Comparison of the non-equilibrium predictions of Intrinsic Quantum Thermodynamics at the atomistic level with experimental evidence.

Charles E Smith and Michael R von Spakovsky
Center for Energy Systems Research, Mechanical Engineering Department Virginia Polytechnic Institute and State University, Blacksburg, VA 24061
E-mail: Michael.von.Spakovsky@vt.edu, cesmith@vt.edu

Abstract. Theoretical predictions from Intrinsic Quantum Thermodynamics (IQT) are compared to published experimental findings in order to examine whether or not calculations using IQT are consistent with experimental data. IQT makes the assertion that entropy is an intrinsic property of matter in the same way that inertial mass, energy, and momentum are and must, thus, exist even for single particles. Entropy as defined by IQT is a measure of the distribution of a system’s internal energy at any given instant of time amongst the available internal degrees of freedom, i.e., the energy eigenlevels of the system. In this paper, it is shown that IQT models the internal relaxation of a 5-level rubidium system in a way that is consistent with the experimental data available in the literature. In addition, other experimental data found in the literature is compared with results obtained from the equation of motion of IQT that allows for heat interactions. It is shown that the decay of so-called “cat states” for single ions that are contained in Paul traps and that interact with a heat reservoir is also consistent with the calculations made using the theory of IQT.

1. Introduction and background
The foundations of Intrinsic Quantum Thermodynamics (IQT) were first presented thirty-five years ago by Hatsopoulos and Gyftopoulos [1] with important preliminary work contributed by Park and Simmons [2,3]. A fundamental dynamical contribution was introduced in 1981 by Beretta [4], and important subsequent work includes Refs. [5-22]. The theory of IQT is based on the assertion that the second law of thermodynamics, with its implications of irreversibility, applies at all physical levels of description from the macroscopic and classical to the atomistic and quantum [1]. Central to the foundations of IQT is the recovery of the concept of “state of a system”, a bedrock of physical thought and a concept lost in quantum statistical mechanics (QSM) in which the state necessarily refers only to the state of an ensemble, which consists of an infinite number of identical systems not identically prepared [1,2]. Also central to IQT is the fact that the dynamics of any change in state is at all times consistent with the laws of physics and thermodynamics [1-7]. To satisfy both the requirements of thermodynamics, particularly that of the second law, as well as those of quantum mechanics (QM), IQT relies on two fundamental insights. The first is that the ontological entity representing any state
of a quantum system\(^1\) is not the density operator (i.e., wave function projector) of QM\(^2\) but instead a density or “state” operator based on an ensemble consisting of an infinite number of identical systems identically prepared \([1]\). The second is that the Schrödinger equation of motion of QM, though correct, is incomplete since it is unable to describe the dynamics of a system with entropies greater than zero \([1,4-7]\).

The rationale behind the concept that the density operator is synonymous with the state of a system is based on the idea that in QM the density operator contains all the information necessary to characterize the state (i.e., the so-called pure state) of a quantum system at any given instant of time. Thus, for example, the expectation value \(\langle S \rangle\) for the entropy, as defined by von Neumann, can be written in terms of the density or “state” operator \(\rho\) via

\[
\langle S \rangle = -k_B \text{Tr}(\rho \ln \rho).
\]

Here \(k_B\) is Boltzmann’s constant. In QM, the value of \(\langle S \rangle\) is necessarily zero, i.e. is zero for all pure states. For values greater than zero, i.e. for non-pure or mixed states, the density operator of QM can be replaced with that of QSM. However, the problem is that not only does this introduce the difficulty mentioned above about the loss of the concept of “state of the system” but it as well leads to an entropy, which is not the entropy of thermodynamics \([12]\). In fact, QSM leads to the so-called ‘irreversibility paradox’, the resolution of which requires a simultaneous consideration of questions that specifically go to the heart of issues surrounding the second law of thermodynamics, namely, i) what the physical roots of “entropy” and “irreversibility” are, ii) whether or not “entropy generation” due to irreversibility is merely a statistical illusion\(^3\), and iii) what a general description of non-equilibrium is \([21]\). Such a general description is not possible with QSM without the addition of a non-thermodynamic principle (microscopic reversibility), assumption (e.g., small perturbations to ensure linear behaviour), or approximation (e.g., sufficiently small deviations from stable equilibrium) \([21]\). In contrast, IQT and its density operator exhibit none of these drawbacks and instead lead to an entropy that is physical and exists for all states (pure and non-pure) and all systems regardless of size. Moreover, the entropy at a fundamental level of description is seen as a measure of how the system energy \(\langle E \rangle\) is distributed amongst the system’s available degrees of freedom, i.e., its energy eigenlevels, while the entropy generation is a measure of how the energy \(\langle E \rangle\) is redistributed in a change of state \([21]\).

The second insight mentioned above that the Schrödinger equation of motion is incomplete has prompted the search for an equation able to describe irreversible processes. In Quantum Thermodynamics (QT), formerly known generally as Quantum Dissipative Dynamics, this has led to master equations of various types \([23, 24]\). These equations have been developed to model the so-called “open quantum systems”\(^4\) introduced by Lindblad and Kossakowski and others \([25-27]\) where the increase in the entropy of a system is brought about through interactions with an external reservoir. In QT, the generalization to irreversible or “dissipative”\(^5\) processes is provided by an equation of motion originally developed by Beretta \([4-7]\), which assumes a priori a tendency for an intrinsic increase in system entropy, i.e., the entropy of thermodynamics. Unlike the master equations of QT, which are often second order approximations \([28]\), the Beretta equation represents the full nonlinear dynamics, which describes the irreversible evolutions in state of systems that are arbitrarily far from stable equilibrium.

Thus, the outlook provided by IQT avoids the inconsistencies pointed out by Loschmidt \([29]\), which arise when trying to force irreversible, non-unitary behaviour from dynamics that is intrinsically reversible and unitary. Avoided as well is the need for the exogenous statistics found in QSM that destroy the concept of state by requiring that a system possessing entropy be described with ensembles

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\(^1\) All systems are in the end quantum systems; but as the size of a system increases, the importance of quantum effects decreases, since the dispersions representing observables approach delta functions.

\(^2\) The density operator of QM only represents a limited class of states and is, thus, a special case of the density operator of QT.

\(^3\) In fact, this is the conclusion drawn from statistical mechanics that entropy generation due to irreversibility does not result from the endogenous dynamics but instead from temporal changes of some exogenous statistical description.

\(^4\) This is the closed-system-plus-reservoir model used as the basis for describing the concept of “dissipation” in QT, which in QT is understood to be a loss of information between the system and the reservoir. This “dissipation” is, thus, not physical.

\(^5\) In contrast to QT, the concept of “dissipation” in IQT is that of a physical entity internal to the system and is not dependent on the closed-system-plus-reservoir model as used in QT.
of “pure” states which themselves have no entropy. Statistical mixes of pure states have the additional inconsistency which arises when work can be extracted from subsets of the ensemble even though none can be extracted from the ensemble as a whole. Clearly, this violates the second law [21].

IQT also avoids the violations of the second law that are inherent with the QT approach. In contrast to QSM, QT is not based on statistical mixes of pure states and, thus, the definition of “state of the system” is preserved. However, because the entropy for the “open system” (i.e., closed system plus reservoir) cannot increase, the potential for extracting energy to do work remains unchanged (i.e., is not degraded) regardless of whether gradients of thermodynamic potentials between the closed system and reservoir exist and change over time. This cannot be since it suggests that regardless at what point in time energy is extracted that the potential to do work remains unchanged even when all thermodynamic potentials have ceased to exist. This is inconsistent with what is observed in nature and, thus, violates the second law. IQT obviates such difficulties because the increase in entropy is a process that is intrinsic to the closed (isolated) system, leading to a degradation in the potential to do work.

The equation of motion of IQT governs how the diagonal and off-diagonal elements of the thermodynamic state or density operator (or matrix) $\rho$ evolve in time. The formulation is based on the hypothesis that physical systems naturally seek the path of local steepest entropy increase on their way to stable equilibrium [4]. For an isolated or non-isolated (experiencing a work interaction), single constituent (i.e., a single particle, a single assembly of indistinguishable particles, or a single field) closed system, this equation is given by

$$\frac{d\rho}{dt} = -\frac{i}{\hbar} [H, \rho] - \frac{1}{\tau_D} D \rho.$$  \hspace{1cm} (2)

Here, $H$ is the Hamiltonian operator, $\tau_D$ a scalar time constant or functional, and $-D / \tau_D$ the so-called dissipation term, which is a function of $\rho$, $\ln \rho$, and $H$, and which pulls the state operator in the direction of the projection of the gradient of the entropy functional $\langle S \rangle$ onto the hyper-plane of the constant energy $\langle E \rangle$ of the system. Forms of this equation for closed systems composed of distinguishable particles (or distinguishable assemblies of particles) and/or experiencing a non-work interaction (i.e., a heat interaction) are found in Beretta [7,19,20] as well as in Section 2.3 below.

Both the first and the second laws of thermodynamics are implied by this equation and its other forms.

The first term on the right hand side of Eq. (2) is the Schrödinger term which governs the reversible (linear) dynamics for the system, and it along with the time-derivative term on the left are equivalent to the time-dependent Schrödinger equation. This part of Eq. (2) governs the relative phases between system energy eigenlevels and quantum interference effects. Equation (2) also includes a dissipation operator $D$ scaled by an associated time functional $\tau_D$. This term governs the dissipation of a system’s adiabatic availability [31] as its state relaxes to one of maximal entropy. In general, due to its high degree of non-linearity, this equation must be solved numerically except in the simplest of cases, e.g., a two-energy-eigenlevel system [8].

Since its development, there has been a limited effort to verify Eq. (2) experimentally and as a consequence the theory of IQT. The first by Beretta [8] uses IQT to model the effect of irreversibilities on the resonance fluorescence, absorption and stimulated emission of a two-level atom driven near resonance by a monochromatic laser beam. Beretta’s results suggest that the discrepancies between experiment and the theoretical predictions of QM are due to an irreversible atomic relaxation to stable equilibrium at constant energy, which can be predicted using the IQT equation of motion.
Nonetheless, further high-resolution experimental work, which has yet to be done, is needed to verify Beretta’s predicted results [8].

In a second attempt, Çubukçu [11] argues that unlike QM, IQT can predict the experimental results developed by Kukolich [32] for the damped-oscillatory behavior seen in the absorption rate of transmitted light by rubidium atoms in the vapor phase in a magnetic field. However, to support this contention, he uses the analytical solution of the IQT equation of motion for a 2-level, spin-$\frac{1}{2}$ system given by Beretta [33] even though the experimental rubidium spin system actually represents a 5-level system. Thus, the match between his solution and the actual experimental results is not perfect. Nonetheless, the implication is that the damping effects predicted by the IQT equation are due to the irreversible relaxation of the spin states of the rubidium atom to stable equilibrium.

To improve on Çubukçu’s results, Kukolich’s experiment [32] is revisited in this paper and the actual five-level system of Kukolich’s experiment numerically (as opposed to analytically) modeled using the IQT equation of motion, Eq. (2). In addition, a new comparison is made with the experimental data of Turchette et al. [34] for the relaxation of superposition states for a single ion in a Paul trap using the IQT equation of motion initially developed by Beretta [19] to include a heat interaction term and subsequently modified by the present authors as outlined in Section 2.3 below and in Smith [35].

2. Comparison of IQT with experiment

2.1 The Kukolich experiment

Kukolich [32] uses the spin states of rubidium to demonstrate the time dependence of the state operator of QM (i.e., the projector of the wave function). A diagram of the experimental apparatus is shown in Figure 1.

The rubidium (Rb) atoms and a helium (He) buffer gas are contained in a closed glass vessel with an applied external magnetic field that is oriented along the z-axis. The technique of optical pumping with circularly polarized light is used to prepare the Rb atoms in the desired spin state. The He is used to slow the relaxation of the Rb due to collisions with other Rb atoms as well as collisions with the walls of the container. Once the Rb atoms are in the uppermost spin energy eigenlevel, the direction of the magnetic field is changed suddenly to the x-direction, perpendicular to the z-axis. A photodiode detector opposite the light source along the z-axis is used to measure the intensity of the light beam as a function of time. The intensity of the light that is transmitted through the Rb vapor is found to oscillate and can be used to determine the quantum eigenstates of the Rb atoms.

![Figure 1. Diagram of the experimental apparatus of Kukolich [32].](image)

The spin states for Rb occur due to the coupling of the \( \frac{3}{2} \) spin of the nucleus with the \( \frac{1}{2} \) spin of the electrons. An energy level diagram is shown in Figure 2. The external magnetic field splits the energy eigenlevels \( E_0 \) and \( E_1 \) into sets of 5-level spin energy eigenlevels denoted as \( F=1 \) and \( F=2 \), respectively. The energies between each spin energy eigenlevel are multiples of Planck’s modified constant \( \hbar \) as shown. The external circularly polarized laser light, which has a wavelength of 7948 Å, pumps the majority of the atoms into the highest energy eigenlevel (i.e., \( F=2, \left| +\frac{1}{2}\right>_z \)), which leaves the Rb atoms in a spin-2 eigenstate.
The switching of the magnetic field to the x-direction changes the thermodynamic state of the Rb atoms. In QM, the new state or density operator (matrix) $\rho_{\text{new}}^{\text{QM}}$ as seen along the z-axis is calculated by means of the time-dependent von Neumann (or equivalent Schrödinger) equation or equivalently by the unitary (non-dissipative) transformation given by

$$
\rho_{\text{new}}^{\text{QM}} = \left| \Psi_{z}^{\text{new}} \right\rangle \left\langle \Psi_{z}^{\text{new}} = U^{-1} \left| \Psi_{z}^{\text{old}} \right\rangle \left\langle \Psi_{z}^{\text{old}} \right| U
$$

where $\left| \Psi_{z}^{\text{new}} \right\rangle$ (or its bra $\left\langle \Psi_{z}^{\text{new}} \right|$) is the new state vector and the unitary transformation matrix $U$ and its inverse $U^{-1} = U^\dagger$. As done in Kukolich [32], the unitary transformation matrix $U$ can be derived using the method outlined in Feynman [36]. The QM solution results in phases of state (i.e., $J_z, \omega_p/\hbar \equiv (\epsilon_i/\hbar)t$ for $i = -2,-1,0,1,2$) that change periodically in time $t$. The precession frequency of the phase, $\omega_p$, is proportional to the absolute magnitude of the spin energy eigenvalues $\epsilon_i$. As a consequence, the resulting non-dissipative state operator $\rho_{\text{new}}^{\text{QM}}$ of the system must contain elements that oscillate with the precession frequency of the Rb atoms as well as twice this precession frequency, with the precession frequency being directly proportional to the strength of the applied magnetic field in the x-direction. After the transformation, the new state vector as seen along the z-axis is expressed as

$$
\left| \Psi_{z}^{\text{new}} \right\rangle = \begin{bmatrix}
\frac{1}{4} \cos 2\omega_p t + \frac{1}{4} \cos \omega_p t + \frac{3}{8} \\
\frac{1}{4} i \sin 2\omega_p t + \frac{1}{4} i \sin \omega_p t \\
\frac{1}{4} i \sqrt{\frac{3}{2}} \left( \cos 2\omega_p t - 1 \right) \\
\frac{1}{4} i \sin 2\omega_p t - \frac{1}{4} i \sin \omega_p t \\
\frac{1}{8} \cos 2\omega_p t - \frac{1}{4} \cos \omega_p t + \frac{3}{8}
\end{bmatrix}
$$

where the transformed state vector $\left| \Psi_{z}^{\text{new}} \right\rangle$ (or state operator $\rho_{\text{new}}^{\text{QM}}$) is that of a pure state (i.e., a thermodynamic state with zero entropy).

After the field direction is switched, the amount of transmitted light from the same light source that is used for the optical pumping is employed to produce a signal whereby the thermodynamic state of the system can be determined. This is deduced from the intensity of the light transmitted through the cell containing the Rb atoms given by [32]

$$
I = I_0 - A = I_0 - \frac{3}{2} C + 2C \cos \omega_p t + \frac{3}{2} C \cos 2\omega_p t
$$

where $I_0$ is the intensity of the light source and $A$ the magnitude of the light absorbed by the atoms expressed as
\[ A = \frac{7}{2} C - 2 C \cos \omega_p t - \frac{1}{2} C \cos 2\omega_p t. \]  

(7)

As seen in Eq. (6), the intensity contains two precession frequencies: \( \omega_p \) and \( 2\omega_p \).

A diagram of \( I \) as a function of time is shown in Figure 3 and clearly shows the oscillatory behaviour of the thermodynamic state of the Rb atoms also seen in the experimental results given in Figure 4. As expected, the damping seen in the experimental results does not appear in Figure 3 since the unitary transformation of QM is reversible and damping is an inherently irreversible phenomenon. The damping, in fact, indicates that there is a relaxation from the initial non-equilibrium state in which the Rb atoms are placed to one of stable equilibrium. In addition, as noted in Kukolich [32], the relative amplitude between the two frequency components in Figure 4 differ from the expected theoretical value in part because the photocell attenuates the fundamental frequency more than the double frequency component. Finally, the braces under some of the oscillations in part (a) of Figure 4 indicate a “stair step” aspect of the data not attributable to a simple exponential decay of the signal. As will be seen below, both this aspect and the damping are captured by the IQT simulation.

**Figure 3.** Time-dependent photocell current as calculated for a spin-2 system without dissipation [32].

**Figure 4.** Experimental trace of the photocell current for two precession frequencies ((a) \( \omega_p \) and (b) \( 2\omega_p \)) after the field is switched to the x-direction [32].

In an experiment similar to that of Kukolich [32], Nagel and Haworth [37] use the magnetic field of the earth, which is oriented in the x-direction, instead of an applied external field to produce the oscillations. Their results shown in Figure 5 indicate an initial spin attenuation that is more gently curved than would be indicated by a simple exponential decay. In fact, these relaxation curves look more like the gradual, S-shaped curves that are predicted by IQT where sparsely occupied energy eigenlevels for a system gradually increase their occupation probabilities at the expense of those with larger initial occupation probabilities. Clearly, the same gradual, S-shaped drop off is not seen in the Kukolich experiment. Although one can only speculate as to why, since Kukolich makes no comment, it is reasonable to assume that only the latter part of the signal, which corresponds in the Nagel-Haworth experiment to the bottom half of the S of the S-shaped decrease, is reported in Kukolich.

To initiate the solution of the IQT equation of motion for the Rb relaxation, an initial density or state operator \( \rho \), which represents the thermodynamic state of the system after the magnetic field is switched to the x-direction, is chosen. Thus, the initial state operator, \( \rho_{\text{ini}} \), is taken as \( \rho_{\text{QM}}^{\text{new}} \) (Eq. (3)) slightly perturbed (see the discussion below following Eq. (9)) and evaluated at \( t = 0 \). The IQT solution assumes that each Rb atom can be treated as a separate, isolated system. Çubukçu [11] sug-
Figure 5. The results of the field switching experiment for Rb atoms by Nagle and Haworth [37]; the sweep time for the signal is 10 ms.

suggests this assumption is valid at sufficiently low pressures based on Franzen’s [38] measurements of relaxation time as a function of Rb vapour pressure which indicate that the time to relax increases with decreasing pressure until the latter is sufficiently low after which time it plateaus out, i.e., collisions as the driving mechanism for relaxation become negligible. Çubukçu concludes that the gradual relaxation to stable equilibrium is attributed to each atom’s own internal relaxation from a state of non-equilibrium to one of stable equilibrium and not due to collisions with other atoms (i.e., Rb or those of the buffer gas or of the wall). However, the recent experiments of Balabas et al. [39] show with refined techniques, which further isolate the Rb atoms from collisions harmful to the spin state, that relaxation times are extended by 2 to 3 orders of magnitude over those viewed in the Franzen [38] experiment. Thus, redoing the latter with the techniques of Balabas et al. would be needed to see if the plateauing at low vapour pressures observed by Franzen indeed still occurs. Nonetheless, for now, the assumption of Çubukçu is made and as seen below, the characteristics of the data of Kukolich and Nagel and Haworth are modelled well using it and the IQT formalism.

To model this relaxation, the system of equations which result from Eq. (2) for this 5-level, spin-2 system is written as

\[
\frac{d\rho_{ij}}{dt} = -\frac{i}{\hbar} [H, \rho]_{ij} - \frac{1}{\tau_D} D_{ij}
\]

where the \(\rho_{ij}\) are the elements of the density matrix (state operator) that are found as functions of time and \(i\) and \(j\) each vary from 1 to 5. The first term on the right hand side of Eq. (8) are the commutator elements that represent the decay of the relative phases between the spin energy eigenlevels of each Rb atom, while the second term are the elements of the dissipation operator of IQT expressed as

\[
D_{ij} = \begin{pmatrix}
(\rho \ln \rho)_{ij} & \rho_{ij} & E_{ij} \rho_{ij} \\
\sum (\rho \ln \rho)_{ii} & 1 & \sum E_{ii} \rho_{ii} \\
\sum E_{ii} (\rho \ln \rho)_{ii} & \sum E_{ii} \rho_{ii} & \sum E_{ii}^2 \rho_{ii}
\end{pmatrix}
\]

(9)

Note that ‘current theory’ explains the plateauing in the following way: when the number of particles is sufficiently small so that collisions with the walls are still much more frequent than collisions with other particles, the relaxation time plateaus because each particle behaves as if the others were not present. To conclusively rule out that the effect being seen is not due to particle-wall interactions, one would have to redo the experiment with different wall materials to see if the relaxation time plateaus at different values or always at the same ‘intrinsic’ value.

Note, that the logarithm of the matrix representation of the density operator \(\rho\) is found by computing its Jordan decomposition and then taking the logarithm of the Jordan blocks.
Because the state involves the decay of the relative phases between the spin energy eigenlevels of each Rb atom, the operators $H$ and $\rho$ do not commute so both diagonal and off-diagonal elements of $\rho$ are included in the solution.

The results from the IQT equation of motion are seen in Figure 6, which shows the evolution of the density operator for the 5-level, spin-2 Rb system with internal dissipation. The initial state operator, $\rho_{\text{init}}$, is constructed from the outer product of the state vector shown in Eqs. (3) and (5). At $t = 0$, this product, $\rho_{\text{OM}}$, represents a pure state having no entropy. In order for the state of the system to evolve in time according to Eq. (8), the elements of $\rho_{\text{new}}^{\text{OM}}$ are perturbed slightly from their starting values; and it is this perturbed density operator, $\rho_{\text{init}}$, which is used as the initial state operator in Eq. (8). The upper blue traces seen in Figure 6 result from the diagonal terms of the state operator, while the traces in red and green represent evolutions due to the off-diagonal terms. The time constant $\tau$ is chosen to qualitatively match the rate of dissipation shown in the Kukolich data. The solution is used in Eq. (6) to calculate the amount of transmitted laser light.

![Figure 6](image1.png)

**Figure 6.** Evolution as predicted by IQT of the density matrix for the 5-level, spin-2 Rb system.

![Figure 7](image2.png)

**Figure 7.** A detailed view of the IQT result for the density matrix evolution of the 5-level, spin-2 Rb system.
A close-up view of the IQT solution is seen in Figure 7 where it is evident that the two different frequencies contained in the waveform play a role in the time evolution of the state operator. In other similar experiments described in Balabas et al. [39] and Happer, Jau, and Walker [40], the light frequency unlike in the Kukolich experiment is detuned far from resonance so as to reduce any disturbance by the probe beam. As a result, the double frequency component is suppressed and the signal is dominated by just the precession frequency.

Since the relaxation to stable equilibrium is due to dissipation (i.e., the destruction of exergy), which is modelled by the second term on the right hand side of the IQT equation of motion (Eq. (8)), the entropy changes and evolves according to the results presented in Figure 8. As is evident from this figure, the entropy evolves somewhat slowly initially and then quickly increases, reaching its maximum or stable equilibrium value after about 80 dimensionless time units.

![Figure 8.](image1)

**Figure 8.** The IQT result for the entropy as a function of time for a 5-level, spin-2 Rb system.

Finally, as is done in Kukolich [32] with Eq. (6), the IQT solution is used to calculate the amount of transmitted light. The relative probabilities of photon absorption for the four lowest eigenenergies are given in Kukolich [32] as derived from Messiah [41,42]. Only the four lowest spin energies are able to absorb photons since there are no transitions above the $|+2\rangle$ energy state. These absorption probabilities are multiplied by their respective lowest four diagonal elements of $\rho$ which are then summed together to represent the IQT version of the absorption function $A$ of Eq. (6). The result is

![Figure 9.](image2)

**Figure 9.** The transmission curve as predicted by IQT for the 5-level, spin-2 Rb spin system.
presented in Figure 9 and follows the same trends as the experimental data of Kukolich and Nagel and Haworth presented in Figures 4 and 5. The initial period of relaxation starts out relatively gradually, much like the result seen in Figure 5, an effect which is commonly seen in IQT simulations. The reason for this is that it takes some time for energy sharing between the occupied and unoccupied energy eigenlevels of the system to grow. For the 5-level, spin-2 Rb system, the lower four system energy eigenlevels start out with very low occupation probabilities due to theoretical pumping of the Rb atom into the fifth and highest level. The IQT simulation predicts a lag before the internal energy begins to be extensively shared with the lower four spin levels.

A close-up view of the predicted IQT transmission curve is shown in Figure 10. The double frequency component of the experiment is captured but is seen to damp out more rapidly than for the Kukolich data since the simulation leaves out the selective damping effects of the primary frequency of the signal by the optical filters and photocell that occur in the experiment. Furthermore, note the uneven stair-step feature of the wave minima in Figure 10, a feature seen in the experiment and one which contrasts with the smooth envelope that would be produced if one simply used decaying exponentials to describe the data (see Figure 11). The capture of these two key features by IQT lends weight to the physical basis for its predictions.

![Figure 10](image1.png)

**Figure 10.** A close-up view of the transmission amplitude as predicted by IQT.

![Figure 11](image2.png)

**Figure 11.** The transmission amplitude as calculated by QM and multiplied by a decaying exponential function with the extrema of the curve following the exponential envelope.

2.3 *The Turchette et al. experiment*

In the experiment of Turchette et al. [34], a thermodynamic system consisting of single trapped Be⁺ ion contained in a Paul trap is put into various quantum superposition states much like in the “particle
in a box” models that are used in physics texts. The decay of the initial state is observed and measured after the ion trap is put into contact with a range of engineered external heat sources. A schematic of the Paul trap is shown in Figure 12.

The edges of the slots serve as electrodes through which the RF (radio frequency) fields are produced to trap the ion as well as to input the noise signals used to serve as an external heat source. The strength of the fields is quadratic, so the particle behaves as a quantum harmonic oscillator within the trap. The harmonic superposition or “cat” or “motional” states that are produced in the experiments are also known as Fock states, and density matrices describing these states contain only diagonal elements [34].

The measurement of the amount of decoherence (i.e., in the view of IQT, the amount of dissipation) over the time interval is done through interferometry techniques. Nuclear spin states (up and down) are excited in the Be⁺ ion and combined by means of optical pumping and laser cooling methods with the superpositions of the motional eigenstates of interest. The spins constitute a “carrier” signal that enables the degree of decoherence of the cat states to be readily measured. The resulting quantum (thermodynamic) state after preparation can be written in terms of the state vector such that

\[ |\psi\rangle = \frac{1}{\sqrt{2}} (|\downarrow\rangle |\alpha\rangle + |\uparrow\rangle |\alpha\rangle) \] (10)

where the arrows signify spin up or spin down and \( \alpha \) is the particular cat state superposition between the ground state \( |0\rangle \) and some higher energy oscillator state \( |n\rangle \). Because the spin states are correlated with the energy eigenstates of the harmonic oscillator, any changes or degradation of the cat state will result in proportional changes between the phases of the up and down (\( |\uparrow\rangle \) and \( |\downarrow\rangle \)) eigenstates.

During the experimental procedure, a state as shown in Eq. (10) is created and immediately coupled to a heat bath. After a given delay, typically 3 \( \mu s \), a measurement is made. The phase shift between the spin components is seen as a loss of signal contrast, from which the magnitude of decoherence of the cat state can be calculated. The heat bath consists of a noise spectrum of a given mean frequency and power that is applied to the fields containing the ion in the Paul trap. The mean frequency of the noise corresponds to the temperature of the heat bath while the power (in volts²) corresponds to the strength of the heat source coupled to the system. Numerous measurements are conducted to produce ensemble average values that make up each experimental data point. The time intervals between the application of the heat source and when the measurements are taken are held constant. The variation of the power turns out to give results that are close to being the same as keeping the strength of the heat source constant and varying the measurement time intervals and is evidently easier to do experimentally.
IQT simulations are compared with the relaxation data for the ion and use a modified form of Eq. (2), which includes an additional term to account for the heat interaction that occurs between the heat source and the system. This form of the IQT equation of motion was initially introduced by Beretta [19] and subsequently modified by Smith [35]. The simulations use 100 equally spaced energy eigenlevels to represent the lowest eigenlevels of the trap. The superposition eigenstates that are studied are the 1, 2 and 3 cat states from Turchette et al. [34] where 1 is the state associated with the energy eigenlevel one level above the ground energy level, 2 two levels above and 3 three levels above. In the experiments, the power applied to the heat source is used to represent the relaxation time.

The initial state and relaxation time constants are varied to fit the IQT simulation results with the experimental probability distribution versus time data of Turchette et al. [34] as well as with the energy versus entropy plots created by Smith [35] using the experimental data of Turchette et al. [34]. The temperatures of the heat reservoirs of the experiment are estimated by noting the tightness of the probability distribution for the data as stable equilibrium is approached. Determining the initial state of the system for the IQT simulations is somewhat problematic since it is not specified in Turchette et al. [34] but is again estimated with reasonable success based on the experimental data.

Comparisons between the IQT results and the experimental data for the lowest 5 energy eigenlevels of the cat state are shown in Figures 13 to 15. The experimental data is indicated by the symbols. The solid lines in part a) of these figures are the theoretical probabilities predicted from the QT master equation used in Turchette et al. [34], while those in part b) are the probabilities predicted by IQT using an equation of motion which includes the heat interaction term as formulated by Smith [35]. The time constants used for the IQT simulation in Figure 13 are $\tau_D = 20.0$ and $\tau_Q = 27.0$ for the dissipation term and heat interaction term, respectively. In Figures 14 and 15, $\tau_D$ is still 20 but $\tau_Q$ changes to 20.0 and 25.0, respectively. The scaled reservoir temperature in each figure for a Boltzmann constant set to 1.0 is estimated to be 0.055, 0.11, and 0.15, respectively.

**Figure 13.** Comparison of the experimentally measured dissipative decay of cat state 1 from Turchette et al. [34] for the lowest 5 energy eigenlevels with a) that predicted by Turchette et al. [34] using a QT master equation and with b) that predicted by the IQT equation of motion that includes a heat interaction term as formulated by Smith [35].

![Figure 13](image-url)
Figure 14. Comparison of the experimentally measured dissipative decay of cat state $|2\rangle$ from Turchette et al. [34] for the lowest 5 energy eigenlevels with a) that predicted by Turchette et al. [34] using a QT master equation and with b) that predicted by the IQT equation of motion that includes a heat interaction term as formulated by Smith [35].

Figure 15. Comparison of the experimentally measured dissipative decay of cat state $|3\rangle$ from Turchette et al. [34] for the lowest 5 energy eigenlevels with a) that predicted by Turchette et al. [34] using a QT master equation and with b) that predicted by the IQT equation of motion that includes a heat interaction term as formulated by Smith [35].

Although both the QT and IQT simulations fit the data well, QT views the “dissipation” predicted by its master equation as a loss of coherence, resulting from the loss of correlations (information) between the system and the heat reservoir, which cyclically build-up and then are lost (i.e., dissipated) as the system relaxes to stable equilibrium. Such a loss is not physical since it is due solely to the
exogenous statistics, i.e., to a loss of information about the state of the system. In contrast, IQT views the “dissipation” as the internal destruction of exergy, i.e., available energy [31]. Thus, the “dissipation” is due to the endogenous measurement statistics of QM alone and is, therefore, physical.

2.4 IQT equation of motion with heat interaction
The IQT equation of motion used for the simulations in the previous section is based on Smith [35] and is a modified version of the equation introduced by Beretta [19]. The latter is expressed as

\[
\frac{d\rho}{dt} = -\frac{1}{\tau_D} \{\Delta G_D, \rho\} - \frac{1}{\tau_Q} \{\Delta G_Q, \rho\}
\]  

(11)

where the Schrödinger term representing the linear dynamics does not appear since for this case the state operator \(\rho\) of the trapped ion and the Hamiltonian \(H\) commute. The curly brackets in this equation represent the anti-commutator. The first term on the right hand side of Eq. (11) is the internal dissipation operator, while the second is the heat interaction operator. Both terms can be expressed in a fashion similar to what appears in Eqs. (2), (8), and (9) but have been put into an equivalent, more compact form here as developed in Beretta [19]. As already indicated in the previous section, \(\tau_D\) and \(\tau_Q\) are relaxation times that are adjusted to change the relative strengths of the two effects.

The quantities \(G_D\) and \(G_Q\) are “non-equilibrium Massieu free energy operators” for internal dissipation and a heat interaction with a reservoir, respectively, i.e.,

\[
G_D(H,S) = S - \frac{H}{\theta_H}
\]  

(12)

and

\[
G_Q(H,S) = S - \frac{H}{\theta_Q}
\]  

(13)

where \(\theta_H\) and \(\theta_Q\) are non-equilibrium temperatures. Here, \(S\) is the entropy operator written as

\[
S = -k_B \ln \rho.
\]  

(14)

Furthermore, the symbol \(\Delta\) in Eq. (11) signifies the deviation of an operator from its mean value. Thus, for any operator \(A\),

\[
\Delta A = A - \langle A \rangle I.
\]  

(15)

where \(I\) is the identity operator. For further details, the reader is referred to Beretta [19].

To address a drawback to the heat interaction term of Eq. (11), Smith [35] has developed a new term that drives the system to mutual stable equilibrium with the heat reservoir with which the system interacts along a path that not only is unique but is the path of steepest entropy ascent and steepest energy descent/ascent. The term results from a rotational transformation of the internal dissipation operator. This leads to a new non-equilibrium Massieu free energy heat interaction operator given by

\[
\tilde{G}_Q(\tilde{H}, \tilde{S}) = \tilde{S} - \frac{\tilde{H}}{\tilde{\theta}_H}
\]  

(16)

where \(\tilde{\theta}_H\) is a non-equilibrium temperature expressed as

\[
\tilde{\theta}_H = \frac{\langle \Delta \tilde{H} \Delta \tilde{S} \rangle}{\langle \Delta \tilde{H} \Delta \tilde{S} \rangle}
\]  

(17)

and the new \(\tilde{S}\) and \(\tilde{H}\) operators result from a rotation of the original \(S\) and \(H\) operators, i.e.,
The angle of rotation $\varphi$ is a function of the slope of the heat interaction trajectory and is expressed as

$$\varphi = \tan^{-1}\left(\frac{T_Q}{T^*}\right).$$

The quantity $T^*$ is a constant with units of temperature and a value of one, while $T_Q$ is yet another non-equilibrium temperature that corresponds to the slope of the line in the energy versus entropy operator plane, which connects the current state of the system and a state in mutual stable equilibrium with the heat reservoir.

By using the rotation matrix as shown in Figure 16, the path for a dissipation process is transformed from being horizontal to one at an angle of $\varphi$. Thus, instead of the $S$ operator following a steepest path with the $H$ operator held constant, the system now follows a steepest path with respect to the transformed $\tilde{S}$ operator while holding the transformed $\tilde{H}$ operator constant. Thus, the dissipation operator in the transformed coordinate space appears as a heat interaction operator in the original coordinate space.

$$\begin{bmatrix} \tilde{S} \\ \tilde{H} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & T^* \end{bmatrix} \begin{bmatrix} \cos \varphi & -\sin \varphi \\ \sin \varphi & \cos \varphi \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & 1/T^* \end{bmatrix} \begin{bmatrix} S \\ H \end{bmatrix}. \quad (18)$$

With this new heat interaction operator, the IQT equation of motion becomes

$$\frac{d\rho}{dt} = -\frac{1}{\tau_D} \{\Delta G_D, \rho\} - \frac{1}{\tau_Q} \{\Delta G_Q, \rho\}. \quad (20)$$

It is this equation, which is solved for the IQT trajectories that match the Turchette et al. [34] experimental relaxation data seen in Figures 13 to 15 above. The results for these IQT simulations are also plotted on the energy $\langle E \rangle$ versus entropy $\langle S \rangle$ diagrams shown in Figures 17 to 19. For the 5 lowest eigenlevels, the experimental data is given in dark blue, the values predicted by the QT master equation are in light blue, and the curve predicted from IQT is in magenta. Note that the fact that the experimental data as well as the QT and IQT trajectories curve back on themselves is, of course, physically impossible, i.e., violates the second law. However, this occurs here solely due to the fact that these trajectories are only based on the lowest 5 energy eigenlevels. When all 100 eigenlevels are considered, the result is the magenta curves, which show the evolution of the 100 energy eigenlevel model as predicted by IQT from the initial state designated by the cross in magenta to a state of mutual
stable equilibrium with the heat reservoir. Clearly, for all three cat state relaxations, the IQT simulations do a good job of matching the experimental data.

**Figure 17.** Non-equilibrium evolutions in thermodynamic state of cat state $|1\rangle$ on an energy versus entropy diagram when only considering the lowest 5 energy eigenlevels and in the case of the IQT simulation 100 eigenlevels as well.

**Figure 18.** Non-equilibrium evolutions in thermodynamic state of cat state $|2\rangle$ on an energy versus entropy diagram when only considering the lowest 5 energy eigenlevels and in the case of the IQT simulation 100 eigenlevels as well.

### 3. Conclusions
Simulations using the equation of motion of IQT are seen to correspond closely to data from two experiments that show non-equilibrium relaxations at atomistic scales. Thus, there appears to be support for the idea as proposed by IQT that dissipation due to internal irreversibilities occur for systems even at these small scales, i.e., that there is no “irreversibility paradox”. The findings though not conclusive nonetheless warrant the development of additional experiments specifically designed to verify the claims of IQT that the entropy is indeed a fundamental property of matter in the same way that inertial mass, energy, and momentum are.
Towards this end, a possible variation of the Turchette et al. experiment which could be used to test for the presence of internal dissipation is to employ an interaction time with the reservoir that is much shorter than the measurement time interval. The short interaction would serve as a perturbation after which the system would be allowed to evolve on its own without further influence from the reservoir. The system could then be examined to see whether the evolution is consistent with the expected magnitude of internal dissipation. Of course, care must be taken to differentiate the results from the effects of $1/f$ noise from the electrodes as well as ambient vacuum noise, which, though relatively weak, is always present. It is also suggested that the time length of the measurement interval be varied instead of varying the strength of the heat reservoir as was done in Turchette et al. By doing so, there is greater assurance that the data represent a single trajectory and not portions of different trajectories that are associated with reservoirs of varying strengths.

Finally, another experiment involving a trapped ion would be to use the same procedure as Turchette et al. but with relatively weak reservoirs to study whether the signature of a gradual initial relaxation evolution can be detected. An initial shape of the relaxation curve that tends to be concave down would support the notion of a gradual increase in energy spreading among the energy eigenlevels of the system as is seen in IQT simulations.

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Appendix
Be$^+$ beryllium ion
c constant
$D$ IQT dissipation operator or matrix
$D_{ij}$ element of IQT dissipation operator or matrix
$\langle E \rangle$ expectation energy
$E_{\mu}$ energy of an element in the density matrix
$E_0, E_1$ Rb spin states without the external magnetic field
$F$ Rb spin states after splitting by external magnetic field
$H$ Hamiltonian operator
$I$ identity matrix, operator
$I_0$ intensity of the laser beam probe
$h$ modified Planck constant
$J$ Rb angular momentum operator
$J_+$ raising operator for the angular momentum
$k_b$ Boltzmann’s constant
$M$ Rb spin operator
$Q$ energy exchange due to a heat interaction
$IQT$ Intrinsic Quantum Thermodynamics
$QSM$ Quantum Statistical Mechanics
$\text{Rb}$ rubidium
$\langle S \rangle$ expectation entropy
$t$ time
$T_R$ temperature of the heat reservoir
$Tr$ trace of a matrix or operator
$U$ unitary transformation matrix
$U^\dagger$ Hermitian conjugate of the unitary transformation matrix
$\langle V^2 \rangle$ average power of the external heat source

**Greek**

$\alpha$ generic index for a harmonic superposition state
$|\Psi_z\rangle$ state vector of the Rb spin state as seen along the z-axis
$\rho$ density matrix or state operator
$\tau$ scalar time constant or functional for the IQT equation of motion
$\tau_0$ time constant or functional for the dissipation term in the IQT equation of motion
$\tau_Q$ time constant for the strength of heat interaction term in the IQT equation of motion
$\omega_p$ precession frequency of a Rb spin state

**Miscellaneous**

$|\uparrow\rangle, |\downarrow\rangle$ spin up and spin down states for the Be$^+$ ion
$|n\rangle$ a harmonic cat state between the ground energy level and the $n^{th}$ energy level

**References**

1. Hatsopoulos, G N and Gyftopoulos, E P 1976a,b,c,d A unified quantum theory of mechanics and thermo-dynamics – Part I: Postulates, Part IIa: Available energy, Part IIb: Stable equilibrium states, Part III: Irreducible quantal dispersions *Foundations of Physics* 6 15-31, 6 127-141, 6 39-455, 6 561-570
2. Park J L 1968 *Am. J. Phys.* 36 211
3. Simmons Jr. R F and Park J L 1981 *Found. Phys.* 11 297
4. Beretta G P 1981 On the general equation of motion of Quantum Thermodynamics and the distinction between quantal and nonquantal uncertainties *Dr. Sc. thesis, MIT, Cambridge, MA.*
5. Park J L and Simmons Jr. R F 1983 The knots of thermodynamics *Old and New Questions in Physics, Cosmology, Philosophy, and Theoretical Biology* ed A van der Merwe (New York: Plenum)
6. Beretta G P, Gyftopoulos E P, Park, J L and Hatsopoulos G N 1984 A new equation of motion for a single constituent of matter *Il Nuovo Cimento B* 82 169-191

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11 In references [4], [7], [10], [20] and [22] the term "Quantum Thermodynamics" is used to refer to what in the present paper is referred to as 'Intrinsic Quantum Thermodynamics.'
[7] Beretta G P, Gyftopoulos E P, and Park J L 1985 Quantum Thermodynamics - A new equation of motion for a general quantum system Nuovo Cimento B 87 77
[8] Beretta G P 1985 Effect of irreversible atomic relaxation on resonance fluorescence, absorption and stimulated emission Int. J. Theor. Phys. 12 1233
[9] Beretta G P 1986 Frontiers of Nonequilibrium Statistical Physics: Proc of the NATO Advanced Study Institute, (Santa Fe, 1984, Series B: Physics, Vol. 135) ed G.T. Moore and M.O. Scully (New York: Plenum) p 205
[10] Beretta G P 1987 Quantum thermodynamics of nonequilibrium. Onsager reciprocity and dispersion-dissipation relations Foundations of Phys. 17 365
[11] Çubukçu E 1993 Thermodynamics as a nonstatistical theory, Sc.D. dissertation, M.I.T.
[12] Gyftopoulos E P and Cubukçu E 1997 The entropy of thermodynamics Physical Review E 55 3851-3858
[13] Gheorghiu-Svirchevski S  2001 and 2001 Nonlinear quantum evolution with maximal entropy production Phys Rev. A 63 022105 and Addendum Phys Rev. A 63 054102
[14] Gyftopoulos E P and von Spakovsky M R 2003 Quantum theoretic shapes of constituents of systems in various states Journal of Energy Resources Technology, (ASME transactions, March, vol. 125, no. 1) pp 1-8
[15] Beretta G P and Gyftopoulos E P 2004 Thermodynamic derivations of conditions for chemical equilibrium and of Onsager reciprocal relations for chemical reactors J. Chem. Phys. 121 2718
[16] Beretta G P 2005 Nonlinear extensions of Schrodinger-von Neumann quantum dynamics: A set of necessary conditions for compatibility with thermodynamics Mod. Phys. Letters A 20 977
[17] Beretta G P 2006 Nonlinear model dynamics for closed-system, constrained, maximal-entropy-generation relaxation by energy redistribution Phys. Rev. E 73 026113
[18] Beretta G P 2008 Modeling non-equilibrium dynamics of a discrete probability distribution: General rate equation for maximal entropy generation in a maximum-entropy landscape with time-dependent constraints Entropy 10 160
[19] Beretta G P 2009 Nonlinear quantum evolution equations to model irreversible adiabatic relaxation with maximal entropy production and other nonunitary processes Reports on Mathematical Physics 64 139
[20] Beretta G P 2010 Maximum entropy production rate in quantum thermodynamics J. Phys.: Conf. Ser. 237 012004
[21] von Spakovsky M R 2008 The second law: A unified approach to thermodynamics applicable to all systems and all states The Entropy Challenge: Proc. Am. Inst. Phys.
[22] Smith C E, Sciacovelli A, von Spakovsky M R and Verda V 2010 3D quantum thermodynamic description of the non-equilibrium behavior of an unbounded system at an atomistic level J. of Phys.: Conf. Series, 237 012022
[23] Blum K 1996 Density Matrix Theory and Applications (New York: Plenum)
[24] Weiss U 1999 Quantum Dissipative Systems (Singapore: World Scientific)
[25] Lindblad G 1976 On the generators of quantum dynamical semigroups Communications in Mathematical Physics 48 119
[26] Kossakowski A 1972 On necessary and sufficient conditions for a generator of a quantum dynamical semi-group Bulletin of Academy Science and Mathematics 20 1021
[27] Kossakowski A 1972 On quantum statistical mechanics of non-Hamiltonian systems Rep. on Math. Phys. 3 247
[28] Zhu W and Rabitz H 2005 Perturbative and nonpertubative master equations for open quantum systems J. of Math. Phys. 46 022105
[29] Loschmidt J 1876 Sitzungsber. Kais. Akad. Wiss. Wien, Math. Naturwiss. Classe 73 128–142
[30] Hatsopoulos G N and Keenan J H 1965 Principles of General Thermodynamics (New York: Wiley)
[31] Gyftopoulos E P and Beretta G P 2005 Thermodynamics – Foundations and Applications (New York: Dover)
[32] Kukolich S G 1968 Time dependence of quantum-state amplitudes demonstrated by free precession of spin Am. J. of Phys. 36 420
[33] Beretta G P 1985 International J. of Theoretical Physics 24 119
[34] Turchette Q A, Myatt C J, King BE, Sackett CA, Kielpinski D, Itano W M, Monroe C and Wineland D J 2000 Decoherence and decay of motional quantum states of a trapped atom coupled to engineered reservoirs Phys Rev A 62 053807
[35] Smith C E 2012 Intrinsic Quantum Thermodynamics: Application to hydrogen storage on a carbon nanotube and theoretical consideration of non-work interactions Ph.D. dissertation (advisor: M. R. von Spakovsky, Virginia Tech, Blacksburg)
[36] Feynman R P, Leighton R B and Sands M 1965 Feynman Lectures on Physics vol. 3. (Reading, MA: Addison-Wesley)
[37] Nagel M and Haworth F E 1966 Advanced laboratory experiments on optical pumping of rubidium atoms—part II: Free precession Am. J. of Phys. 34 559
[38] Franzen W 1959 Spin relaxation of optically aligned rubidium vapor Phys. Rev. 115 850
[39] Balabas M V, Karaulanov T, Ledbetter M P and Budker D 2010 Polarized alkali vapor with minute-long transverse spin-relaxation time Phys. Rev. Lett. 105 070801
[40] Happer W, Jau, Y-Y and Walker T 2010 Optically Pumped Atoms (Weinheim, Germany: Wiley-VCH)
[41] Messiah A 1962 Quantum Mechanics (North-Holland Publishing Co: Amsterdam), Vol. 2, XIII, 19.
[42] Messiah A 1999 Quantum Mechanics (Dover Publications, Inc.: New York), Vols. 1&2, XIII, 19.