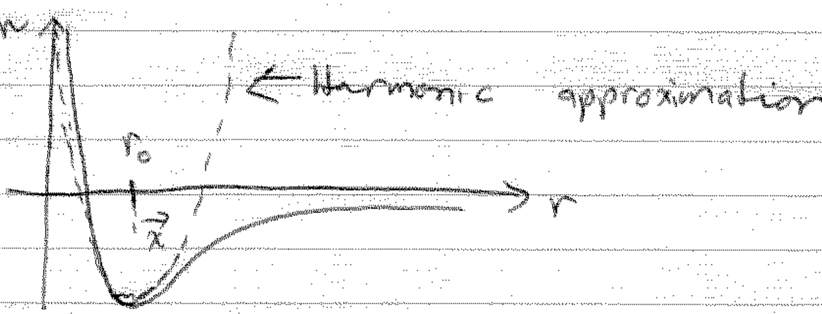
Physics 412 - Quantum II

Problem Set #9 - Solutions

Problem 1: Lennard-Jones Encore

Given $\quad V(r) = \dfrac{C_{12}}{r^{12}} + \dfrac{C_6}{r^6}$



near r_0 $\quad V(x) = \frac{1}{2} m\omega^2 x^2 + \xi x^3$

$$\text{where} \quad \tfrac{1}{2} m\omega^2 = V''(r_0), \quad \xi = \tfrac{1}{6} V'''(r_0)$$

$$\Rightarrow \hat{H} = \hat{H}_0 + \hat{H}_1$$

$$\text{where} \begin{cases} \hat{H}_0 = \dfrac{\hat{P}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2 = \hbar\omega(\hat{N} + \frac{1}{2}) \\ \hat{H}_1 = \xi \hat{x}^3 \end{cases}$$

(a) Small parameter

$$\epsilon = \frac{\xi x_c^3}{\frac{1}{2} m\omega^2 x_c^2} = \frac{1}{6} \frac{V'''(r_0)}{V''(r_0)} x_c$$

$$\text{where} \quad x_c = \sqrt{\frac{2\hbar}{m\omega}}$$

(b) The zeroth order eigenstates $|n\rangle$, $E_n^{(0)} = \hbar\omega(n+\frac{1}{2})$

$\Rightarrow$ First order shift: $E_n^{(1)} = \langle n|\hat{H}_1|n\rangle$

$$E_n^{(1)} = \xi \int_{-\infty}^{\infty} dx \, |\phi_n(x)|^2 \, x^3$$

The wave functions $\phi_n(x)$ are eigenstates of parity

$\Rightarrow |\phi_n(x)|^2$ is even function, but x^3 odd

$\Rightarrow E_n^{(1)} = 0 \quad \forall n$

(c) Second order shift

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle m|\hat{H}_1|n\rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$= \frac{\xi^2 \left(\frac{x_c}{2}\right)^6}{\hbar\omega} \sum_{m \neq n} \frac{|\langle m|(\hat{a}+\hat{a}^{\dagger})^3|n\rangle|^2}{n-m}$$

where I used $\hat{x} = \frac{x_c}{2}(\hat{a}+\hat{a}^{\dagger})$

$$\frac{x_c}{2} = \sqrt{\frac{\hbar}{2m\omega}}$$

(d) $(\hat{a}+\hat{a}^{+})^3 = (\hat{a}+\hat{a}^{+})(\hat{a}+\hat{a}^{+})^2$

$$= (\hat{a}+\hat{a}^{+})(\hat{a}^2+\hat{a}^{+2}+\hat{a}^{+}\hat{a}+\underbrace{\hat{a}\hat{a}^{+}}_{=\hat{a}^{+}\hat{a}+1})$$

(from commutator)

$$\Rightarrow (\hat{a}+\hat{a}^{+})^3 = (\hat{a}+\hat{a}^{+})(\hat{a}^2+\hat{a}^{+2}+2\hat{N}+1)$$

$$= (\hat{a}^3+\hat{a}^{+3}+\hat{a}^{+}\hat{a}^2+\hat{a}\hat{a}^{+2}+$$

$$(\hat{a}+\hat{a}^{+})(2\hat{N}+1))$$

Aside: $\hat{a}^{+}\hat{a}^2 = \hat{N}\hat{a}$

$$\hat{a}\hat{a}^{+2} = \hat{a}\hat{a}^{+}\hat{a}^{+} = (\hat{N}+1)\hat{a}^{+}$$

$$\hat{a}\hat{N} = \hat{N}\hat{a}+[\hat{a},\hat{N}] = \hat{N}\hat{a}+\hat{a} = (\hat{N}+1)\hat{a}$$

$$\hat{a}^{+}\hat{N} = \hat{N}\hat{a}^{+}+[\hat{a}^{+},\hat{N}] = \hat{N}\hat{a}^{+}-\hat{a}^{+} = (\hat{N}-1)\hat{a}^{+}$$

$$\Rightarrow (\hat{a}^3+\hat{a}^{+3}+\hat{N}a+(\hat{N}+1)\hat{a}^{+}+2(\hat{N}+1)\hat{a}$$

$$+2(\hat{N}-1)\hat{a}^{+}+\hat{a}+\hat{a}^{+})$$

$$\Rightarrow \boxed{(\hat{a}+\hat{a}^{+})^3 = (\hat{a}^3+\hat{a}^{+3}+(3\hat{N}+3)\hat{a}+3\hat{N}\hat{a}^{+})}$$

(e) $$E_n^{(2)} = \frac{\xi^2 \left(\frac{\hbar}{2m\omega}\right)^3}{\hbar\omega} \sum_m \frac{|\langle m|(\hat{a}+\hat{a}^\dagger)^3|n\rangle|^2}{n-m}$$

Aside:

Need: $\langle m|\hat{a}^3|n\rangle = \sqrt{n(n-1)(n-2)}\ \delta_{m,n-3}$

$$\langle m|\hat{a}^{\dagger 3}|n\rangle = \sqrt{(n+1)(n+2)(n+3)}\ \delta_{m,n+3}$$

$$\langle m|(3\hat{N}+3)\hat{a}|n\rangle = (3m+3)\sqrt{n}\ \delta_{m,n-1}$$

$$\langle m|3\hat{N}\hat{a}^\dagger|n\rangle = 3m\ \delta_{m,n+1}$$

$$\Rightarrow E_n^{(2)} = \frac{\xi^2\left(\frac{\hbar}{2m\omega}\right)^3}{\hbar\omega}\left[\frac{n(n-1)(n-2)}{3} + \frac{(n+1)(n+2)(n+3)}{-3} + \frac{9n^3}{1} + \frac{9(n+1)^3}{-1}\right]$$

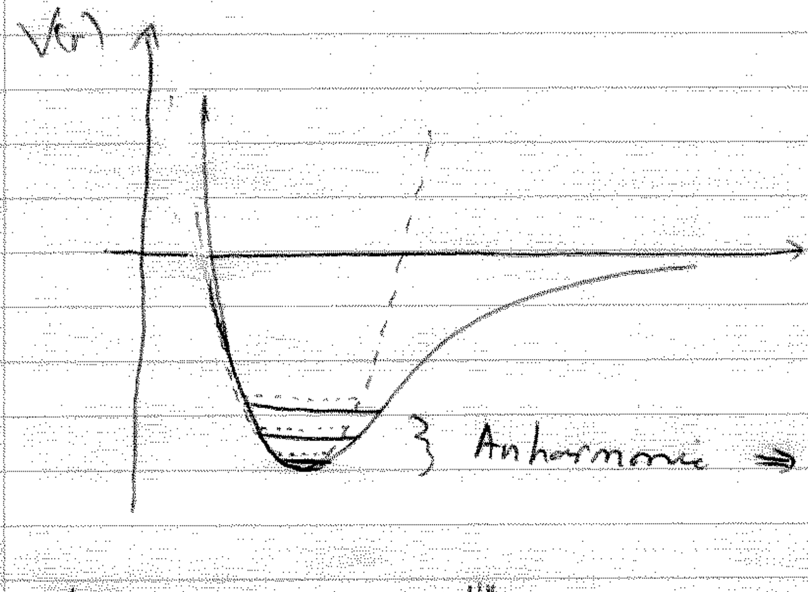
$$\Rightarrow \boxed{E_n^{(2)} = -\frac{\xi^2\hbar^2}{m^3\omega^4}\left[\frac{15}{4}\left(n+\frac{1}{2}\right)^2 + \frac{7}{16}\right]}$$

(f) Carbon - Carbon bonds:

$$C_6 = 15.2 \text{ eV } \mathring{A}^6$$

$$C_{12} = 2.4 \text{ eV } \mathring{A}^{12}$$

Equilibrium point $r_0 = \left(\frac{2C_{12}}{C_6}\right)^{1/6} = 3.8 \mathring{A}$



} Anharmonic $\Rightarrow$ not equally spaced levels

Note $\epsilon = \frac{1}{6} \frac{V'''(r_0)}{V''(r_0)} x_c = 0.35$ for this problem

Perturbation theory is "fair"

Problem 2: Perturbation theory in 2D Hilbert Space

Spin $\frac{1}{2}$ in an magnetic field $\vec{B} = B_x \vec{e}_x + B_z \vec{e}_z$

(a) Hamiltonian $\hat{H} = -\hat{\vec{\mu}} \cdot \vec{B}$

electron $\vec{\mu} = -\underbrace{2}_{\text{g factor}} \mu_B \vec{S} = -\mu_B \vec{\sigma}$

$$\Rightarrow \hat{H} = \mu_B \vec{B} \cdot \vec{\sigma} = \mu_B B_x \hat{\sigma}_x + \mu_B B_z \hat{\sigma}_z$$

$$= \hbar\omega_0 \hat{\sigma}_z + \frac{\hbar\Omega}{2} \hat{\sigma}_x$$

where $\mu_B B_z = \hbar\omega_0$ $\quad$ $\mu_B B_x = \frac{\hbar\Omega}{2}$

(b) If $B_x = 0 \Rightarrow \hat{H}_0 = \hbar\omega_0 \hat{\sigma}_z$

"Zeroth order" $\quad |\uparrow_z\rangle \quad E_\uparrow^{(0)} = \hbar\omega_0$

$|\downarrow_z\rangle \quad E_\downarrow^{(0)} = -\hbar\omega_0$

Now add small field $|B_x| << |B_z| \Rightarrow$ Perturbation theory

$$\hat{H}_1 = \frac{\hbar\Omega}{2} \hat{\sigma}_x$$

First order vanishes $\begin{cases} E_\uparrow^{(1)} = \langle\uparrow|\hat{H}_1|\uparrow\rangle = 0 \\ E_\downarrow^{(1)} = \langle\downarrow|\hat{H}_1|\downarrow\rangle = 0 \end{cases}$

Second order shift

$$E_{\uparrow}^{(2)} = \frac{|\langle\downarrow|\hat{H}_1|\uparrow\rangle|^2}{E_{\uparrow}^{(0)} - E_{\downarrow}^{(0)}} = \left(\frac{\hbar\Omega}{2}\right)^2 \frac{|\langle\downarrow|\hat{\sigma}_x|\uparrow\rangle|^2}{\hbar\omega_0 - (-\hbar\omega_0)}$$

$$= \frac{(\hbar\Omega)^2}{8(\hbar\omega_0)} = \frac{\hbar\omega_0}{8}\left(\frac{\Omega}{\omega_0}\right)^2$$

small parameter

Similarly $$E_{\downarrow}^{(2)} = \frac{(\hbar\Omega)^2}{4} \frac{|\langle\downarrow|\hat{\sigma}_x|\uparrow\rangle|^2}{-\hbar\omega_0 - (\hbar\omega_0)}$$

$$= -\frac{(\hbar\Omega)^2}{8(\hbar\omega_0)} = -\frac{\hbar\omega_0}{8}\left(\frac{\Omega}{\omega_0}\right)^2$$

Shifts

$|\uparrow_z\rangle$ $\quad E_{\uparrow}^{(2)} = \frac{\hbar\omega_0}{8}\epsilon^2$

$2\hbar\omega_0$ $\qquad\qquad \epsilon = \frac{\Omega}{\omega_0}$

$|\downarrow_z\rangle$ $\quad E_{\downarrow}^{(2)} = -\frac{\hbar\omega_0}{8}\epsilon^2$

Lowest correction to state

$$|\uparrow_z\rangle \Rightarrow |\uparrow_z\rangle + |\downarrow_z\rangle \frac{\langle\downarrow_z|\hat{H}_1|\uparrow_z\rangle}{E_{\downarrow}^{(0)} - E_{\uparrow}^{(0)}}$$

so $$|\uparrow_z\rangle \Rightarrow |\uparrow_z\rangle + \frac{\hbar\Omega}{4(\hbar\omega_0)}|\downarrow_z\rangle = |\uparrow_z\rangle + \frac{\Omega}{4\omega_0}|\downarrow_z\rangle$$

Similarly

$$\boxed{|\downarrow_z\rangle \Rightarrow |\downarrow_z\rangle - \frac{\Omega}{4\omega_0}|\uparrow_z\rangle}$$

(c) Now set $B_z = 0$. Now the two state $|\uparrow_z\rangle$ and $|\downarrow_z\rangle$ are degenerate in the absense of any other field.

Using degenerate perturbation theory, we seek the eigenvectors and eigenvalues of

$$\hat{H}_1 = \frac{\hbar\Omega}{2}\hat{\sigma}_x$$

By inspection: New eigenvectors

$$|\uparrow_x\rangle = \frac{1}{\sqrt{2}}(|\uparrow_z\rangle + |\downarrow_z\rangle)$$

$$|\downarrow_x\rangle = \frac{1}{\sqrt{2}}(|\uparrow_z\rangle - |\downarrow_z\rangle)$$

Eigenvalues $E_{\uparrow_x} = +\frac{\hbar\Omega}{2}$

$$E_{\downarrow_x} = -\frac{\hbar\Omega}{2}$$

(d) Exact solution, Write total Hamiltonian

$$\hat{H} = \hbar\omega_0 \hat{\sigma}_z + \frac{\hbar\Omega}{2}\hat{\sigma}_x$$

as a matrix, in the basis $\{|\uparrow_z\rangle, |\downarrow_z\rangle\}$

$$\hat{H} \doteq \hbar \begin{bmatrix} \omega_0 & \Omega/2 \\ \Omega/2 & -\omega_0 \end{bmatrix}$$

Characteristic equation

$$\det(\hat{H} - \hbar\lambda\hat{\mathbb{1}}) = \hbar^2\left[(\omega_0-\lambda)(-\omega_0-\lambda) - \frac{\Omega^2}{4}\right] = 0$$

$$\Rightarrow \lambda^2 = \omega_0^2 + \frac{\Omega^2}{4} \Rightarrow \lambda_\pm = \pm\sqrt{\omega_0^2 + \frac{\Omega^2}{4}}$$

$$\Rightarrow \text{Eigenvalues } \boxed{E_\pm = \pm\hbar\sqrt{\omega_0^2 + \frac{\Omega^2}{4}}}$$

Eigenvectors $\hat{H}|\pm\rangle = \hbar\lambda_\pm |\pm\rangle$ $\quad |\pm\rangle \doteq \begin{bmatrix} c^{\uparrow}_{(\pm)} \\ c^{\downarrow}_{(\pm)} \end{bmatrix}$

$$\Rightarrow \omega_0 c^{\uparrow}_{(\pm)} + \frac{\Omega}{2} c^{\downarrow}_{(\pm)} = \pm\lambda_\pm c^{\uparrow}_{(\pm)}$$

Unnormalized: $c^{\uparrow}_{\pm} = 1 \quad c^{\downarrow}_{\pm} = \dfrac{\pm\lambda_\pm + \omega_0}{\Omega/2}$

$$\Rightarrow \boxed{|\pm\rangle = \underset{\substack{\uparrow \\ \text{normalization}}}{N_\pm}\left(\frac{\Omega}{2}|\uparrow\rangle \pm (\lambda_\pm \mp \omega_0)|\downarrow\rangle\right)}$$

Let us now expand to lowest nonvanishing order in the small parameter $\epsilon = \frac{\Omega}{2\omega_0}$

- $E_{\pm} = \pm \hbar\omega_0 \sqrt{1 + \frac{\Omega^2}{4\omega_0^2}}$

$$\cong \pm\hbar\omega_0 \left(1 + \frac{\Omega^2}{8\omega_0^2}\right) = \underbrace{\pm\hbar\omega_0}_{E_{\pm}^{(0)}} \pm \underbrace{\frac{\hbar^2\Omega^2}{4\omega_0^2}}_{E_{\pm}^{(2)}} \checkmark$$

- Expansion of eigenvectors

Consider $\lambda_{\pm} - \omega_0 = \omega_0 \left(\pm\sqrt{1+\epsilon^2} - 1 \right)$

$$\Rightarrow \cong \omega_0 \left(\pm\left(1 + \frac{\epsilon^2}{2}\right) - 1 \right)$$

$$= \begin{cases} + & \frac{\omega_0}{2}\epsilon^2 = \frac{\Omega^2}{8\omega_0} \\ - & -2\omega_0 \end{cases}$$

$\Rightarrow$ Unnormalized

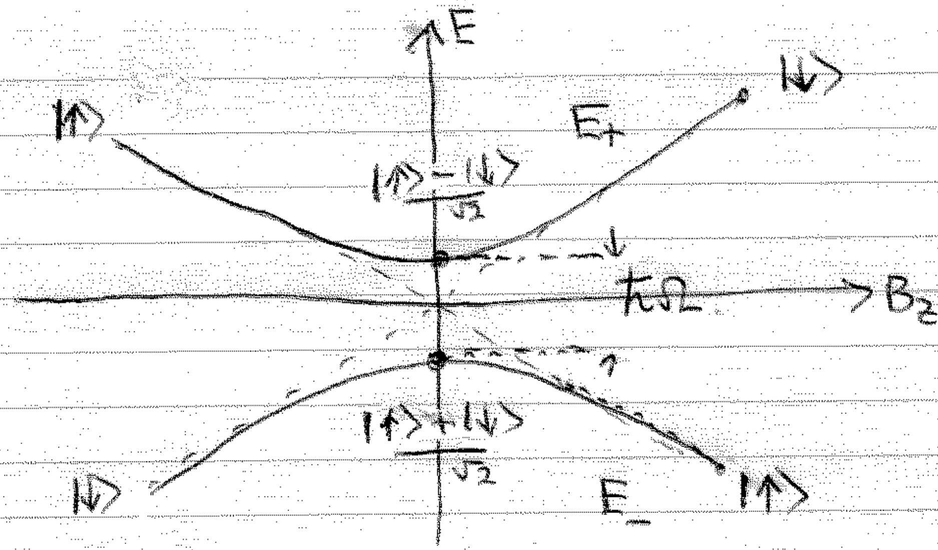
$$|+\rangle = N_+\left(\frac{\Omega}{2}|\uparrow\rangle + \frac{\Omega^2}{8\omega_0}|\downarrow\rangle \right) = \left(N_+\frac{\Omega}{2}\right)\left(|\uparrow\rangle + \frac{\Omega}{4\omega_0}|\downarrow\rangle\right)$$

$$\Rightarrow |+\rangle = \tilde{N}_+\left(|\uparrow\rangle + \frac{\Omega}{4\omega_0}|\downarrow\rangle \right) \checkmark$$

$$|-\rangle = N_-\left(\frac{\Omega}{2}|\downarrow\rangle - 2\omega_0|\downarrow\rangle \right) = (-2N_-\omega_0)\left(|\downarrow\rangle - \frac{\Omega}{4\omega_0}|\uparrow\rangle \right)$$

$$\Rightarrow |-\rangle = \tilde{N}_-\left(|\downarrow\rangle - \frac{\Omega}{4\omega_0}|\uparrow\rangle \right) \checkmark$$

(c)



This energy level diagram is known as an avoided crossing. In the absense of a B_x the two energy levels would become degenerate at $B_z = 0$ (shown here as dotted lines). Including B_x the degeneracy is broken; the new eigenvectors are symmetric and antisymmetric combinations of $|\uparrow\rangle$ and $|\downarrow\rangle$.