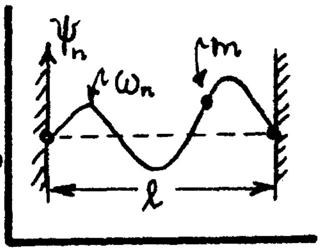
General idea of a perturbation theory

Stationary State Perturbation Theory

ref. Davydov: ¶ 47-50, Sakurai: Secs. 5.1-5.2.

The key idea of a perturbation theory is to start with a well-defined and well-known system, add a small change (i.e perturbation), and then develop a method for specifying the presumably small excursions in system parameters.

In this general sense, the WKB approximation is a perturbation theory -- we start from free particle eigenfcns & eigenvalues (or from ψ's & E's in a cnst external potential), and document how things change when we add "small" (remember $|k'/k^2| \ll 1$) departures from a cnst potential.



A classical example¶ of a perturbation is a string of length ℓ & uniform mass density, pegged at both ends and set into vibration. The wave amplitudes ψ_n and eigenfrequencies ω_n are easy to get. Now a small point mass m (small means m ≪ string mass) is attached to the string -- this changes $\psi_n \to \psi_n'$ and $\omega_n \to \omega_n'$ by small amounts. The problem is to calculate the new ψ_n' & ω_n' from the old (unperturbed) ψ_n & ω_n.

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1) We shall now do the QM version of the above string problem, viz.

> Suppose a stationary (i.e. time-independent), bound-state (i.e. discrete energies) QM system with known eigenfcns $\psi_n^{(0)}$ & eigenenergies $E_n^{(0)}$ is described by: $\mathcal{H}_0(p,x)\,\psi_n^{(0)}(x) = E_n^{(0)}\,\psi_n^{(0)}(x)$. A "small" time-independent potential V(x) is added to $\mathcal{H}_0$, i.e. $\mathcal{H}_0 \to \mathcal{H} = \mathcal{H}_0 + V$. The new QM problem is: $\mathcal{H}\Psi_n = E_n\Psi_n$. How are the perturbed (Ψ_n, E_n) related to the known $(\psi_n^{(0)}, E_n^{(0)})$? (1)

¶ See Sec. 44 of A. Fetter & J. Walecka "Theoretical Mechanics..." (McGraw-Hill, 1980)

Basic perturbation equation.

REMARKS

1. For the unperturbed system, the $\{\psi_n^{(0)}\}$ are a complete orthonormal set. The energies $E_n^{(0)}$ are assumed non-degenerate (we'll treat degeneracy later).
2. $V(x)$ "small" means $|\langle\psi_n^{(0)}|V|\psi_n^{(0)}\rangle| \ll |E_n^{(0)}|$ within n^{th} state, or when $m \neq n$: $|\langle\psi_m^{(0)}|V|\psi_n^{(0)}\rangle| \ll |E_m^{(0)} - E_n^{(0)}|$. So V cannot change the spectrum much.

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2) With V added in, our perturbed problem is:

$$\mathcal{H}(p,x)\,\psi_k(x) = E_k\,\psi_k(x), \quad \text{w/}\ \mathcal{H}(p,x) = \mathcal{H}_0(p,x) + V(x).$$

PROBLEM: Find ψ_k and E_k in terms of $\psi_n^{(0)}$, $E_n^{(0)}$ & V. (2)

Since $\{\psi_n^{(0)}\}$ are a complete set, we can expand the unknown ψ_k as...

$$\rightarrow \psi_k(x) = \sum_n a_{nk}\,\psi_n^{(0)}(x), \quad \text{w/}\ a_{nk} = \langle\psi_n^{(0)}|\psi_k\rangle \quad \text{(3)}$$

at this point, the a_{nk} are unknown.

Plug this version of ψ_k into $\mathcal{H}\psi_k = E_k\psi_k$...

$$\sum_n a_{nk}\,(\mathcal{H}_0 + V)\,\psi_n^{(0)} = \sum_n a_{nk}\,E_k\,\psi_n^{(0)} \leftarrow \text{use } \mathcal{H}_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)},$$

and rearrange terms...

or/

$$\sum_n a_{nk}\,(E_k - E_n^{(0)})\,\psi_n^{(0)} = \sum_n a_{nk}\,V\,\psi_n^{(0)}. \quad \text{(4)}$$

Operate thru Eq. (4) by $\langle\psi_m^{(0)}|\ \ \rangle$, and use $\langle\psi_m^{(0)}|\psi_n^{(0)}\rangle = \delta_{mn}$. Then...

$$\boxed{(E_k - E_m^{(0)})\,a_{mk} = \sum_n V_{mn}\,a_{nk}}, \quad \text{w/}\ V_{mn} = \langle\psi_m^{(0)}|V|\psi_n^{(0)}\rangle. \quad \text{(5)}$$

This is the <u>Fundamental</u> <u>Equation</u> of QM SS perturbation theory. It allows us -- at least in principle -- to solve for the set of coefficients $\{a_{nk}\}$ (which specify $\psi_k = \sum_n a_{nk}\psi_n^{(0)}$) from an ∞ set of linear coupled equations. The energies E_k are gotten from a secular eqtn, as follows...

Existence of solns $\{\psi_k, E_k\}$ from $\{\psi_n^{(0)}, E_n^{(0)}, V_{mn}\}$.

let/ $\rightarrow \mathbb{a}_k = \begin{pmatrix} \vdots \\ a_{nk} \\ \vdots \end{pmatrix}$, $a_{nk} = \langle \psi_n^{(0)} | \psi_k \rangle$ [a repⁿ of ψ_k on basis $\{\psi_n^{(0)}\}$]; (6a)

$\rightarrow \underset{\sim}{V} = \begin{pmatrix} & \vdots & \\ \cdots & V_{mn} & \cdots \\ & \vdots & \end{pmatrix}$, $V_{mn} = \langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle$ [repⁿ of V on $\{\psi_n^{(0)}\}$]; (6b)

$\rightarrow \underset{\sim}{\Delta}_k = \begin{pmatrix} \cdots (E_k - E_m^{(0)}) \delta_{mn} \cdots \end{pmatrix}$, a diagonal energy matrix. (6c)

Then Eq. (5) reads, in these terms...

$$\underset{\sim}{\Delta}_k \mathbb{a}_k = \underset{\sim}{V} \mathbb{a}_k, \text{ or/ } (\underset{\sim}{\Delta}_k - \underset{\sim}{V}) \mathbb{a}_k = 0;$$

and/ $$\det(\underset{\sim}{\Delta}_k - \underset{\sim}{V}) = \det[(E_k - E_m^{(0)})\delta_{mn} - V_{mn}] = 0. \quad \text{secular equation.} \tag{7}$$

The secular eqtn is imposed to avoid the trivial solution $\mathbb{a}_k \equiv 0$. It will evidently give a specific E_k in terms of all the $E_m^{(0)}$ & V_{mn}. Then, with the $\{E_k\}$, we can find the (normalized) eigenvectors $\{\mathbb{a}_k\}$ as usual.

This statement of the perturbation problem in Eq. (5) shows that solutions $\{\psi_k, E_k\}$ exist, and they can be gotten from the $\{\psi_n^{(0)}, E_n^{(0)}\}$ and V alone. But Eq. (7) is not a practical solution, since it involves $\infty \times \infty$ matrices like $\{V_{mn}\}$ and ∞-component eigenvectors $\mathbb{a}_k$.

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3) A practical method of dealing with Eq. (5) capitalizes on the "smallness" of V and the notion we can correct for it by a series of ever smaller terms. Let:

$$\underline{V \rightarrow \lambda V} \left\{ \begin{array}{l} \text{parameter } \lambda = 0 \Rightarrow \text{no perturbation; solns are } \psi_n^{(0)} \text{ \& } E_n^{(0)}; \\ \quad \text{"} \quad \lambda = 1 \Rightarrow \text{full perturbation; solns are } \psi_k \text{ \& } E_k. \end{array} \right. \tag{8}$$

Expansion of Fund.^l Eq. (5) in terms of order parameter λ

In what follows, we will always take $\lim_{\lambda \to 1}$ in the final result, to get the full solution of the $(\mathcal{H}_0 + V)$ problem. λ is just a convenient parameter to keep track of what "order-of-approximation" we are doing; this will soon become clear.

If V is "small", E_k must be close to $E_k^{(0)}$, so we write...

$$\rightarrow E_k = E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \cdots = \sum_{\mu=0}^{\infty} \lambda^\mu E_k^{(\mu)} \quad \int \lim_{\lambda \to 1} \text{ is understood.} \tag{9}$$

$E_k^{(\mu)}$ is called the μ^{th} order correction to $E_k^{(0)}$ [for $\mu \geq 1$].

Hope is: if V is "small", then $\underline{|E_k^{(\mu+1)}| \ll |E_k^{(\mu)}|}$, so series converges.

In the same spirit, we expand the unknown a_{nk}'s in Eq. (5), viz...

$$\rightarrow a_{nk} = a_{nk}^{(0)} + \lambda a_{nk}^{(1)} + \lambda^2 a_{nk}^{(2)} + \cdots = \sum_{\nu=0}^{\infty} \lambda^\nu a_{nk}^{(\nu)} \quad \int \lim_{\lambda \to 1} \text{ is understood.} \tag{10}$$

Put the λ-expansions of Eqs. (9) & (10) into the Fundamental Equation (5);

$$\rightarrow (E_k - E_m^{(0)}) a_{mk} = \sum_n \lambda V_{mn} a_{nk}, \text{ becomes:}$$

$$\underbrace{\left(\sum_{\mu=0}^{\infty} E_k^{(\mu)} \lambda^\mu\right)\left(\sum_{\nu=0}^{\infty} a_{mk}^{(\nu)} \lambda^\nu\right)} - \sum_{\nu=0}^{\infty} E_m^{(0)} a_{mk}^{(\nu)} \lambda^\nu = \sum_n \lambda V_{mn} \left(\sum_{\nu=0}^{\infty} a_{nk}^{(\nu)} \lambda^\nu\right). \tag{11}$$

[use general formula for product of power series] $\left(\sum_{\mu=0}^{\infty} A_\mu \lambda^\mu\right)\left(\sum_{\nu=0}^{\infty} B_\nu \lambda^\nu\right) = \sum_{\mu=0}^{\infty} C_\mu \lambda^\mu, \quad C_\mu = \sum_{\sigma=0}^{\mu} A_{\mu-\sigma} B_\sigma$

So// 1st term LHS in Eq. (11) $= \sum_{\mu=0}^{\infty} \left(\sum_{\sigma=0}^{\mu} E_k^{(\mu-\sigma)} a_{mk}^{(\sigma)}\right) \lambda^\mu$,

and Eq. (11) can be written...

$$\left[\!\left[\sum_{\mu=0}^{\infty} \left[\sum_{\sigma=0}^{\mu} E_k^{(\mu-\sigma)} a_{mk}^{(\sigma)} - E_m^{(0)} a_{mk}^{(\mu)} \right] \lambda^\mu = \sum_{\nu=0}^{\infty} \left[\sum_n V_{mn} a_{nk}^{(\nu)} \right] \lambda^{\nu+1}. \right]\!\right] \tag{12}$$

This is now the Master Equation. It can be simplified, by the following steps:

Master Eqtn for Perturbation Theory as an Iteration

Simplifying Eq. (12)...

1. On the LHS, split off the $\mu=0$ term, and set $\sum_{\mu=1}^{\infty} = \sum_{\nu=0}^{\infty}$, with $\mu=\nu+1$. Then...

$$\left\{\begin{matrix}\text{LHS of}\\ \text{Eq. (12)}\end{matrix}\right\} = (E_k^{(0)}-E_m^{(0)})a_{mk}^{(0)} + \sum_{\nu=0}^{\infty}\Big[\underbrace{\sum_{\sigma=0}^{\nu+1} E_k^{(\nu+1-\sigma)} a_{mk}^{(\sigma)}}_{= E_k^{(0)} a_{mk}^{(\nu+1)} + \sum_{\sigma=0}^{\nu} E_k^{(\nu+1-\sigma)} a_{mk}^{(\sigma)}} - E_m^{(0)} a_{mk}^{(\nu+1)}\Big]\lambda^{\nu+1}; \quad (13)$$

Take entire RHS of (12), and put over to LHS. Then (12) becomes...

$$\rightarrow (E_k^{(0)}-E_m^{(0)})a_{mk}^{(0)} + \sum_{\nu=0}^{\infty}\Big[(E_k^{(0)}-E_m^{(0)})a_{mk}^{(\nu+1)} + \sum_{\sigma=0}^{\nu} E_k^{(\nu+1-\sigma)} a_{mk}^{(\sigma)} - \sum_n V_{mn} a_{nk}^{(\nu)}\Big]\lambda^{\nu+1} = 0. \quad (14)$$

This is the first simplification.

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2. Consider Eq. (14) as a power series in λ for $\lambda \neq 0$ ($0<\lambda\leq 1$ is OK). Since λ is an independently variable parameter, the only way the power series can $=0$ is if every one of its coefficients vanish, i.e.

$$\text{I.} \quad (E_k^{(0)}-E_m^{(0)})a_{mk}^{(0)} = 0; \quad (15a)$$

$$\text{II.} \quad (E_k^{(0)}-E_m^{(0)})a_{mk}^{(\nu+1)} + E_k^{(\nu+1)} a_{mk}^{(0)} = \sum_n V_{mn} a_{nk}^{(\nu)} - \sum_{\sigma=1}^{\nu} E_k^{(\nu+1-\sigma)} a_{mk}^{(\sigma)}. \quad (15b)$$

This extremely powerful simplification justifies the whole procedure of using power series in λ. Note that II is a recursion relation for $a_{mk}^{(\nu+1)} = \text{fcn}\, a_{mk}^{(\mu\leq\nu)}$.

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3. In Eq. (15a), $a_{mk}^{(0)} \equiv 0$ for $m\neq k$ (the $E_n^{(0)}$ are not degenerate). Then, for $m=k$ we need $a_{kk}^{(0)}=1$, so that $\psi_k = \psi_k^{(0)}$ when V vanishes. So: $\boxed{a_{mk}^{(0)} = \delta_{mk}}$. Use of this in Eq. (15b), plus rewrite of last term RHS (let $\mu=\sigma-1$) gives...

$$\boxed{(E_k^{(0)}-E_m^{(0)})a_{mk}^{(\nu+1)} + E_k^{(\nu+1)}\delta_{mk} = \sum_n V_{mn} a_{nk}^{(\nu)} - \sum_{\mu=0}^{\nu-1} E_k^{(\nu-\mu)} a_{mk}^{(\mu+1)}}\ ; \ \nu=0,1,2,\ldots \quad (16)$$

term contributes for $\nu\geq 1$ only.

This is the new version of our Master Eq. for perturbation. The order parameter $\nu=0,1,2,\ldots$ corresponds to working on $O(\lambda)$, $O(\lambda^2)$, $O(\lambda^3)$ terms, i.e. to working on 1st, 2nd, 3rd order perturbative corrections.

SS Perturbation Theory: Iteration of Master Eq. (16).

4) Now we iterate the Master Eqtn to get the $a_{mk}^{(1)}$ from the already known $a_{mk}^{(0)} = \delta_{mk}$, the $a_{mk}^{(2)}$ from the $a_{mk}^{(1)}$ & $a_{mk}^{(0)}$, etc. Also the $E_k^{(1)}$ from the $E_k^{(0)}$, etc. Like this:

In Eq. (16), Choose $\nu = 0$ ($\Rightarrow$ working to $O(\lambda)$, 1st order perturbation theory).

$$\xrightarrow{\text{So}} (E_k^{(0)} - E_m^{(0)})\, a_{mk}^{(1)} + E_k^{(1)}\delta_{mk} = \sum_n V_{mn}\, \overset{\delta_{nk}}{a_{nk}^{(0)}} + (\text{zero}) = V_{mk}. \tag{17}$$

1. $m \neq k$, (17) $\Rightarrow$ $\boxed{a_{mk}^{(1)} = V_{mk}/(E_k^{(0)} - E_m^{(0)})}$. (17a)

So $\psi_k = \psi_k^{(0)} + \underbrace{\sum_m a_{mk}^{(1)}\psi_m^{(0)}}_{\text{"small" correction only if}} + \cdots$ $\int |a_{mk}^{(1)}| \ll 1$, "$\,|V_{mk}| \ll |E_k^{(0)} - E_m^{(0)}|$ (as advertised at top of p. SS 2).

2. $m = k$, (17) $\Rightarrow$ $(\text{zero}) + E_k^{(1)} = V_{kk} + (\text{zero})$, i.e. $\boxed{E_k^{(1)} = V_{kk}}$. (17b)

So $E_k = E_k^{(0)} + \underbrace{V_{kk}}_{\text{"small" only if}} + \cdots$ $\int |V_{kk}| \ll |E_k^{(0)}|$, within state k. (as advertised on top of p. SS 2).

NOTE: the $m=k$ eqtn for $\nu=0$ gives no information on $a_{kk}^{(1)}$.

$\boxed{\text{ASIDE}}$: What value do we give $a_{kk}^{(1)}$? Assertion: we can set $a_{kk}^{(1)} = 0$.

(1) We can defend the assertion on grounds that ψ_k should be normed: $\langle\psi_k|\psi_k\rangle = 1$. The argument goes as follows. Write the wavefcn ψ_k as...

$$\left[\begin{array}{l} \psi_k = \sum_n a_{nk}\psi_n^{(0)} = \sum_n \left(\sum_{\sigma=0}^{\infty} \lambda^\sigma a_{nk}^{(\sigma)}\right)\psi_n^{(0)} = \sum_{\sigma=0}^{\infty}\psi_k^{(\sigma)}, \\ \text{w/}\quad \psi_k^{(\sigma)} = \lambda^\sigma \sum_n a_{nk}^{(\sigma)}\psi_n^{(0)} = \lambda^\sigma\left[a_{kk}^{(\sigma)}\psi_k^{(0)} + \sum_n{}' a_{nk}^{(\sigma)}\psi_n^{(0)}\right]. \end{array}\right. \tag{18}$$

prime means $\sum_{n\neq k}$ (sum w/o $n=k$ term)

$\psi_k^{(\sigma)}$ is the σ^{th} order correction to $\psi_k^{(0)}$; note $\psi_k^{(\sigma)}|_{\sigma=0} = \psi_k^{(0)}$, as should be (here use $a_{nk}^{(0)} = \delta_{nk}$). Now we calculate the norm, $\langle\psi_k|\psi_k\rangle$, after splitting off $\psi_k^{(0)}$, i.e. put $\psi_k = \psi_k^{(0)} + \sum_{\sigma=1}^{\infty}\psi_k^{(\sigma)}$ and calculate...

Normalization of perturbed wavefcn Ψ_k.

$$\rightarrow \langle\psi_k|\psi_k\rangle = \langle \psi_k^{(0)} + \sum_{\sigma=1}^{\infty}\psi_k^{(\sigma)} \,|\, \psi_k^{(0)} + \sum_{\mu=1}^{\infty}\psi_k^{(\mu)}\rangle$$

$$= 1 + 2\,\mathrm{Re}\sum_{\sigma=1}^{\infty}\underbrace{\langle\psi_k^{(0)}|\psi_k^{(\sigma)}\rangle}_{①} + \sum_{\sigma,\mu=1}^{\infty}\underbrace{\langle\psi_k^{(\sigma)}|\psi_k^{(\mu)}\rangle}_{②} \tag{19}$$

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(2) Use $\psi_k^{(\sigma)}$ from Eq. (18) to evaluate the projections ①&②. Thus...

$$① = \lambda^\sigma\langle\psi_k^{(0)} \,|\, a_{kk}^{(\sigma)}\psi_k^{(0)} + \sum_n{}' a_{nk}^{(\sigma)}\psi_n^{(0)}\rangle = \lambda^\sigma a_{kk}^{(\sigma)}\;; \tag{20a}$$

only contrib^n

$$② = \lambda^{\sigma+\mu}\langle a_{kk}^{(\sigma)}\psi_k^{(0)} + \sum_n{}' a_{nk}^{(\sigma)}\psi_n^{(0)} \,|\, a_{kk}^{(\mu)}\psi_k^{(0)} + \sum_m{}' a_{mk}^{(\mu)}\psi_m^{(0)}\rangle$$

$$= \lambda^{\sigma+\mu}\left\{ a_{kk}^{(\sigma)*}a_{kk}^{(\mu)} + \sum_{n,m} a_{nk}^{(\sigma)*}a_{mk}^{(\mu)}\underbrace{\langle\psi_n^{(0)}|\psi_m^{(0)}\rangle}_{\delta_{nm},\text{ now sum over }m.}\right\}. \tag{20b}$$

Put results of Eqs. (20) into Eq. (19) to get the ψ_k norm as...

$$\boxed{\langle\psi_k|\psi_k\rangle = 1 + 2\,\mathrm{Re}\sum_{\sigma=1}^{\infty}\lambda^\sigma a_{kk}^{(\sigma)} + \sum_{\sigma,\mu=1}^{\infty}\lambda^{\sigma+\mu}\left\{a_{kk}^{(\sigma)*}a_{kk}^{(\mu)} + \sum_n{}' a_{nk}^{(\sigma)*}a_{nk}^{(\mu)}\right\}} \tag{21}$$

This expression is exact. Clearly $\langle\psi_k|\psi_k\rangle \neq 1$ in general (despite $\langle\psi_k^{(0)}|\psi_k^{(0)}\rangle = 1$).

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(3) Now suppose we are working in the $\sigma = 1^{st}$ order of perturbation theory, as we did in Eqs. (17) on p. SS6. Eq. (21) prescribes (to $\mathcal{O}(\lambda)$ and no higher)...

$$\rightarrow \langle\psi_k|\psi_k\rangle = 1 + 2\lambda\,\mathrm{Re}\,a_{kk}^{(1)} + \cancelto{0}{\mathcal{O}(\lambda^2)},$$

soy reqt. that $\langle\psi_k|\psi_k\rangle = 1 \Rightarrow \underline{\mathrm{Re}\,a_{kk}^{(1)} = 0}$, or// $a_{kk}^{(1)} = i\,b_k^{(1)}$ ⌠ $a_{kk}^{(1)}$ is pure imaginary

and// $\psi_k \simeq \psi_k^{(0)} + \psi_k^{(1)} = [1 + \lambda a_{kk}^{(1)}]\,\psi_k^{(0)} + \left(\lambda\sum_n{}' a_{nk}^{(1)}\psi_n^{(0)}\right)$ this is $\mathcal{O}(\lambda^2)\to 0$, $\frac{}{}$ w/ $a_{nk}^{(1)} = \dfrac{\lambda V_{nk}}{E_k^{(0)} - E_n^{(0)}}$.

or// $\psi_k \simeq [1 + i\lambda b_k^{(1)}]\,\psi_k^{(0)} \rightarrow [e^{i\lambda b_k^{(1)}}]\,\psi_k^{(0)}$, to $\mathcal{O}(\lambda)$. (22)

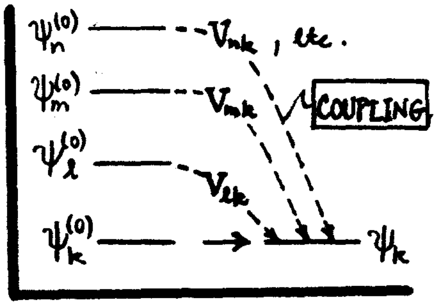
So the evanescent $a_{kk}^{(1)}$ enters 1^{st} order theory at most as a phase factor, which is arbitrary. We can set $b_k^{(1)} \equiv 0$ w/o harm. So, as advertised, $\underline{a_{kk}^{(1)} = 0}$.

Form of theory when all phases $a_{kk}^{(\sigma)} \equiv 0$.

(4) Now we can claim with confidence that in 1^{st} order theory...

$$\left[\begin{array}{l} a_{mk}^{(1)} = \begin{cases} V_{mk}/(E_k^{(0)} - E_m^{(0)}), & \text{for } m \neq k; \\ \underline{\underline{0}}, & \text{for } m = k; \end{cases} \\ \text{so } \psi_k \simeq \psi_k^{(0)} + \sum_n{}' \left(\frac{V_{nk}}{E_k^{(0)} - E_n^{(0)}}\right) \psi_n^{(0)} \quad \text{is } 1^{st} \text{ order perturbed wavefcn } [\text{prime on } \textstyle\sum_n' \Rightarrow n \neq k \text{ in sum}] \end{array}\right] \quad (23)$$

This maneuver removes the possibility that $a_{kk}^{(1)} = \left(\frac{V_{nk}}{E_k^{(0)} - E_n^{(0)}}\right)\Big|_{n=k}$ diverges for $V_{kk} \neq 0$. Also, it ensures that $\langle \psi_k | \psi_k \rangle = 1 + \Theta(\lambda^2)$, i.e. that ψ_k is normed to 1 to within the order of approxn $[\Theta(\lambda)]$. Note that in 1st order theory, the mixed state ψ_k has a contribution from $\psi_n^{(0)}$ only if the "Coupling" $V_{nk} \neq 0$.



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(5) It is clear from the Master Eq. (16) that in general the $a_{kk}^{(\sigma)}$, $\sigma \geq 1$, are free constants (phase factors) because for $m = k$ the eqtn reads...

$$\rightarrow (E_k^{(0)} - \cancelto{0}{E_k^{(0)}}) a_{kk}^{(\nu+1)} + E_k^{(\nu+1)} = \sum_n{}' V_{kn} a_{nk}^{(\nu)} + \left[V_{kk} a_{kk}^{(\nu)} - \sum_{\sigma=1}^{\nu} E_k^{(\nu+1-\sigma)} a_{kk}^{(\sigma)} \right]. \quad (24)$$

Since the first term LHS drops out, we get no restrictions on $a_{kk}^{(\nu+1)}$ from any of the previous iterations for $a_{nk}^{(\sigma)}$ & $E_k^{(\sigma)}$, $\sigma \leq \nu$. We thus have the freedom:

<u>Choose : $a_{kk}^{(\sigma)} \equiv 0$, for all $\sigma \geq 1$</u> $\quad$ (25)

so

<u>1.</u> $\langle \psi_k | \psi_k \rangle = 1 + \sum_n{}' \left(\sum_{\sigma,\mu=1}^{\infty} a_{nk}^{(\sigma)*} a_{nk}^{(\mu)} \lambda^{\sigma+\mu} \right)$, from Eq. (21); $\quad$ 1^{st} term is $\Theta(\lambda^4)$ (usually negligible).

<u>2.</u> $\langle \psi_k^{(\sigma)} | \psi_k \rangle = \lambda^\sigma \sum_n{}' \left(\sum_{\mu=1}^{\infty} a_{nk}^{(\sigma)*} a_{nk}^{(\mu)} \lambda^\mu \right)$ $\quad$ the ( ) = $\Theta(\lambda^2)$ at least, so $\psi_k^{(0)}$ is $\perp$ ψ_k, negl. $\Theta(\lambda^{\sigma+2})$.

<u>3.</u> $\underline{E_k^{(\nu+1)} = \sum_n{}' V_{kn} a_{nk}^{(\nu)}}$, from Eq. (24). ← NICE SIMPLIFICATION!

END of ASIDE

Perturbations to 2nd order [$\mathcal{O}(V^2)$].

5) We have the first-order [i.e. $\mathcal{O}(V)$, same as $\mathcal{O}(\lambda)$] energy corrections $E_k^{(1)} = V_{kk}$ and amplitudes $a_{nk}^{(1)} = V_{nk}/(E_k^{(0)} - E_n^{(0)})$ from Eqs. (17). And we have shown that we can choose $a_{kk}^{(\sigma)} = 0$ for all $\sigma \geq 1$, which simplifies the proceedings.

Now go after second-order corrections. Like this:

In Eq. (16), choose $\nu = 1$ ($\Rightarrow$ working to $\mathcal{O}(V^2)$, 2nd order pert$^{\underline{b}}$n theory).

$$\xrightarrow{\text{So}} (E_k^{(0)} - E_m^{(0)}) a_{mk}^{(2)} + E_k^{(2)} \delta_{mk} = \sum_n{}' V_{mn} a_{nk}^{(1)} - E_k^{(1)} a_{mk}^{(1)} . \qquad (26)$$

1. $m \neq k$, (26) $\Rightarrow$ $(E_k^{(0)} - E_m^{(0)}) a_{mk}^{(2)} = \sum_n{}' V_{mn} a_{nk}^{(1)} - V_{kk} a_{mk}^{(1)}$,

but $a_{nk}^{(1)} = \dfrac{V_{nk}}{E_k^{(0)} - E_n^{(0)}}$, so

$$\boxed{a_{mk}^{(2)} = \frac{1}{E_k^{(0)} - E_m^{(0)}} \sum_{n \neq k} (V_{mn} - V_{kk}\delta_{mn}) \frac{V_{nk}}{E_k^{(0)} - E_n^{(0)}}} . \qquad (26a)$$

Then: $\psi_k = \psi_k^{(0)} + \sum_m{}' a_{mk}^{(1)} \psi_m^{(0)} + \sum_m{}' a_{mk}^{(2)} \psi_m^{(0)} + \ldots$ Gets pretty messy!

2. $m = k$, (26) $\Rightarrow$ $0 + E_k^{(2)} = \sum_n{}' V_{kn} a_{nk}^{(1)} - 0$

but $a_{nk}^{(1)} = \dfrac{V_{nk}}{E_k^{(0)} - E_n^{(0)}}$,

$$\boxed{E_k^{(2)} = \sum_{n \neq k} V_{kn} V_{nk} / (E_k^{(0)} - E_n^{(0)})} . \qquad (26b)$$

Now: $E_k = E_k^{(0)} + V_{kk} + \sum_{n \neq k} \dfrac{V_{kn} V_{nk}}{E_k^{(0)} - E_n^{(0)}} + \ldots$ to $\mathcal{O}(V^2)$. Fairly compact!

REMARKS on 2nd order results.

(a) The iteration can be continued ($\nu = 2, 3$, etc.), but ψ_k up thru $\psi_k^{(1)}$ and E_k up thru $E_k^{(2)}$ are sufficient for most problems.

(b) E_k up thru $E_k^{(2)}$ [i.e. $\mathcal{O}(V^2)$] can be calculated from ψ_k up thru $\psi_k^{(1)}$ [i.e. $\mathcal{O}(V)$] by evaluating: $E_k = \langle \psi_k | \mathcal{H} | \psi_k \rangle / \langle \psi_k | \psi_k \rangle$. Do as exercise.

(c) Both $a_{mk}^{(2)}$ & $E_k^{(2)}$ are 2nd order in V, and the smallness conditions in Eqs. (17) (e.g. $|V_{nk}| \ll |E_k^{(0)} - E_n^{(0)}|$) ensure $|E_k^{(2)}| \ll |E_k^{(1)}|$, etc.

Remarks on $\mathcal{O}(V^2)$ results. Stark effect example.

$\boxed{\text{REMARKS}}$ (cont'd)

(d) Since V is a Hermitian perturbation, then $V_{kn} = V_{nk}^*$, and Eq. (26b) reads $\underline{E_k^{(2)} = \sum_{n \neq k} |V_{nk}|^2/(E_k^{(0)} - E_n^{(0)})}$; the numerator is +ve definite. If $k=0$ is the ground state of the system, then $E_0^{(2)} = (-)\sum_{n>0} |V_{n0}|^2/(E_n^{(0)} - E_0^{(0)})$. When $V_{00} = 0$, the perturbed ground state $E_0 = E_0^{(0)} + E_0^{(2)} + \ldots$ is driven <u>downward</u>, so -- curiously enough -- the applied V (usually) <u>increases</u> the binding.

(e) Notice the way that "coupling" works in forming the energy shift $E_k^{(2)} = \sum_{n \neq k} V_{kn} V_{nk}/(E_k^{(0)} - E_n^{(0)})$. The matrix element V_{kn} mixes $k \rightarrow n$, then V_{nk} takes that contribution $n \rightarrow k$ back to the (perturbed) state k, weighted by the energy denominator $(E_k^{(0)} - E_n^{(0)})$. $E_k^{(2)}$ is formed by state k "exploring" all possible intermediate states n ($\ni V_{kn} \neq 0$) in this way.