The Rotational Spectrum of Tunnelling Methyl Groups

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Dedicated to Professor Werner-Müller Warmuth on the occasion of his 65th birthday

The quantum-classical transition of methyl rotation highlights conflicting assumptions of quantum and classical mechanics, the first assuming that identical fermions are indistinguishable while the second recognises they are distinguishable through their histories. When this is introduced into quantum mechanics, the two are compatible and there is a smooth transition of the methyl rotational spectrum with increasing temperature through the merger of three broadening peaks. The changing character of methyl dynamics through this transition is discussed.

1. The Quantum-Classical Transition

The study of the NMR line shape and the spin lattice relaxation time of hindered methyl groups was one of the outstanding successes of the early development of NMR [1]. Forty years later methyl dynamics remains an active area of research for the way it spans the quantum and classical domains and because of fundamental problems with which it has continued to be associated. One of these problems, the correct way of identifying identical particles is the topic of this paper. The simple triangular geometry of the methyl group and the well understood Zeeman and dipole–dipole Hamiltonians means that only a description of the motion is needed to enable detailed predictions to be made. Experiments are able to probe in great detail the changing character of the motion between the quantum and quasi-classical domains. A simple model of the motion at high temperatures consists of random reorientations of the triangle of protons about its symmetry axis. Three proton sites in the host lattice are assumed to be well defined, and the protons are considered to move round these sites as the methyl triangle rotates through $\pm 2\pi/3$, transporting their spin states from site to site. The depth of modulation of the dipole–dipole interaction is easily calculated, and the motion is characterised by a Lorentzian spectrum with a width determined by a correlation time τ_c. This classical model usually works extremely well down to temperatures around 70 K. As the temperature falls, the nature of the motion changes and the spectrum departs radically from the Lorentzian form. The same change accounts for the failure of the high temperature motionally narrowed NMR spectrum to broaden at low temperature. High temperature quasi-classical hopping rotation changes to more coherent quantum tunnelling.

The low temperature extreme of this transition is represented by the stationary states of a time independent Hamiltonian. A way of describing the eigenstates of a strongly hindered methyl group is to consider three harmonic oscillator states centred at orientations ϕ_0 and $\phi_0 \pm 2\pi/3$. These correspond to the three orientations of the methyl group relative to the crystal lattice. The protons being identical, we may only distinguish these three orientations in stationary states by the spin components at the three sites. If we choose spin states α and β as basis functions there are eight ways with total magnetic quantum numbers $m = \pm 3/2$ or $\pm 1/2$, in which these can be allocated to thre three sites. One of these ways with $m = 1/2$ is represented by $|\alpha, \alpha, \beta\rangle$, the order of the symbols indicating the lattice sites. Now the overlap of the functions introduces matrix elements between the triplet of functions having $m = 1/2$, and one obtains eigenstates

$$|\alpha, \alpha, \beta\rangle + \lambda |\beta, \alpha, \alpha\rangle + \lambda^* |\alpha, \beta, \alpha\rangle \tag{1}$$

in which $\lambda = \exp(\imath 2\pi k/3)$ with $k = \pm 1$ or 0. The E doublet having $k = \pm 1$ is displaced in energy by $\hbar\omega_t$ from the A singlet with $k = 0$. This is the tunnel splitting. The $m = \pm 3/2$ states have $k = 0$. Thus there is an A spin quartet separated from two E doublets. The nuclear Zeeman energy $m\hbar\omega_L$ is easily added, as is the dipole–dipole interaction between the protons at the three sites. The NMR spectrum calculated from this energy level diagram exhibits the observed narrowing due to the tunnel splitting and more interestingly shows observable sidebands [2] separated by the tun-

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nel frequency from the main NMR line. The same feature appears in the temperature dependence of the spin lattice relaxation time [3, 4].

The relaxation time is a parameter which links the low and high temperature descriptions of methyl motion [5]. It depends on the Fourier components of the rotational spectrum at one and two times the Larmor frequency ω_L. The rotational spectrum changes from the high temperature Lorentzian form as the temperature falls, and at low temperatures is consistent with the singlet and doublet energy level diagram whose splittings give the three frequencies $\pm\omega_t$ and 0. These three frequencies constitute the spectrum of the time-evolution of a wavepacket formed by superposition of the eigenstates. The classical expectation that the Lorentzian spectrum merely narrows as the temperature falls is therefore incorrect. A more interesting development occurs in which the spectrum divides into three peaks which continue to narrow and at low temperature are centred on $\pm\omega_t$ and 0. This is illustrated in Figure 1. Relaxation experiments explore this spectrum. Two early observations confirmed the general form of the spectrum. Instead of one minimum in the T_1 versus T curve there are two when ω_t is much larger than ω_L [3]. The usual minimum occurs near the condition $\omega_L \tau_c = 1$ and the second one, known as the Haupt minimum, at $\omega_t \tau_c = 1$. The second feature is that the depth of the first minimum is reduced by the separation of the two minima [4]. Two more properties of this rotational spectrum contribute to its interest. It was found that the three peaks originating at low temperatures from $\pm\omega_t$ and 0 converge as they broaden and merge. The tunnel frequency thus declines with temperature. The second discovery was that the character of the rotational spectrum depends essentially on only two parameters, the hindering barrier height and the temperature. Since the barrier height is linked in a simple way with the tunnel frequency ω_t, the temperature dependence can be predicted from a single low temperature measurement. The host crystal merely plays the role of a heat bath. Methyl rotation is thus almost ideal for the exploration of the quantum-classical transition in a simple well characterised quantum system.

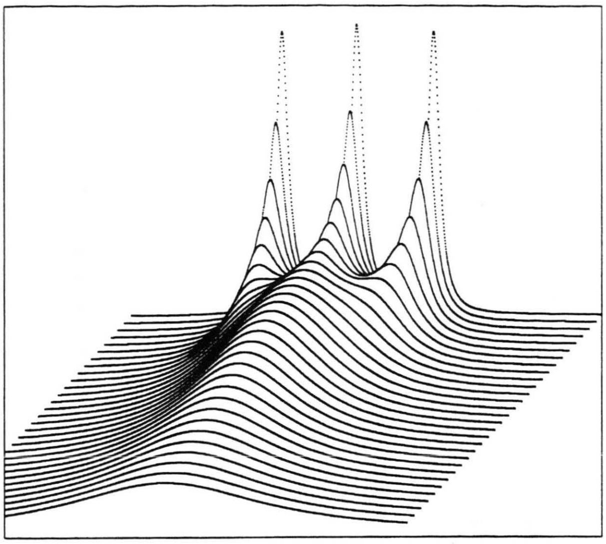

Fig. 1. A mathematical model for the temperature dependent rotational spectrum of a methyl group. Motional averaging of a three-frequency spectrum is combined with random phase modulation. Three frequencies converge and merge while broadening into the high temperature Lorentzian spectrum.

The correlation time τ_c whose reciprocal governs the width of the Lorentzian spectrum at high temperatures is essentially the same parameter which governs the width of the three separate peaks of the spectrum at low temperatures. It typically obeys an Arrhenius relation $\tau_c = \tau_0 \exp(E/kT)$ over a fairly wide temperature range. The temperature at which the change in the character of the rotational spectrum occurs is roughly that at which $\omega_t \tau_c = 1$. The tunnel frequency can be inferred from E, so it is possible to predict the transition temperature from high temperature measurements with some degree of success. Two kinds of dynamics may be presumed to be in competition, a temperature dependent one with a rate τ_c^{-1} and one with a frequency ω_t. Quasi-classical behaviour occurs when the former overtakes the latter. It is possible to model the spectrum [6] using only two parameters ω_t and τ_c by imagining a frequency jumping randomly between the three frequencies $\pm\omega_t$ and 0 at a rate τ_c^{-1} while the phase is also modulated at the same rate. The frequency modulation causes the three peaks to converge and merge while the phase modulation causes the whole spectrum to broaden with increasing temperature. If the activation energy E is related to ω_t, this is a single parameter theory generating a family of temperature dependent rotational spectra for methyl groups with different hindering barrier heights. Figure 1 is calculated in this way. To go beyond this requires a detailed model of the trajectories in the quantum and classical regimes.

2. Proton Identities and the Antisymmetry Law

2.1 *Identities of Identical Objects*

The study of methyl rotation outlined above has been complicated by the existence of two incompatible theories, one employed at high and the other at low temperatures. The reason is a conflict concerning fermion distinguishability. Quantum mechanics asserts that identical fermions are indistinguishable and classical mechanics treats them as distinguishable. Fermion identities are introduced in both cases but quantum mechanics restores indistinguishability through antisymmetrisation. The logical position is that identical objects can be identified if they have relative motion. Two identical twins for example may be identified as one (a) who visited Paris last week and one (b) who was elsewhere. We refer to identities which depend on relative motion as relative identities to distinguish them from absolute identities which would require differences in mass, charge etc. The notion that fermions are indistinguishable can be traced back to the Gibbs paradox in statistical mechanics when it was found that identical fermions have no absolute identities. Because statistical mechanics does not involve relative motion, the existence of relative identities was overlooked and the particles were described as indistinguishable rather than identical. When this was carried over into quantum mechanics, it resulted in the antisymmetry law which then creates the gulf between quantum mechanics and classical mechanics.

The usual low temperature theory of methyl groups [7] is an extension of the well known explanation of ortho and para hydrogen. Freely rotating hydrogen molecules have rotational eigenstates with integer rotational quantum numbers. For even quantum numbers the total proton spin is $F=0$ while for odd numbers it is $F=1$. This is conventionally explained by an antisymmetry law which says that a many-fermion function must be antisymmetric to the exchange of any two fermions. Even quantum numbers belong to functions which are symmetric in the exchange of the space coordinates of the two protons so the spin state is required to be antisymmetric, which means $F=0$. Odd rotational quantum numbers belong to states which are antisymmetric to the exchange of the space coordinates. They have symmetric spin states with $F=1$. These are the two spin symmetry species. To express these properties it is necessary to assign identities to the protons. For example an antisymmetric spin function is written $\alpha(i)\beta(j)-\alpha(j)\beta(i)$ so that it reverses sign when protons i and j are exchanged. The symbols i and j are called proton labels. In this low temperature theory there is no relative motion of i and j.

The absence of relative motion resulting from antisymmetrisation obviously posed a problem for quantum mechanics and led to a reinterpretation of the antisymmetry law [8, 9]. Instead of exchange being an operation on a statefunction it is interpreted to mean a dynamical process in which particles i and j interchange space coordinates over a finite time. During this process it is supposed the wavefunction acquires a phase π if the particles are fermions but not if they are bosons, introducing the factor $\exp(\imath\pi)=-1$. This reinterpretation, however, conflicts with the relativity principle that laws are the same for all observers. Two particles moving round a circle exchange space coordinates according to an observer who is at rest with respect to the circle, but not according to an observer who is moving along the axis of the circle. To this observer the particles follow non-intersecting helical paths. The observers do not agree on whether the particles exchange, so this meaning of exchange can not be part of a physical law. Discarding the antisymmetrisation law solves all the problems and restores the compatibility with classical mechanics. It allows a single description to be given of the whole quantum-classical transition.

2.2 *Relative Identities*

The relative identities may be introduced into quantum mechanics as follows. A set of fermions (electrons say) occupies states $p, q, r\ldots$ at time t_0 and states $u, v, w\ldots$ at the later time t. The statefunction at t is written $P_u Q_v R_w\ldots$, where the upper case letters are identities derived from the states at t_0. The particle trajectories do not merge because this would require a doubly occupied state which is forbidden by the Pauli principle. Now one could change the names of the states p and q to q and p so that the statefunction at t becomes $Q_u P_v R_w\ldots$ These two identity schemes are related though because the vector pq is reversed relative to the vector uv in passing from one to the other. In switching the identities of the particles in u and v the angle between the two vectors changes by π in any reference frame. This geometrical feature is reproduced in the quantum mechanics by a phase change which occurs in passing from one identity scheme to the other. To effect the switch, the identities are based on two orthogonal states $p\cos(\theta/2)+q\sin(\theta/2)$ and $q\cos(\theta/2)-p\sin(\theta/2)$ and then θ is changed from 0 to π. P_u changes to Q_u and Q_v changes to $-P_v$:

$$X_{uv}P_uQ_v=-Q_uP_v. \tag{2}$$

As $v\rightarrow u$ we find that doubly occupied states like P_uQ_u are antisymmetric under the exchange operator X_{uv} and are annihilated by the exclusion operator $1+X_{uv}$. The Pauli principle is satisfied by removing these states. When eigenstates are superposed to form wavepackets there is relative motion of the fermions $P, Q, R\ldots$ etc. The particles have velocities which transform in the usual way under transformation from one reference frame to another, so the relativity principle is satisfied.

As a simple example we consider again the states of ortho and para hydrogen. Henceforth orbital and spin state will be shown separately as subscript and superscript. So far the states u, v have included both. P_u^{α} means that particle P occupies orbital u and has spin state α. In a rotating hydrogen molecule the two protons occupy orbitals $u=\exp(\imath m\phi)$ and $v=\exp(\imath m(\phi+\pi))$. If m is even then $u=v$. If the two spin states are also the same as in $P_u^{\alpha}Q_u^{\alpha}$, the function is doubly occupied and does not exist, being annihilated by $(1+X_{uv})$. States with even m are thus spin singlets with $F=0$. If m is odd $u\neq v$ and the states with the same spin states are not annihilated. States with odd m are consequently spin triplets with $F=1$. By discarding the antisymmetrisation law the Hilbert space is enormously enlarged, but at low temperature the state vectors of an ensemble condense into a small region of that space which has the same structure as that obtained with antisymmetrisation. The number of eigenstates and the energy level diagram are thus the same. The difference appears with increasing temperature since without antisymmetrisation the state vectors move out into the large Hilbert space acquiring the particle-like attributes of quasi-classical behaviour. With antisymmetrisation the statevectors are artificially confined to a small Hilbert space to suppress relative motion and preserve indistinguishability.

2.3 *Application to Methyl Rotation*

When antisymmetrised theory is extended to hindered methyl groups there are three spin symmetry species [7]. The cyclic permutation of three protons ijk is considered. Since this is the same as two pair exchanges, the antisymmetry law requires methyl states to be invariant under cyclic permutation of the space and spin coordinates of the protons. Eigenstates are presumed to be products of spatial functions and spin functions with permutation eigenvalues $\exp(\imath 2\pi k/3)$, where $k=\pm 1$ or 0. They are designated A × A, Ea × Eb and Eb × Ea. They thus have two k values, the one in the spin function being the negative of the spatial one. The lowest lying states of the species are identified with the singlet and doublet levels introduced in the introduction. Because the non-magnetic environment can not affect the spin state it may also not change the symmetry of the spatial state, since if it did so the resulting function would no longer satisfy the antisymmetry law. It is therefore presumed that the fluctuating interaction with the environment must have perfect three-fold symmetry to prevent this happening. It is assumed that only symmetry conserving transitions occur. This three-fold symmetry constraint confines the statevectors to the small Hilbert space. It has of course no parallel in the high temperature theory of methyl rotation and it is the crucial factor which prevents a desciption of the quantum-classical transition based on the antisymmetrised theory.

With relative proton identities the methyl eigenstates are not antisymmetrised and do not have the form of products of space and spin functions. They have only one k value. The Pauli principle is trivially satisfied by confining the basis set to singly occupied states, all functions being of the form $P_uQ_vR_w$ with one of the protons P, Q, R at each of the sites u, v, w. There are still three types of eigenstate as is evident in (1) but interaction with the spin-independent environment may combine them. Wavepackets transport the protons along trajectories which may be followed through the change in associated observables. This is then consistent with the high temperature model of random reorientation.

3. Methyl Group Wavepackets

A superposition of two methyl eigenstates having $k=1$ and 0, both with $m=1/2$, yields

$$\begin{aligned}\psi = (2/3)^{1/2}\,[&P_u^{\alpha} Q_v^{\alpha} R_w^{\beta} \cos(\omega_t t/2) \\ &+ \exp(\imath\pi/3)\, P_v^{\alpha} Q_w^{\alpha} R_u^{\beta} \cos((\omega_t t + 2\pi/3)/2) \\ &+ \exp(\imath 2\pi/3)\, P_w^{\alpha} Q_u^{\alpha} R_v^{\beta} \cos((\omega_t t + 4\pi/3)/2)]. \end{aligned} \tag{3}$$

The observable effect of rotation is due to the different spin state of proton R compared with the other two. The spin components of each proton are unchanging but the magnetisation at a lattice site is time dependent:

$$\begin{aligned}\langle I_{uz}\rangle &= (1/3)(\cos^2(\omega_t t/2) - \cos^2((\omega_t t + 2\pi/3)/2) \\ &\qquad + \cos^2((\omega_t t + 4\pi/3)/2)) \\ &= (1/6)(1 - 2\cos(\omega_t t + 2\pi/3)). \end{aligned} \tag{4}$$

The magnetisation at the other two sites is similar with a different phase. It gives a peak in the dipole–dipole driven NMR spectrum [10] at the tunnel frequency ω_t.

To create independent methyl rotation and spin precession, four eigenstates are superimposed. Two rotating functions like (3) with different m are first constructed and then superimposed:

$$\begin{aligned}\psi = (2/3)^{1/2}\,(&P_u^{\alpha} Q_v^{\alpha} R_w^{+} \cos(\omega_t t/2) \\ &+ \exp(\imath\pi/3)\, P_v^{\alpha} Q_w^{\alpha} R_u^{+} \cos((\omega_t t + 2\pi/3)/2) \\ &+ \exp(\imath 2\pi/3)\, P_w^{\alpha} Q_u^{\alpha} R_v^{+} \cos((\omega_t t + 4\pi/3)/2)), \end{aligned} \tag{5}$$

where

$$\begin{aligned} R_w^{+} &= (1/2)^{1/2}(R_w^{\alpha} \exp(\imath\omega_L t/2) + R_w^{\beta} \exp(-\imath\omega_L t/2)), \\ R_w^{-} &= (1/2)^{1/2}(R_w^{\alpha} \exp(\imath\omega_L t/2) - R_w^{\beta} \exp(-\imath\omega_L t/2)) \end{aligned} \tag{6}$$

and ω_L is the Larmor frequency. The magnetisation associated with the precessing trajectory R is given by

$$\langle I_{x,R}\rangle = \cos(\omega_L t)/2. \tag{7}$$

The transverse magnetisation at a particular lattice site u is given by

$$\langle I_{x,u}\rangle = (2/3)\cos(\omega_L t)\cos^2((\omega_t t + 2\pi/3)/2). \tag{8}$$

According to (7) the precession of spin R occurs at the Larmor frequency ω_L. At a particular lattice site u a succession of protons passes, only one of which, namely R, precesses the other two being in the state α. On each rotation there is a burst of precession at the site u. The resulting amplitude modulated precession has components at the three frequencies ω_L and $\omega_L \pm \omega_t$. This accounts for the observation of sidebands of the Larmor peak of the NMR spectrum, which may be seen in Figure 2. The separation of the sidebands from the central peak gives the tunnel frequency ω_t. Thus it is possible to derive observables pertaining to the lattice sites or to the protons which circulate round the sites. The discussion may be conducted using the lattice frame in which the methyl group rotates or using the methyl frame in which the lattice rotates. The measured observables are relative quantities whose value is the same in all frames.

4. The Environment and Rotational Trajectories

Having now a low temperature description of the trajectories of partially localised protons moving coherently between the three lattice sites, it is possible to ask how these trajectories change with increasing temperature to develop the characteristics of localisation and incoherent motion assumed by the quasi-classical theory. The instrument of the change is the motion of the hindering obstacle which is part of the host lattice. When a rotating wavepacket state of the methyl group is excited, the hindering obstacle participates in the motion. It moves away from the methyl axis as a partially localised proton passes it by, and towards the axis when the proton has gone. It therefore oscillates at three times the rotation frequency. In the idling state in which there is no transfer of energy and angular momentum between the lattice and the rotor it oscillates in phase with the rotation. If the relative phase of the rotation and obstacle oscillation changes, then there is transfer of angular momentum, the direction depending on the sign of the phase change. This is similar to any machine, for example a bicycle in which the phase change causes the upper part of the chain to tighten when accelerating and the lower part when decelerating. The energy transfer explains how the thermal motions of the lattice generate the broad distribution of methyl angular velocities at high temperatures.

With the transfer of angular momentum, the methyl wavepacket is no longer representable as a superposition of eigenstates having integer k. Instead a continuous range of k values may contribute. When the angular velocity of a wavepacket changes, so does its mean k value. The Hilbert space inhabited at high temperatures contains this continuous range of k values, and at low temperatures the state vectors of an ensemble

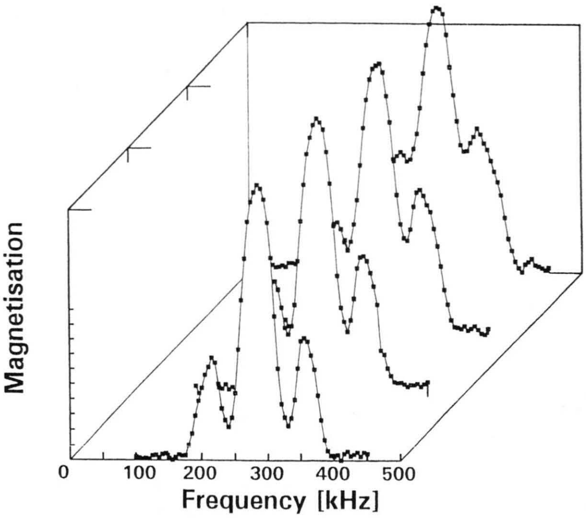

Fig. 2. The low field NMR spectrum of methyl malonic acid showing the tunnelling sidebands 75 kHz on each side of the Larmor peak. The sidebands broaden inwards as the amplitude of the oscillating field increases. The behaviour is similar to the effect of temperature in Figure 1.

condense into a subspace of integer k. The spreading of k about the integer values leads to the broadening of the rotational spectrum. It is not necessary to use high temperatures to induce the broadening. By modulating the dipole–dipole interaction with a sufficiently strong oscillating field the rotational spectrum can be broadened at helium temperatures. An example is shown in Figure 2. This shows the main Larmor peak of the dipole–dipole driven NMR [10] spectrum of methyl malonic acid flanked by tunnel sidebands separated from the central peak by the tunnel frequency 75 kHz. The series of four spectra is obtained with increasing strength of the oscillating field. For a weak field the rotational spectrum has two narrow side peaks as in Figure 1. With increasing strength the peaks broaden towards the central peak but not outwards away from that peak. This again is similar to the behaviour in Fig. 1 and is characteristic of all compounds studied in this way.

The change from three peaks at low temperatures to a single broadening peak at high temperatures is caused by a dynamical influence from outside the methyl group. The low temperature methyl motion described by a superposition of eigenstates with integer k is disturbed by fluctuations of the amplitude and phase of the coupled oscillations of the hindering obstacle. It must either suppress those fluctuations at low temperature or itself be suppressed by them at high temperatures. The decline in the splitting of the three peaks with increasing temperature is evidence of the latter. In Fig. 1 this decline results from the motional averaging of the three angular velocities $\pm\omega_t$ and 0 characteristic of the undisturbed motion. As the free motion with its three frequency spectrum is suppressed it is replaced by driven motion in which the methyl group responds to the fluctuations of the hindering obstacle. An example of the change of character is that an undisturbed wavepacket initially rotating clockwise changes due to the dipole–dipole interaction into a wavepacket rotating anticlockwise, the two motions being superposed. In accomplishing this change the wavepacket shape evolves. When disturbed by fluctuations, angular momentum is transferred from the rotating wavepacket to the environment, a form of friction, and the free motion is damped. The eigenvalues of the undisturbed system become increasingly irrelevant with increasing temperature, as the quasi-classical environment imposes its own character on the quantum system [11]. The change is reflected in the temperature dependent spectrum of Figure 1.

5. Summary

The quantum and quasi-classical theories are both descriptions of the motion of a typical wavepacket in an ensemble of methyl groups, the classical one assuming extreme particle-like properties. The character of the rotational trajectories in the high and low temperature extremes can be plausibly modelled. The manner in which the trajectories change over a fairly narrow temperature range can be perceived qualitatively but not yet described in any detail. Many different types of measurement over a wide temperature range all relate to a characteristic temperature dependent rotational spectrum. Methyl rotation is a good way of probing the quantum-classical transition and presents a continuing challenge to experimentalists. The possibility of studying coherent rotational excitations in the time domain by extending the techniques and concepts of NMR from spin orientational trajectories to the combination of spin and particle trajectories is a particularly interesting possibility for the future.

The growing understanding of methyl dynamics owes much to the large body of work inspired by Professor W. Müller-Warmuth. Besides acknowledging a scientific debt I would like to express my gratitude to him for a friendship based on shared enthusiasms and extending over many years.

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