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Note on the Solution of Secular Problems with Two Non-Orthogonal Basis Functions

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A convenient trigonometric expression for the eigenfunctions and eigenvalues of 2×2 secular problems including overlap is presented.

1. Introduction

Secular equations occur in many applications of quantum mechanics to the electronic structure of atoms and molecules. Using symmetry-adapted basis functions, the secular determinant can often be factorised. The simplest non-trivial factor is a determinant with just 2 rows and columns. The solution of this problem is simple and is given in many textbooks [1–3]. Since the formulae for the coefficients (Eq. (5)) are somewhat awkward, it has become customary to use them in a more convenient trigonometric form [4]; which however is applicable only, if the two basis functions are orthogonal.

For a nonorthogonal basis, which often is required by the nature of the physical problem, no such convenient expressions seem to be available in the literature. They are therefore presented in this note.

2. Secular Problem with Orthogonal Basis

We collect here the pertinent formulae to facilitate a comparison with the results of the next section.

The wave function is written as a linear combination of the two orthonormal basis functions

$$\psi = c_1 \varphi_1 + c_2 \varphi_2 . \tag{1}$$

Minimization of the energy expectation value $\langle H \rangle_\psi$ with respect to c_1 and c_2 then leads to the secular equations

$$\begin{aligned} c_1(H_{11} - E) + c_2 H_{12} &= 0 \\ c_1 H_{12}^* + c_2 (H_{22} - E) &= 0 . \end{aligned} \tag{2}$$

From these we obtain the secular determinant

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{12}^* & H_{22} - E \end{vmatrix} = 0 \tag{3}$$

with roots

$$E_\pm = \tfrac{1}{2}(H_{11} + H_{22}) \pm \sqrt{((H_{22} - H_{11})/2)^2 + |H_{12}|^2} . \tag{4}$$

The coefficients are then obtained from Eq. (2) and the normalization condition $c_1^2 + c_2^2 = 1$

$$c_1 = \{\tfrac{1}{2} \pm (H_{22} - H_{11})/2\sqrt{[(H_{22} - H_{11})^2 + 4|H_{12}|^2]}\}^{\frac{1}{2}}, \tag{5a}$$

$$c_2 = \pm\{\tfrac{1}{2} \mp (H_{22} - H_{11})/2\sqrt{[(H_{22} - H_{11})^2 + 4|H_{12}|^2]}\}^{\frac{1}{2}}. \tag{5b}$$

The last two equations are somewhat awkward, especially if one does not wish to calculate the c_i, but only wants to get an idea of their magnitude from qualitative considerations.

If we write the two solutions (1) in the trigonometric form

$$\psi_- = \cos\theta\,\varphi_1 + \sin\theta\,\varphi_2, \tag{6a}$$

$$\psi_+ = \sin\theta\,\varphi_1 - \cos\theta\,\varphi_2, \tag{6b}$$

then the normalization of ψ_+ and ψ_- as well as their orthogonality are automatically assured and a comparison with Eqs. (5a, b) leads to

$$C\sin 2\theta = -H_{12}, \tag{7a}$$

$$C\cos 2\theta = (H_{22} - H_{11})/2, \tag{7b}$$

$$2C = \sqrt{(H_{22} - H_{11})^2 + 4|H_{12}|^2}, \tag{7c}$$

from which the angle parameter θ can be determined. The two energies (4) are now

$$E_\pm = \tfrac{1}{2}(H_{11} + H_{22}) \pm C. \tag{8}$$

The following points are useful for qualitative discussions of the solution (6a, b):

(a) We will assume that the basis functions φ_i are real and that φ_2 has the higher energy (i.e. $H_{22} \geqq H_{11}$, H_{12} real).

(b) θ is then real and its sign is opposite to that of H_{12}. For H_{12} negative – the usual case in quantum chemistry – the wave function ψ_- with the lower energy is an in-phase-combination and ψ_+ an out-of-phase combination of the two basis functions. For positive H_{12} the situation is reserved.

(c) It follows from (7a, b) that for nondegenerate states ($H_{11} < H_{22}$) the angle $|\theta| < 45°$. This means that in the "lower" solution φ_1 and in the "higher" solution φ_2 makes the larger contribution. For degenerate states ($H_{11} = H_{22}$) $\theta = 45°$ and both solutions are 50 – 50-mixtures of φ_1 and φ_2.

3. Secular Problem with Non-Orthogonal Basis

Corresponding to Eqs. (2)–(4) we now have

$$\begin{aligned} c_1(H_{11} - E) + c_2(H_{12} - S_{12}E) &= 0 \\ c_1(H_{12}^* - S_{12}^*E) + c_2(H_{22} - E) &= 0, \end{aligned} \tag{2'}$$

$$\begin{vmatrix} H_{11} - E & H_{12} - S_{12}E \\ H_{12}^* - S_{12}^*E & H_{22} - E \end{vmatrix} = 0, \tag{3'}$$

$$\begin{aligned} E_\pm = \frac{1}{1 - S_{12}^2}\{&\tfrac{1}{2}(H_{11} + H_{22} - 2S_{12}H_{12}) \\ &\pm\sqrt{((H_{11} + H_{22} - 2S_{12}H_{12})/2)^2 + (1 - S_{12}^2)(H_{12}^2 - H_{11}\cdot H_{22})}\}. \end{aligned} \tag{4'}$$

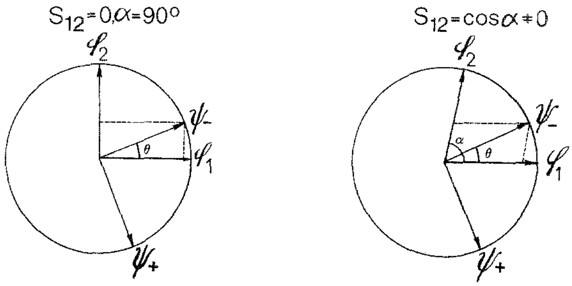

Fig. 1. Relation between basis functions φ_1, φ_2 and wave functions ψ_-, ψ_+ in a 2-dimensional vector space. Note that for both orthogonal and non-orthogonal basis functions ψ_+ is obtained from ψ_- by changing θ to $\theta - 90°$

The Eqs. (5′) for the coefficients are even more cumbersome and will therefore not be given.

The derivation of the trigonometric solution will only be sketched, since it is the final result only that is of interest.

The generalisation of Eqs. (6a, b) turns out to be (cf. Fig. 1)

$$\psi_- = (\sin(\alpha-\theta)\,\varphi_1 + \sin\theta\,\varphi_2)/\sin\alpha\,, \tag{6a′}$$

$$\varphi_+ = (\cos(\alpha-\theta)\,\varphi_1 - \cos\theta\,\varphi_2)/\sin\alpha \tag{6b′}$$

where

$$S_{12} = \cos\alpha\,.$$

To obtain the equations for the angle parameter θ corresponding to (7a, b) the following procedure different from that of Sect. 2 was found more convenient. One calculates the energy expection value with ψ_- of (6a′) and puts its derivative with respect to θ equal to zero. This procedure leads to

$$C\sin 2\theta = \sin\alpha(H_{11}\cos\alpha - H_{12})\,, \tag{7a′}$$

$$C\cos 2\theta = \cos\alpha(H_{11}\cos\alpha - H_{12}) + \tfrac{1}{2}(H_{22} - H_{11}) \tag{7b′}$$

$$C = \sqrt{\{(1-S_{12}^2)(H_{11}S_{12} - H_{12})^2 + ((H_{22}-H_{11})/2 + H_{11}S_{12}^2 - H_{12}S_{12})^2\}}\,.$$

The energy expression (4′) now becomes

$$E_\pm = [\tfrac{1}{2}(H_{11}+H_{22}) - H_{12}\cos\alpha \pm C]/\sin^2\alpha\,. \tag{8′}$$

These results can be checked by putting $\alpha = 90°$, i.e. $S_{12} = 0$ when the corresponding results of Sect. 2 are recovered.

The following points should be noted in using the trigonometric solution (6a′, b′):

(a′) With the assumptions of (a) of Sect. 2 we note, that we can choose the basis functions such that $S_{12} \geqq 0$, leading to $0 < \alpha \leqq \frac{\pi}{2}$.

(b′) θ is again real and from Eq. (7a′) its sign is the same as that of $H_{11}\cos\alpha - H_{12}$.

(c′) We still have the limitation $|\theta| \leqq 45°$; the contributions of φ_1 and φ_2 to ψ_+ and ψ_- for the nondegenerate case are given by the trigonometric ratios in Eqs. (6a′, b′). For the degenerate case ($H_{11} = H_{22}$), we obtain from Eqs. (7a′, b′), that $\theta = \alpha/2 < 45°$. In this case, Eqs. (6a′, b′) simplify to

$$\psi_- = (\varphi_1 + \varphi_2)/\sqrt{2(1 + S_{12})}$$

$$\psi_+ = (\varphi_1 - \varphi_2)/\sqrt{2(1 - S_{12})}$$

and (8′) becomes

$$E_\pm = \frac{H_{11} \mp H_{12}}{1 \mp S_{12}}$$

a wellknown result.

References

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