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## Chapter 2

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# Many-body quantum mechanics

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*Nonlinear Dynamics and Chaos - Where do we go from here?* is the title of this book. My answer for a proposed direction is *many-body quantum mechanics*. In keeping with the informal spirit of the presentation on which this chapter is based, I will pose several questions, though they vary in status from ill-defined to those for which I have a fairly complete answer.

I should start with some preliminaries about quantum mechanics. The experienced reader may find some of what I write to be naive or even misconceived, so I would be grateful for feedback and I ask the inexperienced reader to take everything with a pinch of salt. In addition, I do not propose to give a scholarly account, so some of my references and credits will be a bit haphazard.

The traditional dogma is that quantum mechanics is linear, so there is no nonlinearity and *a fortiori* there is no chaos. Thus, it looks as if my proposal is a backwards step!

I believe that view of quantum mechanics is superficial, however. Any dynamical system, written in terms of its flow map

$$\phi : \mathbb{R} \times M \rightarrow M, \quad (t, x) \mapsto \phi_t(x)$$

on a state space  $M$ , can be viewed as linear via its action on functions  $F : M \rightarrow \mathbb{R}$ ,

$$(\phi_t^* F)(x) = F(\phi_t x) \tag{2.1}$$

(evaluation along trajectories), or equivalently its inverse

$$(\phi_{*,t} F)(x) = F(\phi_{-t} x)$$

(advection of passive scalars). In the common case that  $M$  is a manifold and the dynamical system comes from a vector field

$$\dot{x} = v(x)$$

then (2.1) can alternatively be written as the linear partial differential equation (PDE)

$$\frac{\partial F}{\partial t} = DFv = v \cdot \nabla F \tag{2.2}$$

for how functions  $F$  evolve. For the special case of Hamiltonian vector fields  $v$ , those arising from frictionless classical mechanics, there is another way to write (2.2): its right-hand side is the *Poisson bracket*  $\{H, F\}$ ,

$$\{H, F\} = \sum_{j=1}^d \frac{\partial H}{\partial q_j} \frac{\partial F}{\partial p_j} - \frac{\partial H}{\partial p_j} \frac{\partial F}{\partial q_j}$$

in canonical coordinates  $(p, q)$ , where  $H$  is the Hamiltonian function and  $d$  is the number of degrees of freedom. So (2.2) can be written as

$$\frac{\partial F}{\partial t} = \{H, F\} \tag{2.3}$$

which is one of the standard formulations of Hamiltonian mechanics. In particular, from this point of view, Hamiltonian mechanics is linear. Nonetheless, all the nonlinear and chaotic phenomena are still present.

Quantum mechanics can be expressed in a similar form to (2.3), actually two alternative forms. The first is the Schrödinger form

$$i\hbar\dot{\psi} = H\psi$$

for the evolution of a *wave function*  $\psi$  in some complex Hilbert space  $U$ , where  $H$  is a Hermitian operator and  $\hbar$  is Planck's constant  $h$  divided by  $2\pi$ . The second is the Heisenberg form (or maybe one should say Jordan-Born-Heisenberg form)

$$\dot{A} = -\frac{i}{\hbar}[H, A]$$

for the evolution of any linear operator  $A$  on  $U$ , where  $[H, A]$  denotes the commutator

$$[H, A] = HA - AH.$$

These are linear evolutions for  $\psi$  and  $A$ . The two are related: if every wavefunction evolves by Schrödinger's equation then for all  $\psi$ ,  $i\hbar(A\psi)_t = H(A\psi)$ , so  $i\hbar A_t\psi = HA\psi - i\hbar A\psi_t = [H, A]\psi$ . Conversely, if every operator evolves by Heisenberg's equation, then in particular the rank-1 projections  $P = \psi\eta$ , where  $\psi \in U$  and  $\eta \in U^*$  (the dual space, consisting of linear forms on  $U$ ), evolve this way, so  $\dot{\psi}\eta + \psi\dot{\eta} = -\frac{i}{\hbar}(H\psi\eta - \psi\eta H)$  for all  $\psi, \eta$ , and the only solution is  $i\hbar\dot{\psi} = H\psi$ ,  $-i\hbar\dot{\eta} = \eta H$ .

In particular, the Heisenberg form is closely analogous to (2.3), because  $\{H, F\}$  and  $[H, A]$  are 'derivations' on functions  $F$  and operators

$A$ , respectively, that is, they are linear and satisfy Leibniz rule  $[H, AB] = A[H, B] + [H, A]B$  (and similar for  $\{H, FG\}$ ).

So we are not really justified in saying quantum mechanics has no nonlinearity, because we know that in the case of (2.3) there is, in general, an underlying nonlinearity in the vector field. Who is to say that there is not some analogous underlying nonlinear vector field in the quantum case?

Indeed, the theory of non-commutative manifolds (e.g. [13]) provides a way of thinking of Heisenberg's equation as coming from an underlying vector field, but on a *non-commutative manifold*; see e.g. [5]. Here is a rapid introduction to the subject (which is also known as *quantum geometry*). Consider the algebra  $C(M)$  of (smooth) functions  $F : M \rightarrow \mathbb{C}$  on a normal manifold  $M$ , with the usual operations of pointwise addition and multiplication and complex conjugation. For each point  $x \in M$  we can define a linear functional  $ev_x$  on  $C(M)$ , namely the evaluation map  $ev_x(F) = F(x)$ . It has properties that algebraists call a *Hermitian character*, viz.  $ev_x(FG) = ev_x(F)ev_x(G)$  and  $ev_x(F^*) = (ev_x(F))^*$ , where  $*$  represents complex conjugation. Remarkably, every Hermitian character on  $C(M)$  can be proved to be the evaluation map at some point  $x \in M$ . So one can think of  $M$  as being the set of Hermitian characters on  $C(M)$ . Now  $C(M)$  is commutative, that is,  $FG = GF$  for all  $F$  and  $G \in C(M)$ . It turns out that every commutative algebra  $\mathcal{A}$  satisfying suitable properties (to get the smooth structure) is  $C(M)$  for some  $M$ . The wonderful idea is to define a non-commutative manifold to be the set of Hermitian characters of a non-commutative algebra (with suitable smoothness properties). The basic example of a non-commutative algebra is the algebra of linear operators on a Hilbert space, with the operations of addition, multiplication and Hermitian conjugation. There are variations on the theme, using *prime ideals* of the algebra, or its *irreducible representations*. An unfortunate obstacle is that for even the simplest example of a quantum mechanical algebra, that generated by position  $x$  and momentum  $p$  operators for a one-dimensional (1D) oscillator, with  $[p, x] = i\hbar$ , there are no characters (nor finite-dimensional representations) and only one prime ideal. However, this seems not to be regarded as serious by proponents.

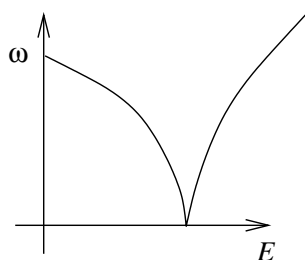
There is a growing literature on non-commutative manifolds, but I am not aware yet of anyone having tried to develop an analogue of the theory of dynamical systems for them, and this is in my opinion very important as it underlies quantum mechanics. So I am ready to pose my first question.

**Question 2.1.** Can a theory of dynamics on non-commutative manifolds be developed?

The first step is to define a vector field on a non-commutative manifold. This is easy. On an ordinary manifold  $M$ , one way of thinking of a vector field  $v$  is as a Hermitian derivation  $L_v$  on  $C(M)$ , defined by  $L_v F = DFv$

(the right hand side of (2.2)). Any Hermitian derivation  $L$  on  $C(M)$  induces a vector field  $v_L$  on  $M$ , namely the unique  $v$  such that  $LF = DFv$  for all  $F$ . So it is natural to define a vector field on a non-commutative manifold to be a Hermitian derivation on its algebra. The right hand side of Heisenberg's equation is an example.

The next step is not so obvious. One might wish to analyse the initial value problem and derive a local flow, as for ordinary (Lipschitz) vector fields. But I do not know if this makes sense in the non-commutative case. An alternative could be to mimic the theory of uniformly hyperbolic systems, which can be formulated entirely in functional analytic terms, so it does not require solution of the initial value problem. Another promising direction would be to mimic the spectral theory of measure-preserving transformations; see e.g. [2]. In any case, there is lots of room for work on this question.



**Figure 2.1.** Frequency  $\omega$  versus energy  $E$  for the ideal pendulum.

## 2.1 Signs of Nonlinearity in Quantum Mechanics

I am now going to move to a different approach, which is to look for signs of nonlinearity in quantum mechanics.

The basic nonlinearity in Hamiltonian mechanics is anharmonicity (which is better called non-isochronicity). An oscillator is said to be *anharmonic* if the frequency  $\omega$  of oscillation varies non-trivially with the energy  $E$ . For example, a pendulum's frequency decreases until one reaches the energy when it can go over the top, as all bell-ringers know; see figure 2.1. Equivalently, when expressed in terms of the *action variable*  $I$ , the Hamiltonian  $H(I)$  is not affine, since  $\omega = \frac{\partial H}{\partial I}$ . Note, however, that there are other oscillators than the harmonic oscillator for which the frequency is constant [10]!

We will say that a 1D quantum oscillator is *anharmonic* if its energy levels are not equally spaced. This is because neighbouring energy levels are thought of as corresponding to actions differing by  $\hbar$ , so the energy difference divided by  $\hbar$  is a discretisation of  $\frac{dH}{dI}$ . Most quantum oscillators



(except for the harmonic one) have non-constant energy level spacing, so we see that in this sense nonlinearity is common in quantum mechanics.

To take this to more degrees of freedom, a classical Hamiltonian system is linear (in a coordinate system for which the Poisson brackets are constant) if and only if the Hamiltonian is a homogeneous quadratic in the coordinates (plus a constant). Similarly, we can say that a quantum system is linear (with respect to a generating set of operators whose commutators are constants) if the Hermitian operator  $H$  is a homogeneous quadratic (plus a constant) when expressed in this basis of operators. For example, if  $H$  is Hermitian and quadratic in operators  $a_j$  and their Hermitian conjugates  $a_j^\dagger$ , satisfying commutation relations  $[a_j, a_k] = 0, [a_j, a_k^\dagger] = \delta_{jk}$ , then there is a unitary change of generators to a set  $\alpha_j, \alpha_j^\dagger$  satisfying the same commutation relations, such that  $H$  takes the form  $\sum_j \lambda_j N_j$  for some real numbers  $\lambda_j$ , where  $N_j = \alpha_j^\dagger \alpha_j$ . Each  $N_j$  is called a *number operator* because its spectrum is precisely the non-negative integers  $\mathbb{Z}_+$ . They commute, so it follows that  $H$  commutes with them and hence the spectrum of  $H$  is  $\{\sum_j \lambda_j n_j : n_j \in \mathbb{Z}_+\}$ .

My next question is to make this more general.

**Question 2.2.** How far can one generalise the above example of a linear quantum system (e.g. fermionic operators are all right too), and when can a new generating set be chosen to make the system linear (cf. Sternberg’s linearisation theorem near an equilibrium of a classical vector field [3])?

We can go a bit further in our translations of properties from classical to quantum. A classical system is *integrable* if the Hamiltonian is a function only of a Poisson commuting set of integrals (conserved quantities), whose derivatives are linearly independent almost everywhere. It follows that its motion can be solved virtually explicitly and the dynamics fully comprehended (equivalent to constant velocity motion on tori). Similarly, a quantum system can be said to be *integrable* if the Hermitian operator  $H$  is a function only of some commuting and independent set of operators. This is the case in the linear example above. Again, it allows one to solve the dynamics virtually explicitly. The only problem with this definition is that it is not yet agreed what counts as independent, but there is a large literature on quantum integrable systems; see e.g. [29].

One can go still further. Many Hamiltonian systems, even if not exactly integrable, turn out to be close to integrable in certain parameter regimes or regions of the state space. For example, near a non-resonant equilibrium of a classical Hamiltonian system one can find canonical coordinate systems — here I have chosen complex co-ordinates  $z_j, \bar{z}_j$  — to put  $H$  into the form

$$\begin{aligned} \text{“integrable”} &+ \text{“remainder”} \\ H(|z_j|^2)_j &+ O(\|z\|^{2N}) \end{aligned}$$

for arbitrary  $N$ , the so-called Birkhoff normal form. Similarly, in many quantum systems one can apply unitary transformations to put them into Birkhoff normal form, in the sense of a function only of a commuting set of operators, plus some ‘high-order’ remainder (Bogoliubov transformations, e.g. as rediscovered by [21]). Note that there are also quantum analogues of KAM theory (e.g. [14]) and Nekhoroshev theory (e.g. [9]).

In classical mechanics, Poincaré made the really important discovery that there are obstacles to integrability. Before his discovery the hope was that for every Hamiltonian system one could perform co-ordinate changes to bring them closer to integrable, and eventually push the remainder to zero; so every Hamiltonian system would be integrable. Poincaré realised that there is an obstacle, a very simple one: classical integrable systems of more than one degree of freedom generically have rational tori, a dense set of them in fact. He showed that they are fragile under general perturbation of the Hamiltonian. So the conclusion is that most Hamiltonian systems are not integrable. There is an analogue of this for quantum systems: if you have an integrable quantum system then degeneracy of energy levels is a codimension-one phenomenon — typically there are no degeneracies. However, in one-parameter families of integrable systems of more than one degree of freedom, energy levels can cross each other as the parameter varies, typically transversely, and so degeneracies occur at isolated parameter values and they are typically unremovable by small change in the family, preserving integrability. For general real symmetric quantum systems, however, Wigner pointed out that degeneracy is a codimension-two phenomenon, and it is of codimension three for general Hermitian ones: there is generically a repulsion of energy levels, leading to avoided crossings.

I regard this as a direct analogue of Poincaré’s observation. It shows that most quantum systems are not integrable, or strictly speaking most *one-parameter families* of quantum systems are not integrable. Actually, the latter comment highlights a subtle distinction between classical and quantum mechanics. I feel that in order to talk about nonlinearity in quantum mechanics it is probably usually necessary to think in terms of one-parameter families. A natural parameter might be Planck’s constant or some equivalent scale of action, but it could be other parameters. There is a huge literature on the distribution of spacings of energy levels, in particular on the repulsion of energy levels as a sign of non-integrability, people at Bristol being key players; see e.g. [7].

Poincaré went much further than just saying that most classical systems are not integrable — he showed what dynamics is substituted for the rational tori in a near integrable system, and he found the notion of homoclinic chaos that we are all familiar with. So my next question is:

**Question 2.3.** Is there a quantum analogue of homoclinic chaos?

Of course, one can answer that avoided crossings take the place of

crossings, but I have a feeling that there should be some consequences of non-integrability of a more dynamical nature. For a snapshot of some views on this, see [6]. One avenue that I consider promising is adiabatic theory: on varying the parameter slowly a quantum system can switch energy levels near an avoided crossing, best described probabilistically (e.g. [27]), which recalls probabilistic interpretations of transitions across a separatrix in classical mechanics; see e.g. [39]. In both cases the transition rate is very small for small perturbation from integrable (exponentially so for analytic systems).

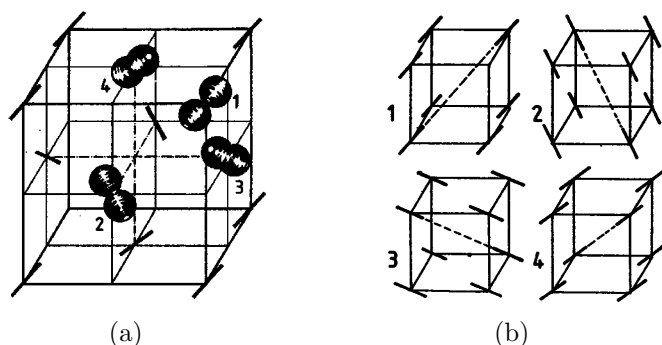
OK, that is all by way of introduction. Now I want to concentrate on the many-body case of quantum mechanics. I am going to discuss in detail one particular phenomenon in many-body quantum mechanics – *quantum discrete breathers* – but before I begin on that I should say that there are many well-known approximations in many-body quantum mechanics that produce obviously nonlinear equations. Hartree-Fock theory is a basic example, where a many-electron problem is replaced by some effective one-electron problem which is nonlinear (e.g. [44]). It is the basis for understanding the periodic table of the elements, for example, though its validity is questionable. Another example is Bose-Einstein condensates, where the Gross-Pitaevskii equation (the nonlinear Schrödinger equation in an external potential) is derived for the wave function that is supposed to describe the condensate [32]. Thus, many-body problems, if you make certain approximations, can boil down to nonlinear few-body problems.

Another direction one could pursue in many-body quantum mechanics is another type of answer to Question 2.3. Arbitrarily small perturbation of some quantum many-body problems can produce qualitatively new effects, an example being superconductivity when electron-phonon interactions are added. The effects even have the property of being exponentially small in the perturbation parameter.

But these are not the directions in which I wish to go. I want to pursue the anharmonicity idea, as we did not have to do anything fancy to see that there is anharmonicity in quantum mechanics, but its implications for many-body systems are less obvious.

## 2.2 Discrete Breathers

First I should tell you what discrete breathers are classically; for one survey see [34]. A classical *discrete breather* (DB) is a time-periodic spatially localized vibration in a Hamiltonian network of oscillators. There are dissipative analogues, but I am going to concentrate entirely on the Hamiltonian case. Imagine that we have some network, it could be sites in a crystal lattice or it could be some amorphous thing like a globular protein, and at each site



**Figure 2.2.** The crystal structure of orthotropic  $\text{H}_2$  at less than 3K. Reproduced from I.F. Silvera, The solid molecular hydrogens in the condensed phase: fundamentals and static properties, *Rev. Mod. Phys.* **52** (1980) 393–452 ©1980 by the American Physical Society.

we have a classical oscillator with Hamiltonian

$$H(x_s, p_s) = \sum_{s \in S} \left( \frac{1}{2} p_s^2 + V(x_s) \right) + \frac{\varepsilon}{2} \sum_{r, s \in S} \Delta_{rs} (x_r - x_s)^2 \quad (2.4)$$

for some network  $S$ , local potential  $V$ , coupling strength  $\varepsilon$  and coupling matrix  $\Delta$ . We will suppose that the potential  $V$  is not harmonic, as is generically the case, and that the coupling is relatively weak and satisfies some decay condition like

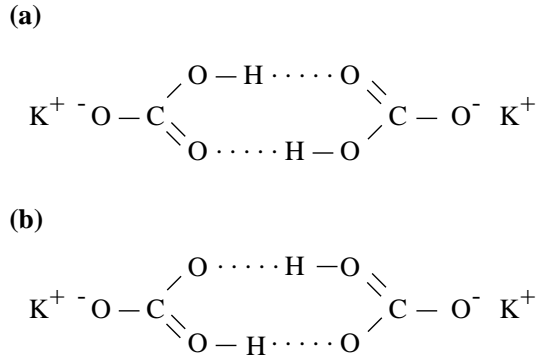
$$|\Delta_{rs}| \leq C e^{-\lambda d(r,s)}$$

or even some summable power law. Many other forms of coupling can be considered too. To avoid confusion let us just think of the case of linear nearest neighbour coupling.

Such models are proposed for vibrations of molecular crystals and I want to mention a few examples here. First, figure 2.2 shows a molecular hydrogen crystal, solid  $\text{H}_2$ , where the molecules arrange themselves in a lattice and orient themselves along the four main diagonals. Now, what is the degree of freedom that I wish to consider here? I am thinking of the stretch of the molecule. The stretches in nearby molecules are coupled by Van der Waals and quadruple–quadruple interactions. Of course, stretch of one molecule also makes forces which shift the centre of mass and change the orientation of nearby molecules, but we will ignore that for present purposes.

Another example, sketched in figure 2.3, is potassium bicarbonate  $\text{K HCO}_3$ . The bicarbonates pair up by hydrogen bonding and one gets

a degree of freedom where the protons can switch sides simultaneously between configurations (a) and (b) in figure 2.3 [25] (though there is now evidence in similar materials for *four*-well dynamics [20]).

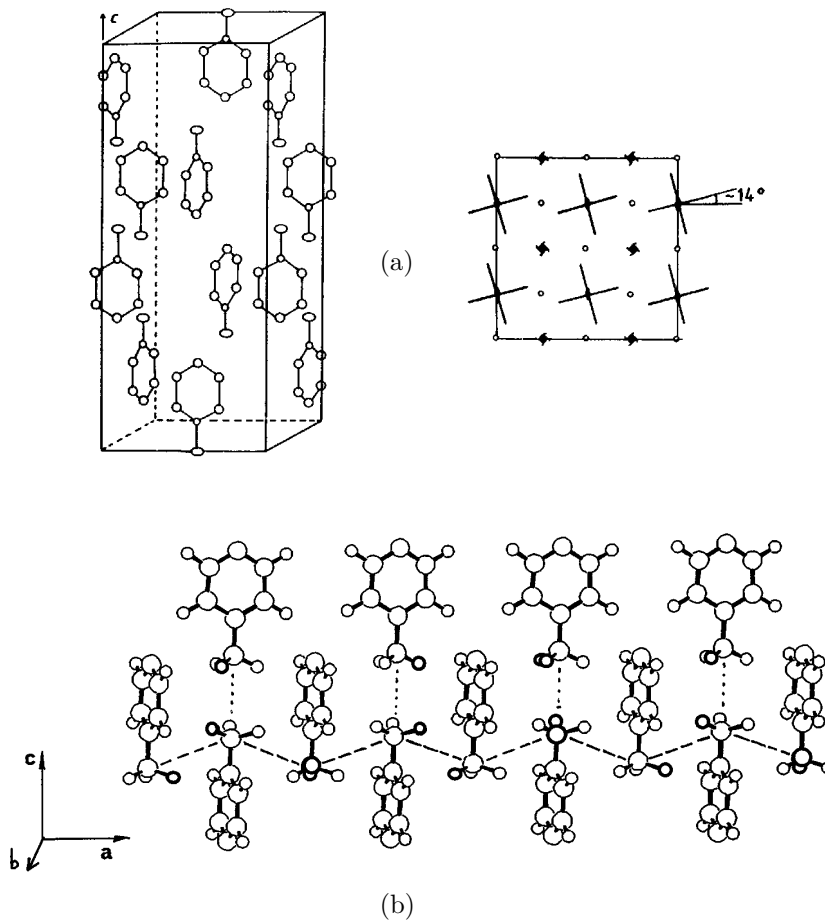


**Figure 2.3.** The two configurations (a) and (b) of the potassium bicarbonate dimers.

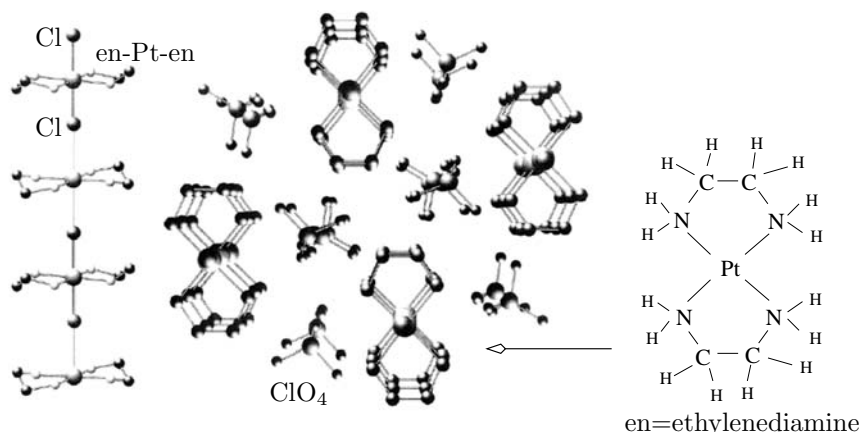
A third example is 4-methyl pyridine; see figure 2.4. This is a crystal of a molecule that has pyridine rings, like benzene but with nitrogen at the bottom, and a methyl group attached to the top. The methyl groups are relatively free to rotate, so it is that rotation that is my degree of freedom here [16]. But each methyl group has another one facing it and they interact quite strongly (along the dotted lines in figure 2.4(b)), so really we have to consider two-degree-of-freedom quantum units consisting of such pairs of methyl groups. Methyl groups in neighbouring pairs interact with each other (e.g. via the dashed lines in the figure, but also along similar lines in the *b* direction), linking the pairs in a 3D lattice.

The final example is a platinum chloride material,  $\text{Pt}(\text{en})_2\text{Cl}_2 \text{Pt}(\text{en})_2 (\text{ClO}_4)_4$  where en stands for ethylenediamine, which contains long chains of alternate platinum and chlorine ions. The chains dimerise (meaning that instead of the Pt and Cl being equally spaced along these chains, the equilibrium position of the *n*th Cl is displaced by  $(-)^n\delta$ , and  $\delta$  is relatively large for this material). This is because the electrons reduce their energy by doing so, more than the energy required to move the Cl ions (Peierls' instability). Essentially one ends up with alternate 'molecules' of  $\text{PtCl}_2(\text{en})_2$  and  $\text{Pt}(\text{en})_2$ ; see figure 2.5 and [43] for more details. The degree of freedom that is relevant here is the symmetric stretch of the  $\text{Cl}_2$  in the  $\text{PtCl}_2(\text{en})_2$  molecules, though the interaction with neighbours forces one to include at least the antisymmetric stretch as well. So again the units have two degrees of freedom.

Now if we suppose that the potential for the local degree of freedom in



**Figure 2.4.** Two views of the crystal structure of 4-methyl pyridine: the 3D structure (a) (reproduced from N. Le Calvé, B. Pasquier, G. Braathen, L. Soulard and F. Fillaux, Molecular mechanism determining phase transitions in the 4-methyl-pyridine crystal, *J. Phys. C* **19** (1986) 6695–6715 ©1986 by Institute of Physics Publishing), and a section (b) (reproduced from F. Fillaux, C.J. Carlile and G. J. Kearley, Inelastic neutron scattering study at low temperature of the quantum sine-Gordon breather in 4-methyl pyridine with partially deuterated methyl groups, *Phys. Rev. B* **44** (1991) 12280–93 ©1991 by the American Physical Society).



**Figure 2.5.** The ‘molecules’ involved in the platinum chloride example. Reproduced from B.I. Swanson, J.A. Brozik, S.P. Love, G.F. Strouse, A.P. Shreve, A.R. Bishop, W.-Z. Wang and M.I. Salkola, Observation of intrinsically localized modes in a discrete low-dimensional material, *Phys. Rev. Lett.* **82** (1999) 3288–91 ©1999 by the American Physical Society.

solid  $\text{H}_2$  or the  $\text{PtCl}$  material, say, is harmonic, meaning a pure parabola,

$$V(x) = \frac{1}{2}\omega_0^2 x^2$$

and we suppose the system has crystal periodicity, so the coupling is translation invariant, then there are no DBs for any positive coupling because, as is well known, any localized initial condition will disperse. For example, if you look at the dispersion relation for a one-dimensional nearest-neighbour-coupled chain

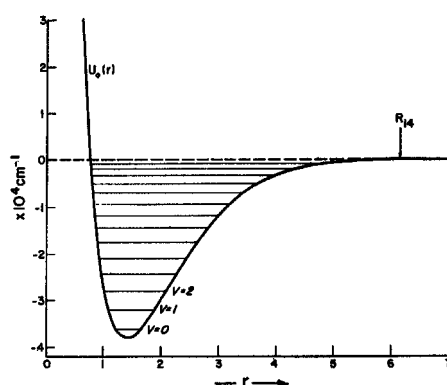
$$\omega^2 = \omega_0^2 + 4\varepsilon \sin^2 \frac{k}{2}$$

it is non-trivial (meaning  $\frac{\partial\omega}{\partial k}$  is not constant) and so any localized initial condition will spread out. Therefore, one never gets any time-periodic spatially localized solutions.

Real molecules are anharmonic; frequency *does* vary with amplitude. Morse found that the so-called Morse potential

$$V(x) = \frac{1}{2}(1 - e^{-x})^2$$

gives a good fit to a lot of spectroscopic data. See, for example, figure 2.6 for the case of solid Hydrogen. Table 2.1 indicates the amount of anharmonicity, of certain gas-phase diatomic molecules (from [24, 42]). These



**Figure 2.6.** The effective potential and the fifteen vibration levels of stretch of an  $\text{H}_2$  molecule. The arrow indicates the classical turning point in level 14 which is not shown. Reproduced from J. van Kranendonk, *Solid Hydrogen*, Plenum 1983 ©1983 by Plenum Publishing Corporation.

figures are obtained by fitting spectroscopic data to a formula of the form

$$E = (n + 1/2)\hbar\omega - x(n + 1/2)^2\hbar\omega + \dots$$

Molecule	$\omega$ ( $\text{cm}^{-1}$ )	anharmonicity $x$
$\text{H}_2$	4401.21	2.757%
HD	3813.1	2.404%
$\text{D}_2$	3115.5	1.984%
$\text{H } ^{35}\text{Cl}$	2990.946	1.766%
$\text{O}_2$	1580.19	0.758%
CO	2169.81	0.612%
$\text{N}_2$	2358.03	0.599%
$^{35}\text{Cl}_2$	599.71	0.482%
$\text{Br}_2$	323.07	0.361%
$\text{I}_2$	214.50	0.268%

**Table 2.1.** Anharmonicities of some diatomic molecules in gas phase

From my results with Aubry [36], if  $V$  in (2.4) is anharmonic and the coupling is weak enough compared with the anharmonicity  $\varepsilon < \varepsilon_0$ , then we proved existence of DBs in the classical system (extended to multi-degree-of-freedom oscillators in [40]). If the coupling is nearest neighbour or exponentially decaying then the amplitude of the DBs decays exponentially in space [40]. (Similarly, if the coupling is a (summable) power law, we obtain power law localisation of the DB [8].) The existence proof is



very constructive — we just continue from the uncoupled case using the Implicit Function Theorem, and that means the proof can essentially be used numerically. Furthermore, the DBs are stable in a sense: if  $\varepsilon$  is small enough,  $\varepsilon < \varepsilon_1$  (where maybe  $\varepsilon_1$  is smaller than  $\varepsilon_0$ ), then the DBs are  $l_2$ -linearly stable, i.e. stable under the linearised evolution of finite energy perturbations [37]. This is the best form of stability one could hope for. So it suggests they could be physically observable.

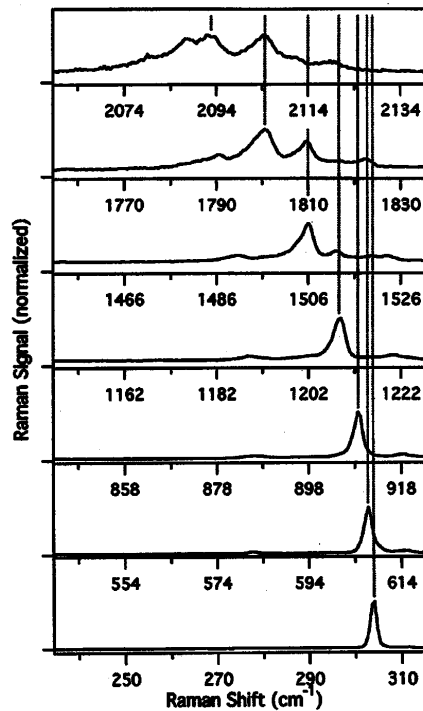
But real molecules are *quantum mechanical*. Just to give an illustration, look again at figure 2.6 showing the effective potential for the stretch of a hydrogen molecule. Classically, any energy of vibration between the minimum and the dissociation energy is possible. But spectroscopists observe only 15 energy levels, labelled from 0...14. (Actually they observe transitions between them and infer the levels.) So real molecules are highly quantum mechanical and we cannot ignore quantum mechanics in trying to understand vibrations in molecular crystals. Notice also the anharmonicity in figure 2.6: the spacing between levels is relatively large at the bottom and shrinks as we go up. The question that poses itself, and the key question to be addressed in this chapter is:

**Question 2.4.** Is there a quantum analogue of discrete breathers?

### 2.3 Experimental Evidence for Quantum Discrete Breathers

Experiments suggest that the answer is yes. Figure 2.7 shows experimental results of Swanson *et al.* [43] on the platinum-chloride material that was represented in figure 2.3.

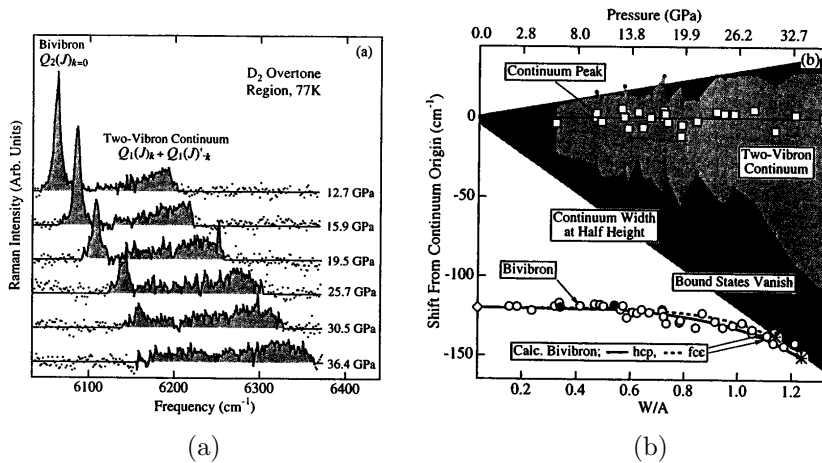
What they do is fire in photons from a laser and have a look for any photons that come out with less energy; the idea is that if they have lost energy they have created a vibration in the crystal. This is called Raman scattering. Spectroscopists measure energy in  $\text{cm}^{-1}$ ! Sorry about that but it is just units. We see that they can create an excitation at  $312 \text{ cm}^{-1}$ , and they can also create one at nearly twice that. To see the difference, they cut up the energy axis and align the pieces above, shifted by multiples of  $312 \text{ cm}^{-1}$ . The second panel from the bottom shows a peak at slightly less than twice the original, the third panel up shows a peak at yet less than three times, the next even less than four times, and so on. So they say “Ah-ha! we are creating some anharmonic vibration here, because we are seeing successive levels of some anharmonic vibration”. They assume that it is a localized  $\text{PtCl}_2$  symmetric stretch. The  $\text{PtCl}_2$  symmetric stretch assumption is fine because for the chosen material that is the only Raman active mode in that range of energies. But the localisation inference is not justified in my opinion. They do not observe spatial localisation at all; they just say that their results are consistent with one molecule that is anharmonic and is picking up various amounts of energy.



**Figure 2.7.** Raman scattering results on  $\text{Pt}^{35}\text{Cl}$ . Reproduced from B.I. Swanson, J.A. Brozik, S.P. Love, G.F. Strouse, A.P. Shreve, A.R. Bishop, W.-Z. Wang and M.I. Salkola, Observation of intrinsically localized modes in a discrete low-dimensional material, *Phys. Rev. Lett.* **82** (1999) 3288–91 ©1999 by the American Physical Society.

I think it would be really interesting to do an experiment to observe the spatial structure of the created excitations. In principle, one could do this by scattering neutrons, instead of photons, because their energy can be chosen to make their de Broglie wavelength comparable to or shorter than the lattice spacing. So I tried it [35], but it turned out that the neutrons excited far too many other modes in the same energy range to even see the  $\text{PtCl}_2$  stretch.

Another experiment that I like is the one by Eggert, Mao & Hemley [15] on solid deuterium  $D_2$ , the results of which are depicted in figure 2.8. The great thing about solid deuterium (and solid hydrogen) is that one can compress it relatively easily, and thereby change the coupling strength between the molecules. This is really fun. What they do is change the



**Figure 2.8.** Pressure-induced bi-vibron bound-unbound transition of  $D_2$ ; shown are Raman spectra of  $D_2$  in the overtone region as a function of pressure (a), and a comparison between experimental results and theoretical calculations (b). Reproduced from J.H. Eggert, H.-K. Mao and R.J. Hemley, Observation of a two-vibron bound-to-unbound transition in solid deuterium at high pressure, *Phys. Rev. Lett.* **70** (1993) 2301–4 ©1993 by the American Physical Society.

pressure, from 12.7 GP (gigapascals) to 36.4 GP (for reference, atmospheric pressure is about 0.1 MP). At 12.7 GP, they can create an excitation that they call a bi-vibron, and a continuum of excitations with a range of slightly higher energies. They interpret the bi-vibron as a second excited state of one deuterium molecule and the continuum as formation of a pair of first excited molecules but where the excitations propagate in opposite directions. As they increase the pressure, the bi-vibron peak merges into the continuum; see figure 2.8(a). In figure 2.8(b) the continuum is depicted above the bi-vibron, but as the pressure increases one can see the bi-vibron energy decreases slightly and then it is absorbed into the continuum. This is nice because this shows that just as in the classical case one gets existence of some localised excitation, provided that coupling strength is smaller than or the same order of magnitude as a measure of the anharmonicity. In fact, in the appropriate dimensionless units, which are plotted on the lower horizontal scale of figure 2.8(b), the threshold is at about 1.2. Note again, however, that the experiment did not measure the spatial structure of the excitation. This material would be much better adapted than PtCl to the inference of spatial structure by neutron scattering and I would very much like to find someone willing to try it. The only problem is that solid deuterium is much harder to handle than PtCl because one needs to keep it cold and under pressure.

These experiments (and others, for example bi-vibrons were reported in solid hydrogen in 1957 [22]!) suggest that there is a quantum analogue of the classical discrete breather concept. But we need a mathematical formulation.

### 2.4 Towards a mathematical theory of quantum discrete breathers

A quantum system is specified by a Hermitian operator  $H$  on a Hilbert space  $U$ . A large part of the game, though not all, is to find the eigenvalues and eigenvectors of this operator. For example, if we had a single degree of freedom  $x$ , like stretch of a hydrogen molecule, then our Hilbert space would be  $L^2$  functions of one variable and our operator would be the standard Schrödinger operator

$$H\psi = -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi \quad \text{for } \psi \in U = L_2(\mathbb{R}, \mathbb{C}).$$

A typical spectrum would consist of a ground state energy (which, without loss of generality, I will chose to be the origin of energy), first excited energy etc., as depicted in figure 2.9. In practice, there would be a continuum corresponding to dissociation for higher energies, but I am not really interested in the high excitations and, to avoid technicalities to do with unbounded operators (or even with infinite-dimensional bounded ones), I will simplify by supposing that my Hilbert spaces are finite-dimensional. The important thing is that typically these spectra have softening anharmonicity as we saw above. So the gaps between the eigenvalues decrease as you go up the spectrum.

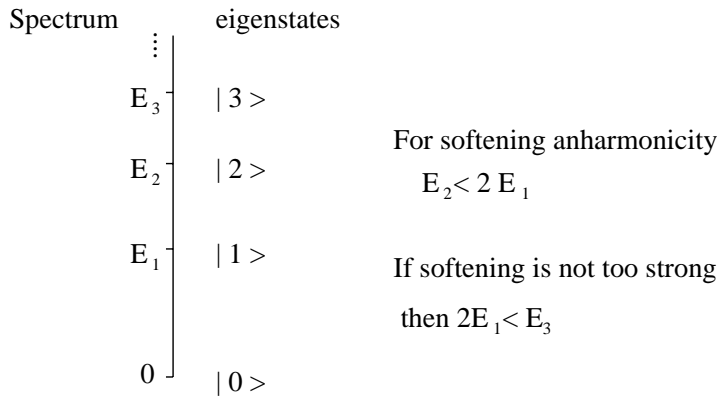


Figure 2.9. A typical spectrum of a one-degree-of-freedom quantum system

Now, how do we describe quantum mechanically the whole molecular crystal? Mathematically, the Hilbert space for  $N$  molecules is the *tensor* product of the individual spaces,

$$U_1 \otimes U_2 \otimes \dots \otimes U_N.$$

It is defined to be the set of multilinear maps  $\psi$  from  $U_1^* \times U_2^* \times \dots \times U_N^*$  to  $\mathbb{C}$  (where  $U^*$  is the dual of  $U$ ), but the easiest way to think about a tensor product is to describe a basis for it. A natural basis is given by the states of the form  $|n_1, \dots, n_N\rangle$ , which represents that molecule # 1 is in its  $n_1$  state, molecule # 2 in its  $n_2$  state etc., and is defined by

$$|n_1, \dots, n_N\rangle \text{ on } \langle m_1 | \langle m_2 | \dots \langle m_N | \text{ gives } \prod_s \delta_{m_s n_s}.$$

The mathematical difficulties in many-body quantum mechanics come about because the dimension of a tensor product is the product of the dimensions rather than the sum, that is

$$\dim(\times_s U_s) = \sum_s \dim U_s,$$

but

$$\dim \otimes_s U_s = \prod_s \dim U_s.$$

Actually, related difficulties occur in probability theory of large networks, so I am developing a parallel theory there. We will see where this difficulty starts to play a role in a moment, but if we think just of an *uncoupled* network then the Hamiltonian is just the sum of the individual Hamiltonian operators

$$H^0 = \sum_s "H_s",$$

where a superscript '0' corresponds to 'uncoupled' and " $H_s$ " is defined on  $\otimes U_s$  by

$$"H_s" \psi(\psi_1^*, \dots) = \psi(\psi_1^*, \dots, H_s \psi_s^*, \dots).$$

Hence the eigenvalues of  $H^0$  are just sums of eigenvalues of  $H_s$ , taking one for each unit.

So what do we get for the spectrum of the uncoupled network? We get a ground state where each molecule is in its ground state. We get a first excited subspace where one molecule is first excited and the rest are in their ground state. But, of course, there are  $N$  ways of choosing which molecule is first excited so this has dimension  $N$ . There is a second excited subspace where one molecule is second excited and the rest are in their ground state, and again that has dimension  $N$ . Then there is a subspace where two molecules are first excited and the rest are in their ground state,

	representative eigenstate	multiplicity	name for spectral projection
$\vdots$			
$E_3$	$ 0\ 3\ 0\ 0\ 0\rangle$	$N$	$P^{(3)}$
$2E_1$	$ 0\ 1\ 0\ 0\ 1\rangle$	$N(N-1)/2$	$P^{(1,1)}$
$E_2$	$ 0\ 2\ 0\ 0\ 0\rangle$	$N$	$P^{(2)}$
$E_1$	$ 0\ 1\ 0\ 0\ 0\rangle$	$N$	$P^{(1)}$
$0$	$ 0\ 0\ 0\ 0\ 0\rangle$	$1$	$P^{(0)}$

**Figure 2.10.** Multiplicity of the spectrum of an uncoupled  $N$ -unit network.

and that has dimension  $N(N-1)/2$ ; see figure 2.10. You can go up as far as you want but this is going to be enough for our present purposes.

Let me give names to the spectral projections corresponding to these subspaces;  $P^{(0)}$ ,  $P^{(1)}$ ,  $P^{(2)}$ ,  $P^{(1,1)}$  and so on, as indicated in figure 2.10. Just to remind you, a *spectral projection*  $P$  (for a finite-dimensional Hermitian operator) is the orthogonal projection onto the span of eigenvectors corresponding to an isolated part of the spectrum. The question that I want to ask is:

**Question 2.5.** What happens to the spectrum of  $H^0$  when one adds some coupling operator, i.e.  $H^\varepsilon = H^0 + \varepsilon\Delta$ ?

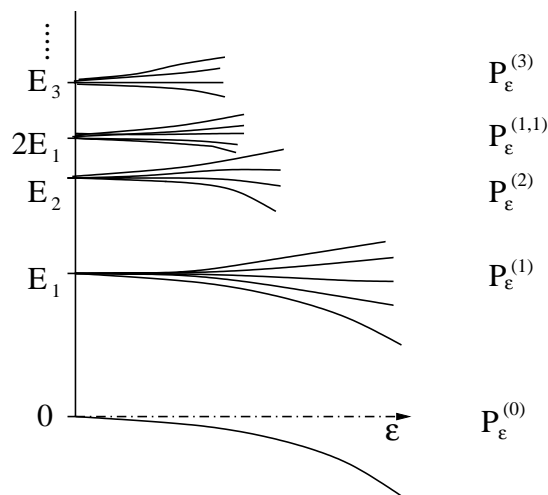
We will suppose the coupling operator takes the form

$$\Delta = \sum_{r,s \in S} \Delta_{rs}$$

together with some decay property, as in the classical case.

Now if the size  $\varepsilon\|\Delta\|$  of the coupling (measured using the Hilbert norm, i.e. the largest eigenvalue in absolute value) is small, then standard perturbation theory tells one that the spectral projections move smoothly and the spectral gaps can not change dramatically in size; in particular they can shrink by at most  $2\varepsilon\|\Delta\|$  if at all. So as we turn on coupling we should get a situation as sketched in figure 2.11.

The ground state energy may move but does so smoothly and remains non-degenerate. The first excited subspace, in general, splits into a variety of energy levels. However, the spectral projection corresponding to the



**Figure 2.11.** The spectrum of the  $N$ -unit quantum system for weak coupling  $\varepsilon$ .

subspace still moves smoothly, and we keep a nice gap of almost the same size between these  $N$  states and the ground state. Similarly, there is a gap between this family and the family of states emerging from the energy of the second excited state, etc.

Here is a nice proof of the smooth persistence of spectral projections, which so far I have not seen in the literature anywhere. (If someone has then please let me know.) It is this strategy of proof that will be useful to me in what follows. The idea is that  $P$  is a spectral projection for  $H$  if and only if it is a non-degenerate equilibrium for the vector field

$$F(P) = i[H, P]$$

on the manifold  $M$  of orthogonal projections ( $P = P^2 = P^\dagger$ ). (It is a manifold, called Grassmannian, though it has connected components of many different dimensions.) It is simple to check that  $F(P)$  is indeed tangent to  $M$  at  $P$  and that the amount of non-degeneracy of an equilibrium is inversely proportional to the spectral gap  $g$ , that is, the shortest distance to the rest of the spectrum. In fact, using the operator norm (induced by the Hilbert norm) on  $DF$ , which takes an infinitesimal change in  $P$  on  $M$  to a change in the tangent vector to  $M$ , we have precisely that

$$\|DF^{-1}\| = 1/g.$$

What we are faced with is just the question of the persistence of a non-degenerate equilibrium  $P_0$ . If you are a dynamical systems person, then you know that that is easy to answer. By the Implicit Function Theorem,

the non-degenerate equilibrium persists under small changes of vector field  $F$ , in particular, if we change the Hamiltonian so that

$$F_\varepsilon(P) = i[H^\varepsilon, P].$$

So we get a continued spectral projection,  $P_\varepsilon$  for  $H^\varepsilon$  and, in fact, we can continue it as long as the equilibrium remains non-degenerate, that is,  $DF_\varepsilon = \partial F/\partial P$  remains invertible. By the chain rule

$$\frac{d}{d\varepsilon}DF_\varepsilon^{-1} = -DF^{-1}\frac{d}{d\varepsilon}DF DF^{-1}.$$

Hence,

$$\frac{d}{d\varepsilon}\|DF^{-1}\|^{-1} \leq 2\|\Delta\|$$

as long as it is defined, and so

$$g_\varepsilon \geq g_0 - 2\varepsilon\|\Delta\|$$

as long as this remains positive, i.e. for  $\varepsilon < \frac{g_0}{2\|\Delta\|}$ . This ends the proof.

## 2.5 Obstructions to the theory

You might say “well that is great, persistence of spectral projections explains those Eggert et al results in figure 2.11”. The bi-vibron would be the zero momentum part (because photons contribute negligible momentum compared with their energy) of the second excited spectral projection, and the continuum band would be that for the  $P^{(1,1)}$  spectral projection. We see that they continue for some range of  $\varepsilon$ , namely up to 1.2. So you might say “that is OK, it just means that we started with a gap larger than 2.4 times the size of the coupling.” But the big problem is that if one works out the Hilbert norm of the coupling operator, it grows like the system size: it is of the order of  $NE$ , where  $E$  is the energy change to a single unit due to coupling to the rest. This is because the quantum mechanics of a product system is a tensor product not a direct product. So the standard persistence result of the last section gives a result only for  $\varepsilon$  up to  $\frac{g_0}{2NE}$ , which is useless if we have  $N \approx 10^{23}$  molecules in our crystal.

**Question 2.6.** Can this persistence of spectral projections result be extended up to  $\varepsilon = O(1)$ ?

Well actually, there are some genuine obstructions to extending the result.

- (i) The first is that a typical coupling operator  $\Delta$  changes all energies by order  $N\varepsilon$ . The easy way to see this is to take the trivial coupling operator

$$\Delta_{rs} = \left\{ \begin{array}{ll} I & r = s \\ 0 & r \neq s \end{array} \right\}$$



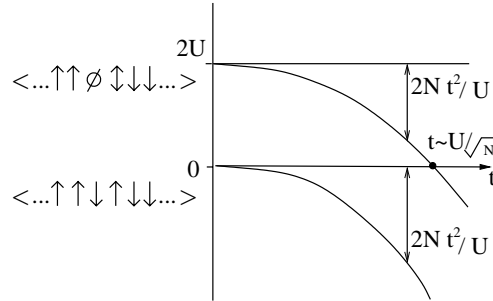
that just adds the identity at each site. That shifts all the energy levels of each unit. Then we add up our sums of energy levels, one per unit, and the whole energies are going to shift by  $N\varepsilon$ . If all the energies are moving roughly by  $N\varepsilon$  then it looks very dubious that we would keep any gaps. It is certainly not going to be an easy argument to show that we keep any gaps for  $\varepsilon$  greater than  $O(1/N)$  because some might move slightly faster with  $\varepsilon$  than others.

- (ii) Another obstruction is that typical coupling turns the ground state through  $O(45^\circ)$  as soon as  $\varepsilon \sim 1/\sqrt{N}$ , and nearly  $90^\circ$  as soon as it becomes significantly bigger than  $1/\sqrt{N}$ . So this means we cannot expect spectral projections to move uniformly smoothly in the standard Hilbert norm, that is, uniformly in system size, because we go from  $0-45^\circ$  in  $O(1/\sqrt{N})$ , which is non-uniform in system size. An easy example of this problem is a set of spin- $\frac{1}{2}$  particles in a magnetic field at angle  $\varepsilon$ , which have a groundstate  $\phi_\varepsilon$  that is always aligned with the field. So we can work out that the overlap with the unperturbed ground state is

$$\langle \phi_0 | \phi_1 \rangle = (\cos \varepsilon)^N$$

which tends to zero as soon as  $\varepsilon$  is significantly bigger than  $1/\sqrt{N}$ .

- (iii) Furthermore, there are examples, admittedly with degenerate ground state (unlike the molecular crystals I am talking about), for which spectral gaps are indeed lost for  $\varepsilon \approx 1/\sqrt{N}$ . For example, if you take a half-filled 1D Hubbard model (e.g. [38]), you lose spectral gaps between the ground state band and the first excited state band when the coupling  $\varepsilon$  reaches the Hubbard constant  $U$  divided by  $\sqrt{N}$ ; see figure 2.12.



**Figure 2.12.** Spectrum for the half-filled Hubbard model, indicating typical states in the  $t = 0$  limit.

So there are real obstacles to extending the result to one that is uniform in system size. However, there is one result which partially extends it: Kennedy & Tasaki [28] proved persistence of a non-degenerate ground state,

with its spectral gap, uniformly in system size. But they did not claim any smoothness for how their ground state moves (fortunately, because it is probably false!). Nor does their method (cluster expansions of  $e^{-\beta H}$ ) look easy to extend to higher spectral projections. If you like, in figure 2.12 the Kennedy & Tasaki result tells you that the ground state persists as a non-degenerate ground state and that the gap between it and the rest of the spectrum remains roughly of the same order. But to understand the Eggert et al. results and the PtCl work I am interested in higher spectral gaps.

## 2.6 A proposed solution

My proposed solution is to introduce new norms on tangent vectors to the manifold  $M$  of projections on  $\otimes_{s \in S} U_s$ , instead of using the standard Hilbert norm. We will find we also need to introduce something I have called a *domination condition* on the coupling in order to rule out systems like the half-filled Hubbard model. So here is the idea. I have to call it an ‘idea’ because I still have not filled in a couple of details in the proof. I am hoping they are just technical details, but I never get around to it so I apologise to those who have seen this before and you must think it is about time I finished it.

The idea goes as follows.

- We start by taking the manifold  $M$  of orthogonal projections on our tensor product

$$P : \otimes_{s \in S} U_s \rightarrow \otimes_{s \in S} U_s$$

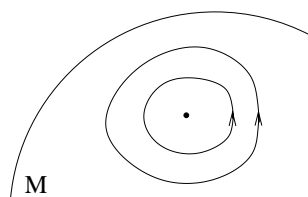
and we might as well restrict attention to the component of this manifold composed of projections which have the same rank as the unperturbed case  $P_0$ .

- As I said earlier, we have a vector field  $F_H$  on  $M$

$$\dot{P} = F_H(P) = i[H, P] \in T_P M.$$

- $P$  is a spectral projection if and only if it is a non-degenerate zero of  $F_H$ . I should say that the typical dynamics is that a spectral projection is an equilibrium and nearby projections rotate around it as depicted in figure 2.13. They rotate at angular rates equal to the differences between eigenvalues corresponding to the spectral projection and its complement, as is easy to see by going into an eigenbasis of  $H$ .
- We want to get results that are uniform in system size. We are going to need to quantify things so we are going to need find norms (and a condition on  $\Delta$ ) such that this vector field is  $C^1$  in our parameter and state space. That is, we require

$$\left. \begin{array}{l} F \text{ is } C^1 \text{ in } (\varepsilon, P) \\ DF_{H_0, P_0} \text{ is invertible} \end{array} \right\} \text{uniformly in } N.$$



**Figure 2.13.** The typical dynamics on  $M$

Note that I use the notation  $DF$  for the derivative of  $F$  with respect to  $P$ , and I will use  $\partial F/\partial \varepsilon$  for the derivative with respect to  $\varepsilon$ .

- Then we just invoke the Implicit Function Theorem, with whatever these norms might be, to obtain that  $P_0$  persists uniformly in  $N$  with respect to  $\varepsilon$ .

Now, to quantify  $F$  being  $C^1$  we have to come up with

- (a) the norms, and
- (b) a co-ordinate chart around  $P_0$  in  $M$ .

### 2.6.1 Norms

Choosing new norms is the key idea. This means assigning a length to each tangent vector  $\pi$  to the manifold  $M$  of projections on  $\otimes_{s \in S} U_s$ . For tangent vectors  $\pi$  at  $P \in M$ , we write  $\pi \in T_P M$ . First we define, for every subset  $\Lambda \subset S$  of our molecular crystal, an operator  $\pi^\Lambda$  on  $\otimes_{s \in \Lambda} U_s$ , which I call the *density matrix* of  $\pi$  on  $\Lambda$ . This is a standard thing in physics — one just takes the trace over the complementary sites

$$\pi^\Lambda = \text{Tr}_{S \setminus \Lambda} \pi : \otimes_{s \in \Lambda} U_s \rightarrow \otimes_{s \in \Lambda} U_s.$$

The only difference is that usually density matrices are defined only for operators  $\pi$  which are non-negative and have  $\text{Tr} \pi = 1$ . It turns out that I need to define two norms.

- I define the  $\theta$ -norm of a tangent vector  $\pi$  to be the supremum over non-empty choices of the subset  $\Lambda$  of the standard Hilbert norm of the density matrix, divided by the size of the subset

$$|\pi|_0 := \sup_{\emptyset \neq \Lambda \subset S} \frac{\|\pi^\Lambda\|}{|\Lambda|}.$$

This is sensible. For example, take the spin- $\frac{1}{2}$  particles in the magnetic field at angle  $\varepsilon$ , and take  $\pi$  to be the rate of change of the projection onto the ground state with  $\varepsilon$ , which corresponds to simultaneously

rotating the state space for each spin. If one works out the Hilbert norm of the density matrix of  $\pi$  for a subset  $\Lambda$  of spins, it turns out to be precisely equal to the size of  $\Lambda$ . So if we take the ratio, we get a nice supremum of 1. This means that the 0-norm in this example — which is of the size of the rate at which the ground state actually moves — is uniform in the system size. This is very promising.

- The 1-norm is just the 0-norm of the commutator with the unperturbed Hamiltonian

$$|\pi|_1 := |i[H_0, \pi]|_0.$$

One can check that it is a norm on  $T_P M$ , because it is at least as big as the gap times the 0-norm. Why do I need the 1-norm? It is because  $F$  takes a  $P$  and gives us  $i[H, P]$ , but the commutator with  $H$  is like taking a derivative (it is a derivation, as we saw near the beginning of this chapter). Also, if we think about the proof that Aubry and I did for the classical case [36], then what we had to do was to take a loop, that is a candidate for a periodic orbit, and evaluate the equations of motion on it, which should give zero if it is a periodic orbit. But evaluating equations of motion involves looking at  $\dot{x}$ , so it means taking a derivative. If our loops are in  $C^1$  then we have to take our tangent loops in  $C^0$ , so there is a loss of one derivative. It is exactly the same here, you have to think of commutator with  $H$  like taking a derivative, and so regard  $F$  as taking  $M$  with the 1-norm to  $TM$  with the 0-norm.

### 2.6.2 Chart

The next thing is that, unfortunately,  $M$  is a nonlinear manifold, so if we are going to quantify  $F$  being  $C^1$  then we are going to have to do something like use a co-ordinate chart. There is an alternative, namely to embed  $M$  into a linear space by adding the equation  $P^2 = P$ , but the chart route is the one I will take here. Figure 2.14 shows a chart around  $P_0$  in  $M$ , which is constructed as follows.

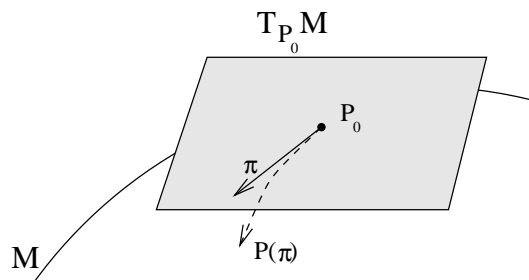


Figure 2.14. The chart.

- First define  $J$  to be the difference between  $P_0$  and its complementary projection  $Q_0 = I - P_0$ ,

$$J := Q_0 - P_0.$$

- We note that if  $\pi$  is in  $T_{P_0}M$ , then  $e^{J\pi}$  is a unitary operator.
- Now we define  $\mathcal{B}$  to be a not too large ball with respect to the 1-norm

$$\mathcal{B} := \{\pi \in T_{P_0}M : |\pi|_1 \leq \delta\}.$$

- Then we co-ordinatise  $P$  within this ball by writing

$$\begin{aligned} P : \mathcal{B} &\rightarrow M \\ \pi &\mapsto e^{J\pi}P_0e^{-J\pi}. \end{aligned}$$

### 2.6.3 The formulation

Having defined appropriate norms and a co-ordinate chart, we can now return to a formulation of the continuation problem. If you express the continuation problem in the chart it turns into this: find zeroes of

$$G_H : \mathcal{B}_{(1)} \times \mathbb{R} \mapsto T_{P_0}M_{(0)} \tag{2.5}$$

$$(\pi, \varepsilon) \mapsto i[A_\pi(H^\varepsilon), P_0] \tag{2.6}$$

$$\text{where } A_\pi(H) := e^{-J\pi}He^{J\pi}. \tag{2.7}$$

Here the subscripts (0) and (1) are used to stress that we have to consider the left-hand side as being in the space of the 1-norm and the right-hand side as being in the space of the 0-norm. Now, if you take a tangent vector at  $P_0$  and you work out the right-hand side of (2.6), then to get the uniform persistence of the spectral projection  $P$  it will be enough to show that

$$\left. \begin{aligned} G \text{ is } C^1 \text{ in } (\varepsilon, \pi) \\ DG \text{ is invertible at } (0, 0) \end{aligned} \right\} \text{ uniformly in } N. \tag{2.8}$$

There are several steps to showing this, I checked most of the things — well the easy parts — which can be summarised as follows:

### 2.6.4 Part of a proof of (2.8)

Here is a formula for  $DG$ :

$$DG(\sigma) = i [[A_\pi(H), B_\pi(\sigma)], P_0]$$

$$\text{where } B_\pi(\sigma) = \int_0^1 A_{t\pi}(J\sigma)dt.$$

Let us see what we need.

- First of all,  $DG$  is invertible, and both it and its inverse are bounded, that is,

$$\begin{aligned} \text{at } \varepsilon = \pi = 0, \quad DG(\sigma) &= i[[H_0, J\sigma], P_0] = i[H_0, \sigma] \\ \text{so } |DG|_{1 \rightarrow 0} &= |DG^{-1}|_{0 \rightarrow 1} = 1 \end{aligned}$$

where again the subscripts refer to the appropriate norms.

- If we assume that the coupling is uniformly summable:

$$\sup_{r \in S} \sum_{s \in S} \|\Delta_{rs}\| \leq K$$

then the rate of change of  $G$  with the coupling parameter is bounded uniformly in system size, at least at the unperturbed projection

$$\frac{\partial G(\pi)}{\partial \varepsilon} = i[A_\pi(\Delta), P_0], \quad \text{so } \left| \frac{\partial G(0)}{\partial \varepsilon} \right|_0 \leq K \quad \text{at } \pi = 0.$$

- The next thing is that we have to show that the derivative is continuous, because for the Implicit Function Theorem it is not enough just to show that  $F$  is differentiable, we have to show it is  $C^1$ . Furthermore, to obtain uniform results we have to show this uniformly in system size, which means showing a uniform module of continuity for the derivative. The easiest way to do that is to bound the second derivative. First consider the mixed second derivative

$$\frac{\partial}{\partial \varepsilon} DG(\sigma) = i[[A_\pi(\Delta), B_\pi(\sigma)], P_0].$$

If we assume a “**domination**” condition:

$$|i[[\Delta, \sigma], P_0]|_0 \leq \frac{K}{g} |i[H_0, \sigma]|_0, \tag{2.9}$$

where  $K$  is as above and  $g$  is the unperturbed spectral gap, which I convinced myself once is satisfied for low lying spectral projections of molecular crystal models with units having non-degenerate ground-state (though I cannot reconstruct the proof now!), then we obtain

$$\left| \frac{\partial}{\partial \varepsilon} DG \right| \leq \frac{K}{g} \quad \text{at } \pi = 0.$$

Interestingly, the domination condition is not satisfied for the ground-state of the half-filled Hubbard model, for which we know the result cannot apply, so it is nice to see where it gets excluded. But really I need a bound like this in a uniform neighbourhood, that is an estimate of the form:

$$\left| \frac{\partial DG}{\partial \varepsilon} \right|_0 \leq f(|\pi|_1) |\sigma|_1 \quad \text{for some function } f. \tag{2.10}$$

I have not yet obtained such an estimate, but I think it is very likely to be possible.

- Similarly, we had better check the second derivative  $D^2G$ :

$$D^2G(\sigma, \tau) = i \left[ [A_\pi(H), B_\pi(\tau)], B_\pi(\sigma), P_0 \right] + \left[ A_\pi(H), \int_0^1 [A_{t\pi}(J_\sigma), B_{t\pi}(\tau)] dt, P_0 \right].$$

It is zero at the unperturbed case, that is,

$$\text{at } \pi = \varepsilon = 0, \quad D^2G(\sigma, \tau) = i [[LH_0, J_\sigma], J_\tau], P] = 0.$$

But we have to show that it remains uniformly small in some neighbourhood. That is, we would like to obtain

$$|D^2G(\sigma, \tau)|_0 \leq h(|\pi|_1, \varepsilon) |\sigma|_1 |\tau|_1 \tag{2.11}$$

for some function  $h$ . Again, I have not yet done this.

So if we were to obtain the estimates (2.10) and (2.11) (and check that the domination condition really holds) then the Implicit Function Theorem would give persistence of a spectral projection from  $P_0$  uniformly in the system size  $N$ .

**Question 2.7.** Can one prove estimates of the forms (2.10) and (2.11)?

If so, I could explain why we should expect the Eggert et al. result to happen up to 1.2 rather than just  $1.2 \times 10^{-23}$ , and similarly why we should expect the Swanson et al. results for PtCl, as follows.

### 2.6.5 Application to quantum discrete breathers

Here is the application to quantum discrete breathers (QDBs). I will define a first excited QDB to be any element of the range of the continued first spectral projection, and so on thus:

- 1st excited QDB = elements of Range  $P_\varepsilon^{(1)}$
- 2nd excited QDB = elements of Range  $P_\varepsilon^{(2)}$
- (1, 1) multi QDB = elements of Range  $P_\varepsilon^{(1,1)}$
- etc.

Many might say “Well OK, that is great, I have got some analogue of the continued periodic orbits that we had in the classical case. But in the classical case we also got that the amplitude decays exponentially in space

away from some site, which leads to ask whether we get a localisation result for quantum discrete breathers.”

There is a standard dogma in quantum mechanics that says that in a periodic crystal nothing is localised, therefore it is ridiculous even trying to prove a general localisation result because it would have to include the periodic case. Well again, that is based on total misconception. It is true that the eigenfunctions in a periodic crystal are, without loss of generality, Bloch waves, so they are not localised. However, there are very strong localisation results, not of wave functions about a particular molecule, but a spatial decorrelation for the spectral projections; see e.g. [23, 26].

Here is a weak localisation result for QDB. One can look at the density matrix for a pair of states  $\{r, s\}$

$$P_\varepsilon^{(1)\{r,s\}} = \begin{bmatrix} N-2 & 0 & 0 & \mathbf{0} \\ 0 & 1 & 0 & \mathbf{0} \\ 0 & 0 & 1 & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \end{bmatrix} + O(2\varepsilon) \quad \text{in basis} \quad \begin{array}{l} |0_r 0_s\rangle \\ |1_r 0_s\rangle \\ |0_r 1_s\rangle \\ \text{the rest.} \end{array}$$

This means that the probability to see  $\{r, s\}$  in state  $|0_r 0_s\rangle$  is approximately  $1 - (2/N)$ , in state  $|1_r 0_s\rangle$  is  $\sim 1/N$ , in state  $|0_r 1_s\rangle$  is  $\sim 1/N$ , and in state  $|1_r 1_s\rangle$  is  $\sim \varepsilon/N$ .

Hence, the spectral projections indeed have some localisation properties. One should also note that the total probability is 1, so the spatial correlation function is summable with respect to distance between sites, which implies a weak form of decay. But one could hope for a stronger result if the coupling decays suitably in space, a feature that we have not used so far.

**Question 2.8.** Can we prove that the spatial correlation decays exponentially with the distance between  $r$  and  $s$  if the coupling  $\Delta_{rs}$  does?

An analogue of the method of [4] could perhaps be developed.

## 2.7 A tentative interpretation of 4-methyl pyridine results

Before I wrap up I would like to say some final words about 4-methyl pyridine.

**Question 2.9.** Could quantum discrete breathers explain experimental results on 4-methyl pyridine?

I think so, if for the quantum units one takes coupled pairs of rotors. Independent coupled pairs of rotors has been a successful explanation of experiments on Lithium acetate [12], but this was dismissed as a possible

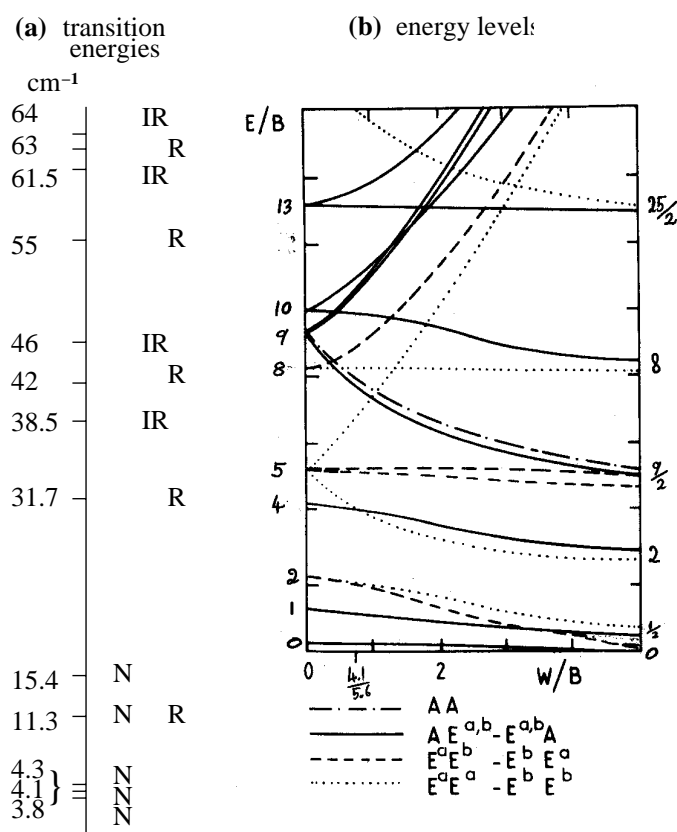


explanation for 4-methyl pyridine in [16], mainly because effects in isotopic mixtures (with a proportion  $p$  of  $\text{CH}_3$  groups replaced by  $\text{CD}_3$ ) do not fit. However, I think that it is possible that the continuation of the excitations of a single coupled pair of rotors to quantum discrete breathers, when coupling between neighbouring pairs of rotors is taken into account, could lead to a good explanation. On the other hand, Fillaux recently showed me some very interesting further experimental results on this material that cast doubt on my interpretation, so this section should be taken with a large dose of salt (or better, with a molecular crystal).

Figure 2.15 shows a summary of various observations of transition energies for 4-methyl pyridine, by three different methods, mainly at 5K. Next to this, I show an approximate spectrum for a pair of methyl rotors coupled by a potential  $\frac{W}{2}(1 + \cos 3\delta)$ , where  $\delta$  is the angle between a chosen arm in each rotor (from [12]). One could obtain a much more accurate spectrum by separating the Schrödinger equation into mean and relative coordinates  $(\theta, \delta)$ , which reduces to a free rotor in  $\theta$  and a standard Mathieu problem in  $\delta$  though one must be careful with the boundary conditions. However, the picture from [12] will do for present purposes. The energy scale  $B$  is the rotation constant  $\hbar^2/2I \approx 5.6 \text{ cm}^{-1}$ , for a single methyl group of moment of inertia  $I$ . Calculations of [16] using an empirical proton-proton potential suggest that  $W \approx 4.1 \text{ cm}^{-1}$ , thus the appropriate value of  $W/B$  to look at is 0.73. It looks to me as if the spectrum is in the right ballpark to interpret all the observed transition energies as excitation energies from the ground state. (One could also allow some transitions from the first excited state, however, as in [1, 16], since 5 K corresponds to a thermal energy of  $3.3 \text{ cm}^{-1}$ , so a  $4.1 \text{ cm}^{-1}$  excited state would have a 30% thermal population. Furthermore, one should pay attention to the selection rules governing which types of transitions between symmetry classes are possible via the three spectroscopic methods.)

To make a more precise comparison with experiments, there are several further steps that would be required. Firstly, one should probably add to the pair of rotors a potential  $V(\theta, \delta) = \alpha \sin 6\theta \sin 3\delta + \gamma \cos 12\theta \cos 6\delta$ , representing the effects of the pyridine rings. This form is dictated by symmetry considerations, which I think make all lower harmonics cancel. But because we are left with only relatively high harmonics, one can expect the amplitudes to be of relative order  $e^{-12C}$  for some order one constant  $C$ , by analyticity arguments, and thus they will probably not be very important.

Much more importantly, one should include the effect of coupling between different pairs. This is estimated *ab initio* to have an energy barrier of  $6.6 \text{ cm}^{-1}$  in [16], so it is highly significant. But I hope that it is not too large compared with anharmonicity (for which a reasonable measure would be  $B \approx 5.6 \text{ cm}^{-1}$ ) so that my continuation theory still applies. (Remember that the theory appears to apply to solid deuterium up to a dimensionless coupling of 1.2.) Thus, one would obtain quantum discrete breathers



**Figure 2.15.** Observed transition energies (measured in  $\text{cm}^{-1}$ ) for 4-methyl pyridine, mostly at 5 K (a), where  $N$  stands for neutron scattering (from [1, 16]),  $R$  for Raman scattering and  $IR$  for infrared absorption (reproduced from N. Le Calvé, B. Pasquier, G. Braathen, L. Soulard and F. Fillaux, Molecular mechanism determining phase transitions in the 4-methyl-pyridine crystal, *J. Phys. C* **19** (1986) 6695–6715 ©1986 by Institute of Physics Publishing). Approximate energy levels for a pair of  $\text{CH}_3$  rotors coupled by a potential  $\frac{W}{2}(1 + \cos 3\delta)$ , scaled to the rotation constant  $B$  for a single methyl group (b) (reproduced from S. Clough, A. Heidemann, A.H. Horsewill and M.N.J. Paley, Coupled tunnelling motion of a pair of methyl groups in Lithium acetate studied by inelastic neutron scattering, *Z. Phys. B* **55** (1984) 1–6 ©1984 by Springer Verlag). The different line styles correspond to different symmetry types of excitation.

which continue each of the low lying excitations of a single pair of methyl rotors. These would have a significant width in space, however, so their energies would be affected significantly by the choices of isotopes in the

four neighbouring methyl pairs. In particular, I suggest that the ‘smooth’ shift of a transition energy from  $516\mu\text{eV} = 4.1\text{ cm}^{-1}$  to  $350\mu\text{eV}$  observed in neutron scattering in [16, 19] as the deuterated proportion  $p$  increases from 0 towards 1, is an effect created by populating a spectrum of discrete energies corresponding to  $(\text{CH}_3)_2$  and  $\text{CH}_3\text{CD}_3$  rotors in the full range of environments (e.g. the four nearest neighbours are all  $(\text{CH}_3)_2$  or one or more is a  $\text{CH}_3\text{CD}_3$  or a  $(\text{CD}_3)_2$  etc.), weighted by the appropriate binomial coefficients, which of course vary significantly with  $p$ .

Finally, the splitting of the  $4.1\text{ cm}^{-1}$  transition into three distinct energies (around 3.8, 4.1 and  $4.3\text{ cm}^{-1}$ ) can be explained by the crystal point group. There are four pairs of rotors per unit cell, and from an examination of the crystal structure given in [11] (which differs little from that of figure 1.4, though in [31] it is mentioned that there might be a phase transition at around 100 K between the two cases), I believe it has  $D_4$  as its point group symmetry, generated by a  $1/4$  screw rotation and inversion in a point not on the screw rotation axis (not the  $C_{4h}$  symmetry claimed in [16]). The three distinct transitions could correspond to the three different symmetry types contained in the relevant representation of  $D_4$ , so-called  $A_g$ ,  $B_u$  and  $E$ , though a calculation would be required to assign them and to explain the splitting ratio. Similar splitting should presumably occur for every excitation, but perhaps the splitting is less for higher excitations or some of the symmetry types are less visible.

But the whole of my interpretation may be wrong. The preferred interpretation of [16] is in terms of moving breathers in the quantum sine-Gordon model

$$H = \int dx \frac{p^2}{2IL} + \frac{n^2 V_c L}{4} \theta_x^2 - \frac{V_0}{2L} \cos n\theta$$

with commutation relation  $[p(x), \theta(x')] = i\hbar L \delta(x - x')$  (one can scale  $p$  by  $L$  to obtain the standard commutation relation if one replaces the first term in  $H$  by  $p^2 L / 2I$ ). This is a continuum model (for  $n = 1$ , think of a heavy elastic band with one edge fixed along a horizontal wire, though free to rotate around it) for the angles of a 1D chain of rotors of moment of inertia  $I$  with  $n = 3$  arms in a cosine potential with barrier energy  $V_0$ , and coupled to nearest neighbours with lattice spacing  $L$  by a cosine force with barrier energy  $V_c$ . Classically, it has breather (and kink) solutions, and the model is Lorentz invariant (with respect to the relevant sound speed  $c$ ,  $c^2 = \frac{V_c L^2 n^2}{2I}$ ) so they can move too. For the quantum version, it is convenient to introduce the rotational constant  $B = \hbar^2 / 2I$ , the dimensionless quantum parameter  $\beta = \sqrt{2n(B/V_c)^{1/4}}$  and associated quantity  $Z = 8\pi/\beta^2 - 1$ , and the energy  $\lambda = \sqrt{nV_0/2(V_c B)^{1/4}}$ . If  $Z > 0$  it is proved [33] that the quantum model has elementary excitations analogous to the classical breathers and kinks, but the quantum breathers are restricted to having rest energies  $E_k = \frac{2\beta\lambda Z}{\pi} \sin \frac{\pi k}{2Z}$ , for  $k = 1, \dots, N_b$ , where  $N_b$  is the integer

part of  $Z$  (and the kink rest energy is  $\frac{\beta\lambda Z}{\pi}$ ). A breather moving with linear momentum  $P$  has energy  $\sqrt{E_k^2 + c^2 P^2}$ . Fillaux and Carlile proposed in [16] that the principal effect of spatial discreteness is to quantise the momentum  $P$  to the values  $j/L, j \in \mathbb{Z}$  (actually, I think they intended  $hj/L$ ), and interpreted the transition energy of  $4.1 \text{ cm}^{-1}$  as corresponding to exciting a pre-existing  $k = 1$  breather from  $j = 0$  to  $j = 1$  (though they interpret the transition energies at  $3.8$  and  $4.3 \text{ cm}^{-1}$  as the extremes of the tunnelling band).

I think their interpretation has fundamental problems. Firstly, where does the quantisation rule come from (e.g. electrons in metals are not restricted to such values of momentum)? Secondly, they make a parameter fit which is a factor 7 out from their prior estimates of the interaction energies of methyl groups. Thirdly, they compute breather energies based on an assumption that the quantum parameter  $\beta = 3$ , but I think this is due to a misunderstanding of the theoretical papers, most of which use scaled versions of the sine-Gordon model like  $H = \int dX \frac{1}{2}(P^2 + U_X^2) - \lambda^2 \cos \beta U$  with  $[P(X), U(X')] = i\delta(X - X')$  and which admittedly do not explain how to get to this from physical variables; the fitted parameter values of [16] would give a value of  $\beta = 1.46$ ; the difference is huge because  $N_b$  for the former is 1, whereas for the latter it is 10. Fourthly, using their parameters, the rest energy of a  $k = 1$  breather would be  $45.7 \text{ cm}^{-1}$ , so its thermal population at 5 K would be only  $10^{-6}$ , so it is surprising that transitions between its momentum states would be observable (in their favour, Fillaux et al do observe that the strength of the transition decays on a timescale of about 70 hours after cooling [17]). Fifthly, the chains of methyl groups in the  $a$ -direction are strongly coupled to those in the  $b$ -direction, and thus all together (including in the  $c$ -direction), so it is doubtful that a 1D model would suffice, a point acknowledged in [16]. Indeed they would have liked to use a theory that allowed for a 3D network of interactions but none was available at the time: hopefully mine will provide what is required, though I would be the first to admit that it is not yet sufficiently mature to provide quantitative predictions.

Nonetheless, further experimental results that Fillaux showed me just after I presented this material at the workshop in June 2001 lend very strong support to the idea that the  $4.1 \text{ cm}^{-1}$  transition energy does correspond to setting something in motion along the  $a$  or  $b$ -directions, so the problem is still wide open! Perhaps I have to generalise my theory to moving QDB.

**Question 2.10.** Can one generalise QDB to mobile QDB?

This may not be too hard, as the range of the spectral projection  $P^{(2)}$ , for example, already contains combinations (Bloch waves) that have any desired (pseudo-) momentum, and I guess one gets true momentum by usual group velocity analysis of the dispersion relation.

## 2.8 Conclusion

Now, I *will* conclude. Modulo checking a couple of technicalities, I think I have a proof of existence (which provides a definition as well) of quantum discrete breathers in models of molecular crystals, provided the coupling strength is sufficiently less than the anharmonicity. I think this will make a firm foundation for the interpretation of many experiments like the two mentioned in section 2.3, and maybe the methyl pyridine that I have just attempted to explain and  $KHCO_3$  which I have not started to analyse (Fillaux tells me the interaction between different dimers is very weak, but this would make my theory all the more applicable). Furthermore, I think the mathematical approach will have many other applications to quantum many-body problems. There is a huge number of quantum many-body problems, e.g. spins, bipolarons, excitons, etc., where what theoretical physicists do currently is work out some power series and then chop things off, despite the fact that the terms grow like powers of  $N$ . I think the new norms I have introduced will sort out what is going on there and justify the procedures ... or maybe not always justify them? It would be interesting if discrepancies arise!

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