Generalized quantum fluctuation-dissipation identities

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Abstract. In this article, we derive the fluctuation-dissipation theorem from Bayesian statistics in the language of quantum statistical mechanics, using density matrices representing the respective state of knowledge about the system. This theorem, which we have called the quantum-fluctuation-dissipation theorem (Q-FDT), allows us to obtain expectation identities between quantum observables depending on a continuous parameter $\gamma \in \mathbb{R}$. In this sense, we consider parameters contained in the observables (e.g. a perturbative parameter), or parameters such as Lagrange multipliers only, excluding parameters that modify the underlying Hilbert space. Using both canonical and grand canonical density matrices in the Q-FDT, we explore the resulting fluctuation-dissipation identities. In this sense, we found that some of the expectation identities in common use in traditional quantum statistics and quantum chemistry, such as the thermodynamical fluctuation-dissipation theorem, the Ehrenfest and the Hellmann-Feynman theorems, among others, are particular instances of the Q-FDT. Lastly, using a *generalized* density matrix arising from a Maximum-Entropy procedure, we derive generalized fluctuation-dissipation identities: these generalized identities allow us to group all the previous cases in a unitary scheme.

1. Introduction

The concept of expectation value plays a central role both in statistical sciences and physics. It corresponds to the prediction that a theory makes on a variable or an

observable of a system under study. Examples of expectation values in physics are the ensemble average in classical statistical mechanics, the pure-state mean value of basic quantum mechanics, and the mixed-state mean value of quantum statistics [1]. In order to give a number to an expectation value, it is necessary to count with a statistical distribution of the accessible states of the respective physical system. For example, to calculate the ensemble average of a phase-space function we only need to integrate that function weighted by a phase-space distribution over all coordinates and all the classical momenta. However, in several cases, the resulting integral can not be evaluated straightforwardly.

On the other hand, following the Bayesian formulation of statistics [2], it is possible to derive an algebraic identity that relates the derivative of an expectation value taken in a certain state of knowledge with another expectation taken in the same state of knowledge. Specifically, for an arbitrary function $\omega(\mathbf{X}; \gamma)$ of a random variable $\mathbf{X}$, which depends parametrically on a continuous parameter γ and follows a nowhere vanishing statistical distribution $P(\mathbf{X}|\gamma, I)$, we have

$$\frac{\partial}{\partial \gamma} \langle \omega(\mathbf{X}; \gamma) \rangle_{\gamma, I} = \int_U d\mathbf{x} \left[\frac{\partial \omega(\mathbf{X}; \gamma)}{\partial \gamma} + \omega(\mathbf{X}; \gamma) \frac{\partial \ln P(\mathbf{X}|\gamma, I)}{\partial \gamma} \right] P(\mathbf{X}|\gamma, I), \qquad (1)$$

where γ is also a parameter contained in the statistical distribution, U is some region such as $\mathbf{x} \in U$, and I points out a certain state of knowledge. It is worth noting that in Eq. (1), the expectation values are taken not only in the state of knowledge given by I, but also by the continuous parameter γ. The identity shown in Eq. (1) is called, for historical reasons, the fluctuation-dissipation theorem (FDT) [3]. With the aid of the FDT, it is possible, for example, to evaluate indirectly the mean value and the variance associated to the discrete variable k in the Poisson distribution without the need to evaluate any integral [3]. Applied to statistical physics, the FDT allows us to recover certain identities such as the relationship between the mean energy with the logarithmic derivative of the canonical partition function and the relationship between the specific heat of a thermodynamical system with its energy fluctuation: this relation corresponds to the thermodynamical version of the fluctuation-dissipation theorem [4].

In the case of quantum mechanics, we have two types of expectation values depending on whether we are dealing with pure quantum states or mixed quantum states. In the first case, we use the wave function ψ_n associated with a certain quantum number n as a probability amplitude, to calculate the expectation value of a Hermitian operator, while in the case of mixed states, it is necessary to know the density matrix $\hat{\rho}$ of the system. Thus, for mixed-state quantum systems, the density matrix becomes a key quantity since it, being the equivalent of the phase-space distribution in quantum mechanics, acts as a probability distribution of the accessible quantum states.

Depending on the type of the system, we have different methodologies to obtain the density matrix $\hat{\rho}$ associated with the quantum state of such a system. For example, in atomic and molecular systems, we can reconstruct the density matrix using some fundamental parameters of the respective model, such as the total charge and the

number of electrons, and also imposing well-known constraints to the statistical weights (probabilities) [5]. On the other hand, within the inferential statistical approach of E. T. Jaynes [6, 7], we can build the least biased quantum distribution only maximizing the von-Neumann entropy

$$S = -k \operatorname{Tr} (\hat{\rho} \log \hat{\rho}), \tag{2}$$

under specific constraints related to whatever we know about the system. This procedure is, indeed, the application of the Maximum Entropy Principle (MaxEnt) to quantum statistics [8]. In practice, the constraints that are used in the MaxEnt procedure are given by different Lagrange multipliers, such as the inverse temperature β or the product $\alpha = -\beta\mu$, etc., where each of them is associated with respective expectation values of key observables of the system (energy and mean particle number, respectively). Additionally, the knowledge of the expectation values of quantum observables allows us to reconstruct the density matrix of a microscopic system. Such a process is known as Quantum State Tomography [9–11], which, nowadays, comprises an important ground to quantum computing [12].

Once we have the density matrix of a system, we only need a states base in order to expand the trace operator in the expression

$$\left\langle \hat{A} \right\rangle_{\hat{\rho}} = \operatorname{Tr} \left\{ \hat{A}\hat{\rho} \right\}, \tag{3}$$

where $\hat{A} = \hat{A}^{\dagger}$ is a Hermitian linear operator acting on the Hilbert space $\mathcal{H}$ of the accessible states of the system. It is important to stress that we have used the density matrix $\hat{\rho}$ as a subscript in the expectation value (3) because, in quantum statistics and following the Bayesian nomenclature, it represents the state of knowledge in which we are calculating the expectation of $\hat{A}$. If the density matrix $\hat{\rho}$ used in Eq. (3) comes from the MaxEnt principle, it depends on a collection of Lagrange multipliers, so that, the expectation value (3) depends on the same parameters too. We will call that collection of Lagrange multipliers **statistical-like** parameters, since these determine the form of the statistical model given by the density matrix. Moreover, there are cases in which the observables of the system may depend on extra parameters, different from those already mentioned, such as an oscillation frequency, a perturbative parameter, time, etc. We will call such a collection of parameters **quantum-like** parameters, because these are only contained in the quantum observables (e.g. the Hamiltonian) and never appear outside of them.

The main goal of this article is to adapt to the quantum world the classical FDT Eq. (1), taking special care in the way how the concepts are translated from classical to quantum statistics. Additionally, we will show that several traditional identities of quantum statistics and quantum mechanics, such as the Hellmann-Feynman and the Ehrenfest theorems, the thermodynamical FDT, and the generalization of the thermodynamic integration identity (useful in determining the Helmholtz free energy difference in numerical simulations) among others, become different instances of our quantum fluctuation-dissipation theorem. Finally, by means of a *generalized* density

matrix coming from the MaxEnt principle we obtain generalized fluctuation-dissipation identities: we will conclude that all of the previous FD identities, such as the canonical and the grand canonical FD identities, are particular instances of such generalized relationships.

The above suggests the following reflection: *Are the FD-like identities (Ehrenfest theorem, thermodynamical FDT, etc.) physical relationships or, on the contrary, are only straightforward applications of the Bayesian reasoning to quantum statistical mechanics?* [13–16]. Without giving a definitive answer, we, at least, will seed the question.

This article is organized as follows: Section 2 is devoted to the derivation of the quantum-FDT (Q-FDT). In Section 3 we review the Hellmann-Feynman theorem as a particular case of the Q-FDT, alluding to its importance in quantum chemistry. Section 4 is dedicated to review applications of Q-FDT to the canonical and grand canonical models from statistical mechanics. Section 5 provides a view of the Ehrenfest theorem from our Q-FDT. At last Section 6 is devoted to the generalized FD identities coming from a MaxEnt density matrix.

A remark about the notation: in this work we use the symbol ln for the natural logarithm of a scalar function, and the symbol log for the natural logarithm of an operator. The circumflex accent or *hat* over a symbol A, namely $\hat{A}$, denotes an operator on the underlying Hilbert space, as is customary in the quantum chemistry and chemical physics literature [17].

2. Derivation

Consider an observable $\hat{A}(\gamma)$ and a mixed quantum state represented by a density matrix $\hat{\rho}(\gamma)$, acting both on a Hilbert space $\mathcal{H}$ with a fixed domain Ω. Both observables are dependent on a continuous parameter $\gamma \in \mathbb{R}$ which can be of the following types:

1) *Quantum-like parameters*: Are parameters that can be contained in the Hamiltonian $\hat{H}(\gamma)$ or other observables of the system, such as a perturbative parameter, time or some coordinate.

2) *Statistical-like parameters*: Are parameters that are not contained in the observables of the system, and appear as Lagrange multipliers associated to some constraint. Examples of this type of parameters are the inverse temperature β, chemical potential μ, etc.

In this article, we exclude parameters that change the underlying Hilbert space. For example, those that change the size or shape of the system (such as the length of the well in the model of the potential-well) are not considered in this work.

We are interested in calculating the derivative of the expectation value of $\hat{A}(\gamma)$ in the state $\hat{\rho}(\gamma)$ with respect to the parameter γ, i.e.

$$\frac{\partial}{\partial \gamma} \left\langle \hat{A}(\gamma) \right\rangle_{\hat{\rho}(\gamma)} = \frac{\partial}{\partial \gamma} \operatorname{Tr} \left\{ \hat{A}(\gamma) \hat{\rho}(\gamma) \right\}. \tag{4}$$

Due to the property of the invariance of the expectation with respect to the basis, we are free to choose, in Eq. (4), a continuous or a discrete basis kets. In this way, in order to expand the trace operator in (4), we use the eigenstates of $\hat{\rho}(\gamma)$, and we assume that they form a countable basis $\{|n; \gamma\rangle\}_{n \in \mathbb{N}}$ labeled both by a quantum number $n \in \mathbb{N}$ and by the parameter γ. We can write

$$
\begin{aligned}
\frac{\partial}{\partial \gamma} \operatorname{Tr} \left\{ \hat{A}(\gamma) \hat{\rho}(\gamma) \right\} &= \frac{\partial}{\partial \gamma} \sum_{n \in \mathbb{N}} \langle n; \gamma | \hat{A}(\gamma) \hat{\rho}(\gamma) | n; \gamma \rangle, \\
&= \sum_{n \in \mathbb{N}} \left[\frac{\partial}{\partial \gamma} \langle n; \gamma | \right] \hat{A}(\gamma) \hat{\rho}(\gamma) | n; \gamma \rangle \\
&\quad + \sum_{n \in \mathbb{N}} \langle n; \gamma | \hat{A}(\gamma) \hat{\rho}(\gamma) \left[\frac{\partial}{\partial \gamma} | n; \gamma \rangle \right] \\
&\quad + \sum_{n \in \mathbb{N}} \langle n; \gamma | \frac{\partial}{\partial \gamma} \left[\hat{A}(\gamma) \hat{\rho}(\gamma) \right] | n; \gamma \rangle.
\end{aligned}
\tag{5}
$$

Now, if we restrict to certain observables $\hat{A}$ compatible with the density matrix of the system, i.e., $\left[\hat{A}, \hat{\rho} \right] = 0$, we have that $\hat{A}$ and $\hat{\rho}$ have the common eigenbasis $\{|n; \gamma\rangle\}$. In this way, the spectral decompositions of $\hat{A}$ and $\hat{\rho}$ are given by

$$
\begin{aligned}
\hat{A}(\gamma) &= \sum_{n \in \mathbb{N}} a_n(\gamma) \hat{P}_n(\gamma), \\
\hat{\rho}(\gamma) &= \sum_{n \in \mathbb{N}} \rho_n(\gamma) \hat{P}_n(\gamma),
\end{aligned}
\tag{6}
$$

where $a_n(\gamma)$ and $\rho_n(\gamma)$ are the eigenvalues of $\hat{A}$ and $\hat{\rho}$, respectively. Moreover, $\rho_n(\gamma)$ represents the associated probabilities to each pure state $\hat{P}_n(\gamma) = |n; \gamma\rangle \langle n; \gamma|$ to which the system has access, and whose form depends on the particular statistical model (e.g. canonical, grand canonical, etc.). Knowing the eigenvalues of $\hat{A}(\gamma)$ and $\hat{\rho}(\gamma)$, we can use them in the first two sums of the left-hand side of (5), thus obtaining

$$
\begin{aligned}
&\left[\frac{\partial}{\partial \gamma} \langle n; \gamma | \right] \hat{A}(\gamma) \hat{\rho}(\gamma) | n; \gamma \rangle + \langle n; \gamma | \hat{A}(\gamma) \hat{\rho}(\gamma) \left[\frac{\partial}{\partial \gamma} | n; \gamma \rangle \right], \\
&= \rho_n(\gamma) \left\{ \left[\frac{\partial}{\partial \gamma} \langle n; \gamma | \right] \hat{A}(\gamma) | n; \gamma \rangle + \langle n; \gamma | \hat{A}(\gamma) \left[\frac{\partial}{\partial \gamma} | n; \gamma \rangle \right] \right\}, \\
&= \rho_n(\gamma) a_n(\gamma) \left\{ \left[\frac{\partial}{\partial \gamma} \langle n; \gamma | \right] | n; \gamma \rangle + \langle n; \gamma | \left[\frac{\partial}{\partial \gamma} | n; \gamma \rangle \right] \right\},
\end{aligned}
\tag{7}
$$

and assuming normalized states $|n; \gamma\rangle$, i.e. $\langle n; \gamma | n; \gamma \rangle = 1$, we recall that

$$
\frac{\partial}{\partial \gamma} \left[\langle n; \gamma | n; \gamma \rangle \right] = \left\{ \left[\frac{\partial}{\partial \gamma} \langle n; \gamma | \right] | n; \gamma \rangle + \langle n; \gamma | \left[\frac{\partial}{\partial \gamma} | n; \gamma \rangle \right] \right\} = 0.
\tag{8}
$$

Thus, Eq. (5) is reduced to

$$
\frac{\partial}{\partial \gamma} \left\langle \hat{A}(\gamma) \right\rangle_{\hat{\rho}(\gamma)} = \sum_{n \in \mathbb{N}} \langle n; \gamma | \frac{\partial \hat{A}(\gamma)}{\partial \gamma} \hat{\rho}(\gamma) | n; \gamma \rangle + \sum_{n \in \mathbb{N}} \langle n; \gamma | \hat{A}(\gamma) \frac{\partial \hat{\rho}(\gamma)}{\partial \gamma} | n; \gamma \rangle,
\tag{9}
$$

where the first sum in Eq. (9) is easily related to the expectation of $\partial \hat{A}/\partial \gamma$ in the state $\hat{\rho}(\gamma)$,

$$\sum_{n \in \mathbb{N}} \langle n; \gamma | \frac{\partial \hat{A}(\gamma)}{\partial \gamma} \hat{\rho}(\gamma) | n; \gamma \rangle = \left\langle \frac{\partial \hat{A}(\gamma)}{\partial \gamma} \right\rangle_{\hat{\rho}(\gamma)}. \tag{10}$$

Then, in order to rewrite as an expectation value the second sum in Eq. (9), we need to assume that $\hat{\rho}$ is a non-singular operator. This can always be done by discarding all possible zero eigenvalues of $\hat{\rho}$ and considering only those that are non-zero (i.e. non-zero probabilities). In this way, if we multiply $\partial \hat{\rho}/\partial \gamma$ by $\mathbb{1} = \hat{\rho}^{-1} \hat{\rho}$ from the right in the second sum of Eq. (9), and using the fact that

$$\frac{\partial \hat{\rho}}{\partial \gamma} \hat{\rho}^{-1} = \frac{\partial \log \hat{\rho}}{\partial \gamma} \tag{11}$$

which follows from the Taylor series of $\hat{\rho}^{-1}$ and $\log \hat{\rho}$, we finally get

$$\begin{aligned} \sum_{n \in \mathbb{N}} \langle n; \gamma | \hat{A}(\gamma) \frac{\partial \hat{\rho}(\gamma)}{\partial \gamma} | n; \gamma \rangle &= \sum_{n \in \mathbb{N}} \langle n; \gamma | \hat{A}(\gamma) \frac{\partial \hat{\rho}(\gamma)}{\partial \gamma} \hat{\rho}^{-1} \hat{\rho} | n; \gamma \rangle, \\ &= \sum_{n \in \mathbb{N}} \langle n; \gamma | \hat{A}(\gamma) \frac{\partial \log \hat{\rho}(\gamma)}{\partial \gamma} \hat{\rho} | n; \gamma \rangle, \\ &= \left\langle \hat{A}(\gamma) \frac{\partial \log \hat{\rho}(\gamma)}{\partial \gamma} \right\rangle_{\hat{\rho}(\gamma)}. \end{aligned} \tag{12}$$

We conclude that the derivative with respect to a continuous parameter γ of the expectation value of an observable $\hat{A}(\gamma)$ is given by

$$\frac{\partial}{\partial \gamma} \left\langle \hat{A}(\gamma) \right\rangle_{\hat{\rho}(\gamma)} = \left\langle \frac{\partial \hat{A}(\gamma)}{\partial \gamma} \right\rangle_{\hat{\rho}(\gamma)} + \left\langle \hat{A}(\gamma) \frac{\partial \log \hat{\rho}(\gamma)}{\partial \gamma} \right\rangle_{\hat{\rho}(\gamma)}. \tag{13}$$

Eq. (13) corresponds to a quantum version of the *fluctuation-dissipation theorem* (Q-FDT) for observables compatible with the density matrix. By means of Eq. (13) we will derive not only standard results of quantum mechanics and thermodynamics (the relation between the partition function and the mean energy of a quantum system, the Ehrenfest theorem, and the thermodynamical version of the fluctuation-dissipation theorem, among others), but also new identities in the field (see Section 4.2 below). This supports the idea of using the name of the fluctuation-dissipation theorem for Eq. (13). At last, it is important to remark that a simple way to ensure that $\left[\hat{A}, \hat{\rho} \right] = 0$, is when both $\hat{A}$ and $\hat{\rho}$ are functions of the Hamiltonian $\hat{H}$, i.e. $\hat{A} = A(\hat{H})$ and $\hat{\rho} = \rho(\hat{H})$.

3. Hellmann-Feynman from quantum fluctuation-dissipation theorem

In the context of classical statistics, the derivative with respect to a continuous parameter γ on the expectation value of a function $\omega(\mathbf{X}; \gamma)$ in the state of knowledge given only by I, is

$$\frac{\partial}{\partial \gamma} \langle \omega(\mathbf{X}; \gamma) \rangle_I = \left\langle \frac{\partial \omega(\mathbf{X}; \gamma)}{\partial \gamma} \right\rangle_I. \tag{14}$$

We observe that Eq. (14) is a particular case of the classical FDT (Eq. (1)): the last reduces to the former in the case when the statistical distribution $P(\mathbf{X}|I)$ does not depend on the parameter γ used in the derivative.

In quantum mechanics, we have an analogous situation. Consider the Q-FDT Eq. (13) for an operator $\hat{A}(\gamma)$ and for the instance where the density matrix $\hat{\rho}$ represents a mixed state but does not contain the parameter γ used in the derivative. In such a case, the Q-FDT reduces to

$$\frac{\partial}{\partial \gamma} \left\langle \hat{A}(\gamma) \right\rangle_{\hat{\rho}} = \left\langle \frac{\partial \hat{A}(\gamma)}{\partial \gamma} \right\rangle_{\hat{\rho}}. \tag{15}$$

Observe that the above identity is the quantum equivalent of the Eq. (14). Then, in the special case in which the operator is the Hamiltonian of the system, i.e. $\hat{A}(\gamma) = \hat{H}(\gamma)$, where γ may be some parameter contained in it (mass, force constant, etc.), we have

$$\frac{\partial}{\partial \gamma} \left\langle \hat{H} \right\rangle_{\hat{\rho}} = \left\langle \frac{\partial \hat{H}(\gamma)}{\partial \gamma} \right\rangle_{\hat{\rho}}. \tag{16}$$

Eq. (16), which is called the *Hellmann-Feynman* theorem, is widely used in the context of quantum chemistry and molecular physics to explore the chemical bonding in molecular systems [17, 18].

Not only the Hellmann-Feynman theorem is recovered when the density matrix $\hat{\rho}$ does not depend on γ, but also when it represents a pure state projector, namely $\hat{\rho} = |n; \gamma\rangle \langle n; \gamma|$ (which may depend on γ). In this case, we have

$$\begin{aligned}
\frac{\partial}{\partial \gamma} \left\langle \hat{H}(\gamma) \right\rangle_n &= \frac{\partial}{\partial \gamma} \mathrm{Tr}\left\{ \hat{H} |n; \gamma\rangle \langle n; \gamma| \right\}, \\
&= \frac{\partial}{\partial \gamma} \sum_{m \in \mathbb{N}} \langle m; \gamma| \hat{H}(\gamma) |n; \gamma\rangle \, \delta_{n,m}, \\
&= \frac{\partial}{\partial \gamma} \left[\langle n; \gamma| \hat{H}(\gamma) |n; \gamma\rangle \right], \\
&= \langle n; \gamma| \frac{\partial \hat{H}(\gamma)}{\partial \gamma} |n; \gamma\rangle,
\end{aligned} \tag{17}$$

where we have assumed that $\{|n; \gamma\rangle\}_{n \in \mathbb{N}}$ is an orthonormal eigenbasis of $\hat{H}(\gamma)$ (cf. Eq. (8)). Hence

$$\frac{\partial E_n(\gamma)}{\partial \gamma} = \left\langle \frac{\partial \hat{H}(\gamma)}{\partial \gamma} \right\rangle_n, \tag{18}$$

where $E_n(\gamma)$ is the energy eigenvalue associated to the state $|n; \gamma\rangle$.

An interesting use of the Hellmann-Feynman theorem, in the context of quantum chemistry, is in the case in which the parameter γ corresponds to a certain nuclear coordinate $R_{i,\alpha}$ (*ith* coordinate of the nucleus α) of a N-electron molecular

system. Considering the molecular Schrödinger equation within the Born-Oppenheimer approximation [17]

$$\left[\hat{H}_{el} + \hat{V}_{NN} \right] |\psi_{el}\rangle = U(\mathbf{R}) |\psi_{el}\rangle, \tag{19}$$

where $\hat{H}_{el} = \hat{T}_{el} + \hat{V}_{el}$ is the *electronic* Hamiltonian (which includes the electronic kinetic energy operator $\hat{T}_{el}$ and the electronic potential operator $\hat{V}_{el}$), $\hat{V}_{NN}$ is the potential due to nuclear repulsion and $|\psi_{el}\rangle$ are the electronic states of the molecule. The energy $U(\mathbf{R})$ corresponds to the electronic energy plus the internuclear repulsion and is called the *Born-Oppenheimer energy* (BO) of the molecule [19]. We notice that the BO energy depends parametrically on the coordinates of the nuclei in the molecule throughout the nuclear coordinate vector $\mathbf{R} = (R_{x,1}, R_{y,1}, R_{z,1}, ..., R_{x,M}, R_{y,M}, R_{z,M})$, where M is the total number of nuclei in the molecule. In such a case, the Hellmann-Feynman theorem can be written as (for $\gamma = R_{i,\alpha}$)

$$\frac{\partial U(\mathbf{R})}{\partial R_{i,\alpha}} = \int d\mathbf{r}_1 ... d\mathbf{r}_N \, \psi_{el}^*(\mathbf{r}_1, ..., \mathbf{r}_N) \left[\frac{\partial V_{el}}{\partial R_{i,\alpha}} + \frac{\partial V_{NN}}{\partial R_{i,\alpha}} \right] \psi_{el}(\mathbf{r}_1, ..., \mathbf{r}_N), \tag{20}$$

where $\mathbf{r}_i$ denotes the coordinates of the *ith* electron. The derivative of the BO energy with respect to $R_{i,\alpha}$ can be seen as the *ith* component of a force on the αth nucleus due to the other nuclei and the electron cloud. See [20] for more details.

4. Canonical and grand canonical identities

Before giving the general results obtained from the Q-FDT for a generalized density matrix, we illustrate the use of (13) in the canonical and grand canonical statistical models. According to Section 2, we are free to choose $\hat{A}$ as any observable compatible with $\hat{\rho}$ such as the identity operator $\mathbb{1}$, the Hamiltonian $\hat{H}$ and the density matrix $\hat{\rho}$ itself, or even an arbitrary function $F(\hat{\rho})$ of $\hat{\rho}$. For the sake of simplicity, we only consider the the cases $\hat{A} = \mathbb{1}$ and $\hat{A} = \hat{H}$.

4.1. Canonical model

We consider a canonical density matrix of the form

$$\hat{\rho}_c(\beta) = \frac{\exp\left\{ -\beta \hat{H} \right\}}{\mathcal{Z}(\beta)}, \tag{21}$$

where β is the inverse temperature and

$$\mathcal{Z}(\beta) = \mathrm{Tr}\left(e^{-\beta \hat{H}} \right) \tag{22}$$

is the canonical partition function, which depends on β and, in certain cases, on a quantum-like parameter λ. If we use the canonical model Eq. (21) in the Q-FDT, we obtain

$$\frac{\partial}{\partial \gamma} \left\langle \hat{A} \right\rangle_{\hat{\rho}_c} = \left\langle \frac{\partial \hat{A}}{\partial \gamma} \right\rangle_{\hat{\rho}_c} - \left\langle \hat{A} \frac{\partial}{\partial \gamma} \left(\beta \hat{H} \right) \right\rangle_{\hat{\rho}_c} - \frac{\partial \ln \mathcal{Z}(\beta)}{\partial \gamma} \left\langle \hat{A} \right\rangle_{\hat{\rho}_c}, \tag{23}$$

where γ may be a quantum-like (λ) or a statistical-like parameter (β). In the following, we will use in the above relation Eq. (23) (which we have called the *canonical Q-FDT*) $\hat{A} = \mathbb{1}$ and $\hat{A} = \hat{H}$ for both types of parameters, obtaining four canonical fluctuation-dissipation identities (which are summarized in Table 1):

i) $\hat{A} = \mathbb{1}$ **and** γ **is a quantum-like parameter** (λ):

In this case, we have that

$$\frac{\partial}{\partial \lambda} \langle \mathbb{1} \rangle = 0 \quad \text{and} \quad \left\langle \frac{\partial \mathbb{1}}{\partial \lambda} \right\rangle = 0,$$

so the second term of the right-hand side of Eq. (13) becomes

$$
\begin{aligned}
0 = \left\langle \frac{\partial \log \hat{\rho}_c}{\partial \lambda} \right\rangle_{\hat{\rho}_c} &= \left\langle \frac{\partial}{\partial \lambda} \left[-\beta \hat{H}(\lambda) - \ln \mathcal{Z}(\beta, \lambda) \mathbb{1} \right] \right\rangle_{\hat{\rho}_c}, \\
&= -\beta \left\langle \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \right\rangle_{\hat{\rho}_c} - \frac{\partial \ln \mathcal{Z}(\beta, \lambda)}{\partial \lambda},
\end{aligned}
\tag{24}
$$

and we obtain

$$\left\langle \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \right\rangle_{\hat{\rho}_c} = -\frac{1}{\beta} \frac{\partial \ln \mathcal{Z}(\beta, \lambda)}{\partial \lambda} \bigg|_{\beta}. \tag{25}$$

Identifying in the above identity the Helmholtz Free energy,

$$\mathcal{F} = -\frac{1}{\beta} \ln \mathcal{Z}(\beta, \lambda), \tag{26}$$

we can rewrite this (Eq. (25)) in the form

$$\left\langle \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \right\rangle_{\hat{\rho}_c} = \frac{\partial \mathcal{F}(\beta, \lambda)}{\partial \lambda}. \tag{27}$$

Finally, we can obtain the free energy difference $\Delta \mathcal{F}$ integrating with respect to $\lambda \in [\lambda_{min}, \lambda_{max}]$ on both sides:

$$\Delta \mathcal{F} = \int_{\lambda_{min}}^{\lambda_{max}} d\lambda \left\langle \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \right\rangle_{\hat{\rho}_c}. \tag{28}$$

This procedure is used to obtain free energy differences via molecular dynamics, such as the ionic hydration free energy difference, and is called the *thermodynamic integration technique* [21, 22].

ii) $\hat{A} = \mathbb{1}$ **and** γ **is a statistical-like parameter** (β):

As in the previous case, we have

$$\frac{\partial}{\partial \beta} \langle \mathbb{1} \rangle = 0 \quad \text{and} \quad \left\langle \frac{\partial \mathbb{1}}{\partial \beta} \right\rangle = 0,$$

and the Q-FDT gives

$$0 = \left\langle \frac{\partial \log \hat{\rho}_c}{\partial \beta} \right\rangle_{\hat{\rho}_c} = \left\langle \frac{\partial}{\partial \beta} \left[-\beta \hat{H} - \ln \mathcal{Z}(\beta) \mathbb{1} \right] \right\rangle_{\hat{\rho}_c},$$
$$= -\left\langle \hat{H} \right\rangle_{\hat{\rho}_c} - \frac{\partial \ln \mathcal{Z}(\beta)}{\partial \beta}, \tag{29}$$

where we have used the fact that $\hat{H}$ does not depend on the inverse temperature β. In this way, we get

$$\left\langle \hat{H} \right\rangle_{\hat{\rho}_c} = -\frac{\partial \ln \mathcal{Z}(\beta)}{\partial \beta}\bigg|_{\lambda}. \tag{30}$$

It is important to observe that the identity shown in Eq. (30) is the well-known relationship between the partition function and the average energy which arises in the context of canonical ensemble in traditional statistical mechanics [1].

iii) $\hat{A} = \hat{H}$ **and** γ **is a quantum-like parameter** (λ):

In this case we have

$$\frac{\partial}{\partial \lambda} \left\langle \hat{H}(\lambda) \right\rangle_{\hat{\rho}_c} = \left\langle \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \right\rangle_{\hat{\rho}_c} + \left\langle \hat{H}(\lambda) \frac{\partial}{\partial \lambda} \left[-\beta \hat{H}(\lambda) - \ln \mathcal{Z}(\beta, \lambda) \mathbb{1} \right] \right\rangle_{\hat{\rho}_c},$$
$$= \left\langle \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \right\rangle_{\hat{\rho}_c} - \beta \left\langle \hat{H} \frac{\partial \hat{H}}{\partial \lambda} \right\rangle_{\hat{\rho}_c} - \frac{\partial \ln \mathcal{Z}(\beta, \lambda)}{\partial \lambda} \left\langle \hat{H} \right\rangle_{\hat{\rho}_c}, \tag{31}$$

and using Eq. (25), we finally get

$$\frac{\partial}{\partial \lambda} \left\langle \hat{H}(\lambda) \right\rangle_{\hat{\rho}_c} = \left\langle \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \right\rangle_{\hat{\rho}_c} - \beta \operatorname{Cov}\left(\hat{H}, \frac{\partial \hat{H}}{\partial \lambda} \right), \tag{32}$$

where $\operatorname{Cov}\left(\hat{H}, \dfrac{\partial \hat{H}}{\partial \lambda} \right)$ stands for

$$\operatorname{Cov}\left(\hat{H}, \frac{\partial \hat{H}}{\partial \lambda} \right) \equiv \left\langle \Delta \hat{H} \, \Delta \left(\frac{\partial \hat{H}}{\partial \lambda} \right) \right\rangle_{\hat{\rho}_c},$$
$$= \left\langle \hat{H} \frac{\partial \hat{H}}{\partial \lambda} \right\rangle_{\hat{\rho}_c} - \left\langle \hat{H} \right\rangle_{\hat{\rho}_c} \left\langle \frac{\partial \hat{H}}{\partial \lambda} \right\rangle_{\hat{\rho}_c}, \tag{33}$$

i.e., corresponds to the covariance between the Hamiltonian and its derivative in the state of knowledge given by $\hat{\rho}$, and measures the correlation between both operators in a statistical sense. In Eq. (33) $\Delta \hat{H}$ means the deviation of $\hat{H}$ from its expectation (mean) value,

$$\Delta \hat{H} = \hat{H} - \left\langle \hat{H} \right\rangle \mathbb{1},$$

and the same for $\partial \hat{H} / \partial \lambda$.

It is worth mentioning two compatible observables (i.e. whose commutator is null), might not be uncorrelated. This can be seen if we recast the covariance between any two observables $\hat{A}$ and $\hat{B}$ as [23]

$$\text{Cov}\left(\hat{A}, \hat{B}\right) = \frac{1}{2}\left\langle\left[\hat{A}, \hat{B}\right]\right\rangle_{\hat{\rho}} + \frac{1}{2}\left\langle\left\{\Delta\hat{A}, \Delta\hat{B}\right\}\right\rangle_{\hat{\rho}}, \tag{34}$$

where

$$\left\{\Delta\hat{A}, \Delta\hat{B}\right\} = \Delta\hat{A}\Delta\hat{B} + \Delta\hat{B}\Delta\hat{A}$$

stands for the anticommutator between the deviations of $\hat{A}$ and $\hat{B}$. In this way, we can easily see that if $\left[\hat{A}, \hat{B}\right] = 0$, the anticommutator term survives and so does the covariance.

iv) $\hat{A} = \hat{H}$ **and** λ **is a statistical-like parameter** (β):
In this case, the Q-FDT gives

$$\begin{aligned}
\frac{\partial}{\partial\beta}\left\langle\hat{H}\right\rangle_{\hat{\rho}_c} &= \left\langle\hat{H}\frac{\partial}{\partial\beta}\left[-\beta\hat{H} - \ln\mathcal{Z}(\beta)\mathbb{1}\right]\right\rangle_{\hat{\rho}_c} \\
&= -\left\langle\hat{H}^2\right\rangle_{\hat{\rho}_c} - \frac{\partial\ln\mathcal{Z}(\beta)}{\partial\beta}\left\langle\hat{H}\right\rangle_{\hat{\rho}_c}.
\end{aligned} \tag{35}$$

where we have used that $\partial\hat{H}/\partial\beta = 0$.
Using Eq. (30) in the second term of Eq. (35), we finally obtain

$$\frac{\partial}{\partial\beta}\left\langle\hat{H}\right\rangle_{\hat{\rho}_c} = -\text{Var}\left(\hat{H}\right), \tag{36}$$

where $\text{Var}\left(\hat{H}\right)$ is the variance in the energy of the system, namely

$$\text{Var}\left(\hat{H}\right) = \left\langle\hat{H}^2\right\rangle_{\hat{\rho}_c} - \left\langle\hat{H}\right\rangle_{\hat{\rho}_c}^2. \tag{37}$$

Then, by means of the chain rule and using $\beta = 1/kT$, we finally obtain

$$C = \frac{\partial}{\partial T}\left\langle\hat{H}\right\rangle_{\hat{\rho}_c} = \frac{1}{kT^2}\text{Var}\left(\hat{H}\right), \tag{38}$$

where C is the heat capacity of the system, T is the absolute temperature and k is the Boltzmann constant. Traditionally, Eq. (38) is understood as one instance of the fluctuation-dissipation theorem [4]; it relates an external change in energy, driven by a change in temperature (hence, dissipation) with the internal fluctuations of the energy in equilibrium [24]. It supports the name given to Eq. (13), namely the fluctuation-dissipation theorem.

Observable	$\gamma = \lambda$ (quantum-like parameter)		$\gamma = \beta$ (statistical-like parameter)
$\hat{A} = \mathbb{1}$	$\left\langle \dfrac{\partial \hat{H}(\lambda)}{\partial \lambda} \right\rangle = -\dfrac{1}{\beta} \dfrac{\partial \ln \mathcal{Z}(\beta, \lambda)}{\partial \lambda}\bigg|_{\beta}$		$\left\langle \hat{H} \right\rangle = -\dfrac{\partial \ln \mathcal{Z}(\beta)}{\partial \beta}\bigg|_{\lambda}$
$\hat{A} = \hat{H}$	$\dfrac{\partial}{\partial \lambda}\left\langle \hat{H}(\lambda) \right\rangle = \left\langle \dfrac{\partial \hat{H}(\lambda)}{\partial \lambda} \right\rangle - \beta \operatorname{Cov}\left(\hat{H}, \dfrac{\partial \hat{H}}{\partial \lambda} \right)$		$\dfrac{\partial}{\partial \beta}\left\langle \hat{H} \right\rangle = -\operatorname{Var}\left(\hat{H} \right)$

Table 1: *Canonical quantum fluctuation-dissipation identities*

4.2. Grand canonical model

The grand canonical density matrix corresponds to the following statistical model:

$$\hat{\rho}_g(\beta, z) = \frac{\exp\left\{ -\beta \left(\hat{H} - \mu \hat{N} \right) \right\}}{\Xi(\beta, z)}, \tag{39}$$

where μ is the chemical potential, $\hat{N}$ is the number operator and $\Xi(\beta, z)$ is the grand partition function which depends on the inverse temperature β and the *fugacity* $z = e^{\beta\mu}$. As in the canonical model, the grand partition function may also depend on a quantum-like parameter λ.

Using the grand canonical model Eq. (39) in the Q-FDT (13), we obtain the *grand canonical Q-FDT*:

$$\frac{\partial}{\partial \gamma}\left\langle \hat{A} \right\rangle_{\hat{\rho}_g} = \left\langle \frac{\partial \hat{A}}{\partial \gamma} \right\rangle_{\hat{\rho}_g} - \left\langle \hat{A}\frac{\partial}{\partial \gamma}\left(\beta \hat{H} \right) \right\rangle_{\hat{\rho}_g} + \left\langle \hat{A}\frac{\partial}{\partial \gamma}\left(\beta \mu \hat{N} \right) \right\rangle_{\hat{\rho}_g} - \frac{\partial \ln \Xi(\beta, z)}{\partial \gamma}\left\langle \hat{A} \right\rangle_{\hat{\rho}_g}, \tag{40}$$

where, in the present case, γ may be a quantum-like (λ) or a statistical-like parameter (β or μ). As above, we can replace $\hat{A}$ with certain observables compatibles with the grand canonical density matrix $\hat{\rho}_g$. In this case we have the following three options:

1) $\hat{A} = \mathbb{1}$
2) $\hat{A} = \hat{H}$
3) $\hat{A} = \hat{N}$

We obtain for the grand canonical statistical model nine different fluctuation-dissipation identities, which are summarized in Table 2. Some of these identities are well-known relations coming from quantum statistics while others are new ones. At this point, it is worth mentioning that the number operator $\hat{N}$ is, in general, a constant operator, so that a quantum-like parameter λ can only appear within the Hamiltonian. Since the calculations concerning the grand canonical model follow in a very similar way to the calculations of the canonical model, here we will omit the details.

Considering the first row in Table 2 for $\hat{A} = \mathbb{1}$. We have that these three cases (using $\gamma = \lambda$, $\gamma = \beta$ and $\gamma = \mu$) lead to known relationships of quantum statistical mechanics. In particular for the pair $(\mathbb{1}, \lambda)$ we obtain

$$\left\langle \frac{\partial \hat{H}}{\partial \lambda} \right\rangle_{\hat{\rho}_g(\lambda)} = -\frac{1}{\beta} \frac{\partial \ln \Xi(\beta, z, \lambda)}{\partial \lambda}\bigg|_{\beta, z}, \tag{41}$$

where the derivative has been taken fixing the fugacity and the inverse temperature. As in the canonical model, we can identify another thermodynamic potential: the grand potential $\Phi(\beta, z, \lambda)$. It is defined by

$$\Phi(\beta, z, \lambda) = -\frac{1}{\beta} \ln \Xi(\beta, z, \lambda). \tag{42}$$

If we integrate Eq. (41) with respect to $\lambda \in [\lambda_{min}, \lambda_{max}]$, using the definition of Φ, we can obtain the grand potential difference:

$$\Delta\Phi(\beta, z, \lambda) = \int_{\lambda_{min}}^{\lambda_{max}} d\lambda \left\langle \frac{\partial \hat{H}}{\partial \lambda} \right\rangle_{\hat{\rho}_g}. \tag{43}$$

Eq. (43) is another instance of the thermodynamic integration technique applied to open quantum systems. Then, for the pairs $(\mathbb{1}, \beta)$ and $(\mathbb{1}, \mu)$, we have

$$\left\langle \hat{H} \right\rangle_{\hat{\rho}_g} = -\frac{\partial \ln \Xi(\beta, z)}{\partial \beta}\bigg|_{\lambda, z} \tag{44}$$

and

$$\left\langle \hat{N} \right\rangle_{\hat{\rho}_g} = \frac{1}{\beta} \frac{\partial \ln \Xi(\beta, z)}{\partial \mu}\bigg|_{\lambda, \beta}, \tag{45}$$

respectively. The identities in Eqs. (44) and (45), which relate, in the first case, the grand partition function with the mean energy for an open quantum system, and in the second case, the grand partition function with the mean particle number, are well-known identities in quantum statistics [1]. It is important to highlight that the derivative in Eq. (44) has been taken fixing both λ and z, while in Eq. (45) both λ and β are fixed.

Consider now the second row in Table 2 for $\hat{A} = \hat{H}$. For the pairs $(\hat{H}, \lambda)$ and $(\hat{H}, \beta)$ we obtain the same identities (Eqs. (32) and (36)) as for the canonical model, but using $\hat{\rho}_g$ in the calculations of the mean values. Because we have the same identities for both canonical and grand canonical models, one may be tempted to interpret this as a consequence of the principle of equivalence between different statistical ensembles. However, such a principle is meaningless in our case, because we are interested in small quantum systems in which it is not possible to employ the *thermodynamic limit* ($N \to \infty$): such equivalence between these canonical and grand canonical identities is an algebraic consequence of the similitude between both statistical models; the grand canonical model can be considered as the canonical model with an extra condition.

Next, for the pair $(\hat{H}, \mu)$ we have the identity

$$\frac{\partial}{\partial \mu} \left\langle \hat{H} \right\rangle_{\hat{\rho}_g} = \beta \operatorname{Cov}\left(\hat{H}, \hat{N} \right), \tag{46}$$

which accounts for the dependence of the variation of the mean energy with respect to the chemical potential expressed as the covariance between the Hamiltonian and the number operator: the stronger the correlation between $\hat{H}$ and $\hat{N}$, the greater dependence of the energy with respect to the chemical potential.

Obs.	$\gamma = \lambda$	$\gamma = \beta$	$\gamma = \mu$
$\hat{A} = \mathbb{1}$	$\left\langle \dfrac{\partial \hat{H}}{\partial \lambda} \right\rangle = -\dfrac{1}{\beta} \dfrac{\partial \ln \Xi(\beta, z, \lambda)}{\partial \lambda} \bigg\|_{\beta, z}$	$\left\langle \hat{H} \right\rangle = -\dfrac{\partial \ln \Xi(\beta, z)}{\partial \beta} \bigg\|_{\lambda, z}$	$\left\langle \hat{N} \right\rangle = \dfrac{1}{\beta} \dfrac{\partial \ln \Xi(\beta, z)}{\partial \mu} \bigg\|_{\lambda, \beta}$
$\hat{A} = \hat{H}$	$\dfrac{\partial}{\partial \lambda} \left\langle \hat{H}(\lambda) \right\rangle = \left\langle \dfrac{\partial \hat{H}(\lambda)}{\partial \lambda} \right\rangle - \beta \operatorname{Cov}\left(\hat{H}, \dfrac{\partial \hat{H}}{\partial \lambda} \right)$	$\dfrac{\partial}{\partial \beta} \left\langle \hat{H} \right\rangle = -\operatorname{Var}\left(\hat{H} \right)$	$\dfrac{\partial}{\partial \mu} \left\langle \hat{H} \right\rangle = \beta \operatorname{Cov}\left(\hat{H}, \hat{N} \right)$
$\hat{A} = \hat{N}$	$\dfrac{\partial}{\partial \lambda} \left\langle \hat{N} \right\rangle = -\beta \operatorname{Cov}\left(\hat{N}, \dfrac{\partial \hat{H}}{\partial \lambda} \right)$	$\dfrac{\partial}{\partial \beta} \left\langle \hat{N} \right\rangle = -\operatorname{Cov}\left(\hat{N}, \hat{H} \right)$	$\dfrac{\partial}{\partial \mu} \left\langle \hat{N} \right\rangle = \beta \operatorname{Var}\left(\hat{N} \right)$

Table 2: *Grand canonical quantum fluctuation-dissipation identities.*

Consider finally the third row of Table 2 for $\hat{A} = \hat{N}$. As above, we obtain three relations, namely for $\gamma = \lambda$, $\gamma = \beta$ and $\gamma = \mu$. The first two cases ($\gamma = \lambda$ and $\gamma = \beta$), along with Eq. (46), to the best of our knowledge, are new identities. Thus, for the pair $(\hat{N}, \lambda)$ we obtain

$$\frac{\partial}{\partial \lambda} \left\langle \hat{N} \right\rangle_{\hat{\rho}_g} = -\beta \operatorname{Cov}\left(\hat{N}, \frac{\partial \hat{H}}{\partial \lambda} \right); \tag{47}$$

identity that has been derived using Eq. (41). Then, for the pair $(\hat{N}, \beta)$, we obtain

$$\frac{\partial}{\partial \beta} \left\langle \hat{N} \right\rangle_{\hat{\rho}_g} = -\operatorname{Cov}\left(\hat{N}, \hat{H} \right), \tag{48}$$

where we have used Eq. (44). As in Eq. (46), the correlation between the Hamiltonian and the number operator allows to predict the change between a property of the system (the mean particle number) driven by the change in a external parameter (the inverse temperature). At last, for the pair $(\hat{N}, \mu)$, and by means of Eq. (45), the following identity is obtained:

$$\frac{\partial}{\partial \mu} \left\langle \hat{N} \right\rangle_{\hat{\rho}_g} = \beta \operatorname{Var}\left(\hat{N} \right). \tag{49}$$

Eq. (49), which can be derived also in a traditional way by applying derivatives with respect to the chemical potential on the grand partition function, allows to predict the change in the mean particle number with an external parameter (chemical potential) only measuring the internal fluctuations in the particle number. For this reason, we can interpret Eq. (49) as another instance of the thermodynamical FDT, but for the conjugate-variable couple $(\hat{N}, \mu)$.

5. Ehrenfest theorem from quantum fluctuation-dissipation theorem

An important result of quantum mechanics is the Eherenfest theorem, which states that [23]

$$\frac{d}{dt} \left\langle \hat{A} \right\rangle_{|\psi\rangle} = \left\langle \frac{\partial \hat{A}}{\partial t} \right\rangle_{|\psi\rangle} + \frac{1}{i\hbar} \left\langle \left[\hat{A}, \hat{H} \right] \right\rangle_{|\psi\rangle}, \tag{50}$$

and accounts for the time evolution of the expectation value of an observable $\hat{A}$ in a closed quantum system with a Hamiltonian $\hat{H}$. Originally, the expectations in Eq. (50)

are taken in a pure state $|\psi\rangle \langle\psi|$, but this can easily be generalized to the case of mixed states.

In order to derive the Ehrenfest theorem (Eq. (50)) from the Q-FDT, we use in Eq. (13) an arbitrary time-dependent density matrix $\hat{\rho}(t)$ with an arbitrary time-dependent observable $\hat{A}(t)$,

$$\frac{d}{dt} \left\langle \hat{A}(t) \right\rangle_{\hat{\rho}(t)} = \left\langle \frac{\partial \hat{A}(t)}{\partial t} \right\rangle_{\hat{\rho}(t)} + \left\langle \hat{A}(t) \frac{\partial \log \hat{\rho}(t)}{\partial t} \right\rangle_{\hat{\rho}(t)}, \tag{51}$$

where we have chosen the time t as the parameter γ. Rewriting the second term in the right side of Eq. (51) as

$$\begin{aligned} \left\langle \hat{A}(t) \frac{\partial \log \hat{\rho}(t)}{\partial t} \right\rangle_{\hat{\rho}(t)} &= \left\langle \hat{A}(t) \frac{\partial \hat{\rho}(t)}{\partial t} \hat{\rho}^{-1}(t) \right\rangle_{\hat{\rho}(t)} \\ &= \mathrm{Tr} \left\{ \hat{A}(t) \frac{\partial \hat{\rho}(t)}{\partial t} \right\}, \end{aligned} \tag{52}$$

where we have used $\hat{\rho}^{-1}\hat{\rho} = \mathbb{1}$, and assuming that $\hat{\rho}(t)$ evolves in an unitary way, i.e., according to the Liouville-von Neumann equation of motion

$$\frac{\partial \hat{\rho}(t)}{\partial t} = \frac{1}{i\hbar} \left[\hat{H}(t), \hat{\rho}(t) \right], \tag{53}$$

we obtain

$$\left\langle \hat{A}(t) \frac{\partial \log \hat{\rho}(t)}{\partial t} \right\rangle_{\hat{\rho}(t)} = \frac{1}{i\hbar} \mathrm{Tr} \left\{ \hat{A}(t) \left[\hat{H}(t), \hat{\rho}(t) \right] \right\}. \tag{54}$$

After some algebra, it is possible to recast the trace operator in (54) as an expectation value in the state $\hat{\rho}(t)$,

$$\mathrm{Tr} \left\{ \hat{A} \left[\hat{H}, \hat{\rho} \right] \right\} = \left\langle \left[\hat{A}, \hat{H} \right] \right\rangle_{\hat{\rho}(t)}, \tag{55}$$

where we have used the cyclic property of the trace operator. Finally, the last expression allows us to recover the Ehrenfest theorem from the the Q-FDT

$$\frac{d}{dt} \left\langle \hat{A}(t) \right\rangle_{\hat{\rho}(t)} = \left\langle \frac{\partial \hat{A}(t)}{\partial t} \right\rangle_{\hat{\rho}(t)} + \frac{1}{i\hbar} \left\langle \left[\hat{A}, \hat{H} \right] \right\rangle_{\hat{\rho}(t)}. \tag{56}$$

6. Generalized MaxEnt density matrix identities

Given a set $\{\alpha_i\}_{i=1,\ldots,n}$ of statistical-like parameters, and another set $\{\lambda_i\}_{i=1,\ldots,m}$ of quantum-like parameters, we can generalize the results of the previous sections introducing a *generalized* density matrix of the form

$$\hat{\rho}(\alpha_1, \ldots, \alpha_n; \lambda_1, \ldots, \lambda_m) = \frac{1}{\mathcal{Z}(\alpha_1, \ldots, \alpha_n; \lambda_1, \ldots, \lambda_m)} \exp \left[-\sum_{j=1}^{n} \alpha_j \hat{F}_j (\lambda_1, \ldots, \lambda_m) \right], \tag{57}$$

where $\left\{ \hat{F}_j \right\}_{j=1,...,n}$ is a set of observables acting on the Hilbert space $\mathcal{H}$ of states of the system (e.g. Hamiltonian, number operator, etc.). These observables are compatible with each other and may depend on one or more quantum-like parameters. It is important to notice that the statistical-like parameters depend on the statistical model only and appear as Lagrange multipliers associated with certain constraints in the MaxEnt procedure, while the quantum-like parameters are related to the particular features of the system, and some of them can be contained in the Hamiltonian or other observables of the system (e.g., perturbation parameters). We have used the appellative *generalized* for the density matrix in the sense given in Ref. [6]: within the approach of MaxEnt inference not only does it have the Hamiltonian the prime role, but all the observables in the set $\left\{ \hat{F}_j \right\}_{j=1,...,n}$ possess equal weight.

The entropy associated to such a generalized density matrix is obtained through the von-Neumann entropy (2), which in this case is given by

$$S = \sum_{j=1}^{n} \alpha_j \left\langle \hat{F}_j \right\rangle_{\hat{\rho}} + \ln \mathcal{Z} \left(\alpha_1, ..., \alpha_n; \lambda_1, ..., \lambda_m \right). \tag{58}$$

We can easily identify the canonical and the grand-canonical cases encoded in the entropy Eq. (58). For instance, considering only one statistical-like parameter α and setting it equal to the inverse temperature β, and choosing $\hat{F} = \hat{H}$, we obtain

$$-kT \ln \mathcal{Z}(\beta; \lambda_1, ..., \lambda_m) = E - TS = \mathcal{F} \tag{59}$$

where $\mathcal{F}$ is the Helmholtz free energy (26). On the other hand, if we consider two statistical-like parameters, namely, $\alpha_1 = \beta$ and $\alpha_2 = -\beta\mu$, and setting $\hat{F}_1 = \hat{H}$ and $\hat{F}_2 = \hat{N}$ for the corresponding observables, we can recover the grand-canonical equation of state

$$\ln \Xi(\beta, \mu; \lambda_1, ..., \lambda_m) = \frac{pV}{kT} = -\frac{\Phi}{kT}, \tag{60}$$

where $\Xi(\beta, \mu; \lambda_1, ..., \lambda_m)$ and Φ are the grand partition function and the grand potential, respectively.

In order to obtain generalized FD identities using the MaxEnt density matrix, it is necessary to bear in mind the different choices for the continuous parameter γ_k in the Q-FDT, i.e., $\gamma_k \in \{\alpha_1, ..., \alpha_n\} \cup \{\lambda_1, ..., \lambda_m\}$, with $k \in \{1, 2, ..., n, n+1, ..., n+m\}$. In this way we have the following ordering of parameters:

$$\gamma_1 = \alpha_1, \gamma_2 = \alpha_2, ..., \gamma_n = \alpha_n, \gamma_{n+1} = \lambda_1, ..., \gamma_{n+m} = \lambda_m. \tag{61}$$

Using the model given by (57) in (13) we obtain the Q-FDT in its generalized form:

$$\frac{\partial}{\partial \gamma_k} \left\langle \hat{A} \right\rangle_{\hat{\rho}} = \left\langle \frac{\partial \hat{A}}{\partial \gamma_k} \right\rangle_{\hat{\rho}} - \sum_{j=1}^{n} \left\langle \hat{A} \frac{\partial}{\partial \gamma_k} \left(\alpha_j \hat{F}_j \right) \right\rangle_{\hat{\rho}} - \frac{\partial \ln \mathcal{Z}}{\partial \gamma_k} \left\langle \hat{A} \right\rangle_{\hat{\rho}}, \tag{62}$$

where $\hat{A}$ is an observable depending on quantum-like parameters only and must be compatible with the generalized density matrix $\hat{\rho}$. As in the previous section, we can

choose different operators for the observable $\hat{A}$. The results for $\hat{A} = \mathbb{1}$ and $\hat{A} = \hat{F}_k$, for both types of continuous parameters, are summarized in Table 3. These four cases encode all the possibilities for the Q-FDT. As a result of introducing a generalized density matrix, we have gained breath and depth: breadth because we can see all the above fluctuation-dissipation identities, using both the canonical and grand canonical models, as particular instances of Eq. (62); depth by being able to frame several quantum-statistical identities within an inferential-statistic (and Bayesian) framework.

Consider the first row in Table 3 for $\hat{A} = \mathbb{1}$. We have for the pairs $(\mathbb{1}, \lambda_k)$ and $(\mathbb{1}, \alpha_k)$ the identities

$$\sum_{j=1}^{n} \alpha_j \left\langle \frac{\partial \hat{F}_j}{\partial \lambda_k} \right\rangle_{\hat{\rho}} = -\frac{\partial \ln \mathcal{Z}}{\partial \lambda_k} \tag{63}$$

and

$$\left\langle \hat{F}_k \right\rangle_{\hat{\rho}} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha_k}, \tag{64}$$

where Eq. (63) is a generalization of the thermodynamic integration formula for n Lagrange multipliers, while Eq. (64) establishes a relation between the mean value of the *kth* observable of the set with its respective conjugate variable (parameter). It is worth mentioning that Eq. (64) agrees with the identity previously obtained, by means of maximum-entropy inference by E. T. Jaynes in the reference [8]. That is how our approach differs from previous approaches: not only are we using a density matrix coming from a MaxEnt procedure, but we are also systematizing all the FD identities within the same general theorem (Eq. (13)).

Finally, for the pairs $(\hat{F}_k, \lambda_l)$ and $(\hat{F}_k, \alpha_l)$ in the second row of Table 3 we have the following identities:

$$\frac{\partial}{\partial \lambda_l} \left\langle \hat{F}_k \right\rangle_{\hat{\rho}} = \left\langle \frac{\partial \hat{F}_k}{\partial \lambda_l} \right\rangle_{\hat{\rho}} - \sum_{j=1}^{n} \alpha_j \operatorname{Cov}\left(\hat{F}_k, \frac{\partial \hat{F}_j}{\partial \lambda_l} \right) \tag{65}$$

and

$$\frac{\partial}{\partial \alpha_l} \left\langle \hat{F}_j \right\rangle_{\hat{\rho}} = -\operatorname{Cov}\left(\hat{F}_j, \hat{F}_l \right), \tag{66}$$

where

$$\begin{aligned} \operatorname{Cov}\left(\hat{F}_k, \hat{F}_l \right) &\equiv \left\langle \Delta \hat{F}_k \Delta \hat{F}_l \right\rangle_{\hat{\rho}} \\ &= \left\langle \hat{F}_k \hat{F}_l \right\rangle_{\hat{\rho}} - \left\langle \hat{F}_k \right\rangle_{\hat{\rho}} \left\langle \hat{F}_l \right\rangle_{\hat{\rho}} \end{aligned} \tag{67}$$

are the covariances between the observables $\hat{F}_k$ and $\hat{F}_l$ in the quantum state $\hat{\rho}$. We observe that Eq. (65) is the generalization of the identity (32) for n different Lagrange multipliers while, Eq. (66) sets up a generalization of the thermodynamical-like FD identities (cf. Eqs (36) for the canonical model, and Eqs. (46), (48) and (49) for the grand canonical model).

Operator	$\gamma_k = \lambda_k$ (quantum-like parameter)	$\gamma_k = \alpha_k$ (statistical-like parameter)
$\hat{A} = \mathbb{1}$	$\sum_{j=1}^{n} \alpha_j \left\langle \dfrac{\partial \hat{F}_j}{\partial \lambda_k} \right\rangle_{\hat{\rho}} = -\dfrac{\partial \ln \mathcal{Z}}{\partial \lambda_k}$	$\left\langle \hat{F}_k \right\rangle_{\hat{\rho}} = -\dfrac{\partial \ln \mathcal{Z}}{\partial \alpha_k}$
$\hat{A} = \hat{F}_k$	$\dfrac{\partial}{\partial \lambda_l} \left\langle \hat{F}_k \right\rangle_{\hat{\rho}} = \left\langle \dfrac{\partial \hat{F}_k}{\partial \lambda_l} \right\rangle_{\hat{\rho}} - \sum_{j=1}^{n} \alpha_j \, \mathrm{Cov}\left(\hat{F}_k, \dfrac{\partial \hat{F}_j}{\partial \lambda_l} \right)$	$\dfrac{\partial}{\partial \alpha_l} \left\langle \hat{F}_j \right\rangle_{\hat{\rho}} = -\mathrm{Cov}\left(\hat{F}_j, \hat{F}_l \right)$

Table 3: *Generalized fluctuation-dissipation identities. Depending on the type of the continuous parameter γ_k and the choice of the observable, we obtain four different cases.*

7. Concluding remarks

In this work we derived the fluctuation-dissipation theorem coming from Bayesian statistics in the language and rules of quantum mechanics, and we exposed the usefulness of this, the Q-FDT, by including all the thermodynamical-like FD identities, among others, *beneath its shade.*

A prospective and interesting challenge would be exploring the scope of another kind of expectation identities, such as the *conjugate-variables* identities, in quantum statistics. In this sense, we would have a complete program of Bayesian expectation identities in the context of quantum statistical mechanics.

8. Acknowledgments

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