

QMS Week 11

①

Perturbation Theory II

Example 2: charged harmonic oscillator in constant E-field.

Consider a 1-d SHO Hamiltonian for \hat{H}_0 , to which we add a term that is linear in \hat{x} :-

$$\begin{aligned}\hat{H} &= \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 + E\hat{x} \\ &= \hat{H}_0 + \delta\hat{H}\end{aligned}$$

The term $\delta\hat{H}$ can arise if we imagine the particle is charged and there is present an electric field (1-d)

$$E = \text{constant} = -\frac{dV}{dx} \Rightarrow V = -Ex$$

The potential energy of the charged particle is qV so if we take $q = -1$ (we don't worry about units here)

(2)

Their $p \cdot E = +\varepsilon x$. In the Q.M.

Hamiltonian this appears as the additional term
 $+\hat{E}x$.

This example is a simple Toy model of the Stark Effect - which is the shift in the energy levels of atoms (e.g. Hydrogen) when placed in a constant \vec{E} -field. For a full treatment in the case of Hydrogen or Hydrogen-like atoms see e.g.

Sakuri Book.

Back to our example - the linear perturbation is in fact exactly solvable because (see Homework questions in past weeks) one can simply define new coordinates

$$\hat{y} = \left(\hat{x} + \frac{\varepsilon}{mw^2} \right)$$

(3)

$$\text{and write } \hat{H} = \frac{\hat{P}_y^2}{2m} + \frac{1}{2} m\omega^2 \hat{y}^2 - \frac{\epsilon^2}{2m\omega^2}$$

where $\hat{P}_y = \hat{P}_x$ since \hat{y} is just \hat{x} up to a constant shift.

\hat{H} is therefore just usual SHO Hamiltonian with a constant shift $-\frac{\epsilon^2}{2m\omega^2}$.

The energy spectrum is thus: - $\hat{H}|\Psi_n\rangle = E_n |\Psi_n\rangle$

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

while the configuration space states: -

$\langle y | \Psi_n \rangle = \Psi_n(y)$ are just usual expressions given in terms of Hermite with x replaced by polynomials

by $(x + \epsilon/m\omega^2)$.

(4)

Recall that the wave functions $\Psi_n(y)$ are:-

$$\Psi_n(y) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} H_n(y\sqrt{\alpha}) e^{-y^2\alpha/2} \times \frac{1}{\sqrt{2^n n!}}$$

where $\alpha \equiv \frac{m\omega}{\pi}$; $y = x + E/m\omega^2$; H_n - Hermite polynomials
 $n=0, 1, 2, \dots$

These are exact results. By considering E small ($E \ll 1$)

we can expand $\Psi_n(x, E)$ and

$E_n(E)$ and compare these expressions to what

we would obtain from perturbation theory -

clearly the result $E_n(E) = n\omega(n+\frac{1}{2}) - E^2/2m\omega^2$

is exact. It says there is no term linear in E

and a single $O(E^2)$ term.

(5)

For the wave-functions $\Psi_n(x + \epsilon/m\omega^2)$
we have to expand $e^{-((x+\epsilon/m\omega^2)^2)/2}$

and the Hermite polynomials $H_n(\sqrt{\alpha}(x + \epsilon/m\omega^2))$.

$$\begin{aligned} e^{-((x+\epsilon/m\omega^2)^2)/2} &= e^{-x^2\alpha/2} + \frac{\epsilon(-2(x)\alpha)}{m\omega^2} e^{-x^2\alpha/2} \\ &\quad + O(\epsilon^2) \\ &= e^{-x^2\alpha/2} \left(1 - \frac{\epsilon x \alpha}{m\omega^2} + O(\epsilon^2) \right) \end{aligned}$$

$$\begin{aligned} H_n(\sqrt{\alpha}(x + \epsilon/m\omega^2)) &= H_n(\sqrt{\alpha}x) \\ &\quad + \frac{\epsilon}{m\omega^2} H'_n(\sqrt{\alpha}x) + O(\epsilon^2) \end{aligned}$$

so that $\Psi_n(x + \epsilon/m\omega^2) = \Psi_n^{(0)}(x)$

$$\begin{aligned} &- \frac{\epsilon x \alpha}{m\omega^2} \Psi_n^{(0)}(x) \\ &+ \frac{\epsilon}{m\omega^2} \left(H'_n \left(\frac{x}{\sqrt{\alpha}} \right)^{\frac{1}{4}} \sqrt{\frac{1}{2^n n!}} \right) e^{-x^2\alpha/2} \\ &+ O(\epsilon^2) \end{aligned}$$

where we have used notation:-

$$\Psi_n^{(0)}(x) = \Psi_n(x + \epsilon/m\omega^2) \Big|_{\epsilon=0}$$

(6)

Results predicted by perturbation theory

We have $\hat{H}_0 |\Psi_n^{(0)}\rangle = E_n^{(0)} |\Psi_n^{(0)}\rangle$

with $E_n^{(0)} = \hbar\omega(n+\frac{1}{2})$; $|\Psi_n^{(0)}\rangle$ usual non-degenerate orthonormal states

$\delta\hat{A} = E\hat{x} = E\hat{V}$ so $\lambda = E$ and $\hat{V} = \hat{x}$ in our previous notation.

1st order:

$$E_n^{(1)} = \langle \Psi_n^{(0)} | \hat{x} | \Psi_n^{(0)} \rangle$$

Now recall \hat{a}, \hat{a}^+ operators we defined as:-

$$\hat{a} = \sqrt{\alpha/2} \hat{x} + i \frac{1}{\sqrt{2\alpha/\hbar^2}} \hat{P}; \quad \hat{a}^+$$

$$\text{so } \hat{x} = (\hat{a} + \hat{a}^+) \frac{1}{2\sqrt{\alpha/2}}; \quad |\Psi_n^{(0)}\rangle \equiv |n\rangle$$

$$E_n^{(1)} = \frac{1}{\sqrt{2\alpha}} \langle n | (\hat{a} + \hat{a}^+) | n \rangle$$

(7)

But \hat{a}^\dagger (\hat{a}^+) lower (raise) the value

of n by 1 unit, so $\hat{a}|n\rangle = \sqrt{n}|n-1\rangle$

$$\hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$$

$$\therefore E_n^{(1)} = \frac{1}{\sqrt{2}\alpha} (\sqrt{n} \langle n | n-1 \rangle + \sqrt{n+1} \langle n | n+1 \rangle)$$

$$= 0 \quad \text{because} \quad \langle n | m \rangle = \delta_{nm}$$

We therefore recover the previous result that

there are no linear terms in ϵ in the

expansion of $E_n(\epsilon)$. [we can also understand $\langle n | \hat{c} | n \rangle = 0$ via parity conservation]

What about 2nd order in ϵ^2 ?

From our formula

$$E_n^{(2)} = \sum_{k \neq n} \left| \frac{\langle \psi_k^{(0)} | \hat{V} | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} \right|^2$$

(8)

$$= \frac{1}{2\alpha} \sum_{k \neq n} \left| \frac{\langle k | (\hat{a} + \hat{a}^\dagger) | n \rangle}{E_n^{(o)} - E_k^{(o)}} \right|^2$$

$$= \frac{1}{2\alpha} \sum_{k \neq n} \left| \frac{\langle k | n-1 \rangle \sqrt{n} + \langle k | n+1 \rangle \sqrt{n+1}}{E_n^{(o)} - E_k^{(o)}} \right|^2$$

using orthonormality we see only contributions come

from $k = n-1$ and $k = n+1$ [also can see this by parity selection rule]

$$E_n^{(2)} = \frac{1}{2\alpha} \left| \frac{\langle n-1 | n-1 \rangle \sqrt{n}}{\hbar\omega(n+\frac{1}{2}) - \hbar\omega(n-1+\frac{1}{2})} \right|^2$$

$$+ \frac{1}{2\alpha} \left| \frac{\langle n+1 | n+1 \rangle \sqrt{n+1}}{\hbar\omega(n+\frac{1}{2}) - \hbar\omega(n+1+\frac{1}{2})} \right|^2$$

$$= \frac{1}{2\alpha} \frac{1}{\hbar\omega} \left\{ \frac{n}{\frac{1}{2} + \frac{1}{2}} + \frac{n+1}{\frac{1}{2} - \frac{3}{2}} \right\}$$

$$= -\frac{1}{2 \frac{m\omega}{\hbar} \hbar\omega} = -\frac{1}{2m\omega^2}$$

(9)

Thus second order perturbation theory predicts :

$$\begin{aligned} E_n &= E_n^{(0)} + \varepsilon \hat{E}_n^{(1)} + \varepsilon^2 \hat{E}_n^{(2)} \\ &\stackrel{\text{def}}{=} \hbar\omega(n+\frac{1}{2}) - \frac{\varepsilon^2}{2m\omega^2} \\ &= \hbar\omega \end{aligned}$$

which is precisely the result found on P3 //

Corrections to $|n\rangle$

Let's just look at 1st order in ε .

Call $|n\rangle \equiv |\psi_n^{(0)}\rangle$ to use our previous notation for unperturbed state.

$$\begin{aligned} \text{Then } |\psi_n^{(1)}\rangle &= \sum_{k \neq n} \frac{\langle \psi_k^{(0)} | \hat{V} | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} |\psi_k^{(0)}\rangle \\ &= \frac{1}{\sqrt{2\alpha}} \sum_{k \neq n} \frac{\langle k | (\hat{a} + \hat{a}^\dagger) | n \rangle}{E_n^{(0)} - E_k^{(0)}} |k\rangle \\ &= \frac{1}{\sqrt{2\alpha}} \left\{ \frac{\langle n-1 | \sqrt{n} | n-1 \rangle}{E_n^{(0)} - E_{n-1}^{(0)}} |n-1\rangle + \frac{\langle n+1 | \sqrt{n+1} | n+1 \rangle}{E_n^{(0)} - E_{n+1}^{(0)}} |n+1\rangle \right\} \end{aligned}$$

(10)

Since again, only non-zero contributions come from $k=n-1$ or $k=n+1$.

$$\begin{aligned} |\Psi_n^{(1)}\rangle &= \frac{1}{\sqrt{2\alpha}} \left\{ \frac{\sqrt{n} |n-1\rangle}{\hbar\omega(\frac{1}{2} + \frac{1}{2})} + \frac{\sqrt{n+1} |n+1\rangle}{\hbar\omega(\frac{1}{2} + \frac{3}{2})} \right\} \\ &= \frac{1}{\sqrt{2\alpha}} \frac{1}{\hbar\omega} (\sqrt{n} |n-1\rangle - \sqrt{n+1} |n+1\rangle). \end{aligned}$$

so that the prediction is

$$\begin{aligned} |\Psi_n\rangle &= |\Psi_n^{(0)}\rangle + \varepsilon |\Psi_n^{(1)}\rangle + O(\varepsilon^2) \\ &= |\Psi_n^{(0)}\rangle + \frac{\varepsilon}{\sqrt{2m\omega^3\hbar}} (\sqrt{n} |n-1\rangle - \sqrt{n+1} |n+1\rangle) \end{aligned}$$

\Rightarrow wave function

$$\begin{aligned} \langle x | \Psi_n \rangle &= \underbrace{\langle x | \Psi_n^{(0)} \rangle}_{\Psi_n^{(0)}(x)} + \frac{\varepsilon}{\sqrt{2m\omega^3\hbar}} \left(\sqrt{n} \langle x | n-1 \rangle - \sqrt{n+1} \langle x | n+1 \rangle \right) \\ &\quad - \text{unperturbed SHO wavefunctions} \end{aligned}$$

(11)

$$\text{i.e. } \Psi_n(x) = \Psi_n^{(0)}(x) + \frac{\epsilon}{\sqrt{2m\omega^3 h}} \left(\sqrt{n} \Psi_{n-1}^{(0)}(x) - \sqrt{n+1} \Psi_{n+1}^{(0)}(x) \right)$$

Now compare with expression obtained earlier

by expanding exact result to linear order in ϵ :-

$$\Psi_n(x) = \Psi_n^{(0)}(x) - \frac{\epsilon}{m\omega^2} x \alpha \Psi_n^{(0)}(x) - \frac{x^2 \alpha^2}{2} \\ + \frac{\epsilon (\alpha/\pi)^{1/4}}{m\omega^2} \sqrt{\frac{1}{2^n n!}} H_n(\Gamma \alpha x) e^{-x^2 \alpha^2/2}$$

Now Hermite polynomials $H_n(x)$ have the
property that

$$H_{n+1}(x) = 2xH_n(x) - H_n'(x). \quad (\text{recursion relation})$$

$$\Psi_n^{(0)}(x) = \left(\frac{x}{\pi}\right)^{1/4} \sqrt{\frac{1}{2^n n!}} H_n(\Gamma \alpha x) e^{-x^2 \alpha^2/2}$$

(12)

The recursion relation satisfied by $H_n(\sqrt{\alpha}x)$

$$\text{is:- } H_{n+1}(\sqrt{\alpha}x) = 2\sqrt{\alpha}x H_n(\sqrt{\alpha}x) - \frac{1}{\sqrt{\alpha}} H'_n(\sqrt{\alpha}x)$$

use this to substitute for $H'(\sqrt{\alpha}x)$

$$\begin{aligned} \Psi_n(x) &= \Psi_n^{(0)}(x) - \frac{\varepsilon x \alpha}{mw^2} \left(\left(\frac{\alpha}{\pi} \right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\sqrt{\alpha}x) e^{-x^2 \alpha/2} \right) \\ &\quad + \frac{\varepsilon (\alpha/\pi)^{1/4}}{mw^2} \frac{1}{\sqrt{2^n n!}} e^{-x^2 \alpha/2} \left(2\alpha x H_n(\sqrt{\alpha}x) \right. \\ &\quad \left. - \sqrt{\alpha} H_{n+1}(\sqrt{\alpha}x) \right) \end{aligned}$$

$$= \Psi_n^{(0)}(x) + \frac{\varepsilon \alpha x}{mw^2} \Psi_n^{(0)}(x) - \frac{\varepsilon \sqrt{\alpha}}{mw^2} \sqrt{n+1} \sqrt{2} \Psi_{n+1}^{(0)}(x)$$

Another Hermite Polynomial identity:

$$H_{n+1}(x) = 2x H_n(x) - 2^n H_{n-1}(x)$$

we can use this in second term:

$$\left(\text{using } H_{n+1}(\sqrt{\alpha}x) = 2\sqrt{\alpha}x H_n(\sqrt{\alpha}x) - 2^n H_{n-1}(\sqrt{\alpha}x) \right)$$

(13)

$$\text{Thus the term } \frac{\epsilon \alpha x}{m\omega^2} \Psi_n^{(0)}(x)$$

$$= \left(\frac{\epsilon \alpha}{m\omega^2}\right) x H_n(\sqrt{\alpha}x) \left(\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} e^{-\frac{x^2 \alpha}{2}}\right)$$

$$= \left(\frac{\epsilon \alpha}{m\omega^2}\right) \left\{ \frac{n}{\sqrt{\alpha}} H_{n-1}(\sqrt{\alpha}x) + \frac{1}{2\sqrt{\alpha}} H_{n+1}(\sqrt{\alpha}x) \right\} \\ \times \left(\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} e^{-\frac{x^2 \alpha}{2}}\right)$$

$$= \frac{\epsilon \alpha}{m\omega^2} \left(\frac{\sqrt{n}}{\sqrt{2\alpha}} \Psi_{n-1}^{(0)}(x) + \frac{\sqrt{n+1} \sqrt{2}}{2\sqrt{\alpha}} \Psi_{n+1}^{(0)}(x) \right)$$

 \Rightarrow

$$\Psi_n(x) = \Psi_n^{(0)}(x) + \frac{\epsilon \sqrt{\alpha}}{\sqrt{2} m\omega^2} \sqrt{n} \Psi_{n-1}^{(0)}(x)$$

$$+ \frac{\epsilon \sqrt{\alpha}}{\sqrt{2} m\omega^2} \sqrt{n+1} \Psi_{n+1}^{(0)}(x) - \frac{\epsilon \sqrt{\alpha} \sqrt{n+1} \sqrt{2}}{m\omega^2} \Psi_{n+1}^{(0)}$$

$$\alpha = \frac{m\omega}{\pi}$$

$$= \Psi_n^{(0)}(x) + \frac{\epsilon}{\sqrt{2 m \omega^3 \pi}} \cdot \left(\sqrt{n} \Psi_{n-1}^{(0)}(x) - \sqrt{n+1} \Psi_{n+1}^{(0)}(x) \right)$$

(14)

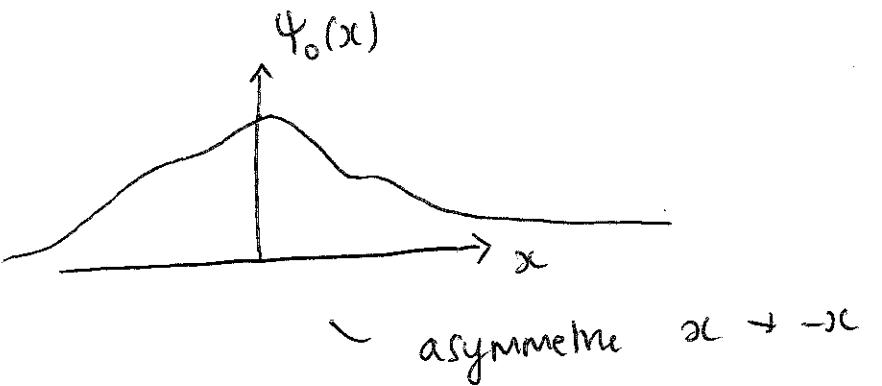
Thus we have verified that this linear in ϵ correction to the wave functions agrees precisely with that predicted from 1st order perturbation theory.

Sketch of Shifted States

Ground State

$$\psi_{n=0}(x) = \psi_0^{(0)}(x) + \frac{\epsilon}{\sqrt{2m\omega^3\hbar}} (-\psi_1^{(0)}(x))$$

Schematically:



(15)

Because parity symmetry of \hat{H}_0 ($x \rightarrow -x$)
is broken by the perturbation $\delta\hat{H} = \varepsilon \hat{x}$;

the new ground state is not a parity eigenstate.

Hence $\langle \Psi_0 | \hat{x} | \Psi_0 \rangle$ need not vanish.

Recall for a system where parity is a symmetry
we find selection rule $\langle \alpha | \hat{x} | \beta \rangle \neq 0$ only if
 $|\alpha\rangle, |\beta\rangle$ have opposite parity assignments.

If we consider initial state of our perturbed
system is the ground state $|\Psi_0\rangle$ then

$$\begin{aligned}\langle \Psi_0 | \hat{x} | \Psi_0 \rangle &= \left\{ \underbrace{\langle \Psi_0^{(0)} | \hat{x} | \Psi_1^{(0)} \rangle}_{\text{parity}} + \underbrace{\langle \Psi_1^{(0)} | \hat{x} | \Psi_0^{(0)} \rangle}_{-} \right\} \left(-\frac{\varepsilon}{\sqrt{2m\omega^3 h}} \right) \\ &= \left(-\frac{\varepsilon}{\sqrt{2m\omega^3 h}} \right) \left(\frac{1}{\sqrt{2\alpha}} + \frac{1}{\sqrt{2\alpha}} \right) \\ &= -\frac{\varepsilon}{m\omega^2}\end{aligned}$$

(16)

The quantity $q \langle \Psi_0 | \hat{x} | \Psi_0 \rangle$

is basically the induced electric dipole moment -

it is 'induced' by the presence of the electric field
and vanishes as $\epsilon \rightarrow 0$.

The fact that the shift in energy levels is

quadratic in ϵ also is indicative of an induced

dipole - because if a system has electric dipole moment

$\vec{\mu}_e$, then the potential energy when we place

it in an \vec{E} -field is $-\vec{\mu}_e \cdot \vec{E}$.

But in our case $\vec{\mu}_e$ is induced and (since 1-d)

$$\mu_e = q \langle \Psi_0 | \hat{x} | \Psi_0 \rangle \approx -\epsilon/m\omega^2 (q=-1) = +\frac{\epsilon}{m\omega^2}$$

$$\Rightarrow -\frac{1}{2} \vec{\mu}_e \cdot \vec{E}^* = -\frac{1}{2} \frac{\epsilon}{m\omega^2} \epsilon = -\frac{\epsilon^2}{2m\omega^2}$$

which is exactly the shift we found!

$$(* \quad \mu_e = -\frac{\partial}{\partial \epsilon} \Delta E = \epsilon/m\omega^2 \Rightarrow \Delta E = -\frac{\epsilon^2}{2m\omega^2})$$

In the case of the Stark effect e.g. in Hydrogen atom; calculating it is more complex in general because this is a degenerate system.

(the energy eigenvalues E_n depend only on principle quantum number n not on $j, m_j \dots |n, j, m_j\rangle$)

- However if we assume atom is in ground state $n=1$
 $|n=1, l=0, m_l=0\rangle$ (we can ignore spin in the Stark effect) - this state is non-degenerate and we can use our results derived in the lectures.

The shift in $E_{n=1}^{(0)}$ at first order is:-

$$E_{n=1}^{(1)} = \epsilon \langle n=1, l=0, m_l=0 | \hat{z} | n=1, l=0, m_l=0 \rangle \\ = 0 \quad (\text{where for simplicity we took } \vec{E} = \epsilon \hat{z})$$

This can be seen by e.g. going to r, θ, ϕ coords:-

$$\langle 100 | \hat{z} | 100 \rangle = \int d^3r R^*(r) (e r \cos\theta) R(r) \sin\theta d\theta d\phi \\ \int d\theta \rightarrow 0$$

(18)

To get a non-vanishing contribution we have to go to 2nd order in perturbation theory:-

$$E_{n=1}^{(2)} = \sum_{n \neq 1, L, M_L} \frac{|\langle 100 | e \vec{E} | n L M_L \rangle|^2}{E_1 - E_n}$$

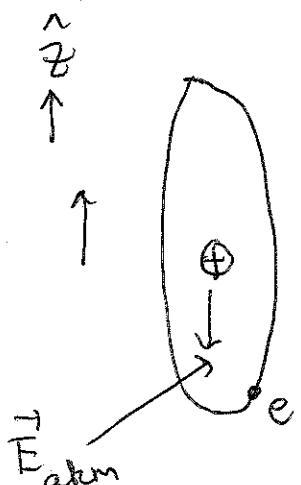
Using the properties of the Spherical Harmonics $Y_{lm}(\theta, \phi)$

and the radial wave-functions R_{nl} one can

discover:-

$$E_{n=1}^{(2)} = -\frac{9}{4} (4\pi f_0) q_0^3 \epsilon^2$$

↑ quadratic
-ve



\vec{E}_{atom} is \vec{E} field
produced by induced dipole moment of Hydrogen atom.

- this is why shift $E_{n=1}^{(2)} < 0$.

The Linear Stark Effect

Can one ever find a contribution $E_n^{(1)}$ to the shift in energy levels at linear order in ϵ ?

For the simple toy model based on 1-d SHO no

... but in the case e.g. Hydrogen atom it is possible - but only for excited states which necessarily means one has to use the technology of degenerate perturbation theory.

This is beyond the scope of this course - but if you are interested see e.g. Sakuri for a good treatment. Conceptually it's the same basic idea we have already studied - but to overcome the technical issues one has to make use of some results in linear algebra...

Note that if one takes the extended \vec{E} -field to have magnitude E , one can define the electric dipole moment as -

$$\mu_e = - \frac{\partial \Delta E}{\partial E} .$$

Therefore if ΔE contains a term linear in E ,

$$\mu_e \neq 0 \text{ even if } E \rightarrow 0 .$$

What this means is that the object (e.g. excited Hydrogen atom) possesses an intrinsic (as opposed to induced) dipole moment.

physically we can understand why because for excited states there may not be a spherically symmetric distribution of charge (i.e. electron's orbital wave function need not be symmetric) and so such states will naturally have an electric dipole moment independent of the \vec{E} -field.