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5.80 Small-Molecule Spectroscopy and Dynamics
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Lecture #24 Supplement: Energy levels of a Rigid Rotor*

$$W_r = \frac{1}{2}I_a\omega_a^2 + \frac{1}{2}I_b\omega_b^2 + \frac{1}{2}I_c\omega_c^2 = \frac{P_a^2}{2I_a} + \frac{P_b^2}{2I_b} + \frac{P_c^2}{2I_c}$$

$$W_r/h = AP_a^2 + BP_b^2 + CP_c^2$$

where a, b, c denote the directions of the three principal axes of inertia (fixed in the molecule), \underline{P} is the total angular momentum vector, with components P_a, P_b, P_c , and the labeling of the axes is chosen so that

$$I_a < I_b < I_c,$$

or

$$A > B > C,$$

in terms of the rotational constants

$$A = \frac{h}{8\pi^2 I_a}, B = \frac{h}{8\pi^2 I_b}, C = \frac{h}{8\pi^2 I_c}.$$

The magnitude of the total angular momentum vector is quantized, and

$$P^2 = P_a^2 + P_b^2 + P_c^2 = J(J+1)\hbar^2$$

$$J = 0, 1, 2, \dots$$

The orientation of \underline{P} with respect to a space fixed z-axis is also quantized. The projection of \underline{P} on this z-axis can have only the values given by

$$P_z = M\hbar$$

where, for each given value of J, the “azimuthal quantum number” M takes on the $2J + 1$ values

$$M = J, J - 1, \dots, 0, \dots, -J.$$

It is convenient to distinguish the following types of rotors:

<u>Moments of Inertia</u>	<u>Symmetry</u>	<u>Rotational Constants</u>	<u>Examples</u>
$I_a = 0; I_b = I_c$	Linear	$A = \infty; B = C$	HCl, CO ₂
$I_a < I_b = I_c$	Prolate symmetric top	$A > B = C$	CH ₃ Cl, C ₂ H ₆ , Football
$I_a = I_b < I_c$	Oblate symmetric top	$A = B > C$	CH ₃ CF ₃ , C ₆ H ₆ , Frisbee
$I_a = I_b = I_c$	Spherical top	$A = B = C$	CH ₄ , SF ₆
$I_a < I_b < I_c$	Asymmetric top	$A > B > C$	H ₂ O, C ₂ H ₄

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Symmetric Top Spectra

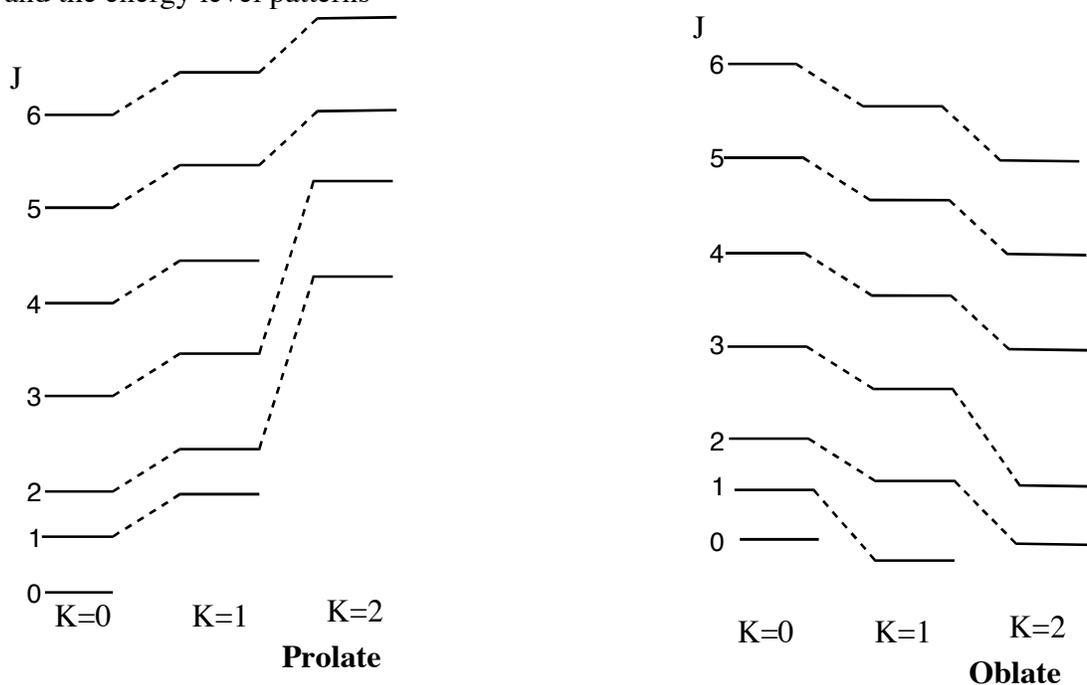
For symmetric top molecules, the component of \underline{P} along the symmetry axis is also quantized, and takes the values

$$P_s = K h$$

with $K = J, J - 1, \dots, 0, \dots, -J$; here s denotes the \underline{a} -axis for prolate tops and the \underline{c} -axis for oblate tops. Thus the rotational energy of a symmetric top is given by

$$\begin{aligned} W_r &= BP^2 + (A - B)P_a^2, && \text{prolate case} \\ &= BP^2 + (C - B)P_c^2, && \text{oblate case} \end{aligned}$$

and the energy level patterns



Since the energy is independent of the sign of K , levels with the same absolute magnitude of K coincide, so that all levels for which K is greater than zero are doubly degenerate, and there are only $J + 1$ distinct energy values for each possible value of J . For each particular value of K , there is an infinite series of levels with different values of J . These are identical in spacing with the linear molecule levels except that the series must start with $J = K$ rather than $J = 0$.

For a symmetric top, the selection rules for J and M are identical to those for a linear molecule, namely:

$$\Delta J = \pm 1$$

$$\Delta M = 0 \quad \text{for radiation polarized along the } z \text{ direction}$$

$$\Delta M = \pm 1 \quad \text{for radiation polarized along the } x \text{ and/or } y \text{ direction.}$$

The selection rule for K is

$$\Delta K = 0.$$

A rigorous quantum mechanical derivation of these selection rules would involve evaluating the transition integrals,

$$\mu_{JMK;J'M'K'} = \int \psi_{JMK}^* \mu \psi_{J'M'K'} d\tau$$

of the dipole moment operator μ between the wavefunctions of the initial and final rotational states, for all possible transitions $JMK \rightarrow J'M'K'$. (A simplified example is treated on page 75 of Brand and Speakman.)

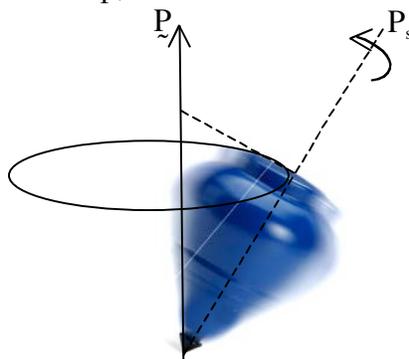
However, an heuristic demonstration of the rules follows from simple semi-classical arguments. Thus, when the electric field vector of the radiation is polarized in the z direction, the result that M cannot change is easily understood: M measures the angular momentum about the z axis (in units of \hbar), and cannot change in this case because an electric vector in the z direction can exert no torque about the z axis on the molecular dipole. Electric fields in the x or y direction, however, can exert a torque about the z axis and then M can change by one unit when a photon is absorbed or emitted. The selection rule for the K quantum number of a symmetric top may be understood in a similar way. Because of the symmetry, there can be no component of the dipole moment perpendicular to the symmetry axis, and hence no torque along this axis due to the electric field associated with radiation. Accordingly, the angular momentum along the symmetry axis cannot change due to radiation, so $\Delta K = 0$.

Because of the above selection rules, the observable frequencies for a rigid symmetric top do not depend on K or on the moment of inertia about the symmetry axis, but are given simply by

$$\nu = 2B(J + 1)$$

for the $J \rightarrow J + 1$ transition, just as for a linear rotor.

This simple spectrum actually corresponds to that which would be predicted from the classical mechanics of the rotation of a symmetric top, familiar from children's toys:



If the dissipative effects of friction were not present, the total angular momentum \underline{P} and its projections P_s (on the top axis) and P_z (on a space fixed axis) would remain constant during the motion, which consists of a combined rotation around the symmetry axis associated with P_s and a precession on this axis around the total angular momentum vector \underline{P} .

Asymmetric Top Spectra

For an asymmetric top, the total angular momentum \underline{P} and its projection P_z on a space fixed axis remain constants of the motion; accordingly, the corresponding quantum numbers J and M are “good” and can be used to specify the state of the rotor. However, there is no longer any direction in the molecule along which \underline{P} has a constant component and thus there is no axis fixed to the molecule that carries out a simple rotation about \underline{P} . The quantum number K is no longer a “good” quantum number and indeed there is no set of convenient quantum numbers that can specify the state and also have simple physical meaning. The usual means of specifying the energy levels is to give the value of J and the values of K_a and K_c for the limiting prolate and limiting oblate symmetric tops. The energy levels in general have a quite complicated functional dependence on J and K_a, K_c , but extensive numerical tables are now available. The energy of a level designated by

$$J_{K_a K_c}$$

would usually be written in the form

$$W_r/h = \frac{A+C}{2} J(J+1) + \frac{A-C}{2} E(\kappa, K_a, K_b)$$

where the quantity $E(\kappa, K_a, K_b)$ is tabulated as a function of the asymmetry parameter

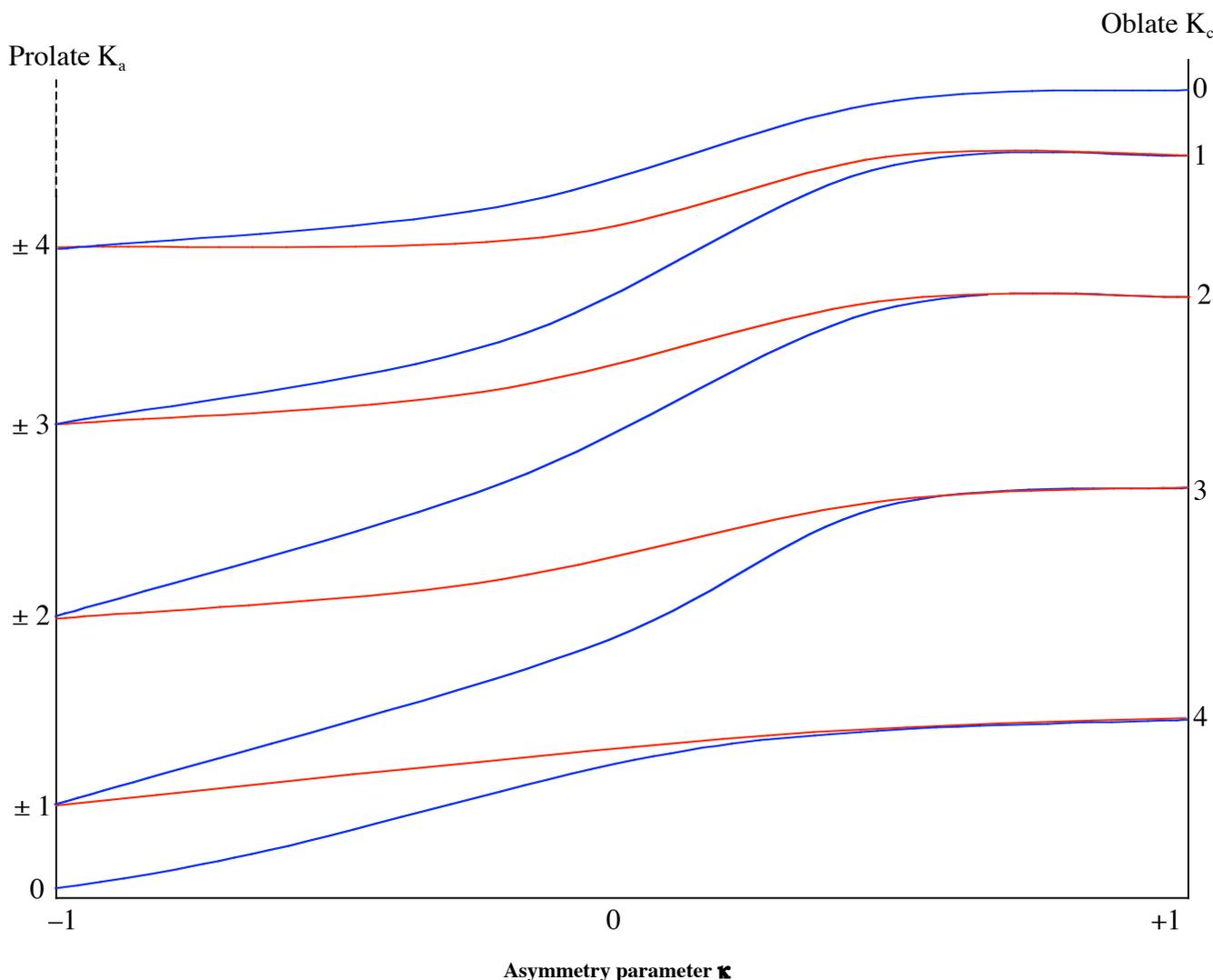
$$\kappa = \left[B - \left(\frac{A+C}{2} \right) \right] / \left(\frac{A-C}{2} \right)$$

The limiting values are

$$\kappa = -1, \text{ prolate symmetric top}$$

$$\kappa = +1, \text{ oblate symmetric top}$$

and the qualitative behavior of the asymmetric rotor levels is readily obtained by interpolating between these limits, as shown in the following example with $J = 4$.



The spectrum of an asymmetric rotor may be extremely complex in contrast to that of a symmetric top. In addition to the irregular distribution of energy levels, the selection rules and transition probabilities between these levels are complicated. In an asymmetric rotor the dipole moment may lie in any arbitrary direction with respect to the principal axes of inertia, and this is one of the main sources of complexity. The transitions can be conveniently classified according to which component of the dipole moment makes them allowed:

<u>Transition</u>	<u>Component</u>	<u>Approximate Selection Rule</u>
“a-type”	μ_a	$\Delta K_a = 0; \Delta K_c = \pm 1$
“b-type”	μ_b	$\Delta K_a = \pm 1; \Delta K_c = \pm 1$
“c-type”	μ_c	$\Delta K_a = \pm 1; \Delta K_c = 0$

In all cases $\Delta J = 0, \pm 1$ and $\Delta M = 0$ (z polarization) or ± 1 (x, y polarization), just as for any type of rotor. [Although the $\Delta J = 0$ situation was not mentioned earlier, it is allowed also for linear and symmetric tops, but for them $\Delta J = 0$ transitions are usually of no interest in rotational spectroscopy.]

The transitions are further classified according to the change in J:

$\Delta J = -1$	P branch
$\Delta J = 0$	Q branch
$\Delta J = +1$	R branch.

ENERGY LEVELS OF AN ASYMMETRIC ROTOR

(Landau & Lifschitz, p. 383-389)

$$H = AJ_a^2 + BJ_b^2 + CJ_c^2 \quad A = \frac{\hbar^2}{2I_a}, \text{ etc. } A > B > C \quad I_a < I_b < I_c$$

Spherical Top:

$$A = B = C$$

$$H = B(J_a^2 + J_b^2 + J_c^2) = BJ^2, \quad E = BJ(J+1)$$

Prolate Symmetric Top:

$$A > B = C$$

$$H = AJ_a^2 + B(J^2 - J_a^2) = BJ^2 + \underbrace{(A-B)}_{>0} J_a^2$$

$$E = BJ(J+1) + (A-B)K^2$$

Oblate Symmetric Top:

$$A = B > C$$

$$H = B(J^2 - J_c^2) + CJ_c^2 = BJ^2 + \underbrace{(C-B)}_{<0} J_c^2$$

$$E = BJ(J+1) + (C-B)K^2$$

Asymmetric Top:

$$A > B > C$$

$$H = AJ_a^2 + BJ_b^2 + CJ_c^2$$

The H matrix will be diagonal in J, non-diagonal in K; will have $\langle K|\mathbf{H}|K\rangle$ and $\langle K|\mathbf{H}|K \pm 2\rangle$ elements. We can choose among three representations:

- I: "Prolate representation", $J_a = K$
- II: "Intermediate", $J_b = K$
- III: "Oblate representation", $J_c = K$

e.g., in the prolate representation, we can write:

$$H = \underbrace{\frac{B+C}{2}(J_a^2 + J_b^2 + J_c^2) + \left(A - \frac{B+C}{2}\right)J_a^2}_{\text{All this diagonal in both J and K}} + \underbrace{\frac{B-C}{2}(J_b^2 - J_c^2)}_{\substack{\text{Diagonal in J,} \\ \text{off-diagonal} \\ \text{by } \pm 2 \text{ in K}}}$$

Thus,

$$\langle J, K | \mathbf{H} | J, K \rangle = \frac{B+C}{2} J(J+1) + \left(A - \frac{B+C}{2} \right) K^2$$

$$\langle J, K | \mathbf{H} | J, K \pm 2 \rangle = \frac{B-C}{4} \left[\{J(J+1) - K(K \pm 1)\} \{J(J+1) - (K \pm 1)(K \pm 2)\} \right]^{1/2}.$$

Returning to the general problem:

it is conventional to define a reduced rotational energy as follows,

$$\mathbf{H}(A, B, C) = \frac{A+C}{2} J^2 + \frac{A-C}{2} E(\kappa)$$

where

$$E(\kappa) = \mathbf{H}(1, \kappa, -1) = J_a^2 + \kappa J_b^2 - J_c^2$$

$$\kappa = \frac{B - \frac{A+C}{2}}{\frac{A-C}{2}} = \text{asymmetry parameter} \rightarrow \begin{matrix} -1 \text{ prolate case} \\ +1 \text{ oblate case} \end{matrix}$$

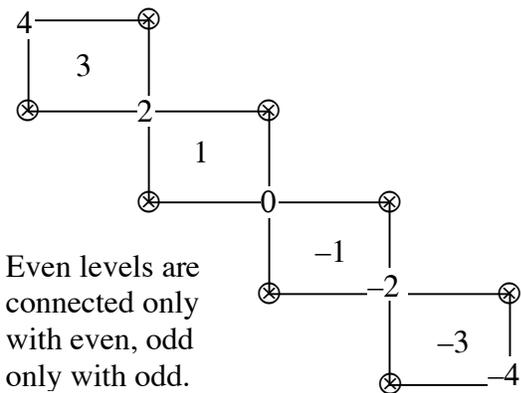
We can set up $E(\kappa)$ in any representation. For a given J , we will have a matrix of dimension $2J + 1$, but we can readily see that this can be factored into four submatrices, as a consequence of the following relations:

$$\langle K | E | K \rangle = \langle -K | E | -K \rangle$$

$$\langle K | E | K \pm 2 \rangle = \langle K \pm 2 | E | K \rangle = \langle -K | E | -K \pm 2 \rangle = \langle -K \pm 2 | E | -K \rangle$$

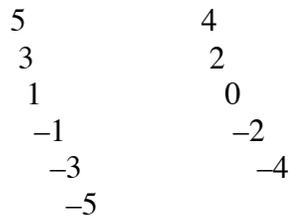
e.g. $J = 5$ case
5

11 levels



Even levels are connected only with even, odd only with odd.

Group into O (odd) and E (even)



-5

MATRIX ELEMENTS OF REDUCED ROTATIONAL ENERGY, E(κ)

$$E(\kappa) = J_a^2 + \kappa J_b^2 - J_c^2$$

$$= D(J^2 - J_z^2) + D'J_z^2 + D''(J_x^2 - J_y^2)$$

$$\langle J, K | E | J, K \rangle = DJ(J + 1) + (D' - D)K^2$$

$$\langle J, K | E | J, K \pm 2 \rangle = \frac{D''}{4} [\{J(J + 1) - K(K \pm 1)\} \{J(J + 1) - (K \pm 1)(K \pm 2)\}]^{1/2}$$

	I Prolate Representation $z \rightarrow a, x \rightarrow b, y \rightarrow c$ K_a	II Intermediate Representation $z \rightarrow b, x \rightarrow c, y \rightarrow a$ K_b	III Oblate Representation $z \rightarrow c, x \rightarrow a, y \rightarrow b$ K_c
D	$\frac{1}{2}(\kappa - 1)$	0	$\frac{1}{2}(\kappa + 1)$
D'	1	κ	-1
D''	$-\frac{1}{2}(\kappa + 1)$	1	$\frac{1}{2}(\kappa - 1)$

Factor further by Wang transformation:

$$X^{-1}E(\kappa)X \text{ where } X = X^{-1} = \frac{1}{\sqrt{2}} \begin{pmatrix} \ddots & & & & \ddots \\ & -1 & & & 1 \\ & & -1 & & 1 \\ & & & \sqrt{2} & \\ & & 1 & & 1 \\ 1 & & & & 1 \\ \ddots & & & & \ddots \end{pmatrix} \quad \text{This is only for even } \kappa$$

e.g., look at $\begin{matrix} 2 \\ 0 \\ -2 \end{matrix}$ block

$$\frac{1}{2} \begin{pmatrix} -1 & 0 & 1 \\ 0 & \sqrt{2} & 0 \\ 1 & 0 & 1 \end{pmatrix} \begin{pmatrix} E_{22} & E_{02} & 0 \\ E_{02} & E_{00} & E_{02} \\ 0 & E_{02} & E_{22} \end{pmatrix} \begin{pmatrix} -1 & 0 & 1 \\ 0 & \sqrt{2} & 0 \\ 1 & 0 & 1 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} -1 & 0 & 1 \\ 0 & \sqrt{2} & 0 \\ 1 & 0 & 1 \end{pmatrix} \begin{pmatrix} -E_{22} & \sqrt{2}E_{02} & E_{22} \\ 0 & \sqrt{2}E_{00} & 2E_{02} \\ E_{22} & \sqrt{2}E_{02} & E_{22} \end{pmatrix}$$

$$= \frac{1}{2} \begin{pmatrix} 2E_{22} & 0 & 0 \\ 0 & 2E_{00} & 2\sqrt{2}E_{02} \\ 0 & 2\sqrt{2}E_{02} & 2E_{22} \end{pmatrix} = \left(\begin{array}{c|cc} E_{22} & & \\ \hline & E_{00} & \sqrt{2}E_{02} \\ & \sqrt{2}E_{02} & E_{22} \end{array} \right)$$

Thus, $E(\kappa)$ factors into four blocks:

E^+			
	E^-		
		O^+	
			O^-

$$E^+ = \begin{bmatrix} E_{00} & \sqrt{2}E_{02} & 0 & \dots \\ \sqrt{2}E_{02} & E_{22} & E_{24} & \\ 0 & E_{24} & E_{44} & \\ \vdots & & & \ddots \end{bmatrix}$$

$$O^\pm = \begin{bmatrix} E_{11} & \pm E_{11} & E_{13} & 0 \\ E_{13} & & E_{33} & E_{35} \\ 0 & & E_{35} & E_{55} \\ \vdots & & & \ddots \end{bmatrix}$$

$$E^- = \begin{bmatrix} E_{22} & E_{24} & 0 & \dots \\ E_{24} & E_{44} & E_{46} & \\ 0 & E_{46} & E_{66} & \\ \vdots & & & \ddots \end{bmatrix}$$

We can solve by continued fraction expansion. E.g. consider the E^+ block for $J = 2$ or $J = 3$.

$$\begin{vmatrix} E_{00} - \lambda & \sqrt{2}E_{02} & 0 \\ \sqrt{2}E_{02} & E_{22} - \lambda & E_{24} \\ 0 & E_{24} & E_{44} - \lambda \end{vmatrix} = 0 = (E_{00} - \lambda) \begin{vmatrix} 1 & \frac{\sqrt{2}E_{02}}{E_{00} - \lambda} & 0 \\ \sqrt{2}E_{02} & E_{22} - \lambda & E_{24} \\ 0 & E_{24} & E_{44} - \lambda \end{vmatrix}$$

$$= (E_{00} - \lambda) \begin{vmatrix} 1 & \frac{\sqrt{2}E_{02}}{E_{00} - \lambda} & 0 \\ 0 & E_{22} - \lambda - \frac{2E_{02}^2}{E_{00} - \lambda} & E_{24} \\ 0 & E_{24} & E_{44} - \lambda \end{vmatrix}$$

So $(E_{00} - \lambda) \begin{vmatrix} E_{22} - \lambda - \frac{2E_{02}^2}{E_{00} - \lambda} & E_{24} \\ E_{24} & E_{44} - \lambda \end{vmatrix}$

Similarly, we get

$$(E_{00} - \lambda)(E_{44} - \lambda) \underbrace{\left[E_{22} - \lambda - \frac{2E_{02}^2}{E_{00} - \lambda} - \frac{E_{24}^2}{E_{44} - \lambda} \right]}_{\lambda = E_{22} - \frac{2E_{02}^2}{E_{00} - \lambda} - \frac{E_{24}^2}{E_{44} - \lambda} \text{ iterate}} = 0$$

In the same way, we get

$$\lambda = E_{00} - \frac{2E_{02}^2}{E_{22} - \lambda - \frac{E_{24}^2}{E_{44} - \lambda \dots}} \quad \text{and} \quad \lambda = E_{44} - \frac{E_{24}^2}{E_{22} - \lambda - \frac{2E_{02}^2}{E_{00} - \lambda \dots}}$$