Approximation methods for stationary states

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chapter 9:

There are many problems in QM that can not be solved exactly. Exact solutions of schrodinger equation exist only for few idealized systems. To solve general problems, one must go to approximation methods. In this chapter we study three approximation methods for stationary states; the perturbation theory, the variational method, and WKB method. (if time permits)

- (1) Perturbation theory: This theory is based on the assumption that the problem we wish to solve is slightly different from a problem that can be solved exactly. the total Hamiltonian can be reduced to an exactly solvable part H_0, plus a small correction λH_1; where $\lambda H_1 << H_0$

$\Rightarrow H = H_0 + \lambda H_1$; λ is a dimensionless quantity that determines the strength of the perturbation

it is called perturbation for its effect on the energy spectrum and eigen functions will be small. in what follows, we are going to consider two separte cases depending on wether the exact solution of H_0 are non degenerate or degenerate.

(a) Non-degenerate Perturbation theory:

Here we limit our study to the case where H_0 has no degenerate eigenvalues

$\therefore$ $\hat{H}_0 |\phi_n\rangle = E_n^{(0)} |\phi_n\rangle$ where $|\phi_n\rangle$ form a complete orthonormal set with $\langle \phi_m | \phi_n \rangle = \delta_{mn}$ ---- (1)

in the presence of Perturbation, our eigenvalue problem reads

$$\hat{H} |\psi_n\rangle = E_n |\psi_n\rangle$$

$$(\hat{H}_0 + \lambda \hat{H}_1) |\psi_n\rangle = E_n |\psi_n\rangle \quad \text{------} \quad (2)$$

Now Recall that we are dealing with very small perturbation where E_n is very close $E_n^{(0)}$ and $|\psi_n\rangle$ is very close to $|\phi_n\rangle$, so both E_n and $|\psi_n\rangle$ can be expanded in a power series in the parameter λ

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \text{----} \quad \text{----} \quad (3)$$

$$|\psi_n\rangle = |\phi_n\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \text{---}$$

See that if $\lambda = 0$ $\Rightarrow$ we recover the unperturbed system

$E_n = E_n^{(0)}$ and $|\psi_n\rangle = |\phi_n\rangle$

in general and when λ is small, the first few terms in the above expansions provide a reliable description of the system. in this chapter, we will be concerned with finding $E_n^{(1)}$, $E_n^{(2)}$, and $|\psi_n^{(1)}\rangle$.

Notice that $E_n^{(k)}$ represents the kth order correction to the eigenvalue $E_n^{(0)}$

$|\psi_n^{(k)}\rangle$ " " " " " the eigenfunctions $|\phi_n\rangle$

Now substitute (3) in (2)

$$(H_0 + \lambda H_1)\left(|\phi_n\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \cdots\right) \quad \text{---- (3-1)}$$

$$= \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots\right)\left(|\phi_n\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \cdots\right)$$

now equating the coefficients of matching powers of λ on both sides gives the zeroth, the first, and the second corrections to $E_n^{(0)}$ and to $|\phi_n\rangle$

i) Zeroth order of λ: $\hat{H}_0|\phi_n\rangle = E_n^{(0)}|\phi_n\rangle$

ii) first order of λ:

$$\hat{H}_0|\psi_n^{(1)}\rangle + \hat{H}_1|\phi_n\rangle = E_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}|\phi_n\rangle$$

multiply by $\langle\phi_m|$

$$\langle\phi_m|H_0|\psi_n^{(1)}\rangle + \langle\phi_m|H_1|\phi_n\rangle = E_n^{(0)}\langle\phi_m|\psi_n^{(1)}\rangle + E_n^{(1)}\underbrace{\langle\phi_m|\phi_n\rangle}_{\delta_{mn}} \quad \text{---- (4)}$$

now need to find how $|\phi_n\rangle$ and $|\psi_n^{(1)}\rangle$ overlap. since $|\psi_n\rangle$ is considered not very different from $|\phi_n\rangle$, then

$\langle\phi_n|\psi_n\rangle \simeq 1$

in fact $|\psi_n\rangle$ can be normalized so that

$$\langle\phi_n|\psi_n\rangle = 1 \quad \text{--- (5)}$$

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

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

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

but $\lambda \neq 0 \Rightarrow \langle\phi_n|\psi_n^{(1)}\rangle = \langle\phi_n|\psi_n^{(2)}\rangle = \cdots = 0$

Coming back to equation (4), we have two cases

Case 1: if $m = n$

$$\langle \phi_n | \cancelto{0}{H_0 | \psi_n^{(1)}} \rangle + \langle \phi_n | H_1 | \phi_n \rangle = E_n^{(0)} \cancelto{0}{\langle \phi_n | \psi_n^{(1)} \rangle} + E_n^{(1)} \underbrace{\langle \phi_n | \phi_n \rangle}_{1}$$

$\Downarrow$

H_0 is hermitian $\Rightarrow$ $H_0 |\phi_n\rangle = E_n^{(0)} |\phi_n\rangle$

$$\langle \phi_n | H_0 = E_n^{(0)} \langle \phi_n |$$

$$\Rightarrow \langle \phi_n | H_0 | \psi_n^{(1)} \rangle = E_n^{(0)} \cancelto{0}{\langle \phi_n | \psi_n^{(1)} \rangle} = 0$$

$$\Rightarrow E_n^{(1)} = \langle \phi_n | H_1 | \phi_n \rangle \quad \text{---- (5)}$$

so the energy to first order correction $E_n = E_n^{(0)} + \lambda E_n^{(1)}$

$$E_n = E_n^{(0)} + \lambda \langle \phi_n | H_1 | \phi_n \rangle = E_n^{(0)} + \langle \phi_n | \lambda H_1 | \phi_n \rangle$$

$$= E_n^{(0)} + \langle \phi_n | H' | \phi_n \rangle$$

where $H' = \lambda H_1$

Case 2: if $m \neq n$

$$E_m^{(0)} \langle \phi_m | \psi_n^{(1)} \rangle + \langle \phi_m | H_1 | \phi_n \rangle = E_n^{(0)} \langle \phi_m | \psi_n^{(1)} \rangle \; ; \quad m \neq n$$

$$\left(E_n^{(0)} - E_m^{(0)} \right) \langle \phi_m | \psi_n^{(1)} \rangle = \langle \phi_m | H_1 | \phi_n \rangle$$

$$\Rightarrow \langle \phi_m | \psi_n^{(1)} \rangle = \frac{\langle \phi_m | H_1 | \phi_n \rangle}{E_n^{(0)} - E_m^{(0)}} = \frac{(H_1)_{mn}}{E_n^{(0)} - E_m^{(0)}} \quad \text{--- (6)}$$

Now how this can help ?!

$|\psi_n^{(1)}\rangle$ can be expanded in terms of $|\phi_n\rangle$ basis

$$|\psi_n^{(1)}\rangle = \left(\sum_m |\phi_m\rangle\langle\phi_m|\right)|\psi_n^{(1)}\rangle = \sum_{m\neq n} \underbrace{\langle\phi_m|\psi_n^{(1)}\rangle}\,|\phi_m\rangle$$

the term $m=n$ does not contribute as $\langle\phi_n|\psi_n^{(1)}\rangle = 0$

$$\Rightarrow |\psi_n^{(1)}\rangle = \sum_{m\neq n} \frac{(H_1)_{mn}}{E_n^{(0)} - E_m^{(0)}} |\phi_m\rangle \quad \text{---} \quad (6\text{-}A)$$

the eigenfunction $|\psi_n\rangle$ of $\hat{H}$ to first order is

$$|\psi_n\rangle = |\phi_n\rangle + \sum_{m\neq n} \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} |\phi_m\rangle \; ; \; H'_{mn} = \lambda (H_1)_{mn}$$

Notice that $|\psi_n^{(1)}\rangle$ is valid as long as the H_0 spectrum is not degenerate i.e $E_n^{(0)} \neq E_m^{(0)}$

(iii) Second order in λ

Now equating the coefficient of λ^2 on both sides of equation (3-1) yields

$$\hat{H}_0|\psi_n^{(2)}\rangle + H_1|\psi_n^{(1)}\rangle = E_n^{(0)}|\psi_n^{(2)}\rangle + E_n^{(1)}|\psi_n^{(1)}\rangle + E_n^{(2)}|\phi_n\rangle$$

multiply by $\langle\phi_m|$

$$\langle\phi_m|\hat{H}_0|\psi_n^{(2)}\rangle + \langle\phi_m|H_1|\psi_n^{(1)}\rangle = E_n^{(0)}\langle\phi_m|\psi_n^{(2)}\rangle + E_n^{(1)}\langle\phi_m|\psi_n^{(1)}\rangle + E_n^{(2)}\langle\phi_m|\phi_n\rangle$$

now if $m=n$

$$\langle\phi_n|\hat{H}_0|\psi_n^{(2)}\rangle + \langle\phi_n|H_1|\psi_n^{(1)}\rangle = E_n^{(0)}\cancel{\langle\phi_n|\psi_n^{(2)}\rangle}^{\to 0} + E_n^{(1)}\cancel{\langle\phi_n|\psi_n^{(1)}\rangle}^{\to 0} + E_n^{(2)}\underbrace{\langle\phi_n|\phi_n\rangle}_{1}$$

$$\Downarrow$$

$$E_n^{(0)}\cancel{\langle\phi_n|\psi_n^{(2)}\rangle}^{\to 0}$$

$\therefore \; E_n^{(2)} = \langle \phi_n | H_1 | \psi_n^{(1)} \rangle$

but we found that $|\psi_n^{(1)}\rangle = \sum_{m \neq n} \dfrac{\langle \phi_m | H_1 | \phi_n \rangle}{E_n^{(0)} - E_m^{(0)}} |\phi_m\rangle$

$$\Rightarrow E_n^{(2)} = \sum_{m \neq n} \frac{\langle \phi_n | H_1 | \phi_m \rangle \langle \phi_m | H_1 | \phi_n \rangle}{E_n^{(0)} - E_m^{(0)}}$$

$$= \sum_{m \neq n} \frac{\langle \phi_m | H_1 | \phi_n \rangle^{*} \langle \phi_m | H_1 | \phi_n \rangle}{E_n^{(0)} - E_m^{(0)}}$$

$$= \sum_{m \neq n} \frac{|\langle \phi_m | H_1 | \phi_n \rangle|^2}{E_n^{(0)} - E_m^{(0)}} \qquad (6\text{-}B)$$

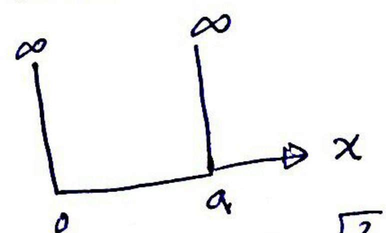
so the energy to 2nd order is $E_n = E_n^{0} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)}$

$$E_n = E_n^{(0)} + \langle \phi_n | H' | \phi_n \rangle + \sum_{m \neq n} \frac{|\langle \phi_m | H' | \phi_n \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

or shortly

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

<u>Ex:</u> infinite square well



$$\phi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right)$$

$$E_n^{(0)} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

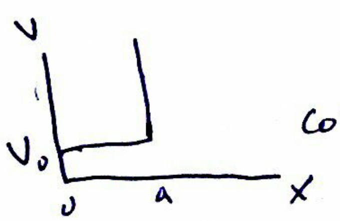
$\phi_n(x) = \sqrt{\frac{2}{a}} \sin kx$

$\Rightarrow \sin(ka) = 0, \quad ka = n\pi$

$k = \frac{n\pi}{a}$

$E = \frac{\hbar^2 k^2}{2m}$

i) let $H' = V_0$



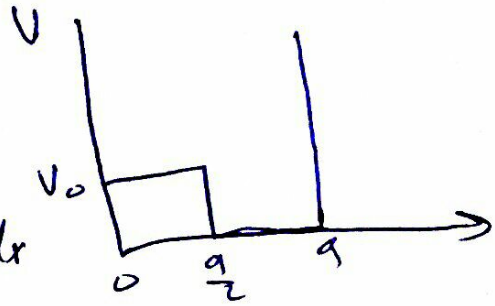
constant Perturbation

$$E_n^{(1)} = \langle \phi_n | H' | \phi_n \rangle = \langle \phi_n | V_0 | \phi_n \rangle = V_0 \langle \phi_n | \phi_n \rangle = V_0$$

constant

$\Rightarrow E_n \approx E_n^{(0)} + V_0$ in this case it is exact answer

(ii) let $H' = \begin{cases} V_0, & 0<x<a/2 \\ 0, & \frac{a}{2}<x<a \end{cases}$



$$E_n^{(1)} = \langle \phi_n | H' | \phi_n \rangle = \frac{2}{a}\int_0^{a/2} V_0 \sin^2\left(\frac{n\pi}{a}x\right) dx$$

$= \frac{V_0}{2}$; using $\int \sin^2(ax)\,dx = -\frac{1}{2a}\cos(ax)\sin(ax) + \frac{x}{2}$

$\Rightarrow E_n \approx E_n^{(0)} + \frac{V_0}{2}$

Remark: for a constant perturbation, like the above example, only $E_n^{(1)}$ survive and the higher order energy corrections vanish i.e $E_n^{(2)} = E_n^{(3)} = \dots = 0$. This hold for any constant perturbation, Recall that

$$E_n^{(2)} = \sum_{n\neq m} \frac{|\langle \phi_m | H' | \phi_n \rangle|^2}{E_n^{(0)} - E_m^{(0)}} \text{ ; }$$ if H' is constant $= V_0$

$$= V_0^2 \sum_{n\neq m} \frac{|\cancelto{0}{\langle \phi_m | \phi_n \rangle}|^2}{E_n^{(0)} - E_m^{(0)}}$$ as ϕ_m, ϕ_n orthogonal

in addition, there are no corrections to the wave functions for a constant perturbation, for example

$$|\psi_n^{(1)}\rangle = \sum_{m\neq n} \frac{\langle \phi_m | H' | \phi_n \rangle}{E_n^{(0)} - E_m^{(0)}} |\phi_m\rangle$$; $H' = V_0$

$$= V_0 \sum_{m\neq n} \frac{\cancelto{0}{\langle \phi_m | \phi_n \rangle}}{E_n^{(0)} - E_m^{(0)}} |\phi_m\rangle = 0$$

same for higher orders $\Rightarrow |\psi_n\rangle = |\phi_n\rangle$

Example 11-1: consider a charged particle in a S.H.O for which $H_0 = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2$ subject to a constant electric field so that $H_1 = qEX$:

a) Find the exact expression for the energy

$$H = H_0 + H_1 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2} m\omega^2 x^2 + qEX$$

we can do this part without using perturbation theory. changing variables $y = x + \frac{qE}{m\omega^2}$ leads to

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dy^2} + \frac{1}{2} m\omega^2 y^2 - \frac{q^2E^2}{2m\omega^2}$$

this is again S.H.O from which a constant $\frac{q^2E^2}{2m\omega^2}$ is subtracted

$$\Rightarrow E_n = (n+\tfrac{1}{2})\hbar\omega - \frac{q^2E^2}{2m\omega^2} \quad , \text{when } E_n^{(0)} = \cancel{(n+\tfrac{1}{2})} (n+\tfrac{1}{2})\hbar\omega$$

b) Calculate the energy to first non zero correction and compare it with result of a)

$$H_1 = qEX \quad ; \quad E_n^{(1)} = \langle n|H_1|n\rangle = qE\langle n|X|n\rangle = 0$$

this can be shown from $\hat{X} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{A} + \hat{A}^\dagger)$

with $A|n\rangle = \sqrt{n}\,|n-1\rangle \quad \Rightarrow \quad \langle n|A|n\rangle = \sqrt{n}\,\delta_{n,n-1} = 0$

$A^\dagger|n\rangle = \sqrt{n+1}\,|n+1\rangle \qquad \langle n|A^\dagger|n\rangle = \sqrt{n+1}\,\delta_{n,n+1} = 0$

Now to second order

$$E_n^{(2)} = \sum_{m\neq n} \frac{|\langle m|H_1|n\rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

the only contribution comes from $m = n-1$ and $m = n+1$

$$= q^2E^2\left[\frac{|\langle n-1|X|n\rangle|^2}{E_n^{(0)} - E_{n-1}^{(0)}} + \frac{|\langle n+1|X|n\rangle|^2}{E_n^{(0)} - E_{n+1}^{(0)}}\right].$$

Now using $E_n^{(0)} = (n+1/2)\hbar\omega$

$$\Rightarrow E_n^{(0)} - E_{n+1}^{(0)} = -\hbar\omega \quad \text{and} \quad E_n^{(0)} - E_{n-1}^{(0)} = \hbar\omega$$

Now need to find $\langle n-1|x|n\rangle$ and $\langle n+1|x|n\rangle$

starting from $x = \sqrt{\frac{\hbar}{2m\omega}}(A + A^{+})$

$$x|n\rangle = \sqrt{\frac{\hbar}{2m\omega}}\left[A|n\rangle + A^{+}|n\rangle\right]$$

$$= \sqrt{\frac{\hbar}{2m\omega}}\left[\sqrt{n}\,|n-1\rangle + \sqrt{n+1}\,|n+1\rangle\right]$$

now $\langle n-1|x|n\rangle = \sqrt{\frac{\hbar}{2m\omega}}\sqrt{n}$ and similarly $\langle n+1|x|n\rangle = \sqrt{\frac{\hbar}{2m\omega}}\sqrt{n+1}$

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

same as a)

$$\text{now } |\psi_n\rangle = |n\rangle + \sum_{m \neq n} \frac{\langle m|H_1|n\rangle}{E_n^{(0)} - E_m^{(0)}}|m\rangle$$

Again taking $m = n-1$ and $m = n+1$ as only contributions

$$|\psi_n\rangle = |n\rangle + \left[\frac{\langle n-1|H_1|n\rangle}{E_n^{(0)} - E_{n-1}^{(0)}}|n-1\rangle + \frac{\langle n+1|H_1|n\rangle}{E_n^{(0)} - E_{n+1}^{(0)}}|n+1\rangle\right]$$

$$= |n\rangle + qE\left[\frac{\langle n-1|x|n\rangle}{\hbar\omega}|n-1\rangle - \frac{\langle n+1|x|n\rangle}{\hbar\omega}|n+1\rangle\right]$$

$$= |n\rangle + qE\left[\sqrt{\frac{\hbar}{2m\omega}}\right]\left(\sqrt{n}\,|n-1\rangle - \sqrt{n+1}\,|n+1\rangle\right)$$

exact eigenstate

Degenerate Perturbation theory:

Here, we have more than one eigenfunction corresponding to the same eigenvalue. the general procedure is to eliminate the degeneracy first and then go on as before.

let us assume that the energy level $E_n^{(0)}$ is f-fold degenerate i.e there exist a set of different eigenstates $|\phi_{n\alpha}\rangle$ that correspond to the same eigenvalue $E_n^{(0)}$

$$\hat{H}_0 |\phi_{n\alpha}\rangle = E_n^{(0)} |\phi_{n\alpha}\rangle \quad --- \quad (1) \quad ; \quad \alpha = 1, 2, -- f$$

Now considering the states $|\phi_{n\alpha}\rangle$ to be orthonormal i.e

$\langle\phi_{n\alpha}|\phi_{n\beta}\rangle = \delta_{\alpha,\beta}$, then when we apply a perturbation H'

$\Rightarrow (H_0 + H')|\psi_n\rangle = E_n|\psi_n\rangle$, where $|\psi_n\rangle$ can be expanded in terms of the states $|\phi_{n\alpha}\rangle$

$$|\psi_n\rangle = \sum_{\alpha=1}^{f} |\phi_{n\alpha}\rangle\langle\phi_{n\alpha}| \, |\psi_n\rangle = \sum_{\alpha=1}^{f} \underbrace{\langle\phi_{n\alpha}|\psi_n\rangle}_{a_\alpha} |\phi_{n\alpha}\rangle$$

$$= \sum_{\alpha=1}^{f} a_\alpha |\phi_{n\alpha}\rangle \quad ; \text{ when } |\psi_n\rangle \text{ is normalized}$$

$$\langle\psi_n|\psi_n\rangle = 1 \Rightarrow \sum_{\alpha,\beta} a_\alpha^* a_\beta \delta_{\alpha,\beta} = \sum_{\alpha=1}^{f} |a_\alpha|^2 = 1$$

Now $(H_0 + H')|\psi_n\rangle = E_n|\psi_n\rangle$

$$\sum_\alpha a_\alpha [H_0|\phi_{n\alpha}\rangle + H'|\phi_{n\alpha}\rangle] = E_n \sum_\alpha a_\alpha|\phi_{n\alpha}\rangle$$

$$\sum_\alpha a_\alpha [E_n^{(0)}|\phi_{n\alpha}\rangle + H'|\phi_{n\alpha}\rangle] = E_n \sum_\alpha a_\alpha|\phi_{n\alpha}\rangle$$

multiply by $\langle\phi_{n\beta}|$ and integrate

$$\sum_{\alpha} a_\alpha \left[E_n^{(0)} \delta_{\alpha,\beta} + \langle \phi_{n\beta} | H' | \phi_{n\alpha} \rangle \right] = E_n \sum_{\alpha} a_\alpha \delta_{\alpha,\beta}$$

$$a_\beta E_n^{(0)} + \sum_{\alpha=1}^{f} a_\alpha \underbrace{\langle \phi_{n\beta} | H' | \phi_{n\alpha} \rangle}_{H'_{\beta\alpha}} = a_\beta E_n$$

let $E_n^{(1)} = E_n - E_n^{(0)}$

$$\Rightarrow \cancel{a_\beta E_n^{(0)}} + \sum_{\alpha=1}^{f} a_\alpha H'_{\beta\alpha} = a_\beta E_n^{(1)} + \cancel{a_\beta E_n^{(0)}}$$

$$\sum_{\alpha=1}^{f} \left(H'_{\beta\alpha} - E_n^{(1)} \delta_{\alpha,\beta} \right) a_\alpha = 0 \quad (7)$$

, This is a system of f homogeneous linear equations for the coefficients a_α. these coefficients are non vanishing only if $\det\left(H'_{\beta\alpha} - E_n^{(1)} \delta_{\beta,\alpha}\right) = 0$.

$$\begin{vmatrix} H'_{11} - E_n^{(1)} & H'_{12} & \cdots & H'_{1f} \\ H'_{21} & H'_{22} - E_n^{(1)} & & \\ \vdots & & & \\ H'_{f1} & \cdots & \cdots & H'_{ff} - E_n^{(1)} \end{vmatrix} = 0$$

we end up with a polynomial of degree f in $E_n^{(1)}$ which has f different real roots $E_{n\alpha}^{(1)}$. these roots are the first order correction to the eigenvalues $E_{n\alpha}$ of $H = H_0 + H'$.
Now to find the coefficient a_α, we need to substitute these roots into equation (7) and then solve the resulting expression. knowing the coefficients a_α, we can find the eigenfunctions $|\psi_n\rangle$ of $\hat{H}$ in the zeroth approximation