Potentials for linear prolate and oblate

- symmetric about $\theta = \pi/2$ (in contrast to $\mu_0$-Interaction)
- as $|M|$ increases $|\Psi(\theta = 0, \pi)|^2$ decreases (centrifugal contribution)
- prolate $\rightarrow$ double well
  $\Rightarrow$ for each $|M|$: pairing of levels (tunneling)
**Pendular states in Symmetric Tops**

W. Kim, P. M. Felker, JCP 108, 6763 (1998); JCP 104, 1147 (1996)

- Schrödinger equation similar as for linear rotor:

\[
\left[ \frac{d}{dz} \left[ (1 - z^2) \frac{d}{dz} \right] - \frac{1}{(1-z^2)} \left( M^2 + K^2 - 2MK \cos \theta \right) + \lambda_{n,M,K} + c^2z^2 \right] F_{n,M,K} = 0
\]

Eigenvalues: \( E_{n,M,K} = B\lambda_{n,M,K} - B\alpha_\perp \varepsilon_0^2/4B + (A(C) - B)K^2 \)

- \( M, K \): good quantum number; for given set of \( M, K \) more than one solution \( \rightarrow n \) as integer

- Eigenfunctions expanded in symmetric-top free-rotational eigenfunctions:

\[
\Psi(\varphi, \theta, \chi) \propto F_{n,M,K} e^{iM\varphi} e^{iK\chi} = |nMK\rangle = \sum_J \ldots
\]

- analytical solution feasible if \( c^2 \gg 1 \Rightarrow \text{different characteristics} \) for Prolate and Oblate
Pendular states – Oblate versus Prolate

Oblate

- Eigenfunctions $F$: independent of $M$ and $K$, no restriction for $n$
- Eigenvalues:
  $$E_{nMK} = CK^2 + B \left[ -\frac{\alpha + \varepsilon_0^2}{4B} + (2n + 1)i\epsilon + M^2 - \frac{(2n^2 + 2n + 3)}{4} \right]$$
  - infinite number of \{M, K\}-manifolds
  - for $M, K \neq 0$: four manifolds coincide

Prolate

- Eigenfunctions $F$: two types of solutions (double well !) characterized by $n - |M - K| = 0, 2, 4, \ldots$ and $n - |M + K| = 0, 2, 4, \ldots$
  - dependent on $M$ and $K$, $n$ quantum number restricted
- Eigenvalues:
  $$E_{nMK} = AK^2 + B \left[ -\frac{\alpha ||\varepsilon_0||}{4B} + (2n + 1)c + \frac{M^2}{2} - \frac{K^2}{2} - \frac{(n+1)^2}{2} - \frac{1}{2} \right]$$
  - particular pair of $M$ and $K$: two submanifolds, offset in energy levels
  - for $M, K \neq 0$: $|M|$ or $|K|$ (whichever is smaller) states that are fourfold degenerated, all other states eightfold degenerated (for finite $c \to$ mixed states through tunneling)
Pendular states — Eigenfunctions

\[ F_n(\theta) \] (oblate)

level structure for prolate

\[ F_{nMK}(\theta) \] (prolate, \(|M - K|\)-manifold)

\[ \text{sign}(M) = \text{sign}(K) \]
Pendular states – Spectroscopy

- Dipole allowed vibrational or vibronic transitions

⇒ matrix elements: \( \langle v'; n'M'K'\Pi'|\vec{\mu}|v; nMK\Pi \rangle \)

\((\Pi, \Pi': \text{submanifolds in prolate case})\)

### Oblate

| Selection Rules \((\Delta |M|, \Delta |K|)\) | Propensity rules\(^a\) \(\Delta n\) | fig. |
|----------------|-----------------|-----|
| (0,0)          | ±1              | a   |
| (1,0)          | 0               | b   |
| (0,1)          | 0               | c   |
| (1,1)          | 0, ±1           | d   |

\(^a\Delta n\text{ with appreciable matrix element}\)

### Prolate

<table>
<thead>
<tr>
<th>Selection Rules ((\Delta M, \Delta K))</th>
<th>Propensity rules (\Delta n)</th>
<th>fig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,0)</td>
<td>0, ±2</td>
<td>a</td>
</tr>
<tr>
<td>(± 1,0)</td>
<td>±1</td>
<td>b</td>
</tr>
<tr>
<td>(0, ± 1)</td>
<td>±1</td>
<td>c</td>
</tr>
<tr>
<td>(± 1, ± 1)</td>
<td>0</td>
<td>d</td>
</tr>
</tbody>
</table>

Pendular states – selection rules

• important: $\vec{\varepsilon} \mu \psi(\theta, \varphi) \sim e^{iM\varphi}$

• for parallel type-bands ($\vec{\mu}_{tr} \parallel z$-axis): $\Delta K = 0$

• for $\vec{\varepsilon} \parallel Z$-axis:
  $\langle \psi_2(\theta, \varphi)|\mu_{tr}\varepsilon\parallel \cos\theta|\psi_1(\theta, \varphi)\rangle$
  $\Delta M = 0$
  - prolate: WF centered at $\theta = 0^\circ$ $\Rightarrow \Delta n$ gerade
  - oblate: WF centered at $\theta = 90^\circ$ $\Rightarrow \Delta n$ ungerade

• for $\vec{\varepsilon} \bot Z$-axis:
  $\langle \psi_2(\theta, \varphi)|\mu_{tr}\varepsilon\bot \sin\theta \cos\varphi|\psi_1(\theta, \varphi)\rangle$
  $\Delta M = \pm 1$
  - prolate: WF centered at $\theta = 0^\circ$
    $\Rightarrow \Delta n$ ungerade
  - oblate: WF centered at $\theta = 90^\circ$ $\Rightarrow \Delta n$ gerade
Pendular states – calculated spectra

Oblate

\[ icB = 0.15 \text{ cm}^{-1} \]
\[ icB = 0.38 \text{ cm}^{-1} \]

\[ \Delta |M|, \Delta |K| = 0,0 \text{ (a); } 1,0 \text{ (b); } 0,1 \text{ (c); } 1,1 \text{ (d)} \]

Prolate

\[ cB = 0.15 \text{ cm}^{-1} \]
\[ cB = 0.38 \text{ cm}^{-1} \]

\[ \Delta M, \Delta K = 0,0 \text{ (a); } \pm 1,0 \text{ (b); } 0,\pm 1 \text{ (c); } \pm 1,\mp 1 \text{ (d)} \]

Pendular states – experimental spectra

- Comparison of experimental and calculated Raman-spectra gives impression of reliability of theory (qualitative agreement)

→ Naphthalene trimer (Prolate case)
  - experimental spectrum: $\vec{\varepsilon}_0 \parallel \vec{\varepsilon}_{laser}$, except for (a)
    Average power of aligning field: 20MW (a,b); 10 MW (c); 4 MW (d); 2 MW (e)
  - calculated spectrum: values correspond to $\Delta \alpha \varepsilon_0^2 / 6B$