Approximate Methods

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SECULAR EQUATION

In many examples, It is generally desirable to express the variation function in terms of a set of function, ϕ. These functions are of class Q and are generally normalized. Thus,

$$\psi = a_1\phi_1 + a_2\phi_2 + \cdots a_n\phi_n \quad -① $$

where a_1 $a_2 \cdots a_n$ are arbitary parameters; their values can be varied to give a minimum in energy. for the sake of simplicity, we will consider the variation function in terms of two functions only. i.e

$$\psi = a_1\phi_1 + a_2\phi_2 \quad \cdots (2)$$

from the variation method, we know

$$E = \int \psi^* H \psi \, d\tau \quad - (3)$$

substituting equation (2) & (3), we get

$$E = \frac{\int (a_1\phi_1^* + a_2\phi_2^*) H (a_1\phi_1 + a_2\phi_2) \, d\tau}{\int (a_1\phi^* + a_2\phi_2^*)(a_1\phi_1 + a_2\phi_2) \, d\tau} \quad - (4)$$

$$E \int (a_1\phi_1^* + a_2\phi_2^*)(a_1\phi_1 + a_2\phi_2) \, d\tau = \int (a_1\phi_1^* + a_2\phi_2^*) H (a_1\phi_1 + a_2\phi_2) \, d\tau$$

or $E \left(a_1^2 \int \phi_1^*\phi_1 \, d\tau + 2a_1a_2 \int \phi_1^*\phi_2 \, d\tau + a_2^2 \int \phi_2^*\phi_2 \, d\tau \right)$

$$= a_1^2 \int \phi_1^* H \phi_1 \, d\tau + 2a_1a_2 \int \phi_1^* H \phi_2 \, d\tau + a_2^2 \int \phi_2^* H \phi_2 \, d\tau \quad -(5)$$

In order to get the minimum value of E, it is required to minimise E with respect to both a_1 and a_2 for this, differentiation is used with respect to both a_1 and a_2. Differentiating equation (5) with respect to a_1, we get

$$E\left[2a_1\int\phi_1^*\phi_1\,d\tau + 2a_2\int\phi^*\phi_2\,d\tau\right.$$
$$+\frac{\partial E}{\partial a_1}\left[a_1^2\int\phi_1^*\phi_1\,d\tau + 2a_1a_2\int\phi_1\phi_2^*\,d\tau + a_2^2\int\phi_2^*\phi_2\,d\tau\right.$$
$$= 2a_1\int\phi_1^* H\phi_1\,d\tau + 2a_2\int\phi_2^* H\phi_2\,d\tau \quad -(6)$$

If we differentiate equation (5) with respect to a_2, we get an equivalent equation to (6). According to the rules of differential calculus, the minimum value of E with respect to a_1 and a_2 is obtained by putting

$$\left(\frac{\delta E}{\partial a_1}\right)_{a_2} = \left(\frac{\delta E}{\partial a_2}\right)_{a_1} \quad -(7)$$

For the sake of simplicity, it is desirable to introduce the symbolism

$$H_{ij} = \int\phi_i^* H\phi_j\,d\tau \text{ and } S_{ij} = \int\phi_i^*\phi_j\,d\tau \quad -(8)$$

By applying the condition of equation (7), i.e

$\frac{\partial E}{\partial a_1} = 0$ to equation (6), we obtained an equation which on substitution according to equation (8) yields a new equation

$$(H_{11} - ES_{11})a_1 + (H_{12} - ES_{12})a_2 = 0 \quad -(9)$$

The equivalent equation will be obtained, by applying the condition

$\frac{\partial E}{\partial a_2} = 0$, i.e

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$$(H_{21} - ES_{21})a_1 + (H_{22} - ES_{22})a_2 = 0 \quad - (10)$$

equation 9 & 10 are known as secular equations.
These equations are of the form

$$ax + by = 0$$
$$cx + dy = 0$$

The above two equations can be expressed in the determinantal form as.

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = 0$$

obviously, the above condition can be applied to equation 9 & 10, we get

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \quad (11)$$

In order to express in terms of n independent terms, the secular determinant of equation (11) becomes as follows:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2n} - ES_{2n} \\ \vdots & & & \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \cdots & H_{nn} - ES_{nn} \end{vmatrix} = 0$$