INTRINSIC QUANTUM THERMODYNAMICS:
WHAT IT IS AND WHAT CAN BE DONE WITH IT

Michael R. von Spakovsky

Mechanical Engineering Department
Virginia Tech, Blacksburg, Virginia, 24061, USA

ABSTRACT

Experimental evidence over the last three decades has seen the emergence at atomistic scales of the phenomenon of "spontaneous decoherence", which in turn has led to a revival of interest in matters related to the unitary foundations of quantum mechanics (QM) and what, if anything, non-equilibrium thermodynamics may have to say about this. Decoherence at these scales suggests the presence of non-linearities not envisioned by the unitary dynamics of QM, non-linearities that, in contrast, are foreseen by the dynamics of intrincic quantum thermodynamics (IQT). IQT provides a reasonable, coherent, and comprehensive explanation for these non-linearities, unifying QM and thermodynamics into a single kinematics and dynamics applicable to all systems and all states and doing so in part by supplementing the postulates of QM by the 2nd law from which a physically meaningful nonlinear dynamics emerges. This paper provides a brief summary of a number of applications of this theory to non-reactive and reactive systems by the author and his co-workers along with comparisons of predicted results to experimental and numerical data found in the literature.

INTRODUCTION

New experimental evidence (e.g., [1-8]) over the last three decades has seen the emergence at atomistic scales of the phenomenon of "spontaneous decoherence", which in turn has led to a revival of interest in matters related to the unitary foundations of quantum mechanics (QM) and what if anything non-equilibrium thermodynamics (NET) may have to say about this. This renewed interest is fuelled to a large extent by the impact that this phenomenon has on a large number of applications. Thus, understanding and predicting modern physics phenomena such as decoherence, entanglement and coherence structure, and dynamics in applications involving nanometric devices, fast switching times, clock synchronization, super-dense coding, quantum computation, teleportation, quantum cryptography, etc. [9-27] is of great importance. Since "spontaneous decoherence" at these scales suggests the presence of non-linearities not envisioned by the unitary dynamics of QM, a number of recent publications [28-33] have proposed possible fundamental tests of standard unitary QM, emphasizing on the basis of the fairly general ansatz developed in [28-32] "that if the pure states happen to be attractors of a nonlinear evolution, then testing the unitary propagation of pure states alone cannot rule out a nonlinear propagation of mixtures" [33].

This last statement is illustrated in the context of recent work on nonlinear Lie-Poisson dynamics [29-32]. However, testing these particular dynamics experimentally is necessarily a matter of guesswork since the physicality of these theories is quite obscure. In contrast, a physically meaningful nonlinear dynamics emerges when the postulates of QM are supplemented by both the 1st and 2nd laws of thermodynamics. In such an approach, the evolution of state of a quantum system is no longer unitarily constrained but can, in fact, occur non-unitarily in time. Thus, at the expense of only violating the unitary constraint, an approach such as intrinsic quantum thermodynamics (IQT) [34-56] (not to be confused with quantum thermodynamics (QT), i.e., dissipative quantum dynamics [27,57]) provides an overall physical framework for such non-unitary evolutions. 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 [34-40]. To satisfy both the requirements of thermodynamics, particularly that of the 2nd law, as well as those of 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, i.e., a projector onto a wave function,[2] but instead a density or "state" operator based on an ensemble consisting of an infinite number of identical systems identically prepared [34]. 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 [34,37-40]. IQT completes this equation on the basis of the steepest-entropy-ascent (SEA) principle or today better known as the locally-maximal entropy generation (LMEG) dynamical law, which encompasses the Hatsopoulos-Keenan statement of the 2nd law via the Hatsopoulos-Gyftopoulos ansatz [34] as a theorem about the dynamical (Lyapunov) stability of equilibrium states [53]. This equation is able to describe the irreversible (i.e., non-linear and non-unitary) relaxation of system state to one of stable equilibrium based solely on changes occurring intrinsic to the system.

In contrast, QT, which presents an alternative framework, is based on the so-called "open-system model" in which the dynamics of relaxation to stable equilibrium result from assumed "weak-interactions", i.e., statistical perturbations (the so-called Born-Markov approximation), with an environment or heat bath. However, the "dissipative" state evolutions,

---

[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 IQT.

which this approach predicts, are still linear in nature and, thus, can at best only mimic the non-linear dynamics that may be in play. Despite this weakness, QT has engendered a great deal of work over the last few decades [27,57-71]. Even so, whatever the reality of the assumed "weak interactions", Nakatani and Ogawa [60] have shown that the Born-Markov approximation for obtaining evolution equations, i.e., quantum master equations (QMEs), cannot be used for composite systems in the strong-coupling regime, no matter how short the reservoir correlation time. Indeed, the assumption of very short correlation times is problematic even in the weak-coupling regime, since it comes at the expense of introducing the so-called Loschmidt paradox [72]. In other words, because the overall linear dynamics of the closed and isolated system-plus-environment composite is reversible and unitary, the assumption of weak coupling is equivalent to assuming that system and environment are effectively maintained decorrelated, which in turn gives rise to an irreversible and non-unitary linear dynamics of the system alone. This paradox as well as the inherent weaknesses outlined in [52] limit the applicability of these QMEs.

Other more traditional approaches to the modelling at the atomistic level of phenomena typically viewed as irreversible (e.g., heat transfer) are the so-called "closed quantum systems" (CQS) approach [73] and the two heat reservoirs mediated by a quantum system (HRQS) approach [74-95]. Results shown to date with the former [73] indicate that as long as a "persistent coherence" is maintained between the amplitudes of the different energy eigenlevels, the heat flux remains constant. This observation may indeed have important implications for other "irreversible" phenomena such as the decoherence of qubits, which is a major obstacle to the construction of quantum computers [18]. Thus, if a qubit were placed, for example, in contact with a non-equilibrium environment so that a persistent energy flux through the qubit could be induced, would it protect the qubit from complete decoherence? This question requires an answer, which needs further investigation to see if it can be answered generally in the affirmative and if so, how such a system and interaction could be set up. Note that an early candidate for the role of qubit, i.e., a trapped ion, can be described to *some* extent by the model of a particle confined to a harmonic potential well exposed to statistical perturbations due to electromagnetic noise [96–99]. It is also interesting to note that it can be described quite well by IQT [56], which is able to describe its behaviour in terms of a relaxation from a state of non-equilibrium to that of stable equilibrium.

As to the HRQS approach, results to date (e.g., [74]) show that certain quantities (i.e., a non-equilibrium temperature T_p equal to the kinetic energy of the quantum system (mediator) and another, T_x, to its potential energy) have proven useful in quantifying the strengths of the couplings between the mediator (quantum particle or system) and the heat reservoirs [91]. When the so-called friction kernel, which is a measure of the interaction between mediator and reservoirs, is non-zero, the difference between these two temperatures as well as between T_x and the average of the two reservoir temperatures is also non-zero; and, therefore, these temperatures and differences can be used as a measure of the quantum entanglement, i.e., the degree of coherence, between the mediator and reservoirs [91]. As a criterion for quantifying the coupling strength, these quantities are equally applicable to steady as well as unsteady state. Nonetheless, it is doubtful that the HRQS model even if modified could be used to determine

the rate of decoherence, which takes place as the composite system relaxes to stable equilibrium. In contrast, IQT is not limited in this way.

THE IQT APPROACH

At the heart of IQT is the concept that irreversible relaxations of state occur due to the intrinsic characteristics, i.e., endogenous (as opposed to exogenous) statistics, of the system itself. Thus, the framework of IQT suggests that "spontaneous decoherence" is a consequence of intrinsic system irreversibilities and that thermodynamics and in particular NET do indeed have a great deal to say about it. Beyond the theoretical work, which has laid the foundations for IQT, this assertion has found a number of verifications via experimental comparisons found in [41,44,56,100,101] and is reasonable in the context of a quantum system (even a one-particle system) in a non-equilibrium state spontaneously[3] relaxing to stable equilibrium.

The foundations of IQT were developed by Hatsopoulos and Gyftopoulos [34] with important preliminary work by Park [35]. In 1981, Beretta contributed a fundamental dynamical postulate embodied in a non-linear equation of motion [37] consistent with the proof by Simmons and Park [36] that the evolution in state of a closed thermodynamic system to stable equilibrium is necessarily non-linear. Important subsequent work includes [38-56,100,101,106,107]. IQT asserts that the 2nd law of thermodynamics, with its implications of intrinsic irreversibility, applies at all physical levels of description from the macroscopic and classical to the atomistic and quantum [34]. 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) where the state necessarily refers only to the state of an ensemble, which consists of an infinite number of identical systems not identically prepared [34,35]. 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 [34-40].

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 ρ via

$$\langle S \rangle = -k_B \text{Tr}(\rho \ln \rho) \qquad (1)$$

Here k_B is Boltzmann's constant. In QM, the value of $\langle S \rangle$ is necessarily zero for all pure states. For states whose entropy is greater than zero, the density operator of QM can be replaced with the von Neumann statistical operator of QSM. However, the problem which arises with using QSM to describe non-zero entropy states is that not only does this introduce the difficulty mentioned above about the loss of the concept of "state of the system" but as well leads to an entropy, which is not the entropy of thermodynamics [45]. 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 2nd law of thermodynamics, namely, i) what the physical roots of

---

[3] A physical mechanism for such relaxations may, for example, be spontaneous emissions resulting from vacuum fluctuations and/or self-radiation reactions [102-105].

"*entropy*" and "*irreversibility*" are, ii) whether or not "*entropy generation*" due to irreversibility is merely a *statistical illusion*[4], and iii) what a general description of *non-equilibrium* is [54]. 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) [54]. 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 zero-entropy and non-zero entropy states 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 [54].

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 QT, this has led to master equations of various types [27,57]. These equations have been developed to model the "open quantum systems" introduced by Lindblad and Kossakowski and others [62-65] where the increase in the entropy of a system is brought about through interactions with an external reservoir. In IQT, the generalization to irreversible or "dissipative" processes is provided by an equation of motion originally developed by Beretta [37,39,40], which assumes a priori a tendency for an intrinsic increase in system entropy, i.e., the entropy of thermodynamics, along the direction of steepest entropy ascent compatible with the system's constraints. Unlike the master equations of QT, which are often second order approximations [108], 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 [72], which arise when trying to force the emergence of 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 of a system by requiring that a system possessing entropy be described with heterogeneous ensembles of identical systems in "pure" states. Statistical mixtures 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 2nd law [54].

IQT also avoids the violations of the 2nd law that are inherent with the QT approach. In contrast to QSM, QT is not based on statistical mixtures of pure states and, thus, the definition of "state of the system" is preserved. However, because the entropy for the "overall closed system" (i.e., open 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 open 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 2nd 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 IQT EQUATION OF MOTION

The equation of motion of IQT governs how the diagonal and off-diagonal elements of the thermodynamic state or density operator (or matrix) ρ [5] 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 [4,46,53,109]. For an isolated or non-isolated, single elementary constituent (i.e., a single particle, a single assembly of indistinguishable particles, or a single field) closed (i.e., not experiencing a non-work interaction) system, this equation is given by

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H,\rho] + \frac{1}{2k_B\tau}\{\Delta M,\rho\} \qquad (2)$$

where H is the Hamiltonian operator and τ a scalar time constant or functional [6]. Both the 1st and 2nd laws of thermodynamics are implied by this equation and its other forms given below[7]. The first term on the right of this equation 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 temporal part of the Schrödinger equation. This term governs the relative phases between system energy eigenlevels and quantum interference effects. The second term on the right, $\{\Delta M,\rho\}/2k_B\tau$, the so-called dissipation term, depends on ρ, $\ln\rho$, and H and 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 constant system energy $\langle E \rangle$. This term governs the dissipation of a system's adiabatic availability [111] as its state relaxes to one of maximal entropy and is written as

$$\{\Delta M,\rho\} = \Delta M\rho + \rho\Delta M \qquad (3)$$

where $\quad M = S - H/\theta_H(\rho) \qquad (4)$

$$\theta_H(\rho) = \langle \Delta H \Delta H \rangle / \langle \Delta S \Delta H \rangle \qquad (5)$$

Here M is a non-equilibrium Massieu function and ΔH and ΔS are the deviation operators of H and S defined as

$$\Delta H = H - I\langle H \rangle \qquad (6)$$

$$\Delta S = S - I\langle S \rangle \qquad (7)$$

The S operator is expressed as

$$S = -k_B\ln(\rho + P_o) = -k_B B\ln\rho \qquad (8)$$

with P_o and B, respectively, the projection operators onto the range and the kernel of ρ.

For a closed composite system composed of two distinguishable particles, assemblies of particles, fields, or a

---

[4] 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.

[5] The state operator is a linear, self-adjoint, non-negative definite, unit-trace operator (i.e., an operator whose diagonal elements sum to one) on Hilbert space $\mathcal{H}$.

[6] Note, that a lower bound for τ and, thus, an upper bound on $\{\Delta M,\rho\}/2k_B$ may be suggested by the time-energy Heisenberg uncertainty relation [53].

[7] This equation implies the *1st law* because as is proven in Beretta et al. [39], each of the generators (e.g., the identity and Hamiltonian operators) of the motion (i.e., the evolution or change in state of the system) is also a constant of the motion of the system. Thus, $\langle E \rangle = Tr(\rho H)$ is conserved and the ΔE in any adiabatic process is uniquely related to the amount of work involved in the process. This equation also implies the *2nd law* since as proven in Beretta et al. [39], a system admits of one and only one stable equilibrium state for given finite mean values of the generators of the motion. This, of course, is simply a generalization of the Hatsopoulos-Keenan statement of the second law [34,110].

combination of these, Eq. (2) is replaced by the following equation [40,52,53]:

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H,\rho] + \frac{1}{2k_B\tau_A}\left\{(\Delta M)^A, \rho_A\right\} \otimes \rho_B$$

$$+ \frac{1}{2k_B\tau_B}\rho_A \otimes \left\{(\Delta M)^B, \rho_B\right\} \qquad (9)$$

where $\quad (\Delta M)^J = (\Delta S)^J - (\Delta H)^J / \theta_H(\rho)$ (10)

$$(\Delta H)^J \equiv Tr_{\bar{J}}\left[(I_J \otimes \rho_{\bar{J}})\Delta H\right] \qquad (11)$$

$$(\Delta S)^J \equiv Tr_{\bar{J}}\left[(I_J \otimes \rho_{\bar{J}})\Delta S\right] \qquad (12)$$

and $J = A,B$, while $\bar{J} = B,A$. Equation (9) is easily generalized to three or more distinguishable constituents.

Finally, for a system experiencing a non-work interaction (i.e., a heat or mass interaction), the IQT equation of motion in the form of Eq. (2) may be extended to the following [56,112]:

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H,\rho] + \frac{1}{2k_B\tau}\{\Delta M,\rho\} + \frac{1}{2k_B\tau_G}\{\Delta\tilde{G},\rho\} \qquad (13)$$

where the last term on the right accounts for either a heat or mass interaction. If the latter, $\tilde{G}$ is a non-equilibrium, Massieu-like, mass-interaction operator as described in detail in [112]. If the former, $\tilde{G}$ is a non-equilibrium Massieu heat interaction operator expressed as

$$\tilde{G} = \tilde{G}_Q(\tilde{H},\tilde{S}) = \tilde{S} - \frac{\tilde{H}}{\bar{\theta}_H} \qquad (14)$$

where $\tilde{\theta}_H$ is a non-equilibrium temperature defined as

$$\tilde{\theta}_H = \frac{\langle\Delta\tilde{H}\Delta\tilde{H}\rangle}{\langle\Delta\tilde{H}\Delta\tilde{S}\rangle} \qquad (15)$$

and the $\tilde{S}$ and $\tilde{H}$ operators result from a rotation of the original S and H operators, i.e.,

$$\begin{bmatrix}\tilde{S} \\ \tilde{H}\end{bmatrix} = \begin{bmatrix}1 & 0 \\ 0 & T^*\end{bmatrix}\begin{bmatrix}\cos\varphi & -\sin\varphi \\ \sin\varphi & \cos\varphi\end{bmatrix}\begin{bmatrix}1 & 0 \\ 0 & 1/T^*\end{bmatrix}\begin{bmatrix}S \\ H\end{bmatrix}. \qquad (16)$$

The angle of rotation φ is a function of the slope of the heat interaction trajectory and is expressed as

$$\varphi = \tan^{-1}(T_Q/T^*). \qquad (17)$$

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.

We now turn to a brief discussion of the application of each one of these equations of motion and a comparison of the results generated with experimental data found in the literature. The results presented and discussed are taken from [56,100,101]. Equation (2) is used to predict the reaction rate constant of the chemically reactive systems in [101] based on the IQT framework laid out by Beretta and von Spakovsky in [107], while Eq. (9) is employed to predict the rate of decoherence of a composite atom-field system [100]. Finally, Eq. (13) is utilized to predict the relaxation to stable equilibrium of a single ion in a cat state contained in a Paul trap as it interacts with a heat reservoir [56].

CHEMICALLY REACTIVE SYSTEM RESULTS

Since the IQT equation of motion implements the principle of SEA, its application to chemical kinetics is consistent with the idea put forward by Ziegler [113] concerning the thermodynamic consistency of the standard model of chemical kinetics. In [107], Beretta and von Spakovsky develop a general modeling framework for applying IQT to chemically reactive systems at very small scales, i.e., to an isolated, chemically reactive mixture with one or more active reaction mechanisms. In modeling the non-equilibrium time evolution of state of these systems, both the system energy and particle number eigenvalue problems as well as the non-linear IQT equation of motion must be solved, i.e., in this case Eq. (2). The former establish the so-called energy and particle number eigenstructure of the system, i.e., the landscape of quantum eigenstates available for the system, while the latter determines the unique non-equilibrium thermodynamic path, i.e., unique cloud of trajectories, taken by the system, showing how the density operator, which represents the thermodynamic state of the system at every instant of time, evolves from a given initial non-equilibrium state to the corresponding stable chemical equilibrium state. Once this path is established, the time dependences of all the non-equilibrium thermodynamic properties (e.g., composition, chemical potentials, chemical affinities, reaction coordinates, reaction rates), including, of course, the entropy, are known. In fact, the reaction rate in the literature is typically reported at a given temperature in terms of the so-called reaction rate constant (i.e., the forward reaction rate constant), which is determined both experimentally as well as numerically via a phletora of classical (e.g., [114]), quasi-classical (e.g., [115-121]), and time-independent (e.g., [122,123]) and time-dependent quantum methods (e.g., [123,124]). The IQT results presented here and the more extensive ones in [101] are reported in terms of this parameter. It should be noted that no a priori limiting assumption of stable equilibrium via a specific choice of temperature nor of pseudo-equilibrium between reactant and activated complex, both of which are common to the other methods in the literature, is made. In addition, the reaction rate constants found via the IQT formulation are in reality not constants but instead instantaneous values found at each instant of time along the non-equilibrium path determined by the IQT equation of motion.

The IQT kinematic model for the chemically reactive system, which establishes the energy and particle number eigenstructure of the system, is not repeated here due to its complexity and, thus, the reader is referred to [101,107] for details. This model includes vibrational, rotational, and translational degrees of freedom consistent with the number and types of degrees of freedom used by other models found in the literature. The dynamic model is that of Eq. (2).

For purposes of the comparisons given below, the system considered here initially consists of 1 particle of F and 1 of H_2 and is governed by the following reaction mechanism:

$$F + H_2 \Leftrightarrow FH + H \qquad (18)$$

An initial non-equilibrium state is established by finding a metastable equilibrium state far from equilibrium, which is then perturbed into the initial non-equilibrium state used by the equation of motion, Eq. (2). This equation evolves the system density or state operator ρ for the reacting mixture in time at constant system energy until a state of stable equilibrium is reached. The temperature at this final state is found to be 298 K. The degrees of freedom for each of the molecules and atoms in the IQT model are given in Table 1. Results for the non-equilibrium compositional changes of the reacting mixture are shown in Figure 1, while Figure 2 provides the instantaneous values of the forward and backward reaction rate

constants $k_f(T,t)$ and $k_b(T,t)$, respectively, at every instant of time t. Included as well is the equilibrium constant $K(T)$, which is the ratio between k_f and k_b. The time evolutions of the net, forward and backward reaction rates (i.e., r, r_f, and r_b) corresponding to these rate constants are shown in Figure 3. Similar time-evolutions for other non-equilibrium thermody-

Table 1. Degrees of freedom for each of the molecules and atoms in the IQT model [101].

Species	Translational quantum #'s[a]	Vibrational quantum #'s	Rotational quantum #'s
F	1,...,400		
H_2	1,...,400	0	0,1
FH	1,...,400	0,1,2,3	0,1,...,7
H	1,...,400		

[a] Although the translational principal quantum number k varies here from 1 to 400 for each species, only a sampling (30) of these quantum numbers across this range is used for each species in the IQT model.
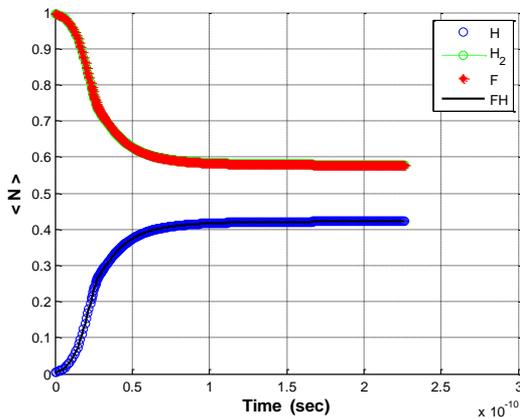

Figure 1. IQT time evolution of the non-equilibrium compositions of the reacting mixture reported as the number of particles for each species for a system expectation energy, which at stable equilibrium corresponds to a temperature of 298 K [101].
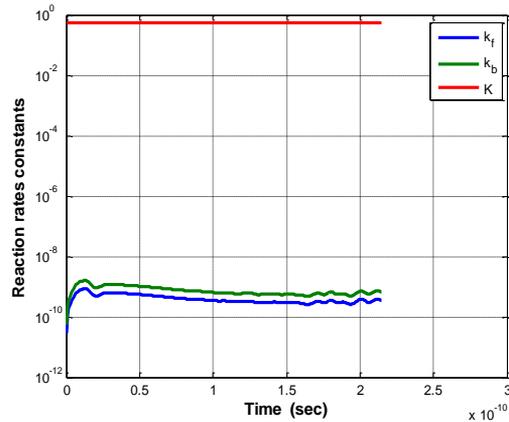

Figure 2. IQT time evolution of the forward and backward reaction rate constants and the equilibrium constant for a system expectation energy, which at stable equilibrium corresponds to a temperature of 298 K [101].

namic properties such as the reaction coordinate, reaction coordinate rate, entropy, entropy generation, species energies, non-equilibrium temperature, etc. can be generated. The relaxation time τ for the time evolutions presented in the previous figures is 3.8×10^{-15} sec and is based on a fit of the IQT results to the value of k_f at 298 K reported in the fourth column of Table 2 [101, 124]. This table also includes the values of k_f from a number of other researchers. Note that the computational time to complete a single evolution, which

provides a complete picture of the non-equilibrium quantum and thermodynamic evolution in time of the system is on the order of seconds for this size system on a conventional PC with a dual-core processor. Much larger systems have already been simulated.
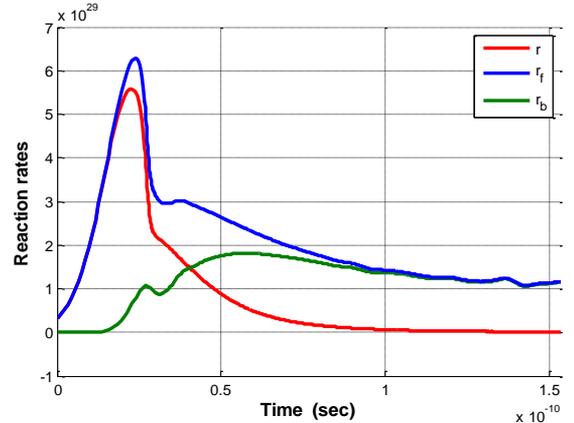
Figure 3. The forward, reverse and net reaction rates for a system expectation energy, which at stable equilibrium corresponds to a temperature of 298 K [101].

Table 2. Values of the forward reaction rate constant reported in the literature for the reaction mechanism of Eq. (18) [101,124].

k_f(T)/10^{-11} (cm^3/molecule-sec)					
T (K)	WH[a]	SBA[b]	HBGM[c]	RHPB[d]	WTM[e]
298	2.33	2.48	2.93	2.81	2.26

[a] Wurzberg and Houston; [b] Stevens, Brune, and Anderson; [c] Heidner, Bott, Gardner, and Melzer; [d] Rosenman, Hochman-Kowal, Persky, and Baer; [e] Wang, Thompson and Miller.

Finally, additional validation of the IQT predictions is needed via a comparison of the forward reaction rate constants predicted with IQT to those given in Table 2 based on a τ, which is a functional of the density operator ρ and which reflects the physics of the problem. This validation has not yet been done. The present author and his co-authors in [101] are currently working on identifying a unique functional $\tau(\rho)$ capable of capturing the dynamics of the reaction without the use of adjustable parameters.

COMPOSITE ATOM-FIELD SYSTEM RESULTS

In [100], the modeling of the non-linear dynamic change in state of a composite system formed by an atom and an electromagnetic field mode is accomplished using IQT (Eq. (9)). The state of the composite (closed and adiabatic) microscopic system evolves in time towards stable equilibrium, resulting in the loss of correlations between its constituents. The IQT description assumes the composite system to be isolated and the time evolution of its state to be intrinsically both Hamiltonian and non-Hamiltonian. In so doing, a loss of quantum entanglement or coherence is fully predicted.

The IQT model of the composite system considered here is that given in [100] and for sake of brevity is not repeated here. A description of the Cavity Quantum Electrodynamic (CQED) experimental system upon which the IQT theoretical model is based is given in [125-131,100]. A very brief description is provided here beginning with the experimental configuration depicted in Figure 4. Rb atoms are contained in oven B from which one atom in an excited state $|\psi_B\rangle = |e\rangle$ is selected and subsequently subjected to a classical resonant microwave

$\pi/2$ pulse in R_1 supplied by source S'. This creates a state in a superposition of circular Rydberg levels $|e\rangle$ and $|g\rangle$ (ground level) for the atom, corresponding to principal quantum numbers 51 and 50, respectively. The atom is then allowed to enter the high-Q quantum cavity C that contains an electromagnetic field mode in a Fock state $|\alpha\rangle$ previously injected into the cavity by an external source S. The atom-field interaction lasts for a time t_i and since the atom and cavity are off-resonant, absorption of photons is not exhibited during the interaction; and the atom only shifts the phase of the field mode by an amount ϕ. This dephasing provokes the coupling of the excited level of the atom to the field mode state with phase $|\alpha e^{i\phi}\rangle$ and the coupling of the ground state of the atom to the field mode state with phase $|\alpha e^{-i\phi}\rangle$. In this maner, an entanglement between the states of the constituents is created. After leaving the cavity, the atom is

Figure 4. Schematic representation of an atom-field Cavity QED experiment [126,100].

subjected again to a resonant microwave pulse in R_2 equal to that at R_1, mixing the atom energy levels and creating a "*blurred*" state for the composite, $|\psi_{R_2}\rangle$, which preserves the quantum ambiguity of the field phase. The excited level state of the Rb atom is then observed and recorder at D.

To measure the decay of coherence left on the field mode state by the Rb atom, a second atom of identical characteristics to the first is sent along the same path after a delay time of t_d. The state of the second atom recorded at D reveals the effects left by the first atom on the state of the field mode. A theoretical description of the experimental observations in [127] provides a functional for the correlation signal which is plotted in Figure 5 relative to the measured data found in [128]. The red triangles with error bars correspond to the experimental values, while the blue line corresponds to the theoretical prediction made using the correlation functional of [127]. The initial point of the correlation has been moved con sistent with [128] from a value of 0.5 to 0.18 on the vertical axis to account for experimental imperfections. As can be seen the fit is good for the initial points but deviates at the end and even becomes negative, which is inconsistent with what is observed.

The IQT prediction is given by the green line, which is the norm $\|C\|$ of the commutator operator ($C = i[H, \rho]$). It is used as a direct indicator of how the coherence of the electromagnetic field mode is dissipated in time since the detection of the atom in the excited level state projects the state of the field in a maximally coherent local state. The green line corresponds to a value for the internal relaxation times of $\tau_A = \tau_B = 0.26$ for the atom and field in Eq. (9). This value is comparable to that reported in [132]. As in the case of the correlation functional, the maximum value for $\|C\|$ is moved to

0.18 on the vertical axis. As seen in this figure, IQT predicts the experimental data well. A very slight deviation from the

Figure 5. Comparison of the loss of coherence predicted by IQT and by the correlation function of [127] with the CQED experimental results of the group at Paris [128].

experimental values is observed with the fourth and fifth points but is well within the experimental error bars. The deviation may correspond to normal imperfections in the experimental equipment (e.g., the quality of mirror reflections which allows a leak of photons from the cavity [130, 133]); or it may be that the value chosen for τ_A and τ_B do not completely take into acount the physical characteristics of the contituents. For example, it may be that slightly differing values for each realaxation time are needed or that these times are instead functionals of the state operator as described in [37, 134].

SINGLE TRAPPED ION SYSTEM RESULTS

In [56], the modeling of the non-linear dynamic change in state of a single ion system in an excited cat state interacting with a heat reservoir is accomplished using IQT and Eq. (13). In this case, the system is not isolated and experiences a heat interaction. The time evolution of its state is intrinsically governed by the dissipation term and extrinsically by the heat interaction term in Eq. (13).

The IQT model for this system is that given in [56] and for sake of brevity is not repeated here. A description of the experimental system upon which the theoretical model is based is given in [96,97,56] and involves a single trapped ion contained in a Paul trap put into various quantum superposition states. A very brief description is provided here beginning with the experimental configuration depicted in Figure 6. The decay of the initial state is observed and measured after the ion trap is

Figure 6. Schematic of the Paul trap used in the experiment of Turchette et al. [97].

put into contact with a range of engineered external electromagnetic sources. Radio frequency fields are produced to trap an ion, while noise signals serve as an external electromagnetic 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 [96]. The amount of decoherence over time is measured using interferometry techniques. Nuclear spin states in the ion are excited 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. Because the spin states are correlated with the energy eigenstates of the harmonic oscillator, any changes or degradation of the cat state result in proportional changes between the phases of the spin eigenstates. During the experimental procedure, a state is created and immediately coupled to the electromagnetic source. After a given delay, 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 is calculated. The electromagnetic source 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. Numerous measurements are conducted to produce ensemble average values that make up each experimental data point.

Both Turchette et al. [96] using QT and Smith and von Spakovsky using IQT [56] have successfully modelled the decay (i.e. decoherence) observed in this first experiment. Levin et al. have studied this problem minus the external source using CQS [73]. The IQT simulations use 100 equally spaced energy eigenlevels to represent the lowest eigenlevels of the trap. Results are presented here for one of the superposition eigenstates experimentally studied in [97], i.e., cat state $|3\rangle$ which is the state associated with the energy eigenlevel three levels above the ground energy level. In the experiments, the power applied to the heat source $\langle V^2 \rangle$ is used to represent the relaxation time.

Results for the IQT simulations are compared with the experimental probability distribution versus time data in Figure 7 as well as with experimental data plotted on the energy-entropy diagram in Figure 8 [56]. 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. In Figure 7, comparisons between the IQT results and the experimental data for the lowest 5 energy eigenlevels of the cat state are shown. The experimental data is indicated by the symbols. The solid lines are the probabilities predicted by IQT using Eq. (13). The time constants used for the IQT simulation are $\tau = 20.0$ and $\tau_G = 25.0$ for the dissipation term and heat interaction term, respectively. The scaled reservoir temperature in each figure for a Boltzmann constant set to 1.0 is estimated to be 0.15. As can be seen, the IQT simulation matches the data quite well.

Comparisons with the experimental data shown in Figure 8 include predictions from the QT quantum master equation used in [97] and from the IQT equation of motion, Eq. (13). Comparisons are made for the 5 lowest eigenlevels with the experimental data given in dark blue, those for QT in light blue
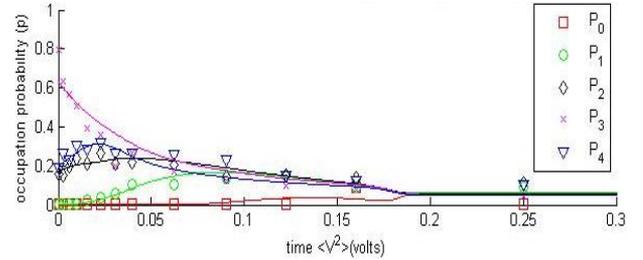

Figure 7. Comparison of the experimentally measured dissipative decay of cat state $|3\rangle$ with IQT predictions [56].
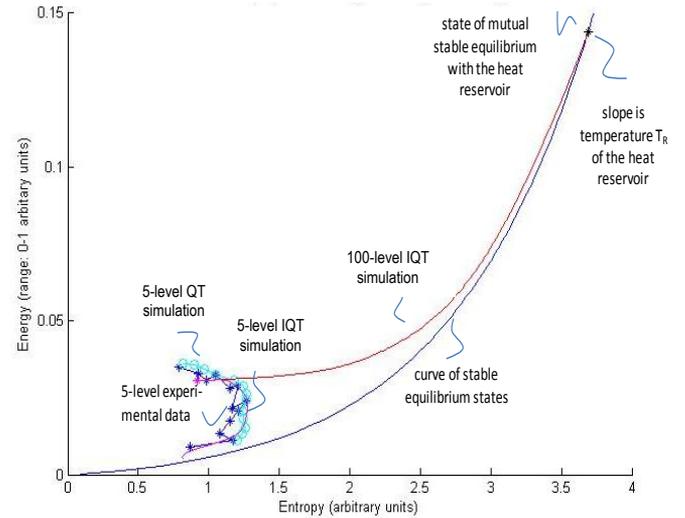

Figure 8. Non-equilibrium evolutions in thermodynamic state for the lowest 5 energy eigenlevels as well as for the lowest 100 [56].

and those for IQT 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 2nd law. However, this occurs here solely due to the fact that these trajectories are only based on the lowest 5 energy eigenlevels. When 100 eigenlevels are considered, the result for the IQT equation of motion is the magenta curve, which shows the evolution in state 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, the IQT simulations do a good job of matching the experimental data, providing an alternative, comprehensive, and reasonable explanation to that provided by QT.

CONCLUSIONS

This paper has provided a brief summary of what IQT is and what can be done with it. The power of this rather unique approach has been illustrated via a number of applications of the IQT framework to non-reactive and reactive systems. Validations of this theory via comparisons of predicted results to experimental and numerical data found in the literature demonstrate the power of this approach and support the claim that IQT provides an alternative, comprehensive, and reasonable explanation of irreversible phenomena at an atomistic level.

REFERENCES

[1]   Bollinger, J. J., et al., 1989, *Phys. Rev. Lett.* **63**, 1031.
[2]   Walsworth, R. L., Silvera, F.,Mattison, E. M., Vessot, R. F. C., 1990, *Phys. Rev. Lett.* **64**, 2599.
[3]   Chupp T. E., Hoare, R. J., 1990, *Phys. Rev. Lett.* **64**, 2261.

[4] P .K. Majumder, P. K., et al., 1990, *Phys. Rev. Lett.* **65**, 2931.

[5] Benatti, F., Floreanini, R., 1996, *Phys. Lett. B* **389**, 100 and 1999, *Phys. Lett. B* **451**, 422.

[6] Lisi, E., Marrone, A., Montanino, D., 2000, *Phys. Rev. Lett.* **85**, 1166.

[7] Klapdor-Kleingrothaus, H. V., Päs, H., Sarkar, U., 2000, *Eur. Phys. J. A* **8**, 577.

[8] D. Hooper, D., Morgan, D., E. Winstanley, E., 2005, *Phys. Lett. B* **609**, 206.

[9] Weinberg, S., 1989, *Phys. Rev. Lett.* **62**, 485.

[10] Stern, A., Aharonov, Y., Imry, Y., 1990, *Phys. Rev. A* **41**, 3436.

[11] Ekert, A. K., 1991, *Phys. Rev. Lett.* **67**, 661.

[12] Holyst, J, A., Turski, L. A., 1992, *Phys. Rev. A* **45**, 6180.

[13] Vidal, G., Werner, R. F., 1993, *Phys. Rev. A* **65**, 032314.

[14] Unruh, W. G., Wald, R. M., 1995, *Phys. Rev. D* **52**, 2176.

[15] Bennett, C. H., Brassard, G., Popescu, S. Schumacher, B., Smolin, J. A., Wootters, W. K., 1996, *Phys. Rev. Lett.* **76**, 722.

[16] Grigorescu, M., 1998, *Physica A* **256**, 149.

[17] Miranowicz, A., Matsueda, H., Wahiddin, M. R. B., 2000, *J. Phys. A: Math. Gen.* **33**, 5159.

[18] Nielsen, M. A., Chung. I. L., 2002, *Quantum Computation and Quantum Information*. Cambridge Univ. Pres., Cambridge.

[19] Bergmann, G., 1984, *Phys. Rep.* **107**, 1.

[20] Pierre, F., Gougam, A. B., Anthore, A., Pothier, H., Estève, D., Birge, N., 2003, *Phys. Rev. B.* **68**, 085413.

[21] Washburn, S., Webb, R., 1986, *Adv. Phys.* **35**, 375.

[22] Pierre, F., Birge, N., 2002, *Phys. Rev. Lett.* **89**, 206804.

[23] Sigwarth, O., Labeyrie, G., Jonckheere T., Delande, D., Kaiser, R., Miniatura, C., 2004, *Phys. Rev. Lett.* **93**, 143906.

[24] Buchleitner, A., Viviescas, C., Tiersch, M. (eds.), 2009, *Entanglement and Decoherence: Foundations and Modern Trends*, Lect. Notes in Phys. 768, Springer.

[25] Kleinekathöfer, U., 2009, *Time-local quantum master equations and their applications to dissipative dynamics and molecular wires, energy transfer dynamics in biomaterial systems*, Springer Series in Chemical Physics **93**, 339, DOI 10.1007/978-3-642-02306-4_10.

[26] Rand, S. C., 2010, *Lectures on Light: Nonlinear and Quantum Optics using the Density Matrix*. Oxford Univ. Press, Oxford, UK

[27] Weiss, U., 2008, *Quantum Dissipative Systems*. World Scientific, series in Modern Condensed Matter Physics – vol. 13, Singapore-London

[28] Domokos, G., Kovesi-Domokos, S., 1999, *J. Phys. A: Math. Gen.* **32**, 4105.

[29] Czachor, M., 1998, *Phys. Rev. A* **57**, 4122

[30] Czachor, M., Kuna, M., 1998, *Phys. Rev. A* **58**, 128

[31] Czachor, M., Naudts, J., 1999,, *Phys. Rev. E* **59**, R2497

[32] Jordan, T. F., 1993, *Ann. Phys. (N.Y.)*, **225**, 83 .

[33] S. Gheorghiu-Svirschevski, S., 2001, *Phys. Rev. A* **63**, 022105 and the Addendum, *Phys. Rev. A* **63**, 054102.

[34] Hatsopoulos, G. N., Gyftopoulos, E. P., 1976, *Found. Phys.* **6**, 15-31, 127-141, 439-455, 561-570.

[35] Park, J. L., 1968, *Am. J. Phys.* **36**, 211.

[36] Simmons Jr., R. F., Park, J. L., 1981, *Found. Phys.* **11**, 297.

[37] Beretta. G. P., 1981, *On the general equation of motion of Quantum Thermodynamics and the distinction between quantal and nonquantal uncertainties*, Sc.D.

dissertation, (advisor: E. P. Gyftopoulos, MIT, Cambridge, MA). arXiv:quant-ph/0509116

[38] Park, J. L., 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).

[39] Beretta, G. P., Gyftopoulos, E. P., Park, J. L., Hatsopoulos, G. N., 1984, *Il Nuovo Cimento B*, **82**, 169.

[40] Beretta, G. P., Gyftopoulos, E. P., Park, J. L., 1985, *Nuovo Cimento B*, **87**, 77.

[41] Beretta, G. P., 1985, *Int. J. Theor. Phys.* **24**(12), 1233.

[42] Beretta, G. P., 1986, *Frontiers of Nonequilibrium Statistical Physics: Proc. of the NATO Advanced Study Institute (Santa Fe, 1984) Series B: Physics* **135**, ed. G. T. Moore, M.O. Scully (N.Y.: Plenum) p.193 and p.205.

[43] Beretta, G. P., 1987, *Found. Phys.* **17**, 365.

[44] Çubukçu, E., 1993, *Thermodynamics as a nonstatistical theory*, Sc.D. dissertation, M.I.T.

[45] Gyftopoulos, E. P., Cubukçu, E., 1997, *Phys. Rev. E* **55**, 3851-3858.

[46] Beretta, G. P., 1986, *Lecture Notes in Physics*, **278**, 441.

[47] Gyftopoulos, E. P., von Spakovsky, M. R., 2003, *J. of En. Res. Tech.* ASME transactions, **125**, 1, 1-8.

[48] Beretta, G. P., Gyftopoulos, E. P., 2004, *J. Chem. Phys.* **121**, 2718.

[49] Beretta, G. P., 2005, *Mod. Phys. Letters A.* **20**, 977.

[50] Beretta, G. P., 2006, *Phys. Rev. E.* **73**, 026113.

[51] Beretta, G. P., 2008, *Entropy.* **10**, 160.

[52] Beretta, G. P., 2009, *Reports on Math. Phys.* **64**, 139.

[53] Beretta, G. P., 2010, *J. Phys.: Conf. Ser.* **237**, 012004.

[54] von Spakovsky, M. R., 2008, *Am. Inst. Phys. CP Series* **1033**, 1, 302.

[55] Smith, C. E., Sciacovelli, A., von Spakovsky, M. R., Verda, V., 2010, *J. of Phys.: Conf. Series.* **237**, 012022.

[56] Smith, C. E., von Spakovsky, M. R., 2012, *J. of Phys.: Conf. Series*, **380,** 012015.

[57] Blum,, K., 1996, *Density Matrix Theory and Applications*, 2nd ed., Physics of Atoms and Molecules Series, Plenum Press, NY.

[58] Coffey, W. T., Kalmykov, Y. P., Titov, S. V., Mulligan, B. P., 2007, *A Lett. J. Explor. Front. Phys.*, EPL, **77**, 20011.

[59] Yu, T., Diosi, L., Gisin, N., Strunz, W. T., 2000, *Phys. Lett. A.* **265**, 331–336.

[60] Nakatani, M., Ogawa, T., 2010, *J. Phys. Soc. Jpn.* **79**, 084401.

[61] Pomyalov, A., Tannor, D. J., 2005, *J. of Chem. Phys.* **123**, 20, 204111.

[62] Kossakowski, A., 1972, *Bull. Acad. Sci. and Math.* **20**, 1021.

[63] Kossakowski, A., 1972, *Rep. on Math. Phys.* **3**, 247.

[64] Ingarden, R. S., Kossakowski, A., 1975, *Annals of Phys.* **89**, 451.

[65] Lindblad, G., 1976, *Comm. in Math. Phys.* **48**, 2, 119.

[66] Giddings, S. B., Strominger, A., 1988, *Nucl. Phys. B.* **307**, 854.

[67] Ellis, J., Mavromatos, N. E., Nanopoulos, D., 1992, *Phys. Lett. B.* **293**, 142.

[68] Huet, P., Peskin, M. E., 1995, *Nucl. Phys. B.* **434**, 3.

[69] Ellis, J., Lopez, J. L., Mavromatos, N. E., Nanopoulos, D., 1996, *Phys. Rev. D.* **53**, 3846.

[70] Chang, C.-H., Dong, H.-S., Feng, X.-C., Li, X.-Q., Ma, F.-C., Tao, Z.-J., 1997, arxiv.org:hep-ph/9711310.

[71] Benatti, F., Floreanini, R., 2000, *J. High Energy Phys.* **2**,

32.

[72] Loschmidt, J., 1876, Sitzungsber. Kais. Akad. Wiss. Wien, *Math. Naturwiss*. Classe **73**, 128–142.

[73] Levin, G. A., Jones, W. A., Walzcak, K., Yerkes, K. L., 2012, *Phys. Rev. E*. **85**, 031109

[74] Panysyuk G. Y., Levin, G. A., Yerkes, K. L., 2012, *Phys. Rev. E*., **86**, 021116.

[75] Landauer, R., 1970, *Philos. Mag*. **21**, 83.

[76] Anderson, P. W., Thouless, D. J., Abrahams, E., Fisher, D. S., 1980, *Phys. Rev. B*. **22**, 3519.

[77] Imry, Y., Landauer, R., 1999, *Rev. Mod. Phys*. **71**, S306.

[78] Lepri, S., Livi, R., Politi, A., 2003, *Phys. Rep*. **377**, 1.

[79] Dhar, A., 2008, *Advances in Phys*. **57**, 457.

[80] Dubi, Y., Di Ventra, M., 2011, *Rev. of Modern Phys*. **83**, 131.

[81] Jortner, J., Ratner, M. (eds.), 1997, *Molecular Electronics*, Blackwell Science, Oxford.

[82] Hanggi, P., Ratner, M., Yalikari, S., 2002, *Chem. Phys*. **281**, 111.

[83] Boneto, F., Lebowitz, J. L., Rey-Bellet, L., 2000, *Fourier law: A challenge to theorists*, in Mathematical Physics 2000, Imperial College Press, London.

[84] Senitzky, I. R., 1960, *Phys. Rev. 119*, 670.

[85] Mori, H., 1965, *Prog. Theor. Phys*. **33**, 423.

[86] Ford, G.W., Cac, M., Mazur, P., 1965, *J. Math. Phys*. **6**, 504.

[87] Haken, H., 1975, *Rev. Mod. Phys*. **47**, 67.

[88] Klimontovich, Y. L., 1997, *Statistical Theory of Open Systems*, Kluwer, Amsterdam.

[89] Caldeira, A. O., Leggett, A. J., 1983, *Physica A* **121**, 587.

[90] Allahverdyan, A. E., Nieuwenhuizen, Th. M., 2000, *Phys. Rev. Lett*. **85**, 1799.

[91] Nieuwenhuizen, Th. M., Allahverdyan, A. E., 2002, *Phys. Rev. E*. **66**, 036102.

[92] Zürcher, U., Talkner, P., 1990, *Phys. Rev. A* **42**, 3278.

[93] Saito, K., Takesue, S., Miyashita, S., 2000, *Phys. Rev. E* **61**, 2397.

[94] Dhar, A., Shastry, B. S., 2003, *Phys. Rev. B* **67**, 195405.

[95] Segal, D., Nitzan, A., Hanggi, P., 2003, *J. Chem. Phys*. **119**, 6840

[96] Turchette, Q. A., Kielpinski, D., King, B. E., Leibfreid, D., Meekhof, D. M., Myatt, Rowe, M. A., C. J., Sackett, C. A., Wood, C. S., Itano, W. M., Monroe, C., Wineland, D. J., 2000, *Phys. Rev. A* **61**, 063418.

[97] Turchette, Q. A., Myatt, C. J., King, B. E., Sackett, C. A., Kielpinski, D., Itano, W. M., Monroe, C., Wineland, D. J., 2000, *Phys. Rev. A* **62**, 053807.

[98] Myatt, C. J., King, B. E., Turchette, Q. A., Sackett, C. A., Kielpinski, D., Itano, W. M., Monroe, C., Wineland, D. J., 2000, *Nature* (London) **403**, 269.

[99] Leibfreid, D., Blatt, R., Monroe, C., Wineland, D., 2003, *Rev. Mod. Phys*. **75**, 281.

[100] Cano-Andrade, S., Beretta, G. P., von Spakovsky, M. R., 2013, *12th Joint European Thermodynamics Conference*, Brescia, Italy, July 1-5.

[101] Al-Abbasi, O., von Spakovsky, M. R., Beretta, G. P., 2013, *12th Joint European Thermodynamics Conference*, Brescia, Italy, July 1-5.

[102] Milonni, P. W., 1984, *Am. J. of Phys*. **52**(4), 340.

[103] Milonni, P. W., 1982, *Phys. Rev. A*. **25**(3), 1315.

[104] Armijo, J., 2012, *Phys. Rev. Lett*. **108**, 225306

[105] Monroe, D., 2012, *Phys*. **5**, 62.

[106] Cano-Andrade, S., Beretta, G. P., von Spakovsky, M. R., 2013, *ASME IMECE,* paper no. IMECE2013–63596,

Nov. 15-21, San Diego, CA.

[107] Beretta, G. P., von Spakovsky, M. R., 2013, in preparation.

[108] Zhu, W., Rabitz, H., 2005, *J. of Math. Phys*. **46**, 022105.

[109] Beretta, G. P., 2008, *Am. Inst. of Phys. CP Series*, **1033**, 180.

[110] Hatsopoulos, G. N., Keenan, J. H., 1965, *Principles of General Thermodynamics* (New York: Wiley).

[111] Gyftopoulos, E. P., Beretta, G. P., 2005, *Thermodynamics: Foundations and Applications* (2nd ed., New York: Dover).

[112] 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).

[113] Ziegler H., 1983 *J of Applied Math. and Phys*. (ZAMP) **34** 832-844.

[114] Wilkins, R. L., 1972, *J. of Chem. Phys.,* **57**(2), pp. 912-917.

[115] Karplus, M., Porter, R. N., Sharma, R. D., 1965, *Journal of Chemical Physics,* **43**(9), pp. 3259-3287.

[116] Fernandez-Ramos, A., Ellingson, B. A., Garrett, B. C. *et al.*, 2007, *Rev. in Compu.l Chem.*, pp. 125-232: Wiley.

[117] Simons, J. *An introduction to theoretical chemistry*, Cambridge; N. Y.: Cambridge University Press, 2003.

[118] Manthe, U., Miller, W. H., *Journal of chemical physics,* **99**, pp. 3411, 1993.

[119] Garrett, B. C., Truhlar, D. G., Grev, R. S. *et al.*, 1980, *J. of Phys. Chem.,* **84**(13), 1730-1748, 1980/06/01.

[120] Marcus, R. A., Coltrin, M. E., 1977, *Journal of Chemical Physics,* **67**(6), pp. 2609-2613.

[121] Yang, X. and Liu, K., 2004, *Modern Trends in Chemical Reaction Dynamics: Experiment and Theory*: World Scientific Publishing Company Incorporated.

[122] Schatz, G. C., 1996, *Journal of Physical Chemistry,* **100**(31), pp. 12839-12847, 1996/01/01.

[123] Neuhauser, D., Baer, M., Judson, R. S. *et al.*, 1991, *Computer Physics Communications,* **63**(1), pp. 460-481.

[124] Wang, H., Thompson, W. H., and Miller, W. H., 1998, *J. of Physical Chemistry A*, 102(47), pp. 9372-9379.

[125] Zhou, X., Dotsenko, I., Peaudecerf, B., Rybarczyk, T., Sayrin, C., Gleyzes, S., Raimond, J. M., Brune, M. and Haroche, S., 2012, *Phys. Rev. Lett.,* **108**, p. 243602.

[126] Haroche, S., Brune, M, Raimond, J. M., 2013, *Physics Today, 66*, 1, 27..

[127] Raimond, J. M., Brune, M., Haroche, S., 1997, *Phys. Rev. Lett.,* **79**.

[128] Brune, M., Hagley, E., Dreyer, J., Maıtre, X., Maali, A., Wunderlich, C., Raimond, J. M., Haroche, S., 1996, *Phys. Rev. Lett.,* **77**, 4887–4890.

[129] Deleglise, S., Dotsenko, I., Sayrin, C., Bernu, J., Brune, M., Raimond, J. M. and Haroche, S., 2008, *Nature Letters, 455*, 510-514.

[130] Haroche, S., Raimond, J. M., *Exploring the quantum*. Oxford, UK: Oxford University Press, 2006.

[131] Raimond J. M., Haroche, S., 2007, *Quantum Decoherence*. **48**, ed: Birkhäuser Verlag Basel, p. 33-83.

[132] Brune, M., Schmidt-Kaler, F., Maali, A., Dreyer, J., Hagley, E., Raimond, J. M., Haroche, S., 1996, *Phys. Rev. Lett.,* **76**, 1800–1803.

[133] Raimond, J. M., Brune, M., Haroche, S., 2001, *Reviews of Modern Physics, 73*, 565-582.

[134] Beretta, G. P., 2006, *Int. J. of Thermodynamics, 9*, 117.