GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-1, 29/08/2024)

Time-independent non-degenerate state perturbation theory

Solution of the Schrödinger equation: $H\psi_n = E_n\psi_n$

* PIB model: $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$, for $0 \le x \le L$, $V(x) = 0$ or constant; $V(x) = \infty$, otherwise

$E_n = \frac{n^2h^2}{8mL^2}$, $\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$

* SHO model: $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$, $E_n = (n+\frac{1}{2})h\nu = (n+\frac{1}{2})\hbar\omega$

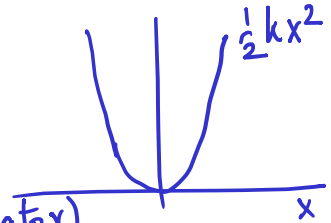
$\psi_n(x) = N_n H_n(x) e^{-\alpha x^2}$

* RR model: $\hat{H} = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right]$

$E_J = \frac{\hbar^2}{2I}J(J+1)$, $J = 0, 1, 2, 3, \ldots, \infty$; $Y_L^M(\theta,\phi)$

* H atom: $\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$, $E_n = \frac{-e^2}{8\pi\epsilon_0 a_0 n^2}$, $\psi_{nlm}(r,\theta,\phi) = R_{nL}(r)Y_L^M(\theta,\phi)$

* Approximation methods: ① Variational methods
② Perturbation theory



$\hat{H} = \underbrace{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}}_{KE} + \underbrace{\frac{1}{2}kx^2}_{PE} + cx^3 + Dx^4$ (anharmonic oscillator)

$H\psi_n = E_n\psi_n$

$\hat{H} = \underbrace{\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right)}_{E_n = (n+\frac{1}{2})\hbar\omega,\ \psi_n(x) = N_n H_n(x) e^{-\alpha x^2},\ \langle\psi_n|\psi_m\rangle = \delta_{nm}} + \underbrace{(cx^3 + Dx^4)}_{?\ 0} = H_0 + V$ ← perturbation

partitioning of the Hamiltonian

unperturbed Hamiltonian

$\hat{H} = H_0 + \lambda V \quad 0 \le \lambda \le 1$

λ : perturbation parameter / strength

$H\psi_n = E_n\psi_n \Rightarrow (H_0 + \lambda V)\psi_n = E_n\psi_n$

$\psi_n = \psi_n(\lambda, q)$: function of λ and coordinates q

$E_n = E_n(\lambda)$: function of λ only; $E_n = \langle\psi_n|\hat{H}|\psi_n\rangle = \int_{\text{all space}} \psi_n^* \hat{H} \psi_n \, dq$

$\lambda = 0$

$H_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$: unperturbed Schrödinger eqn.

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-1, 29/08/2024)

Taylor series expansion

$$E_n = E_n\Big|_{\lambda=0} + \frac{dE_n}{d\lambda}\Big|_{\lambda=0}\lambda + \frac{1}{2!}\frac{d^2E_n}{d\lambda^2}\Big|_{\lambda=0}\lambda^2 + \frac{1}{3!}\frac{d^3E_n}{d\lambda^3}\Big|_{\lambda=0}\lambda^3 + \cdots + \frac{1}{k!}\frac{d^kE_n}{d\lambda^k}\Big|_{\lambda=0}\lambda^k + \cdots$$

$$\frac{1}{k!}\frac{d^kE_n}{d\lambda^k}\Big|_{\lambda=0} = E_n^{(k)}$$

kth order correction to the energy

$$\text{or, } E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} + \cdots + \lambda^k E_n^{(k)} + \cdots \quad \text{——— (1)}$$

$$\psi_n = \psi_n\Big|_{\lambda=0} + \frac{\partial\psi_n}{\partial\lambda}\Big|_{\lambda=0}\lambda + \frac{1}{2!}\frac{\partial^2\psi_n}{\partial\lambda^2}\Big|_{\lambda=0}\lambda^2 + \frac{1}{3!}\frac{\partial^3\psi_n}{\partial\lambda^3}\Big|_{\lambda=0}\lambda^3 + \cdots + \frac{1}{k!}\frac{\partial^k\psi_n}{\partial\lambda^k}\Big|_{\lambda=0}\lambda^k + \cdots$$

$$\frac{1}{k!}\frac{\partial^k\psi_n}{\partial\lambda^k}\Big|_{\lambda=0} = \psi_n^{(k)}$$

kth order correction to the wavefunction

$$\text{or, } \psi_n = \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \lambda^3\psi_n^{(3)} + \cdots + \lambda^k\psi_n^{(k)} + \cdots \quad \text{——— (2)}$$

$\psi_n^{(0)}$s are normalized functions, ie., $\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle = 1$ $\quad \langle\psi_m^{(0)}|\psi_n^{(0)}\rangle = \delta_{mn}$

$\Rightarrow$ unperturbed functions are an orthonormal set of functions.

Instead of taking ψ_n to be normalized, we assume $\langle\psi_n^{(0)}|\psi_n\rangle = 1$

IN simplifies mathematical steps. intermediate normalization (IN)

If ψ_n does not satisfy IN, then multiplication of ψ_n by the constant $\frac{1}{\langle\psi_n^{(0)}|\psi_n\rangle}$ gives a function, say ψ_n', which will satisfy IN.

Now, $\psi_n = \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots$

$$\text{or, } \langle\psi_n^{(0)}|\psi_n\rangle = \langle\psi_n^{(0)}|\psi_n^{(0)}\rangle + \lambda\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle + \lambda^2\langle\psi_n^{(0)}|\psi_n^{(2)}\rangle + \cdots$$

$$\text{or, } 1 = 1 + \lambda\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle + \lambda^2\langle\psi_n^{(0)}|\psi_n^{(2)}\rangle + \cdots$$

$$\text{or, } \lambda\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle + \lambda^2\langle\psi_n^{(0)}|\psi_n^{(2)}\rangle + \cdots = 0$$

$$\therefore \langle\psi_n^{(0)}|\psi_n^{(1)}\rangle = 0,\ \langle\psi_n^{(0)}|\psi_n^{(2)}\rangle = 0,\ \cdots,\ \langle\psi_n^{(0)}|\psi_n^{(k)}\rangle = 0,\ \cdots$$

Chapter 9

Perturbation Theory

9.1 Perturbation Theory

This chapter discusses the second major quantum-mechanical approximation method, perturbation theory.

Suppose we have a system with a time-independent Hamiltonian operator $\hat{H}$ and we are unable to solve the Schrödinger equation

$$\hat{H}\psi_n = E_n\psi_n \tag{9.1}$$

for the eigenfunctions and eigenvalues of the bound stationary states. Suppose also that the Hamiltonian $\hat{H}$ is only slightly different from the Hamiltonian $\hat{H}^0$ of a system whose Schrödinger equation

$$\hat{H}^0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} \tag{9.2}$$

we can solve. An example is the one-dimensional anharmonic oscillator with

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + cx^3 + dx^4 \tag{9.3}$$

The Hamiltonian (9.3) is closely related to the Hamiltonian

$$\hat{H}^0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 \tag{9.4}$$

of the harmonic oscillator. If the constants c and d in (9.3) are small, we expect the eigenfunctions and eigenvalues of the anharmonic oscillator to be closely related to those of the harmonic oscillator.

We shall call the system with Hamiltonian $\hat{H}^0$ the **unperturbed system.** The system with Hamiltonian $\hat{H}$ is the **perturbed system.** The difference between the two Hamiltonians is the **perturbation** $\hat{H}'$:

$$\hat{H}' \equiv \hat{H} - \hat{H}^0 \tag{9.5}$$

$$\boxed{\hat{H} = \hat{H}^0 + \hat{H}'} \tag{9.6}$$

(The prime does not denote differentiation.) For the anharmonic oscillator with Hamiltonian (9.3), the perturbation on the related harmonic oscillator is $\hat{H}' = cx^3 + dx^4$.

In $\hat{H}^0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$ [Eq. (9.2)], $E_n^{(0)}$ and $\psi_n^{(0)}$ are called the **unperturbed energy** and **unperturbed wave function** of state n. For $\hat{H}^0$ equal to the harmonic-oscillator

Hamiltonian (9.4), $E_n^{(0)}$ is $(n + \frac{1}{2})h\nu$ [Eq. (4.45)], where n is a nonnegative integer. (n is used instead of v for consistency with the perturbation-theory notation.) Note that the superscript $^{(0)}$ does not mean the ground state. Perturbation theory can be applied to any state. The subscript n labels the state we are dealing with. The superscript $^{(0)}$ denotes the unperturbed system.

Our task is to relate the unknown eigenvalues and eigenfunctions of the perturbed system to the known eigenvalues and eigenfunctions of the unperturbed system. To aid in doing so, we shall imagine that the perturbation is applied gradually, giving a continuous change from the unperturbed to the perturbed system. Mathematically, this corresponds to inserting a parameter λ into the Hamiltonian, so that

$$\hat{H} = \hat{H}^0 + \lambda \hat{H}' \tag{9.7}$$

When λ is zero, we have the unperturbed system. As λ increases, the perturbation grows larger, and at $\lambda = 1$ the perturbation is fully "turned on." We inserted λ to help relate the perturbed and unperturbed eigenfunctions, and ultimately we shall set $\lambda = 1$, thereby eliminating it.

Sections 9.1 to 9.7 deal with time-independent Hamiltonians and stationary states. Section 9.8 deals with time-dependent perturbations.

9.2 Nondegenerate Perturbation Theory

The perturbation treatments of degenerate and nondegenerate energy levels differ. This section examines the effect of a perturbation on a nondegenerate level. If some of the energy levels of the unperturbed system are degenerate while others are nondegenerate, the treatment in this section will apply to the nondegenerate levels only.

Nondegenerate Perturbation Theory

Let $\psi_n^{(0)}$ be the wave function of some particular unperturbed nondegenerate level with energy $E_n^{(0)}$. Let ψ_n be the perturbed wave function into which $\psi_n^{(0)}$ is converted when the perturbation is applied. From (9.1) and (9.7), the Schrödinger equation for the perturbed state is

$$\hat{H}\psi_n = (\hat{H}^0 + \lambda \hat{H}')\psi_n = E_n \psi_n \tag{9.8}$$

Since the Hamiltonian in (9.8) depends on the parameter λ, both the eigenfunction ψ_n and the eigenvalue E_n depend on λ:

$$\psi_n = \psi_n(\lambda, q) \quad \text{and} \quad E_n = E_n(\lambda)$$

where q denotes the system's coordinates. We now expand ψ_n and E_n as Taylor series (Prob. 4.1) in powers of λ:

$$\psi_n = \psi_n|_{\lambda=0} + \left.\frac{\partial \psi_n}{\partial \lambda}\right|_{\lambda=0} \lambda + \left.\frac{\partial^2 \psi_n}{\partial \lambda^2}\right|_{\lambda=0} \frac{\lambda^2}{2!} + \cdots \tag{9.9}$$

$$E_n = E_n|_{\lambda=0} + \left.\frac{dE_n}{d\lambda}\right|_{\lambda=0} \lambda + \left.\frac{d^2 E_n}{d\lambda^2}\right|_{\lambda=0} \frac{\lambda^2}{2!} + \cdots \tag{9.10}$$

By hypothesis, when λ goes to zero, ψ_n and E_n go to $\psi_n^{(0)}$ and $E_n^{(0)}$:

$$\psi_n|_{\lambda=0} = \psi_n^{(0)} \quad \text{and} \quad E_n|_{\lambda=0} = E_n^{(0)} \tag{9.11}$$

We introduce the following abbreviations:

$$\psi_n^{(k)} \equiv \frac{1}{k!} \left.\frac{\partial^k \psi_n}{\partial \lambda^k}\right|_{\lambda=0}, \qquad E_n^{(k)} \equiv \frac{1}{k!} \left.\frac{d^k E_n}{d\lambda^k}\right|_{\lambda=0}, \qquad k = 1, 2, \ldots \tag{9.12}$$

Equations (9.9) and (9.10) become

$$\psi_n = \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots + \lambda^k\psi_n^{(k)} + \cdots \tag{9.13}$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots + \lambda^k E_n^{(k)} + \cdots \tag{9.14}$$

For $k = 1, 2, 3, \ldots$, we call $\psi_n^{(k)}$ and $E_n^{(k)}$ the ***k*th-order corrections** to the wave function and energy. We shall assume that the series (9.13) and (9.14) converge for $\lambda = 1$, and we hope that for a small perturbation, taking just the first few terms of the series will give a good approximation to the true energy and wave function. (Quite often, perturbation-theory series do not converge, but even so, the first few terms of a nonconvergent series can often give a useful approximation.)

We shall take $\psi_n^{(0)}$ to be normalized: $\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle = 1$. Instead of taking ψ_n as normalized, we shall require that ψ_n satisfy

$$\langle \psi_n^{(0)} | \psi_n \rangle = 1 \tag{9.15}$$

If ψ_n does not satisfy this equation, then multiplication of ψ_n by the constant $1/\langle \psi_n^{(0)} | \psi_n \rangle$ gives a perturbed wave function with the desired property. The condition (9.15), called **intermediate normalization,** simplifies the derivation. Note that multiplication of ψ_n by a constant does not change the energy in the Schrödinger equation $\hat{H}\psi_n = E_n\psi_n$, so use of intermediate normalization does not affect the results for the energy corrections. If desired, at the end of the calculation, the intermediate-normalized ψ_n can be multiplied by a constant to normalize it in the usual sense.

Substitution of (9.13) into $1 = \langle \psi_n^{(0)} | \psi_n \rangle$ [Eq. (9.15)] gives

$$1 = \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle + \lambda \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + \lambda^2 \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle + \cdots$$

Since this equation is true for all values of λ in the range 0 to 1, the coefficients of like powers of λ on each side of the equation must be equal, as proved after Eq. (4.11). Equating the λ^0 coefficients, we have $1 = \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle$, which is satisfied since $\psi_n^{(0)}$ is normalized. Equating the coefficients of λ^1, of λ^2, and so on, we have

$$\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0, \qquad \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle = 0, \quad \text{etc.} \tag{9.16}$$

The corrections to the wave function are orthogonal to $\psi_n^{(0)}$ when intermediate normalization is used.

~~Substituting (9.13) and (9.14) into the Schrödinger equation (9.8), we have~~

~~$$(\hat{H}^0 + \lambda\hat{H}')(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots)$$~~

~~$$= (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots)(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots)$$~~

~~Collecting like powers of λ, we have~~

~~$$\hat{H}^0\psi_n^{(0)} + \lambda(\hat{H}'\psi_n^{(0)} + \hat{H}^0\psi_n^{(1)}) + \lambda^2(\hat{H}^0\psi_n^{(2)} + \hat{H}'\psi_n^{(1)}) + \cdots$$~~

~~$$= E_n^{(0)}\psi_n^{(0)} + \lambda(E_n^{(1)}\psi_n^{(0)} + E_n^{(0)}\psi_n^{(1)}) + \lambda^2(E_n^{(2)}\psi_n^{(0)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(0)}\psi_n^{(2)}) + \cdots \quad (9.17)$$~~

~~Now (assuming suitable convergence) for the two series on each side of (9.17) to be equal to each other for all values of λ, the coefficients of like powers of λ in the two series must be equal.~~

~~Equating the coefficients of the λ^0 terms, we have $\hat{H}^0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$, which is the Schrödinger equation for the unperturbed problem, Eq. (9.2), and gives us no new information.~~

~~Equating the coefficients of the λ^1 terms, we have~~

~~$$\hat{H}'\psi_n^{(0)} + \hat{H}^0\psi_n^{(1)} = E_n^{(1)}\psi_n^{(0)} + E_n^{(0)}\psi_n^{(1)}$$~~

~~$$\hat{H}^0\psi_n^{(1)} - E_n^{(0)}\psi_n^{(1)} = E_n^{(1)}\psi_n^{(0)} - \hat{H}'\psi_n^{(0)} \quad (9.18)$$~~

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-2, 30/08/2024)

From the last class:

all energy states are non-degenerate in this perturbation theory

* partitioning of the Hamiltonian: $\hat{H} = \hat{H}_0 + \lambda V$

* Taylor series expansions of E_n and ψ_n:

$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots$ and $\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots$

* Intermediate normalization: $\langle \psi_n^{(0)} | \psi_n \rangle = 1$

We want to solve: $\boxed{H\psi_n = E_n \psi_n}$

$$(H_0 + \lambda V)(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots) = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots)(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots)$$

$$\text{or, } H_0\psi_n^{(0)} + \lambda H_0\psi_n^{(1)} + \lambda^2 H_0\psi_n^{(2)} + \dots + \lambda V\psi_n^{(0)} + \lambda^2 V\psi_n^{(1)} + \lambda^3 V\psi_n^{(2)} + \dots$$
$$= E_n^{(0)}\psi_n^{(0)} + \lambda E_n^{(0)}\psi_n^{(1)} + \lambda^2 E_n^{(0)}\psi_n^{(2)} + \dots + \lambda E_n^{(1)}\psi_n^{(0)} + \lambda^2 E_n^{(1)}\psi_n^{(1)} + \lambda^3 E_n^{(1)}\psi_n^{(2)} + \dots$$

$$\text{or, } \boxed{H_0\psi_n^{(0)}} + \lambda(H_0\psi_n^{(1)} + V\psi_n^{(0)}) + \lambda^2(H_0\psi_n^{(2)} + V\psi_n^{(1)}) + \dots$$
$$= \boxed{E_n^{(0)}\psi_n^{(0)}} + \lambda(E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)}) + \lambda^2(E_n^{(0)}\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)}) + \dots$$

This equation can only be satisfied only when the coefficients of different powers of λ on both sides of the equation are equal.

λ^0: $H_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$: unperturbed problem. ——— (1)

λ^1: $H_0\psi_n^{(1)} + V\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)}$ ——— (2)

λ^2: $H_0\psi_n^{(2)} + V\psi_n^{(1)} = E_n^{(0)}\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)}$ ——— (3)

From Eq. (2): $H_0\psi_n^{(1)} + V\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)}$

$$\text{or, } H_0\psi_n^{(1)} - E_n^{(0)}\psi_n^{(1)} = E_n^{(1)}\psi_n^{(0)} - V\psi_n^{(0)}$$

Left multiplication by $\psi_m^{(0)*}$ and integration over all space

$$\boxed{\langle \psi_m^{(0)} | H_0 | \psi_n^{(1)} \rangle} - E_n^{(0)}\langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = E_n^{(1)}\langle \psi_m^{(0)} | \psi_n^{(0)} \rangle - \langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle$$

$$\langle \psi_m^{(0)} | H_0 | \psi_n^{(1)} \rangle = \langle \psi_n^{(1)} | H_0 | \psi_m^{(0)} \rangle^* = E_m^{(0)*}\langle \psi_n^{(1)} | \psi_m^{(0)} \rangle^* = E_m^{(0)}\langle \psi_m^{(0)} | \psi_n^{(1)} \rangle$$

$$\therefore E_m^{(0)}\langle \psi_m^{(0)} | \psi_n^{(1)} \rangle - E_n^{(0)}\langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = E_n^{(1)}\delta_{mn} - \langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle$$

$$\text{or, } (E_m^{(0)} - E_n^{(0)})\langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = E_n^{(1)}\delta_{mn} - \langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle \quad \text{——— (4)}$$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-2, 30/08/2024)

(a) If $m=n$, $\delta_{mn}=1$, $\quad 0 = E_n^{(1)} - \langle \psi_n^{(0)} | V | \psi_n^{(0)} \rangle$

$$\therefore \boxed{E_n^{(1)} = \langle \psi_n^{(0)} | V | \psi_n^{(0)} \rangle = \int_{\text{all space}} \psi_n^{(0)*} V \psi_n^{(0)} d\tau}$$

(b) If $m \neq n$, $\delta_{mn}=0$

$$\therefore \left(E_m^{(0)} - E_n^{(0)}\right) \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = - \langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle \quad (m \neq n)$$

$\{\psi_m^{(0)}\}$: is a complete orthonormal set of functions

$$\psi_n^{(1)} = \sum_m a_m \psi_m^{(0)} \qquad a_m = \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle$$

$$\langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = a_m$$

$$\therefore \left(E_m^{(0)} - E_n^{(0)}\right) a_m = - \langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle \quad \text{or,} \quad a_m = \frac{\langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \quad \text{for } m \neq n$$

$$\boxed{\psi_n^{(1)} = \sum_{\substack{m \\ (m \neq n)}} \frac{\langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}}$$

$$H_0 \psi_n^{(2)} + V \psi_n^{(1)} = E_n^{(0)} \psi_n^{(2)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(2)} \psi_n^{(0)}$$

Left multiplication by $\psi_m^{(0)*}$ and integration over all space

$$\boxed{\langle \psi_m^{(0)} | H_0 | \psi_n^{(2)} \rangle} - E_n^{(0)} \langle \psi_m^{(0)} | \psi_n^{(2)} \rangle = E_n^{(2)} \langle \psi_m^{(0)} | \psi_n^{(0)} \rangle + E_n^{(1)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle - \langle \psi_m^{(0)} | V | \psi_n^{(1)} \rangle$$

$$\langle \psi_m^{(0)} | H_0 | \psi_n^{(2)} \rangle = \langle \psi_n^{(2)} | H_0 | \psi_m^{(0)} \rangle^* = E_m^{(0)*} \langle \psi_n^{(2)} | \psi_m^{(0)} \rangle^* = E_m^{(0)} \langle \psi_m^{(0)} | \psi_n^{(2)} \rangle$$

$$\therefore \left(E_m^{(0)} - E_n^{(0)}\right) \langle \psi_m^{(0)} | \psi_n^{(2)} \rangle = E_n^{(2)} \delta_{mn} + E_n^{(1)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle - \langle \psi_m^{(0)} | V | \psi_n^{(1)} \rangle \quad \text{—(5)}$$

(a) If $m=n$, $\delta_{mn}=1$

0 (as a result of the intermediate normalization)

$$0 = E_n^{(2)} + E_n^{(1)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle - \langle \psi_n^{(0)} | V | \psi_n^{(1)} \rangle$$

$$\therefore E_n^{(2)} = \langle \psi_n^{(0)} | V | \psi_n^{(1)} \rangle = \langle \psi_n^{(0)} | V \Big| \sum_{\substack{m \\ (m \neq n)}} \frac{\langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)} \rangle$$

$$\text{or,} \quad \boxed{E_n^{(2)} = \sum_{\substack{m \\ (m \neq n)}} \frac{\langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \langle \psi_n^{(0)} | V | \psi_m^{(0)} \rangle = \sum_{\substack{m \\ (m \neq n)}} \frac{|\langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}}$$

Equations (9.9) and (9.10) become

$$\psi_n = \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots + \lambda^k\psi_n^{(k)} + \cdots \tag{9.13}$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots + \lambda^k E_n^{(k)} + \cdots \tag{9.14}$$

For $k = 1, 2, 3, \ldots$, we call $\psi_n^{(k)}$ and $E_n^{(k)}$ the ***k*th-order corrections** to the wave function and energy. We shall assume that the series (9.13) and (9.14) converge for $\lambda = 1$, and we hope that for a small perturbation, taking just the first few terms of the series will give a good approximation to the true energy and wave function. (Quite often, perturbation-theory series do not converge, but even so, the first few terms of a nonconvergent series can often give a useful approximation.)

We shall take $\psi_n^{(0)}$ to be normalized: $\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle = 1$. Instead of taking ψ_n as normalized, we shall require that ψ_n satisfy

$$\langle\psi_n^{(0)}|\psi_n\rangle = 1 \tag{9.15}$$

If ψ_n does not satisfy this equation, then multiplication of ψ_n by the constant $1/\langle\psi_n^{(0)}|\psi_n\rangle$ gives a perturbed wave function with the desired property. The condition (9.15), called **intermediate normalization,** simplifies the derivation. Note that multiplication of ψ_n by a constant does not change the energy in the Schrödinger equation $\hat{H}\psi_n = E_n\psi_n$, so use of intermediate normalization does not affect the results for the energy corrections. If desired, at the end of the calculation, the intermediate-normalized ψ_n can be multiplied by a constant to normalize it in the usual sense.

Substitution of (9.13) into $1 = \langle\psi_n^{(0)}|\psi_n\rangle$ [Eq. (9.15)] gives

$$1 = \langle\psi_n^{(0)}|\psi_n^{(0)}\rangle + \lambda\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle + \lambda^2\langle\psi_n^{(0)}|\psi_n^{(2)}\rangle + \cdots$$

Since this equation is true for all values of λ in the range 0 to 1, the coefficients of like powers of λ on each side of the equation must be equal, as proved after Eq. (4.11). Equating the λ^0 coefficients, we have $1 = \langle\psi_n^{(0)}|\psi_n^{(0)}\rangle$, which is satisfied since $\psi_n^{(0)}$ is normalized. Equating the coefficients of λ^1, of λ^2, and so on, we have

$$\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle = 0, \qquad \langle\psi_n^{(0)}|\psi_n^{(2)}\rangle = 0, \quad \text{etc.} \tag{9.16}$$

The corrections to the wave function are orthogonal to $\psi_n^{(0)}$ when intermediate normalization is used.

Substituting (9.13) and (9.14) into the Schrödinger equation (9.8), we have

$$(\hat{H}^0 + \lambda\hat{H}')(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots)$$
$$= (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots)(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots)$$

Collecting like powers of λ, we have

$$\hat{H}^0\psi_n^{(0)} + \lambda(\hat{H}'\psi_n^{(0)} + \hat{H}^0\psi_n^{(1)}) + \lambda^2(\hat{H}^0\psi_n^{(2)} + \hat{H}'\psi_n^{(1)}) + \cdots$$
$$= E_n^{(0)}\psi_n^{(0)} + \lambda(E_n^{(1)}\psi_n^{(0)} + E_n^{(0)}\psi_n^{(1)}) + \lambda^2(E_n^{(2)}\psi_n^{(0)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(0)}\psi_n^{(2)}) + \cdots \tag{9.17}$$

Now (assuming suitable convergence) for the two series on each side of (9.17) to be equal to each other for all values of λ, the coefficients of like powers of λ in the two series must be equal.

Equating the coefficients of the λ^0 terms, we have $\hat{H}^0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$, which is the Schrödinger equation for the unperturbed problem, Eq. (9.2), and gives us no new information.

Equating the coefficients of the λ^1 terms, we have

$$\hat{H}'\psi_n^{(0)} + \hat{H}^0\psi_n^{(1)} = E_n^{(1)}\psi_n^{(0)} + E_n^{(0)}\psi_n^{(1)}$$
$$\hat{H}^0\psi_n^{(1)} - E_n^{(0)}\psi_n^{(1)} = E_n^{(1)}\psi_n^{(0)} - \hat{H}'\psi_n^{(0)} \tag{9.18}$$

The First-Order Energy Correction

To find $E_n^{(1)}$ we multiply (9.18) by $\psi_m^{(0)*}$ and integrate over all space, which gives

$$\langle \psi_m^{(0)} | \hat{H}^0 | \psi_n^{(1)} \rangle - E_n^{(0)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = E_n^{(1)} \langle \psi_m^{(0)} | \psi_n^{(0)} \rangle - \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle \quad (9.19)$$

where bracket notation [Eqs. (7.1) and (7.3)] is used. $\hat{H}^0$ is Hermitian, and use of the Hermitian property (7.12) gives for the first term on the left side of (9.19)

$$\begin{aligned} \langle \psi_m^{(0)} | \hat{H}^0 | \psi_n^{(1)} \rangle &= \langle \psi_n^{(1)} | \hat{H}^0 | \psi_m^{(0)} \rangle^* = \langle \psi_n^{(1)} | \hat{H}^0 \psi_m^{(0)} \rangle^* \\ &= \langle \psi_n^{(1)} | E_m^{(0)} \psi_m^{(0)} \rangle^* = E_m^{(0)*} \langle \psi_n^{(1)} | \psi_m^{(0)} \rangle^* = E_m^{(0)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle \end{aligned} \quad (9.20)$$

where we used the unperturbed Schrödinger equation $\hat{H}^0 \psi_m^{(0)} = E_m^{(0)} \psi_m^{(0)}$, the fact that $E_m^{(0)}$ is real, and (7.4). Substitution of (9.20) into (9.19) and use of the orthonormality equation $\langle \psi_m^{(0)} | \psi_n^{(0)} \rangle = \delta_{mn}$ for the unperturbed eigenfunctions gives

$$(E_m^{(0)} - E_n^{(0)}) \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = E_n^{(1)} \delta_{mn} - \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle \quad (9.21)$$

If $m = n$, the left side of (9.21) equals zero, and (9.21) becomes

$$\boxed{E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle = \int \psi_n^{(0)*} \hat{H}' \psi_n^{(0)} \, d\tau} \quad \textbf{(9.22)}$$

The first-order correction to the energy is found by averaging the perturbation $\hat{H}'$ over the appropriate unperturbed wave function.

Setting $\lambda = 1$ in (9.14), we have

$$E_n \approx E_n^{(0)} + E_n^{(1)} = E_n^{(0)} + \int \psi_n^{(0)*} \hat{H}' \psi_n^{(0)} \, d\tau \quad (9.23)$$

EXAMPLE

For the anharmonic oscillator with Hamiltonian (9.3), evaluate $E^{(1)}$ for the ground state if the unperturbed system is taken as the harmonic oscillator.

The perturbation is given by Eqs. (9.3) to (9.5) as

$$\hat{H}' = \hat{H} - \hat{H}^0 = cx^3 + dx^4$$

and the first-order energy correction for the state with quantum number v is given by (9.22) as $E_v^{(1)} = \langle \psi_v^{(0)} | cx^3 + dx^4 | \psi_v^{(0)} \rangle$, where $\psi_v^{(0)}$ is the harmonic-oscillator wave function for state v. For the $v = 0$ ground state, use of $\psi_0^{(0)} = (\alpha/\pi)^{1/4} e^{-\alpha x^2/2}$ [Eq. (4.53)] gives

$$E_0^{(1)} = \langle \psi_0^{(0)} | cx^3 + dx^4 | \psi_0^{(0)} \rangle = \left(\frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2} (cx^3 + dx^4) \, dx$$

The integral from $-\infty$ to ∞ of the odd function $cx^3 e^{-\alpha x^2}$ is zero. Use of the Appendix integral (A.10) with $n = 2$ and (4.31) for α gives

$$E_0^{(1)} = 2d \left(\frac{\alpha}{\pi} \right)^{1/2} \int_0^{\infty} e^{-\alpha x^2} x^4 \, dx = \frac{3d}{4\alpha^2} = \frac{3dh^2}{64\pi^4 \nu^2 m^2}$$

The unperturbed ground-state energy is $E_0^{(0)} = \frac{1}{2} h\nu$ and $E_0^{(0)} + E_0^{(1)} = \frac{1}{2} h\nu + 3dh^2/64\pi^4 \nu^2 m^2$.

EXERCISE Consider a one-particle, one-dimensional system with $V = \infty$ for $x < 0$ and for $x > l$, and $V = cx$ for $0 \leq x \leq l$, where c is a constant. (a) Sketch V for $c > 0$. (b) Treat the system as a perturbed particle in a box and find $E^{(1)}$ for the state with quantum number n. Then use Eq. (3.88) to state why the answer you got is to be expected. (*Partial Answer:* (b) $\frac{1}{2} cl$.)

The First-Order Wave-Function Correction

For $m \neq n$, Eq. (9.21) is

$$(E_m^{(0)} - E_n^{(0)})\langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = -\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle, \quad m \neq n \tag{9.24}$$

To find $\psi_n^{(1)}$, we expand it in terms of the complete, orthonormal set of unperturbed eigenfunctions $\psi_m^{(0)}$ of the Hermitian operator $\hat{H}^0$:

$$\psi_n^{(1)} = \sum_m a_m \psi_m^{(0)}, \qquad \text{where} \quad a_m = \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle \tag{9.25}$$

where Eq. (7.41) was used for the expansion coefficients a_m. Use of $a_m = \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle$ in (9.24) gives

$$(E_m^{(0)} - E_n^{(0)}) a_m = -\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle, \quad m \neq n$$

By hypothesis, the level $E_n^{(0)}$ is nondegenerate. Therefore $E_m^{(0)} \neq E_n^{(0)}$ for $m \neq n$, and we may divide by $(E_m^{(0)} - E_n^{(0)})$ to get

$$a_m = \frac{\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}, \quad m \neq n \tag{9.26}$$

The coefficients a_m in the expansion (9.25) of $\psi_n^{(1)}$ are given by (9.26) except for a_n, the coefficient of $\psi_n^{(0)}$. From the second equation in (9.25), $a_n = \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle$. Recall that the choice of intermediate normalization for ψ_n makes $\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0$ [Eq. (9.16)]. Hence $a_n = \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0$, and Eqs. (9.25) and (9.26) give the first-order correction to the wave function as

$$\psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)} \tag{9.27}$$

The symbol $\sum_{m \neq n}$ means we sum over all the unperturbed states except state n.

Setting $\lambda = 1$ in (9.13) and using just the first-order wave-function correction, we have as the approximation to the perturbed wave function

$$\psi_n \approx \psi_n^{(0)} + \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)} \tag{9.28}$$

For $\psi_n^{(2)}$ and the normalization of ψ, see *Kemble*, Chapter XI.

The Second-Order Energy Correction

Equating the coefficients of the λ^2 terms in (9.17), we get

$$\hat{H}^0 \psi_n^{(2)} - E_n^{(0)} \psi_n^{(2)} = E_n^{(2)} \psi_n^{(0)} + E_n^{(1)} \psi_n^{(1)} - \hat{H}' \psi_n^{(1)} \tag{9.29}$$

Multiplication by $\psi_m^{(0)*}$ followed by integration over all space gives

$$\langle \psi_m^{(0)} | \hat{H}^0 | \psi_n^{(2)} \rangle - E_n^{(0)} \langle \psi_m^{(0)} | \psi_n^{(2)} \rangle = E_n^{(2)} \langle \psi_m^{(0)} | \psi_n^{(0)} \rangle + E_n^{(1)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle - \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(1)} \rangle \tag{9.30}$$

The integral $\langle \psi_m^{(0)} | \hat{H}^0 | \psi_n^{(2)} \rangle$ in this equation is the same as the integral in (9.20), except that $\psi_n^{(1)}$ is replaced by $\psi_n^{(2)}$. Replacement of $\psi_n^{(1)}$ by $\psi_n^{(2)}$ in (9.20) gives

$$\langle \psi_m^{(0)} | \hat{H}^0 | \psi_n^{(2)} \rangle = E_m^{(0)} \langle \psi_m^{(0)} | \psi_n^{(2)} \rangle \tag{9.31}$$

Use of (9.31) and orthonormality of the unperturbed functions in (9.30) gives

$$(E_m^{(0)} - E_n^{(0)}) \langle \psi_m^{(0)} | \psi_n^{(2)} \rangle = E_n^{(2)} \delta_{mn} + E_n^{(1)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle - \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(1)} \rangle \tag{9.32}$$

For $m = n$, the left side of (9.32) is zero and we get

$$E_n^{(2)} = -E_n^{(1)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(1)} \rangle$$

$$E_n^{(2)} = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(1)} \rangle \tag{9.33}$$

since $\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0$ [Eq. (9.16)]. Note from (9.33) that to find the *second*-order correction to the energy, we have to know only the *first*-order correction to the wave function. In fact, it can be shown that knowledge of $\psi_n^{(1)}$ suffices to determine $E_n^{(3)}$ also.

In general, it can be shown that *if we know the corrections to the wave function through order k, then we can compute the corrections to the energy through order* $2k + 1$ (see *Bates*, Vol. I, p. 184).

Substitution of (9.27) for $\psi_n^{(1)}$ into (9.33) gives

$$E_n^{(2)} = \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \langle \psi_n^{(0)} | \hat{H}' | \psi_m^{(0)} \rangle \tag{9.34}$$

since the expansion coefficients a_m [Eq. (9.26)] are constants that can be taken outside the integral. Since $\hat{H}'$ is Hermitian, we have

$$\begin{aligned} \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle \langle \psi_n^{(0)} | \hat{H}' | \psi_m^{(0)} \rangle &= \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle^* \\ &= | \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle |^2 \end{aligned}$$

and (9.34) becomes

$$E_n^{(2)} = \sum_{m \neq n} \frac{| \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle |^2}{E_n^{(0)} - E_m^{(0)}} \tag{9.35}$$

which is the desired expression for $E_n^{(2)}$ in terms of the unperturbed wave functions and energies.

Inclusion of $E_n^{(2)}$ in (9.14) with $\lambda = 1$ gives the approximate energy of the perturbed state as

$$E_n \approx E_n^{(0)} + H'_{nn} + \sum_{m \neq n} \frac{|H'_{mn}|^2}{E_n^{(0)} - E_m^{(0)}} \tag{9.36}$$

where the integrals are over the unperturbed normalized wave functions.

For formulas for higher-order energy corrections, see *Bates,* Volume I, pages 181–185. The form of perturbation theory developed in this section is called *Rayleigh–Schrödinger perturbation theory*; other approaches exist.

Discussion

Equation (9.28) shows that the effect of the perturbation on the wave function $\psi_n^{(0)}$ is to "mix in" contributions from other states $\psi_m^{(0)}$, $m \neq n$. Because of the factor $1/(E_n^{(0)} - E_m^{(0)})$, the most important contributions (aside from $\psi_n^{(0)}$) to the perturbed wave function come from states nearest in energy to state n.

To evaluate the first-order correction to the energy, we must evaluate only the single integral H'_{nn}, whereas to evaluate the second-order energy correction, we must evaluate the matrix elements of $\hat{H}'$ between the nth state and all other states m, and then perform the infinite sum in (9.35). In many cases the second-order energy correction cannot be evaluated exactly. It is even harder to deal with third-order and higher-order energy corrections.

The sums in (9.28) and (9.36) are sums over different states rather than sums over different energy values. If some of the energy levels (other than the nth) are degenerate, we must include a term in the sums for each linearly independent wave function corresponding to the degenerate levels.

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-3, 01/09/2024)

From the last class:

$$E_n^{(1)} = \langle \psi_n^{(0)} | V | \psi_n^{(0)} \rangle = \int_{\text{all space}} \psi_n^{(0)*} V \psi_n^{(0)} dq \; ; \quad \psi_n^{(1)} = \sum_{\substack{m \\ (m \neq n)}} \frac{\langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}$$

$$E_n^{(2)} = \sum_{\substack{m \\ (m \neq n)}} \frac{|\langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

Limitation of non-degenerate PT: if $(E_n^{(0)} - E_m^{(0)})$ is extremely small, the perturbation series diverges rapidly.

A review of the SHO model $\quad K = m\omega^2$

$$H = \frac{p_x^2}{2m} + \frac{Kx^2}{2} \quad \text{or,} \quad \frac{H}{\hbar\omega} = \frac{1}{2}\left[\frac{p_x^2}{m\hbar\omega} + \frac{m\omega^2 x^2}{\hbar\omega}\right] = \frac{1}{2}\left[\left(\frac{p_x}{\sqrt{m\hbar\omega}}\right)^2 + \left(\sqrt{\frac{m\omega}{\hbar}}x\right)^2\right]$$

$\frac{H}{\hbar\omega} = H$ (dimensionless Hamiltonian) $\qquad \sqrt{\frac{m\omega}{\hbar}}x = q$ (dimensionless position)

$\frac{p_x}{\sqrt{m\hbar\omega}} = p$ (dimensionless momentum) $\qquad H = \frac{1}{2}(p^2 + q^2)$

Define: $a = \frac{1}{\sqrt{2}}(q + ip)$; $a^\dagger = \frac{1}{\sqrt{2}}(q - ip)$; $a + a^\dagger = \sqrt{2}q$

or, $\sqrt{2}\left(\frac{m\omega}{\hbar}\right)^{1/2} x = a + a^\dagger$ or, $x = \left(\frac{\hbar}{2m\omega}\right)^{1/2}(a + a^\dagger)$

$$aa^\dagger = \frac{1}{\sqrt{2}}(q + ip)\cdot\frac{1}{\sqrt{2}}(q - ip) = \frac{1}{2}(q^2 + p^2) - \frac{1}{2}i(qp - pq) = \frac{1}{2}(q^2 + p^2) - \frac{1}{2}i[q, p]$$

or, $aa^\dagger = \frac{1}{2}(q^2 + p^2) - \frac{1}{2}i \cdot i$ or, $aa^\dagger = \frac{1}{2}(q^2 + p^2) + \frac{1}{2}$ $\qquad a\psi_n = \sqrt{n}\,\psi_{n-1}$

Similarly, $a^\dagger a = \frac{1}{2}(q^2 + p^2) - \frac{1}{2}$ $\qquad \therefore aa^\dagger + a^\dagger a = q^2 + p^2$ $\qquad a^\dagger \psi_n = \sqrt{n+1}\,\psi_{n+1}$

Anharmonic oscillator: $H = \left(\frac{p_x^2}{2m} + \frac{1}{2}Kx^2\right) + (Cx^3 + Qx^4)$

K = quadratic force constant

C = cubic " "

Q = quartic force constant

$\therefore H = H_0 + V$ (partitioning of the Hamiltonian)

$H_0 = \frac{1}{2}(q^2 + p^2)$; $V = Cx^3 + Qx^4$

$\therefore H_0 = \frac{1}{2}(aa^\dagger + a^\dagger a)$; $E_n^{(0)} = (n + \frac{1}{2})\hbar\omega$; $\psi_n^{(0)} = |n\rangle$

Now, $E_n^{(1)} = \langle \psi_n^{(0)} | V | \psi_n^{(0)} \rangle = \langle n | Cx^3 + Qx^4 | n \rangle = C\langle n | x^3 | n \rangle + Q\langle n | x^4 | n \rangle$

$x^3 = \left(\frac{\hbar}{2m\omega}\right)^{3/2}(a + a^\dagger)^3 \Rightarrow x^3 \sim (a + a^\dagger)^3$ $\qquad (\alpha + \beta)^3 = \alpha^3 + 3\alpha^2\beta + 3\alpha\beta^2 + \beta^3$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-3, 01/09/2024)

$x^3 \sim (a+a^\dagger)^3 = a^3 + a^{\dagger 3} + aaa^\dagger + aa^\dagger a + a^\dagger aa + aa^\dagger a^\dagger + a^\dagger aa^\dagger + a^\dagger a^\dagger a$

Now, $\langle n|x^3|n\rangle = \langle n|a^3|n\rangle + \langle n|a^{\dagger 3}|n\rangle + \langle n|aaa^\dagger|n\rangle + \cdots + \langle n|a^\dagger a^\dagger a|n\rangle$

$\downarrow \langle n|n-3\rangle \quad \downarrow \langle n|n+3\rangle \quad \downarrow \langle n|n-1\rangle \quad \downarrow \langle n|n+1\rangle$

$\langle n|aaa^\dagger|n\rangle \xrightarrow{\sqrt{n+1}} \langle n|aa|n+1\rangle = \sqrt{n+1}\sqrt{n+1}\langle n|a|n\rangle = (n+1)\sqrt{n}\langle n|n-1\rangle = (n+1)\sqrt{n}\,\delta_{n,n-1}$

$\therefore \langle n|x^3|n\rangle = 0$

$\therefore E_n^{(1)} = c\times 0 + Q\langle n|x^4|n\rangle$ or, $E_n^{(1)} = Q\langle n|x^4|n\rangle$

$x^4 \sim (a+a^\dagger)^4 = a^4 + a^{\dagger 4} + \cdots$

$aaa^\dagger a^\dagger, a^\dagger a^\dagger aa, aa^\dagger aa^\dagger, a^\dagger aa^\dagger a, a^\dagger aaa^\dagger, aa^\dagger a^\dagger a$

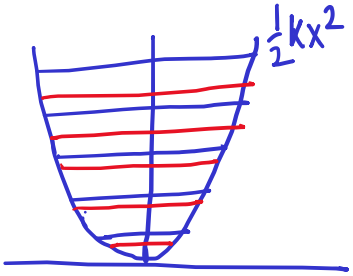
$a\psi_n = \sqrt{n}\,\psi_{n-1}$

$a\psi_{n+2} = \sqrt{n+2}\,\psi_{n+2-1} = \sqrt{n+2}\,\psi_{n+1}$

$\therefore \langle n|x^4|n\rangle = \langle n|aaa^\dagger a^\dagger|n\rangle + \cdots + \langle n|a^\dagger aaa^\dagger|n\rangle$

$\langle n|aaa^\dagger a^\dagger|n\rangle = \sqrt{n+1}\langle n|aaa^\dagger|n+1\rangle = \sqrt{n+1}\sqrt{n+2}\langle n|aa^\dagger|n+2\rangle = \sqrt{n+1}\sqrt{n+2}\sqrt{n+2}\langle n|a|n+1\rangle$

$= \sqrt{n+1}\sqrt{n+2}\sqrt{n+2}\sqrt{n+1}\langle n|n\rangle = (n+1)(n+2)$



$\langle n|a^\dagger a^\dagger aa|n\rangle = n(n-1) \qquad \langle n|aa^\dagger a^\dagger a|n\rangle = n(n+1)$

$\langle n|aa^\dagger aa^\dagger|n\rangle = (n+1)^2 \qquad \langle n|a^\dagger aaa^\dagger|n\rangle = (n+1)n$

$\langle n|a^\dagger aa^\dagger a|n\rangle = n^2 \qquad \therefore \langle n|x^4|n\rangle = 6\left(n^2+n+\frac{1}{2}\right)$

$\therefore E_n^{(1)} = Q\langle n|x^4|n\rangle = Q\left\langle n\left|\left(\frac{\hbar}{2m\omega}\right)^2(a+a^\dagger)^4\right|n\right\rangle = Q\left(\frac{\hbar}{2m\omega}\right)^2 6\left(n^2+n+\frac{1}{2}\right)$

$E_n \simeq E_n^{(0)} + E_n^{(1)} = \left(n+\frac{1}{2}\right)\hbar\omega + \frac{3}{2}\frac{Q\hbar^2}{m^2\omega^2}\left(n^2+n+\frac{1}{2}\right)$

* Energy levels of the perturbed oscillator are not equally spaced.
* $E_n^{(1)}$ grows with n faster than $E_n^{(0)}$.
* For real molecules, the levels of the perturbed oscillator gets close together.

The Anharmonic Oscillator

- Vibrational potential of molecules not harmonic.
- Approximately harmonic near potential minimum.
- Expand potential in power series.

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dX^2} + \frac{1}{2}kX^2 + CX^3 + QX^4 = \frac{P^2}{2m} + \frac{1}{2}kX^2 + CX^3 + QX^4$$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-3, 01/09/2024)

C and Q are cubic and quartic force constants, respectively.

$$\hat{H}^0 = \frac{P^2}{2m} + \frac{1}{2}kX^2; \hat{V} = CX^3 + QX^4$$

where,

$$\hat{H}^0 = \frac{P^2}{2m} + \frac{1}{2}m\omega^2X^2$$

$$\frac{\hat{H}^0}{\hbar\omega} = \frac{1}{2}\left[\frac{P^2}{m\omega\hbar} + \frac{m\omega}{\hbar}X^2\right] = \frac{1}{2}\left[\frac{P^2}{\left(\sqrt{m\omega\hbar}\right)^2} + \left(\sqrt{\frac{m\omega}{\hbar}}\right)^2 X^2\right]$$

Define: $\mathcal{H}^0 = \hat{H}^0/\hbar\omega,\ p = P/\sqrt{m\omega\hbar}$ and $q = \sqrt{m\omega/\hbar}\,X$

$$\therefore \mathcal{H}^0 = \frac{1}{2}(q^2 + p^2)$$

Define: $a = \frac{1}{\sqrt{2}}(q + ip)$ and $a^\dagger = \frac{1}{\sqrt{2}}(q - ip)$

$$\hat{X} = \left(\frac{\hbar}{2m\omega}\right)^{1/2}\left(a + a^\dagger\right)$$

We already know:

$$aa^\dagger = \frac{1}{2}(q^2 + p^2) + \frac{1}{2} \text{ and } a^\dagger a = \frac{1}{2}(q^2 + p^2) - \frac{1}{2}$$

$$\Rightarrow aa^\dagger + a^\dagger a = (q^2 + p^2)$$

$$\because \mathcal{H}^0 = \frac{1}{2}(q^2 + p^2)$$

$$\frac{\hat{H}^0}{\hbar\omega} = \frac{1}{2}(q^2 + p^2) = \frac{1}{2}\left(aa^\dagger + a^\dagger a\right)$$

$$\hat{H}^0 = \frac{1}{2}\hbar\omega\left(aa^\dagger + a^\dagger a\right)$$

Unperturbed energies, $E_n^{(0)} = (n + 1/2)\hbar\omega$

Unperturbed wavefunctions, $\psi_n^{(0)} = |n\rangle$; perturbation, $\hat{V} = CX^3 + QX^4$; C and Q are expansion coefficients, like λ; when $C \to 0$ and $Q \to 0$, $\hat{H} \to \hat{H}^0$.

$$E_n^{(1)} = \langle n|\hat{V}|n\rangle = \langle n|CX^3 + QX^4|n\rangle = C\langle n|X^3|n\rangle + Q\langle n|X^4|n\rangle$$

First consider the cubic term.

$$X \propto \left(a + a^\dagger\right)^3$$

Multiply out...; there will be many terms...

$$aaa,\ aaa^\dagger,\ aa^\dagger a, a^\dagger aa, a^\dagger a^\dagger a,\ \ldots, a^\dagger a^\dagger a^\dagger$$

None of the terms have the same number of raising and lowering operators.

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

$$\langle n|X^3|n\rangle = 0$$

$$\langle n|X^4|n\rangle = \left(\frac{\hbar}{2m\omega}\right)^2\left\langle n\middle|\left(a + a^\dagger\right)^4\middle|n\right\rangle$$

$\left(a + a^\dagger\right)^4$ has terms with same number of raising and lowering operators.

$$\therefore \left\langle n\middle|\left(a + a^\dagger\right)^4\middle|n\right\rangle \neq 0$$

Using $a|n\rangle = \sqrt{n}|n-1\rangle$ and $a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$. Only terms with the same number of raising and lowering operators are non-zero. There are **six** terms.

$$\langle n|aaa^\dagger a^\dagger|n\rangle = (n+1)(n+2)$$

$$\langle n|a^\dagger a^\dagger aa|n\rangle = n(n-1)$$

$$\langle n|aa^\dagger aa^\dagger|n\rangle = (n+1)^2$$

$$\langle n|a^\dagger aa^\dagger a|n\rangle = n^2$$

$$\langle n|aa^\dagger a^\dagger a|n\rangle = n(n+1)$$

$$\langle n|a^\dagger aaa^\dagger|n\rangle = (n+1)n$$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-3, 01/09/2024)

$$\therefore \left\langle n\left|(a+a^{\dagger})^{4}\right|n\right\rangle = \langle n|aaa^{\dagger}a^{\dagger} + a^{\dagger}a^{\dagger}aa + aa^{\dagger}aa^{\dagger} + a^{\dagger}aa^{\dagger}a + aa^{\dagger}a^{\dagger}a + a^{\dagger}aaa^{\dagger}|n\rangle$$

$$\Rightarrow \left\langle n\left|(a+a^{\dagger})^{4}\right|n\right\rangle = \langle n|aaa^{\dagger}a^{\dagger}|n\rangle + \langle n|a^{\dagger}a^{\dagger}aa|n\rangle + \langle n|aa^{\dagger}aa^{\dagger}|n\rangle + \langle n|a^{\dagger}aa^{\dagger}a|n\rangle + \langle n|aa^{\dagger}a^{\dagger}a|n\rangle + \langle n|a^{\dagger}aaa^{\dagger}|n\rangle$$

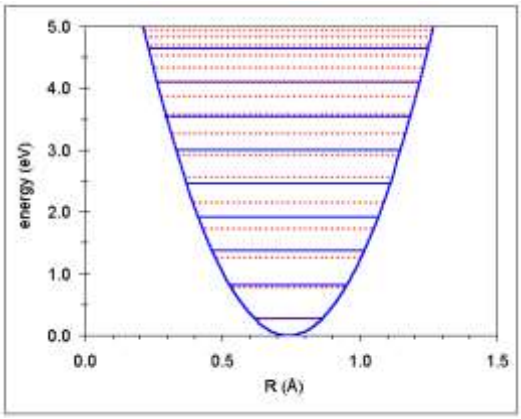
$$\therefore \left\langle n\left|(a+a^{\dagger})^{4}\right|n\right\rangle = 6\left(n^{2}+n+\frac{1}{2}\right)$$

$$E_n^{(1)} = C\langle n|X^3|n\rangle + Q\langle n|X^4|n\rangle = C\times 0 + Q\times\left(\frac{\hbar}{2m\omega}\right)^{2}\left\langle n\left|(a+a^{\dagger})^{4}\right|n\right\rangle$$

$$\therefore E_n^{(1)} = Q\times\left(\frac{\hbar}{2m\omega}\right)^{2} 6\left(n^{2}+n+\frac{1}{2}\right) = \frac{3}{2}\frac{Q\hbar^{2}}{m^{2}\omega^{2}}\left(n^{2}+n+\frac{1}{2}\right)$$

$$\therefore E_n \approx E_n^{(0)} + E_n^{(1)} + E_n^{(2)} = \left(n+\frac{1}{2}\right)\hbar\omega + \frac{3}{2}\frac{Q\hbar^{2}}{m^{2}\omega^{2}}\left(n^{2}+n+\frac{1}{2}\right)$$

- Energy levels not equally spaced.
- Real molecules, levels get closer together – Q is negative.
- Correction grows with *n* faster than zeroth order term → decrease in level spacing.



GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-4, 02/09/2024)

A SHO perturbed by an external electric field

a particle of charge q and mass m is subjected to an external constant electric field $\vec{\mathcal{E}}$.

$$\hat{H} = \frac{p_x^2}{2m} + \frac{1}{2}kx^2 + q|\vec{\mathcal{E}}|x = \underbrace{\frac{p_x^2}{2m} + \frac{1}{2}kx^2}_{\hat{H}_0} + \underbrace{q\mathcal{E}x}_{V} = \hat{H}_0 + V \text{ ; full perturbation, } \lambda = 1$$

$$E_n^{(0)} = \left(n+\tfrac{1}{2}\right)\hbar\omega \text{ ; } \psi_n^{(0)} = |n\rangle \qquad x = \left(\frac{\hbar}{2m\omega}\right)^{1/2}(a+a^\dagger)$$

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \cdots \cong E_n^{(0)} + E_n^{(1)} + E_n^{(2)}$$

$$E_n^{(1)} = \langle \psi_n^{(0)} | V | \psi_n^{(0)} \rangle = \langle n | q\mathcal{E}x | n \rangle = q\mathcal{E}\langle n | x | n \rangle$$

$$\text{or, } E_n^{(1)} = q\mathcal{E}\left(\frac{\hbar}{2m\omega}\right)^{1/2}\langle n | a + a^\dagger | n \rangle = q\mathcal{E}\left(\frac{\hbar}{2m\omega}\right)^{1/2}\left[\langle n|a|n\rangle + \langle n|a^\dagger|n\rangle\right]$$

$$\text{or, } E_n^{(1)} = q\mathcal{E}\left(\frac{\hbar}{2m\omega}\right)^{1/2}\left[\sqrt{n}\underbrace{\langle n|n-1\rangle}_{\delta_{n,n-1}=0} + \sqrt{n+1}\underbrace{\langle n|n+1\rangle}_{\delta_{n,n+1}=0}\right] = 0$$

$$\therefore E_n = E_n^{(0)} + E_n^{(2)}$$

$$E_n^{(2)} = \sum_{\substack{m \\ (m \neq n)}} \frac{|\langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} = q^2\mathcal{E}^2 \sum_{\substack{m \\ (m \neq n)}} \frac{|\langle m | x | n \rangle|^2}{E_n^{(0)} - E_m^{(0)}} \text{ ; } E_n^{(0)} = \left(n+\tfrac{1}{2}\right)\hbar\omega$$

∵ For the calculation of $E_n^{(2)}$, $m \neq n$, so m can either be $n+1$ or, $n-1$.

$$\therefore E_n^{(2)} = q^2\mathcal{E}^2\left[\frac{|\langle n+1|x|n\rangle|^2}{E_n^{(0)} - E_{n+1}^{(0)}} + \frac{|\langle n-1|x|n\rangle|^2}{E_n^{(0)} - E_{n-1}^{(0)}}\right] \text{ ; } x = \left(\frac{\hbar}{2m\omega}\right)^{1/2}(a+a^\dagger)$$

Now, $E_n^{(0)} - E_{n+1}^{(0)} = \left(n+\tfrac{1}{2}\right)\hbar\omega - \left(n+1+\tfrac{1}{2}\right)\hbar\omega = -\hbar\omega$

$E_n^{(0)} - E_{n-1}^{(0)} = \left(n+\tfrac{1}{2}\right)\hbar\omega - \left(n-1+\tfrac{1}{2}\right)\hbar\omega = \hbar\omega$

$$\langle n+1|x|n\rangle = \left(\frac{\hbar}{2m\omega}\right)^{1/2}\langle n+1|a+a^\dagger|n\rangle = \left(\frac{\hbar}{2m\omega}\right)^{1/2}\left[\langle n+1|a|n\rangle + \langle n+1|a^\dagger|n\rangle\right]$$

$$= \left(\frac{\hbar}{2m\omega}\right)^{1/2}\left[\sqrt{n}\underbrace{\langle n+1|n-1\rangle}_{\delta_{n+1,n-1}=0} + \sqrt{n+1}\underbrace{\langle n+1|n+1\rangle}_{\delta_{n+1,n+1}=1}\right] = \left(\frac{\hbar}{2m\omega}\right)^{1/2}\sqrt{n+1}$$

$$\therefore |\langle n+1|x|n\rangle|^2 = \left(\frac{\hbar}{2m\omega}\right)(n+1)$$

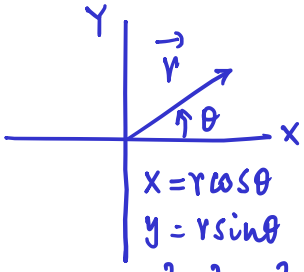
GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-4, 02/09/2024)

Similarly, $|\langle n-1|x|n\rangle|^2 = \left(\frac{\hbar}{2m\omega}\right) n$

$$\therefore E_n^{(2)} = q^2\varepsilon^2\left[\frac{\frac{\hbar}{2m\omega}(n+1)}{-\hbar\omega} + \frac{\frac{\hbar}{2m\omega}\,n}{\hbar\omega}\right] = q^2\varepsilon^2\frac{\hbar}{2m\omega}\cdot\frac{1}{\hbar\omega}\left[-(n+1)+n\right]$$

$$\text{or, } E_n^{(2)} = -\frac{q^2\varepsilon^2}{2m\omega^2} \qquad E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} = \left(n+\tfrac{1}{2}\right)\hbar\omega - \frac{q^2\varepsilon^2}{2m\omega^2}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + q\varepsilon x = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2 + q\varepsilon x$$



variable transformation, $y = x + \frac{q\varepsilon}{m\omega^2} \Rightarrow x = y - \frac{q\varepsilon}{m\omega^2}$

$\therefore dx = dy$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dy^2} + \frac{1}{2}m\omega^2\left(y - \frac{q\varepsilon}{m\omega^2}\right)^2 + q\varepsilon\left(y - \frac{q\varepsilon}{m\omega^2}\right)$$

$$= -\frac{\hbar^2}{2m}\frac{d^2}{dy^2} + \frac{1}{2}m\omega^2\left[y^2 + \left(\frac{q\varepsilon}{m\omega^2}\right)^2 - \frac{2q\varepsilon}{m\omega^2}y\right] + q\varepsilon\left(y - \frac{q\varepsilon}{m\omega^2}\right)$$

$$= -\frac{\hbar^2}{2m}\frac{d^2}{dy^2} + \frac{1}{2}m\omega^2y^2 + \cancel{\frac{1}{2}m\omega^2}\frac{(q\varepsilon)^2}{(m\omega^2)^{\cancel{2}}} - \cancel{\frac{1}{2}m\omega^2}\frac{\cancel{2}q\varepsilon}{\cancel{m\omega^2}}y + q\varepsilon y - \frac{(q\varepsilon)^2}{m\omega^2}$$

$$= -\frac{\hbar^2}{2m}\frac{d^2}{dy^2} + \frac{1}{2}m\omega^2y^2 + \frac{1}{2}\frac{(q\varepsilon)^2}{m\omega^2} - \cancel{q\varepsilon y} + \cancel{q\varepsilon y} - \frac{(q\varepsilon)^2}{m\omega^2}$$

$$= \left[-\frac{\hbar^2}{2m}\frac{d^2}{dy^2} + \frac{1}{2}m\omega^2y^2\right] - \frac{q^2\varepsilon^2}{2m\omega^2}$$

$\therefore$ for this system, we arrive at the same result without performing the perturbative treatment.

$\downarrow$

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

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + \beta x \rightarrow \text{constant shift in } E$$

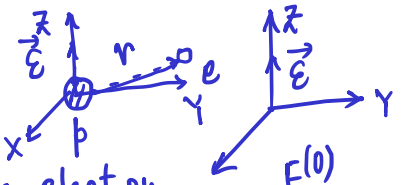
$+\gamma x^2 \rightarrow$ no perturbation : $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \left(\frac{1}{2}k+\gamma\right)x^2$

$+\delta x^3 \rightarrow$ no effect, at $E_n^{(1)}$

$+\varepsilon x^4 \rightarrow$ effect, $E_n^{(1)} \neq 0$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-5, 05/09/2024)

Stark effect on the H atom



$\vec{\mathcal{E}} = |\vec{\mathcal{E}}|\hat{k} = \mathcal{E}\hat{k}$: applied along the z axis

$H_0 = \frac{p^2}{2\mu} - \frac{e^2}{r}$, $\mu = \frac{m_e m_p}{m_e + m_p}$ Spin of the electron is ignored completely

$E^{(0)}_{nlm}$

$\psi^{(0)}_{nlm} = R_{nl}(r)\, Y_{lm}(\theta,\phi)$

$H = H_0 + V$

V will be determined by the energy of interaction between the electron of the H atom and the applied electric field.

$\vec{a} = a_x\hat{i} + a_y\hat{j} + a_z\hat{k}$

$V = e\vec{\mathcal{E}}\cdot\vec{r} = e\,\mathcal{E}\hat{k}\cdot(x\hat{i} + y\hat{j} + z\hat{k}) = e\mathcal{E}z$

$H = \left(\frac{p^2}{2\mu} - \frac{e^2}{r}\right) + e\mathcal{E}z = H_0 + V$ (partioning of the Hamiltonian)

Ground state of H atom: $n=1, l=0, m=0$

$E_{100} \cong E^{(0)}_{100} + E^{(1)}_{100} + E^{(2)}_{100}$

$E^{(0)}_{100}$ ↑ known, −13.6 eV

$E^{(1)}_n = \langle\psi^{(0)}_n|V|\psi^{(0)}_n\rangle = \int \psi^{(0)*}_n V \psi^{(0)}_n\, dq$

$E^{(2)}_n = \sum_{m\,(m\neq n)} \frac{|\langle\psi^{(0)}_m|V|\psi^{(0)}_n\rangle|^2}{E^{(0)}_n - E^{(0)}_m}$

$E_{100} \cong E^{(0)}_{100} + E^{(1)}_{100} + E^{(2)}_{100} = E^{(0)}_{100} + e\mathcal{E}\langle 100|z|100\rangle + e^2\mathcal{E}^2 \sum_{nlm\,(nlm\neq 100)} \frac{|\langle nlm|z|nlm\rangle|^2}{E^{(0)}_{100} - E^{(0)}_{nlm}}$

$\langle 100|z|100\rangle = \int |\psi^{(0)}_{100}|^2 z\, dq$

$x = r\sin\theta\cos\phi$

$y = r\sin\theta\sin\phi$

$z = r\cos\theta$

$dq = r^2 dr \sin\theta\, d\theta\, d\phi$

all space

$$\text{or, } \langle 100|z|100\rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} |\psi^{(0)}_{100}|^2 (r\cos\theta)\, r^2 dr \sin\theta\, d\theta\, d\phi$$

$$= \int_0^\infty |\psi^{(0)}_{100}|^2 r^3 dr \int_0^\pi \sin\theta\cos\theta\, d\theta \int_0^{2\pi} d\phi = 0$$

($\int_0^\pi \sin\theta\cos\theta\, d\theta = 0$)

$E^{(1)}_{100} = 0$: there is no linear Stark effect in H atom

H atom has no dipole moment in the ground state.

* Quantum mechanical treatment of the H atom problem..
* Solutions: energies; wavefunctions
* Shapes of orbitals
* plots of radial and angular prob. dist. functions.

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-5, 05/09/2024)

STARK EFFECT ON HYDROGEN ATOM

Effect of an applied electric field on the energy levels of a hydrogen atom. External uniform weak electric field $\vec{\mathcal{E}} = \mathcal{E}\vec{k}$ applied along the +ve Z axis. Hydrogen atom is in its ground state. The spin degrees of freedom are **ignored**. The unperturbed Hamiltonian:

$$H^0 = \frac{p^2}{2\mu} - \frac{e^2}{r}$$

The unperturbed eigenvalues are $E^{(0)}_{nlm}$, and the corresponding eigenfunctions are $\psi^{(0)}_{nlm} = R_{nl}(r)Y_{lm}(\theta,\phi)$. When the electric field $\vec{\mathcal{E}} = \mathcal{E}\vec{k}$ (applied along the +ve Z axis) is switched on, the system "sees" the perturbation, $H' = e\vec{\mathcal{E}} \cdot \vec{r} = e\mathcal{E}z$. The overall Hamiltonian: $H = H^0 + V$. The ground state of the H atom $\left(E^{(0)}_{100}, \psi^{(0)}_{100}\right)$ is non-degenerate; non-degenerate perturbation theory is applicable. The ground state energy of the H atom that is correct up to second-order in perturbation:

$$E_{100} \approx E^{(0)}_{100} + E^{(1)}_{100} + E^{(2)}_{100}$$

A quick recap: If $\mathrm{m} = \mathrm{n}, \delta_{mn} = 1$

$$E^{(1)}_n = \left\langle \psi^{(0)}_n \middle| V \middle| \psi^{(0)}_n \right\rangle = \int {\psi^{(0)}_n}^* V \psi^{(0)}_n dq$$

$$E^{(2)}_n = \sum_{m \neq n} \frac{\left| \left\langle \psi^{(0)}_m \middle| V \middle| \psi^{(0)}_n \right\rangle \right|^2}{E^{(0)}_n - E^{(0)}_m}$$

$$E_{100} \approx E^{(0)}_{100} + E^{(1)}_{100} + E^{(2)}_{100} = E^{(0)}_{100} + e\mathcal{E}\langle 100|z|100\rangle + e^2\mathcal{E}^2 \sum_{nlm \neq 100} \frac{|\langle nlm|z|100\rangle|^2}{E^{(0)}_{100} - E^{(0)}_{nlm}}$$

$$\langle 100|z|100\rangle = \int \left|\psi^{(0)}_{100}\right|^2 z d\tau = \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \left|\psi^{(0)}_{100}\right|^2 (r\cos\theta) r^2 dr \sin\theta \, d\theta d\phi = 0$$

There can be no correction term to the energy which is proportional to the first power (linear) of the electric field $\mathcal{E} \rightarrow$ **No linear Stark effect.** In the ground state, the H atom has no dipole moment.

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-6, 12/09/2024)

TWO-ELECTRON SYSTEMS: PERTURBATIVE TREATMENT

He atom, Li^+, Be^{2+}, ... $\left[-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}\right]\phi = \varepsilon\phi$

Hamiltonian Operator in atomic units

$\nabla^2 = \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$; $r = \sqrt{x^2+y^2+z^2}$

$x, y, z \longrightarrow \lambda x', \lambda y', \lambda z'$ choice of λ is arbitrary

$\phi \equiv \phi(x,y,z)$; ε is independent of x, y, z

$\phi(x,y,z) \longrightarrow \phi'(x',y',z')$ $\quad \nabla^2 \longrightarrow \frac{1}{\lambda^2}\nabla'^2$; $r \to \lambda r'$

$\therefore \left[-\frac{\hbar^2}{2m_e\lambda^2}\nabla'^2 - \frac{e^2}{4\pi\epsilon_0\lambda r'}\right]\phi' = \varepsilon\phi'$

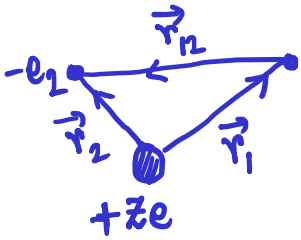
We choose λ in such a way, such that, $\frac{\hbar^2}{m_e\lambda^2} = \frac{e^2}{4\pi\epsilon_0\lambda} = \varepsilon_a$

$\frac{\hbar^2}{m_e\lambda^2} = \frac{e^2}{4\pi\epsilon_0\lambda} \Rightarrow \lambda = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = a_0$ (Bohr radius)

a_0 (Bohr radius): atomic unit of length.

$\left[-\frac{1}{2}\varepsilon_a\nabla'^2 - \frac{\varepsilon_a}{r'}\right]\phi' = \varepsilon\phi$ or, $\left[-\frac{1}{2}\nabla'^2 - \frac{1}{r'}\right]\phi' = \left(\frac{\varepsilon}{\varepsilon_a}\right)\phi'$

$\left[-\frac{1}{2}\nabla'^2 - \frac{1}{r'}\right]\phi' = \varepsilon'\phi'$: Hamiltonian Operator in atomic unit.



$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$

Hamiltonian in atomic units

Born-Oppenheimer type approximation

$H = -\frac{1}{2}(\nabla_1^2+\nabla_2^2) - \frac{Z}{R_1} - \frac{Z}{R_2} + \frac{1}{R_{12}}$

or, $H = \left[-\frac{1}{2}\nabla_1^2 - \frac{Z}{R_1}\right] + \left[-\frac{1}{2}\nabla_2^2 - \frac{Z}{R_2}\right] + \frac{1}{R_{12}}$

↳ Hamiltonian for a one-electron system whose effective nuclear charge is Z.

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-6, 12/09/2024)

$H = H_0 + V$, $H_0 = \left[-\frac{1}{2}\nabla_1^2 - \frac{Z}{R_1}\right] + \left[-\frac{1}{2}\nabla_2^2 - \frac{Z}{R_2}\right]$

$H_0\psi^{(0)} = E^{(0)}\psi^{(0)}$, $V = R_{12}^{-1}$

$\psi^{(0)} = \psi^{(0)}(1)\,\psi^{(0)}(2)$; $E^{(0)} = E^{(0)}(1) + E^{(0)}(2)$

$\psi^{(0)}(1) = \frac{1}{\sqrt{\pi}} Z^{3/2} e^{-ZR_1}$; $\psi^{(0)}(2) = \frac{1}{\sqrt{\pi}} Z^{3/2} e^{-ZR_2}$

$\psi^{(0)} = \psi^{(0)}(1,2) = \frac{Z^3}{\pi} e^{-ZR_1} e^{-ZR_2}$

$\boxed{E^{(0)} = 2Z^2 E_{1s}(H)}$, $E_{1s}(H) = -\frac{1}{2}\frac{e^2}{4\pi\epsilon_0 a_0} = -13.6\ eV$

unperturbed system ≡ two non-interacting one-electron systems.

$E^{(1)} = \langle\psi^{(0)}|V|\psi^{(0)}\rangle = \langle\psi^{(0)}|R_{12}^{-1}|\psi^{(0)}\rangle = \int\int \psi^{(0)} V \psi^{(0)}\, d\tau_1\, d\tau_2$

$d\tau_1 = R_1^2\, dR_1 \sin\theta_1\, d\theta_1\, d\phi_1$

$d\tau_2 = R_2^2\, dR_2 \sin\theta_2\, d\theta_2\, d\phi_2$

$E^{(1)} = \frac{e^2}{4\pi\epsilon_0 a_0}\frac{Z^6}{\pi^2}\int\int \frac{e^{-2ZR_1} e^{-2ZR_2}}{R_{12}} d\tau_1\, d\tau_2 = \frac{5}{8} Z \frac{e^2}{4\pi\epsilon_0 a_0}$

$= \left(-\frac{5}{4}Z\right)\left(-\frac{1}{2}\frac{e^2}{4\pi\epsilon_0 a_0}\right) = \left(-\frac{5}{4}Z\right) E_{1s}(H)$

E = energy correct upto first order $= E^{(0)} + E^{(1)}$

$= \left(2Z^2 - \frac{5}{4}Z\right) E_{1s}(H)$

For He atom, $Z = 2$, $\boxed{E = -74.8\ eV}$

% Error ~ 5.5%

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-7, 13/09/2024)

DEGENERATE-STATE PERTURBATION THEORY

Need: A perturbation theory for energy states that are degenerate…

A two-fold degenerate system

Same unperturbed energy, $E^{(0)}$

Different unperturbed eigenfunctions, $\psi_a^{(0)}$, $\psi_b^{(0)}$

$$H^0\psi_a^{(0)} = E^{(0)}\psi_a^{(0)};\ H^0\psi_b^{(0)} = E^{(0)}\psi_b^{(0)}$$

Unperturbed functions are orthonormal,

$$\left\langle \psi_a^{(0)} \middle| \psi_b^{(0)} \right\rangle = \delta_{ab}$$

Define: an arbitrary linear combination of $\psi_a^{(0)}$, $\psi_b^{(0)}$

$$\psi^{(0)} = \alpha\psi_a^{(0)} + \beta\psi_b^{(0)}$$

$\psi^{(0)}$ is also an eigenfunction of H^0 with an eigenvalue $E^{(0)}$

Proof:

$$H^0\psi^{(0)} = H^0\left(\alpha\psi_a^{(0)} + \beta\psi_b^{(0)}\right) = H^0\left(\alpha\psi_a^{(0)}\right) + H^0\left(\beta\psi_b^{(0)}\right)$$

$$H^0\psi^{(0)} = \alpha\left(H^0\psi_a^{(0)}\right) + \beta\left(H^0\psi_b^{(0)}\right) = \alpha\left(E^{(0)}\psi_a^{(0)}\right) + \beta\left(E^{(0)}\psi_b^{(0)}\right)$$

$$H^0\psi^{(0)} = E^{(0)}\left(\alpha\psi_a^{(0)} + \beta\psi_b^{(0)}\right) = E^{(0)}\psi^{(0)}\ (\text{unperturbed problem})$$

Problem to solve: $H\psi = E\psi$; with the partitioning: $H = H^0 + H'(\lambda = 1)$

Taylor's series expansion: $(\lambda = 1)$

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \cdots;\ \psi = \psi^{(0)} + \psi^{(1)} + \psi^{(2)} + \cdots$$

$$(H^0 + H')\left(\psi^{(0)} + \psi^{(1)} + \psi^{(2)} + \cdots\right) = \left(E^{(0)} + E^{(1)} + E^{(2)} + \cdots\right)\left(\psi^{(0)} + \psi^{(1)} + \psi^{(2)} + \cdots\right)$$

Equating the coefficients of the like powers of λ

$$H^0\psi^{(0)} = E^{(0)}\psi^{(0)}(\text{unperturbed problem}):\ \text{coefficients of } \lambda^0$$

$$H^0\psi^{(1)} + H'\psi^{(0)} = E^{(0)}\psi^{(1)} + E^{(1)}\psi^{(0)};\ \text{coefficients of } \lambda^1$$

$$H^0\psi^{(1)} - E^{(0)}\psi^{(1)} = E^{(1)}\psi^{(0)} - H'\psi^{(0)}$$

Left multiplication by $\psi_a^{(0)*}$ (complex conjugate of one of the degenerate unperturbed functions) and integration over all space

$$\left\langle \psi_a^{(0)} \middle| H^0 \middle| \psi^{(1)} \right\rangle - E^{(0)}\left\langle \psi_a^{(0)} \middle| \psi^{(1)} \right\rangle = E^{(1)}\left\langle \psi_a^{(0)} \middle| \psi^{(0)} \right\rangle - \left\langle \psi_a^{(0)} \middle| H' \middle| \psi^{(0)} \right\rangle$$

Hermitian property of H^0

$$\left\langle \psi_a^{(0)} \middle| H^0 \middle| \psi^{(1)} \right\rangle = \left\langle \psi^{(1)} \middle| H^0 \middle| \psi_a^{(0)} \right\rangle^* = E^{(0)*}\left\langle \psi^{(1)} \middle| \psi_a^{(0)} \right\rangle^* = E^{(0)}\left\langle \psi_a^{(0)} \middle| \psi^{(1)} \right\rangle$$

$$\therefore 0 = E^{(1)}\left\langle \psi_a^{(0)} \middle| \psi^{(0)} \right\rangle - \left\langle \psi_a^{(0)} \middle| H' \middle| \psi^{(0)} \right\rangle$$

$$\text{or, } E^{(1)}\left\langle \psi_a^{(0)} \middle| \psi^{(0)} \right\rangle = \left\langle \psi_a^{(0)} \middle| H' \middle| \psi^{(0)} \right\rangle$$

Now, $\psi^{(0)} = \alpha\psi_a^{(0)} + \beta\psi_b^{(0)}$

$$E^{(1)}\left\langle \psi_a^{(0)} \middle| \alpha\psi_a^{(0)} + \beta\psi_b^{(0)} \right\rangle = \left\langle \psi_a^{(0)} \middle| H' \middle| \alpha\psi_a^{(0)} + \beta\psi_b^{(0)} \right\rangle$$

$$E^{(1)}\left\{\alpha\left\langle \psi_a^{(0)} \middle| \psi_a^{(0)} \right\rangle + \beta\left\langle \psi_a^{(0)} \middle| \psi_b^{(0)} \right\rangle\right\} = \alpha\left\langle \psi_a^{(0)} \middle| H' \middle| \psi_a^{(0)} \right\rangle + \beta\left\langle \psi_a^{(0)} \middle| H' \middle| \psi_b^{(0)} \right\rangle$$

$$\left\langle \psi_a^{(0)} \middle| \psi_a^{(0)} \right\rangle = 1;\ \left\langle \psi_a^{(0)} \middle| \psi_b^{(0)} \right\rangle = 0$$

$$\alpha E^{(1)} = \alpha\left\langle \psi_a^{(0)} \middle| H' \middle| \psi_a^{(0)} \right\rangle + \beta\left\langle \psi_a^{(0)} \middle| H' \middle| \psi_b^{(0)} \right\rangle = \alpha W_{aa} + \beta W_{ab}$$

where, $W_{ij} = \left\langle \psi_i^{(0)} \middle| H' \middle| \psi_j^{(0)} \right\rangle,\ (i, j = a, b)$

$$\alpha E^{(1)} = \alpha W_{aa} + \beta W_{ab}$$

We will use this equation very soon…

$$H^0\psi^{(1)} - E^{(0)}\psi^{(1)} = E^{(1)}\psi^{(0)} - H'\psi^{(0)}$$

Left multiplication by $\psi_b^{(0)*}$ (complex conjugate of the other degenerate unperturbed function) and integration over all space

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-7, 13/09/2024)

$$\left\langle \psi_b^{(0)} \middle| H^0 \middle| \psi^{(1)} \right\rangle - E^{(0)} \left\langle \psi_b^{(0)} \middle| \psi^{(1)} \right\rangle = E^{(1)} \left\langle \psi_b^{(0)} \middle| \psi^{(0)} \right\rangle - \left\langle \psi_b^{(0)} \middle| H' \middle| \psi^{(0)} \right\rangle$$

Hermitian property of H^0

$$\left\langle \psi_b^{(0)} \middle| H^0 \middle| \psi^{(1)} \right\rangle = \left\langle \psi^{(1)} \middle| H^0 \middle| \psi_b^{(0)} \right\rangle^* = E^{(0)*} \left\langle \psi^{(1)} \middle| \psi_b^{(0)} \right\rangle^* = E^{(0)} \left\langle \psi_b^{(0)} \middle| \psi^{(1)} \right\rangle$$

$$\therefore 0 = E^{(1)} \left\langle \psi_b^{(0)} \middle| \psi^{(0)} \right\rangle - \left\langle \psi_b^{(0)} \middle| H' \middle| \psi^{(0)} \right\rangle$$

$$\text{or, } E^{(1)} \left\langle \psi_b^{(0)} \middle| \psi^{(0)} \right\rangle = \left\langle \psi_b^{(0)} \middle| H' \middle| \psi^{(0)} \right\rangle$$

Now, $\psi^{(0)} = \alpha\psi_a^{(0)} + \beta\psi_b^{(0)}$

$$E^{(1)} \left\langle \psi_b^{(0)} \middle| \alpha\psi_a^{(0)} + \beta\psi_b^{(0)} \right\rangle = \left\langle \psi_b^{(0)} \middle| H' \middle| \alpha\psi_a^{(0)} + \beta\psi_b^{(0)} \right\rangle$$

$$E^{(1)} \left\{ \alpha \left\langle \psi_b^{(0)} \middle| \psi_a^{(0)} \right\rangle + \beta \left\langle \psi_b^{(0)} \middle| \psi_b^{(0)} \right\rangle \right\} = \alpha \left\langle \psi_b^{(0)} \middle| H' \middle| \psi_a^{(0)} \right\rangle + \beta \left\langle \psi_b^{(0)} \middle| H' \middle| \psi_b^{(0)} \right\rangle$$

$$\left\langle \psi_b^{(0)} \middle| \psi_a^{(0)} \right\rangle = 0; \left\langle \psi_b^{(0)} \middle| \psi_b^{(0)} \right\rangle = 1$$

$$\beta E^{(1)} = \alpha \left\langle \psi_b^{(0)} \middle| H' \middle| \psi_a^{(0)} \right\rangle + \beta \left\langle \psi_b^{(0)} \middle| H' \middle| \psi_b^{(0)} \right\rangle = \alpha W_{ba} + \beta W_{bb}$$

where, $W_{ij} = \left\langle \psi_i^{(0)} \middle| H' \middle| \psi_j^{(0)} \right\rangle$, $(i, j = a, b)$

$$\beta E^{(1)} = \alpha W_{ba} + \beta W_{bb}$$

$$\alpha E^{(1)} = \alpha W_{aa} + \beta W_{ab}$$

$$\beta W_{ab} = \alpha E^{(1)} - \alpha W_{aa}$$

$$\beta E^{(1)} = \alpha W_{ba} + \beta W_{bb}$$

$$\left(\beta E^{(1)} = \alpha W_{ba} + \beta W_{bb}\right) \times W_{ab}$$

$$E^{(1)} \beta W_{ab} = \alpha W_{ba} W_{ab} + \beta W_{ab} W_{bb}$$

$$E^{(1)} \left(\alpha E^{(1)} - \alpha W_{aa}\right) = \alpha W_{ba} W_{ab} + W_{bb} \left(\alpha E^{(1)} - \alpha W_{aa}\right)$$

$$\alpha \left(E^{(1)} - W_{aa}\right) \left(E^{(1)} - W_{bb}\right) = \alpha W_{ba} W_{ab}$$

If $\alpha \neq 0$, then

$$\left(E^{(1)} - W_{aa}\right) \left(E^{(1)} - W_{bb}\right) = W_{ba} W_{ab}$$

$$E^{(1)^2} - E^{(1)} (W_{aa} + W_{bb}) + (W_{aa} W_{bb} - W_{ab} W_{ba}) = 0$$

By definition, $W_{ba} = \left\langle \psi_b^{(0)} \middle| H' \middle| \psi_a^{(0)} \right\rangle = \left\langle \psi_a^{(0)} \middle| H' \middle| \psi_b^{(0)} \right\rangle^* = W_{ab}^*$

$$\therefore W_{ab} W_{ba} = W_{ab} W_{ab}^* = |W_{ab}|^2$$

$$E^{(1)^2} - E^{(1)} (W_{aa} + W_{bb}) + (W_{aa} W_{bb} - W_{ab} W_{ba}) = 0$$

$$E^{(1)^2} - (W_{aa} + W_{bb}) E^{(1)} + (W_{aa} W_{bb} - |W_{ab}|^2) = 0$$

$$E_{\pm}^{(1)} = \frac{(W_{aa} + W_{bb}) \pm \sqrt{(W_{aa} + W_{bb})^2 - 4(W_{aa} W_{bb} - |W_{ab}|^2)}}{2}$$

$$E_{\pm}^{(1)} = \frac{1}{2} \left[(W_{aa} + W_{bb}) \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right]$$

This is a fundamental result of the degenerate perturbation theory.

$$\alpha E^{(1)} = \alpha W_{aa} + \beta W_{ab}$$

$$\beta E^{(1)} = \alpha W_{ba} + \beta W_{bb}$$

The above is equivalent to

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^{(1)} \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

$E^{(1)}$ are the eigenvalues of the matrix

$$W = \begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix}$$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-13, 03/10/2024)

$$\left.\begin{aligned}\alpha E^{(1)} &= \alpha W_{aa} + \beta W_{ab}\\ \beta E^{(1)} &= \alpha W_{ba} + \beta W_{bb}\end{aligned}\right\} \quad E_{\pm}^{(1)} = \frac{1}{2}\left[(W_{aa}+W_{bb}) \pm \sqrt{(W_{aa}-W_{bb})^2 + 4|W_{ab}|^2}\right]$$

$$\psi^{(0)} = \alpha\psi_a^{(0)} + \beta\psi_b^{(0)}$$

For $\alpha=0, \beta=1 \Rightarrow W_{ab}=0$

$$E_-^{(1)} = \frac{1}{2}\left[(W_{aa}+W_{bb}) - \sqrt{(W_{aa}-W_{bb})^2+0}\right] = \frac{1}{2}\left[W_{aa}+W_{bb}-W_{aa}+W_{bb}\right] = W_{bb}$$

For $\alpha=1, \beta=0 \Rightarrow W_{ba}=0$

$$E_+^{(1)} = \frac{1}{2}\left[(W_{aa}+W_{bb}) + (W_{aa}-W_{bb})\right] = W_{aa}$$

$$E_-^{(1)} = W_{bb} = \langle\psi_b^{(0)}|V|\psi_b^{(0)}\rangle$$

$$E_+^{(1)} = W_{aa} = \langle\psi_a^{(0)}|V|\psi_a^{(0)}\rangle$$

"Good" linear combination

Say, A = a Hermitian Operator → real eigenvalues, orthonormal eigenfunctions

A commutes with $H_0 \Rightarrow [A, H_0] = 0$

A commutes with $V \Rightarrow [A, V] = 0$

} $\psi_a^{(0)}, \psi_b^{(0)}$: degenerate eigenfunctions of H_0

$A\psi_a^{(0)} = \mu\psi_a^{(0)}$, $A\psi_b^{(0)} = \nu\psi_b^{(0)}$, $\mu \neq \nu$

$\therefore W_{ab} = 0 \Rightarrow \psi_a^{(0)}, \psi_b^{(0)}$ are good states

$$\langle\psi_a^{(0)}|[A,V]|\psi_b^{(0)}\rangle = 0$$

$$\therefore \langle\psi_a^{(0)}|[A,V]|\psi_b^{(0)}\rangle = \langle\psi_a^{(0)}|AV-VA|\psi_b^{(0)}\rangle = \langle\psi_a^{(0)}|AV|\psi_b^{(0)}\rangle - \langle\psi_a^{(0)}|VA|\psi_b^{(0)}\rangle$$

$$= \langle A\psi_a^{(0)}|V|\psi_b^{(0)}\rangle - \nu\langle\psi_a^{(0)}|V|\psi_b^{(0)}\rangle = \mu\langle\psi_a^{(0)}|V|\psi_b^{(0)}\rangle - \nu\langle\psi_a^{(0)}|V|\psi_b^{(0)}\rangle$$

$$= (\mu-\nu)\langle\psi_a^{(0)}|V|\psi_b^{(0)}\rangle = (\mu-\nu)W_{ab}$$

$$\because \langle\psi_a^{(0)}|[A,V]|\psi_b^{(0)}\rangle = 0 \quad \Rightarrow (\mu-\nu)W_{ab} = 0$$

$$\because (\mu-\nu) \neq 0, \quad \boxed{W_{ab} = 0}$$

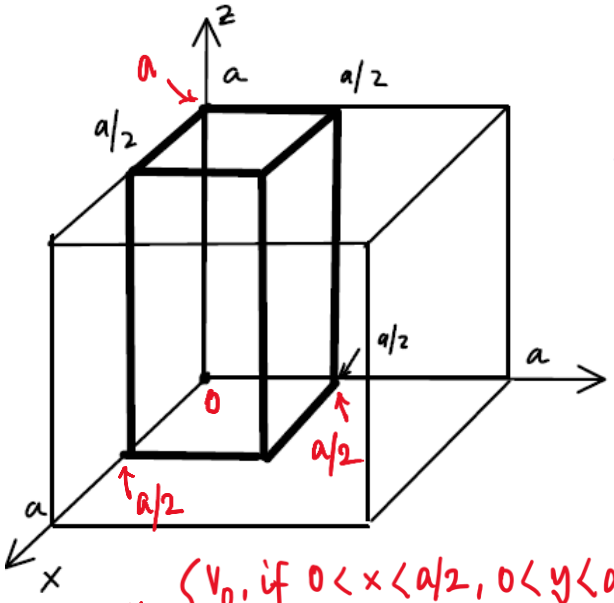
Particle in a 3D box (infinite square well)

$$V(x,y,z) = \begin{cases} 0, & \text{if } 0<x<a, 0<y<a, 0<z<a \\ \infty, & \text{elsewhere}\end{cases}$$

$$\psi^{(0)}_{n_x,n_y,n_z}(x,y,z) = \left(\frac{2}{a}\right)^{3/2}\sin\left(\frac{n_x\pi}{a}\right)x\sin\left(\frac{n_y\pi}{a}\right)y\sin\left(\frac{n_z\pi}{a}\right)z$$

$$E^{(0)}_{n_x,n_y,n_z} = \frac{\pi^2\hbar^2}{2ma^2}\left(n_x^2+n_y^2+n_z^2\right)$$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-13, 03/10/2024)



$E^{(0)}_{111} = 3\frac{\pi^2\hbar^2}{2ma^2} = E^{(0)}_0$, $\psi^{(0)}_{111}$: non-degenerate

First excited state : (112) (121) (211)

3-fold degenerate state

$E^{(0)}_{112} = E^{(0)}_{121} = E^{(0)}_{211} = 6\frac{\pi^2\hbar^2}{2ma^2} = E^{(0)}_1$

$\psi^{(0)}_{112}, \psi^{(0)}_{121}, \psi^{(0)}_{211}$

$$V = \begin{cases} V_0, \text{ if } 0<x<a/2,\ 0<y<a/2,\ 0<z<a \\ 0, \text{ elsewhere} \end{cases}$$

$$E^{(1)}_0 = \langle \psi^{(0)}_{111} | V | \psi^{(0)}_{111} \rangle = \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin^2\left(\frac{\pi}{a}\right)x\,dx \int_0^{a/2} \sin^2\left(\frac{\pi}{a}\right)y\,dy \int_0^{a} \sin^2\left(\frac{\pi}{a}\right)z\,dz$$

$$\int \sin^2(ax)\,dx = -\frac{1}{2a}\cos(ax)\sin(ax) + \frac{x}{2} + C$$

$$\therefore E^{(1)}_0 = \left(\frac{2}{a}\right)^3 V_0 \left(\frac{a/2}{2}\right)^2 \frac{a}{2} = \frac{V_0}{4}$$

For first excited state : $W = \begin{pmatrix} W_{aa} & W_{ab} & W_{ac} \\ W_{ba} & W_{bb} & W_{bc} \\ W_{ca} & W_{cb} & W_{cc} \end{pmatrix}_{3\times 3}$, $W_{ij} = \langle \psi^{(0)}_i | V | \psi^{(0)}_j \rangle$

$\psi^{(0)}_{112} = \psi^{(0)}_a$ $\quad W_{aa} = \langle \psi^{(0)}_a | V | \psi^{(0)}_a \rangle = \langle \psi^{(0)}_{112} | V | \psi^{(0)}_{112} \rangle$

$\psi^{(0)}_{121} = \psi^{(0)}_b$ or, $W_{aa} = \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin^2\left(\frac{\pi}{a}\right)x\,dx \int_0^{a/2} \sin^2\left(\frac{\pi}{a}\right)y\,dy \int_0^{a} \sin^2\left(\frac{2\pi}{a}\right)z\,dz$

$\psi^{(0)}_{211} = \psi^{(0)}_c$

or, $W_{aa} = \frac{V_0}{4}$

Applications to Simple Systems

$\alpha E^{(1)} = \alpha W_{aa} + \beta W_{ab}$. If $\alpha = 0, \beta = 1$, so that $W_{ab} = 0$.

$\beta E^{(1)} = \alpha W_{ba} + \beta W_{bb}$. $E^{(1)} = W_{bb}$.

$$E^{(1)}_{\pm} = \frac{1}{2}\left[(W_{aa} + W_{bb}) \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2}\right]$$

For $\alpha = 0, \beta = 1$, so that $W_{ab} = 0$. Consider the '–' sign...

$$E^{(1)}_{-} = \frac{1}{2}\left[(W_{aa} + W_{bb}) - \sqrt{(W_{aa} - W_{bb})^2 + 4 \times 0}\right]$$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-13, 03/10/2024)

$$E_{-}^{(1)} = \frac{1}{2}[(W_{aa} + W_{bb}) - (W_{aa} - W_{bb})] = W_{bb}$$

Similarly, $\alpha = 1, \beta = 0$, we will have $W_{ba} = 0$, and $E^{(1)} = W_{aa}$.

$$E_{+}^{(1)} = \frac{1}{2}[(W_{aa} + W_{bb}) + (W_{aa} - W_{bb})] = W_{aa}$$

$$E_{+}^{(1)} = W_{aa} = \left\langle \psi_a^{(0)} \middle| H' \middle| \psi_a^{(0)} \right\rangle$$

$$E_{-}^{(1)} = W_{bb} = \left\langle \psi_b^{(0)} \middle| H' \middle| \psi_b^{(0)} \right\rangle$$

This result can be obtained using the non-degenerate perturbation theory. We are lucky! The states $\psi_a^{(0)}$ and $\psi_b^{(0)}$ were already the "good" linear combinations. Obviously, it would be greatly to our advantage if we could somehow guess the "good" states right from the start – then we could go ahead and use non-degenerate perturbation theory.

An important theorem: Let A be a Hermitian operator that commutes with both H^0 and H'. If $\psi_a^{(0)}$ and $\psi_b^{(0)}$(the degenerate eigenfunctions of H^0) are also eigenfunctions of A, with distinct eigenvalues, $A\psi_a^{(0)} = \mu\psi_a^{(0)}$ and $A\psi_b^{(0)} = \nu\psi_b^{(0)}$, and $\mu \neq \nu$, then $W_{ab} = 0$ (and hence $\psi_a^{(0)}$ and $\psi_b^{(0)}$ are the "good" states to use in perturbation theory.

Proof: By assumption, as the Hermitian operator A commutes with both H^0 and H', $[A, H'] = 0$. Therefore, $\left\langle \psi_a^{(0)} \middle| [A, H'] \middle| \psi_b^{(0)} \right\rangle = 0$. Now,

$$\left\langle \psi_a^{(0)} \middle| [A, H'] \middle| \psi_b^{(0)} \right\rangle = \left\langle \psi_a^{(0)} \middle| AH' - H'A \middle| \psi_b^{(0)} \right\rangle = \left\langle \psi_a^{(0)} \middle| AH' \middle| \psi_b^{(0)} \right\rangle - \left\langle \psi_a^{(0)} \middle| H'A \middle| \psi_b^{(0)} \right\rangle$$

$$= \left\langle A\psi_a^{(0)} \middle| H' \middle| \psi_b^{(0)} \right\rangle - \nu \left\langle \psi_a^{(0)} \middle| H' \middle| \psi_b^{(0)} \right\rangle = (\mu - \nu) \left\langle \psi_a^{(0)} \middle| H' \middle| \psi_b^{(0)} \right\rangle = (\mu - \nu) W_{ab}$$

$\because \mu \neq \nu, W_{ab} = 0.$

Moral: If we encounter degenerate states, we should look around (that is, search for) some Hermitian operator A that commutes with both H^0 and H'; we pick as our unperturbed states ones that are simultaneously eigenfunctions of H^0 and A; then we use the ordinary (non-degenerate) first-order perturbation theory.

What if we do not find some Hermitian operator A that commutes with both H^0 and H'?

Degenerate perturbation on a three-dimensional infinite cubical well:

$$V(x, y, z) = \begin{cases} 0, & \text{if } 0 < x < a,\ 0 < y < a,\ 0 < z < a \\ \infty, & \text{elsewhere} \end{cases}$$

The stationary states are (here, the unperturbed ones):

$$\psi_{n_x,n_y,n_z}^{(0)}(x, y, z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{\pi n_x}{a}x\right) \sin\left(\frac{\pi n_y}{a}y\right) \sin\left(\frac{\pi n_z}{a}z\right)$$

n_x, n_y, n_z are positive integers (excluding zero); the energies are given by

$$E_{n_x,n_y,n_z}^{(0)} = \frac{\pi^2\hbar^2}{2ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

What are energies of the ground and the first excited states? Are these states degenerate? If so, what are the degeneracies? The ground state $(n_x = n_y = n_z = 1)$ is non-degenerate: $\psi_{111}^{(0)}$

$$E_{111}^{(0)} = 3\frac{\pi^2\hbar^2}{2ma^2} = E_0^{(0)}$$

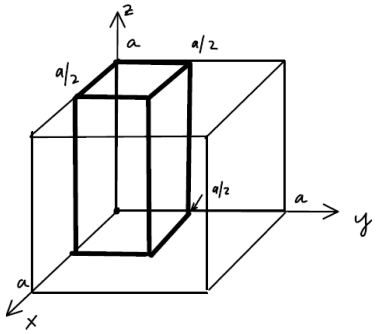
The next state is the first excited state and is triply degenerate: (n_x, n_y, n_z): (112), (121), (211); the eigenfunctions are: $\psi_{112}^{(0)}, \psi_{121}^{(0)}, \psi_{211}^{(0)}$

$$E_{112}^{(0)} = E_{121}^{(0)} = E_{211}^{(0)} = 6\frac{\pi^2\hbar^2}{2ma^2} = E_1^{(0)}$$

We introduce a perturbation, H'

$$H' = \begin{cases} V_0, & \text{if } 0 < x < a/2\,,\ 0 < y < a/2\,,\ 0 < z < a \\ 0, & \text{elsewhere} \end{cases}$$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-13, 03/10/2024)



What is the first-order correction to the ground state energy, $E_0^{(0)}$? Note that:

$$\int \sin^2(ax)dx = -\frac{1}{2a}\cos(ax)\sin(ax) + \frac{x}{2}$$

The first-order correction to $E_0^{(0)}$:

$$E_0^{(1)} = \left\langle \psi_{111}^{(0)} \middle| H' \middle| \psi_{111}^{(0)} \right\rangle = \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin^2\left(\frac{\pi}{a}x\right)dx \int_0^{a/2} \sin^2\left(\frac{\pi}{a}y\right)dy \int_0^{a} \sin^2\left(\frac{\pi}{a}z\right)dz$$

$$\therefore E_0^{(1)} = \left(\frac{2}{a}\right)^3 V_0 \left(\frac{a/2}{2}\right)^2 \frac{a}{2} = \frac{V_0}{4}$$

Our next mission is to calculate the first-order correction to the energy of the first excited state. Here, the states are degenerate and we need to use degenerate perturbation theory, i.e. we need to calculate all elements of the 3×3 matrix

$$W_{ij} = \left\langle \psi_i^{(0)} \middle| H' \middle| \psi_j^{(0)} \right\rangle$$

$$W = \begin{pmatrix} W_{aa} & W_{ab} & W_{ac} \\ W_{ba} & W_{bb} & W_{bc} \\ W_{ca} & W_{cb} & W_{cc} \end{pmatrix}$$

$$\psi_{112}^{(0)} = \psi_a^{(0)}; \psi_{121}^{(0)} = \psi_b^{(0)}; \psi_{211}^{(0)} = \psi_c^{(0)}$$

Now, let us calculate all the matrix elements. Note that:

$$\int \sin^2(ax)dx = -\frac{1}{2a}\cos(ax)\sin(ax) + \frac{x}{2}$$

$$\int \sin(b_1x)\sin(b_2x)\,dx = \frac{\sin[(b_1-b_2)x]}{2(b_1-b_2)} - \frac{\sin[(b_1+b_2)x]}{2(b_1+b_2)}, \text{ for } |b_1| \neq |b_2|$$

Evaluation of the matrix elements:

$$W_{aa} = \left\langle \psi_a^{(0)} \middle| H' \middle| \psi_a^{(0)} \right\rangle = \left\langle \psi_{112}^{(0)} \middle| H' \middle| \psi_{112}^{(0)} \right\rangle$$

$$= \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin^2\left(\frac{\pi x}{a}\right)dx \int_0^{a/2} \sin^2\left(\frac{\pi y}{a}\right)dy \int_0^{a} \sin^2\left(\frac{2\pi z}{a}\right)dz = \left(\frac{2}{a}\right)^3 V_0 \left(\frac{a/2}{2}\right)^2 \frac{a}{2}$$

$$\therefore W_{aa} = \frac{V_0}{4}$$

Similarly, $W_{bb} = W_{cc} = V_0/4 = W_{aa}$ (same as the ground state).

$$W_{ab} = \left\langle \psi_a^{(0)} \middle| H' \middle| \psi_b^{(0)} \right\rangle = \left\langle \psi_{112}^{(0)} \middle| H' \middle| \psi_{121}^{(0)} \right\rangle$$

$$= \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin^2\left(\frac{\pi x}{a}\right)dx \int_0^{a/2} \sin\left(\frac{\pi y}{a}\right)\sin\left(\frac{2\pi y}{a}\right)dy \int_0^{a} \sin\left(\frac{2\pi z}{a}\right)\sin\left(\frac{\pi z}{a}\right)dz$$

$$\int_0^{a/2} \sin\left(\frac{\pi y}{a}\right)\sin\left(\frac{2\pi y}{a}\right)dy = \left[\frac{\sin(-\pi y/a)}{2(-\pi/a)} - \frac{\sin(3\pi y/a)}{2\times 3\pi/a}\right]^{a/2} = a\frac{\sin(\pi/2)}{2\pi} - \frac{a}{6\pi}\sin\left(\frac{3\pi}{2}\right) = \frac{a}{2\pi} + \frac{a}{6\pi}$$

$$= \frac{2a}{3\pi}$$

$$\int \sin(b_1x)\sin(b_2x)\,dx = \frac{\sin[(b_1-b_2)x]}{2(b_1-b_2)} - \frac{\sin[(b_1+b_2)x]}{2(b_1+b_2)}, \text{ for } |b_1| \neq |b_2|$$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-13, 03/10/2024)

$$b_1 = \frac{\pi}{a}, b_2 = \frac{2\pi}{a}; \int_0^a \sin\left(\frac{2\pi z}{a}\right)\sin\left(\frac{\pi z}{a}\right)dz = 0,$$

since we will get $\sin\pi$ and $\sin 3\pi$.

$$W_{ab} = \left\langle \psi_a^{(0)} \middle| H' \middle| \psi_b^{(0)} \right\rangle = \left\langle \psi_{112}^{(0)} \middle| H' \middle| \psi_{121}^{(0)} \right\rangle = 0$$

$$W_{ab} = \left\langle \psi_a^{(0)} \middle| H' \middle| \psi_b^{(0)} \right\rangle = \left\langle \psi_{112}^{(0)} \middle| H' \middle| \psi_{121}^{(0)} \right\rangle = \left\langle \psi_{121}^{(0)} \middle| H' \middle| \psi_{112}^{(0)} \right\rangle = W_{ba} = 0$$

$W_{ac} = \left\langle \psi_a^{(0)} \middle| H' \middle| \psi_c^{(0)} \right\rangle = \left\langle \psi_{112}^{(0)} \middle| H' \middle| \psi_{211}^{(0)} \right\rangle = \left\langle \psi_{211}^{(0)} \middle| H' \middle| \psi_{112}^{(0)} \right\rangle = W_{ca} = 0$, since we get the same z dependent integral as in W_{ab}.

$$W_{bc} = \left\langle \psi_b^{(0)} \middle| H' \middle| \psi_c^{(0)} \right\rangle = \left\langle \psi_{121}^{(0)} \middle| H' \middle| \psi_{211}^{(0)} \right\rangle$$

$$= \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi x}{a}\right)dx \int_0^{a/2} \sin\left(\frac{2\pi y}{a}\right)\sin\left(\frac{\pi y}{a}\right)dy \int_0^a \sin^2\left(\frac{\pi z}{a}\right)dz$$

$$\therefore W_{bc} = \left(\frac{2}{a}\right)^3 V_0 \frac{a}{3\pi}\frac{a}{3\pi}\frac{a}{2} = \frac{4}{9\pi^2}V_0 = W_{cb}$$

$$W = \begin{pmatrix} W_{aa} & W_{ab} & W_{ac} \\ W_{ba} & W_{bb} & W_{bc} \\ W_{ca} & W_{cb} & W_{cc} \end{pmatrix} = \begin{pmatrix} V_0/4 & 0 & 0 \\ 0 & V_0/4 & 16V_0/9\pi^2 \\ 0 & 16V_0/9\pi^2 & V_0/4 \end{pmatrix}$$

$$\therefore W = \frac{V_0}{4}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & (8/3\pi)^2 \\ 0 & (8/3\pi)^2 & 1 \end{pmatrix} = \frac{V_0}{4}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & \kappa \\ 0 & \kappa & 1 \end{pmatrix}; \kappa = (8/3\pi)^2 = 0.7205$$

$$\therefore W = \frac{V_0}{4}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & \kappa \\ 0 & \kappa & 1 \end{pmatrix}; \kappa = (8/3\pi)^2 = 0.7205 \Rightarrow \frac{4W}{V_0} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & \kappa \\ 0 & \kappa & 1 \end{pmatrix}$$

Therefore, the characteristic equation for $4W/V_0$ will be:

$$\begin{vmatrix} 1-W & 0 & 0 \\ 0 & 1-W & \kappa \\ 0 & \kappa & 1-W \end{vmatrix} = 0$$

$$\Rightarrow (1-W)[(1-W)^2 - \kappa^2] = 0$$

$$\text{or, } (1-W)(1-W-\kappa)(1-W+\kappa) = 0$$

$$W_1 = 1$$

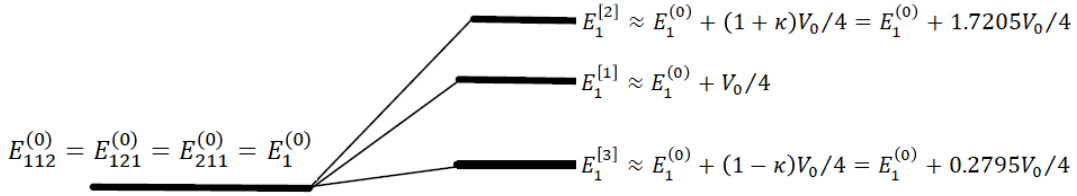
$$W_2 = 1 + \kappa = 1.7205$$

$$W_3 = 1 - \kappa = 0.2795$$

$$E_{112}^{(0)} = E_{121}^{(0)} = E_{211}^{(0)} = 6\frac{\pi^2\hbar^2}{2ma^2} = E_1^{(0)}$$

$$E_1 \approx E_1^{(0)} + W_i V_0/4,\ i = 1,\ 2,\ 3$$

$E_1^{[1]} \approx E_1^{(0)} + V_0/4$; $E_1^{[2]} \approx E_1^{(0)} + (1+\kappa)V_0/4$; $E_1^{[3]} \approx E_1^{(0)} + (1-\kappa)V_0/4$



"Good" unperturbed states are linear combination of the form

$$\psi^{(0)} = \alpha\psi_a^{(0)} + \beta\psi_b^{(0)} + \gamma\psi_c^{(0)}$$

The coefficients α, β and γ are eigenvectors of W

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & \kappa \\ 0 & \kappa & 1 \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = W\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$$

Let us now determine the eigenvectors corresponding to W_1, W_2 and W_3

For the root $W_1 = 1$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-13, 03/10/2024)

$$\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & \kappa\\ 0 & \kappa & 1\end{pmatrix}\begin{pmatrix}\alpha\\ \beta\\ \gamma\end{pmatrix} = W_1\begin{pmatrix}\alpha\\ \beta\\ \gamma\end{pmatrix} = 1\begin{pmatrix}\alpha\\ \beta\\ \gamma\end{pmatrix} \Rightarrow \begin{pmatrix}\alpha\\ \beta+\kappa\gamma\\ \kappa\beta+\gamma\end{pmatrix} = \begin{pmatrix}\alpha\\ \beta\\ \gamma\end{pmatrix}$$

$$\therefore \alpha = 1,\ \beta = \gamma = 0$$

$$\therefore \psi_1^{(0)} = \psi_a^{(0)}$$

For the root $W_2 = 1 + \kappa$

$$\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & \kappa\\ 0 & \kappa & 1\end{pmatrix}\begin{pmatrix}\alpha\\ \beta\\ \gamma\end{pmatrix} = W_2\begin{pmatrix}\alpha\\ \beta\\ \gamma\end{pmatrix} = (1+\kappa)\begin{pmatrix}\alpha\\ \beta\\ \gamma\end{pmatrix} \Rightarrow \begin{pmatrix}\alpha\\ \beta+\kappa\gamma\\ \kappa\beta+\gamma\end{pmatrix} = (1+\kappa)\begin{pmatrix}\alpha\\ \beta\\ \gamma\end{pmatrix}$$

$$\therefore \alpha = 0,\ \beta = \gamma = 1/\sqrt{2}$$

$$\therefore \psi_2^{(0)} = \frac{1}{\sqrt{2}}\left(\psi_b^{(0)} + \psi_c^{(0)}\right)$$

For the root $W_3 = 1 - \kappa$

$$\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & \kappa\\ 0 & \kappa & 1\end{pmatrix}\begin{pmatrix}\alpha\\ \beta\\ \gamma\end{pmatrix} = W_3\begin{pmatrix}\alpha\\ \beta\\ \gamma\end{pmatrix} = (1-\kappa)\begin{pmatrix}\alpha\\ \beta\\ \gamma\end{pmatrix} \Rightarrow \begin{pmatrix}\alpha\\ \beta+\kappa\gamma\\ \kappa\beta+\gamma\end{pmatrix} = (1-\kappa)\begin{pmatrix}\alpha\\ \beta\\ \gamma\end{pmatrix}$$

$$\therefore \alpha = 0,\ \beta = -\gamma$$

$$\therefore \psi_3^{(0)} = \frac{1}{\sqrt{2}}\left(\psi_b^{(0)} - \psi_c^{(0)}\right)$$

If we apply non-degenerate perturbation theory to these three states, we will get correct results. We will not get correct results if we apply non-degenerate perturbation theory to original unperturbed states $\psi_a^{(0)}, \psi_b^{(0)}$ and $\psi_c^{(0)}$.