Quantum Monodromy.

Quantum states in a champagne bottle

Hamiltonian + Quantum energies

Classical motions

Quantum monodromy

Quantum states of H_2O

Bohr-Sommerfeld corrections

Spherical pendulum

Quantum states of HCP

Acknowledgement Richard Cushman

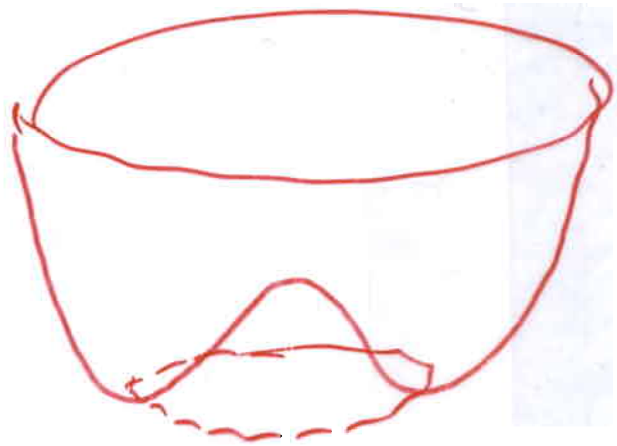
Refs.

L M Bates ZAMP 42, 837 (1991)

M S Child J. Phys A 31, 657 (1998)

M S Child et al Molecular Physics 96, 371 (1991)

Hamiltonian



$$H = \frac{1}{2m}\left(P_x^2 + P_y^2\right) - A\left(X^2 + Y^2\right) + B\left(X^2 + Y^2\right)^2$$

Scaling

$$X \doteq \left(\hbar^2 / 2mA\right)^{1/4} x$$

$$P_X = \left(2mA\hbar^2\right)^{1/4} p_x$$

$$E = \left(\frac{2A\hbar^2}{m}\right)^{1/2} \epsilon$$

$$B = \left(\frac{2mA^3}{\hbar^2}\right) \beta$$

$$h = \frac{1}{2}\left(p_x^2 + p_y^2\right) - \frac{1}{2}\left(x^2 + y^2\right) + \beta\left(x^2 + y^2\right)^2$$

$$= \frac{1}{2}\left(p_r^2 + \frac{p_\theta^2}{r^2}\right) - \frac{1}{2} r^2 + \beta r^4 = \epsilon$$

Quantum energy levels.

Ang mom $\quad p_\theta = k\,(\hbar)$

Hamiltonian matrix elements (2d SHO basis) $|v, k\rangle$

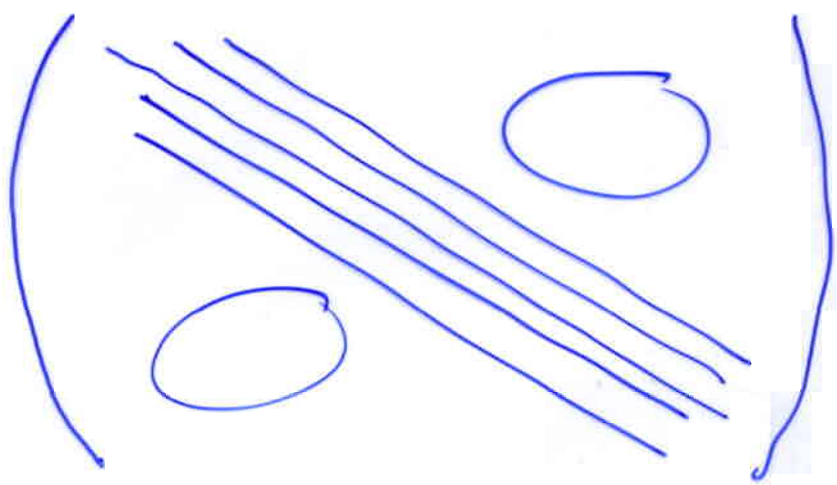
$$H = T - \tfrac{1}{2} r^2 + \beta r^4$$

$$\langle v k | T | v k\rangle = \langle v k | r^2 | v k \rangle = v + 1$$

$$\langle v{+}2\ k | T | v k \rangle = - \langle v{+}2\ k | r^2 | v k \rangle = \tfrac{1}{2}\sqrt{(v+2)^2 - k^2}$$

$$\langle v' k | r^4 | v k \rangle = \sum_{v''} \langle v' k | r^2 | v'' k \rangle \langle v'' k | r^2 | v k \rangle$$

$H =$



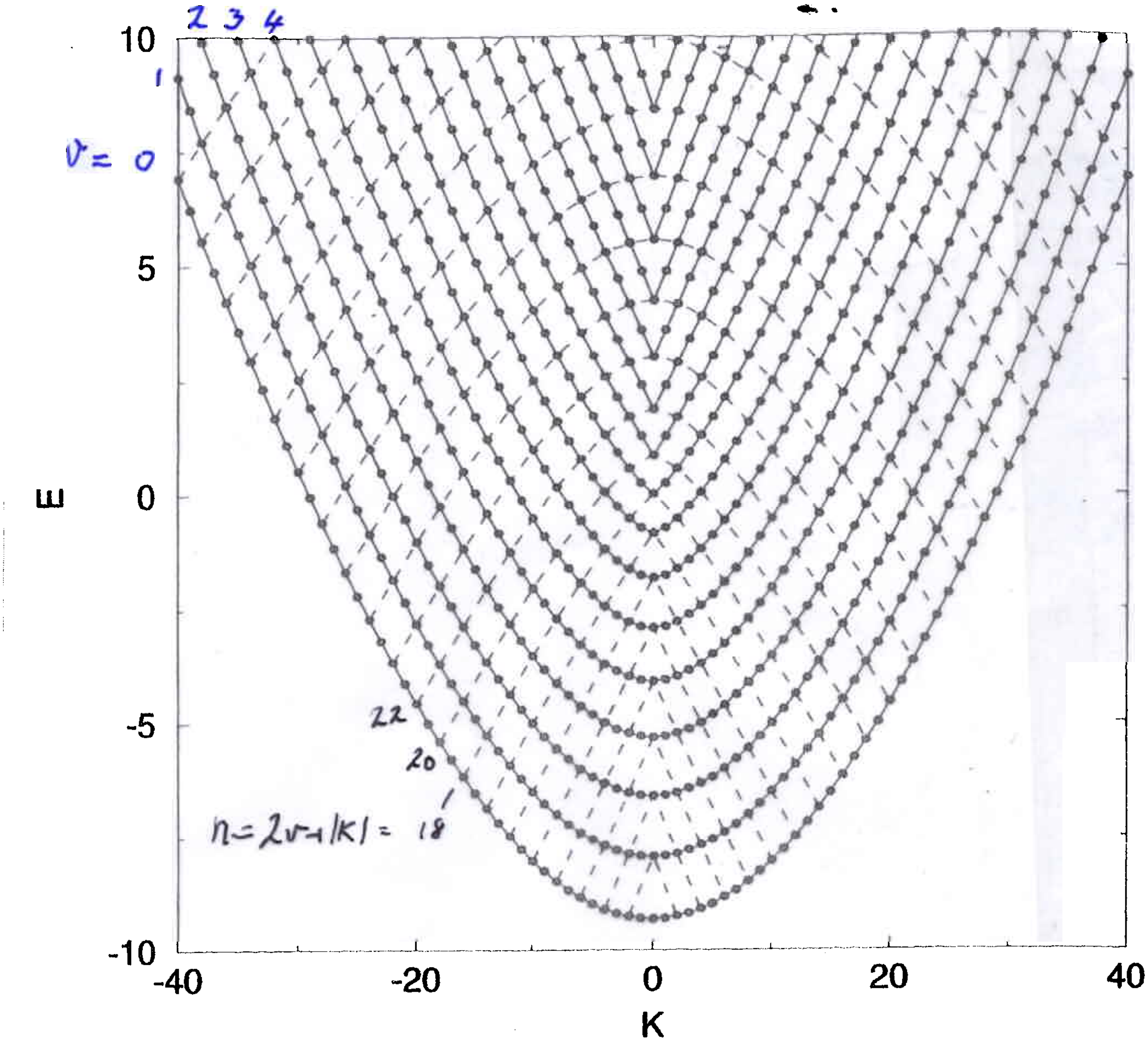


Figure 2. The computed quantal spectrum for the scaled champagne-bottle model with $\beta = 0.006\,25$. Points indicate the computed eigenvalues. Solid and dashed lines join those with common values of the bent molecule quantum number v and the linear molecule number $n = 2v + |K|$ respectively. Note the abrupt transition from smooth to kinked variations in both sets of curves around the critical point at $K = 0$, $E = 0$.

Classical correspondence

$$H(\underset{\sim}{p}, \underset{\sim}{r}) \Longrightarrow \tilde{H}(I_r, I_\theta)$$

$$I_r = (v + \tfrac{1}{2})\hbar , \quad I_\theta = k\hbar$$

$$\left(\frac{\partial E}{\partial v}\right)_k = \hbar \left(\frac{\partial \tilde{H}}{\partial I_r}\right)_{I_\theta} = \hbar\, \omega_r$$

$$\left(\frac{\partial E}{\partial k}\right)_v = \hbar \left(\frac{\partial \tilde{H}}{\partial I_\theta}\right)_{I_r} = \hbar\left(\frac{d\theta}{dt}\right)$$

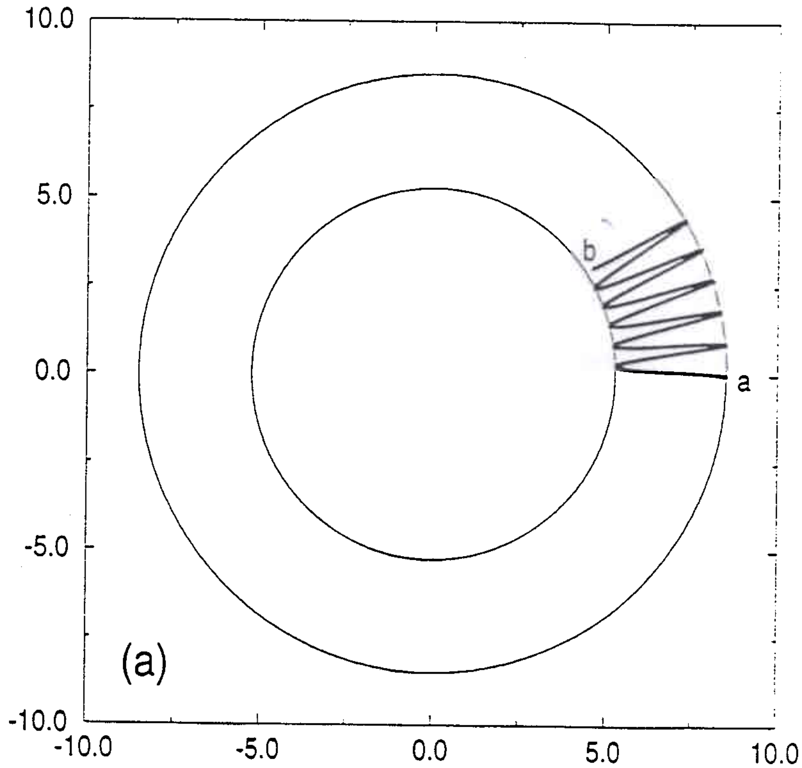
$$= \hbar \ \frac{\Delta\theta}{\Delta T}$$

$$= \hbar \ \frac{(\text{Angle change over a radial cycle})}{(\text{radial time period})}$$

$\beta = 0.005$ trajectories

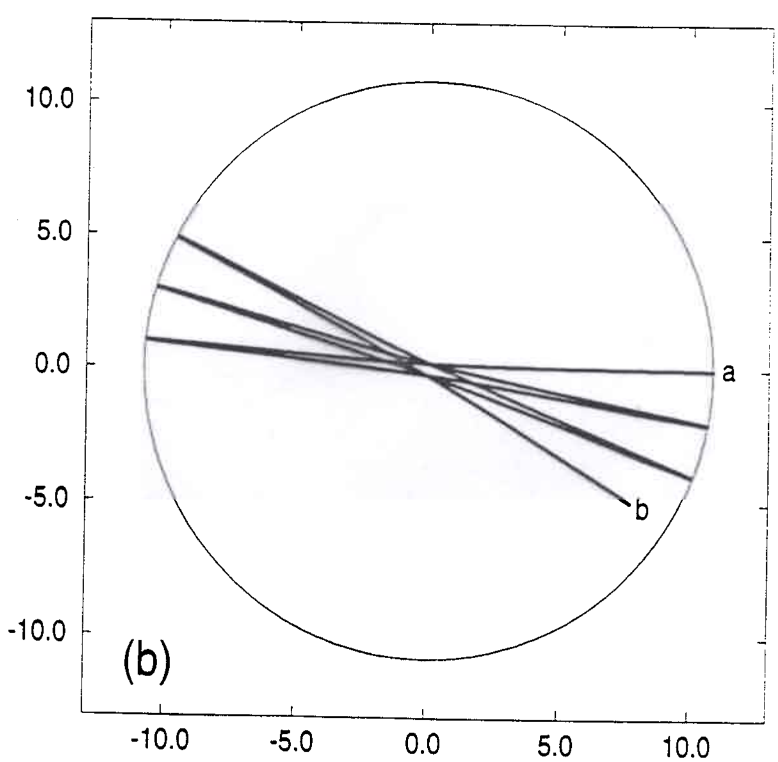
$|k| = 1$

$\epsilon = -10$



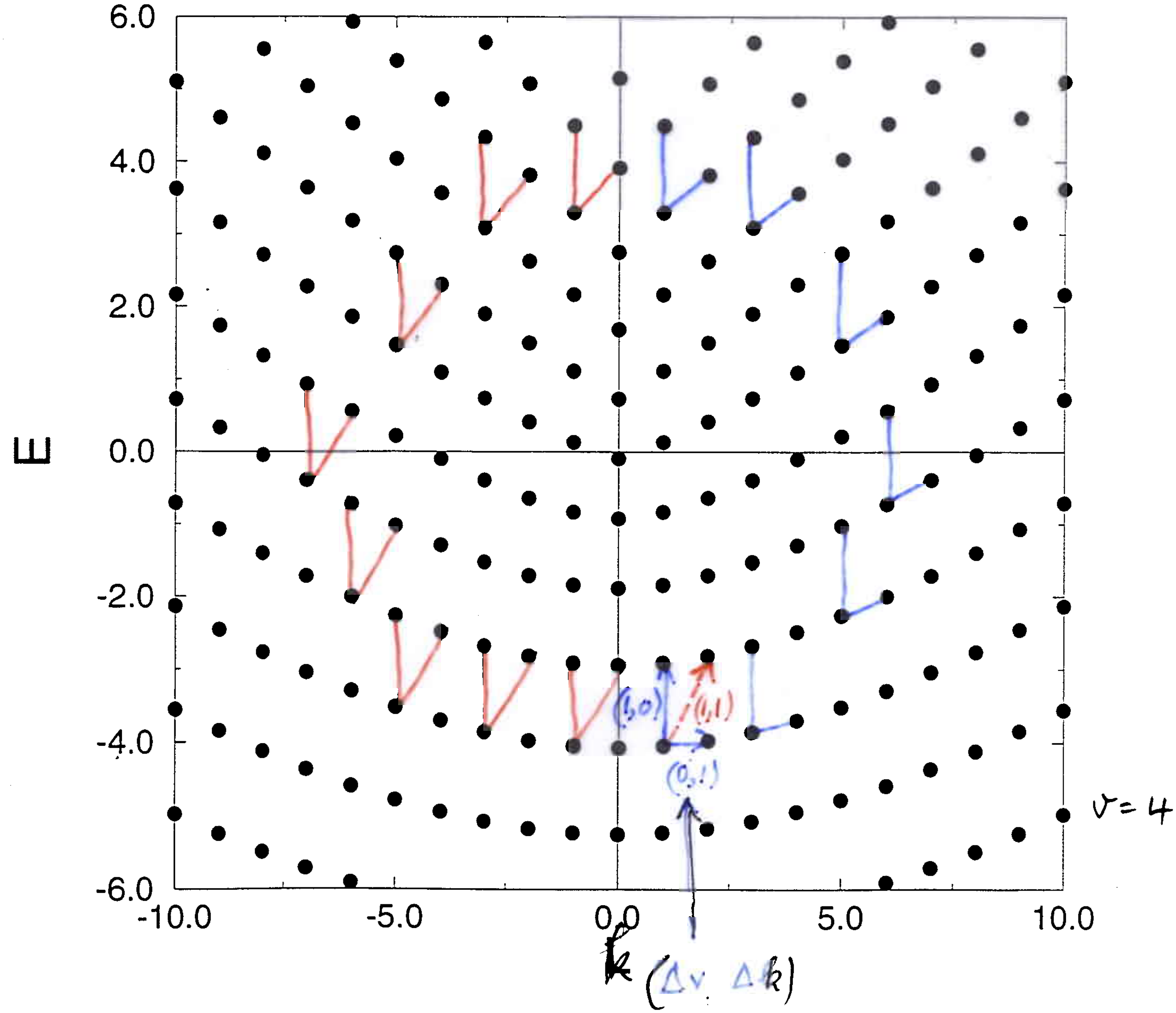
$|k| = 1$

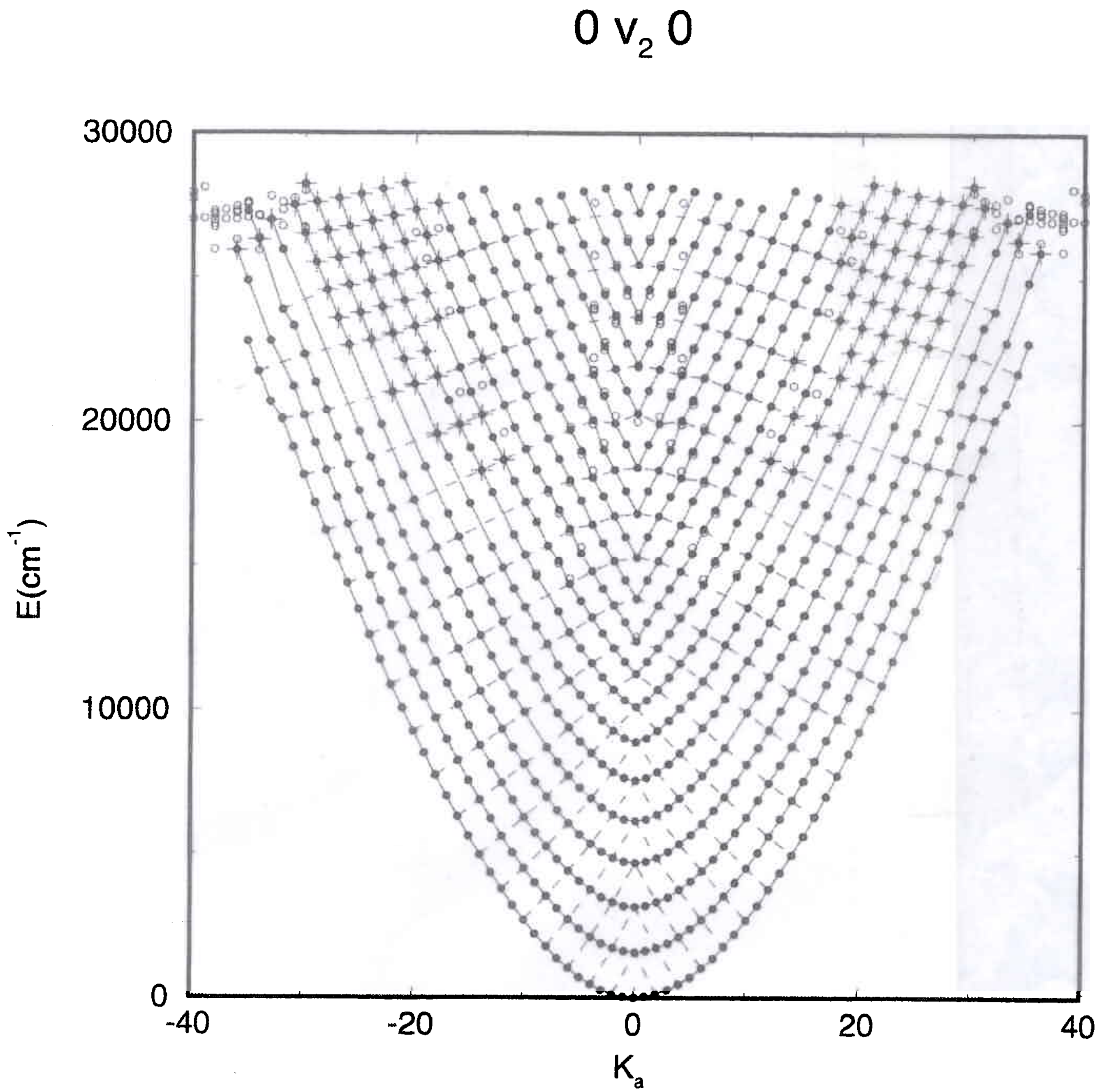
$\epsilon = 10$



Quantum Monodromy

$$\begin{pmatrix} \Delta k' \\ \Delta v' \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} \Delta k \\ \Delta v \end{pmatrix}$$




0 v$_2$ 0
30000
20000
10000
0
E(cm^{-1})
-40
-20
0
20
40
K_a

Bohr Sommerfeld

$$I_r = [\nu(\epsilon, k) + \tfrac{1}{2}]\hbar$$

$$= \frac{1}{2\pi}\oint p_r \, dr$$

$$= \frac{1}{\pi}\int_{r_{min}}^{r_{max}} \sqrt{2\left(\epsilon + \tfrac{1}{2}r^2 - \beta r^4 - k^2/2r^2\right)}\, dr$$

$$= f(\epsilon, k, \beta) - \frac{1}{2\pi}\, \mathrm{Im}\left\{(k + i\epsilon)\ln\left(\frac{k+i\epsilon}{2}\right)\right\}$$

multivalued

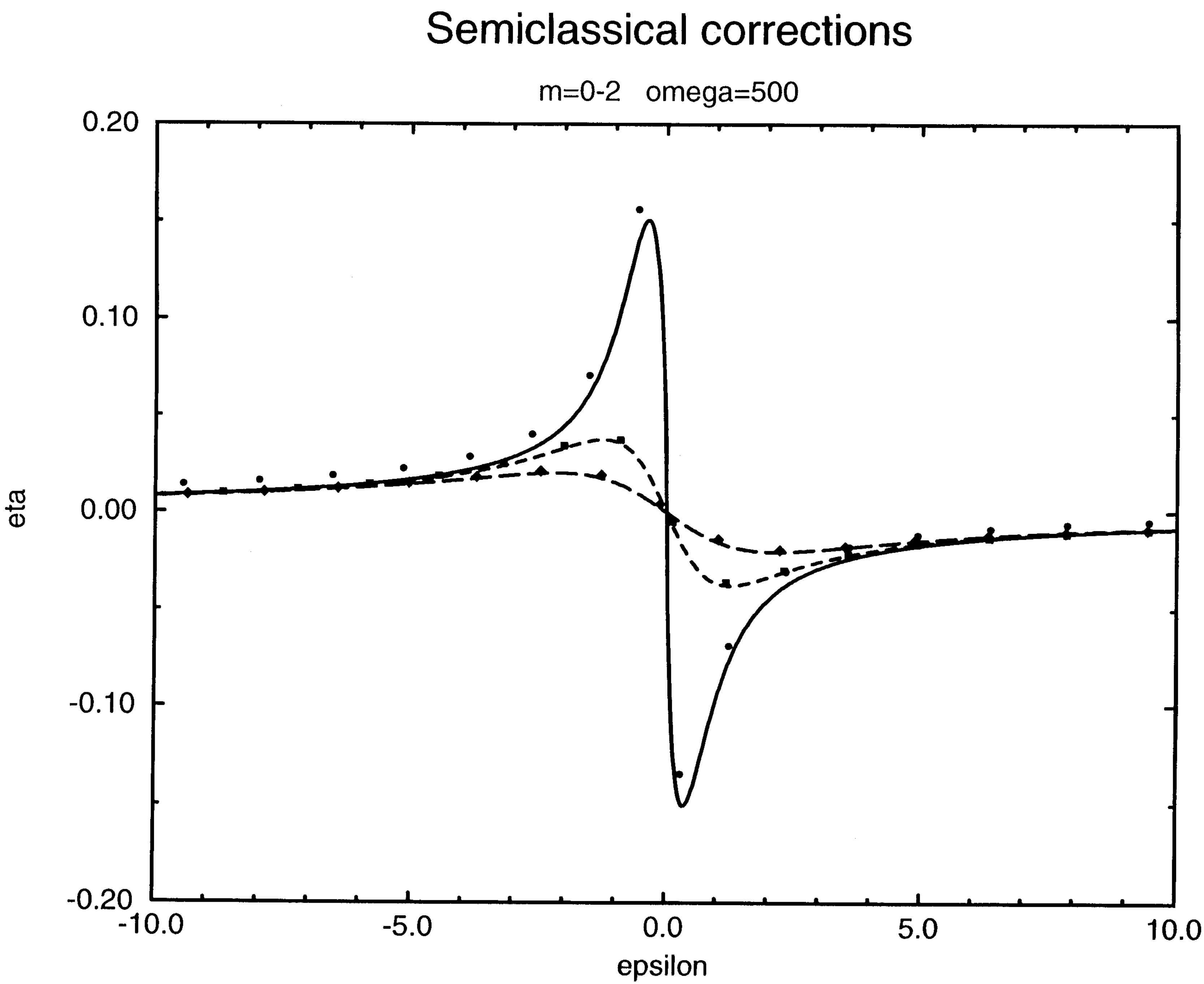
Bohr Sommerfeld phase correction

Asymptotic solution of confluent hypergeometric (Whittaker) equation

$$\left(\frac{d^2}{dx^2} + \underbrace{2\epsilon + x^2 - \frac{k^2}{x^2}}_{q^2(x)} + \frac{1}{4x^2}\right) f = 0$$

$$f \sim q^{-1/2}(x) \cos\left[\int_{x_{min}}^{x} q(x)\,dx - \frac{\pi}{4} + \eta(\epsilon, k)\right]$$

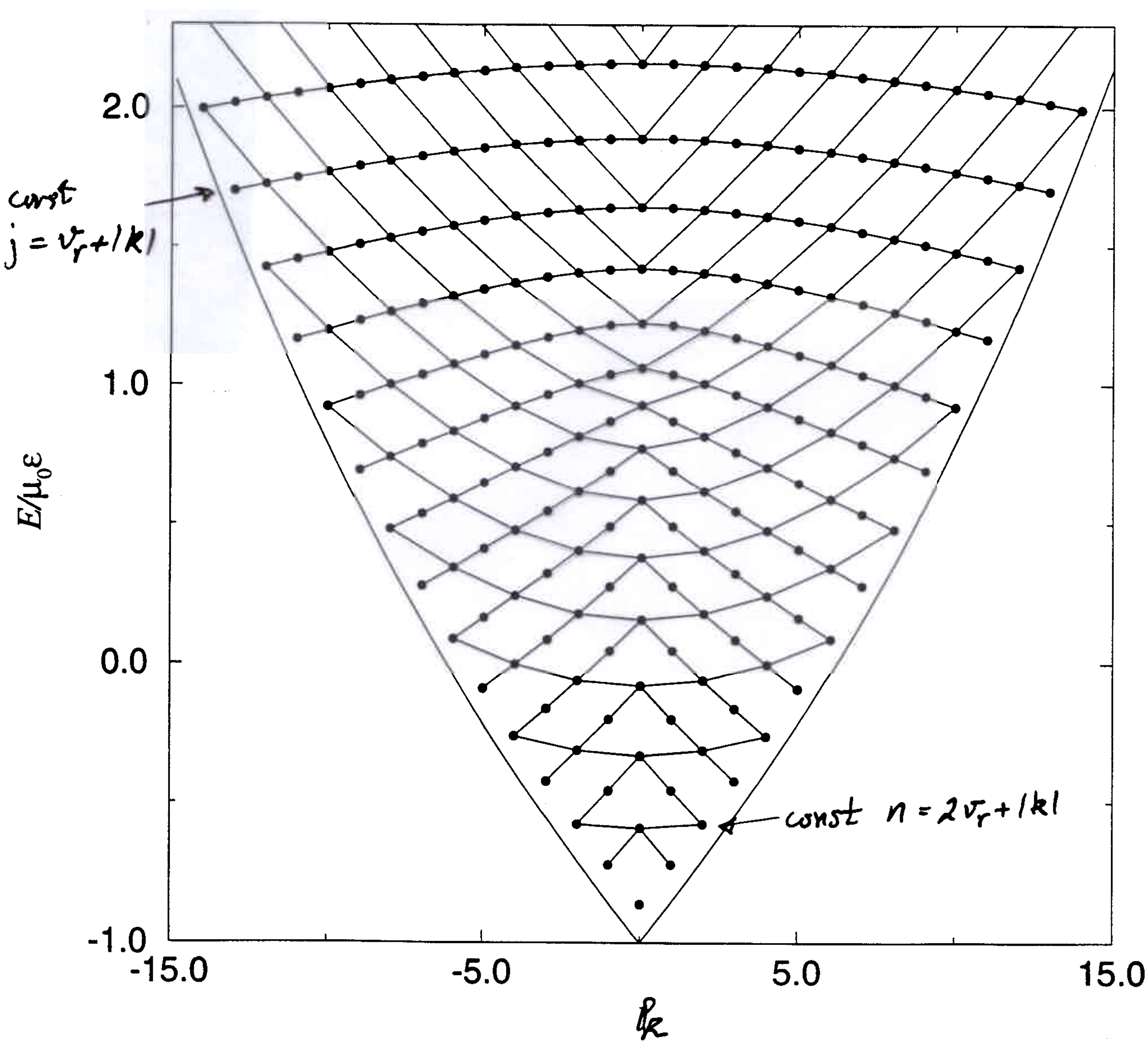
$$\boxed{\eta(\epsilon,k) = \frac{\epsilon}{2}\ln\left(\frac{\epsilon^2+k^2}{4}\right) - \frac{k}{2} + \frac{k}{2}\arctan\left(\frac{\epsilon}{k}\right) - \arg\Gamma\left(\frac{|k|+1}{2} + \frac{i\epsilon}{2}\right)}$$



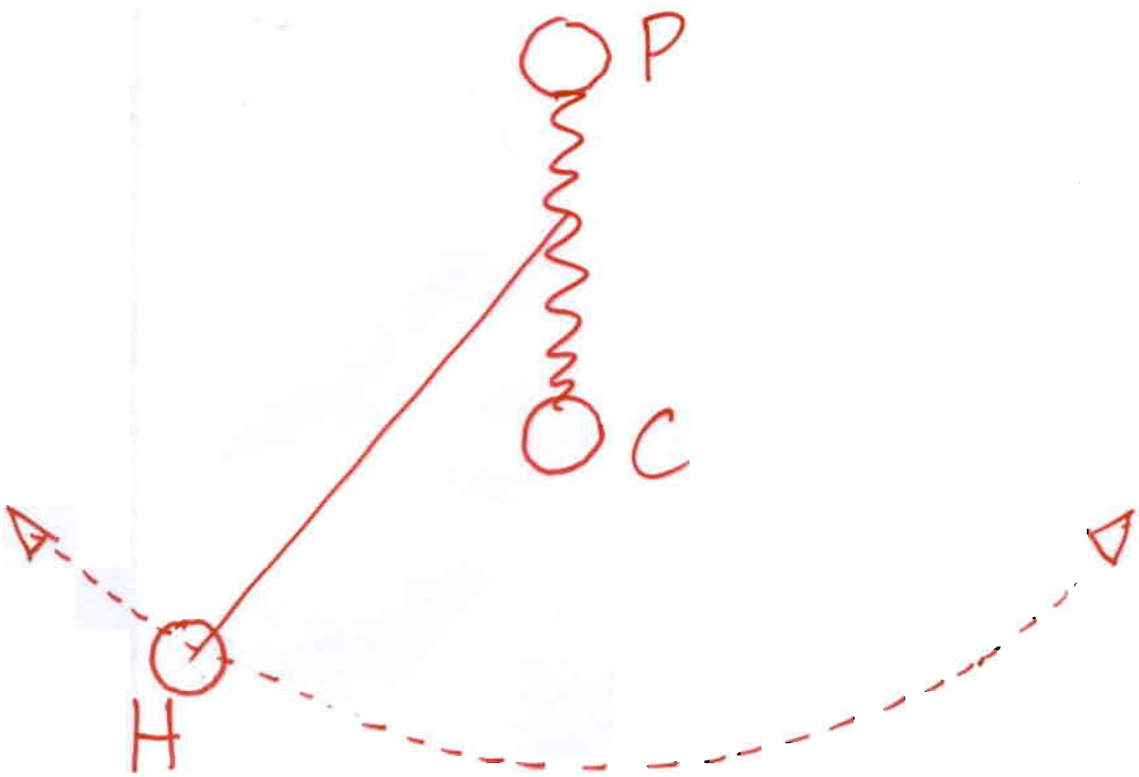
Semiclassical corrections
m=0-2 omega=500
0.20
0.10
0.00
-0.10
-0.20
eta
-10.0
-5.0
0.0
5.0
10.0
epsilon

Spherical pendulum – joint spectrum

$$\hat{H} = BJ^2 + \mu_0 \mathcal{E} \cos\theta$$



Dynamics of HCP



Pendulum / harmonic oscillator model.

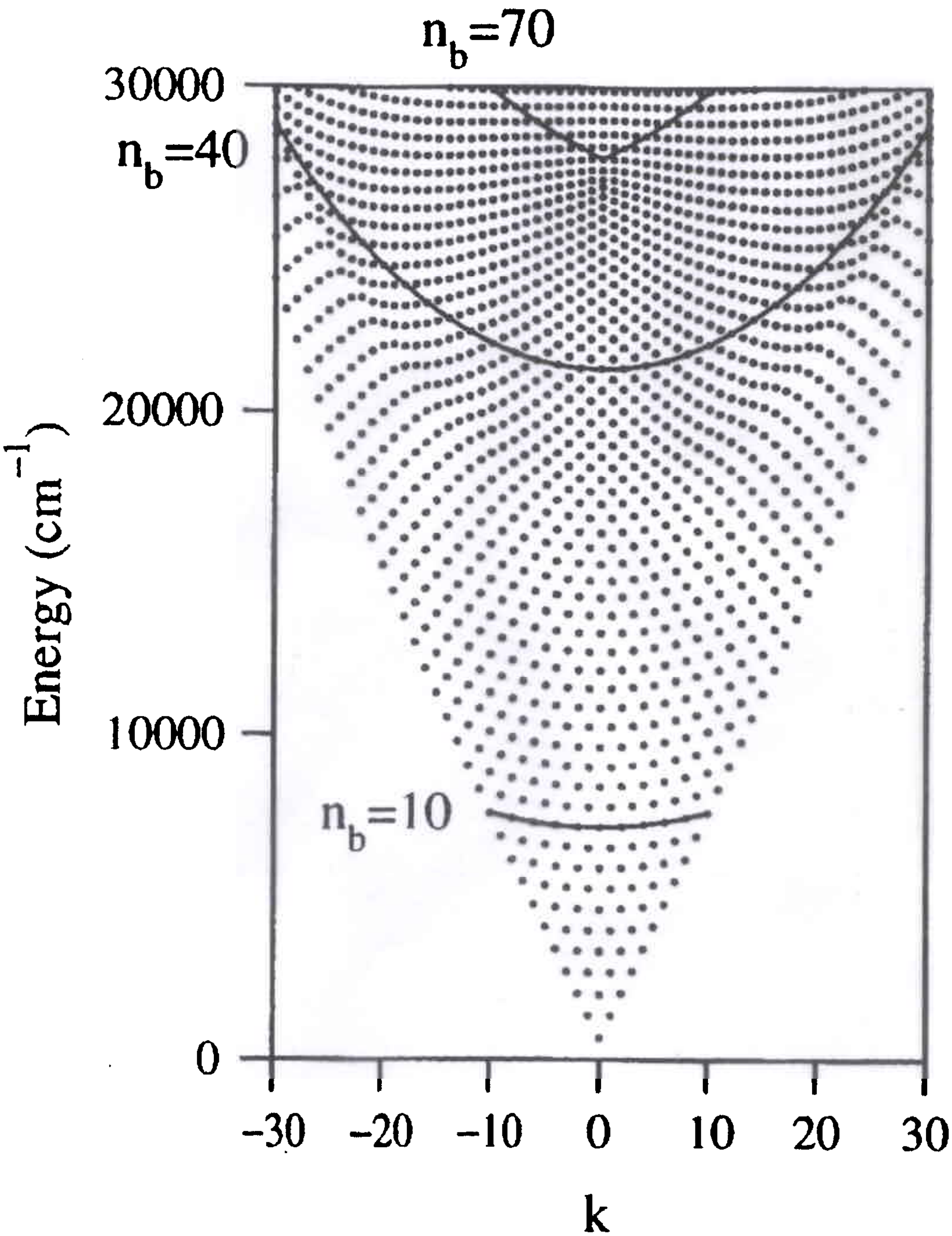
Pendular states in a rotating frame.

$$H = Bj^2 + V(\theta)$$ ← pendulum

$$+ A(\underset{\sim}{J} - \underset{\sim}{j}).(\underset{\sim}{J} - \underset{\sim}{j})$$

$\underset{\sim}{J}$ = total ang. mom^{m}.

$\underset{\sim}{j}$ = internal ang mom^{m}, $j_z = k$



n_b=70
n_b=40
n_b=10
30000
20000
10000
0
Energy (cm^{-1})
-30
-20
-10
0
10
20
30
k

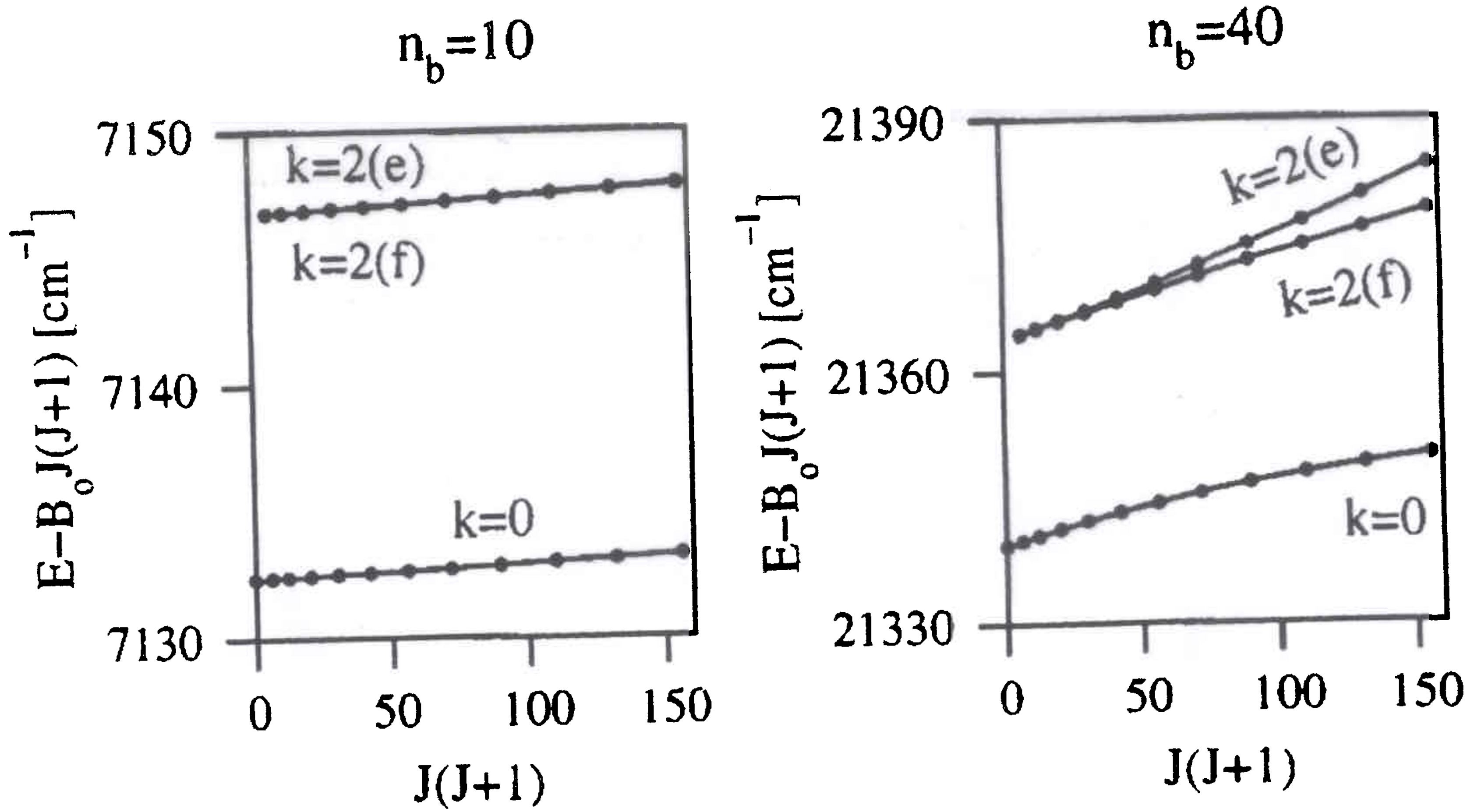


FIG. 6. Reduced term value plots similar to those those which might be constructed for experimental data. Only those levels which can be assigned as $k=0$ or $k=2$ (both parities) are included, for $n_b=10$ and $n_b=40$. The value of $B_\circ$ is chosen to be 0.68.