MULTIELECTRON ATOMS

Dr. M. Monirul Islam
Professor of Chemistry
University of Rajshahi

APPROXIMATION METHODS

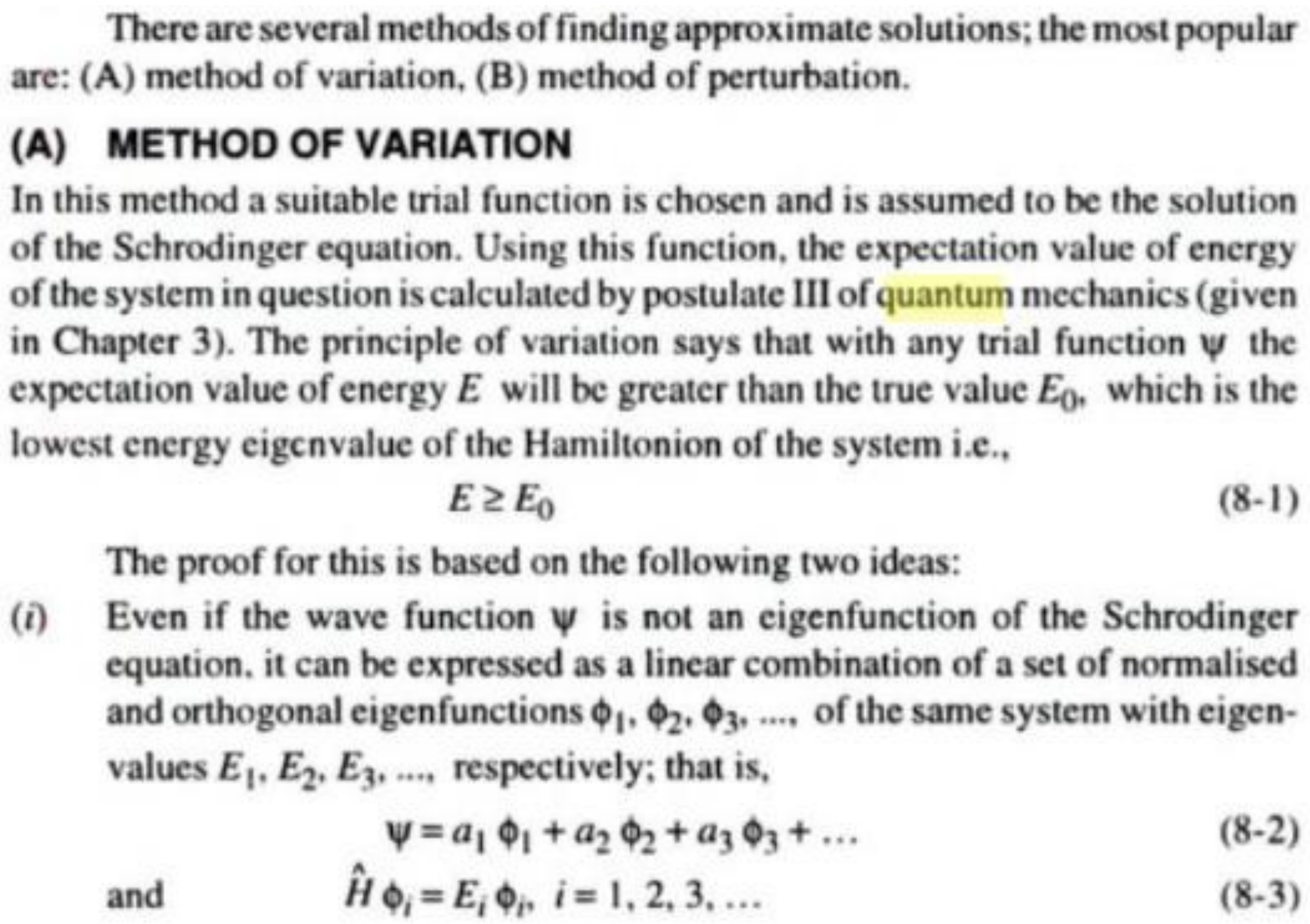
- ✓ For hydrogenic atoms (one-electron), SE can be solved after lengthy mathematical manipulation. The difficulties arise due to single potential term, $-\frac{Z}{r}$ in SE.
- ✓ Now let n electrons are in an atom, then SE can be written as

$$\left(-\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2-\sum_{i=1}^{n}\frac{Z}{r_i}+\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\frac{1}{r_{ij}}\right)\psi=E\psi\quad\text{(in au)}$$

where, 2nd terms in first bracket are potential due to electron-nucleus attractions (n number) and 3rd terms in first bracket due to electron-electron repulsions (${}^nC_2$ number).

- ✓ The enormous electron-nucleus and electron-electron potential terms make SE more complicated.
- ✓ The exact solutions of SE is rather impossible because of many potentials terms.
- ✓ To get approximate eigenfunctions and eigenvalues, approximation methods are applied to solve SE.

APPROXIMATION METHODS



There are several methods of finding approximate solutions; the most popular are: (A) method of variation, (B) method of perturbation.

(A) METHOD OF VARIATION

In this method a suitable trial function is chosen and is assumed to be the solution of the Schrodinger equation. Using this function, the expectation value of energy of the system in question is calculated by postulate III of quantum mechanics (given in Chapter 3). The principle of variation says that with any trial function ψ the expectation value of energy E will be greater than the true value E_0, which is the lowest energy eigenvalue of the Hamiltonion of the system i.e.,

$$E \geq E_0 \tag{8-1}$$

The proof for this is based on the following two ideas:

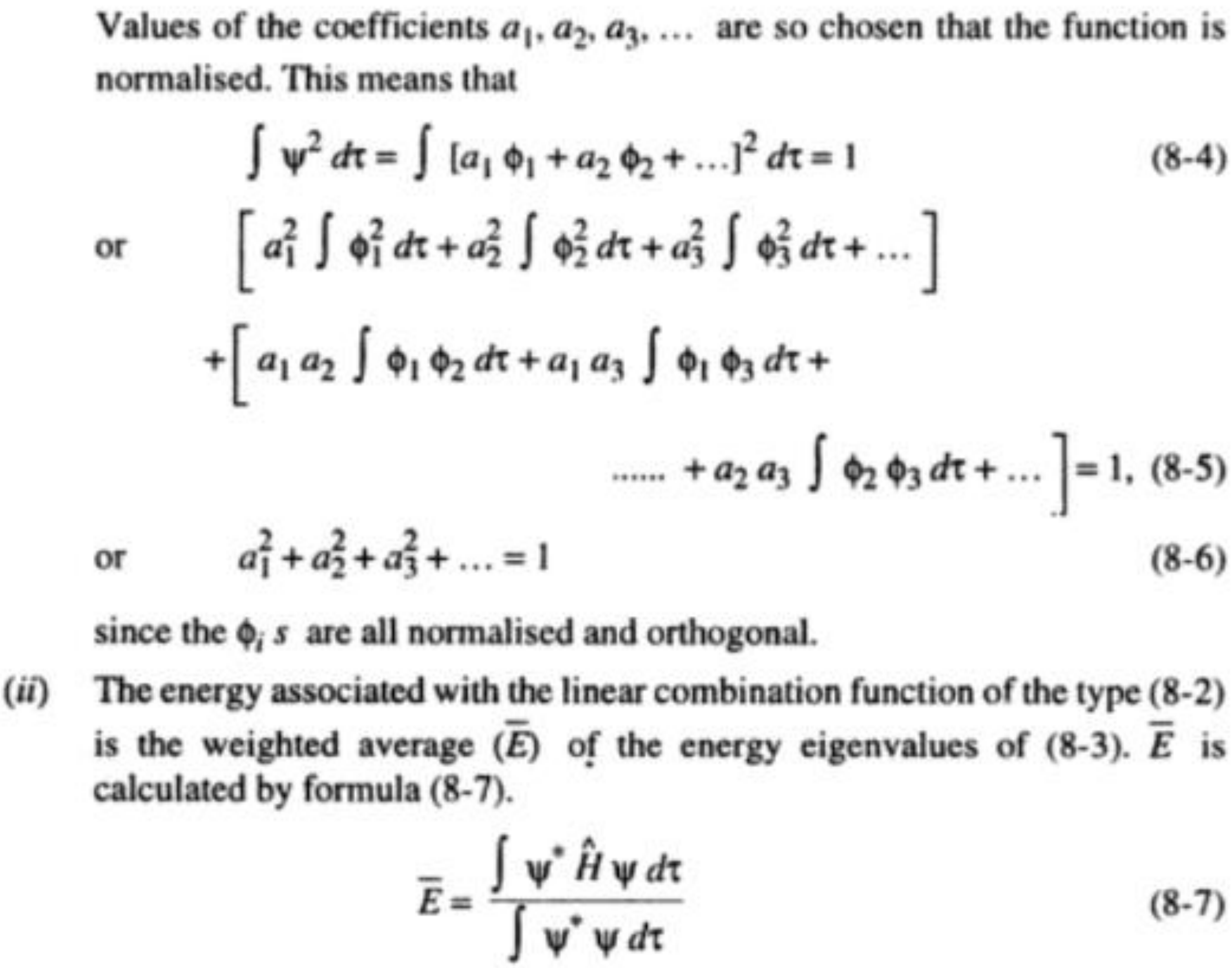
(*i*) Even if the wave function ψ is not an eigenfunction of the Schrodinger equation, it can be expressed as a linear combination of a set of normalised and orthogonal eigenfunctions $\phi_1, \phi_2, \phi_3, \ldots,$ of the same system with eigenvalues $E_1, E_2, E_3, \ldots,$ respectively; that is,

$$\psi = a_1 \phi_1 + a_2 \phi_2 + a_3 \phi_3 + \ldots \tag{8-2}$$

and

$$\hat{H} \phi_i = E_i \phi_i, \quad i = 1, 2, 3, \ldots \tag{8-3}$$

APPROXIMATION METHODS



Values of the coefficients $a_1, a_2, a_3, \ldots$ are so chosen that the function is normalised. This means that

$$\int \psi^2 \, d\tau = \int [a_1 \phi_1 + a_2 \phi_2 + \ldots]^2 \, d\tau = 1 \tag{8-4}$$

or

$$\left[a_1^2 \int \phi_1^2 \, d\tau + a_2^2 \int \phi_2^2 \, d\tau + a_3^2 \int \phi_3^2 \, d\tau + \ldots \right] + \left[a_1 a_2 \int \phi_1 \phi_2 \, d\tau + a_1 a_3 \int \phi_1 \phi_3 \, d\tau + \ldots\ldots + a_2 a_3 \int \phi_2 \phi_3 \, d\tau + \ldots \right] = 1, \tag{8-5}$$

or

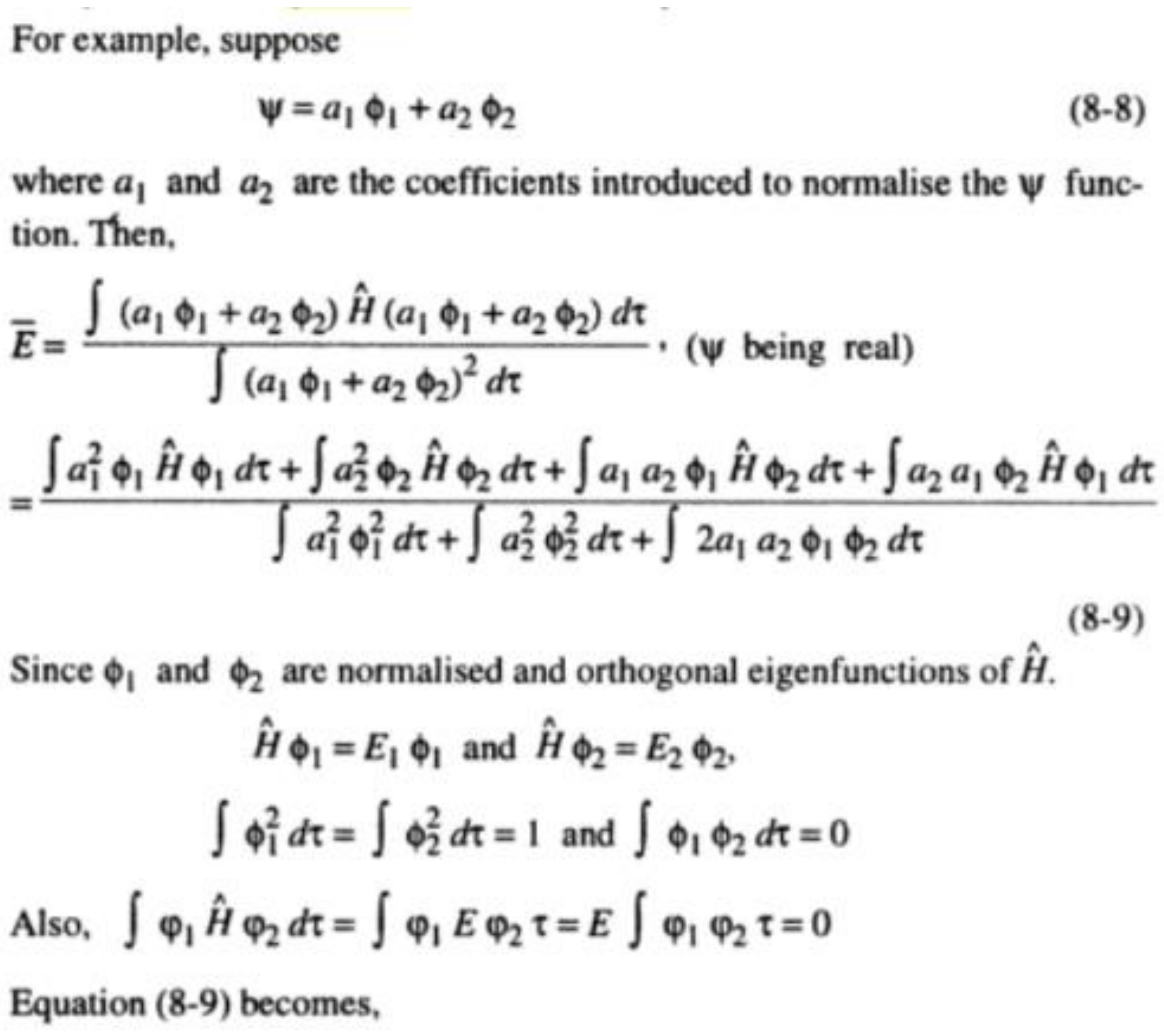
$$a_1^2 + a_2^2 + a_3^2 + \ldots = 1 \tag{8-6}$$

since the $\phi_i\, s$ are all normalised and orthogonal.

(*ii*) The energy associated with the linear combination function of the type (8-2) is the weighted average $(\overline{E})$ of the energy eigenvalues of (8-3). $\overline{E}$ is calculated by formula (8-7).

$$\overline{E} = \frac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau} \tag{8-7}$$

APPROXIMATION METHODS



For example, suppose

$$\psi = a_1 \phi_1 + a_2 \phi_2 \tag{8-8}$$

where a_1 and a_2 are the coefficients introduced to normalise the ψ function. Then,

$$\bar{E} = \frac{\int (a_1 \phi_1 + a_2 \phi_2)\, \hat{H}\, (a_1 \phi_1 + a_2 \phi_2)\, d\tau}{\int (a_1 \phi_1 + a_2 \phi_2)^2\, d\tau}, \text{ (}\psi\text{ being real)}$$

$$= \frac{\int a_1^2 \phi_1 \hat{H} \phi_1\, d\tau + \int a_2^2 \phi_2 \hat{H} \phi_2\, d\tau + \int a_1 a_2 \phi_1 \hat{H} \phi_2\, d\tau + \int a_2 a_1 \phi_2 \hat{H} \phi_1\, d\tau}{\int a_1^2 \phi_1^2\, d\tau + \int a_2^2 \phi_2^2\, d\tau + \int 2a_1 a_2 \phi_1 \phi_2\, d\tau} \tag{8-9}$$

Since ϕ_1 and ϕ_2 are normalised and orthogonal eigenfunctions of $\hat{H}$.

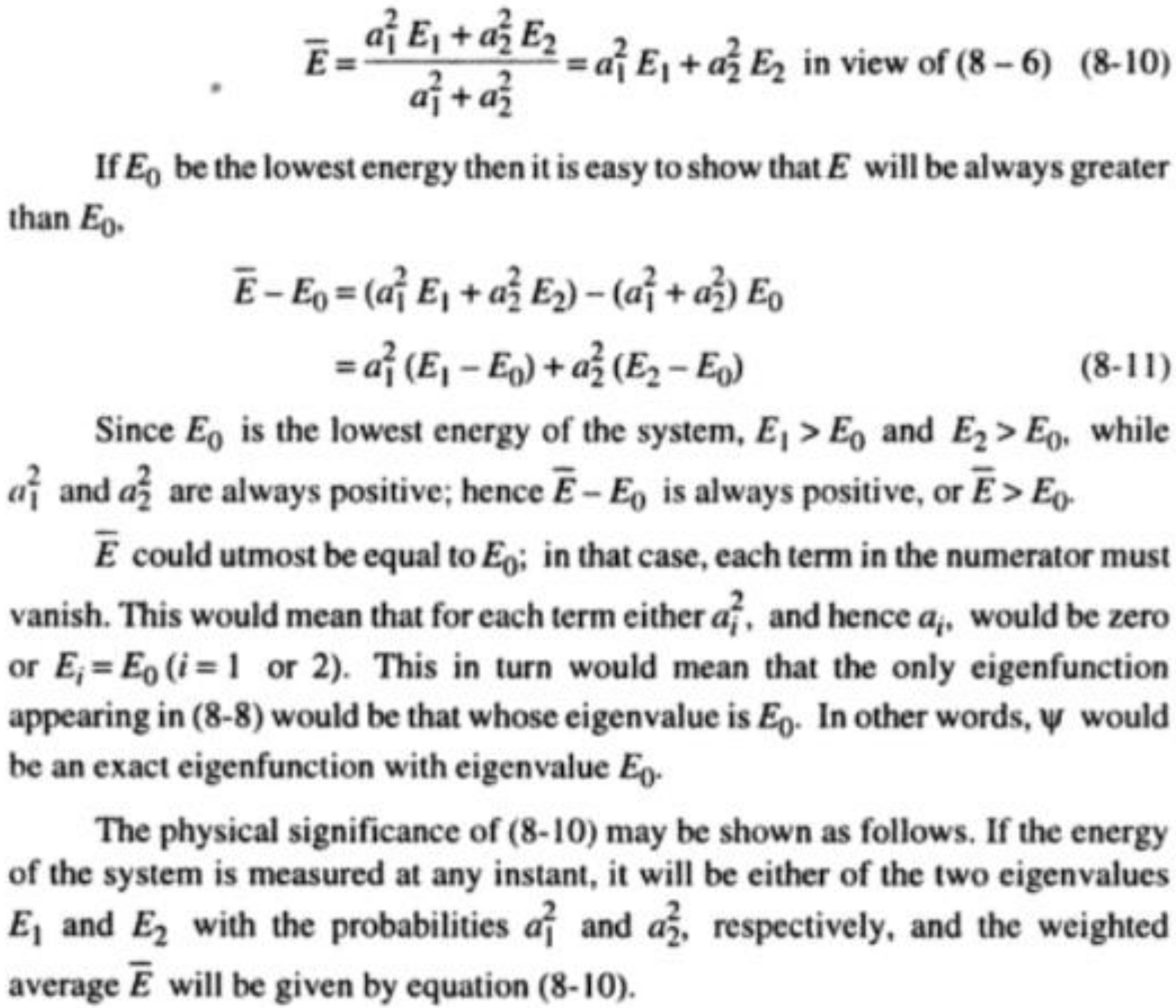
$$\hat{H} \phi_1 = E_1 \phi_1 \text{ and } \hat{H} \phi_2 = E_2 \phi_2,$$

$$\int \phi_1^2\, d\tau = \int \phi_2^2\, d\tau = 1 \text{ and } \int \phi_1 \phi_2\, d\tau = 0$$

Also, $\int \varphi_1 \hat{H} \varphi_2\, d\tau = \int \varphi_1 E \varphi_2 \tau = E \int \varphi_1 \varphi_2 \tau = 0$

Equation (8-9) becomes,

APPROXIMATION METHODS



$$\bar{E} = \frac{a_1^2 E_1 + a_2^2 E_2}{a_1^2 + a_2^2} = a_1^2 E_1 + a_2^2 E_2 \text{ in view of } (8-6) \quad (8\text{-}10)$$

If E_0 be the lowest energy then it is easy to show that E will be always greater than E_0.

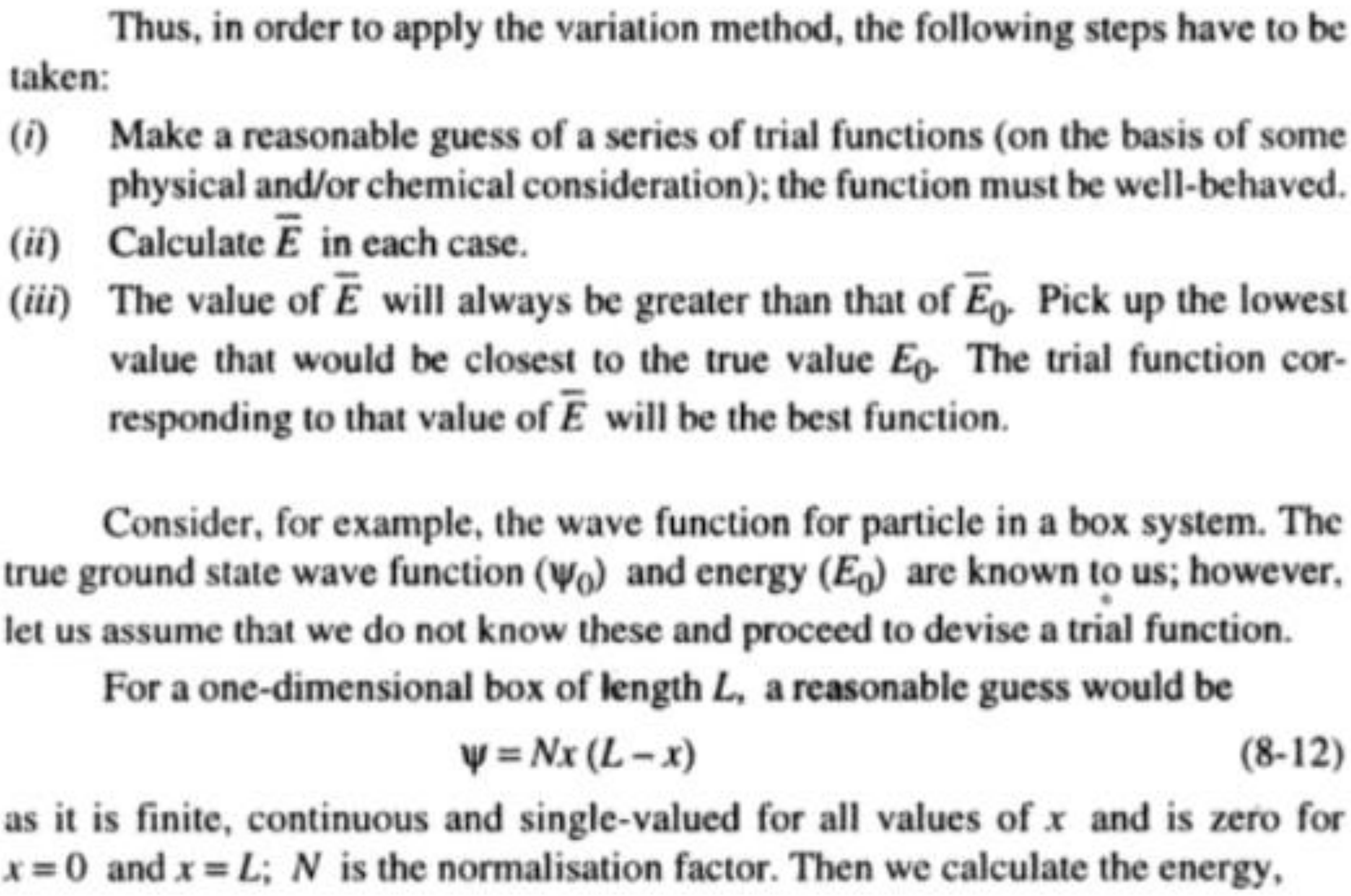
$$\begin{aligned} \bar{E} - E_0 &= (a_1^2 E_1 + a_2^2 E_2) - (a_1^2 + a_2^2) E_0 \\ &= a_1^2 (E_1 - E_0) + a_2^2 (E_2 - E_0) \end{aligned} \quad (8\text{-}11)$$

Since E_0 is the lowest energy of the system, $E_1 > E_0$ and $E_2 > E_0$, while a_1^2 and a_2^2 are always positive; hence $\bar{E} - E_0$ is always positive, or $\bar{E} > E_0$.

$\bar{E}$ could utmost be equal to E_0; in that case, each term in the numerator must vanish. This would mean that for each term either a_i^2, and hence a_i, would be zero or $E_i = E_0$ ($i = 1$ or 2). This in turn would mean that the only eigenfunction appearing in (8-8) would be that whose eigenvalue is E_0. In other words, ψ would be an exact eigenfunction with eigenvalue E_0.

The physical significance of (8-10) may be shown as follows. If the energy of the system is measured at any instant, it will be either of the two eigenvalues E_1 and E_2 with the probabilities a_1^2 and a_2^2, respectively, and the weighted average $\bar{E}$ will be given by equation (8-10).

APPROXIMATION METHODS



Thus, in order to apply the variation method, the following steps have to be taken:

(*i*) Make a reasonable guess of a series of trial functions (on the basis of some physical and/or chemical consideration); the function must be well-behaved.

(*ii*) Calculate $\overline{E}$ in each case.

(*iii*) The value of $\overline{E}$ will always be greater than that of $\overline{E}_0$. Pick up the lowest value that would be closest to the true value E_0. The trial function corresponding to that value of $\overline{E}$ will be the best function.

Consider, for example, the wave function for particle in a box system. The true ground state wave function (ψ_0) and energy (E_0) are known to us; however, let us assume that we do not know these and proceed to devise a trial function.

For a one-dimensional box of length L, a reasonable guess would be

$$\psi = Nx\,(L-x) \tag{8-12}$$

as it is finite, continuous and single-valued for all values of x and is zero for $x=0$ and $x=L$; N is the normalisation factor. Then we calculate the energy,

APPROXIMATION METHODS

$$E = \frac{\int \psi \hat{H} \psi \, d\tau}{\int \psi^2 \, d\tau} = \frac{\int_0^L Nx\,(L-x)\left[-\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}\,[Nx\,(L-x)]\,dx\right]}{\int_0^L N^2 x^2 (L-x)^2 \, dx} \qquad (8\text{-}13)$$

$$= \frac{\frac{h^2}{4\pi^2 m}\int_0^L x\,(L-x)\,dx}{\int_0^L x^2 (L^2 - 2Lx + x^2)\,dx}$$

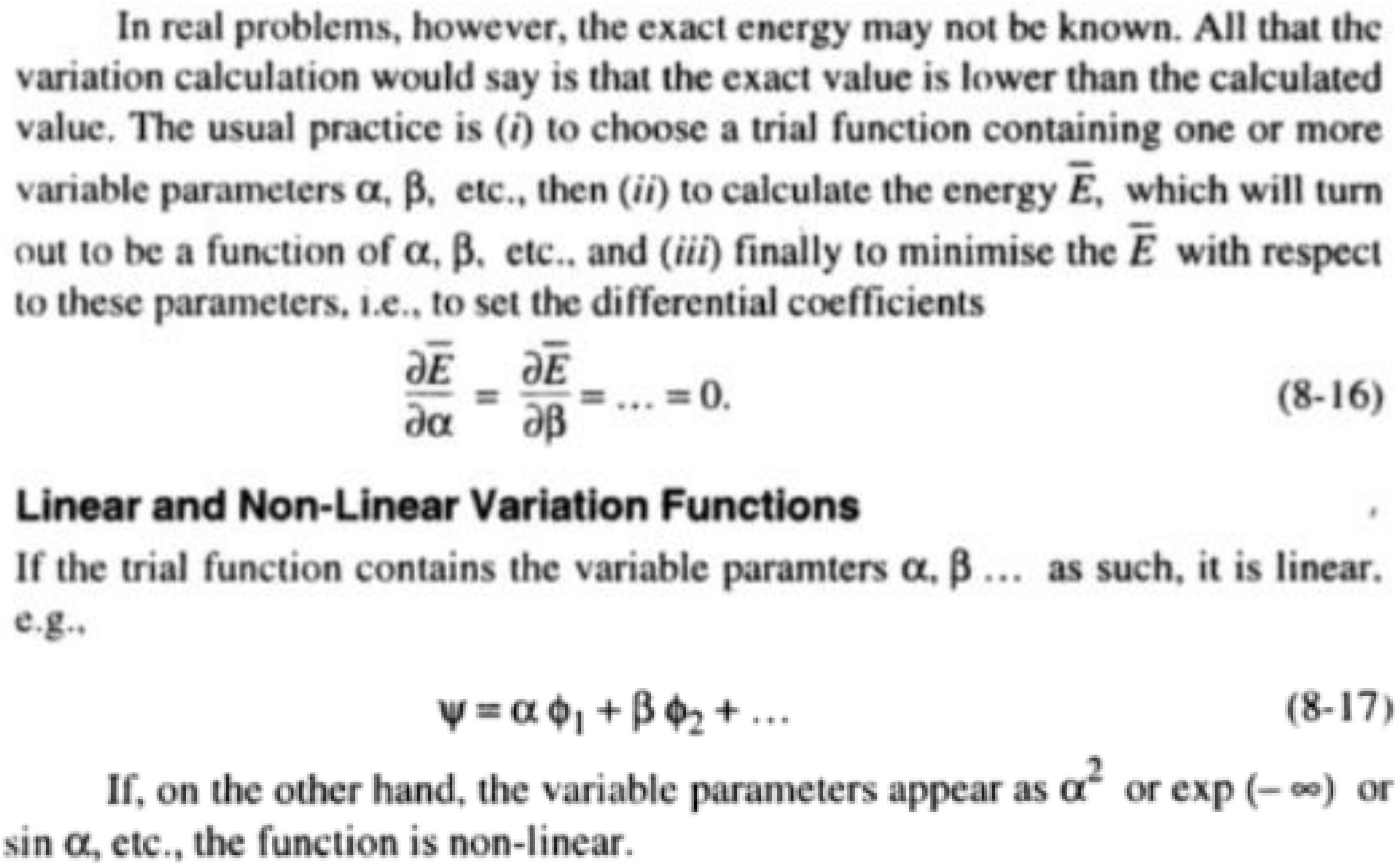
$$= \frac{\frac{h^2}{4\pi^2 m}\cdot\frac{L^3}{6}}{\frac{L^5}{30}} = \frac{5h^2}{4\pi^2 mL^2} = 0.12665\left(\frac{h^2}{mL^2}\right) \qquad (8\text{-}14)$$

The true ground state energy E is known to us to be,

$$E = \frac{h^2}{8mL^2} = 0.125\left(\frac{h^2}{mL^2}\right) \qquad (8\text{-}15)$$

The calculated energy E (8-14) given by the trial function (8-14) is greater than the true energy E (8-15) by 1.3%.

APPROXIMATION METHODS



In real problems, however, the exact energy may not be known. All that the variation calculation would say is that the exact value is lower than the calculated value. The usual practice is (*i*) to choose a trial function containing one or more variable parameters α, β, etc., then (*ii*) to calculate the energy $\overline{E}$, which will turn out to be a function of α, β, etc., and (*iii*) finally to minimise the $\overline{E}$ with respect to these parameters, i.e., to set the differential coefficients

$$\frac{\partial \overline{E}}{\partial \alpha} = \frac{\partial \overline{E}}{\partial \beta} = \ldots = 0. \qquad (8\text{-}16)$$

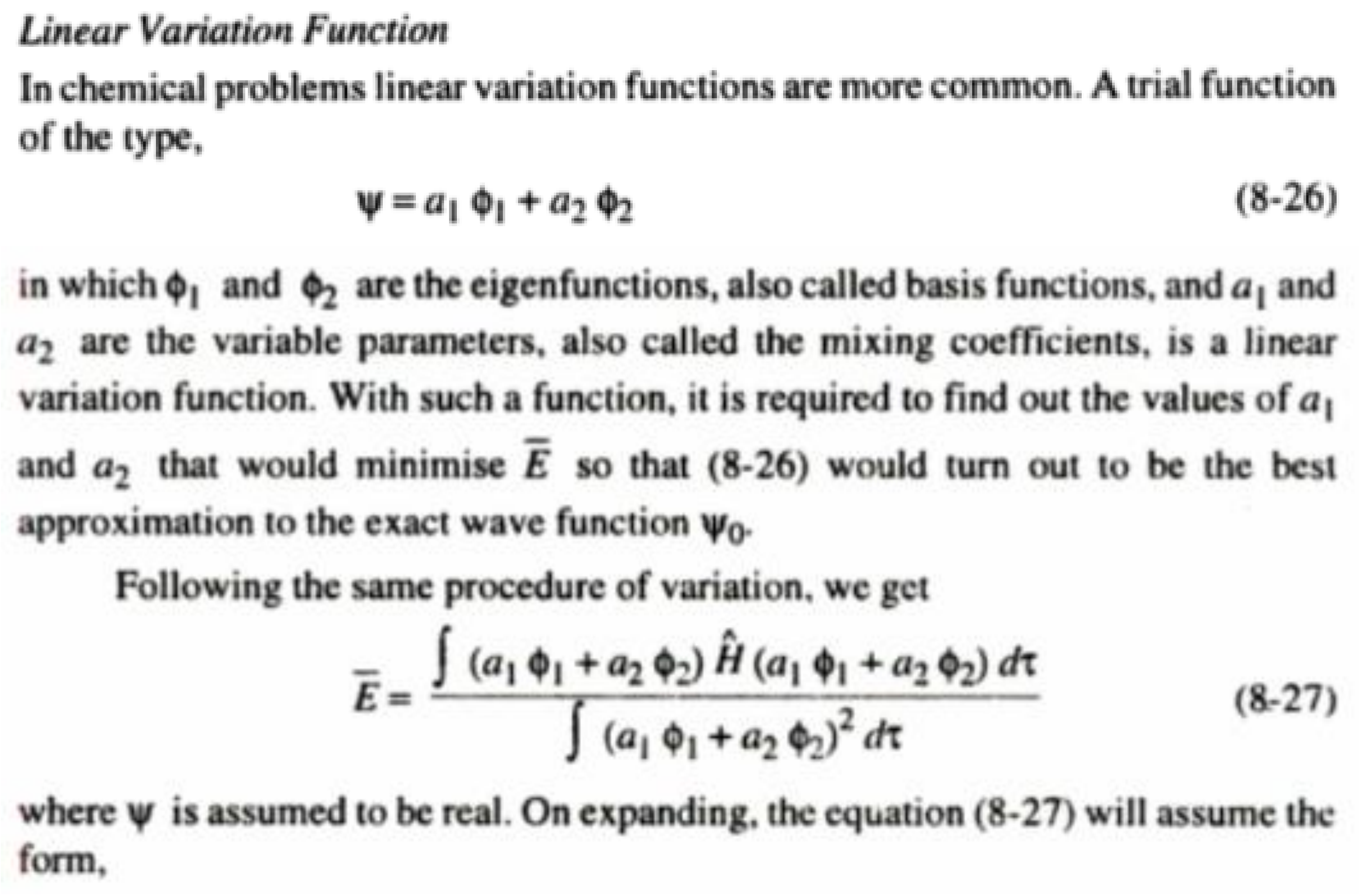
Linear and Non-Linear Variation Functions

If the trial function contains the variable paramters α, β … as such, it is linear. e.g.,

$$\psi = \alpha\,\phi_1 + \beta\,\phi_2 + \ldots \qquad (8\text{-}17)$$

If, on the other hand, the variable parameters appear as α^2 or $\exp(-\infty)$ or $\sin\alpha$, etc., the function is non-linear.

APPROXIMATION METHODS



Linear Variation Function

In chemical problems linear variation functions are more common. A trial function of the type,

$$\psi = a_1 \phi_1 + a_2 \phi_2 \qquad (8\text{-}26)$$

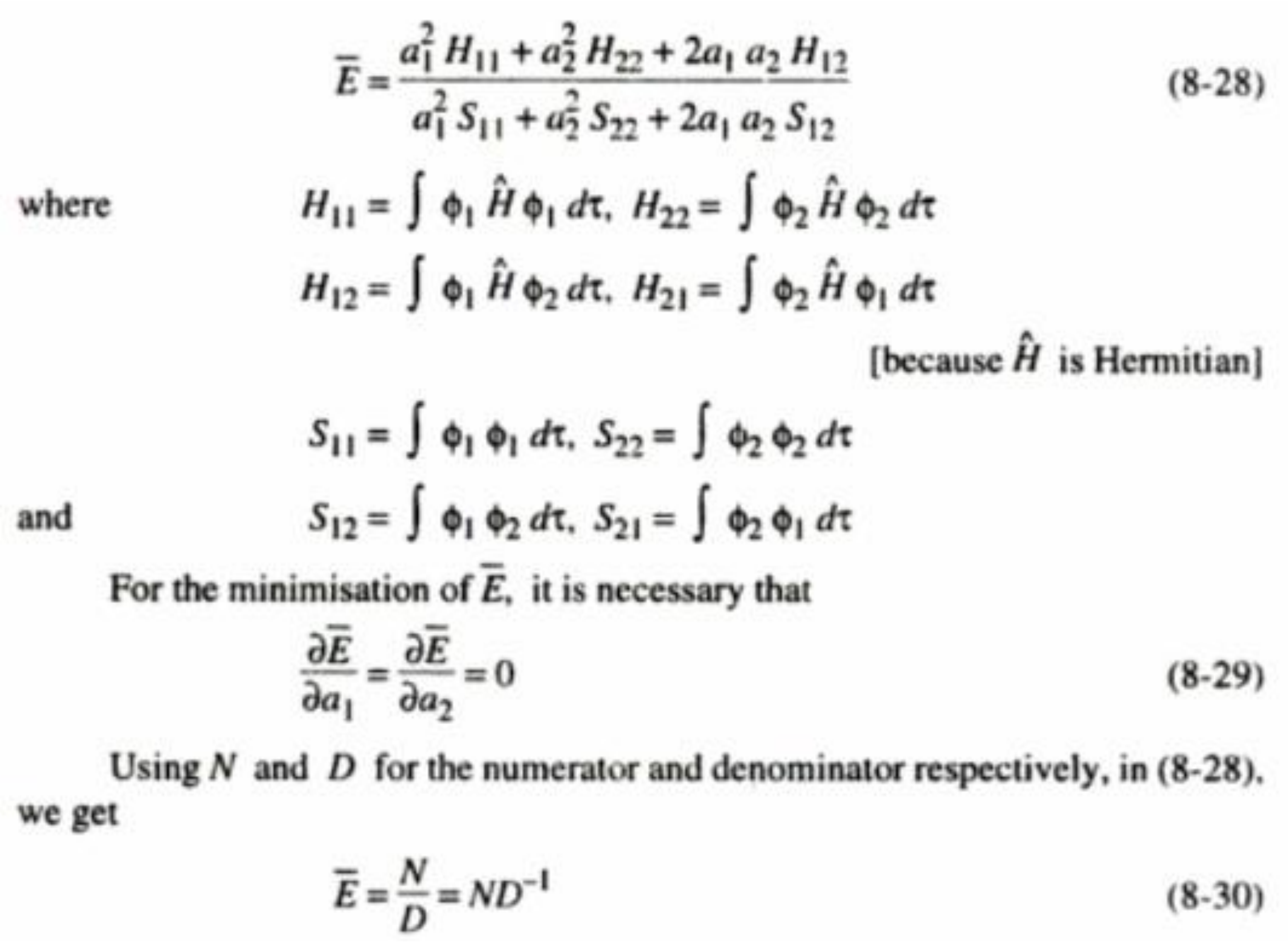
in which ϕ_1 and ϕ_2 are the eigenfunctions, also called basis functions, and a_1 and a_2 are the variable parameters, also called the mixing coefficients, is a linear variation function. With such a function, it is required to find out the values of a_1 and a_2 that would minimise $\overline{E}$ so that (8-26) would turn out to be the best approximation to the exact wave function ψ_0.

Following the same procedure of variation, we get

$$\overline{E} = \frac{\int (a_1 \phi_1 + a_2 \phi_2)\, \hat{H}\, (a_1 \phi_1 + a_2 \phi_2)\, d\tau}{\int (a_1 \phi_1 + a_2 \phi_2)^2\, d\tau} \qquad (8\text{-}27)$$

where ψ is assumed to be real. On expanding, the equation (8-27) will assume the form,

APPROXIMATION METHODS



$$\bar{E} = \frac{a_1^2 H_{11} + a_2^2 H_{22} + 2a_1 a_2 H_{12}}{a_1^2 S_{11} + a_2^2 S_{22} + 2a_1 a_2 S_{12}} \tag{8-28}$$

where
$$H_{11} = \int \phi_1 \hat{H} \phi_1 \, d\tau, \quad H_{22} = \int \phi_2 \hat{H} \phi_2 \, d\tau$$

$$H_{12} = \int \phi_1 \hat{H} \phi_2 \, d\tau, \quad H_{21} = \int \phi_2 \hat{H} \phi_1 \, d\tau$$

[because $\hat{H}$ is Hermitian]

$$S_{11} = \int \phi_1 \phi_1 \, d\tau, \quad S_{22} = \int \phi_2 \phi_2 \, d\tau$$

and
$$S_{12} = \int \phi_1 \phi_2 \, d\tau, \quad S_{21} = \int \phi_2 \phi_1 \, d\tau$$

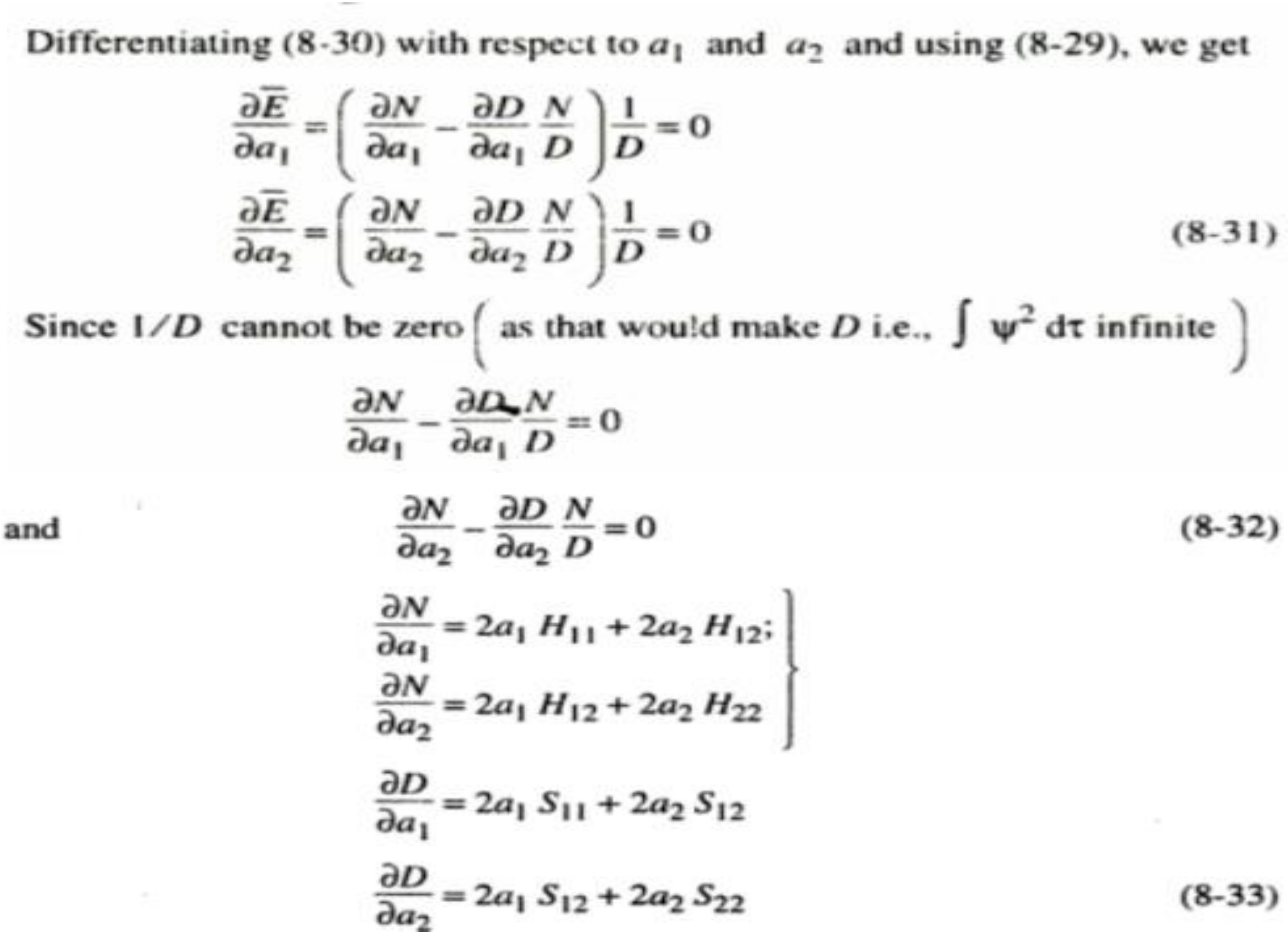
For the minimisation of $\bar{E}$, it is necessary that

$$\frac{\partial \bar{E}}{\partial a_1} = \frac{\partial \bar{E}}{\partial a_2} = 0 \tag{8-29}$$

Using N and D for the numerator and denominator respectively, in (8-28), we get

$$\bar{E} = \frac{N}{D} = ND^{-1} \tag{8-30}$$

APPROXIMATION METHODS



Differentiating (8-30) with respect to a_1 and a_2 and using (8-29), we get

$$\frac{\partial \bar{E}}{\partial a_1} = \left(\frac{\partial N}{\partial a_1} - \frac{\partial D}{\partial a_1} \frac{N}{D} \right) \frac{1}{D} = 0$$

$$\frac{\partial \bar{E}}{\partial a_2} = \left(\frac{\partial N}{\partial a_2} - \frac{\partial D}{\partial a_2} \frac{N}{D} \right) \frac{1}{D} = 0 \qquad (8\text{-}31)$$

Since $1/D$ cannot be zero $\left(\text{as that would make } D \text{ i.e., } \int \psi^2 \, d\tau \text{ infinite} \right)$

$$\frac{\partial N}{\partial a_1} - \frac{\partial D}{\partial a_1} \frac{N}{D} = 0$$

and

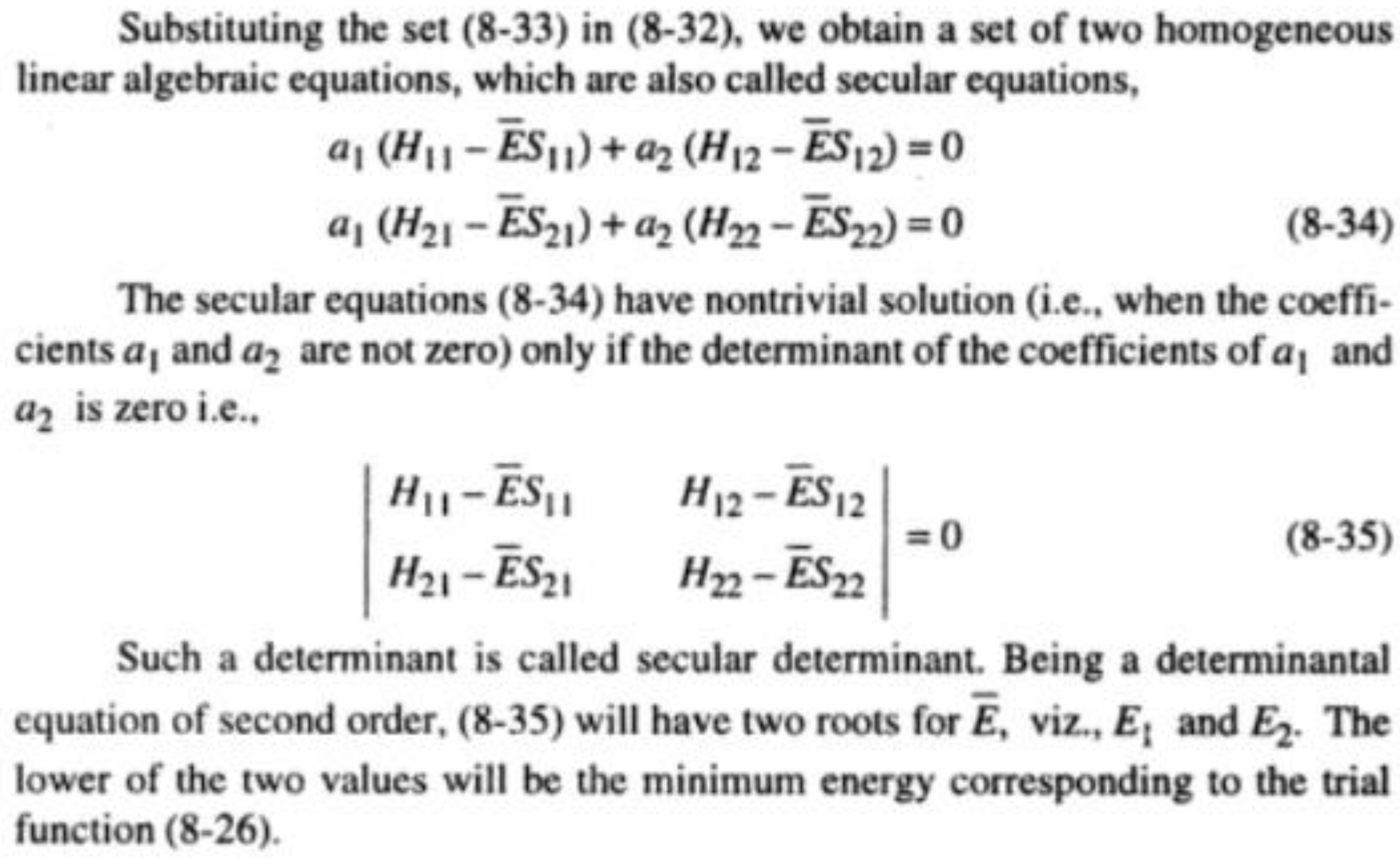
$$\frac{\partial N}{\partial a_2} - \frac{\partial D}{\partial a_2} \frac{N}{D} = 0 \qquad (8\text{-}32)$$

$$\left. \begin{aligned} \frac{\partial N}{\partial a_1} &= 2a_1 H_{11} + 2a_2 H_{12}; \\ \frac{\partial N}{\partial a_2} &= 2a_1 H_{12} + 2a_2 H_{22} \end{aligned} \right\}$$

$$\frac{\partial D}{\partial a_1} = 2a_1 S_{11} + 2a_2 S_{12}$$

$$\frac{\partial D}{\partial a_2} = 2a_1 S_{12} + 2a_2 S_{22} \qquad (8\text{-}33)$$

APPROXIMATION METHODS



Substituting the set (8-33) in (8-32), we obtain a set of two homogeneous linear algebraic equations, which are also called secular equations,

$$a_1 (H_{11} - \bar{E}S_{11}) + a_2 (H_{12} - \bar{E}S_{12}) = 0$$

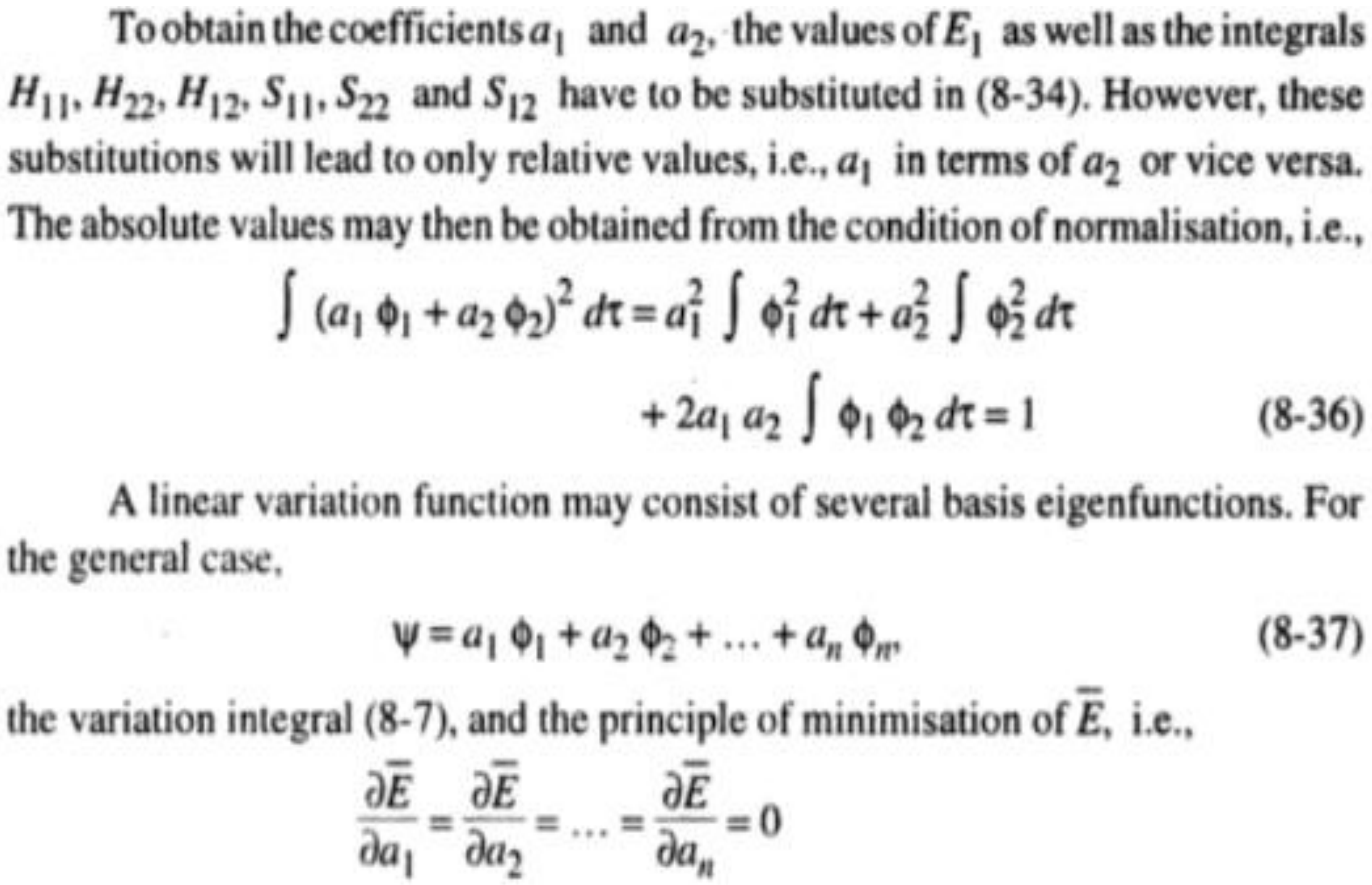
$$a_1 (H_{21} - \bar{E}S_{21}) + a_2 (H_{22} - \bar{E}S_{22}) = 0 \qquad (8\text{-}34)$$

The secular equations (8-34) have nontrivial solution (i.e., when the coefficients a_1 and a_2 are not zero) only if the determinant of the coefficients of a_1 and a_2 is zero i.e.,

$$\begin{vmatrix} H_{11} - \bar{E}S_{11} & H_{12} - \bar{E}S_{12} \\ H_{21} - \bar{E}S_{21} & H_{22} - \bar{E}S_{22} \end{vmatrix} = 0 \qquad (8\text{-}35)$$

Such a determinant is called secular determinant. Being a determinantal equation of second order, (8-35) will have two roots for $\bar{E}$, viz., E_1 and E_2. The lower of the two values will be the minimum energy corresponding to the trial function (8-26).

APPROXIMATION METHODS



To obtain the coefficients a_1 and a_2, the values of E_1 as well as the integrals $H_{11}, H_{22}, H_{12}, S_{11}, S_{22}$ and S_{12} have to be substituted in (8-34). However, these substitutions will lead to only relative values, i.e., a_1 in terms of a_2 or vice versa. The absolute values may then be obtained from the condition of normalisation, i.e.,

$$\int (a_1 \phi_1 + a_2 \phi_2)^2 \, d\tau = a_1^2 \int \phi_1^2 \, d\tau + a_2^2 \int \phi_2^2 \, d\tau + 2a_1 a_2 \int \phi_1 \phi_2 \, d\tau = 1 \qquad (8\text{-}36)$$

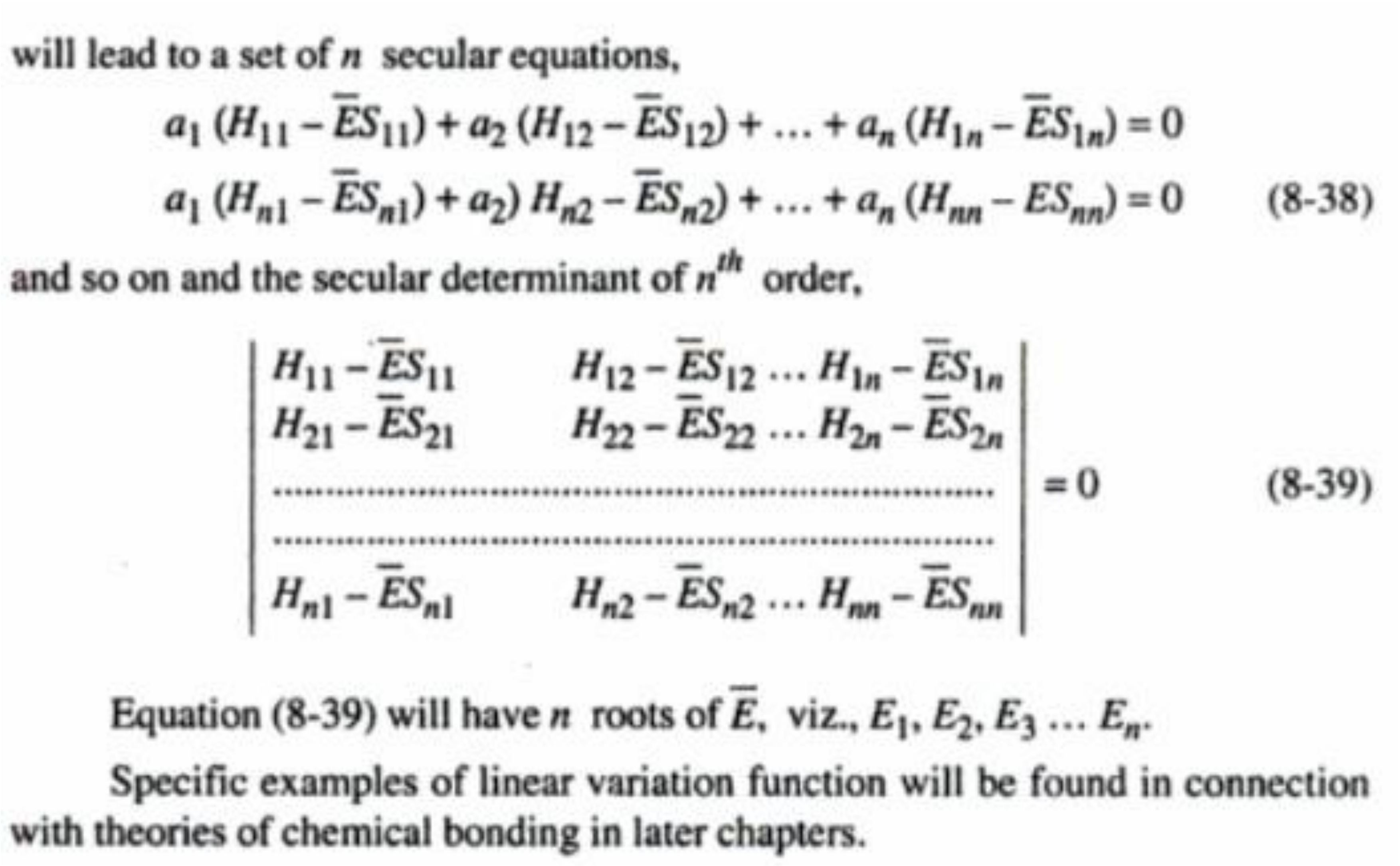
A linear variation function may consist of several basis eigenfunctions. For the general case,

$$\psi = a_1 \phi_1 + a_2 \phi_2 + \ldots + a_n \phi_n, \qquad (8\text{-}37)$$

the variation integral (8-7), and the principle of minimisation of $\bar{E}$, i.e.,

$$\frac{\partial \bar{E}}{\partial a_1} = \frac{\partial \bar{E}}{\partial a_2} = \ldots = \frac{\partial \bar{E}}{\partial a_n} = 0$$

APPROXIMATION METHODS



will lead to a set of n secular equations,

$$a_1\,(H_{11}-\overline{E}S_{11})+a_2\,(H_{12}-\overline{E}S_{12})+\ldots+a_n\,(H_{1n}-\overline{E}S_{1n})=0$$

$$a_1\,(H_{n1}-\overline{E}S_{n1})+a_2)\,H_{n2}-\overline{E}S_{n2})+\ldots+a_n\,(H_{nn}-ES_{nn})=0 \qquad (8\text{-}38)$$

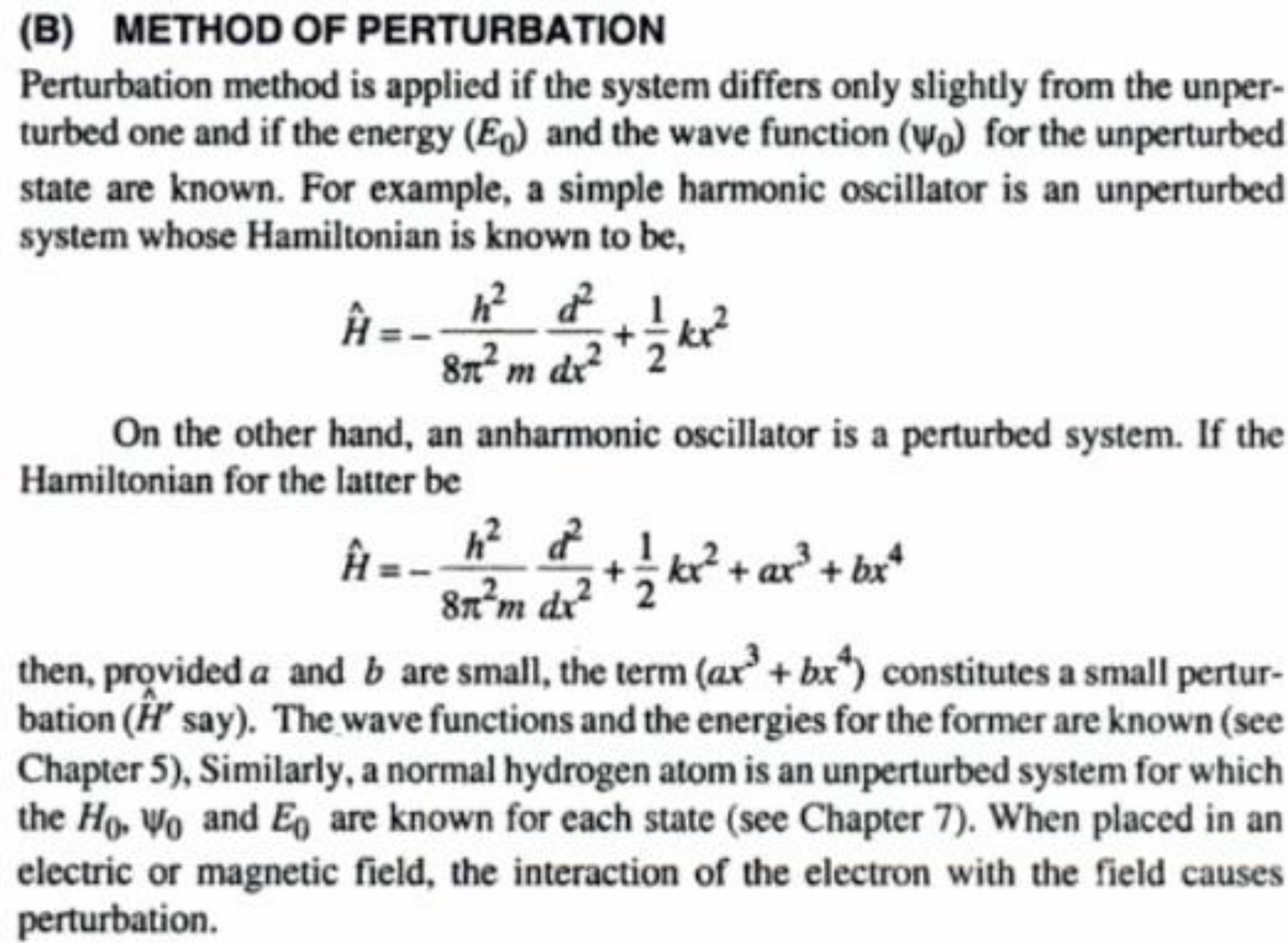
and so on and the secular determinant of n^{th} order,

$$\begin{vmatrix} H_{11}-\overline{E}S_{11} & H_{12}-\overline{E}S_{12}\ \ldots\ H_{1n}-\overline{E}S_{1n} \\ H_{21}-\overline{E}S_{21} & H_{22}-\overline{E}S_{22}\ \ldots\ H_{2n}-\overline{E}S_{2n} \\ \cdots\cdots\cdots\cdots & \cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots & \cdots\cdots\cdots\cdots \\ H_{n1}-\overline{E}S_{n1} & H_{n2}-\overline{E}S_{n2}\ \ldots\ H_{nn}-\overline{E}S_{nn} \end{vmatrix}=0 \qquad (8\text{-}39)$$

Equation (8-39) will have n roots of $\overline{E}$, viz., $E_1, E_2, E_3 \ldots E_n$.

Specific examples of linear variation function will be found in connection with theories of chemical bonding in later chapters.

APPROXIMATION METHODS



(B) METHOD OF PERTURBATION

Perturbation method is applied if the system differs only slightly from the unperturbed one and if the energy (E_0) and the wave function (ψ_0) for the unperturbed state are known. For example, a simple harmonic oscillator is an unperturbed system whose Hamiltonian is known to be,

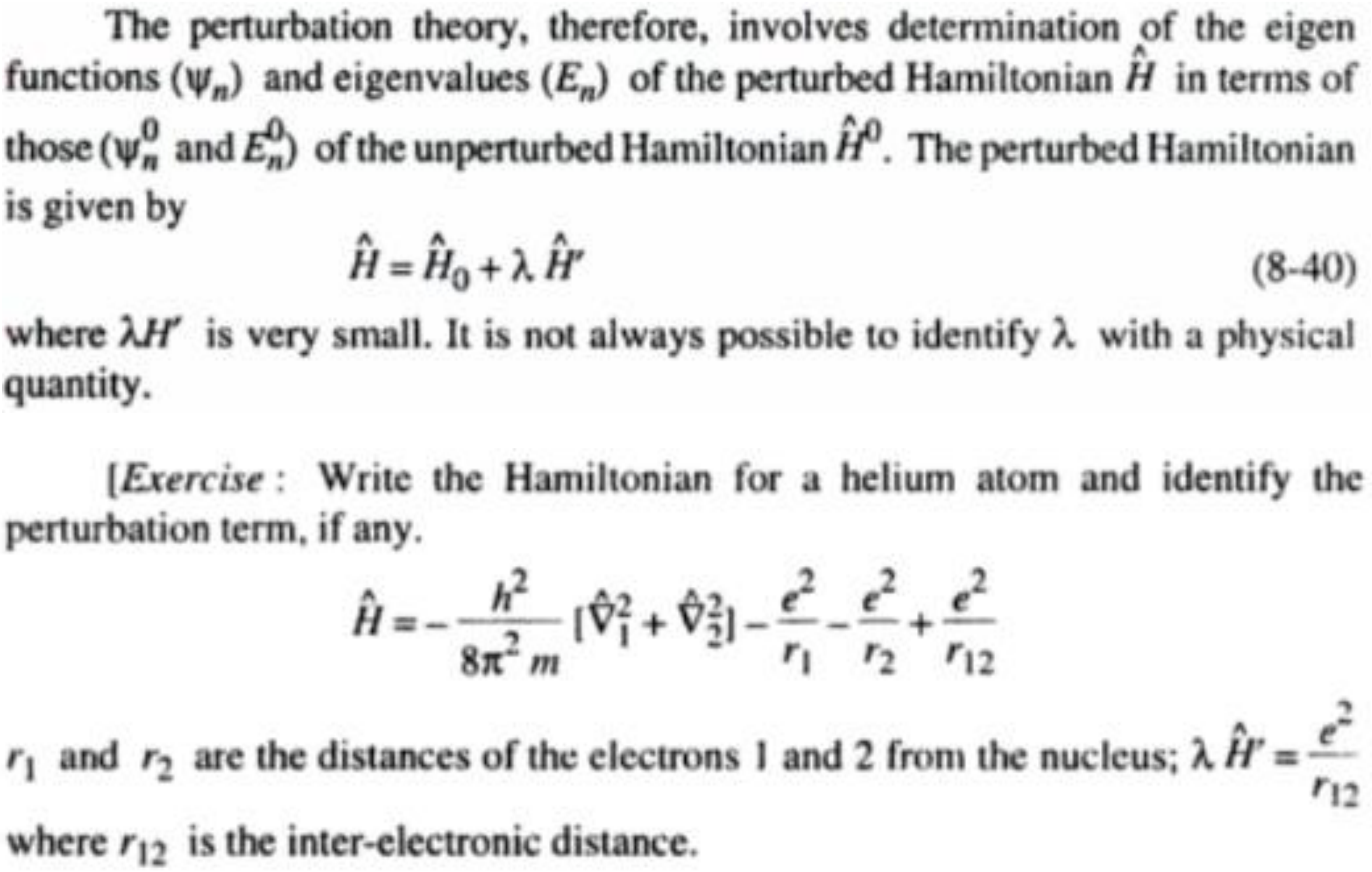
$$\hat{H} = -\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

On the other hand, an anharmonic oscillator is a perturbed system. If the Hamiltonian for the latter be

$$\hat{H} = -\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + ax^3 + bx^4$$

then, provided a and b are small, the term $(ax^3 + bx^4)$ constitutes a small perturbation ($\hat{H}'$ say). The wave functions and the energies for the former are known (see Chapter 5), Similarly, a normal hydrogen atom is an unperturbed system for which the H_0, ψ_0 and E_0 are known for each state (see Chapter 7). When placed in an electric or magnetic field, the interaction of the electron with the field causes perturbation.

APPROXIMATION METHODS



The perturbation theory, therefore, involves determination of the eigen functions (ψ_n) and eigenvalues (E_n) of the perturbed Hamiltonian $\hat{H}$ in terms of those (ψ_n^0 and E_n^0) of the unperturbed Hamiltonian $\hat{H}^0$. The perturbed Hamiltonian is given by

$$\hat{H} = \hat{H}_0 + \lambda\,\hat{H}' \qquad (8\text{-}40)$$

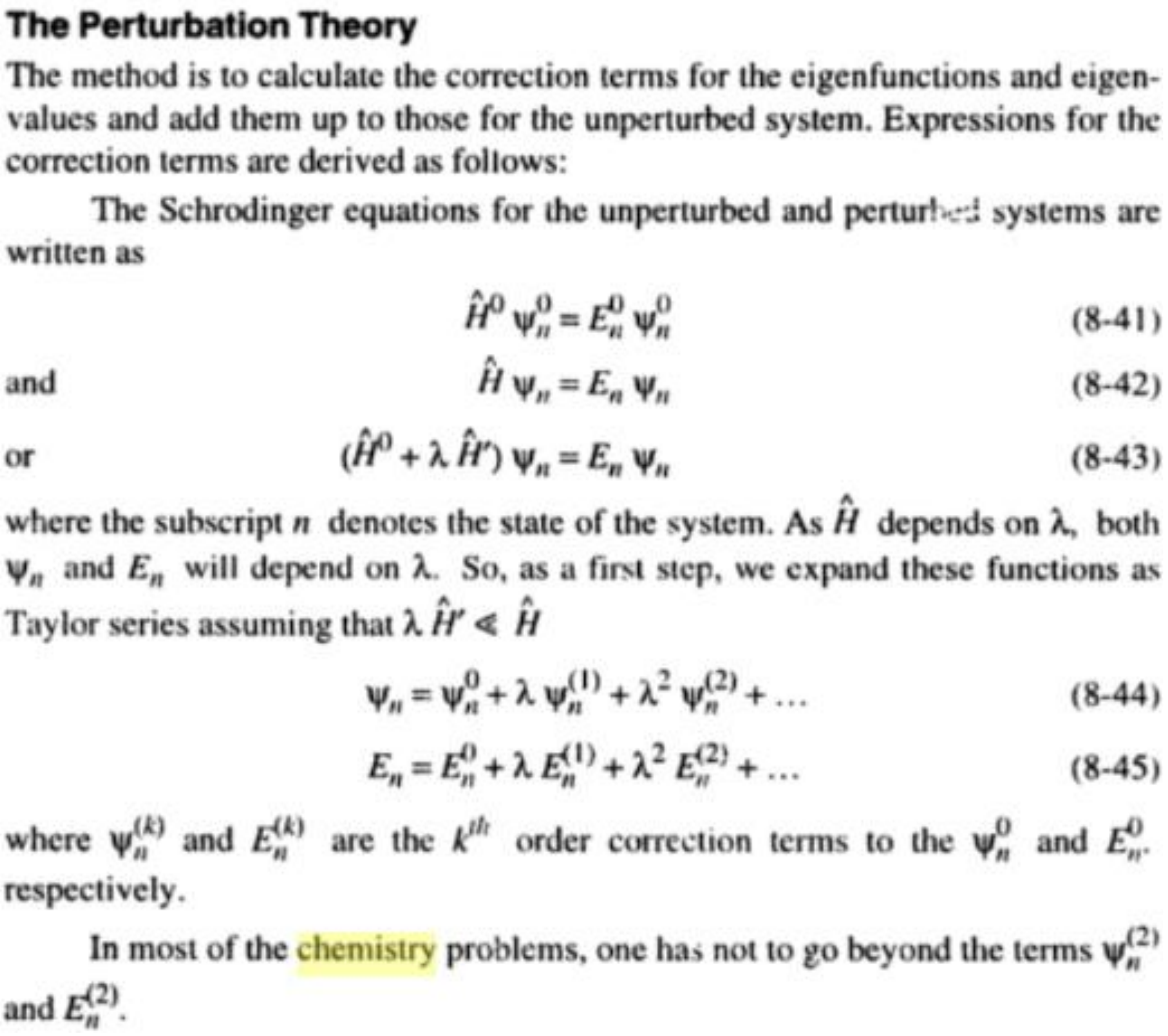
where $\lambda H'$ is very small. It is not always possible to identify λ with a physical quantity.

[*Exercise* : Write the Hamiltonian for a helium atom and identify the perturbation term, if any.

$$\hat{H} = -\frac{h^2}{8\pi^2 m}[\hat{\nabla}_1^2 + \hat{\nabla}_2^2] - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{r_{12}}$$

r_1 and r_2 are the distances of the electrons 1 and 2 from the nucleus; $\lambda\,\hat{H}' = \dfrac{e^2}{r_{12}}$ where r_{12} is the inter-electronic distance.

APPROXIMATION METHODS



The Perturbation Theory

The method is to calculate the correction terms for the eigenfunctions and eigenvalues and add them up to those for the unperturbed system. Expressions for the correction terms are derived as follows:

The Schrodinger equations for the unperturbed and perturbed systems are written as

$$\hat{H}^0 \psi_n^0 = E_n^0 \psi_n^0 \tag{8-41}$$

and

$$\hat{H} \psi_n = E_n \psi_n \tag{8-42}$$

or

$$(\hat{H}^0 + \lambda \hat{H}') \psi_n = E_n \psi_n \tag{8-43}$$

where the subscript n denotes the state of the system. As $\hat{H}$ depends on λ, both ψ_n and E_n will depend on λ. So, as a first step, we expand these functions as Taylor series assuming that $\lambda \hat{H}' \ll \hat{H}$

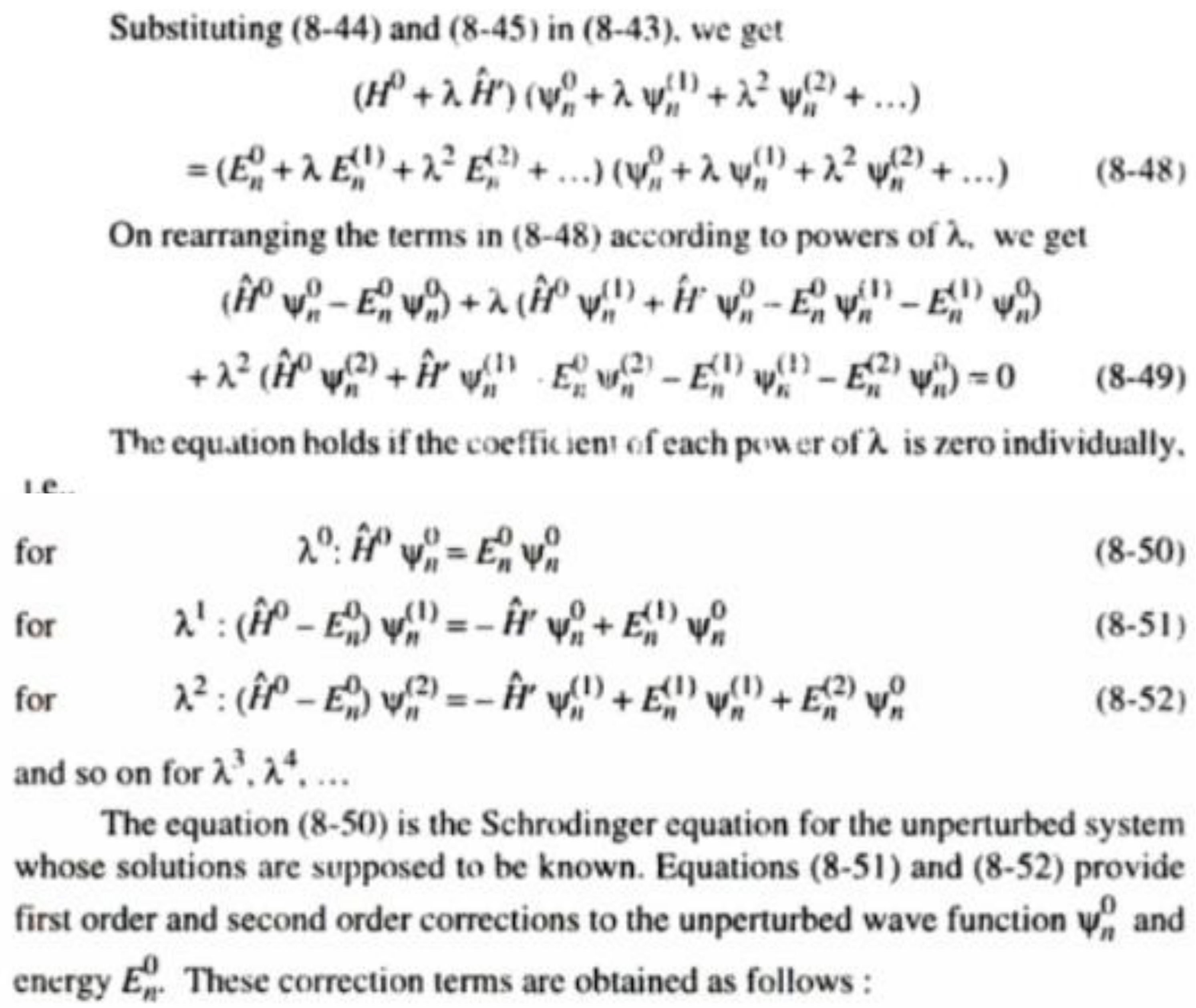
$$\psi_n = \psi_n^0 + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \ldots \tag{8-44}$$

$$E_n = E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots \tag{8-45}$$

where $\psi_n^{(k)}$ and $E_n^{(k)}$ are the k^{th} order correction terms to the ψ_n^0 and E_n^0, respectively.

In most of the chemistry problems, one has not to go beyond the terms $\psi_n^{(2)}$ and $E_n^{(2)}$.

APPROXIMATION METHODS



Substituting (8-44) and (8-45) in (8-43), we get

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

$$= (E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots)(\psi_n^0 + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \ldots) \qquad (8\text{-}48)$$

On rearranging the terms in (8-48) according to powers of λ, we get

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

$$+ \lambda^2 (\hat{H}^0 \psi_n^{(2)} + \hat{H}' \psi_n^{(1)} - E_n^0 \psi_n^{(2)} - E_n^{(1)} \psi_n^{(1)} - E_n^{(2)} \psi_n^0) = 0 \qquad (8\text{-}49)$$

The equation holds if the coefficient of each power of λ is zero individually, i.e.,

for $\lambda^0 : \hat{H}^0 \psi_n^0 = E_n^0 \psi_n^0$ (8-50)

for $\lambda^1 : (\hat{H}^0 - E_n^0)\psi_n^{(1)} = -\hat{H}' \psi_n^0 + E_n^{(1)} \psi_n^0$ (8-51)

for $\lambda^2 : (\hat{H}^0 - E_n^0)\psi_n^{(2)} = -\hat{H}' \psi_n^{(1)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(2)} \psi_n^0$ (8-52)

and so on for $\lambda^3, \lambda^4, \ldots$

The equation (8-50) is the Schrodinger equation for the unperturbed system whose solutions are supposed to be known. Equations (8-51) and (8-52) provide first order and second order corrections to the unperturbed wave function ψ_n^0 and energy E_n^0. These correction terms are obtained as follows :

APPROXIMATION METHODS

Correction to Energy and wavefunction

- ✓ Multiplying both sides of (8-51) by ψ_n^0 and integration results

$$\int \psi_n^0 \widehat{H}^0 \psi_n^{(1)} d\tau - E_n^0 \int \psi_n^0 \psi_n^{(1)} d\tau = -\int \psi_n^0 \widehat{H}' \psi_n^0 d\tau + E_n^{(1)} \int \psi_n^0 \psi_n^0 d\tau \qquad (8\text{-}53)$$

- ✓ Hermitian property of $\widehat{H}^0$ $\left[\int \psi_n^0 \widehat{H}^0 \psi_n^{(1)} d\tau = \int \psi_n^{(1)} \widehat{H}^0 \psi_n^0 d\tau = E_n^0 \int \psi_n^0 \psi_n^{(1)} d\tau\right]$

  reduces (8-53) to

$$\underbrace{E_n^0 \int \psi_n^0 \psi_n^{(1)} d\tau - E_n^0 \int \psi_n^0 \psi_n^{(1)} d\tau}_{0} = -\int \psi_m^0 \widehat{H}' \psi_n^0 d\tau + E_n^{(1)} \underbrace{\int \psi_n^0 \psi_n^0 d\tau}_{1}$$

$$\Longrightarrow 0 = -\int \psi_m^0 \widehat{H}' \psi_n^0 d\tau + E_n^{(1)} \Rightarrow E_n^{(1)} = \int \psi_n^0 \widehat{H}' \psi_n^0 d\tau = H'_{nn}$$

$$E_n^{(1)} = H'_{nn} \qquad (8\text{-}54)$$

APPROXIMATION METHODS

Correction to wavefunction

- Multiplying both sides of (8-51) by ψ_m^0 and integration results

$$\int \psi_m^0 \hat{H}^0 \psi_n^{(1)} d\tau - E_n^0 \int \psi_m^0 \psi_n^{(1)} d\tau = -\int \psi_m^0 \hat{H}' \psi_n^0 d\tau + E_n^{(1)} \int \psi_m^0 \psi_n^0 d\tau \qquad (8\text{-}55)$$

- Hermitian property of $\hat{H}^0$ $\left[\int \psi_m^0 \hat{H}^0 \psi_n^{(1)} d\tau = \int \psi_n^{(1)} \hat{H}^0 \psi_m^0 d\tau = E_m^0 \int \psi_m^0 \psi_n^{(1)} d\tau\right]$ reduces (8-55) to

$$E_m^0 \int \psi_m^0 \psi_n^{(1)} d\tau - E_n^0 \int \psi_m^0 \psi_n^{(1)} d\tau = -\int \psi_m^0 \hat{H}' \psi_n^0 d\tau + E_n^{(1)} \int \psi_m^0 \psi_n^0 d\tau$$

$$\Rightarrow (E_m^0 - E_n^0) \int \psi_m^0 \psi_n^{(1)} d\tau = -\int \psi_m^0 \hat{H}' \psi_n^0 d\tau + E_n^{(1)} \underbrace{\int \psi_m^0 \psi_n^0 d\tau}_{0}$$

$$\Rightarrow (E_m^0 - E_n^0) \int \psi_m^0 \psi_n^{(1)} d\tau = -\int \psi_m^0 \hat{H}' \psi_n^0 d\tau$$

$$\Rightarrow \int \psi_m^0 \psi_n^{(1)} d\tau = \frac{\int \psi_m^0 \hat{H}' \psi_n^0 d\tau}{(E_n^0 - E_m^0)} \qquad (8\text{-}56)$$

APPROXIMATION METHODS

Correction to Energy and wavefunction

- ✓ Now $\psi_n^{(1)}$ can be evaluated through linear combination of unperturbed wavefunctions of different states,

$$\psi_n^{(1)} = a_{1n}\psi_1^0 + a_{2n}\psi_2^0 + \cdots + a_{nn}\psi_n^0 + \cdots + a_{mn}\psi_m^0 \qquad (8\text{-}57)$$

Multiplying both sides of (8-57) by ψ_m^0 and integration give

$$\int \psi_m^0\psi_n^{(1)}d\tau = a_{1n}\underbrace{\int \psi_m^0\psi_1^0 d\tau}_{0} + a_{2n}\underbrace{\int \psi_m^0\psi_2^0 d\tau}_{0} + \cdots + a_{mn}\underbrace{\int \psi_m^0\psi_m^0 d\tau}_{1}$$

$$a_{mn} = \int \psi_m^0\psi_n^{(1)}d\tau = \frac{\int \psi_m^0\hat{H}'\psi_n^0 d\tau}{(E_n^0 - E_m^0)}$$

Similarly

$$a_{1n} = \frac{\int \psi_1^0\hat{H}'\psi_n^0 d\tau}{(E_n^0 - E_1^0)},\quad a_{2n} = \frac{\int \psi_2^0\hat{H}'\psi_n^0 d\tau}{(E_n^0 - E_2^0)},\ a_{3n} = \frac{\int \psi_3^0\hat{H}'\psi_n^0 d\tau}{(E_n^0 - E_3^0)},\ \cdots \qquad a_{nn} = ?$$

APPROXIMATION METHODS

Correction to Energy and wavefunction

- ✓ Now $\psi_n^{(1)} = ?$

$$\psi_n^{(1)} = \underbrace{a_{1n}}_{?}\psi_1^0 + \underbrace{a_{2n}}_{?}\psi_2^0 + \cdots + \underbrace{a_{nn}}_{?}\psi_n^0 + \cdots + \underbrace{a_{mn}}_{?}\psi_m^0 \quad (8\text{-}53)$$

$$a_{1n} = \frac{\int \psi_1^0 \hat{H}' \psi_n^0 d\tau}{(E_n^0 - E_1^0)} \quad (8\text{-}54)$$

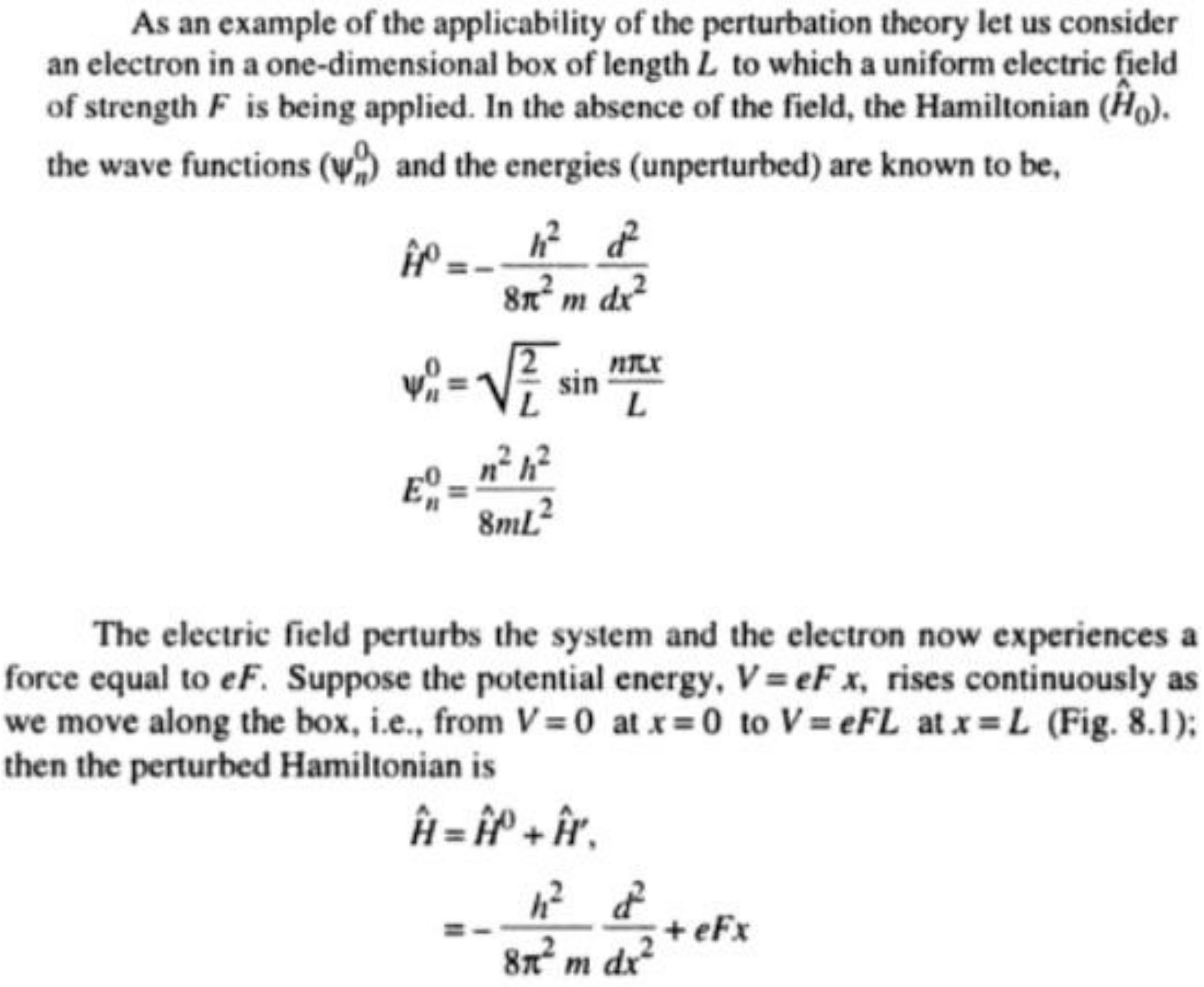
$$a_{2n} = \frac{\int \psi_2^0 \hat{H}' \psi_n^0 d\tau}{(E_n^0 - E_2^0)}$$

$$\cdots$$

$$a_{nn} = ?$$

$$a_{mn} = \frac{\int \psi_m^0 \hat{H}' \psi_n^0 d\tau}{(E_n^0 - E_m^0)}$$

APPROXIMATION METHODS



As an example of the applicability of the perturbation theory let us consider an electron in a one-dimensional box of length L to which a uniform electric field of strength F is being applied. In the absence of the field, the Hamiltonian $(\hat{H}_0)$, the wave functions (ψ_n^0) and the energies (unperturbed) are known to be,

$$\hat{H}^0 = -\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}$$

$$\psi_n^0 = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$$

$$E_n^0 = \frac{n^2 h^2}{8mL^2}$$

The electric field perturbs the system and the electron now experiences a force equal to eF. Suppose the potential energy, $V = eF\,x$, rises continuously as we move along the box, i.e., from $V = 0$ at $x = 0$ to $V = eFL$ at $x = L$ (Fig. 8.1); then the perturbed Hamiltonian is

$$\hat{H} = \hat{H}^0 + \hat{H}',$$

$$= -\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2} + eFx$$

APPROXIMATION METHODS

$$E_1^0 = \frac{h^2}{8mL^2}$$

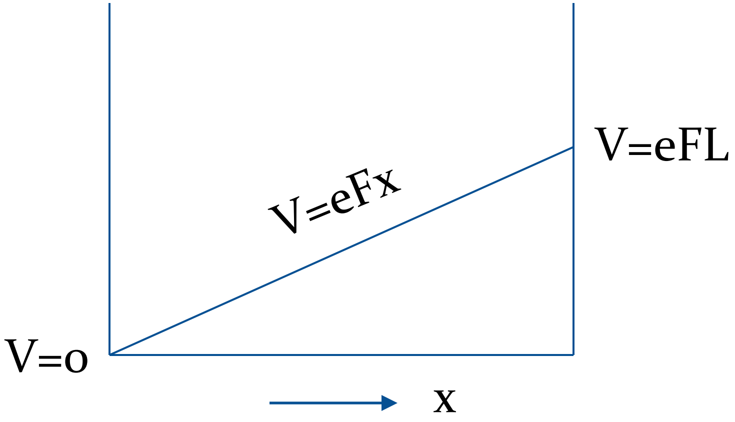
$$E_1^{(1)} = \int_0^L \psi_1^0 H' \psi_1^0 \, d\tau$$

$$= \frac{2}{L} \int_0^L \left[\sin\frac{\pi x}{L} (eFx) \sin\frac{\pi x}{L} \right] dx$$

$$= \frac{2eF}{L} \int_0^L x \sin^2\frac{\pi x}{L} \, dx$$

$$E_1^{(1)} = \frac{2eFL}{\pi^2} \frac{\pi^2}{4} = \frac{eFL}{2}$$

$$E_1 = E_1^0 + E_1^{(1)} = \frac{h^2}{8mL^2} + \frac{eFL}{2}$$



APPROXIMATION METHODS

Correction to the wave function

Correction $\psi_1^{(1)}$ to the ground state wave function ψ_1^0 is calculated as follows:

Using (8.61), we get

$$\psi_1^{(1)} = \sum_{m \neq 1} \frac{\int \psi_m^0 \, \hat{H}' \, \psi_1^0 \, d\tau}{E_1^0 - E_m^0} \psi_m^0$$

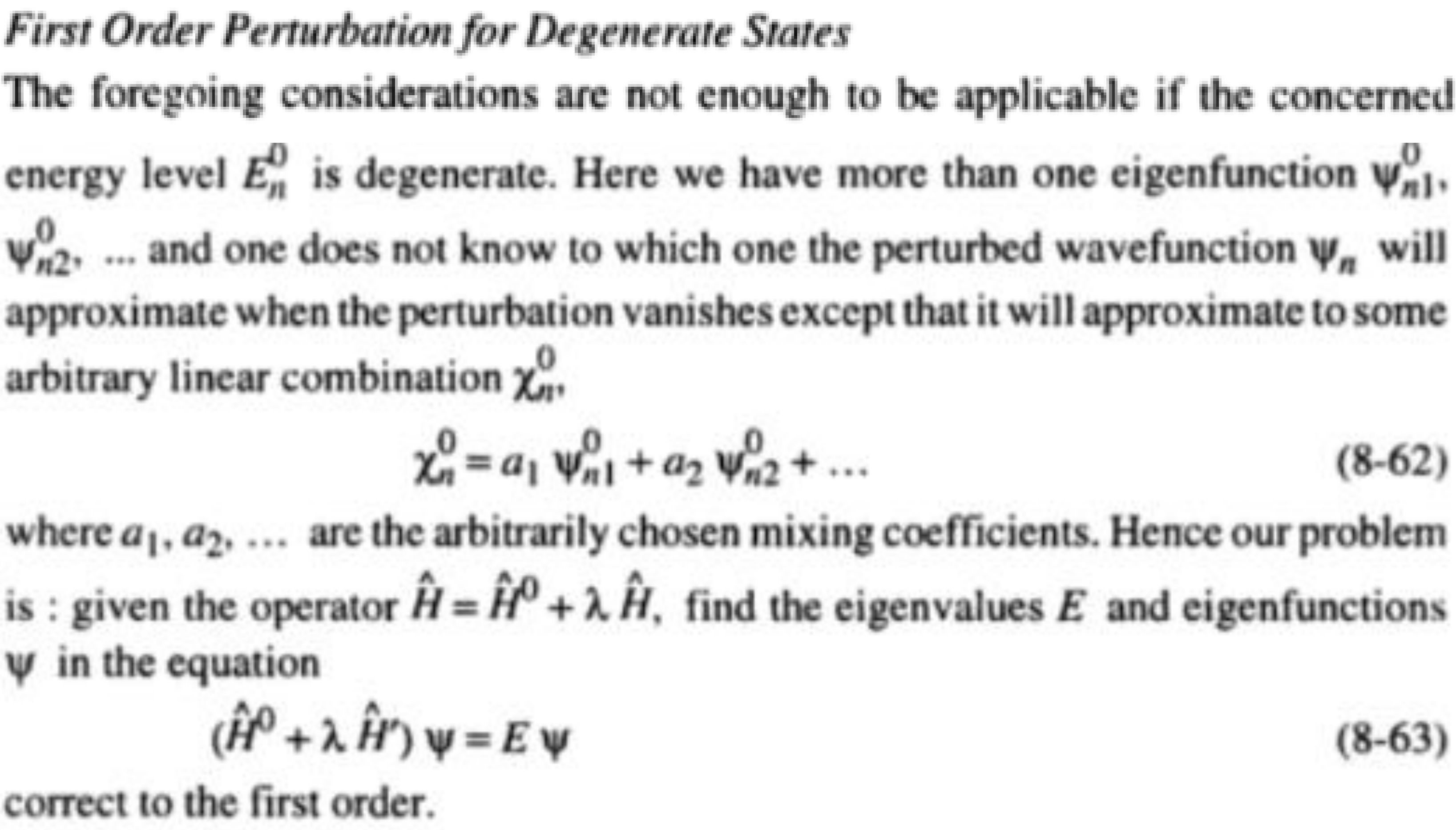
$$= \left[\frac{\int \psi_2^0 \, \hat{H}' \, \psi_1^0 \, d\tau}{E_1^0 - E_2^0} \psi_2^0 + \frac{\int \psi_3^0 \, \hat{H}' \, \psi_1^0 \, d\tau}{E_1^0 - E_3^0} \psi_3^0 + \frac{\int \psi_4^0 \, \hat{H}' \, \psi_1^0 \, d\tau}{E_1^0 - E_4^0} \psi_4^0 + \ldots \right]$$

First term within the brackets in the above equation is,

$$\frac{\int \psi_2^0 \, \hat{H}' \, \psi_1^0 \, d\tau}{E_1^0 - E_2^0} \psi_2^0 = \frac{\int_0^L \sqrt{\frac{2}{L}} \sin \frac{2\pi x}{L} (eFx) \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L} \, dx}{-\left(\frac{3h^2}{8mL^2} \right)} \psi_2^0 = \frac{\frac{2eF}{L} \int_0^L \sin \frac{2\pi x}{L} \sin \frac{\pi x}{L} \, x \, dx}{-\left(\frac{3h^2}{8mL^2} \right)} \psi_2^0$$

$$\psi_1 = \psi_1^0 + 0.48 \, (eFL) \left(\frac{mL^2}{h^2} \right) \psi_2^0.$$

APPROXIMATION METHODS



First Order Perturbation for Degenerate States

The foregoing considerations are not enough to be applicable if the concerned energy level E_n^0 is degenerate. Here we have more than one eigenfunction ψ_{n1}^0, ψ_{n2}^0, ... and one does not know to which one the perturbed wavefunction ψ_n will approximate when the perturbation vanishes except that it will approximate to some arbitrary linear combination χ_n^0,

$$\chi_n^0 = a_1\,\psi_{n1}^0 + a_2\,\psi_{n2}^0 + \ldots \tag{8-62}$$

where $a_1, a_2, \ldots$ are the arbitrarily chosen mixing coefficients. Hence our problem is : given the operator $\hat{H} = \hat{H}^0 + \lambda\,\hat{H}$, find the eigenvalues E and eigenfunctions ψ in the equation

$$(\hat{H}^0 + \lambda\,\hat{H}')\,\psi = E\,\psi \tag{8-63}$$

correct to the first order.

APPROXIMATION METHODS

It is convenient to take a simple case of 2-fold degenerate level E_n^0 with ψ_{n1}^0 and ψ_{n2}^0 as the two eigenfunctions in the unperturbed state. Both are orthogonal to all other eigenfunctions ψ^0 but not necessarily orthogonal to each other. As before, we expand

$$E_n = E_n^0 + \lambda E_n^{(1)} + \ldots \tag{8-64}$$

$$\psi_n = x_n^0 + \lambda \psi_n^{(1)} + \ldots \tag{8-65}$$

As the perturbation $\lambda \hat{H}'$ becomes smaller and smaller, $E_n \rightarrow E_n^0$ while $\psi_n \rightarrow \chi_n^0$. The first thing, therefore, is to determine χ_n^0 which is the correct "zero order wavefunction".

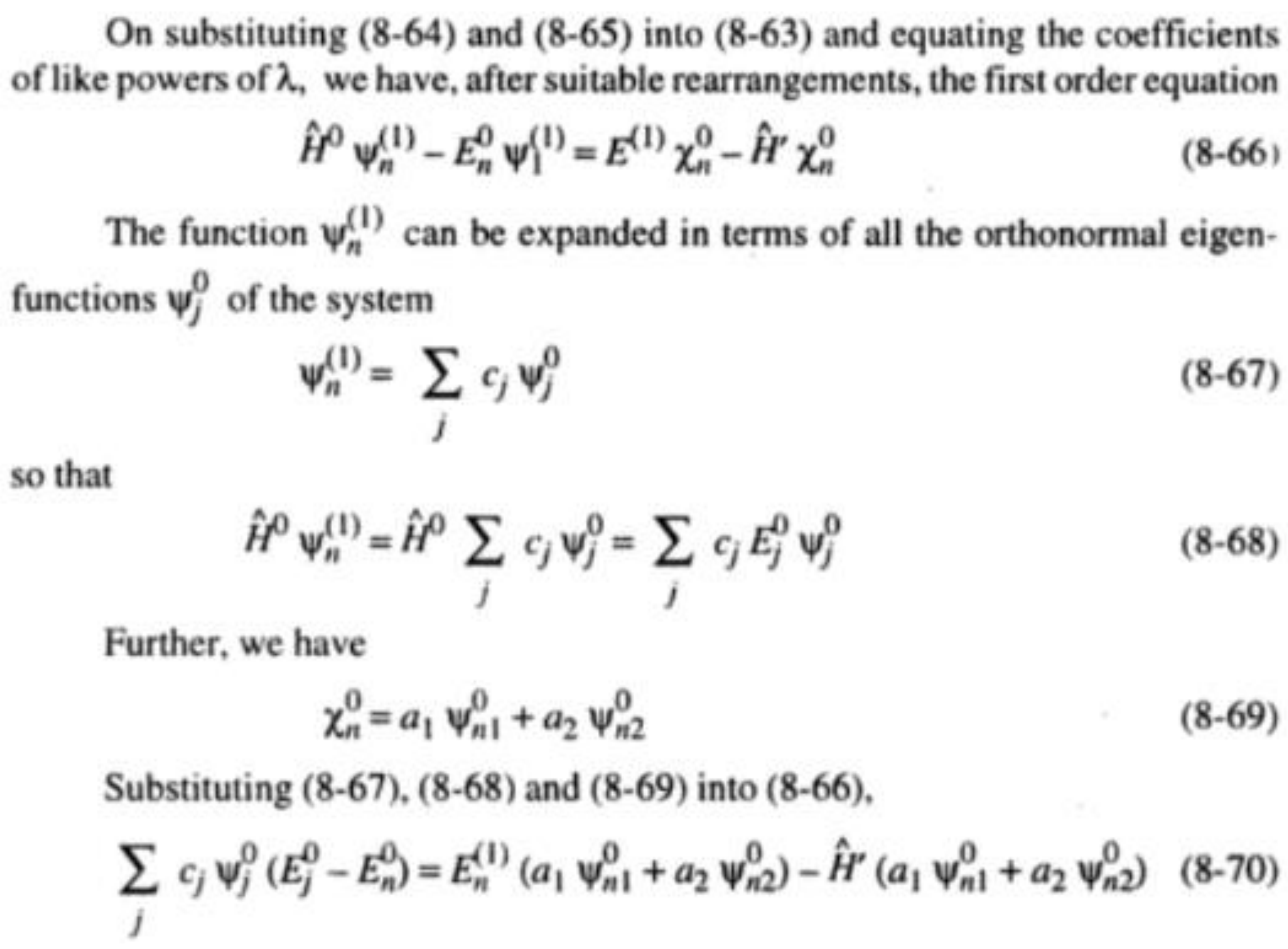
On substituting (8-64) and (8-65) into (8-63) and equating the coefficients of like powers of λ, we have, after suitable rearrangements, the first order equation

$$\hat{H}^0 \psi_n^{(1)} - E_n^0 \psi_1^{(1)} = E^{(1)} \chi_n^0 - \hat{H}' \chi_n^0 \tag{8-66}$$

The function $\psi_n^{(1)}$ can be expanded in terms of all the orthonormal eigenfunctions ψ_j^0 of the system

$$\psi_n^{(1)} = \sum_j c_j \psi_j^0 \tag{8-67}$$

APPROXIMATION METHODS



On substituting (8-64) and (8-65) into (8-63) and equating the coefficients of like powers of λ, we have, after suitable rearrangements, the first order equation

$$\hat{H}^0 \psi_n^{(1)} - E_n^0 \psi_1^{(1)} = E^{(1)} \chi_n^0 - \hat{H}' \chi_n^0 \qquad (8\text{-}66)$$

The function $\psi_n^{(1)}$ can be expanded in terms of all the orthonormal eigenfunctions ψ_j^0 of the system

$$\psi_n^{(1)} = \sum_j c_j \psi_j^0 \qquad (8\text{-}67)$$

so that

$$\hat{H}^0 \psi_n^{(1)} = \hat{H}^0 \sum_j c_j \psi_j^0 = \sum_j c_j E_j^0 \psi_j^0 \qquad (8\text{-}68)$$

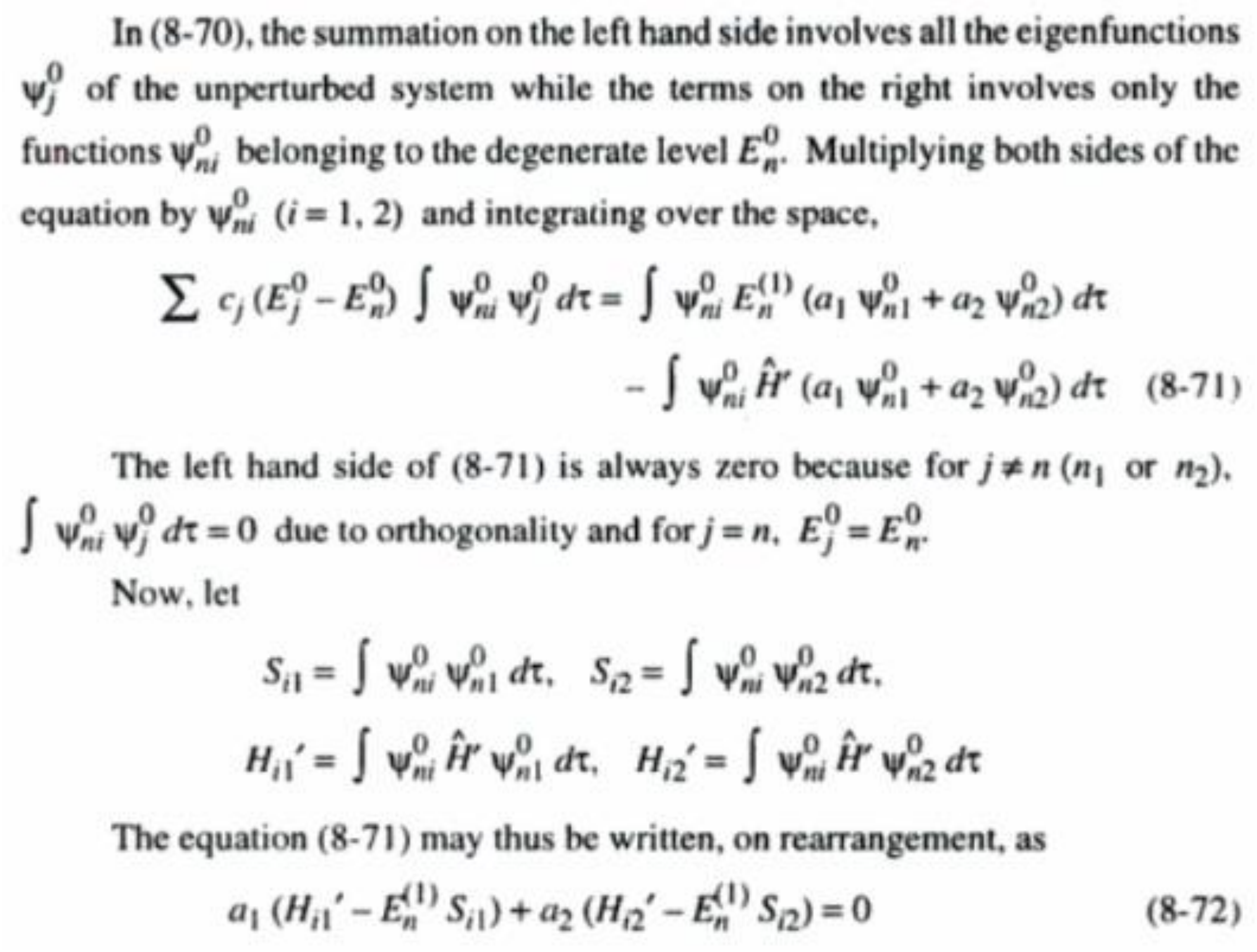
Further, we have

$$\chi_n^0 = a_1 \psi_{n1}^0 + a_2 \psi_{n2}^0 \qquad (8\text{-}69)$$

Substituting (8-67), (8-68) and (8-69) into (8-66),

$$\sum_j c_j \psi_j^0 (E_j^0 - E_n^0) = E_n^{(1)} (a_1 \psi_{n1}^0 + a_2 \psi_{n2}^0) - \hat{H}' (a_1 \psi_{n1}^0 + a_2 \psi_{n2}^0) \qquad (8\text{-}70)$$

APPROXIMATION METHODS



In (8-70), the summation on the left hand side involves all the eigenfunctions ψ_j^0 of the unperturbed system while the terms on the right involves only the functions ψ_{ni}^0 belonging to the degenerate level E_n^0. Multiplying both sides of the equation by ψ_{ni}^0 $(i = 1, 2)$ and integrating over the space,

$$\sum c_j (E_j^0 - E_n^0) \int \psi_{ni}^0 \psi_j^0 \, d\tau = \int \psi_{ni}^0 E_n^{(1)} (a_1 \psi_{n1}^0 + a_2 \psi_{n2}^0) \, d\tau$$

$$- \int \psi_{ni}^0 \hat{H}' (a_1 \psi_{n1}^0 + a_2 \psi_{n2}^0) \, d\tau \qquad (8\text{-}71)$$

The left hand side of (8-71) is always zero because for $j \neq n$ $(n_1$ or $n_2)$, $\int \psi_{ni}^0 \psi_j^0 \, d\tau = 0$ due to orthogonality and for $j = n$, $E_j^0 = E_n^0$.

Now, let

$$S_{i1} = \int \psi_{ni}^0 \psi_{n1}^0 \, d\tau, \quad S_{i2} = \int \psi_{ni}^0 \psi_{n2}^0 \, d\tau,$$

$$H_{i1}' = \int \psi_{ni}^0 \hat{H}' \psi_{n1}^0 \, d\tau, \quad H_{i2}' = \int \psi_{ni}^0 \hat{H}' \psi_{n2}^0 \, d\tau$$

The equation (8-71) may thus be written, on rearrangement, as

$$a_1 (H_{i1}' - E_n^{(1)} S_{i1}) + a_2 (H_{i2}' - E_n^{(1)} S_{i2}) = 0 \qquad (8\text{-}72)$$

APPROXIMATION METHODS

If the energy level E_n^0 of the unperturbed system were k-fold degenerate there would be k such equations. These are called "secular equations".

Nontrivial solution of (8-73) is possible only if the determinant of the coefficients of a_1 and a_2 is equal to zero,

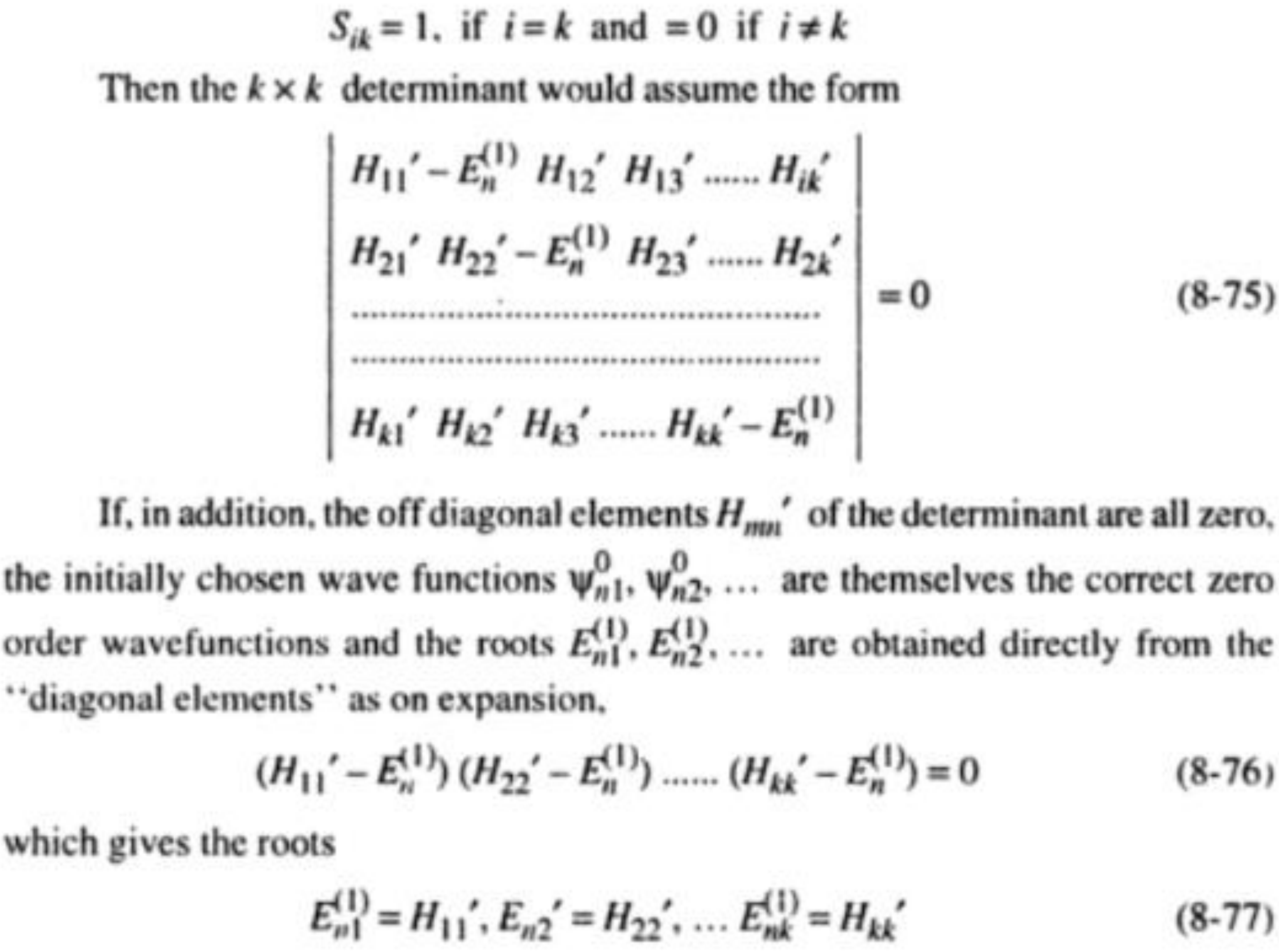
$$\begin{vmatrix} H_{11}' - E_n^{(1)} S_{11} & H_{12}' - E_n^{(1)} S_{12} \\ H_{21}' - E_n^{(1)} S_{21} & H_{22}' - E_n^{(1)} S_{22} \end{vmatrix} = 0 \qquad (8\text{-}74)$$

This, on expanding, gives a 2nd degree polynomial yielding two roots of $E_n^{(1)}$, viz., $E_{n1}^{(1)}$ and $E_{n2}^{(1)}$. In other words, the originally doubly degenerate energy level E_n^0 is split into two levels $E_n^0 + E_{n1}^{(1)}$ and $E_n^0 + E_{n2}^{(1)}$ due to perturbation.

In case of k-fold degeneracy there will be $k \times k$ determinant yielding a kth degree polynomial and hence k values of $E_n^{(1)}$, i.e., $E_{n1}^{(1)}$, $E_{n2}^{(1)}$, … $E_{nk}^{(1)}$.

We started with the premise that the original eigenfunctions ψ_{n1}^0, ψ_{n2}^0, … ψ_{nk}^0 belonging to the k-fold degenerate level E_n^0 are not necessarily orthogonal. But if they are so, we have the advantage that

APPROXIMATION METHODS



$$S_{ik} = 1, \text{ if } i = k \text{ and } = 0 \text{ if } i \neq k$$

Then the $k \times k$ determinant would assume the form

$$\begin{vmatrix} H_{11}' - E_n^{(1)} & H_{12}' & H_{13}' & \ldots\ldots & H_{ik}' \\ H_{21}' & H_{22}' - E_n^{(1)} & H_{23}' & \ldots\ldots & H_{2k}' \\ \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots \\ \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots \\ H_{k1}' & H_{k2}' & H_{k3}' & \ldots\ldots & H_{kk}' - E_n^{(1)} \end{vmatrix} = 0 \qquad (8\text{-}75)$$

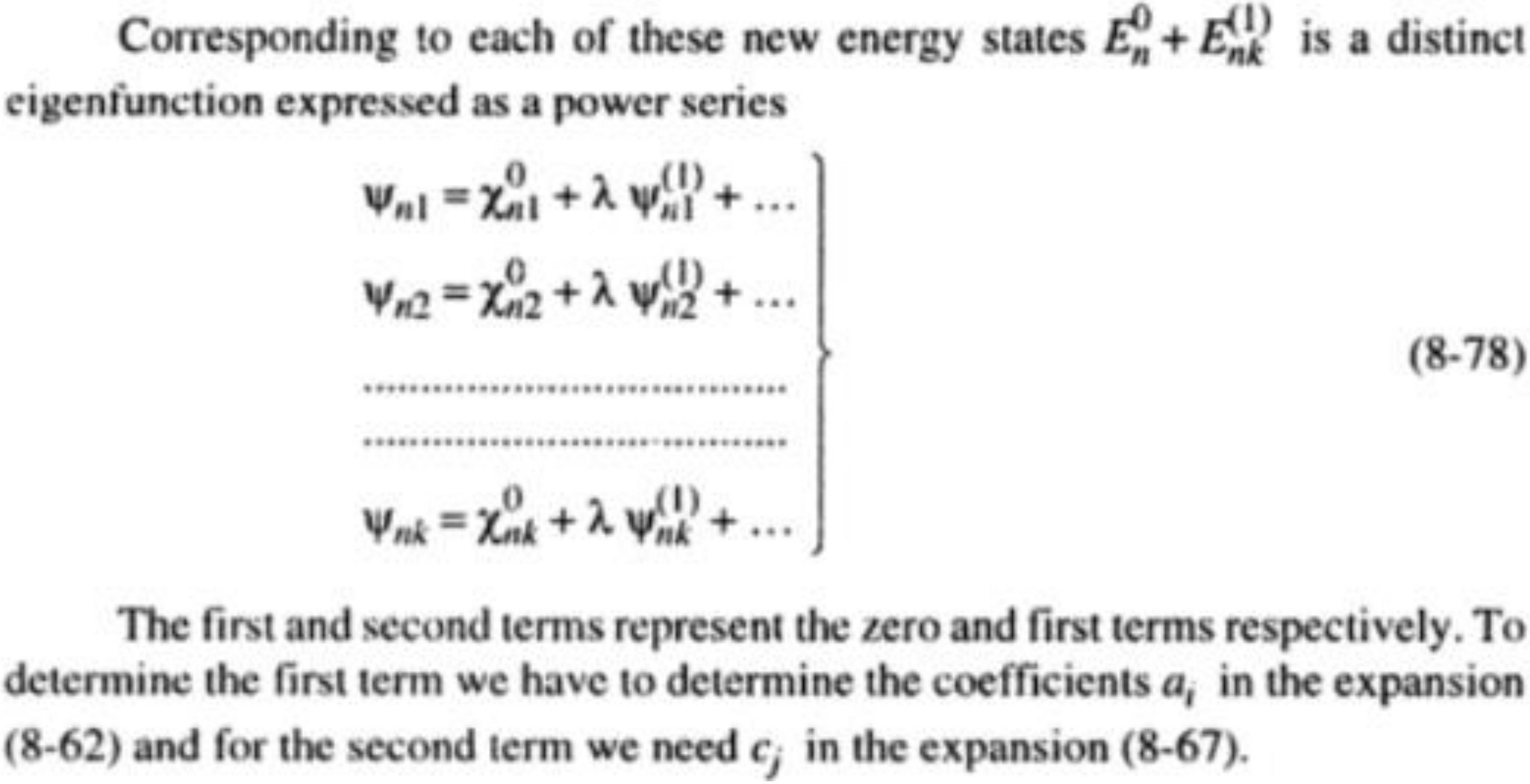
If, in addition, the off diagonal elements H_{mn}' of the determinant are all zero, the initially chosen wave functions $\psi_{n1}^{0}, \psi_{n2}^{0}, \ldots$ are themselves the correct zero order wavefunctions and the roots $E_{n1}^{(1)}, E_{n2}^{(1)}, \ldots$ are obtained directly from the "diagonal elements" as on expansion,

$$(H_{11}' - E_n^{(1)})\,(H_{22}' - E_n^{(1)}) \ldots\ldots (H_{kk}' - E_n^{(1)}) = 0 \qquad (8\text{-}76)$$

which gives the roots

$$E_{n1}^{(1)} = H_{11}', E_{n2}' = H_{22}', \ldots E_{nk}^{(1)} = H_{kk}' \qquad (8\text{-}77)$$

APPROXIMATION METHODS



Corresponding to each of these new energy states $E_n^0 + E_{nk}^{(1)}$ is a distinct eigenfunction expressed as a power series

$$\left.\begin{aligned}
\psi_{n1} &= \chi_{n1}^0 + \lambda\,\psi_{n1}^{(1)} + \ldots \\
\psi_{n2} &= \chi_{n2}^0 + \lambda\,\psi_{n2}^{(1)} + \ldots \\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
\psi_{nk} &= \chi_{nk}^0 + \lambda\,\psi_{nk}^{(1)} + \ldots
\end{aligned}\right\} \qquad (8\text{-}78)$$

The first and second terms represent the zero and first terms respectively. To determine the first term we have to determine the coefficients a_i in the expansion (8-62) and for the second term we need c_j in the expansion (8-67).