(B1)

Time-Independent Perturbation Theory

I. Non Degenerate Perturbation Theory

$$\mathcal{H} = \mathcal{H}_0 + \lambda W \qquad \lambda \ll 1$$

where $\mathcal{H}_0 |p\rangle = E_p^0 |p\rangle$

$$\langle p'|p\rangle = \delta_{p'p}$$

$$\sum_p |p\rangle\langle p| = 1$$

We are interested in solutions & eigenvalues of $\mathcal{H}$:

$$\mathcal{H}\,|\psi(\lambda)\rangle = E(\lambda)\,|\psi(\lambda)\rangle$$

Expand E & $|\psi\rangle$ in powers of λ:

$$E(\lambda) = \varepsilon_0 + \lambda\,\varepsilon_1 + \lambda^2 \varepsilon_2 + \cdots$$

$$|\psi(\lambda)\rangle = |0\rangle + \lambda\,|1\rangle + \lambda^2 |2\rangle + \cdots$$

Plug this into the Schrodinger Eqn.:

$$(\mathcal{H}_0 + \lambda W)\left(|0\rangle + \lambda|1\rangle + \lambda^2|2\rangle\right) = \left(\varepsilon_0 + \lambda\varepsilon_1 + \lambda^2\varepsilon_2\right) \times \left(|0\rangle + \lambda|1\rangle + \lambda^2|2\rangle\right)$$

Collect Powers of λ:

0^{th} $\qquad \mathcal{H}_0|0\rangle = \varepsilon_0|0\rangle$

1^{st} $\qquad \mathcal{H}_0|1\rangle + W|0\rangle = \varepsilon_1|0\rangle + \varepsilon_0|1\rangle$

2^{nd} $\qquad \mathcal{H}_0|2\rangle + W|1\rangle = \varepsilon_2|0\rangle + \varepsilon_1|1\rangle + \varepsilon_0|2\rangle$

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Note that $|0\rangle$, $|1\rangle$ & $|2\rangle$ are not single eigenstates.
Normalization Requires that:

$$\langle 0|0\rangle = 1$$

1ST $\quad \langle\psi(\lambda)|\psi(\lambda)\rangle = \left(\langle 0| + \lambda\langle 1|\right)\left(|0\rangle + \lambda|1\rangle\right) + O(\lambda^2)$

$$= \langle 0|0\rangle + \lambda\left(\langle 1|0\rangle + \langle 0|1\rangle\right) + O(\lambda^2)$$

We choose $\langle 0|1\rangle$ to be real, so that

$$\langle 0|1\rangle = \langle 1|0\rangle = 0$$

2nd To Second Order:

$$\langle\psi(\lambda)|\psi(\lambda)\rangle = 1 =$$

$$= \left(\langle 0| + \lambda\langle 1| + \lambda^2\langle 2|\right)\left(|0\rangle + \lambda|1\rangle + \lambda^2|2\rangle\right)$$

$$= \underbrace{\langle 0|0\rangle}_{\to 1} + \lambda\underbrace{\left(\langle 1|0\rangle + \langle 0|1\rangle\right)}_{=0} + \lambda^2\left(\langle 2|0\rangle + \langle 0|2\rangle + \langle 1|1\rangle\right) + O(\lambda^3)$$

Thus:

$$\langle 0|2\rangle = \langle 2|0\rangle = -\tfrac{1}{2}\langle 1|1\rangle$$

A. Zero Order Energy Correction

$$\mathcal{H}_0|0\rangle = \varepsilon_0|0\rangle$$

$\therefore$ for state n, $|0\rangle = |n\rangle$

$$\mathcal{H}_0|n\rangle = E_n^0|n\rangle$$

B. First Order Energy Correction

$$\mathcal{H}_0|1\rangle + W|0\rangle = \mathcal{E}_1|0\rangle + \mathcal{E}_0|1\rangle$$

$$\mathcal{H}_0|1\rangle + W|n\rangle = \mathcal{E}_1|n\rangle + E_n^\circ|1\rangle$$

Multiply by $\langle n|$

$$\langle n|\mathcal{H}_0|1\rangle + \langle n|W|n\rangle = \mathcal{E}_1\langle n|n\rangle + E_n^\circ\langle n|1\rangle$$

$\langle n|\mathcal{H}_0|1\rangle = E_n^\circ\langle n|1\rangle = 0$; $\mathcal{E}_1\langle n|n\rangle \to 1$; $E_n^\circ\langle n|1\rangle = \langle 0|1\rangle = 0$

* $$\boxed{\mathcal{E}_1 = \langle n|W|n\rangle}$$

C. First Order Wavevector Correction

Let $|p\rangle \neq |n\rangle$

$$\langle p|\mathcal{H}_0|1\rangle + \langle p|W|n\rangle = \mathcal{E}_1\langle p|n\rangle + E_n^\circ\langle p|1\rangle$$

$\langle p|\mathcal{H}_0|1\rangle \to E_p^\circ\langle p|1\rangle$; $\mathcal{E}_1\langle p|n\rangle \to 0$

$$\langle p|1\rangle = \frac{\langle p|W|n\rangle}{E_n^\circ - E_p^\circ} \qquad p \neq n \quad ; \quad \langle n|1\rangle = 0$$

$\langle p|1\rangle$ are the coefficients in an expansion of $|1\rangle$:

$$|1\rangle = \sum_p |p\rangle\langle p|1\rangle$$

$$|1\rangle = \sum_{p\neq n} |p\rangle \frac{\langle p|W|n\rangle}{E_n^\circ - E_p^\circ}$$

* $$\boxed{|\psi_n\rangle \approx |n\rangle + \sum_{p\neq n} \frac{\langle p|W|n\rangle}{E_n^\circ - E_p^\circ}|p\rangle}$$

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D. Second Order Eigenvalue Correction

$$\mathcal{H}_0|2\rangle + W|1\rangle = \varepsilon_2|0\rangle + \varepsilon_1|1\rangle + \varepsilon_0|2\rangle$$

$$\langle n|\mathcal{H}_0|2\rangle + \langle n|W|1\rangle = \varepsilon_2\langle n|n\rangle + \varepsilon_1\langle n|1\rangle + E_n^\circ\langle n|2\rangle$$

$\hookrightarrow = E_n^\circ\langle n|2\rangle$ $\quad\quad$ $\hookrightarrow 1$ $\quad\quad$ $\hookrightarrow 0$

$$\therefore \quad \varepsilon_2 = \langle n|W|1\rangle$$

$$= \langle n|W\Big|\sum_{p\neq n}|p\rangle\frac{\langle p|W|n\rangle}{E_n^\circ - E_p^\circ}$$

$$\varepsilon_2 = \sum_{p\neq n}\frac{|\langle p|W|n\rangle|^2}{E_n^\circ - E_p^\circ}$$

$$* \quad \boxed{E_n \approx E_n^\circ + \langle n|W|n\rangle + \sum_{p\neq n}\frac{|\langle p|W|n\rangle|^2}{E_n^\circ - E_p^\circ}}$$

E. Degenerate Levels

If a subset of the energy levels are degenerate, calculate the matrix W of that subspace & diagonalize.

For example:

$$S^{(2)} = \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix}$$

diagonalize this 2×2 to get the new energies & eigenvectors.

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Exact Solutions: Angular Momentum States

I. Operators & Observables

$$\underline{L} = \underline{R} \times \underline{P} \quad \text{angular momentum}$$

$$L_z = X P_y - Y P_x$$

$$L_x = Y P_z - Z P_y$$

$$L_y = Z P_x - X P_z$$

$$[L_x, L_y] = i\hbar L_z$$

$$[L_y, L_z] = i\hbar L_x$$

$$[L_z, L_x] = i\hbar L_y$$

For generalized angular momentum systems we use J in lieu of L.

$$J^2 = J_x^2 + J_y^2 + J_z^2$$

$$[J^2, \underline{J}] = 0$$

We also define the operators

$$J_+ = J_x + i J_y$$

$$J_- = J_x - i J_y$$

$$[J_z, J_+] = \hbar J_+$$

$$[J_z, J_-] = -\hbar J_-$$

$$[J_+, J_-] = 2\hbar J_z$$

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II. Eigenvectors

J_z and J^2 have eigenvectors $|j,m\rangle$ where $j \to J^2$ & $m \to J_z$:

$$J^2 |j,m\rangle = j(j+1)\hbar^2 |j,m\rangle \qquad j \geq 0 \quad \text{(integer or half-integer)}$$

$$J_z |j,m\rangle = m\hbar |j,m\rangle \qquad -j \leq m \leq j \quad (2j+1 \text{ values})$$

C-T use another index k to remind us that J^2 & J_z are not at C.S.C.O.: for atoms, the radial degree of freedom will supply the additional quantum number.

In addition,

$$J_\pm |j,m\rangle = \hbar\sqrt{j(j+1) - m(m\pm1)}\ |m\pm1\rangle$$

(This equation works assuming that $J_+|j,j\rangle = J_-|j,-j\rangle = 0$)

III. Matrix Representations

Matrices are $2j+1$ dimensional

$$\langle j,m|\ J_x\ |j',m'\rangle = \frac{\hbar}{2}\delta_{jj'}\left[\sqrt{j(j+1)-m'(m'+1)}\,\delta_{m,m'+1} + \sqrt{j(j+1)-m'(m'-1)}\,\delta_{m,m'-1}\right]$$

$$\langle j,m|\ J_y\ |j',m'\rangle = \frac{\hbar}{2i}\delta_{jj'}\left[\sqrt{j(j+1)-m'(m'+1)}\,\delta_{m,m'+1} - \sqrt{j(j+1)-m'(m'-1)}\,\delta_{m,m'-1}\right]$$

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$$\langle j,m \mid J_z \mid j',m' \rangle = m\hbar\, \delta_{jj'}\, \delta_{mm'}$$

$$\langle j,m \mid J_\pm \mid j',m' \rangle = \hbar \sqrt{j(j+1) - m'(m'\pm 1)}\; \delta_{jj'}\, \delta_{m,m'\pm 1}$$

$$\langle j,m \mid J^2 \mid j',m' \rangle = \hbar^2 j(j+1)\, \delta_{jj'}\, \delta_{mm'}$$

For Example, the matrices for a spin = 1 particle in the $|j,m\rangle$ basis are given by:

$$J_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad J_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \qquad J_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}$$

$$J_+ = \hbar \begin{pmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix} \qquad J_- = \hbar \begin{pmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{pmatrix} \qquad J^2 = 2\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

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I. Charged Harmonic Oscillator in an Electric Field - Exact Solution

"Stark Effect"

$$\mathcal{H}_0 = p^2/2m + \tfrac{1}{2} m\omega^2 x^2$$

$$W = -q\mathcal{E}x \qquad \mathcal{E} = \text{Electric Field Strength}$$

This can be solved exactly by completing the square:

$$\mathcal{H} = p^2/2m + \tfrac{1}{2} m\omega^2 x^2 - q\mathcal{E}x$$

$$= p^2/2m + \tfrac{1}{2} m\omega^2 \left(x^2 - \frac{2q\mathcal{E}}{m\omega^2} x + \frac{q^2\mathcal{E}^2}{m^2\omega^4} \right) - \frac{q^2\mathcal{E}^2}{2m\omega^2}$$

$$= p^2/2m + \tfrac{1}{2} m\omega^2 \left(x - \frac{q\mathcal{E}}{m\omega^2} \right)^2 - \frac{q^2\mathcal{E}^2}{2m\omega^2}$$

If we change $x' \Rightarrow x - q\mathcal{E}/m\omega^2$, $p \Rightarrow p$ (same for both x & x')

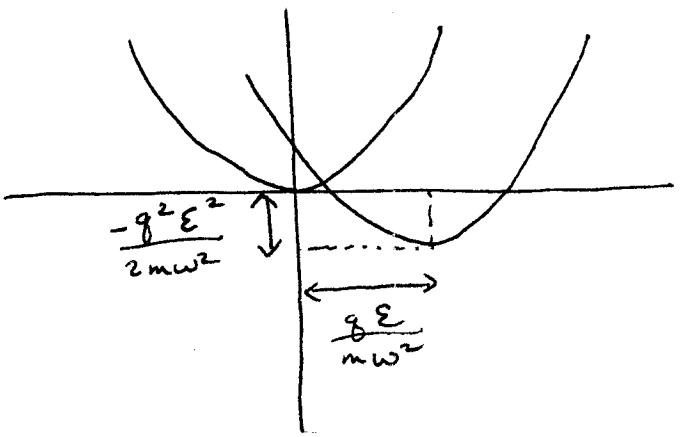
$$\mathcal{H} = p^2/2m + \tfrac{1}{2} m\omega^2 x'^2 - \frac{q^2\mathcal{E}^2}{2m\omega^2}$$

$$= \hbar\omega \hat{N} - \frac{q^2\mathcal{E}^2}{2m\omega^2}$$

$$\therefore \; E_n = \hbar\omega\left(n + \tfrac{1}{2}\right) - q^2\mathcal{E}^2/2m\omega^2$$

The wavefunctions are given by:

$$|\phi'_n\rangle = e^{\frac{-i q\mathcal{E} p}{m\hbar\omega^2}} |\phi_n\rangle \qquad \text{translated by } \frac{q\mathcal{E}}{m\omega^2}$$



II. Charged Harmonic Oscillator in an Electric Field - Perturbation Theory.

$$H_0 = p^2/2m + \tfrac{1}{2} m\omega^2 x^2$$

$$W = -q\mathcal{E}x = -q\mathcal{E}\sqrt{\frac{\hbar}{2m\omega}}\,(a^+ + a)$$

a. 1st order solution -

$$E_n = E_n^\circ + \langle n|W|n\rangle$$

$$= \hbar\omega(n+\tfrac{1}{2}) + \langle n|W|n\rangle$$

but $W|n\rangle \Rightarrow \alpha|n-1\rangle + \beta|n+1\rangle$, $\therefore \langle n|W|n\rangle = 0$

$$E_n = \hbar\omega(n+\tfrac{1}{2}) \quad \text{to } 1^{st} \text{ order.} \longleftarrow$$

b. 2nd order solution -

$$E_n' = E_n^\circ + W_{nn} + \sum_{n'\neq n} \frac{|\langle n'|W|n\rangle|^2}{E_n^\circ - E_{n'}^\circ}$$

The last term is nonzero only for $n' = n+1$ or $n-1$.

$$\langle n+1|W|n\rangle = -q\mathcal{E}\sqrt{\frac{\hbar}{m\omega}}\sqrt{\frac{n+1}{2}}$$

$$\langle n-1|W|n\rangle = -q\mathcal{E}\sqrt{\frac{\hbar}{m\omega}}\sqrt{\frac{n}{2}}$$

$$E_n^\circ - E_{n'}^\circ = (n-n')\hbar\omega$$

$\therefore$

$$E_n = \hbar\omega(n+\tfrac{1}{2}) + \frac{q^2\mathcal{E}^2}{2m\omega^2}\left(\frac{n}{n-(n-1)} + \frac{n+1}{n-(n+1)}\right)$$

$$= \hbar\omega(n+\tfrac{1}{2}) - \frac{q^2\mathcal{E}^2}{2m\omega^2} \longleftarrow \text{same as } \underline{\text{exact}} \text{ result.}$$

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Perturbation Theory Example: Two Spin ½'s coupled by dipole-dipole interactions.

Consider two spins $\underline{S}_1$ & $\underline{S}_2$ that have different magnetic moment (e.g., C & H):

$$\underline{M}_1 = \gamma_1 \underline{S}_1$$
$$\underline{M}_2 = \gamma_2 \underline{S}_2$$

We are interested in the states $|\pm\pm\rangle$ of $\mathcal{H}_0$

$$\mathcal{H}_0 = \omega_1 S_{1z} + \omega_2 S_{2z}$$

$$\omega_1 = -\gamma_1 B_0 \qquad \omega_2 = -\gamma_2 B_0$$

The dipole-dipole interaction we will treat as a perturbation W on $\mathcal{H}_0$:

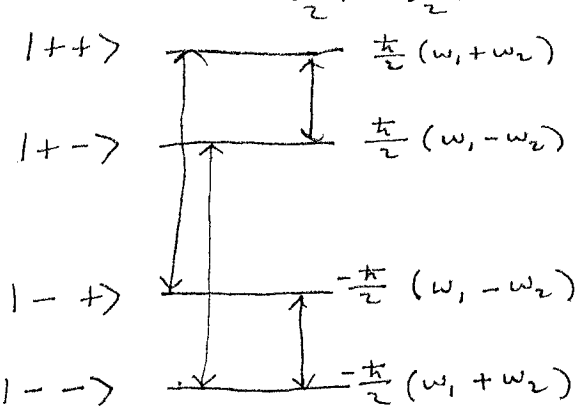
$$\mathcal{H} = \mathcal{H}_0 + W$$

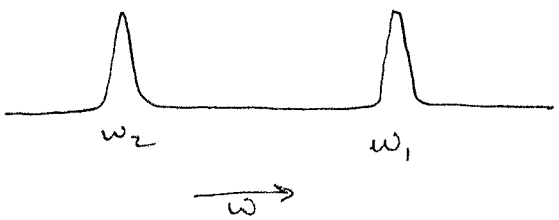
$$W \simeq A(3\cos^2\theta - 1)\left[S_{1z} S_{2z} - \tfrac{1}{4}\left(S_{1+} S_{2-} + S_{1-} S_{2+} \right)\right]$$

where θ is the angle between $\underline{S}_1$ & $\underline{S}_2$.

0th order Energy Eigenvalues:

$$E^\circ = \pm\tfrac{\hbar}{2}\omega_1 \pm \tfrac{\hbar}{2}\omega_2 \qquad \text{assume } \omega_1 > \omega_2$$





The <u>selection rules</u> for transitions between these states are only one spin flip is allowed (lines represent allowed transitions).

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1st order energy levels:

We need to calculate $\langle \pm\pm | W | \pm\pm \rangle$. Only the $S_{1z}S_{2z}$ term leads to diagonal matrix elements:

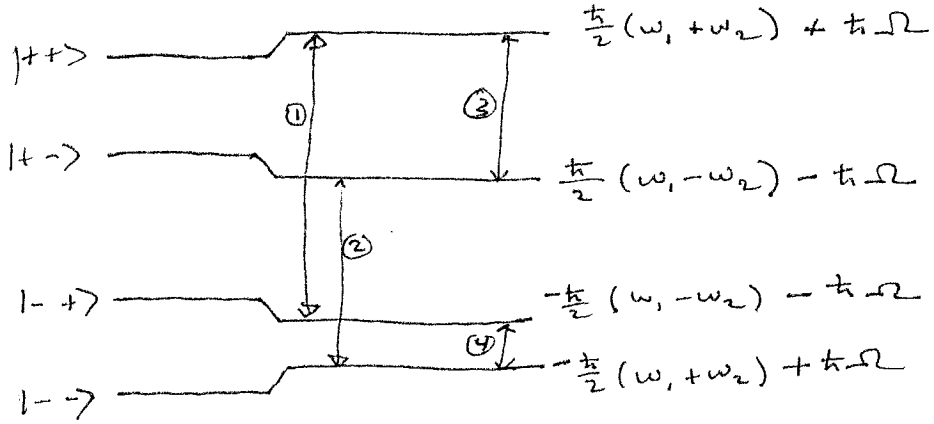
$\langle ++|W|++\rangle = A(3\cos^2\theta - 1)\cdot\frac{\hbar^2}{4} \equiv \hbar\Omega$ ← $\langle ++|S_{1z}S_{2z}|++\rangle = \frac{\hbar^2}{4}$

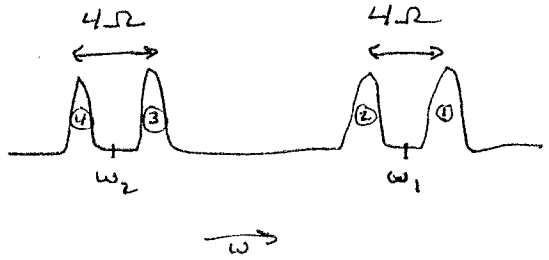
$\Omega \equiv \frac{\hbar^2}{4}A(3\cos^2\theta - 1)$

$\langle +-|W|+-\rangle = A(3\cos^2\theta - 1)\cdot\frac{-\hbar^2}{4} = -\hbar\Omega$

$\langle -+|W|-+\rangle = A(3\cos^2\theta - 1)\cdot\frac{-\hbar^2}{4} = -\hbar\Omega$

$\langle --|W|--\rangle = A(3\cos^2\theta - 1)\cdot\frac{\hbar^2}{4} = \hbar\Omega$



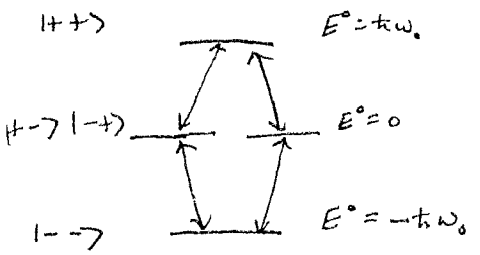


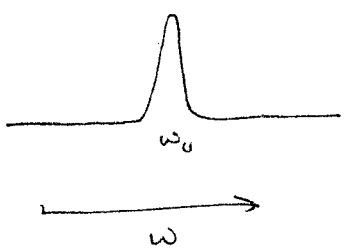
$\mathcal{H}_0 + W$

Selection Rules are unchanged since eigenstates are unchanged (to 1st order).

Degenerate case: $\omega_1 = \omega_2 \equiv \omega_0$ two identical spins.

0th Order:





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1st Order Correction:

Non degenerate shifts for $|++\rangle$ & $|--\rangle$ states are the same as before, but the $|+-\rangle$ & $|-+\rangle$ states mix due to the $S_{1+}S_{2-}$ terms:

$$W = \begin{pmatrix} \hbar\Omega & 0 & 0 & 0 \\ 0 & -\hbar\Omega & -\hbar\Omega & 0 \\ 0 & -\hbar\Omega & -\hbar\Omega & 0 \\ 0 & 0 & 0 & \hbar\Omega \end{pmatrix} \qquad H_0 = \begin{pmatrix} \hbar\omega & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\hbar\omega \end{pmatrix}$$

We have diagonalized a similar matrix before. It leads to the eigenstates of S^2:

$|++\rangle = |1,1\rangle$ $\quad \langle 1,1|W|1,1\rangle = \hbar\Omega$

$\frac{1}{\sqrt{2}}(|+-\rangle + |-+\rangle) = |1,0\rangle$ $\quad \langle 1,0|W|1,0\rangle = -2\hbar\Omega$

$|--\rangle = |1,-1\rangle$ $\quad \langle 1,-1|W|1,-1\rangle = +\hbar\Omega$

$\frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle) = |0,0\rangle$ $\quad \langle 0,0|W|0,0\rangle = 0$

$$\begin{pmatrix} -1 & -1 \\ -1 & -1 \end{pmatrix}$$

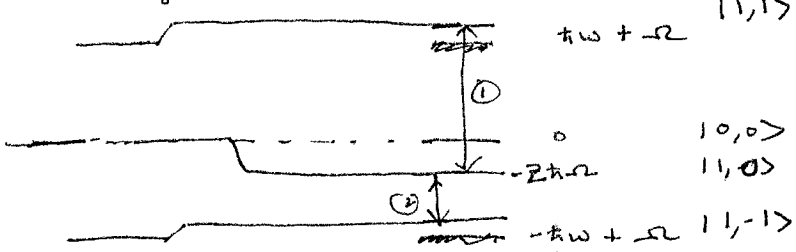
$(-1-\lambda)^2 - 1 = 0$

$1+\lambda = \pm 1$

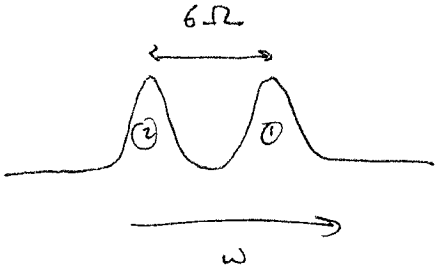
$\lambda = \pm 1 - 1$

$= -2, 0$

Thus the energies are



Only transitions between triplet states are allowed.



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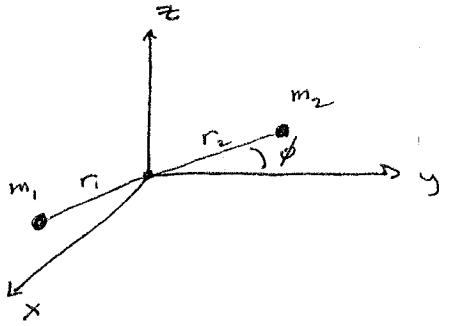
Perturbation Theory Example: Rotation of Diatomic Molecules & the Stark Effect

Consider a rigid diatomic rotator where center of mass is positioned at the origin of our reference frame:



$r_e = r_1 + r_2$ = bond distance

$I = m_1 r_1^2 + m_2 r_2^2$ = moment of inertia

$\mu = \frac{m_1 m_2}{m_1 + m_2}$ = reduced mass

A. Unperturbed Eigenvalues & Eigenstates.

1. The Hamiltonian for the free rotations of this diatomic is

$$\mathcal{H}_0 = \frac{L^2}{2I}$$ L^2 is the angular momentum operator

∴ the eigenstates are $|\ell, m\rangle$ as in our generalized angular momentum problems.

$$\mathcal{H}_0 |\ell, m\rangle = \frac{\hbar^2}{2I} \ell(\ell+1) = hB\ell(\ell+1) \qquad B = \frac{\hbar}{4\pi I}$$

2. If the motion of the diatomic is restricted to the x-y plane, then it is called a plane rigid rotor, and only the m quantum number is important:

$$\mathcal{H}_0 |m\rangle = \frac{L_z^2}{2I} = \frac{\hbar^2}{2I} m^2 \qquad m = 0, \pm 1, \pm 2 \ldots$$

$4hB$ ——— $|2\rangle, |-2\rangle$

hB ——— $|1\rangle, |-1\rangle$

0 ——— $|0\rangle$

The ground state is non-degenerate, & all excited states are two-fold degenerate.

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B. Stark Effect on the Plane Rigid Rotor

If we now apply an electric field in the +x direction of strength E_0, & if the rigid rotor has a charge $\pm q$ on each mass, then the energy of interaction of this dipole & the field is given by:

$$W = -\underline{d}\cdot\underline{E} = -(q r_e \hat{r})\cdot(E_0 \hat{x}) = -q r_e E_0 \cos\phi$$

where ϕ is the angle between $\hat{r}$ & $\hat{x}$.

I will assert that this perturbation has the following matrix elements:

$$\langle m' | W | m \rangle = -\frac{q r_e E_0}{2} \delta_{m', m\pm 1} \equiv -\alpha\, \delta_{m', m\pm 1}$$

(You can derive this relation rather easily).

The perturbation modifies the Hamiltonian in the following fashion:

$$\mathcal{H} = \mathcal{H}_0 + W = \begin{pmatrix} E_0^\circ & -\alpha & -\alpha & 0 & 0 \\ -\alpha & E_{-1}^\circ & 0 & -\alpha & 0 \\ -\alpha & 0 & E_1^\circ & 0 & -\alpha \\ 0 & -\alpha & 0 & E_{-2}^\circ & 0 \\ 0 & 0 & -\alpha & 0 & E_2^\circ \end{pmatrix}$$

Perturbation Energies:

$$\mathcal{E}_0 = E_m^\circ = \frac{\hbar^2}{2I} m^2$$

$\mathcal{E}_1 = 0$

This is true because (i) $W_{mm} = 0$ for all m, & (ii) $W_{m,-m} = 0$ for all m (i.e., degenerate states are not mixed with W).

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Second Order Energy Correction:

$$\mathcal{E}_2 = \sum_{m' \neq m} \frac{|\langle m' | W | m \rangle|^2}{E^\circ_m - E^\circ_{m'}}$$

$$= \alpha^2 \left[\frac{1}{E^\circ_m - E^\circ_{m-1}} + \frac{1}{E^\circ_m - E^\circ_{m+1}} \right]$$

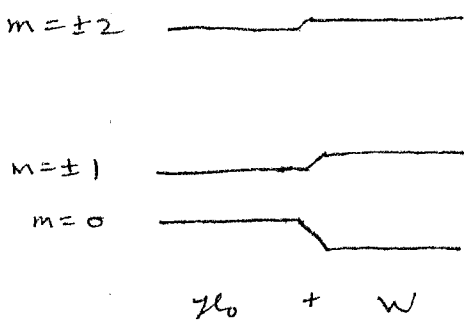
$$= \frac{2I\alpha^2}{\hbar^2} \left[\frac{1}{m^2 - (m-1)^2} + \frac{1}{m^2 - (m+1)^2} \right]$$

$$m^2 - (m-1)^2 = m^2 - (m^2 - 2m + 1) = 2m - 1$$
$$m^2 - (m+1)^2 = m^2 - (m^2 + 2m + 1) = -(2m+1)$$

$$\mathcal{E}_2 = \frac{2I\alpha^2}{\hbar^2} \left[\frac{1}{2m-1} - \frac{1}{2m+1} \right]$$

$$\mathcal{E}_2 = \frac{4I\alpha^2}{\hbar^2} \cdot \frac{1}{(4m^2-1)} \equiv \frac{\delta}{4m^2-1} \qquad \delta \equiv \frac{4I\alpha^2}{\hbar^2}$$

$\mathcal{E}_2(m=0) = -\delta$
$\mathcal{E}_2(m=\pm 1) = +\frac{1}{3}\delta$
$\mathcal{E}_2(m=\pm 2) = +\frac{1}{15}\delta$



Note that:

1) The shift in energy (δ) is proportional to E^2. This is the second order Stark shift. The first order Stark Shift is zero for this system since $\mathcal{E}_1 = 0$
2) Degenerate levels stay degenerate ($\pm m$), as expected.
3) For a 3-d rigid rotor:

$$\mathcal{E}_2 = \frac{4\alpha^2}{2hB\,\ell(\ell+1)} \cdot \frac{\ell(\ell+1) - 3m^2}{(2\ell-1)(2\ell+3)}$$

cf. Townes & Schawlow, "Microwave Spectroscopy"

(B16)

Eigenvalues & Eigenvectors for S^2

$$S^2 = S_1^2 + S_2^2 + 2\,\underline{S}_1 \cdot \underline{S}_2$$

$$= S_1^2 + S_2^2 + 2(S_{1z}S_{2z} + S_{1x}S_{2x} + S_{1y}S_{2y})$$

a) S_1^2, S_2^2 & $S_{1z}S_{2z}$ are diagonal in the $|\pm\pm\rangle$ basis:

$$S_1^2\,|\pm\pm\rangle = S_2^2\,|\pm\pm\rangle = \tfrac{3}{4}\hbar^2$$

$$2\,S_{1z}S_{2z}\,|++\rangle = \tfrac{\hbar^2}{2}\,|++\rangle$$
$$2\,S_{1z}S_{2z}\,|--\rangle = \tfrac{\hbar^2}{2}\,|--\rangle$$
$$2\,S_{1z}S_{2z}\,|+-\rangle = -\tfrac{\hbar^2}{2}\,|+-\rangle$$
$$2\,S_{1z}S_{2z}\,|-+\rangle = -\tfrac{\hbar^2}{2}\,|-+\rangle$$

In general:
$S_x\,|\pm\rangle = \frac{\hbar}{2}\,|\mp\rangle$
$S_y\,|\pm\rangle = \pm i\frac{\hbar}{2}\,|\mp\rangle$

b) $2(S_{1x}S_{2x} + S_{1y}S_{2y})$ is not diagonal in the $|\pm\pm\rangle$ basis:

$$2(S_{1x}S_{2x} + S_{1y}S_{2y})\,|++\rangle = 2\cdot\tfrac{\hbar^2}{4}\,(|--\rangle - |--\rangle) = 0$$

$$2(S_{1x}S_{2x} + S_{1y}S_{2y})\,|--\rangle = 2\cdot\tfrac{\hbar^2}{4}\,(|++\rangle - |++\rangle) = 0$$

$$2(S_{1x}S_{2x} + S_{1y}S_{2y})\,|+-\rangle = 2\cdot\tfrac{\hbar^2}{4}\,(|-+\rangle + |-+\rangle) = \hbar^2\,|-+\rangle$$

$$2(S_{1x}S_{2x} + S_{1y}S_{2y})\,|-+\rangle = 2\cdot\tfrac{\hbar^2}{4}\,(|+-\rangle + |+-\rangle) = \hbar^2\,|+-\rangle$$

c) The matrix for S^2 is block diagonal:

$$S^2 = \hbar^2 \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix}$$

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d) Diagonalize the $|+-\rangle$ & $|-+\rangle$ states:

$$\begin{pmatrix} 1-\lambda & 1 \\ 1 & 1-\lambda \end{pmatrix} = 0 = (1-\lambda)^2 - 1$$

$$(1-\lambda)^2 = 1$$

$$1-\lambda = \pm 1$$

$$\lambda = 1 \pm 1 = 2, 0$$

Two values, Two States:

$$|\lambda = 2\rangle = \frac{1}{\sqrt{2}}\left(|+-\rangle + |-+\rangle\right)$$

$$|\lambda = 0\rangle = \frac{1}{\sqrt{2}}\left(|+-\rangle - |-+\rangle\right)$$

Thus $|++\rangle$, $|--\rangle$, & $\frac{1}{\sqrt{2}}(|+-\rangle + |-+\rangle)$ have an S^2 eigenvalue of $2\hbar^2$

There are called the <u>triplet</u> states.

The vector $\frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle)$ has an S^2 eigenvalue of $0\hbar^2$.

It is called the <u>singlet</u> state.

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What are the eigenvalues of S_z?

$$S_z = S_{1z} + S_{2z}$$

$$S_z|++\rangle = \hbar|++\rangle$$
$$S_z|--\rangle = -\hbar|--\rangle$$
$$S_z|1=2\rangle = (S_{1z} + S_{2z})\frac{1}{\sqrt{2}}(|+-\rangle + |-+\rangle) = 0$$
$$S|1=0\rangle = (S_{1z} + S_{2z})\frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle) = 0$$

S_z is diagonal:

$$S_z = \hbar \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

We can rewrite the coupled spin states in terms of an $S=1$ & an $S=0$ set:

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

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

(B19)

$\underline{J} \cdot \underline{S}$ coupling

As a final note, consider the coupling of two spins / angular momenta $\underline{J}$ & $\underline{S}$. Such a coupling is usually a dot product:

$$\mathcal{H}_{int} = a\, \underline{J} \cdot \underline{S}$$

$$\underline{J} \cdot \underline{S} = J_x S_x + J_y S_y + J_z S_z$$

consider the term $J_+ S_- + J_- S_+$

$$J_+ S_- + J_- S_+ = (J_x + i J_y)(S_x - i S_y) + (J_x - i J_y)(S_x + i S_y)$$

$$= J_x S_x + J_y S_y + i (J_y S_x - J_x S_y) + J_x S_x + J_y S_y + i (J_x S_y - J_y S_x)$$

$$= 2 (J_x S_x + J_y S_y)$$

Therefore:

$$\underline{J} \cdot \underline{S} = J_z S_z + \tfrac{1}{2} (J_+ S_- + S_- J_+)$$

This form will be useful when calculating the eigenstates of coupled systems