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Annotatio

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

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W. A. Bingel
Theoretical Chemistry Group, University of Göttingen, Germany

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1. Introduction

The results of the previous paper were obtained under the restriction that both the basis functions and the matrix elements H_{12} and S_{12} are real. Since in practical applications cases occur where these quantities may be complex, we give here the generalized results[1]. The restriction $H_{11} \leqq H_{22}$ is also dropped.

2. Secular Problem with Orthogonal Basis

The trigonometric form of the two solutions now reads

$$\psi_- = \cos\theta \cdot \varphi_1 - s\sin\theta \cdot \varphi_2 \tag{6a}$$

$$\psi_+ = \sin\theta \cdot \varphi_1 + s\cos\theta \cdot \varphi_2 \tag{6b}$$

with $s = \exp(-ih)$, $h = \arg H_{12}$. The angle θ is obtained from

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

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

Eqs. (7c) for C and (8) for the energy remain unchanged.

(a) The basis functions φ_i and H_{12} can be complex; both cases $H_{11} \lessgtr H_{22}$ will be treated on the same footing.

(b) θ is real and always positive. For H_{12} real $s = \operatorname{sign} H_{12}$ and the statement about the relative signs of φ_1 and φ_2 remains correct.

(c) For *nondegenerate* states $(H_{11} \neq H_{22})$ $0 < \theta < \frac{\pi}{4}$ for $H_{11} < H_{22}$ and $\frac{\pi}{4} < \theta < \frac{\pi}{2}$ for $H_{11} > H_{22}$. For *degenerate* states $(H_{11} = H_{22})$ $\theta = 45°$ and both solutions are 50-50 mixtures:

$$\psi_+ = 2^{-\frac{1}{2}}(\varphi_1 \pm s\varphi_2)\,, \qquad E_\pm = H_{11} \pm |H_{12}|\,.$$

[1] Equation numbers are the same as in the previous paper.

3. Secular Problem with Non-Orthogonal Basis

By using the orthogonalized function

$$\varphi_2^{\perp} = (\varphi_2 - S_{12}\varphi_1)/(1 - |S_{12}|^2)^{\frac{1}{2}}$$
$$= (\varphi_2 - \cos\alpha\, e^{i\sigma}\varphi_1)/\sin\alpha$$

instead of φ_2 in the equations of Section 2 and rewriting the results in terms of the nonorthogonal basis one obtains

$$\sin\alpha \cdot \psi_- = (\sin\alpha \cos\theta + \cos\alpha \sin\theta\, e^{i(\sigma-h)})\varphi_1 - \sin\theta \cdot e^{-ih}\varphi_2 \qquad (6a')$$
$$\sin\alpha \cdot \psi_+ = (\sin\alpha \sin\theta - \cos\alpha \cos\theta\, e^{i(\sigma-h)})\varphi_1 + \cos\theta \cdot e^{-ih}\varphi_2 \qquad (6b')$$

where

$$|S_{12}| = \cos\alpha\,, \sigma = \arg S_{12}\,.$$

The angle θ is now determined from

$$C \sin 2\theta = \sin\alpha \cdot |H_{11} \cos\alpha - |H_{12}| e^{i(h-\sigma)}| \qquad (7a')$$
$$C \cos 2\theta = \cos\alpha \cdot (H_{11} \cos\alpha - |H_{12}| \cos(h-\sigma)) + \tfrac{1}{2}(H_{12} - H_{11}) \qquad (7b')$$
$$C = \{\sin^2\alpha |H_{11} \cos\alpha - |H_{12}| e^{i(h-\sigma)}|^2 + ((H_{22} - H_{11})/2 + H_{11} \sin^2\alpha - |H_{12} S_{12}| \cos(h-\sigma))^2\}^{\frac{1}{2}}$$

The two energies are then given by

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

(a′) Since $|S_{12}| = \cos\alpha \geqq 0$ we will have $0 < \alpha \leqq \frac{\pi}{2}$.

(b′) θ is real and always positive.

(c′) θ lies in the range $0 \leqq \theta \leqq 45°$. For the *nondegenerate* case the contributions of φ_1 and φ_2 to ψ_+ and ψ_- are given by the trigonometric ratios in Eqs. (6a′, b′). For the *degenerate* case ($H_{11} = H_{22}$) a marked simplification of the equations occurs only for H_{12} and S_{12} real, which is given in the previous paper.

Prof. Dr. W. A. Bingel
Lehrstuhl für Theoretische Chemie
der Universität Göttingen
D-3400 Göttingen
Tammannstr. 6
Federal Republic of Germany