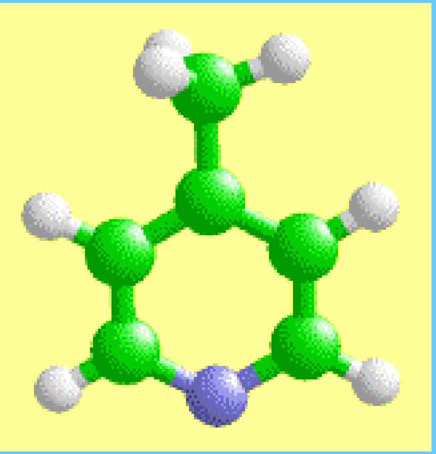
Rotational dynamics of methyl groups in solids: from tunnelling to quantum solitons

Experimental studies of infinite chains of coupled CH_3 rotors and the sine-Gordon theory

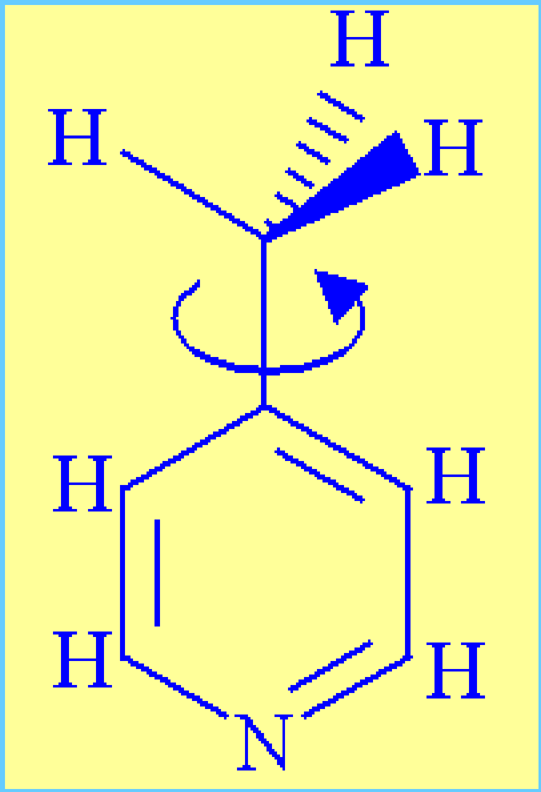
4-Methylpyridine (γ-picoline)



F Fillaux, Nonlinear Double Day, Sevilla 2004

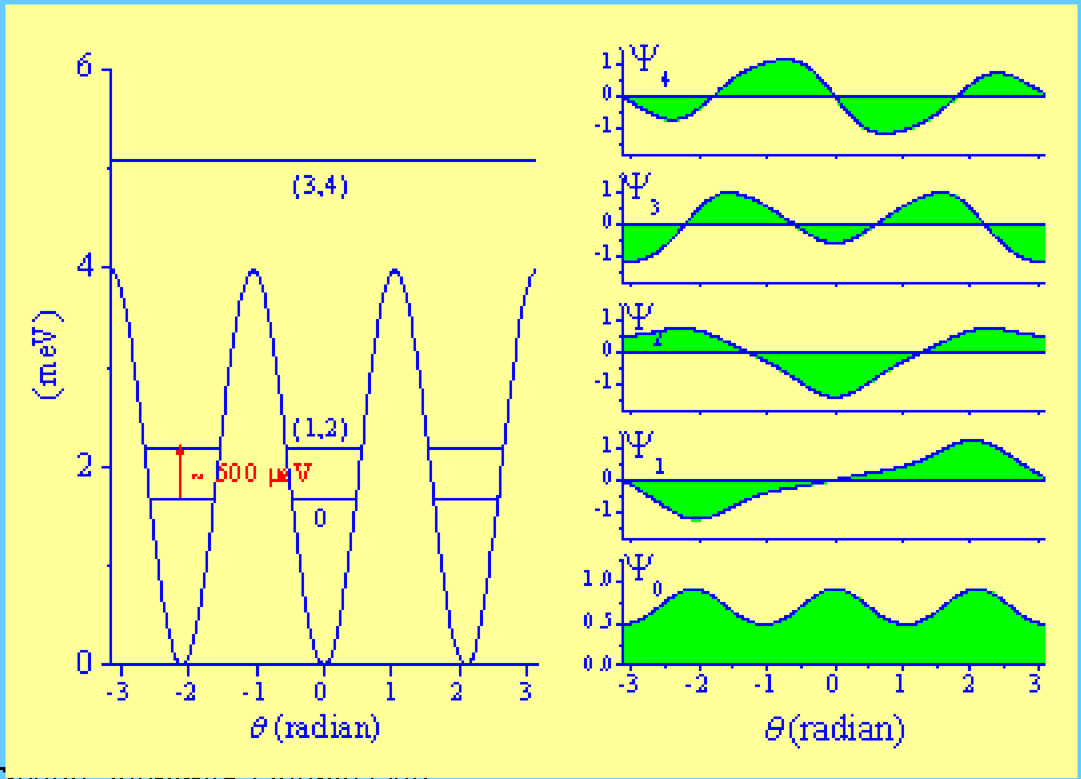
4-METHYL-PYRYDINE
(γ-picoline)

CH_3	$B_H \sim 650$ μeV
CD_3	$B_D \sim 325$ μeV



The single quantum rotor

$$H_0 = -\frac{\hbar^2}{2I_r}\frac{\partial^2}{\partial\theta^2} + V_0(3\theta)$$



F Fillaux, Nonlinear Double Day,
Sevilla 2004.

MOTIVATIONS

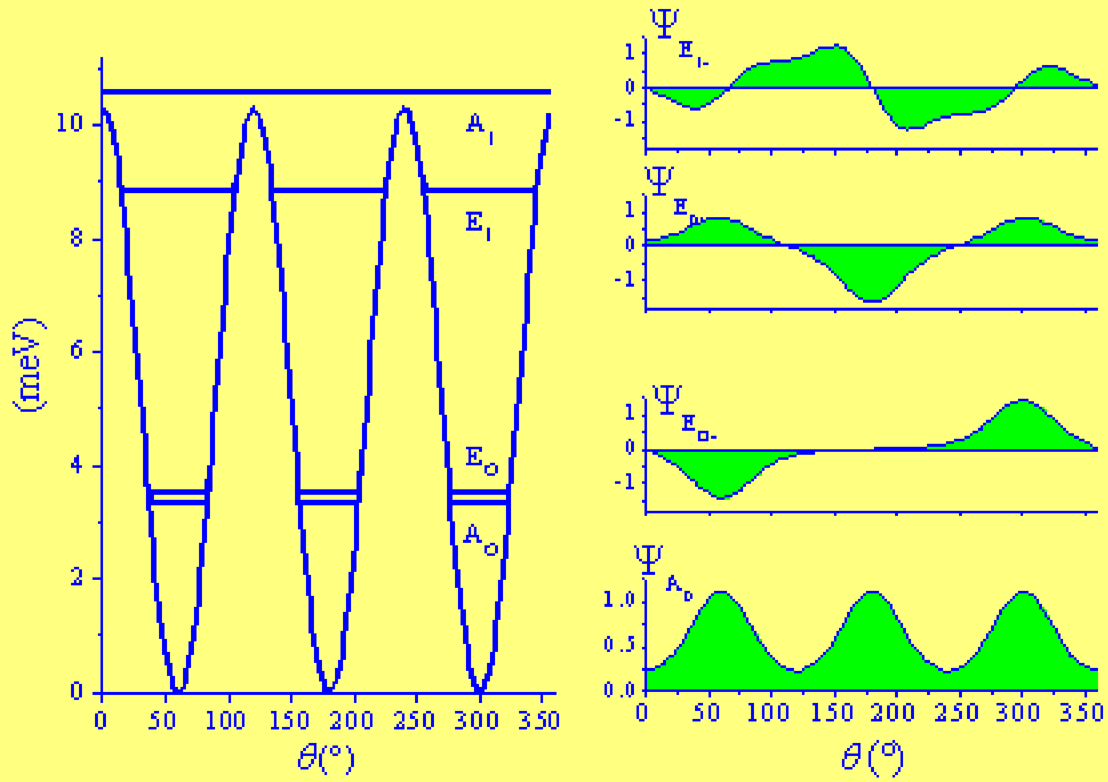
Quantum dynamics in complex environments

Nonlinearity in the quantum regime

Isolated dynamic $h\omega_t = h\omega_{ph}$

Experiments: Spectroscopy
Inelastic neutron scattering
Neutron diffraction
Deuteration

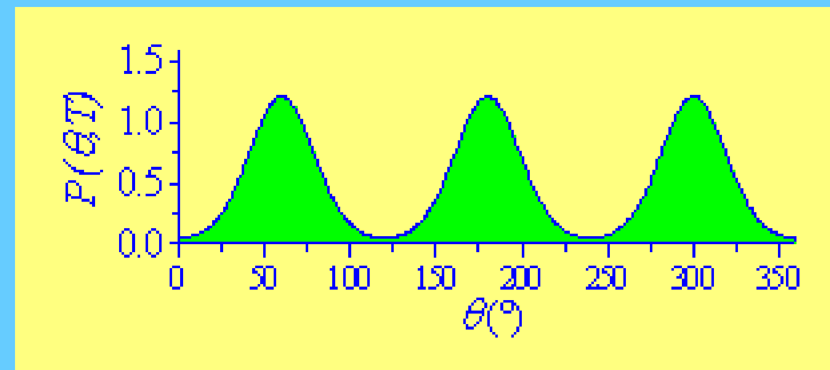
Neutron diffraction and the density probability



F Fillaux, Nonliner Double Day,
Sevilla 2004.

Neutron diffraction and the density probability

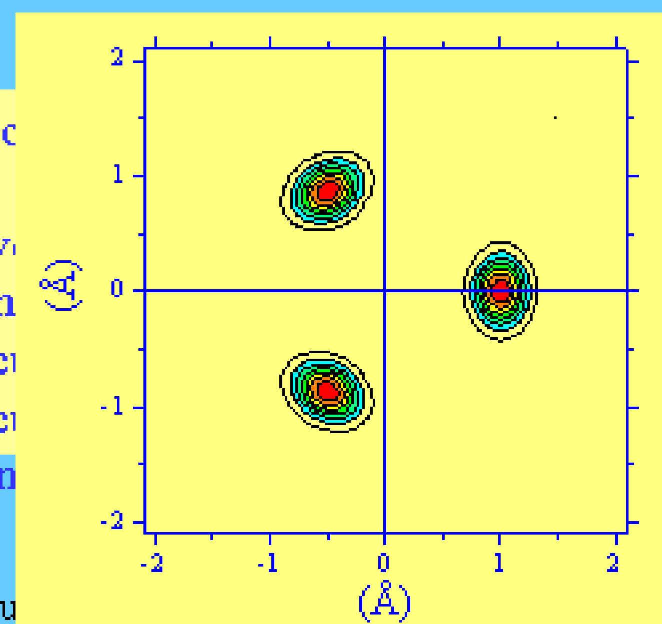
$$P(\phi,T)=\frac{\sum_n \psi_n^2(\phi)\exp\left(-\frac{E_n}{kT}\right)}{\sum_n \exp\left(-\frac{E_n}{kT}\right)}$$



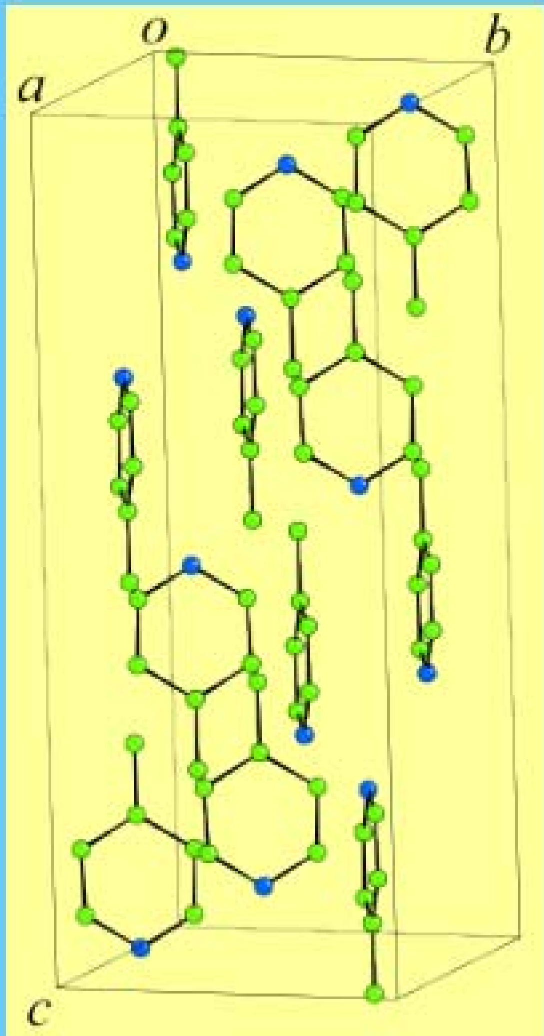
Fourier difference

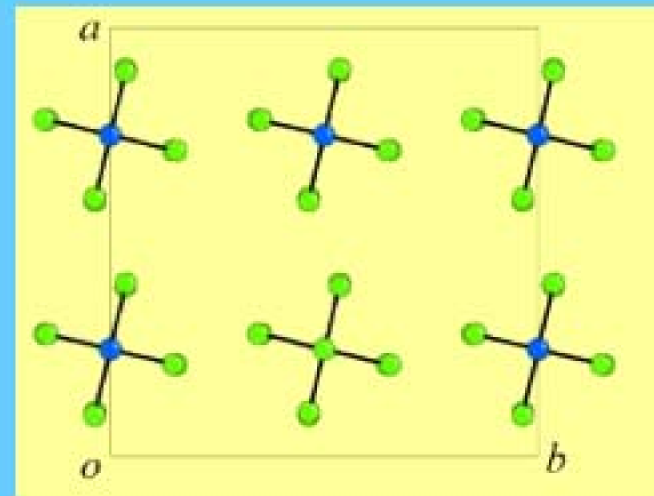
$$\rho(r,\theta,T)=P(\theta,T)\otimes f(r,\theta,T)$$

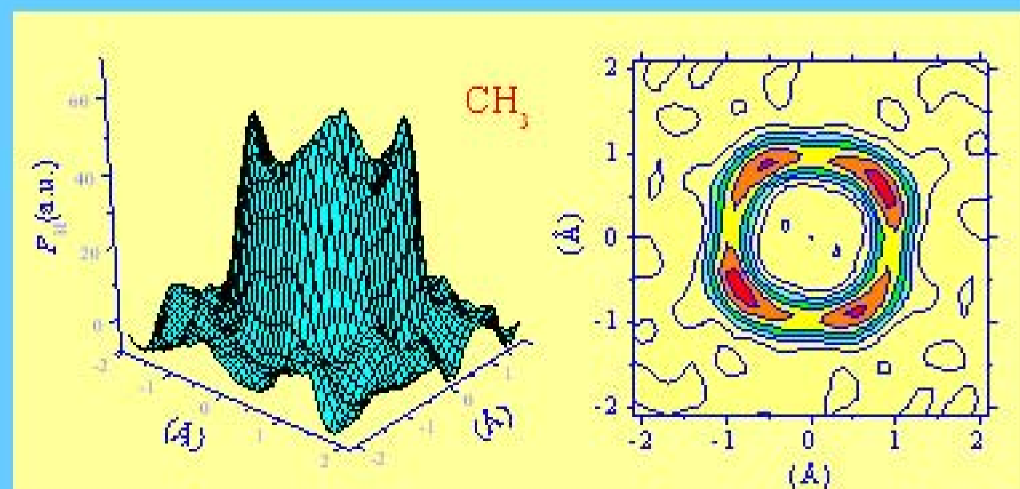
1 Reco ... n pattern D_{exp}
2 Solv
3 Rem ... structure
4 Calc ... tern D_{cal}
5 Calc ... l
6 Tran



γ-Picoline 10 K

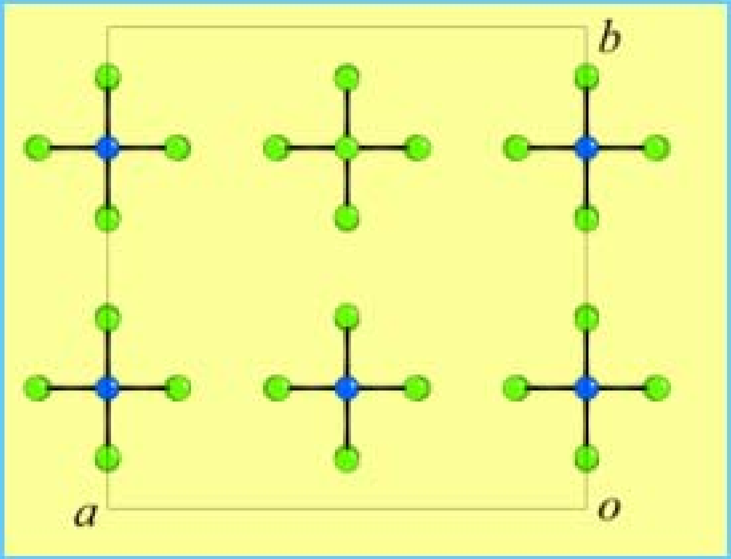


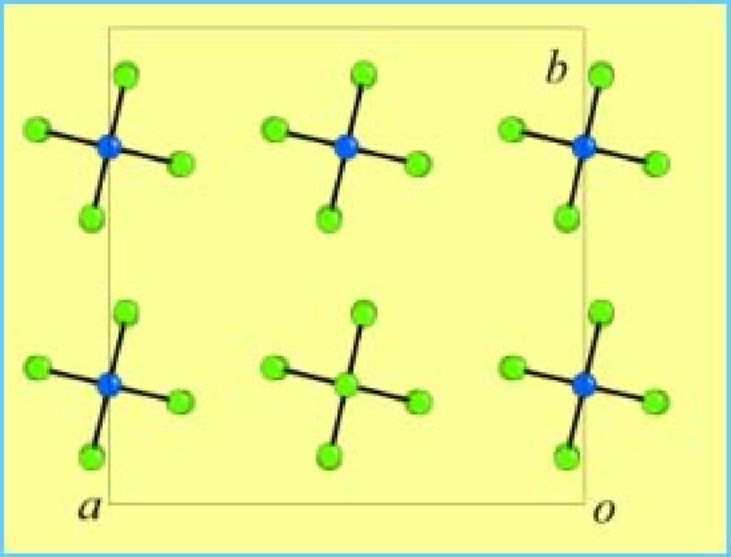




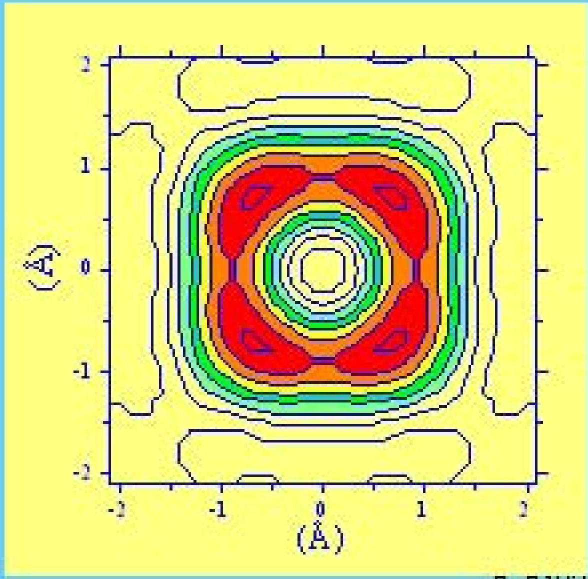
E. Keiser-Morris *et al*, F Fillaux, Nonliner Double Day, Sevilla 2004.

γ-Picoline

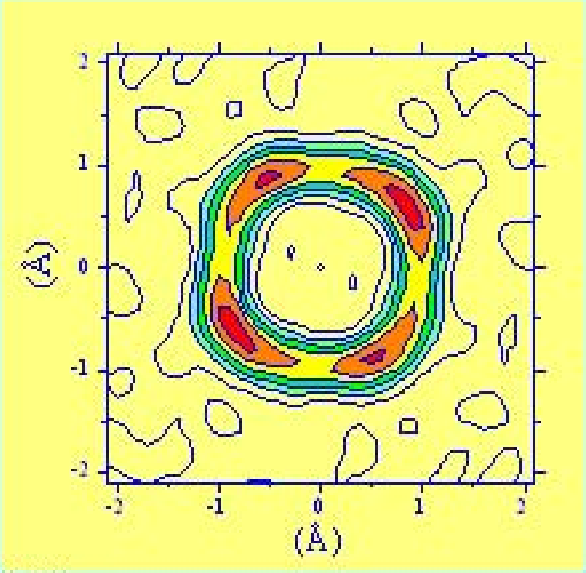




260 K

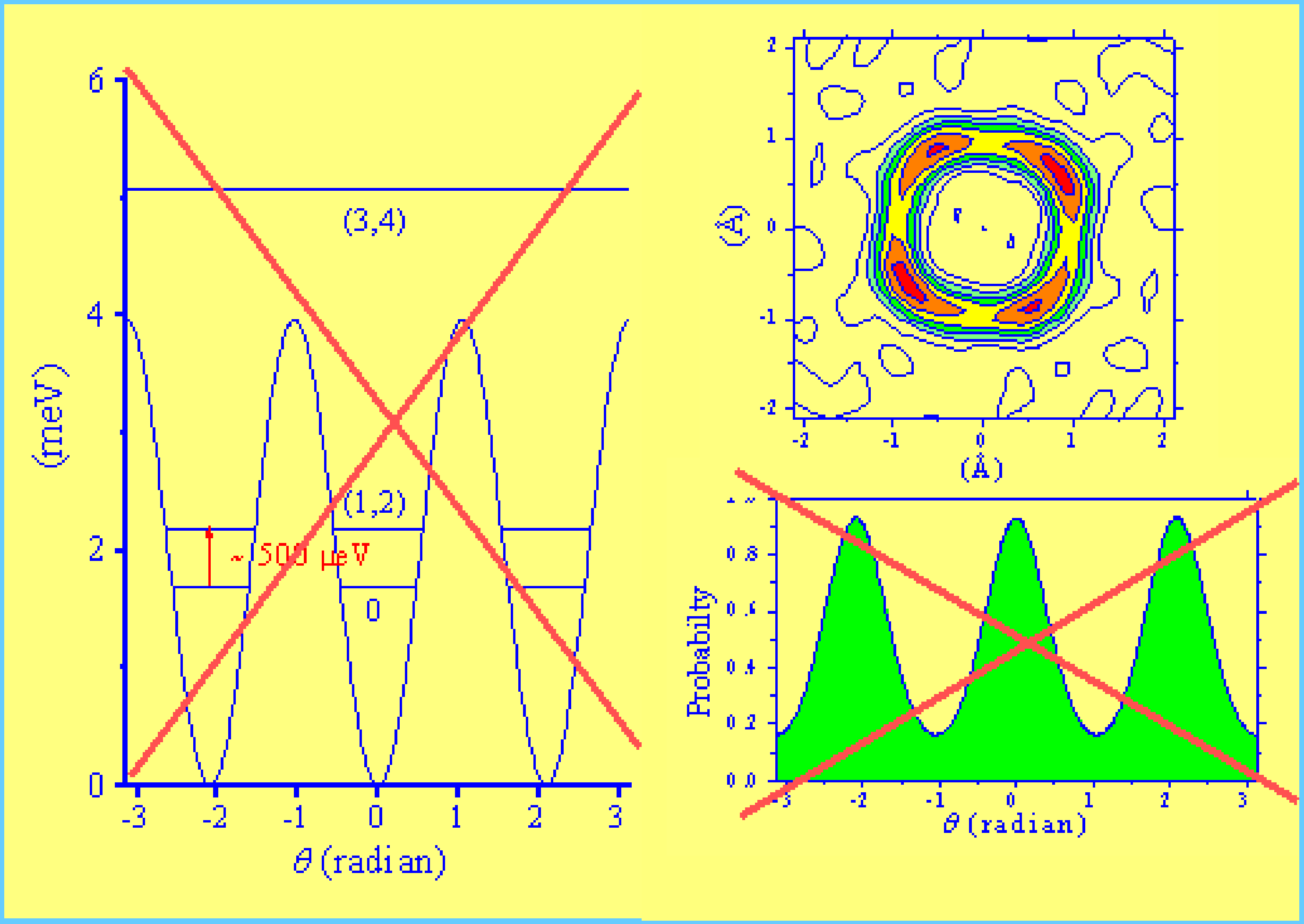


10 K



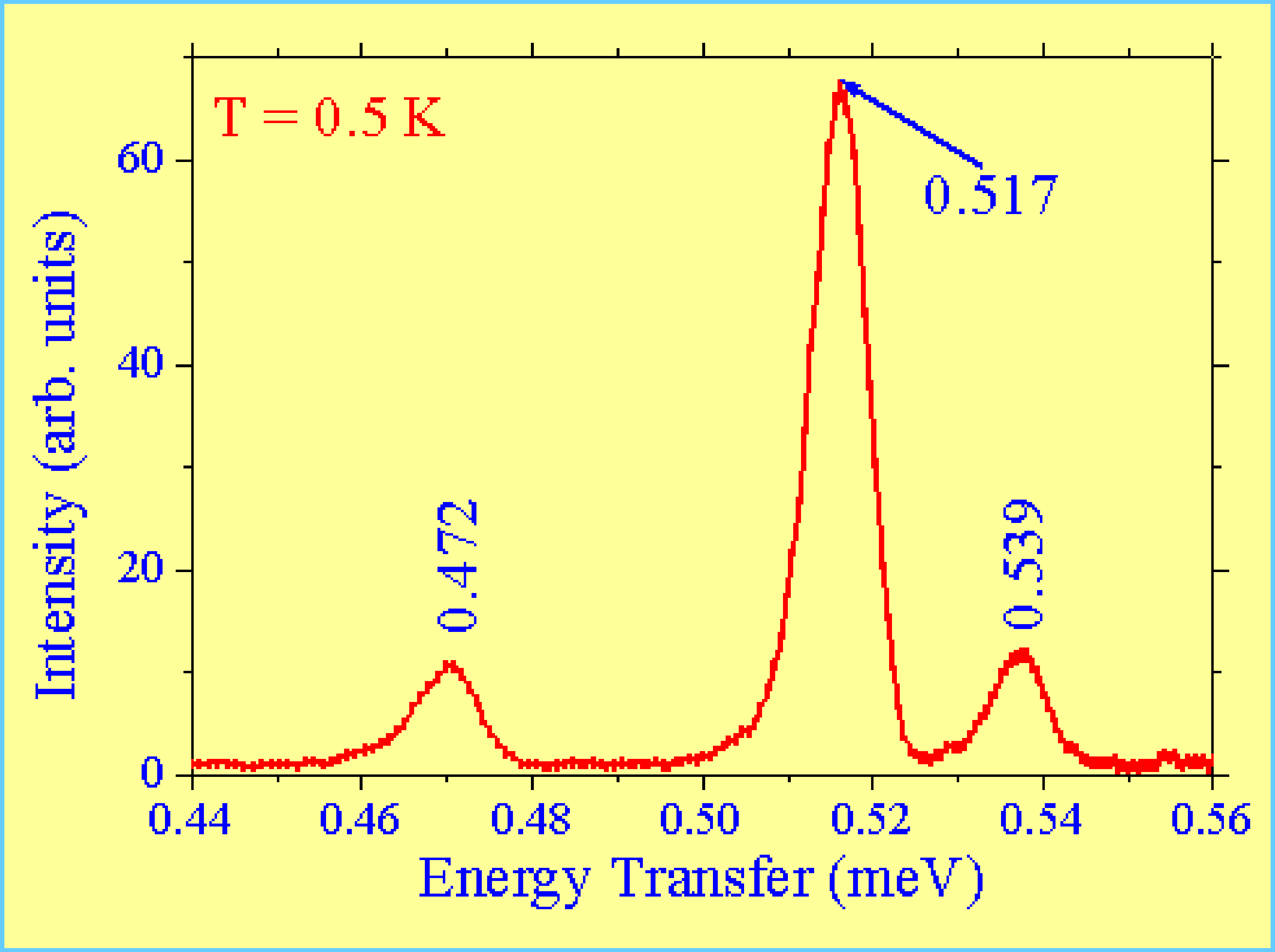
F Fillaux, Nonliner Double Day,
Sevilla 2004.

γ-Picoline Inelastic Neutron Scattering



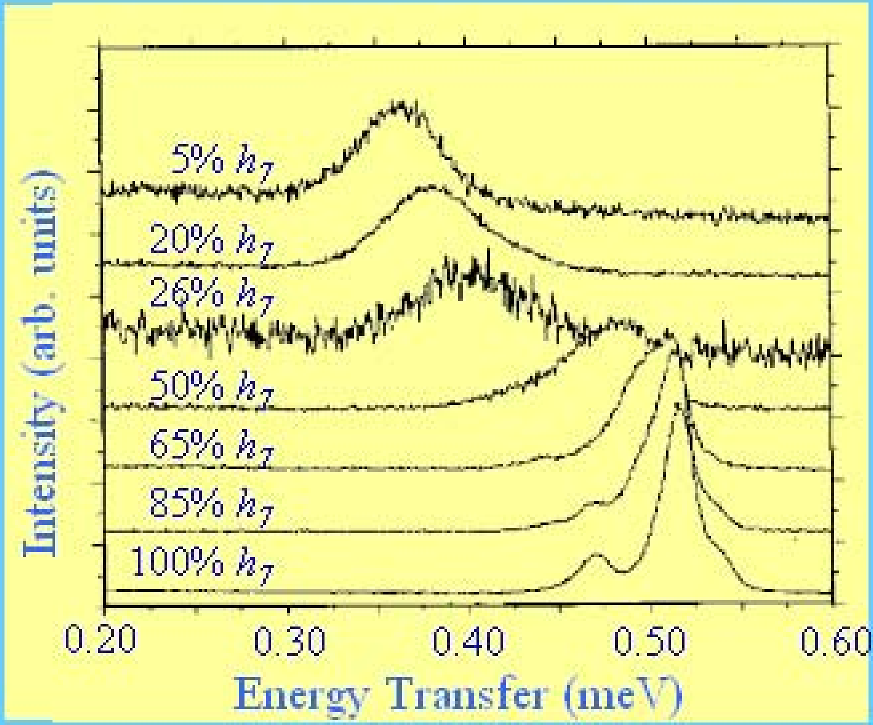
F Fillaux, Nonliner Double Day,
Sevilla 2004.

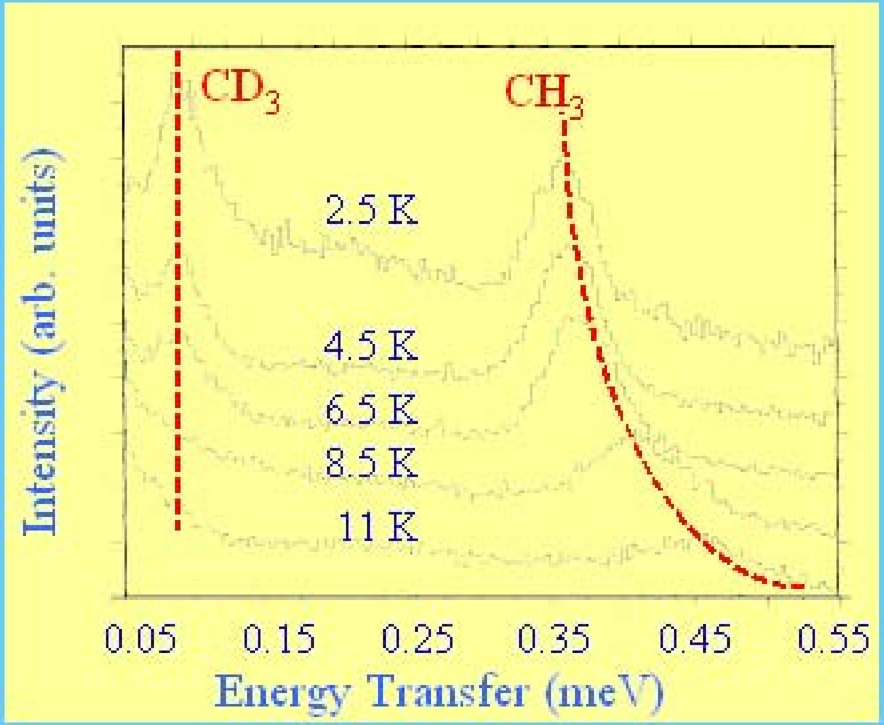
γ-Picoline Inelastic Neutron Scattering



F.Fillaux, C. J. Carlile and G. J. Kearley, Phys. Rev. B **58** (1998) 11416

Isotopic mixtures of 4MP-h_7 (%) and 4MP-d_7

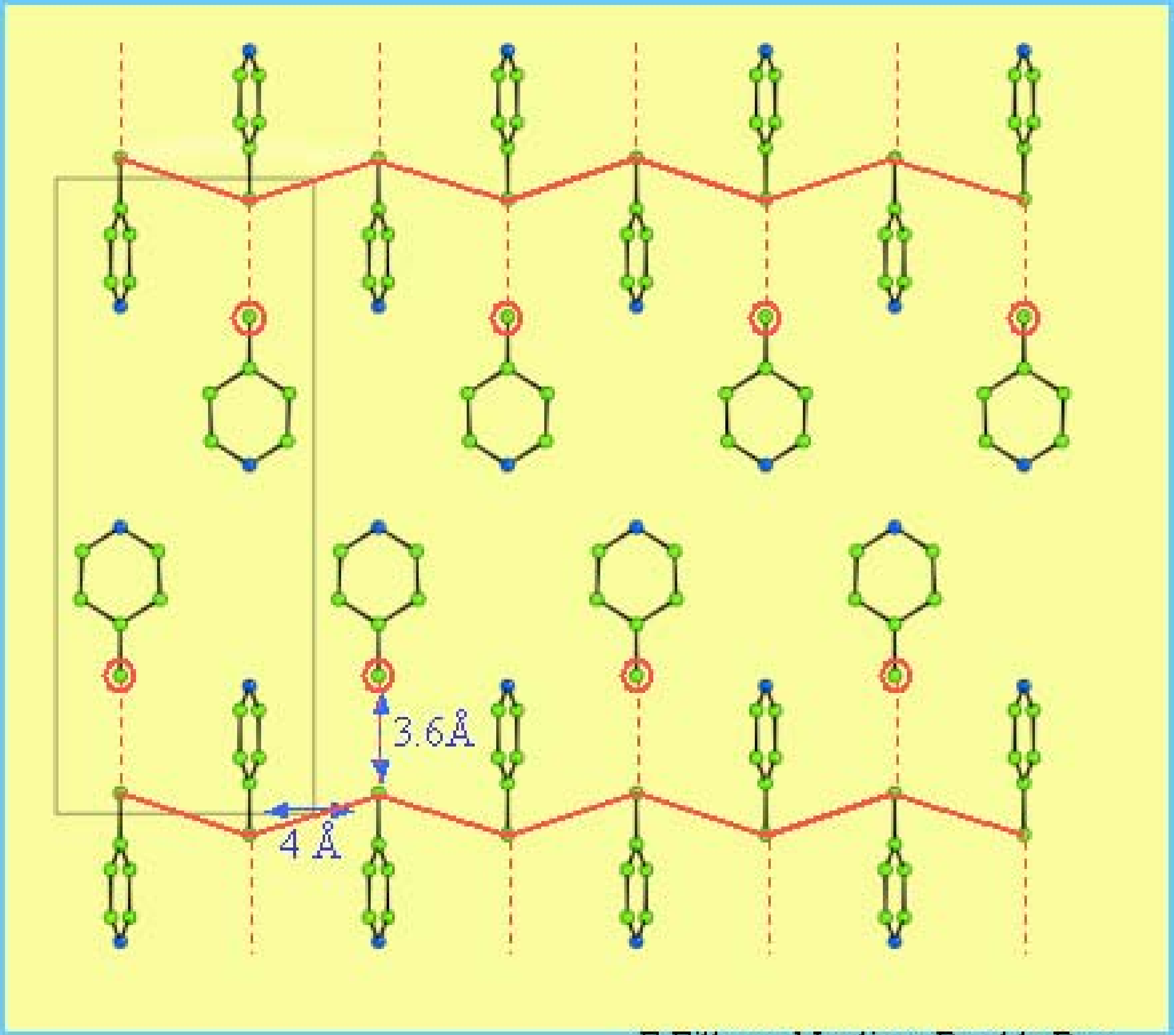


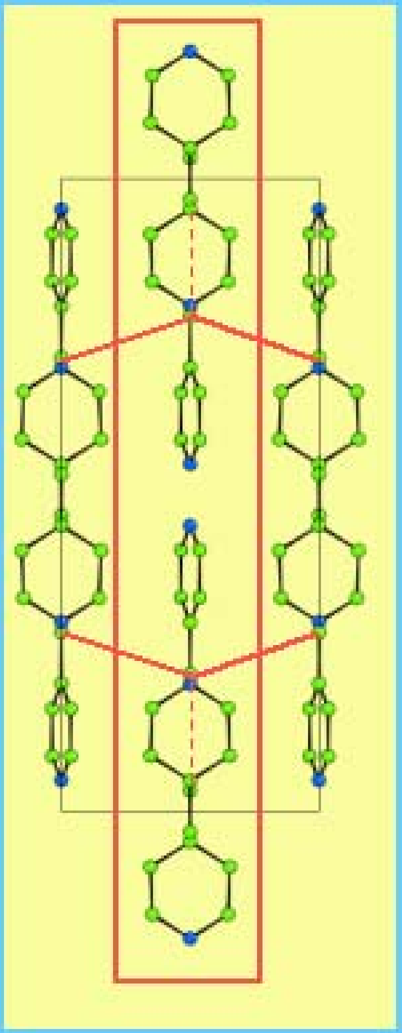


F.Fillaux and C. J. Carlile, Phys. Rev. B **42** (1990) 5990

F Fillaux, Nonliner Double Day,
Sevilla 2004.

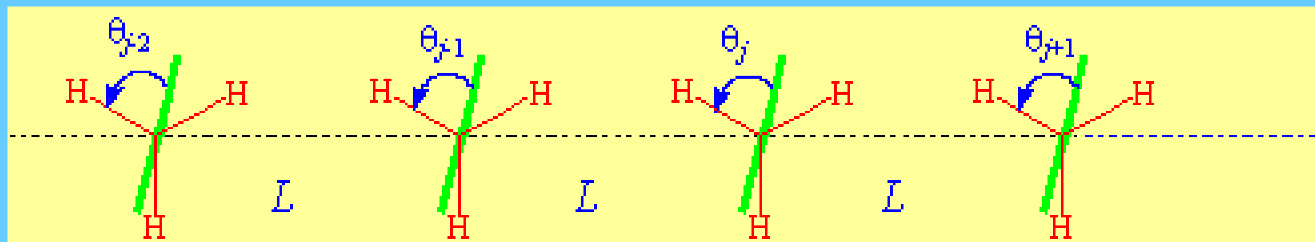
Infinite chains





F Fillaux, Nonliner Double Day,
Sevilla 2004.

The isolated chain of coupled methyl groups



Hamiltonian

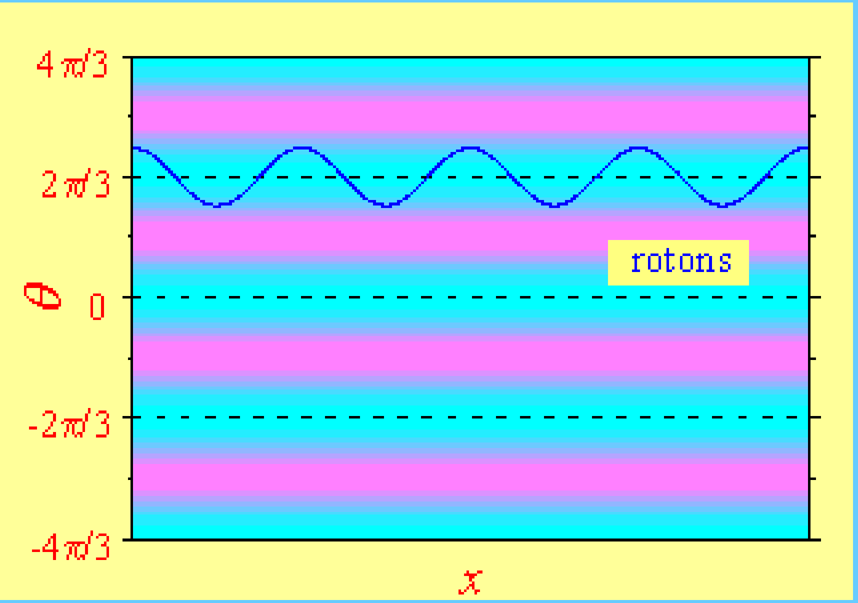
$$H_\theta = \sum_j -\frac{h^2}{2I_r}\frac{\partial^2}{\partial\theta_j^2} + \frac{V_0}{2}\left(1-\cos 3i\,\theta_j\right) + \frac{V_c}{2}\left[1-\cos 3i\left(\theta_{j+1}-\theta_j\right)\right]$$

Linearization

$$H \cong \sum_j -\frac{h^2}{2I_r}\frac{\partial^2}{\partial\theta_j^2} + \frac{V_0}{2}\left(1-\cos 3i\,\theta_j\right) + \frac{(3i)^2 V_c}{4}\left(\theta_{j+1}-\theta_j\right)^2$$

F Fillaux, Nonliner Double Day,
Sevilla 2004.

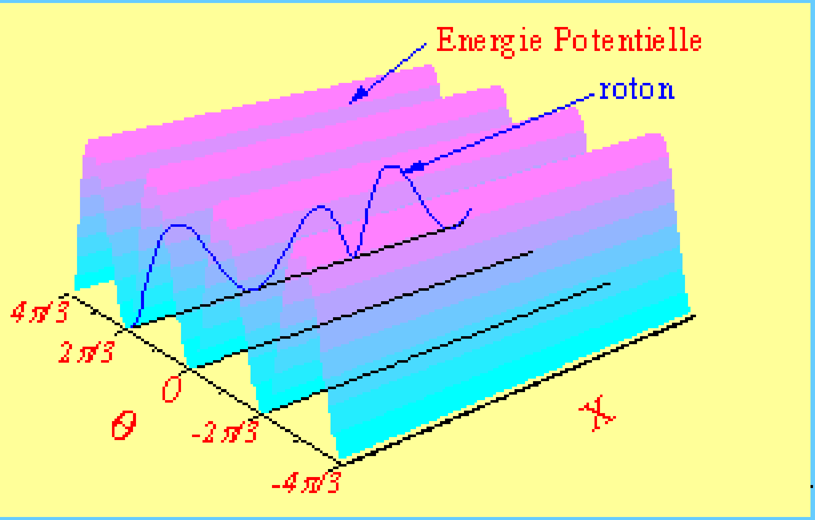
The sine-Gordon excitations (classical)



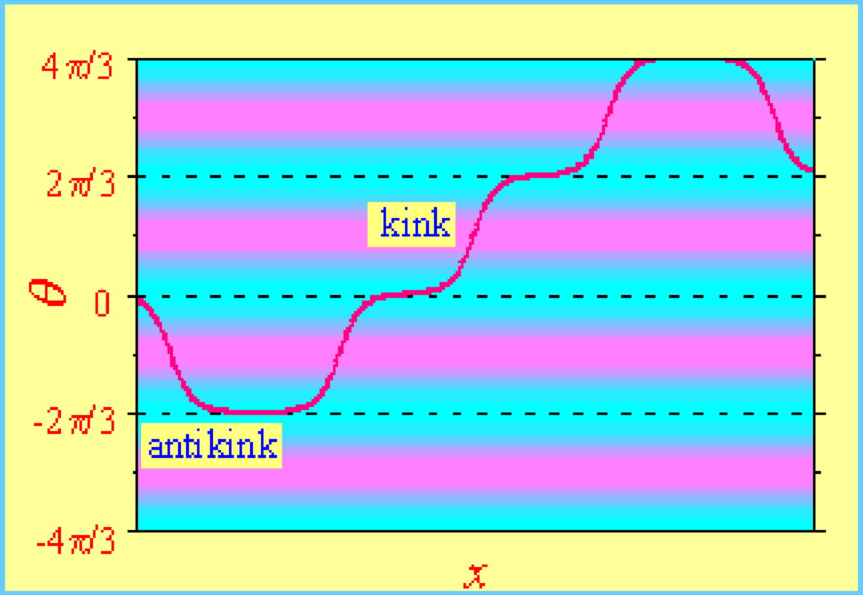
Small amplitude oscillations
(rotons)

$$H \cong \sum_j -\frac{\mathbf{h}^2}{2I_r}\frac{\partial^2}{\partial\theta_j^2} + \frac{9V_0 l^2}{4}\theta_j^2 + \frac{(3l)^2 V_c}{4}\theta_j'^2$$

$$\omega_k^2 = \omega_0^2 + c_0^2 k^2$$



The sine-Gordon excitations (classical)



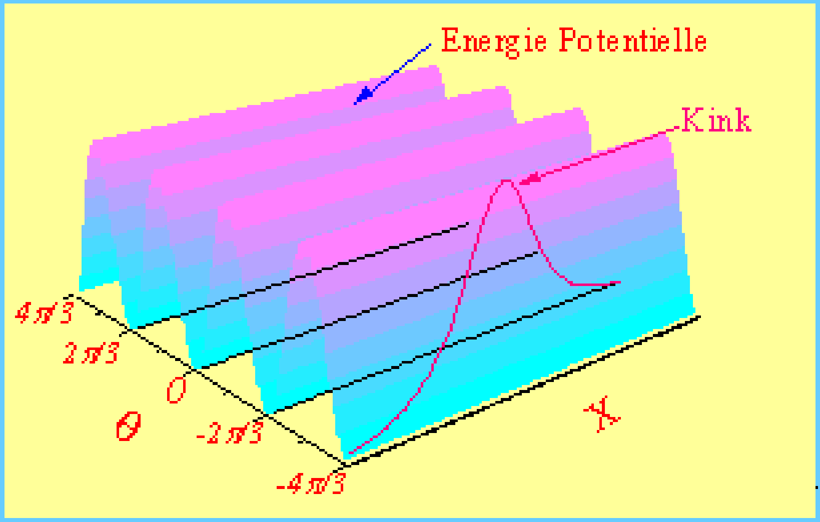
Kink-antikink
(soliton-antisoliton)

$$\theta^{v}_{K\pm}(x,t) = 4\,\mathrm{Arct}\left\{\exp\left[\pm\frac{x-vt}{d\sqrt{1-v^2/c_0^2}}\right]\right\}$$

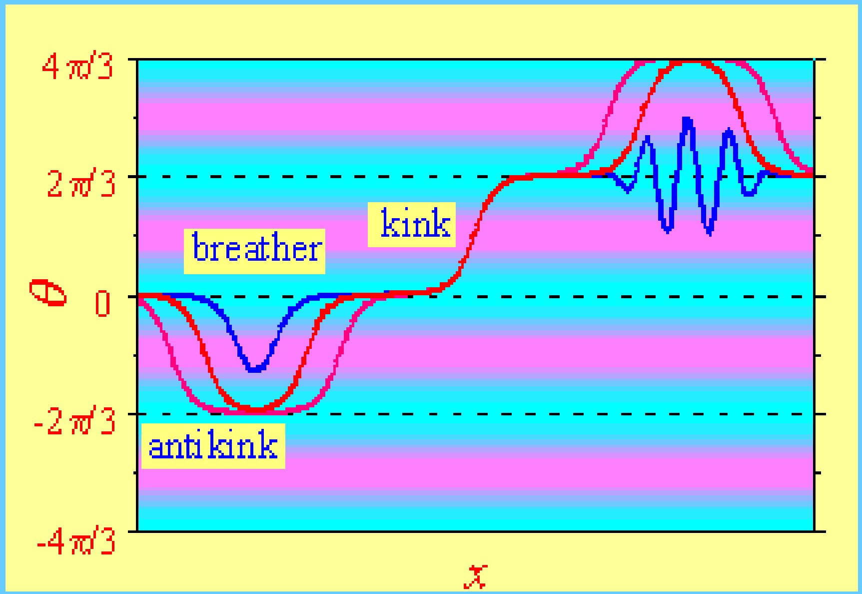
$$d = \frac{c_0}{\omega_0};$$

$$E^{v}_{K\pm} = \frac{E^{0}_{K\pm}}{\sqrt{1-v^2/c_0^2}};$$

$$E^{0}_{K\pm} = M^{0}_{K\pm}c_0^2 = 4\sqrt{V_0 V_c}$$

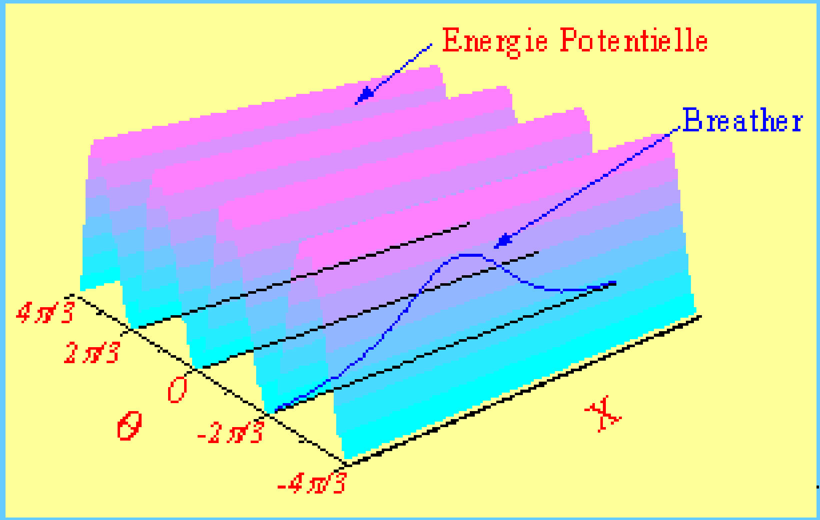


The sine-Gordon excitations (classical)



Breather or Doublet

$$\varphi_B^v(x,t) = 4\,\mathrm{Arct}\left[\frac{\sqrt{\dfrac{\omega_0^2}{\omega_B^2}-1}\,\sin\dfrac{\omega_B\left(t - vx/c_0^2\right)}{\sqrt{1-v^2/c_0^2}}}{\cosh\dfrac{(x-vt)\sqrt{1-\omega_B^2/\omega_0^2}}{d\sqrt{1-v^2/c_0^2}}}\right]$$



$$E_B^v = 2E_{K\pm}^0\,\frac{\sqrt{1-\omega_B^2/\omega_0^2}}{\sqrt{1-v^2/c_0^2}}$$

$$E_B^0 = 2E_{K\pm}^0\sqrt{1-\frac{\omega_B^2}{\omega_0^2}}$$

QUANTIZATION (Semi-classical)

Kink-mass renormalization

$$^{q}M^{0}_{K\pm} = M^{0}_{K\pm}\left[1-\frac{(3i)^2}{8\pi}\right] \quad ; \mathbf{3i} < \sqrt{8\pi} \approx 5$$

Breather mass

$$^{q}M^{0}_{B,l} = 2\,{}^{q}M^{0}_{K\pm}\,\sin\frac{l\,(3i)^2}{16\left[1-\frac{(3i)^2}{8\pi}\right]} \quad ; \quad l = 1,2,\ldots < \frac{8\pi}{(3i)^2}-1$$

Threefold potential: only the l=1 state

Dashen *et al.*, Phys. Rev. D **11** (1975) 3424

QUANTIZATION

Kinetic energy

$${}^{q}E^{p}_{B,l} = \sqrt{{}^{q}E^{2}_{B,l} + p^{2}c_{0}^{2}}$$

Quantization rule

$$\lambda = \frac{h}{p} = \frac{L}{n} \quad ; \quad n = 0, \pm 1, \pm 2, \ldots$$

The energy spectrum

$${}^{q}E^{n}_{B,l} = \sqrt{{}^{q}E^{2}_{B,l} + n^{2}\mathrm{h}^{2}\omega_{c}^{2}}$$

F.Fillaux and C. J. Carlile, Phys. Rev. B **42** (1990) 5990

Tunnelling

$$H = \sum_j -\frac{\hbar^2}{2I_r}\frac{\partial^2}{\partial\theta_j^2} + \frac{V_0}{2}\left(1-\cos 3i\theta_j\right) + \frac{V_c}{2}\left[1-\cos 3i\left(\theta_{j+1}-\theta_j\right)\right]$$

Bloch functions

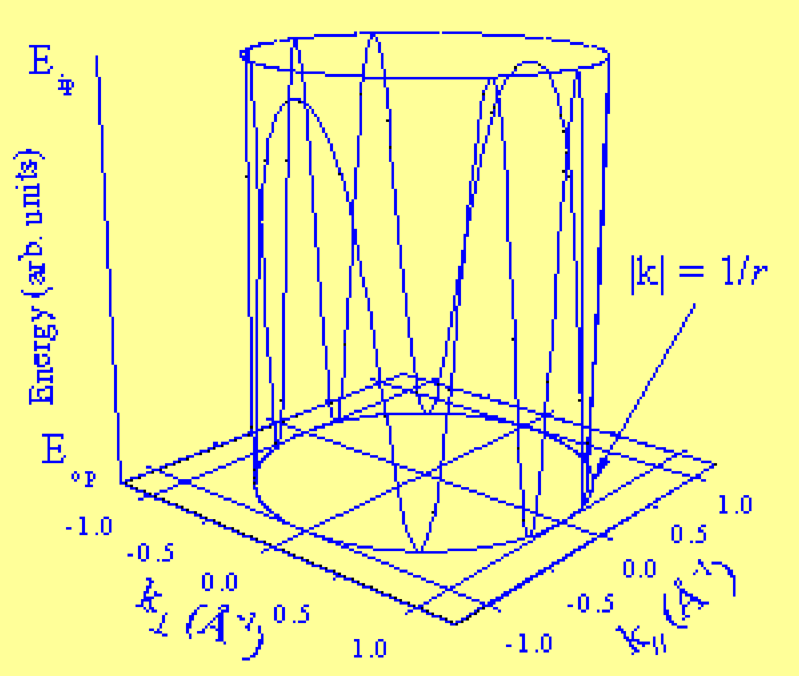
$$\begin{cases} \Psi_{\nu\sigma,k}(\theta) = \exp(ikjL)\,u_{\nu\sigma,k}(\theta) \\ u_{\nu\sigma,k}\left(\theta+\dfrac{2\pi}{3i}\right) = u_{\nu\sigma,k}(\theta) \end{cases}$$

Energy Band Structure

$$\left.\begin{aligned} \varphi_{\upsilon A}(k_p,\theta) &= (2\pi)^{-1/2} a_{\upsilon A0}(k_p) + \pi^{-1/2}\sum_{n=1}^{\infty} a_{\upsilon An}(k_p)\cos(3n\theta) \\ \varphi_{\upsilon\sigma+}(k_p,\theta) &= \pi^{-1/2}\sum_{n=1}^{\infty}\left[a_{\upsilon\sigma+(1n+1)}(k_p)\cos(3n+1)\theta + a_{\upsilon\sigma+(1n+1)}(k_p)\cos(3n+2)\theta\right] \\ \varphi_{\upsilon\sigma-}(k_p,\theta) &= \pi^{-1/2}\sum_{n=1}^{\infty}\left[a_{\upsilon\sigma-(1n+1)}(k_p)\sin(3n+1)\theta + a_{\upsilon\sigma-(1n+1)}(k_p)\sin(3n+2)\theta\right] \end{aligned}\right\}$$

$$H_{\varphi} = -\frac{\hbar^2}{2I_r}\frac{\partial^2}{\partial\theta_j^2} + \frac{V_0}{2}\left(1-\cos 3\theta\right)$$

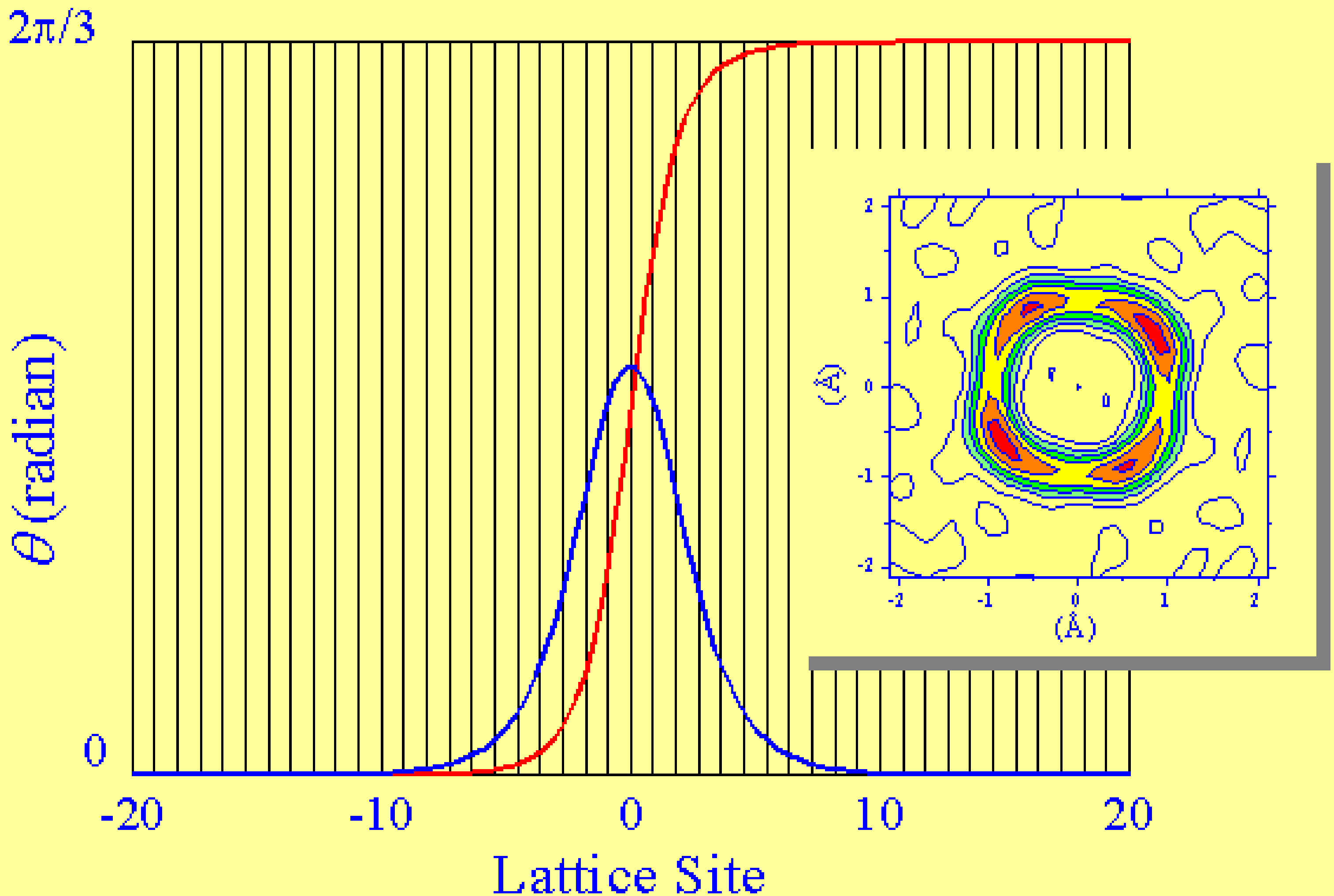
$$H_{c\varphi} = -\frac{\hbar^2}{2I_r}\frac{\partial^2}{\partial\theta_j^2} + \frac{V_0}{2}\left(1-\cos 3\theta\right) + \frac{V_c}{2}\left(1-\cos 6\theta\right)$$



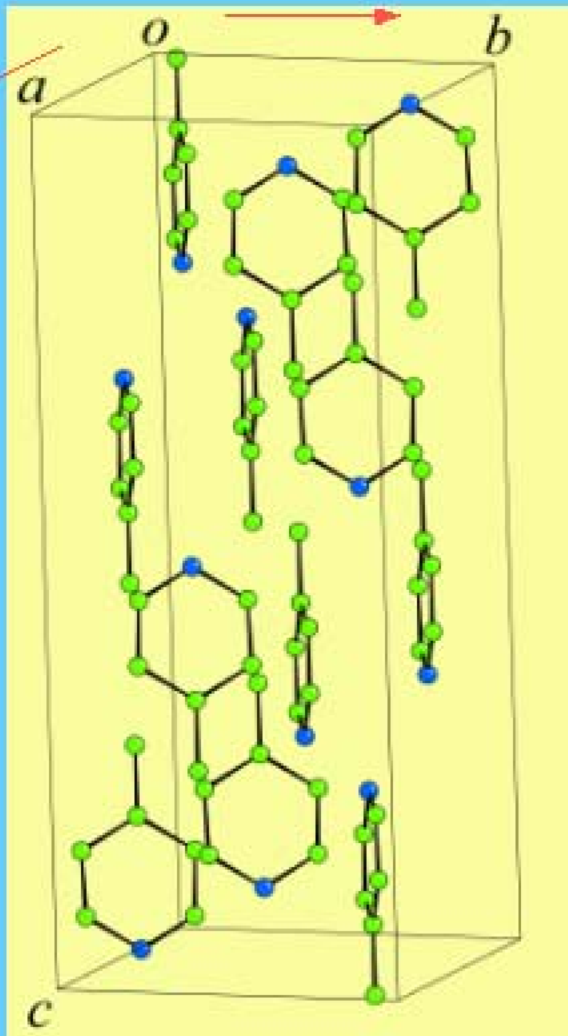
F Fillaux, Nonliner Double Day,
Sevilla 2004.

The sine-Gordon potential

$$V\left(\theta_j\right)_{meV} = \frac{3.66}{2}\left(1-\cos 3\theta_j\right) + \frac{5.46}{2}\left[1-\cos 3\left(\theta_{j+1}-\theta_j\right)\right]$$



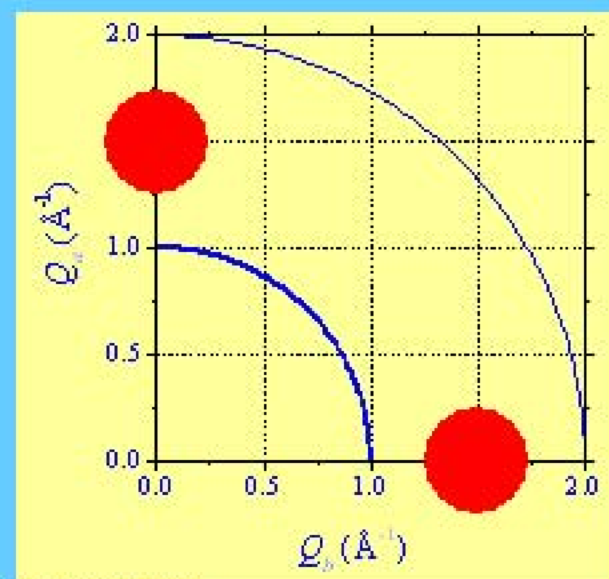
γ-Picoline Single X`stal



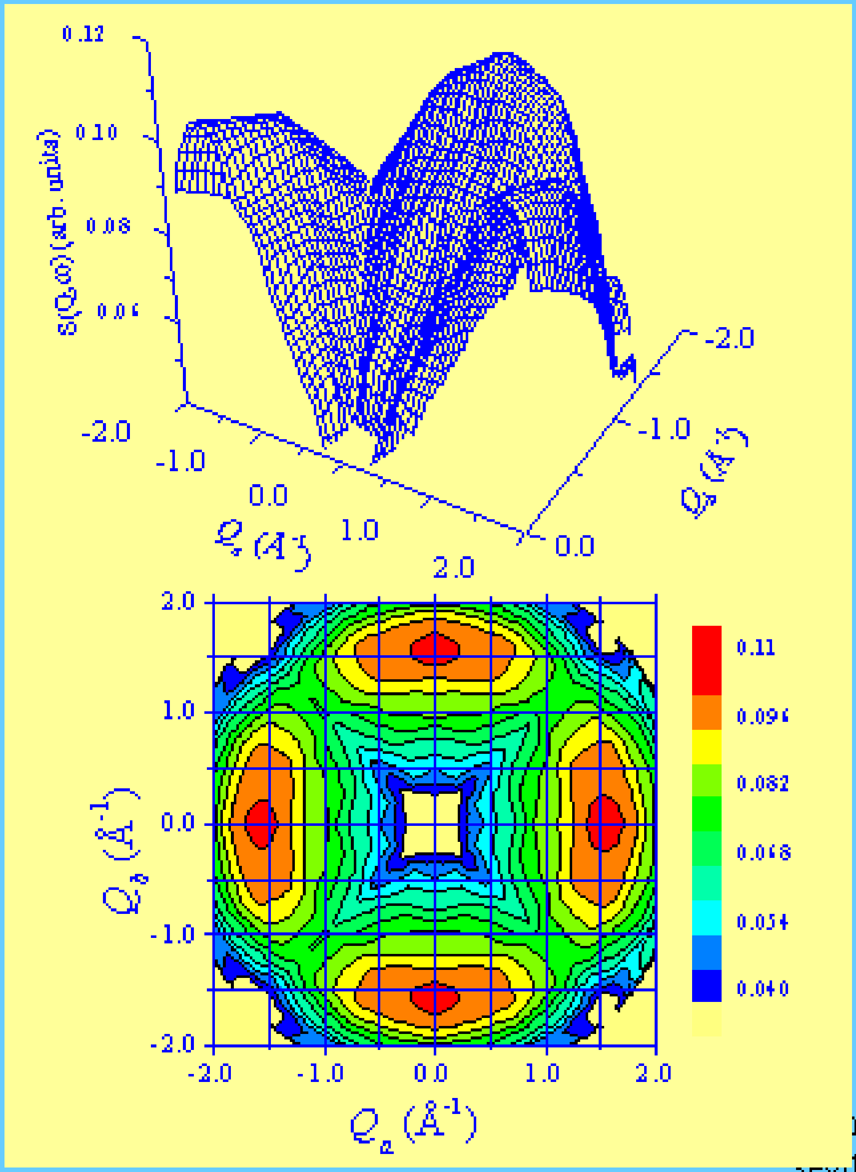
Quantization rule for a free particle in a periodic lattice

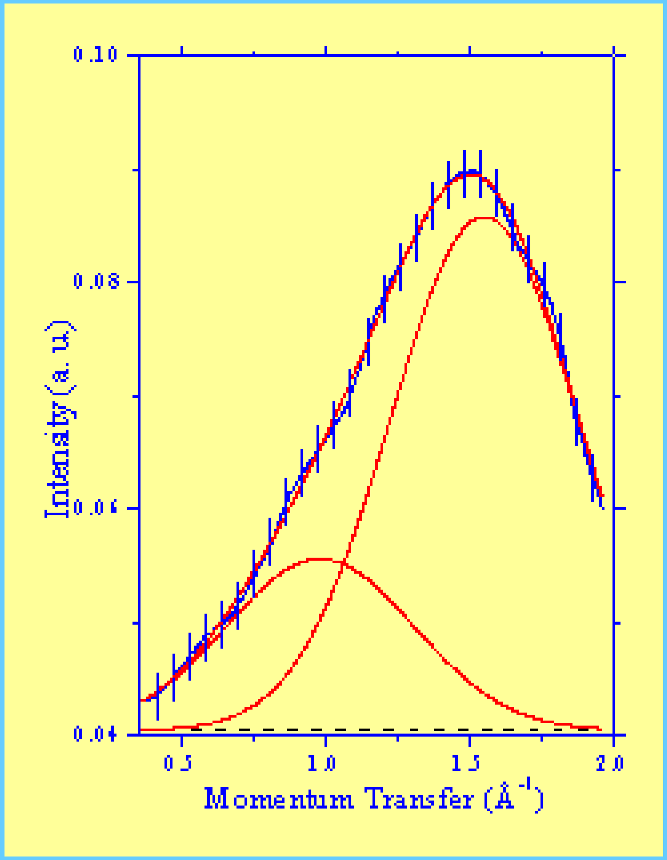
$$\lambda = \frac{h}{p} = \frac{L}{n} \quad ; \quad n = 0, \pm 1, \pm 2, \ldots$$

$$Q = \frac{2\pi}{\lambda} = n\,\frac{2\pi}{L}$$



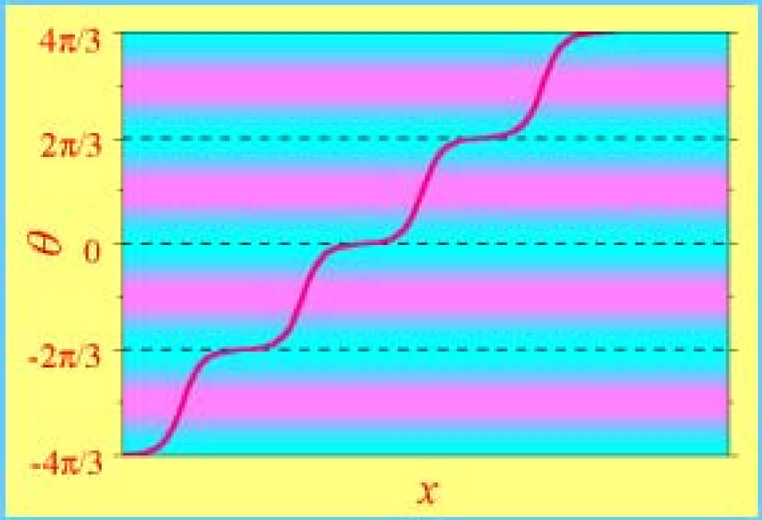
γ-Picoline Single X'stal





$$\hbar\omega = (500 \pm 60)\,\mu eV$$

Multisolitons



$$N\text{-}\left\{\begin{matrix}\text{kinks}\\ \text{antikinks}\end{matrix}\right\} E(N) = N^{q} E_{k}$$

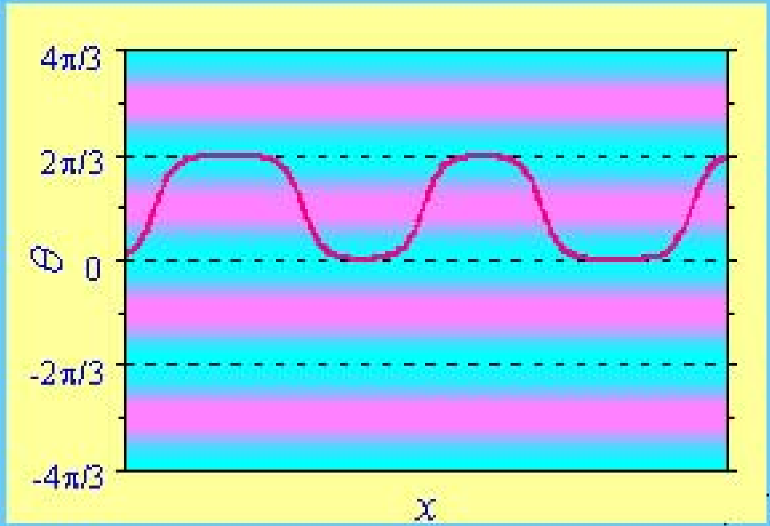
$$E_{k} \approx 11.5\,\text{meV}$$

$$\lambda_{NK} = L / n_{NK}; \quad n_{NK} = 0, \pm 1, \pm 2, K$$
$$p_{NK} = n_{NK} h / L$$

$$E_{op} \leq E(N, n_{NK}) = \sqrt{N^{2q} E_{0k}^{2} + n_{NK}^{2} h^{2} \omega_{c}^{2}} \leq E_{ip}$$

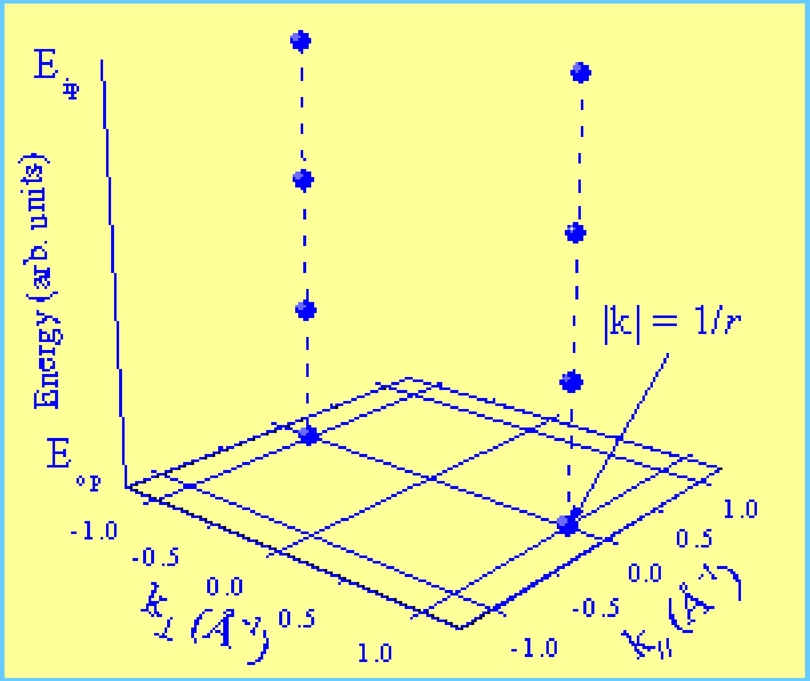
$$E(N, n_{NK}) = N^{q} E_{0K} + E_{0K} - \frac{E_{0K}^{2}}{2NE_{0K}} L$$

$$E_{0K} = n_{NK}^{2} h^{2} \omega_{c}^{2} / 2NE_{0K} \approx (0.742\ \text{meV}) n_{NK}^{2} / N$$



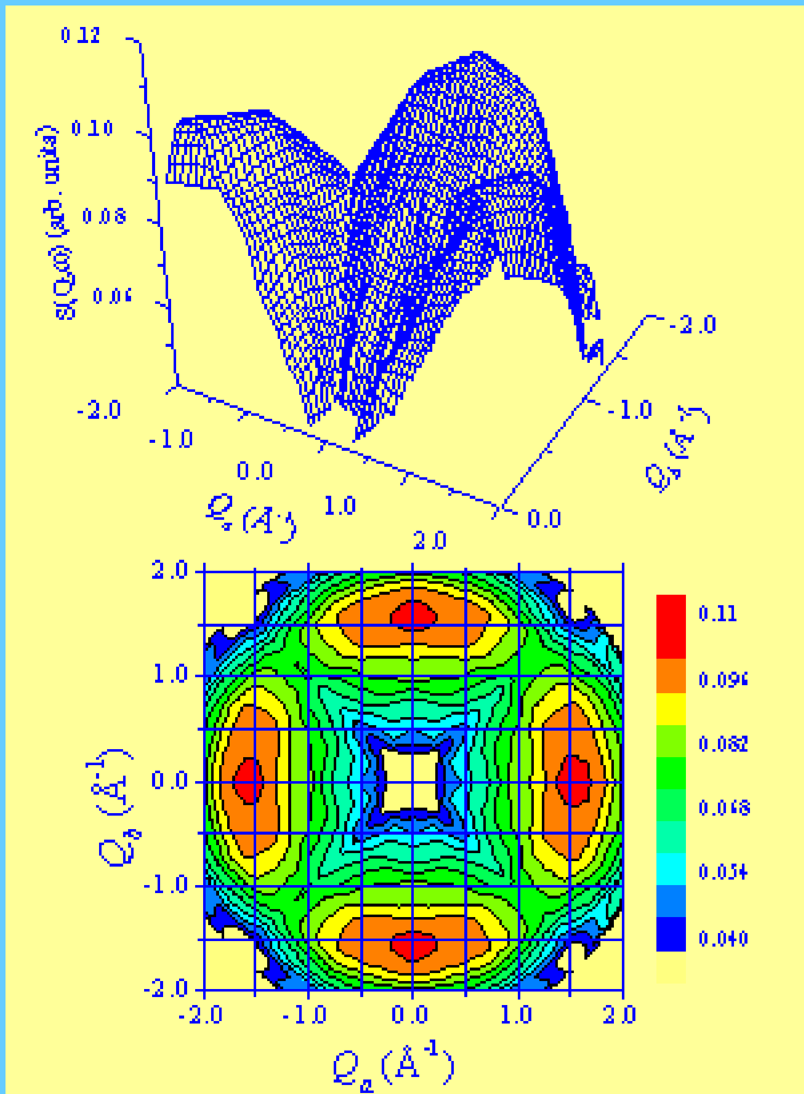
Multisolitons

	$n_{NK} = 4$		
N	$N^{a}E_{0K}$ (meV)	$h\omega$ Calc. (μeV)	$h\omega$ Obs. (μeV)
22	253.0	539	539
23	264.5	515	514
24	276.0	494	500
25	287.5	474	472

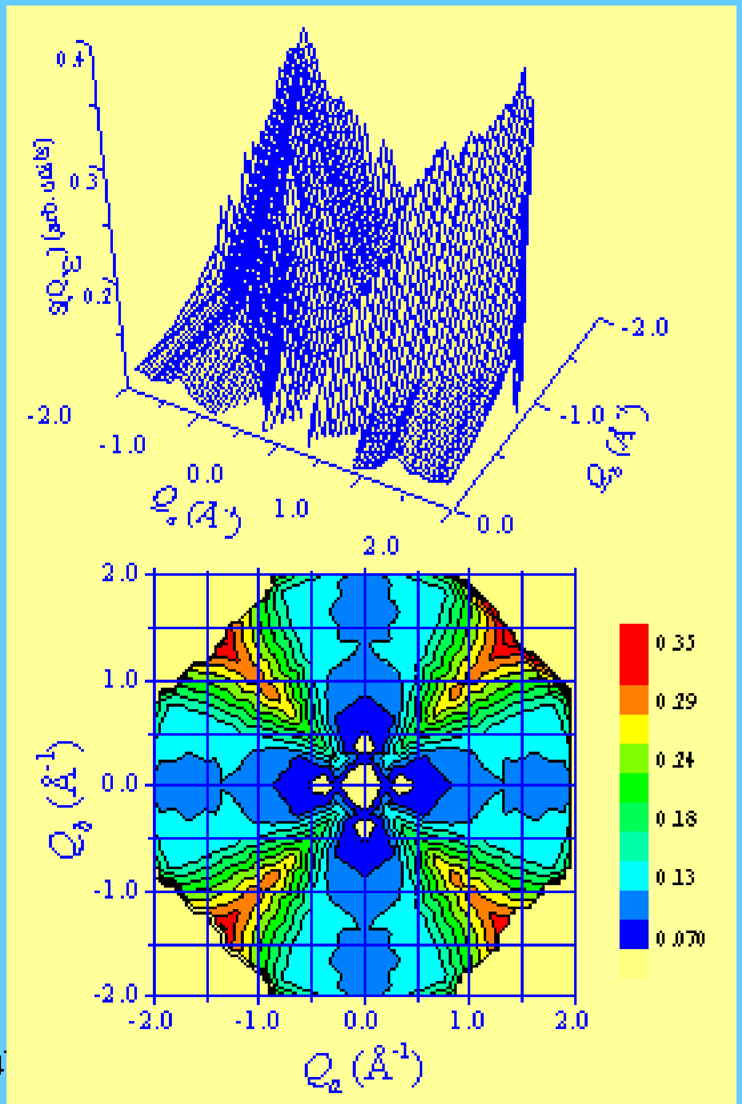


γ-Picoline Single X'stal

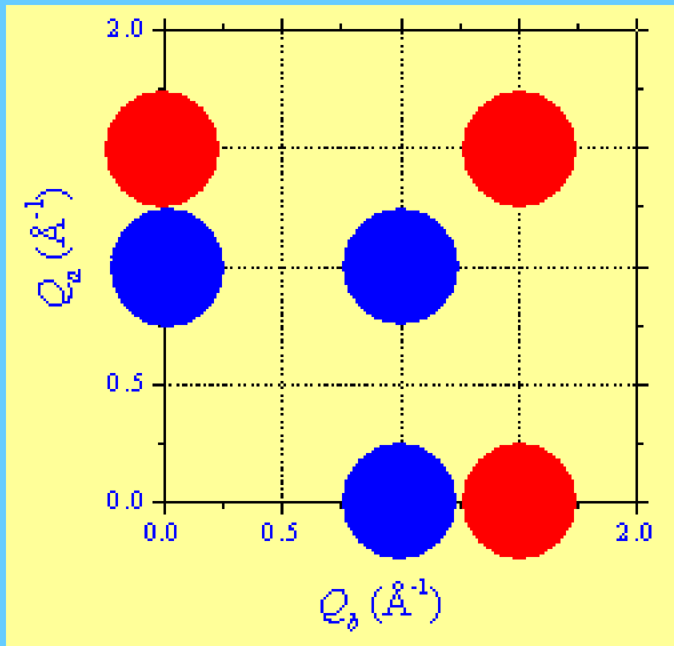
$\hbar\omega = (500 \pm 60)\,\mu eV$



$\hbar\omega = -(500 \pm 60)\,\mu eV$



Bound states

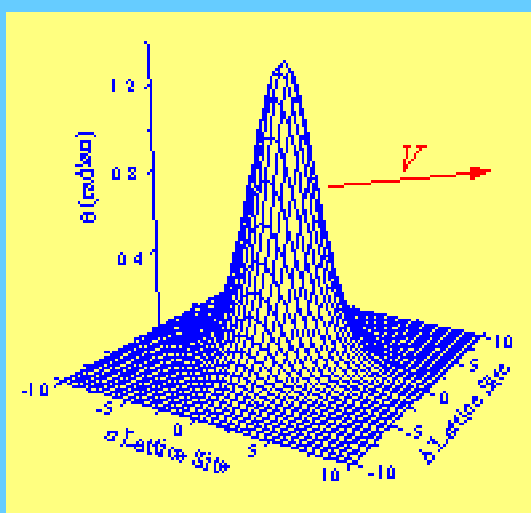


Multikinks

$$p_{2NK} = \sqrt{2}\, n_{NK} h / L; \quad n_{NK} = 0, \pm 1, \pm 2, K$$

$$E_{2K}(N, n_{NK}) = 2N^q E_{0K} + E_{0K} - \frac{E_{0K}^2}{4NE_{0K}} L$$

$$\Delta E(N, n_{NK}) = 2E(N, n_{NK}) - E_{2K}(N, n_{NK})$$
$$= E_{0K} - \frac{3E_{0K}^2}{4NE_{0K}} L$$



Beathers

$$\Delta E(n_B) = E_{0B} - \frac{3E_{0K}^2}{4NE_{0K}} L$$

F Fillaux, Nonliner Double Day, Sevilla 2004.

CONCLUSION

Quantum sine-Gordon

- Multikinks: Thermally activated collective rotational tunnelling
- Breathers: Harmonic oscillations in the ground state
- Exact Hamiltonian in the ground state

Experiments

- Powders and single X'stals
- Diffraction and spectroscopy
- Neutrons, infrared and Raman
- Isotope substitutions (chemistry)

4-Methylpyridine: A "natural" quantum computer for the sine-Gorodon equation ($\neq$ molecular dynamics simulations)

ACKNOWLEDGEMENTS

Collaborations

LADIR (Thiais)

Spectroscopy: N. Le Calvé, B. Pasquier, L. Soulard, G. Braathen, B. Nicolaï

Chemistry: M. F. Lautié, N. Leygues

ISIS (Chilton) C. J. Carlile, M. A. Adams

ILL (Grenoble) G. J. Kearley, A. Heidemann, J. C. Cook

KEK (Tsukuba) S. Ikeda

Chemistry Lab (Osaka) A. Inaba

Opponents (a few among them)

A. Hüller, W. Press, R. Scherm, H. P. Trommsdorff...

4-Methyl-Pyridine

Historical Perspective

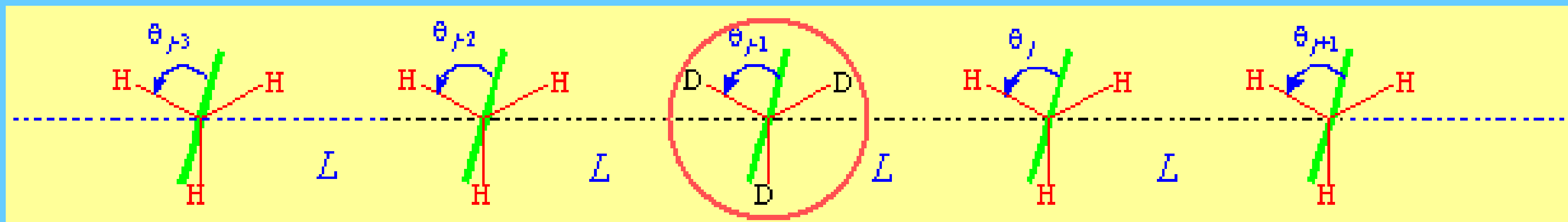
1965	INS ~ 500 μeV	B. Alefeld, *et al.*, J. Chem. Phys. **63** 4415.
1983	RQN	A. Péneau *et al.*, J. Mol. Struct. **111** 227
1985	Neutron Diffr. 120 K	U. Ohms *et al.*, J. Chem. Phys. **83** 273.
1986	Raman	L. Soulard *et al.*, J. Phys. C **19** 6695.
1987	INS high resolution	J. Abed *et al.*, Chem. Phys. Lett., **141** 215.
1989	"	C. J. Carlile *et al.*, Chem. Phys. **134** 437.
1990	Neutron Diffr. 5 K	C. J. Carlile *et al.*, Z. Kristallogr. **193** 243.
1990	INS isotope mixtures	F. Fillaux *et al.*, Phys. Rev. B **42** 5990.
1991	INS CH_2D	F. Fillaux *et al.*, Phys. Rev. B **44** 12280.
1995	INS IN10 and LAM 80	F. Fillaux *et al.*, Physica B **213&214** 646.
1998	INS IN5	F. Fillaux *et al.*, Phys. Rev. B **58** 11416.
2000	Raman	M. Plazanet *et. al.*, Chem. Phys. Letters, **320** 651
2003	Diffr. & INS single X'stal	F. Fillaux *et al.*, Phys. Rev. B **68** 224301.

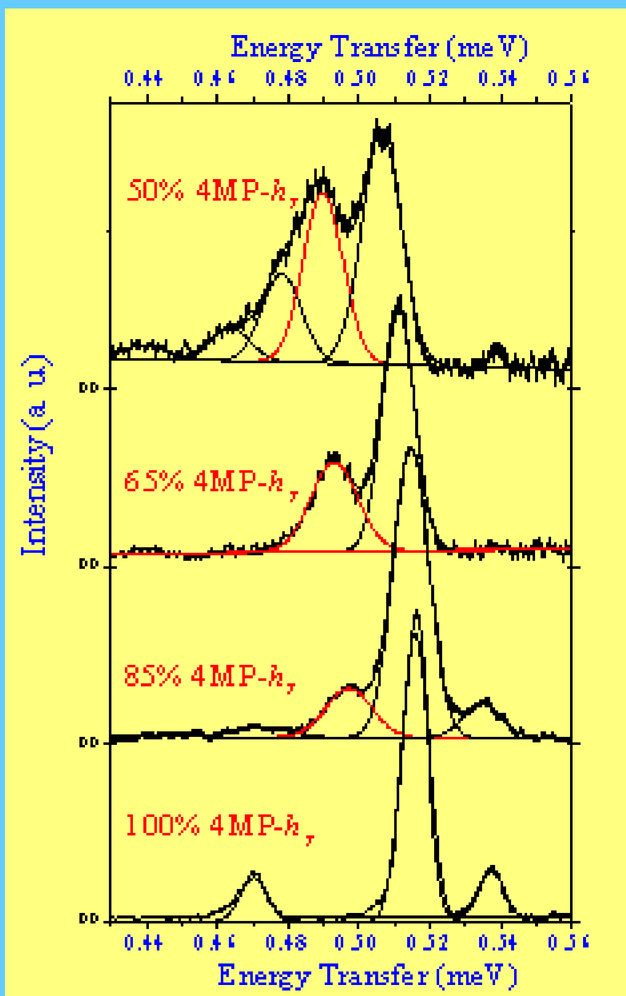
ISOTOPE MIXTURES: CH_3/CD_3

1- Breathers trapped by local impurities

F.Fillaux, C. J. Carlile and G. J. Kearley, Phys. Rev. B **58** (1998) 11416

Breather trapped by a local impurity

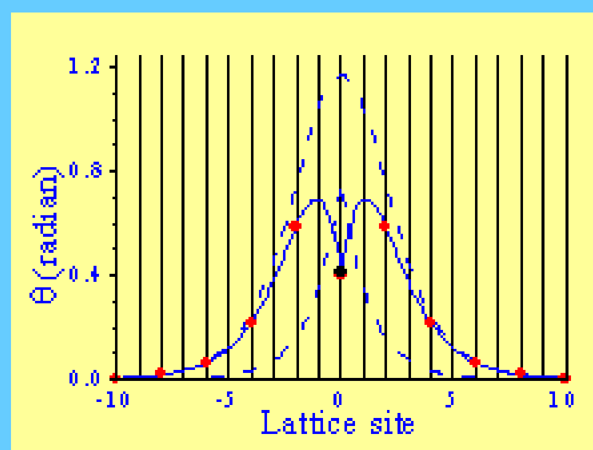


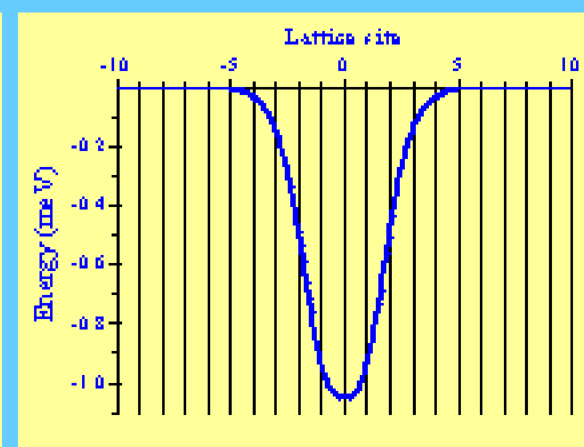


$$H=\sum_j -\frac{\hbar^2}{2I_r}\frac{\partial^2}{\partial\theta_j^2}+\frac{V_0}{2}\left(1-\cos 3i\theta_j\right)+\frac{V_c}{2}\left[1-\cos 3i\left(\theta_{j+1}-\theta_j\right)\right]+\frac{\hbar^2}{4I_r}\frac{\partial^2}{\partial\theta_0^2}$$

$$U_{eff}(x)=-4F\cot\mu\cosh(x\sin\mu)\left[1+\cot^2\mu\cosh^2(x\sin\mu)\right]^{-3/2}$$

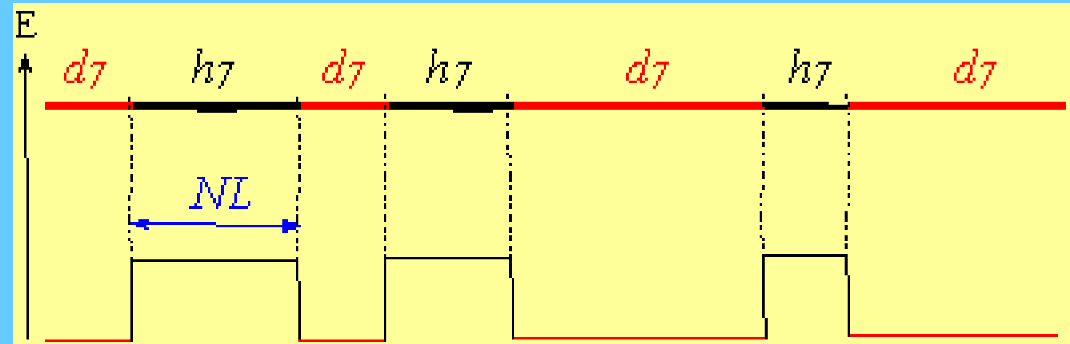
$$\mu=\frac{(3i)^2}{16\left[1-(3i)^2/8\pi\right]}$$



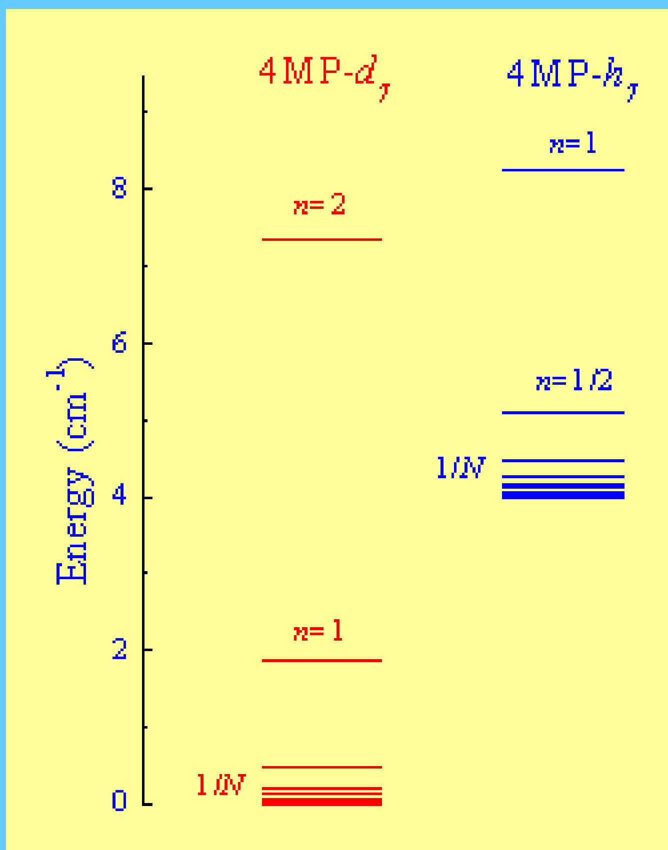


F Fillaux, Nonliner Double Day,
Sevilla 2004.

Isotope Mixtures CH_3/CD_3



2-Breathers in boxes



$$E_{l,N} = \left[E_B^2(l) + \omega_c^2 / N^2 \right]^{1/2}$$

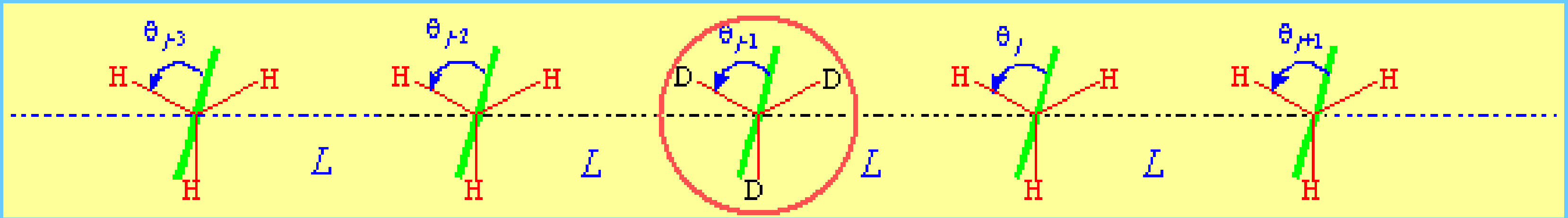
$$N = \pm 1, \pm 2, \ldots$$

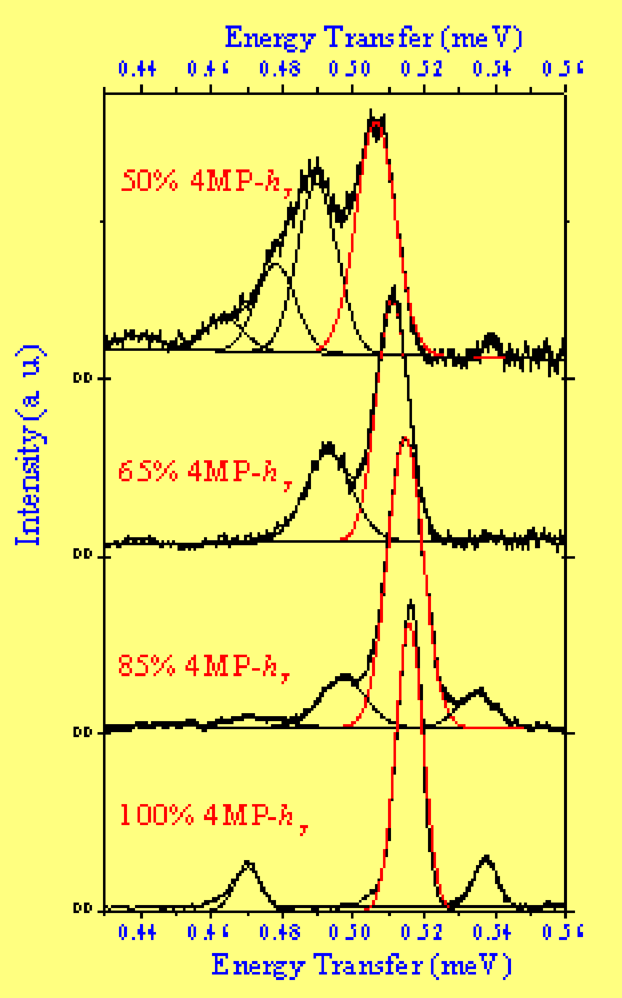
$$E_{l,n} = \left[E_B^2(l) + n^2 \omega_c^2 \right]^{1/2}$$

$$n = \pm 1, \pm 2, \ldots$$

F.Fillaux and C. J. Carlile, Phys. Rev. B (1990) 5990

Low Concentration of CD_3: Breathers in boxes

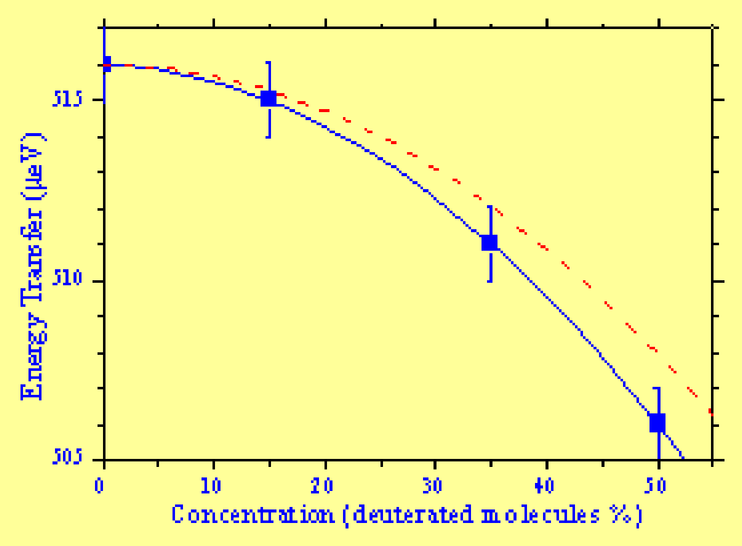




$$\nu_{nm} = \sqrt{4E^2_{B,1,0} + n^2\hbar^2\omega_c^2} - \sqrt{4E^2_{B,1,0} + \hbar^2\frac{\omega_c^2}{N^2}}$$

$n = \pm 1, \pm 2, L \; ; \; N = 1, 2, L$

$$\bar{\nu}_{01} \cong \frac{\hbar^2\omega_c^2}{2\,4E^2_{B,1,0}}\left(1 - \frac{c_d^2}{16}\right) \;, \; c_d << 1$$



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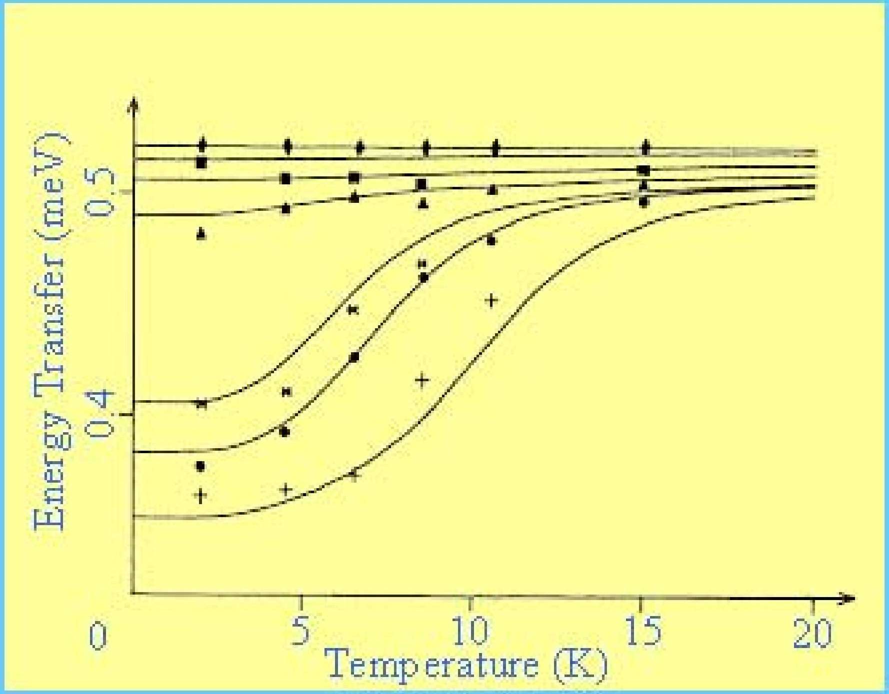
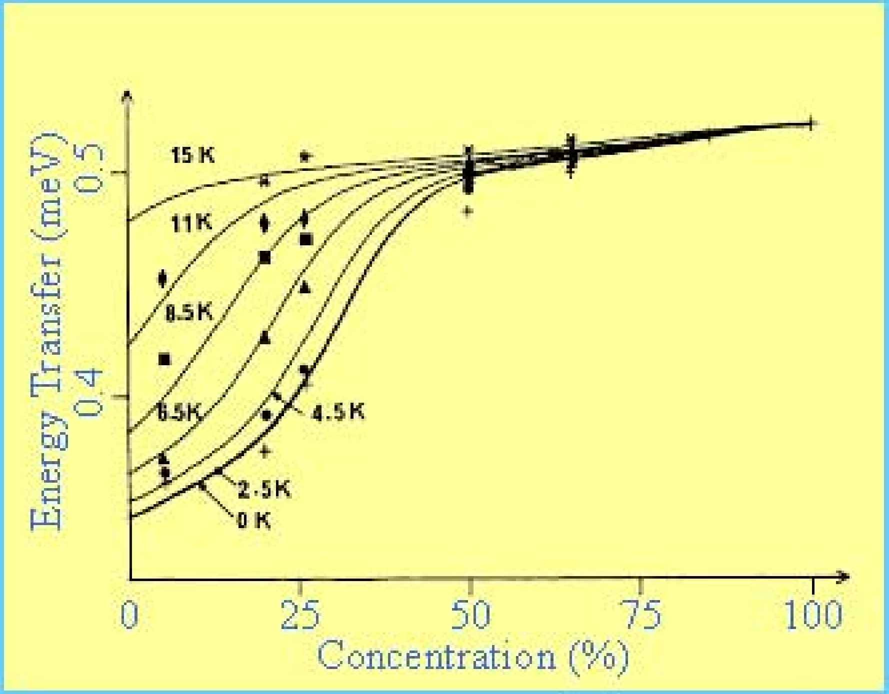
Sevilla

F. Fillaux *et al.*, PRB **58** (1998) 11416

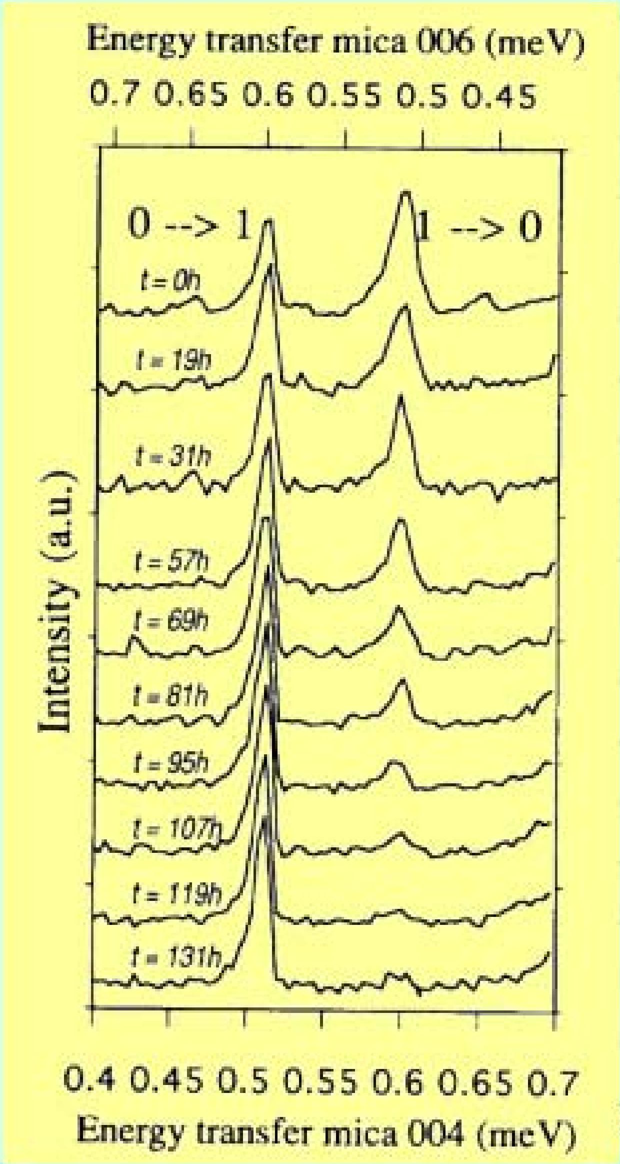
Isotope mixtures CH_3/CD_3: Breathers in boxes



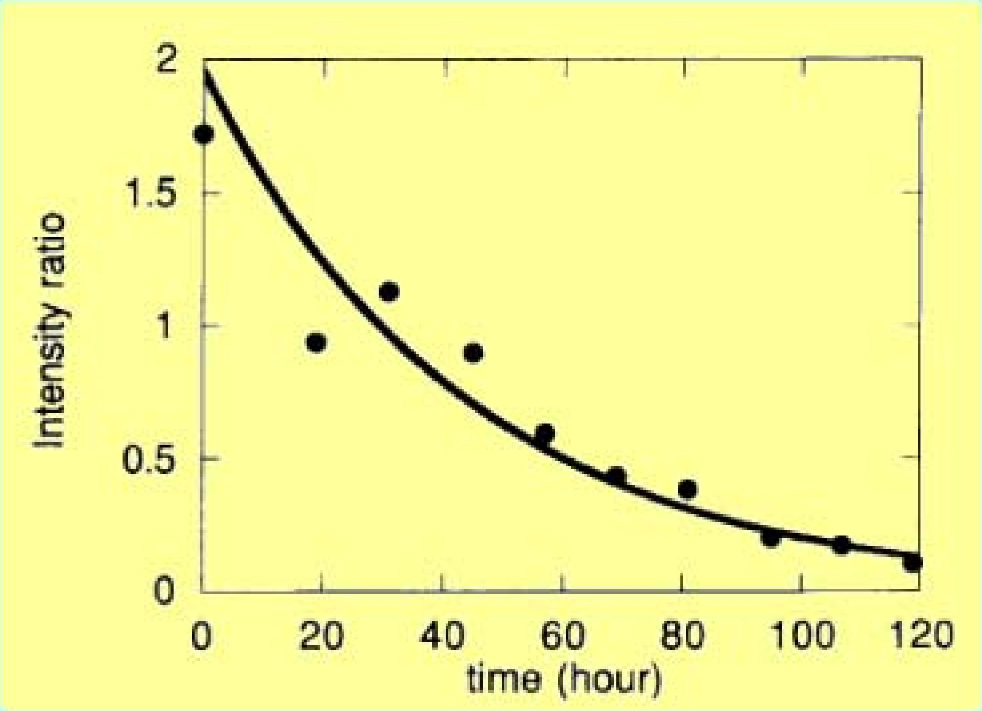


F Fillaux, Nonliner Double Day,
Sevilla 2004.

Life-time of the Breather Travelling State in 2D

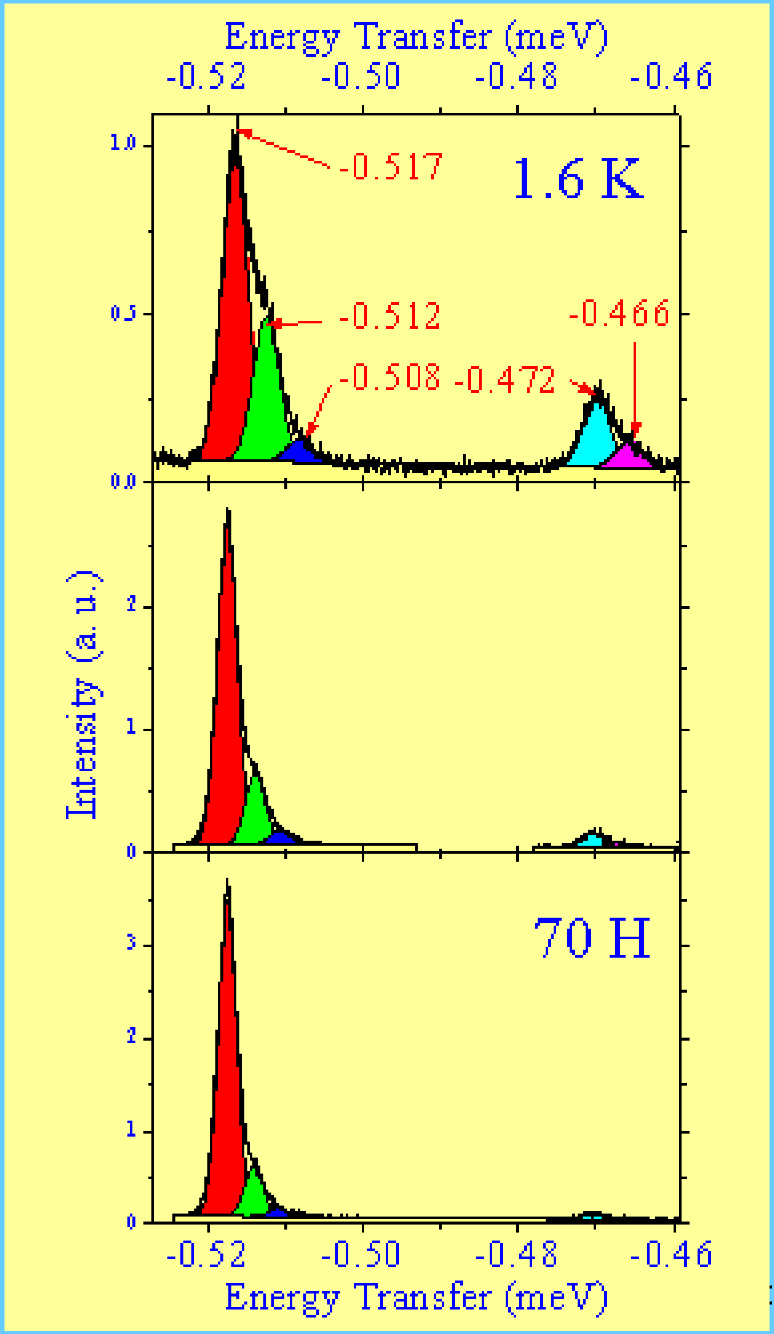


LAM 80 ET, Tsukuba, Japon



F.Fillaux *et al.*, Physica B **213&214** (1995) 646

aux, Nonliner Double Day,
Sevilla 2004.



γ-Picoline

Relaxation of the "Tunnelling" Bands

IN10, ILL, France

F.Fillaux *et al.*, Physica B **213&214** (1995) 646

:, Nonliner Double Day,
Sevilla 2004.