt{2 + \frac{\delta(\delta + \sqrt{4p^2 + \delta^2}}{2p^2}}}[\frac{\delta + \sqrt{4p^2 + \delta^2}}{2p}|2P_{1/2}, m = -1/2\rangle + |2S_{1/2}, m = -1/2\rangle]$$

$$E_2 = \frac{\delta}{2} + \frac{\sqrt{4p^2 + \delta^2}}{2}$$

$$|\psi_2\rangle = \frac{1}{\sqrt{2 + \frac{\delta(\delta + \sqrt{4p^2 + \delta^2}}{2p^2}}}[-\frac{\delta + \sqrt{4p^2 + \delta^2}}{2p}|2P_{1/2}, m = 1/2\rangle + |2S_{1/2}, m = 1/2\rangle]$$

$$E_3 = \frac{\delta}{2} + \frac{\sqrt{4p^2 + \delta^2}}{2}$$

$$|\psi_3\rangle = \frac{1}{\sqrt{2 + \frac{\delta(\delta - \sqrt{4p^2 + \delta^2}}{2p^2}}}[\frac{\delta - \sqrt{4p^2 + \delta^2}}{2p}|2P_{1/2}, m = -1/2\rangle + |2S_{1/2}, m = -1/2\rangle]$$

$$E_4 = \frac{\delta}{2} + \frac{\sqrt{4p^2 + \delta^2}}{2}$$

$$|\psi_3\rangle = \frac{1}{\sqrt{2 + \frac{\delta(\delta - \sqrt{4p^2 + \delta^2}}{2p^2}}}[\frac{-\delta + \sqrt{4p^2 + \delta^2}}{2p}|2P_{1/2}, m = 1/2\rangle + |2S_{1/2}, m = 1/2\rangle]$$

The energy levels (E_1=E_2, E_3=E_4) are degenerate. The perturbation (Stark effect) $\hat{H}_1 = e\mathcal{E}\hat{z}$ is invariant under the time reversal. Since j = 1/2, each level are still doubly degenerate (Kramers doublet).

In the limit of $\delta >> p$

$$E_1 = E_2 = -\frac{p^2}{\delta} + \frac{p^4}{\delta^3}$$

$$E_3 = E_4 = \delta + \frac{p^2}{\delta} - \frac{p^4}{\delta^3}$$

The change of energy is quadratic in ε.

In the limit of $\delta << p$

$$E_1 = E_2 = \frac{\delta}{2} - p + \frac{\delta^2}{8p} + \frac{\delta^4}{128p^3}$$

$$E_3 = E_4 = \frac{\delta}{2} + p + \frac{\delta^2}{8p} - \frac{\delta^4}{128p^3}$$

The change of energy is linear in δ

((**Mathematica**))

```
Clear["Global`*"];
```

$$M = \begin{pmatrix} 0 & 0 & p & 0 \\ 0 & 0 & 0 & -p \\ p & 0 & \delta & 0 \\ 0 & -p & 0 & \delta \end{pmatrix};$$

```
eq1 = Eigensystem[M] // Simplify;
```

```
E1 = eq1[[1, 1]]
```

$$\frac{1}{2}\left(\delta - \sqrt{4\,p^2 + \delta^2}\right)$$

```
E2 = eq1[[1, 2]]
```

$$\frac{1}{2}\left(\delta - \sqrt{4\,p^2 + \delta^2}\right)$$

```
E3 = eq1[[1, 3]]
```

$$\frac{1}{2}\left(\delta + \sqrt{4\,p^2 + \delta^2}\right)$$

```
E4 = eq1[[1, 4]]
```

$$\frac{1}{2}\left(\delta + \sqrt{4\,p^2 + \delta^2}\right)$$

```
E11 = E1 /. δ → 1
```

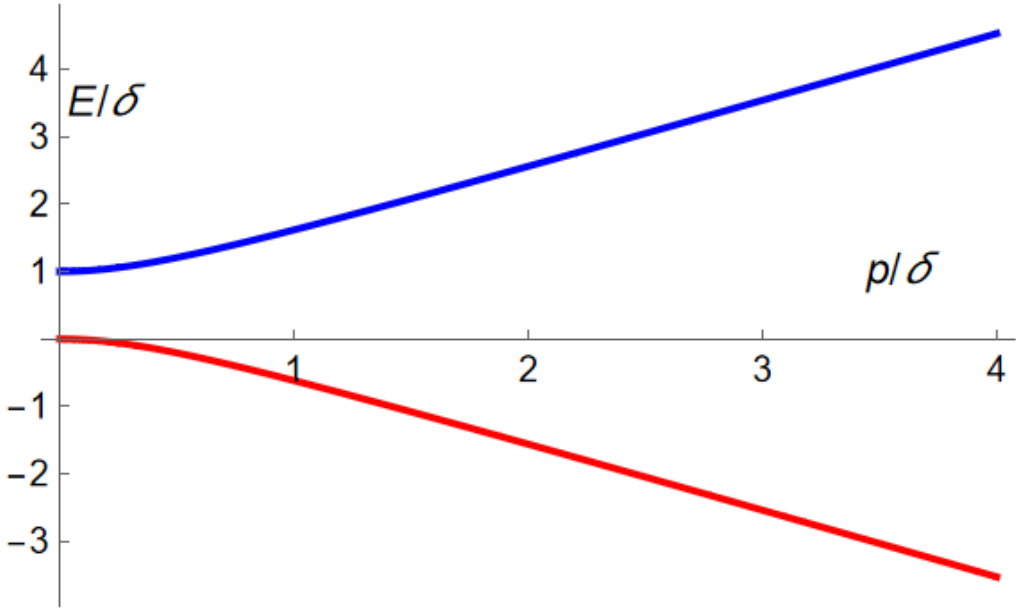
$$\frac{1}{2} \times \left(1 - \sqrt{1 + 4\,p^2}\right)$$

```
E31 = E3 /. δ → 1
```

$$\frac{1}{2} \times \left(1 + \sqrt{1 + 4\,p^2}\right)$$

```
g1 = Plot[Evaluate[{E11, E31}], {p, 0, 4},
  PlotStyle → {{Red, Thick},
    {Blue, Thick}},
  Ticks → {Range[0, 5, 1], Range[-5, 5, 1]}];
```

```
g2 =
 Graphics[
  {Text[Style["p/δ", Black, Italic, 12],
    {3.6, 1}],
   Text[Style["E/δ", Black, Italic, 12],
    {0.2, 3.51}]}];
Show[g1, g2 ]
```



((5-20)) **Stark effect**

5.20 Work out the Stark effect to lowest nonvanishing order for the $n = 3$ level of the hydrogen atom. Ignoring the spin-orbit force and relativistic correction (Lamb shift), obtain not only the energy shifts to lowest nonvanishing order but also the corresponding zeroth-order eigenket.

((**Solution**))
Stark effect $n = 3$
is the Hamiltonian of the hydrogen atom. We apply an external electric field ε (along the z axis) to the hydrogen atom, producing the Stark effect.

where $-e$ (e>0) is the electron charge and $\boldsymbol{\mu}_e$ (=$-e\mathbf{r}$) is an electric dipole moment. The vector $\boldsymbol{r}$ is the position vector of electron, where the proton (e) is located at the origin.

We use this selection rule

$$\langle n_2, l_2, m_2 | \hat{z} | n_1, l_1, m_1 \rangle = 0 \qquad \text{unless } l_2 = l_1 \pm 1,\ m_2 = m_1.$$

For $n = 3$, there are nine states.

$l = 2$ $m = 2, 1, 0, -1, -2,$

$$|3,2,2\rangle, |3,2,1\rangle, |3,2,0\rangle, |3,2,-1\rangle, |3,2,-2\rangle$$

$l = 1$ $m = 1, 0, -1$

$$|3,1,1\rangle, |3,1,0\rangle, |3,1,-1\rangle$$

$l = 0,$ $m = 0.$

$$|3,0,0\rangle$$

Matrix elements $\langle 3, l'm' | \hat{z} | 3, l, m \rangle$ can be calculated using the selection rule and ((**Mathematica**))

	$\lvert 3,2,2\rangle$	$\lvert 3,2,1\rangle$	$\lvert 3,2,0\rangle$	$\lvert 3,2,-1\rangle$	$\lvert 3,2,-2\rangle$	$\lvert 3,1,1\rangle$	$\lvert 3,1,0\rangle$	$\lvert 3,1,-1\rangle$	$\lvert 3,0,0\rangle$
$\langle 3,2,2\rvert$	0	0	0	0	0	0	0	0	0
$\langle 3,2,1\rvert$	0	0	0	0	0	α	0	0	0
$\langle 3,2,0\rvert$	0	0	0	0	0	0	β	0	0
$\langle 3,2,-1\rvert$	0	0	0	0	0	0	0	γ	0
$\langle 3,2,-2\rvert$	0	0	0	0	0	0	0	0	0
$\langle 3,1,1\rvert$	0	α^*	0	0	0	0	0	0	0
$\langle 3,1,0\rvert$	0	0	β^*	0	0	0	0	0	δ
$\langle 3,1,-1\rvert$	0	0	0	γ^*	0	0	0	0	0
$\langle 3,0,0\rvert$	0	0	0	0	0	0	δ^*	0	0

where

$\alpha = \langle 3,2,1|\hat{z}|3,1,1\rangle = -\frac{9a_0}{2}$, $\beta = \langle 3,2,0|\hat{z}|3,1,0\rangle = -3\sqrt{3}a_0$, $\gamma = \langle 3,2,-1|\hat{z}|3,1,-1\rangle = -\frac{9a_0}{2}$

$\delta = \langle 3,1,0|\hat{z}|3,0,0\rangle = -3\sqrt{6}a_0$. Note that $\alpha = \gamma$.

	$\lvert 3,2,1\rangle$	$\lvert 3,2,0\rangle$	$\lvert 3,2,-1\rangle$	$\lvert 3,1,1\rangle$	$\lvert 3,1,0\rangle$	$\lvert 3,1,-1\rangle$	$\lvert 3,0,0\rangle$
$\langle 3,2,1\rvert$	0	0	0	α	0	0	0
$\langle 3,2,0\rvert$	0	0	0	0	β	0	0
$\langle 3,2,-1\rvert$	0	0	0	0	0	α	0
$\langle 3,1,1\rvert$	α	0	0	0	0	0	0
$\langle 3,1,0\rvert$	0	β	0	0	0	0	δ
$\langle 3,1,-1\rvert$	0	0	α	0	0	0	0
$\langle 3,0,0\rvert$	0	0	0	0	δ	0	0

This matrix consists of three submatrices.

$$\hat{z}|3,1,0\rangle = \beta|3,2,0\rangle + \delta|3,0,0\rangle$$
$$\hat{z}|3,0,0\rangle = \delta|3,1,0\rangle$$
$$\hat{z}|3,2,0\rangle = \beta|3,1,0\rangle$$

$$\hat{z}|3,2,1\rangle = \alpha|3,1,1\rangle,$$
$$\hat{z}|3,1,1\rangle = \alpha|3,2,1\rangle,$$

$$\hat{z}|3,1,-1\rangle = \alpha|3,2,-1\rangle$$
$$\hat{z}|3,2,-1\rangle = \alpha|3,1,-1\rangle,$$

or

	$\lvert 3,2,0\rangle$	$\lvert 3,1,0\rangle$	$\lvert 3,0,0\rangle$
$\langle 3,2,0\rvert$	0	β	0
$\langle 3,1,0\rvert$	β	0	δ
$\langle 3,0,0\rvert$	0	δ	0

or

$$M_1 = \begin{pmatrix} 0 & \beta & 0 \\ \beta & 0 & \delta \\ 0 & \delta & 0 \end{pmatrix}$$

Eigensystem[M_1]

$$E_1 = 9e\varepsilon a_0, \qquad |\psi_1\rangle = \frac{1}{\sqrt{3}}\left[\frac{1}{\sqrt{2}}|3,2,0\rangle - \sqrt{\frac{3}{2}}|3,1,0\rangle + |3,0,0\rangle\right]$$
$$E_2 = 0, \qquad |\psi_2\rangle = \frac{1}{\sqrt{3}}\left[\sqrt{2}|3,2,0\rangle - |3,0,0\rangle\right]$$
$$E_3 = -9e\varepsilon a_0 \qquad |\psi_3\rangle = \frac{1}{\sqrt{3}}\left[\frac{1}{\sqrt{2}}|3,2,0\rangle + \sqrt{\frac{3}{2}}|3,1,0\rangle + |3,0,0\rangle\right]$$

	$\lvert 3,2,-1\rangle$	$\lvert 3,1,-1\rangle$
$\langle 3,2,-1\rvert$	0	α
$\langle 3,1,-1\rvert$	α	0

$$M_2 = \begin{pmatrix} 0 & \alpha \\ \alpha & 0 \end{pmatrix}$$

Eigensystem[M_1]

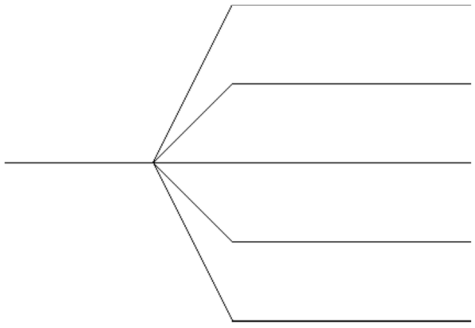
$$E_4 = \frac{9}{2} e\varepsilon a_0, \quad |\psi_4\rangle = \frac{1}{\sqrt{2}}[|3,2,-1\rangle - |3,1,-1\rangle]$$
$$E_5 = -\frac{9}{2} e\varepsilon a_0 \quad |\psi_5\rangle = \frac{1}{\sqrt{2}}[[|3,2,-1\rangle + |3,1,-1\rangle]]$$

	$\|3,2,1\rangle$	$\|3,1,1\rangle$
$\langle 3,2,1\|$	0	α
$\langle 3,1,1\|$	α	0

$$M_3 = \begin{pmatrix} 0 & \alpha \\ \alpha & 0 \end{pmatrix}$$

Eigensystem[M_3]

$$E_4 = \frac{9}{2} e\varepsilon a_0, \quad |\psi_6\rangle = \frac{1}{\sqrt{2}}[|3,2,1\rangle - |3,1,1\rangle]$$
$$E_5 = -\frac{9}{2} e\varepsilon a_0 \quad |\psi_7\rangle = \frac{1}{\sqrt{2}}[[|3,2,1\rangle + |3,1,1\rangle]]$$



((**Mathematica**)) Stark effect $n = 3$

See lecture note 6.2 Stark effect.

((5-21))

5.21 Suppose the electron had a very small intrinsic *electric* dipole moment analogous to the spin magnetic moment (that is, $\boldsymbol{\mu}_{el}$ proportional to σ). Treating the hypothetical $-\boldsymbol{\mu}_{el} \cdot \mathbf{E}$ interaction as a small perturbation, discuss qualitatively how the energy levels of the Na atom $(Z = 11)$ would be altered in the absence of any external electromagnetic field. Are the level shifts first order or second order? State explicitly which states get mixed with each other. Obtain an expression for the energy shift of the lowest level that is affected by the perturbation. Assume throughout that only the valence electron is subjected to the hypothetical interaction.

((**Solution**))

The perturbation is given by

$$\hat{V} = -\boldsymbol{\mu}_{el} \cdot \boldsymbol{E} = -\mu_{el} \frac{\hat{\boldsymbol{\sigma}} \cdot \hat{\boldsymbol{r}}}{r} \frac{dV_c(r)}{dr}$$

where $V_c(r)$ is a potential due to a central force from nucleus and other electrons. This perturbation is a pseudo scalar operator. Using the Wigner-Eckart theorem,

$$\left\langle n', l'; j', m' \middle| \hat{T}^{(=0)}_{q=0} \middle| n, l; j, m \right\rangle = 0 \qquad \text{unless } m' = m \text{ and } j' = j$$

From the property of the parity operator associated with the space inversion, the matrix element is equal to zero unless $l' = l \pm 1$.

Na: $(1s)^2(2s)^2(2p)^6(3s)$

The inner 10 electrons can be visualized to form a spherically symmetrical electron cloud. We are interested in the excitation of the 11-th electron from 3s to a possible higher state.

$$\begin{aligned} \left| 3S_{1/2}, m \right\rangle &= \left| n = 3, l = 0, s = 1/2; j = 1/2, m \right\rangle \\ &= \sqrt{m + 1/2} \left| l = 0, s = 1/2; m_l = m - 1/2, m_s = 1/2 \right\rangle \\ &\quad + \sqrt{\frac{-m + 1/2}{1}} \left| l = 0, s = 1/2; m_l = m + 1/2, m_s = -1/2 \right\rangle \end{aligned}$$

$$\left| 3S_{1/2}, m = 1/2 \right\rangle = \left| l = 0, s = 1/2; m_l = 0, m_s = 1/2 \right\rangle$$
$$\left| 3S_{1/2}, m = -1/2 \right\rangle = \left| l = 0, s = 1/2; m_l = 1, m_s = 1/2 \right\rangle$$

$$|3P_{1/2},m\rangle = |n=3,l=1,s=1/2;j=1/2,m\rangle$$
$$= -\sqrt{\frac{-m+3/2}{3}}|l=1,s=1/2;m_l=m-1/2,m_s=1/2\rangle$$
$$+\sqrt{\frac{m+3/2}{3}}|l=1,s=1/2;m_l=m+1/2,m_s=-1/2\rangle$$

$$|3P_{1/2},m=1/2\rangle = -\sqrt{\frac{1}{3}}|l=1,s=1/2;m_l=0,m_s=1/2\rangle + \sqrt{\frac{2}{3}}|l=1,s=1/2;m_l=1,m_s=-1/2\rangle$$
$$|3P_{1/2},m=-1/2\rangle = -\sqrt{\frac{2}{3}}|l=1,s=1/2,m_l=-1,m_s=1/2\rangle + \sqrt{\frac{1}{3}}|l=1,s=1/2;m_l=0,m_s=-1/2\rangle$$

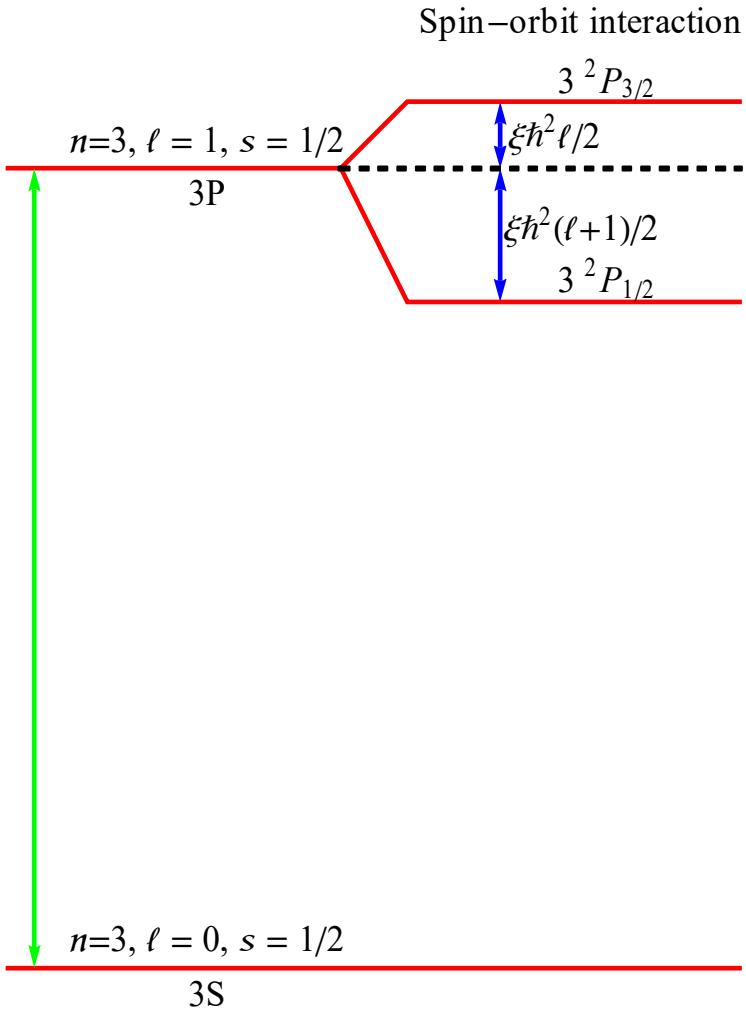


Fig. Energy levels of Na with and without spin-orbit interaction. The 3P level is slightly different from the 3S level (the ground state is 3 $^2S_{1/2}$).
The 3P level is split into 3 $^2P_{3/2}$ (4 degeneracies) and 3 $^2P_{1/2}$ (3 degeneracies) due to the spin-orbit interaction. The Lande g-factor is g = 4/3 for into 3 $^2P_{3/2}$, g = 2/3 for into 3 $^2P_{1/2}$, and g = 2 for into 3 $^2P_{1/2}$.

The matrix element of the pseudo potential,

$$\begin{pmatrix} & |3S_{1/2}, m=1/2\rangle & |3S_{1/2}, m=-1/2\rangle & |3P_{1/2}, m=1/2\rangle & |3P_{1/2}, m=-1/2\rangle \\ \langle 3S_{1/2}, m=1/2| & 0 & 0 & \alpha & 0 \\ \langle 3S_{1/2}, m=-1/2| & 0 & 0 & 0 & \alpha \\ \langle 3P_{1/2}, m=1/2| & \alpha & 0 & 0 & 0 \\ \langle 3P_{1/2}, m=-1/2| & 0 & \alpha & 0 & 0 \end{pmatrix}$$

where

$$\alpha = \langle 3S_{1/2}, m=\pm/2|\hat{V}|3P_{1/2}, m=\pm 1/2\rangle$$

Or simply

$$\hat{V} = \begin{pmatrix} & |3S_{1/2}, m=\pm 1/2\rangle & |3P_{1/2}, m=\pm 1/2\rangle \\ \langle 3S_{1/2}, m=\pm 1/2| & 0 & \alpha \\ \langle 3P_{1/2}, m=\pm 1/2| & \alpha & 0 \end{pmatrix}$$

We use the perturbation theory (non-degenerate case). Before the perturbation, the electron is in the state $|3S_{1/2}, m=\pm 1/2\rangle$.

Perturbation energy (to the second order)

$$E(3S_{1/2}) + \langle 3S_{1/2}, m=\pm/2|\hat{V}|3S_{1/2}, m=\pm 1/2\rangle + \frac{\left|\langle 3P_{1/2}, m=\pm/2|\hat{V}|3S_{1/2}, m=\pm 1/2\rangle\right|^2}{E(3S_{1/2}) - E(3P_{1/2})}$$

$$= E(3S_{1/2}) + \frac{|\alpha|^2}{E(3S_{1/2}) - E(3P_{1/2})}$$

Note that

$$\frac{|\alpha|^2}{E(3S_{1/2}) - E(3P_{1/2})} < 0$$

Perturbed state

$$\left|3S_{1/2}, m = \pm 1/2\right\rangle + \frac{\left|3P_{1/2}, m = \pm 1/2\right\rangle\left\langle 3P_{1/2}, m = /2\right|\hat{V}\left|3S_{1/2}, m = \pm 1/2\right\rangle}{E(3S_{1/2}) - E(3P_{1/2})}$$

$$= \left|3S_{1/2}, m = \pm 1/2\right\rangle + \frac{\alpha\left|3P_{1/2}, m = \pm 1/2\right\rangle}{E(3S_{1/2}) - E(3P_{1/2})}$$

Note that the energy is lowered after the application of the electric field. The new state is a state where the rotation of the electric dipole leads to the lowering of the energy of the system.

((5-22))

5.22 Consider a particle bound to a fixed center by a spherically symmetric potential $V(r)$.

a. Prove

$$|\psi(0)|^2 = \left(\frac{m}{2\pi\hbar^2}\right)\left\langle\frac{dV}{dr}\right\rangle$$

for all s states, ground and excited.

b. Check this relation for the ground state of a three-dimensional isotropic oscillator, the hydrogen atom, and so on. (*Note*: This relation has actually been found to be useful in guessing the form of the potential between a quark and an antiquark. See Moxhay and Rosner, *J. Math. Phys.*, **21** (1980) 1688.)

((**Solution**))

$$-\frac{\hbar^2}{2m}\frac{1}{r}\frac{d^2}{dr^2}(rR)+[\frac{\hbar^2 l(l+1)}{2mr^2}+V(r)]R(r)=ER(r)$$

We assume that

$$rR=u$$

$$-\frac{\hbar^2}{2m}\frac{d^2u(r)}{dr^2}+[\frac{\hbar^2 l(l+1)}{2mr^2}+V(r)]u(r)=Eu(r)=-\frac{\hbar^2\kappa^2}{2m}u(r)$$

where

$$E=-\frac{\hbar^2\kappa^2}{2m},\qquad \kappa=\sqrt{\frac{2m|E|}{\hbar^2}}$$

For $l = 0$ (s-state), we have

$$\frac{d^2u(r)}{dr^2}-\frac{2m}{\hbar^2}V(r)u(r)=\kappa^2u(r),$$

or simply

$$u''-\kappa^2u=\frac{2m}{\hbar^2}V(r)u$$

In the limit of $r \to \infty$

$$\frac{d^2u(r)}{dr^2} = \kappa^2 u(r)$$

$$u(r) = e^{-\kappa r} \qquad (r \to \infty)$$

In the limit of $r \to 0$, we assume that

$$\lim_{r\to 0} R(r) = \text{constant}, \qquad \lim_{r\to 0} u(r) = 0$$

We now calculate

$$\begin{aligned}\left\langle \frac{dV}{dr} \right\rangle &= \int_0^\infty r^2 dr [R(r)]^2 \frac{dV}{dr} \\ &= \int_0^\infty dr u^2 \frac{dV}{dr} \\ &= \left[V(r) u^2 \right]_0^\infty - \int_0^\infty dr V(r) 2u \frac{du}{dr} \\ &= -2 \int_0^\infty dr V(r) u \frac{du}{dr}\end{aligned}$$

We note that

$$\frac{\hbar^2}{2m}(u'' - \kappa^2 u) = V(r)u$$

$$\left\langle \frac{dV}{dr} \right\rangle = \frac{\hbar^2}{m}\int_0^\infty dr(\kappa^2 u - u'')u'$$

$$= \frac{\hbar^2}{2m}\int_0^\infty dr \frac{d}{dr}(\kappa^2 u^2 - u'^2)$$

$$= \frac{\hbar^2}{2m}\left[\kappa^2 u^2 - u'^2\right]_0^\infty$$

$$= \frac{\hbar^2}{2m}\left[\kappa^2 (rR)^2 - (rR)'^2\right]_0^\infty$$

$$= -\frac{\hbar^2}{2m}\left[(rR)'^2\right]_0^\infty$$

$$= -\frac{\hbar^2}{2m}\left[(R + rR')^2\right]_0^\infty$$

$$= \frac{\hbar^2}{2m}[R(r=0)]^2$$

or

$$\left\langle \frac{dV}{dr} \right\rangle = \frac{\hbar^2}{2m}[R(r=0)]^2$$

The wave function of the Hydrogen atom (*s* state)

$$\psi_{n00}(\boldsymbol{r}) = R_{n,0}(r)Y_0^0(\theta,\phi) = \frac{1}{2\sqrt{\pi}}R_{n0}(r),$$

where

$$Y_0^0(\theta,\phi) = \frac{1}{2\sqrt{\pi}}$$

$$\left|\psi_{n00}(\boldsymbol{r})\right|^2 == \frac{1}{4\pi}[R_{n0}(r)]^2$$

$$\left\langle \frac{dV}{dr} \right\rangle = \frac{\hbar^2}{2m}[R_{n0}(r=0)]^2 = \frac{\hbar^2}{2m}4\pi[R_{n0}(r=0)]^2$$

or

$$[R_{n0}(r=0)]^2 = \frac{m}{2\pi\hbar^2}\left\langle \frac{dV}{dr} \right\rangle$$

(b)

(i) Hydrogen ground state

$$V(r) = -\frac{e^2}{r}, \qquad \psi_{100}(\boldsymbol{r}) = R_{10}(r)Y_0^0(\theta,\phi) = \frac{1}{2\sqrt{\pi}}\frac{2}{a_B^{3/2}}e^{-\frac{r}{a_B}}$$

$$\psi_{100}(0) = \frac{1}{\sqrt{\pi}}\frac{1}{a_B^{3/2}}$$

where a_B is the Bohr radius,

$$a_B = \frac{\hbar^2}{me^2}$$

$$R_{1,0}(r) = \frac{2}{a_B^{3/2}}e^{-\frac{r}{a_B}}, \quad Y_0^0(\theta,\phi) = \frac{1}{2\sqrt{\pi}}$$

$$\begin{aligned}
\frac{m}{2\pi\hbar^2}\left\langle \frac{dV}{dr} \right\rangle &= \frac{m}{2\pi\hbar^2}4\pi\int_0^\infty r^2 dr \frac{1}{4\pi}\frac{4}{a_B^3}e^{-\frac{2r}{a_B}}\frac{e^2}{r^2} \\
&= \frac{m}{2\pi\hbar^2}\frac{4e^2}{a_B^3}\int_0^\infty dr e^{-\frac{2r}{a_B}} \\
&= \frac{m}{2\pi\hbar^2}\frac{4e^2}{a_B^3}\frac{a_B}{2} \\
&= \frac{1}{\pi a_B^3} \\
&= |\psi_{100}(0)|^2
\end{aligned}$$

(ii) 3D isotropic simple harmonics ground state

The ground state with the energy $\frac{3}{2}\hbar\omega$

$$\psi(\boldsymbol{r}) = \left\langle xyz \middle| n_x = 0, n_y = 0, n_z = 0 \right\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{3/4} e^{-\frac{m\omega}{2\hbar}r^2}.$$

$$|\psi(0)|^2 = (\frac{m\omega}{\pi\hbar})^{3/2}$$

$$V(r) = \frac{1}{2}m\omega^2 r^2, \qquad \frac{dV}{dr} = m\omega^2 r$$

$$\begin{aligned}
\frac{m}{2\pi\hbar^2}\left\langle\frac{dV}{dr}\right\rangle &= \frac{m}{2\pi\hbar^2}4\pi\int_0^\infty r^2 dr(\frac{m\omega}{\pi\hbar})^{3/2}e^{-\frac{m\omega}{\hbar}r^2}m\omega^2 r \\
&= 2(\frac{m\omega}{\pi\hbar})^{7/2}\int_0^\infty r^3 dr e^{-\frac{m\omega}{\hbar}r^2} \\
&= 2(\frac{m\omega}{\pi\hbar})^{7/2}\frac{\hbar^2}{2m^2\omega^2} \\
&= (\frac{m\omega}{\pi\hbar})^{3/2} \\
&= |\psi(0)|^2
\end{aligned}$$

((5-23))

5.23 a. Suppose the Hamiltonian of a rigid rotator in a magnetic field perpendicular to the axis is of the form (Merzbacher 1970, Problem 17-1)

$$A\mathbf{L}^2 + BL_z + CL_y$$

if terms quadratic in the field are neglected. Assuming $B \gg C$, use perturbation theory to lowest nonvanishing order to get approximate energy eigenvalues.

b. Consider the matrix elements

$$\langle n'l'm_l'm_s'|(3z^2 - r^2)|nlm_lm_s\rangle,$$
$$\langle n'l'm_l'm_s'|xy|nlm_lm_s\rangle$$

of a one-electron (for example, alkali) atom. Write the selection rules for Δl, Δm_l, and Δm_s. Justify your answer.

((**Solution**))

(a)

$$\hat{H}_0 = A\hat{\boldsymbol{L}}^2 + B\hat{L}_z, \qquad \hat{H}' = C\hat{L}_y$$

$|l,m\rangle$ is the eigenket of $\hat{H}_0$ with

$$E_{lm}^{(0)} = A\hbar^2 l(l+1) + B\hbar m .$$

$|l,m\rangle$ is non-degenerate state,

$$E_{lm} = E_{lm}^{(0)} + E_{lm}^{(1)} + E_{lm}^{(2)} + ...$$

with

$$E_{lm}^{(1)} = \langle lm|\hat{H}'|lm\rangle$$

$$E_{lm}^{(2)} = \sum \frac{\left|\langle lm'|\hat{H}'|lm\rangle\right|^2}{E_{lm}^{(0)} - E_{lm'}^{(0)}}$$

Here

$$\langle lm'|\hat{H}'|lm\rangle = \langle lm'|C\hat{L}_y|lm\rangle$$
$$= \frac{C}{2i}\langle lm'|\hat{L}_+ - \hat{L}_-|lm\rangle$$

$$\langle l,m+1|\hat{H}'|lm\rangle = \frac{C}{2i}\langle l,m+1|\hat{L}_+|lm\rangle$$
$$= \frac{C}{2i}\hbar\sqrt{(l-m)(l+m+1)}$$

$$\langle l,m-1|\hat{H}'|lm\rangle = -\frac{C}{2i}\langle l,m-1|\hat{L}_-|lm\rangle$$
$$= -\frac{C}{2i}\hbar\sqrt{(l+m)(l-m+1)}$$

where

$$\hat{L}_+|l,m\rangle = \hbar\sqrt{(l-m)(l+m+1)}|l,m+1\rangle$$

$$\hat{L}_-|l,m\rangle = \hbar\sqrt{(l+m)(l-m+1)}|l,m-1\rangle$$

Then we have

$$E_{lm}^{(1)} = \langle lm|\hat{H}'|lm\rangle = 0$$

$$E_{lm}^{(2)} = \frac{\left|\langle l,m+1|\hat{H}'|lm\rangle\right|^2}{E_{lm}^{(0)} - E_{l,m+1}^{(0)}} + \frac{\left|\langle l,m-1|\hat{H}'|lm\rangle\right|^2}{E_{lm}^{(0)} - E_{l,m-1}^{(0)}}$$
$$= -\frac{|C|^2\hbar}{4B}(l-m)(l+m+1) + \frac{|C|^2\hbar}{4B}(l+m)(l-m+1)$$
$$= \frac{|C|^2\hbar}{2B}m$$

(b)
We note that

$$\hat{x}\hat{y} = \frac{\hat{T}_2^{(2)} - \hat{T}_{-2}^{(2)}}{2i}$$

$$\langle n',l',m_l',m_s'|\hat{x}\hat{y}|n,l,m_l,m_s\rangle = \langle n',l',m_l',m_s'|\frac{\hat{T}_2^{(2)}-\hat{T}_{-2}^{(2)}}{2i}|n,l,m_l,m_s\rangle$$

$$= \frac{1}{2i}\delta(m_s',m_s)[\langle n',l',m_l'|\hat{T}_2^{(2)}|n,l,m_l\rangle$$

$$-\langle n',l',m_l'|\hat{T}_{-2}^{(2)}|n,l,m_l\rangle]$$

From the term $\delta(m_s',m_s)$, we have the selection rule for the spin

$$m_s' = m_s, \qquad \text{or} \qquad \Delta m_s = 0$$

From the term $\langle n',l',m_l'|\hat{T}_2^{(2)}|n,l,m_l\rangle$, we have the selection rule for

$$\langle n',l',m_l'|\hat{T}_2^{(2)}|n,l,m_l\rangle$$

$$\Delta l = l'-l = 2,1,0,-1,-2$$

$$\Delta m_l = m_l'-m_l = 2$$

using the Wigner-Eckart theorem. Since

$$\hat{\pi}|n,l,m_l\rangle = (-1)^l|n,l,m_l\rangle, \qquad \hat{\pi}\hat{T}_2^{(2)}\hat{\pi} = \hat{T}_2^{(2)} \text{ (even parity)}$$

we get the selection rule for Δl as

$$\Delta l = 2, 0, -2$$

Similarly, for the term $\langle n',l',m_l'|\hat{T}_{-2}^{(2)}|n,l,m_l\rangle$, we have the selection rule as

$$\Delta m_s = 0, \qquad \Delta m_l = -2, \qquad \Delta l = 2,0,-2$$

In summary, we get

$$\Delta m_s = 0, \qquad \Delta m_l = \pm 2, \qquad \Delta l = \pm 2, 0$$

Next we consider

$$\left(\frac{-\hat{x}^2-\hat{y}^2+2\hat{z}^2}{\sqrt{6}}\right)=\hat{T}_0^{(2)}$$

The matrix element:

$$\left\langle n',l',m_l',m_s'\left|\hat{T}_0^{(2)}\right|n,l,m_l,m_s\right\rangle=\delta(m_s',m_s)\left\langle n',l',m_l'\left|\hat{T}_0^{(2)}\right|n,l,m_l\right\rangle$$

From the term $\delta(m_s',m_s)$, we have the selection rule for the spin

$$m_s'=m_s, \qquad \text{or} \qquad \Delta m_s=0$$

From the term $\left\langle n',l',m_l'\left|\hat{T}_0^{(2)}\right|n,l,m_l\right\rangle$, we have the selection rule for

$$\left\langle n',l',m_l'\left|\hat{T}_0^{(2)}\right|n,l,m_l\right\rangle$$

$$\Delta l=l'-l=2,1,0,-1,-2$$

$$\Delta m_l=m_l'-m_l=0$$

using the Wigner-Eckart theorem. Since

$$\hat{\pi}\left|n,l,m_l\right\rangle=(-1)^l\left|n,l,m_l\right\rangle, \qquad \hat{\pi}\hat{T}_2^{(2)}\hat{\pi}=\hat{T}_2^{(2)} \text{ (even parity)}$$

we get the selection rule for Δl as

$$\Delta l=2,0,-2$$

In summary, we get

$$\Delta m_s=0, \qquad \Delta m_l=0, \qquad \Delta l=\pm 2,0$$

((5-25))

5.25 Work out the *quadratic* Zeeman effect for the ground-state hydrogen atom due to the usually neglected $e^2\mathbf{A}^2/2m_ec^2$-term in the Hamiltonian taken to first order. Write the energy shift as

$$\Delta = -\tfrac{1}{2}\chi \mathbf{B}^2$$

and obtain an expression for *diamagnetic susceptibility*, χ.

((**Solution**))
1s state for the hydrogen atom ground state

$$\langle \boldsymbol{r} | 1s \rangle = \frac{1}{\sqrt{\pi a_0^{\,3}}} \exp(-\frac{r}{a_0})$$

The perturbation:

$$\hat{V} = \frac{e^2}{2mc^2}\boldsymbol{A}^2 = \frac{e^2B^2}{8mc^2}(\hat{x}^2 + \hat{y}^2)$$

where

$$\boldsymbol{A} = \frac{1}{2}\boldsymbol{B} \times \hat{\boldsymbol{r}} = \frac{1}{2}B(-\hat{y}, \hat{x}, 0)$$

The ground state hydrogen atom is a nondegenerate state. Using the theory of perturbation for the non-degenerate state, we have

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots$$

where

$$
\begin{aligned}
E_n^{(1)} &= \langle 1s|\hat{V}|1s\rangle \\
&= \int d\boldsymbol{r}\langle \boldsymbol{r}|1s\rangle^* \frac{e^2B^2}{8mc^2}(\hat{x}^2+\hat{y}^2)\langle \boldsymbol{r}|1s\rangle \\
&= \int d\boldsymbol{r}\frac{1}{\sqrt{\pi a_0{}^3}}\exp(-\frac{r}{a_0})\frac{e^2B^2}{8mc^2}(x^2+y^2)\frac{1}{\sqrt{\pi a_0{}^3}}\exp(-\frac{r}{a_0}) \\
&= \frac{1}{\pi a_0{}^3}\frac{e^2B^2}{8mc^2}\int d\boldsymbol{r}\exp(-\frac{2r}{a_0})(x^2+y^2)
\end{aligned}
$$

or

$$
\begin{aligned}
E_n^{(1)} &= \frac{1}{\pi a_0{}^3}\frac{e^2B^2}{8mc^2}\int_0^\infty drr^4\exp(-\frac{2r}{a_0})\int_0^\pi \sin^3 d\theta \\
&= \frac{1}{\pi a_0{}^3}\frac{e^2B^2}{8mc^2}2\pi a_0{}^5 \\
&= \frac{e^2B^2a_0{}^2}{4mc^2}
\end{aligned}
$$

Since

$$
\Delta = -\frac{1}{2}\chi B^2 = E_n^{(1)}
$$

we have

$$
\chi = -\frac{e^2a_0{}^2}{2mc^2}
$$

((**Mathematica**))
Evaluation of $N_A\chi$ = -2.37606 x 10^{-6} emu/mol

```
Clear["Global`*"];
rule1 = {kB → 1.3806504 × 10^-16, NA → 6.02214179 × 10^23,
   c → 2.99792 × 10^10, ℏ → 1.054571628 10^-27,
   me → 9.10938215 10^-28, mp → 1.672621637 × 10^-24,
   mn → 1.674927211 × 10^-24, qe → 4.8032068 × 10^-10,
   eV → 1.602176487 × 10^-12, meV → 1.602176487 × 10^-15,
   keV → 1.602176487 × 10^-9, MeV → 1.602176487 × 10^-6,
   rB → 0.52917720859 × 10^-8};

s1 = (qe^2 rB^2)/(2 me c^2) NA //. rule1
```

$$2.37606 \times 10^{-6}$$