1 Examples of Stationary Perturbation Theory

Here we will consider two examples that will illustrate how we can calculate the corrections to the known energy levels if a small perturbation is applied to the system. We will consider:

(A) The Stark effect in a potential well

(B) The shifted Harmonic oscillator problem

(A) The Stark Effect in a Potential Well

Consider an infinte potential well that has a linear, rather than constant potential within the well.

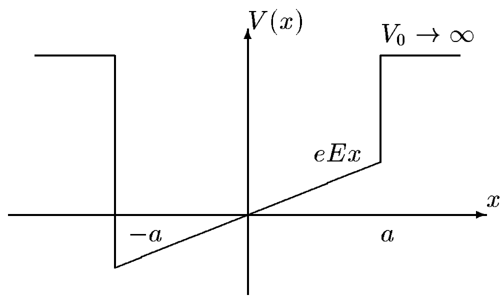

Figure 1: Figure

The eigenfunctions and the eigenvalues of the TISE for infinte potential well $[V(x) = 0, \quad x < a]$ (unperturbed) are

$$\psi_n(x) = \sqrt{\frac{2}{2a}} \sin\left[\frac{n\pi}{2a}(x+a)\right] \tag{1}$$

$$\begin{aligned} E_n &= \frac{\hbar^2}{2m}\left(\frac{n\pi}{2a}\right)^2 & (2) \\ &= \frac{n^2\pi^2\hbar^2}{8ma^2} & (3) \end{aligned}$$

The perturbing potential is described with

$$V(x) = eEx \tag{4}$$

Since this is a system in which we do not have degeneracies, the first and the second order corrections to the energy levels are given by

$$E_n^{(1)} = V_{nn} \tag{5}$$

and

$$E_n^{(2)} = \sum_{j \neq n} \frac{V_{jn} V_{nj}}{E_n^{(0)} - E_j^{(0)}} \tag{6}$$

$$= \sum_{j \neq n} \frac{|V_{jn}|^2}{E_n^{(0)} - E_j^{(0)}} \tag{7}$$

Hence, we need to calculate the diagonal and the off-diagonal matrix elements to calculate the corrections to the energy levels using $V(x)$ as a perturbation and $\psi_n(x)$, i.e., the solutions of the unperturbed problem as a basis set.

Diagonal matrix elements

$$V_{nn} = \langle n|eEx|n\rangle \tag{8}$$

$$= \frac{1}{a}\int_{-a}^{a} x \sin^2\left[\frac{n\pi}{2a}(x+a)dx\right] \tag{9}$$

$$= \frac{1}{2a}\int_{-a}^{a} x\left\{1 - \cos\left[\frac{n\pi}{2a}(x+a)\right]\right\} dx \tag{10}$$

$$= 0 \tag{11}$$

The above result suggests that there is no first-order shift to the energy levels and this is because of the choice of our coordinate system. if the coordinate system was chosen so that $V(-a) = 0$, then it can be shown that $\langle n|V(x)|n\rangle = eEa$ and this would correspond to the linear Start-shift of the energy levels.

Off-diagonal matrix elements

To calculate the higher-order corrections to the energy levels, we need the off-diagonal matrix elements

$$V_{ij} = \langle i|eEx|j\rangle \tag{12}$$

$$= \frac{eE}{a}\int_{-a}^{a} x \sin\left[\frac{i\pi}{2a}(x+a)\right] \sin\left[\frac{j\pi}{2a}(x+a)\right] dx \tag{13}$$

To evaluate this integral, we will use the following trigonometric identities

$$\cos(a+b) = \cos a \cos b - \sin a \sin b \tag{14}$$

$$\cos(a-b) = \cos a \cos b + \sin a \sin b \tag{15}$$

Hence

$$\cos(a-b) - \cos(a+b) = 2\sin a \sin b \tag{16}$$

or

$$\sin a \sin b = \frac{1}{2}\left[\cos(a-b) - \cos(a+b)\right] \tag{17}$$

where

$$\begin{aligned} a - b &= \frac{i\pi}{2a}(x+a) - \frac{j\pi}{2a}(x+a) && (18) \\ &= \frac{(i-j)\pi}{2a}(x+a) && (19) \end{aligned}$$

$$\begin{aligned} a + b &= \frac{i\pi}{2a}(x+a) + \frac{j\pi}{2a}(x+a) && (20) \\ &= \frac{(i+j)\pi}{2a}(x+a) && (21) \end{aligned}$$

This means that

$$\begin{aligned} V_{ij} &= \frac{eE}{2a}\left\{\int_{-a}^{a} x\cos\left[\frac{(i-j)\pi}{2a}(x+a)\right]dx\right. \\ &- \left.\int_{-a}^{a} x\cos\left[\frac{(i+j)\pi}{2a}(x+a)\right]dx\right\} && (22) \end{aligned}$$

i.e., we need to solve the integrals of the form

$$\begin{aligned} I &= \int_{-a}^{a} x\cos\left[\frac{m\pi}{2a}(x+a)\right]dx \\ &= \frac{2a}{m\pi}\cancelto{0}{x\sin}\left[\frac{m\pi}{2a}(x+a)\right]\Bigg|_{-a}^{a} && (23) \\ &- \frac{2a}{m\pi}\int_{-a}^{a}\sin\left[\frac{m\pi}{2a}(x+a)\right]dx && (24) \\ &= \left(\frac{2a}{m\pi}\right)^2\cos\left[\frac{m\pi}{2a}(x+a)\right]\Bigg|_{-a}^{a} && (25) \\ &= \left(\frac{2a}{m\pi}\right)^2\left[\cos(m\pi) - 1\right] && (26) \\ &= \left(\frac{2a}{m\pi}\right)^2\left[(-1)^m - 1\right] && (27) \end{aligned}$$

Now if m is even, then

$$\begin{aligned} I &= \left(\frac{2a}{m\pi}\right)^2 (1-1) && (28)\\ &= 0 && (29) \end{aligned}$$

and if m is odd then

$$\begin{aligned} I &= \left(\frac{2a}{m\pi}\right)^2 (-1-1) && (30)\\ &= -\frac{8a^2}{m^2\pi^2} && (31) \end{aligned}$$

Using this result we arrive at

$$\begin{aligned} V_{ij} &= \frac{eE}{2a}\left(-\frac{8a^2}{\pi^2}\right)\left[\frac{1}{(i-j)^2}-\frac{1}{(i+j)^2}\right] && (32)\\ &= -\frac{4a}{\pi^2}\frac{\left[(i+j)^2-(i-j)^2\right]eE}{(i^2-j^2)^2} && (33)\\ &= -\frac{4a}{\pi^2}eE\frac{i^2+j^2+2ij-i^2-j^2+2ij}{(i^2-j^2)^2} && (34)\\ &= -\frac{16aeE}{\pi^2}\frac{ij}{(i^2-j^2)^2} && (35) \end{aligned}$$

To summarize

$$V_{ij} = \begin{cases} -\dfrac{16aeE}{\pi^2}\dfrac{ij}{(i^2-j^2)^2} & (i \pm j) \text{ odd} \\ 0 & (i \pm j) \text{ even} \end{cases} \qquad (36)$$

The above result suggests that the odd potential will mix only those states that have different parity. The denominator in the expression for V_{ij}, aside from some constants, represents the square of the difference of the associated energy levels.

Harmonic oscillator with linear perturbation

As a second example for the application of the perturbation theory, we consider a microscopic harmonic oscillator subject to a linear potential that can arise due to the application of an electric field. In this case

$$\hat{H} = \hat{H}_0 + \hat{V} \qquad (37)$$

where

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega_0^2 x^2 \tag{38}$$

and

$$\hat{V} = eEx \tag{39}$$

For this case too, we can find the exact solution, i.e.,

$$\begin{aligned} \hat{H} &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega_0^2 x^2 + eEx & (40) \\ &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega_0^2\left(x^2 + \frac{2eEx}{m\omega_0^2}\right) & (41) \end{aligned}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega_0^2\left(x + \underbrace{\frac{eE}{m\omega_0^2}}_{x_0=a}\right)^2 - \frac{1}{2}\cancel{m\omega_0^2}\frac{(eE)^2}{(m\omega_0^2)^{\cancel{2}}} \tag{42}$$

If we define $y = x + a = x + x_0$, then the TISE becomes

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}\psi + \frac{1}{2}m\omega_0^2 y^2\psi = \left(\underbrace{E + \frac{(eE)^2}{2m\omega_0^2}}_{E^1}\right)\psi \tag{43}$$

i.e.,

$$\begin{aligned} E_n^1 &= \left(1 + \frac{1}{2}\right)\hbar\omega_0 & (44) \\ &= E_n + \frac{(eE)^2}{2m\omega_0^2} & (45) \end{aligned}$$

or

$$\boxed{E_n = \left(n + \frac{1}{2}\right)\hbar\omega_0 - \frac{e^2E^2}{2m\omega_0^2}} \tag{46}$$

We can arrive at this result using perturbation theory. We again need to calculate the diagonal and the off-diagonal matrix elements, but in this case we will make use of $\hat{a}$ and $\hat{a}^\dagger$, i.e., we will express $\hat{x}$ as

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega_0}}\left(\hat{a} + \hat{a}^\dagger\right) \tag{47}$$

Then

$$V_{nm} = \langle n|eEx|m\rangle \tag{48}$$

$$= \sqrt{\frac{\hbar}{2m\omega_0}} eE\langle n|\hat{a}+\hat{a}^\dagger|m\rangle \tag{49}$$

$$= eE\sqrt{\frac{\hbar}{2m\omega_0}}\left[\langle n|\hat{a}|m\rangle + \langle n|\hat{a^\dagger}|m\rangle\right] \tag{50}$$

$$= eE\sqrt{\frac{\hbar}{2m\omega_0}}\left[\sqrt{m}\underbrace{\langle n|m-1\rangle}_{\substack{\delta_{n,m-1}\\ n=m-1\Rightarrow m=n+1}} + \sqrt{m+1}\underbrace{\langle n|m+1\rangle}_{\substack{\delta_{n,m+1}\\ n=m+1\Rightarrow m=n-1}}\right] \tag{51}$$

$$= eE\sqrt{\frac{\hbar}{2m\omega_0}}\left[\sqrt{n+1}\delta_{n,m-1} + \sqrt{n}\delta_{n,m+1}\right] \tag{52}$$

(1) Obviously, the diagonal matrix elements, for which $n = m$, will be identically zero due to the Kroneker delta-functions.

(2) If we are considering the second order shift to the energy levels, we will need

$$E_n^{(2)} = \underbrace{\sum_{m\neq n}\frac{V_{nm}V_{mn}}{E_n - E_m}}_{\substack{\text{only two terms}\\ \text{will contribute}\\ m=n+1 \text{ and}\\ m=n-1}} \tag{53}$$

$$= (eE)^2\frac{\hbar}{2m\omega_0}\underbrace{\left[\frac{n+1}{E_n - E_{n+1}} + \frac{n}{E_n - E_{n-1}}\right]}_{\substack{\Downarrow\\ \frac{n+1}{(n+1/2)\hbar\omega_0 - (n+1+1/2)\hbar\omega_0} + \frac{n}{(n+1/2)\hbar\omega_0 - (n-1-1/2)}\\ = \frac{n+1}{-\hbar\omega_0} + \frac{n}{\hbar\omega_0}\\ = -\frac{1}{\hbar\omega_0}}} \tag{54}$$

Thus

$$E_n^{(2)} = -(eE)^2\frac{\hbar}{2m\omega_0}\frac{1}{\hbar\omega_0} \tag{55}$$

$$= -\frac{e^2E^2}{2m\omega_0^2} \longrightarrow \text{the full shift of the energy levels} \tag{56}$$