

# An effective Hamiltonian for the simulation of open quantum molecular systems

Luigi Delle Site\*  and Ana Djurdjevac

Freie Universität Berlin, Department of Mathematics and Computer Science, Berlin, Germany

E-mail: [luigi.dellesite@fu-berlin.de](mailto:luigi.dellesite@fu-berlin.de) and [adjurdjevac@zedat.fu-berlin.de](mailto:adjurdjevac@zedat.fu-berlin.de)

Received 9 January 2024; revised 4 May 2024

Accepted for publication 24 May 2024

Published 12 June 2024



CrossMark

## Abstract

We discuss the derivation of an effective Hamiltonian for open quantum many-particle systems. The aim is to define an operator that can be used for (molecular) simulations where, through the exchange of energy and matter with the surrounding environment (reservoir), the number of particles,  $n$ , becomes a variable of the problem. The Hamiltonian is formally derived from the Von Neumann equation; specifically, we derive an  $n$ -hierarchy of equations for the density matrix,  $\hat{\rho}_n$ , for near equilibrium situations. Such a hierarchy, in case of stationary equilibrium, delivers the standard grand canonical density matrix as it would be expected. We report that a similar Hamiltonian was conjectured, from empirical considerations, in the field of superconductivity. Thus our result also provide a formal basis for this long-standing hypothesis. Finally, an application is discussed for Path Integral simulations of molecular systems.

Keywords: open systems, quantum many-particle systems, Von Neumann equation, molecular dynamics schemes

## 1. Introduction

The simulation of open quantum many-particle systems that exchange matter with the environment is becoming a pressing request by modern research and associated technology (see e.g. [1] and references therein). In current research a systematic description of an open quantum system derived from the Von Neumann equation. i.e. from first principles, is achieved by the Lindblad equation and related approaches [2–4]. However, the equation is used mostly for

\* Author to whom any correspondence should be addressed.



Original Content from this work may be used under the terms of the [Creative Commons Attribution 4.0 licence](https://creativecommons.org/licenses/by/4.0/). Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

problems of transport (see e.g. [2–7] and references therein) and, at the best of our knowledge, does not describe the situation of open systems in equilibrium with a reservoir where the number of particles naturally fluctuates in a grand canonical fashion [2, 3, 8]. On the other hand, an effective Hamiltonian for open quantum systems in equilibrium with a particle's reservoir has been conjectured long time ago in the field of superconductivity; such a conjecture is based on physical intuition, but so far has not been explicitly derived from the Von Neumann equation (see e.g. [9, 10]). Systems in equilibrium are of high interest in current research thus, the key question to address is whether it is possible to explicitly derive an  $n$ -dependent operator, with  $n$  being the variable number of particles, physically consistent and mathematically well defined, so that one can treat the evolution of a system that exchanges energy and matter with a bath at equilibrium or near equilibrium and as a consequence is characterized by particle number fluctuations that are not induced by any external source. For near equilibrium it is meant that the deviation from equilibrium can be eventually added to the system as a (small) perturbation

As an example of system of interest, a relevant class of problems that falls in the category is that of numerical algorithms for *ab initio* molecular dynamics for open molecular systems [1, 11, 12]. In such systems, within the Born–Oppenheimer approximation [13], that is under the hypothesis of nuclear and electronic scale separation, nuclei are considered classical objects while electrons are treated at quantum mechanical level; these latter require a proper quantum treatment as open system and a corresponding numerical prescription for calculations. This field is, in our view, still in its infancy, since most of the current open-system *ab initio* algorithms are built on empirical basis and thus are often numerically not reliable [14] due to conceptual inconsistencies that lead to incorrect statistical sampling [1, 15]. This means that the construction of a solid theoretical framework would assure physical consistency and computational robustness to the underlying numerical methods, as it occurred for molecular dynamics of classical and semi-classical open systems with a system-reservoir exchange of particles [16–20].

Using basic statistical mechanics arguments, for the *ab initio* treatment of open molecular systems the following condition has been proposed: the electronic chemical potential of the open system must have the same value of the electronic chemical potential of reference (i.e. of a large system)[12]; the results of this work provides an explicit formal justification to the idea described above. Furthermore, the current model sets the formal basis for moving beyond equilibrium by adding, on the equilibrium set up, possible physical perturbations to the molecular system.

Actually, in molecular simulations of open systems where the quantum effects of spatial delocalization of atoms in space are included, the numerical algorithm makes use of the effective Hamiltonian derived in this work. This specific example of practical application will be explicitly discussed in the paper. From the conceptual point of view, the key aspect at the basis of this work, is that for situations of equilibrium or near equilibrium, the fundamental principles of quantum statistical mechanics state that the density matrix of a quantum system takes the form of a grand canonical operator (see e.g. [21]). In this context, the necessary request to assure physical consistency for an equation with system-reservoir exchange of particles is that it should deliver the grand canonical density matrix in the limiting case of full statistical equilibrium. As anticipated above, interestingly, from empirical considerations within the framework of statistical mechanics, N.N.Bogoljubov in the treatment of superconductivity introduced a scalar parameter (identified *a posteriori* as the chemical potential of the system) associated to the particle number operator with the task of fixing the particle's number variation and conjectured an effective Hamiltonian for open systems with similar form as the one that we will derive here [9, 10]. However, in our work, differently from the empirical derivation of [9, 10], we propose a formal derivation of the effective Hamiltonian starting

from the Von Neumann equation for the density matrix of the entire system. Next, having in mind systems typically treated in molecular simulations, we integrate out the degrees of freedom of the bath region and derive an  $n$ -hierarchy of equations for the density matrix of the subsystem of interest,  $\hat{\rho}_n$ . This procedure is conceptually equivalent to the procedure followed for the Liouville equation in the classical case [16, 17] developed within the framework of molecular dynamics [22]. The novelty of our proposal lies in the explicit (step-by-step) formal derivation of the equation from first principles, having in mind a molecular system for numerical simulations. The relevant implication is that the procedure employed allows us to explicitly define the physical conditions of validity of the model; this aspect may be rather relevant in a computational set up. It must be noticed that, in our knowledge, the principle that the grand canonical density matrix should be **automatically and explicitly** obtained from the Von Neumann equation in the limiting case of equilibrium has not been applied to any of the currently used quantum master equations where the number of particles are a variable of the problem.

## 2. Quantum grand canonical ensemble

In statistical mechanics, an open system of particles,  $S$ , that exchanges energy and matter in equilibrium with a reservoir  $B$ , is characterized by a grand canonical density matrix:  $\hat{\rho}_n = \frac{1}{Q_{GC}} \exp(-\frac{1}{kT}(\hat{H}_n - \mu\hat{n}))$ , where  $\hat{H}_n$  is the Hamiltonian operator at  $n$  particles in the system  $S$ , where  $n$  is a variable quantity and  $\hat{n}$  the number operator that counts the number of particles in a given quantum state. Finally,  $\mu$  is the chemical potential, that is a quantity that regulates the exchange of particles with the bath and  $Q_{GC}$  a normalization factor. In essence,  $\mu$  can be seen as a rate of change of the free energy of the system w.r.t. the change of number of particles, and  $\hat{n}$ , the particle number operator [21]. This latter, in a Fock space formalism, is defined as [23]  $\hat{n} = \sum_k \hat{n}_k$  and  $\hat{n}_k = \hat{a}_k^\dagger \hat{a}_k$ , with  $\hat{a}_k^\dagger$  and  $\hat{a}_k$  the creation and annihilation operators that act on the  $k$ -orbital of a particle wavefunction, (with basis set  $\phi_1, \phi_2, \dots, \phi_m$ ),  $|\psi\rangle = |\phi_1 \dots \phi_{k-1}, \phi_k, \phi_{k+1} \dots \phi_m\rangle$  so that  $\hat{a}_k |\phi_1 \dots \phi_{k-1}, \phi_k, \phi_{k+1} \dots \phi_m\rangle = \sqrt{n_k} |\phi_1 \dots \phi_{k-1}, \phi_{k+1} \dots \phi_m\rangle$  and  $\hat{a}_k^\dagger |\phi_1 \dots \phi_{k-1}, \phi_{k+1} \dots \phi_m\rangle = \sqrt{n_k+1} |\phi_1 \dots \phi_{k-1}, \phi_k, \phi_{k+1} \dots \phi_m\rangle$ , so that  $\hat{n}_k |\psi\rangle = n_k |\psi\rangle$  with  $n_k$  the number of particles in the  $k$ -orbital of the many-particle wave function  $|\psi\rangle$ .

## 3. Quantum equation in the limiting case of equilibrium: grand canonical operator

The approach employed in this work to derive a quantum equation for the density matrix of a (sub-)system embedded in a large reservoir of energy and particles starts from the Von Neumann equation [24] for the density matrix  $\hat{\rho}$  of a (large) total system with a given Hamiltonian  $\hat{H}$ :

$$i\hbar \frac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}]. \quad (1)$$

In the following, instead of a pure dynamical view, as done for example in the derivation of the Lindblad equation, we consider a statistical view, that is consider a partitioning of the total system with  $N$  particles in a subsystem  $S$  with  $n$  particles and a reservoir  $B$  with  $N - n$  particles, as done for the Liouville equation in the case of classical systems [16, 17]. Next we trace out the degrees of freedom of  $B$  in the Von Neumann equation, considering all the partitioning of

$N$  particles in  $n$  and  $N - n$  sets. The result is a hierarchy of equations for  $\hat{\rho}_n(t) = \frac{N!}{(N-n)!n!} \hat{\rho}_S(t)$ , which in the case of stationary state of equilibrium must deliver the grand canonical density matrix:  $\hat{\rho}_n = \frac{1}{Q_{GC}} \exp(-\frac{1}{kT}(\hat{H}_n - \mu\hat{n}))$  as a solution. For hierarchy here is meant that one obtains a set of equations, one for each value of  $n$ , so that the  $n$ -dimensional operator  $\hat{\rho}_n$  represents the  $n$ -fluctuating ensemble for the open system.

### 3.1. Partitioning the total system into a system of interest and reservoir

We consider the following Hamiltonian for the total system:  $\hat{H} = \hat{H}_S \otimes \mathbb{1}_B + \mathbb{1}_S \otimes \hat{H}_B + \hat{H}_{int}$ ; where the notation  $\mathbb{1}_S$  and  $\mathbb{1}_B$  represent the identity operator of the Hilbert space associated to the domain  $S$  and  $B$  respectively. In essence, we consider the total Hamiltonian partitioned in the Hamiltonian of particles in  $S$ , the Hamiltonian of the particles in  $B$  and the Hamiltonian of interaction between the particles of  $S$  and  $B$ .

We assume  $||\hat{H}_{int}|| \ll ||\hat{H}_S||$  always, this is the so-called surface-to-volume ratio approximation used in the statistical derivation of grand canonical ensemble that can be found in the most popular textbooks of statistical mechanics (see e.g. [21]). In essence, one neglects the direct interaction between  $S$  and  $B$  and considers the total Hamiltonian partitioned between the part of  $S$  and the part of  $B$ :  $\hat{H} = \hat{H}_S \otimes \mathbb{1}_B + \mathbb{1}_S \otimes \hat{H}_B = \hat{H}_n \otimes \mathbb{1}_B + \mathbb{1}_S \otimes \hat{H}_{N-n}$ , thus the particle exchange between  $S$  and  $B$  happens according to the balance of free energy between  $S$  and  $B$ . The free energy of  $S$  and the free energy of  $B$  are characterized by the particle-particle interactions between particles only in  $S$  and particles only in  $B$  respectively, and by a particle-particle interaction between particles in  $S$  and particles in  $B$  (direct interactions). Under the hypothesis that  $S$  is large enough, the direct particle-particle interaction between  $S$  and  $B$  is negligible compared to the effect of all the other interactions, e.g. surface-to-volume ratio hypothesis (see e.g. [21]). The density matrix of the whole system needs to be defined according to the partitioning in a system  $S$  with  $n$  (instantaneous) particles and a bath  $B$  with  $N - n$  (instantaneous) particles, this means that, for indistinguishable particles, one must consider all possible partitioning (realizations) of  $N$  in  $n$  particles for  $S$  and  $N - n$  particles for  $B$ , i.e.  $\frac{N!}{(N-n)!n!}$ . It follows that a consistent definition of the total density matrix is (see also [16]):

$$\hat{\rho} = \frac{N!}{(N-n)!n!} \hat{\rho}_{S_n} \hat{\rho}_{B_{N-n}} \quad (2)$$

with  $\hat{\rho}_{S_n}$  being the  $n$ -realization of the density matrix that represents  $S$  and  $\hat{\rho}_{B_{N-n}}$  the corresponding  $N - n$ -realization of the density matrix that represents  $B$ .

We then define:

$$\hat{\rho}_n = \text{Tr}_B \frac{N!}{(N-n)!n!} \hat{\rho}_{S_n} \hat{\rho}_{B_{N-n}}. \quad (3)$$

At this point we make a first step in the modeling, that is we employ the Born–Markov approximation [25]:  $\hat{\rho}(t) = \frac{N!}{(N-n)!n!} \hat{\rho}_{S_n}(t) \otimes \hat{\rho}_{B_{N-n}}(0)$ , with  $\text{Tr}_B \hat{\rho}_{B_{N-n}}(0) = 1 \forall n$ . In essence we assume that the bath is large enough and thermodynamically in a stationary state where the exchange of particle with  $S$  can be ignored (for the properties of  $B$ ). One can formally see it also in the following manner: one can write  $\hat{\rho}_B = \frac{1}{Q_B} \hat{\gamma}_B$ , where  $Q_B$  is the partition function of  $B$ , that is:  $Q_B = \text{Tr}_B \hat{\gamma}_B$  and  $\hat{\gamma}_B$  is the density matrix operator of  $B$  not normalized, for example in the canonical form:  $\hat{\gamma}_B = e^{-\beta H_B}$ . It is known from statistical mechanics that  $-kT \ln Q_B = F_B$  which is the free energy of  $B$ . Since we assumed that  $B$  is large enough and in equilibrium so that its properties do not significantly change with time, then the exchange of particles with  $S$

can be ignored (w.r.t. the properties of  $B$ ), thus  $F_B$  can be considered constant and thus independent of  $N - n$ , it follows:  $\text{Tr}_B \hat{\rho}_B(0) = 1$ . The followed approach corresponds to the standard procedure of statistical mechanics when the grand canonical partition function is derived from statistical considerations (see e.g. [21]). Proceeding further with the model, since this is a statistical approach where in  $S$  the particle number  $n$  can take values from zero to  $N$ , one has to count all such possible realizations in the ensemble and thus:  $\sum_{n=0,N} \text{Tr} \hat{\rho}_n = 1$ , which implies that  $\text{Tr} \hat{\rho} = \sum_{n=0,N} \text{Tr}_S \text{Tr}_B \frac{N!}{(N-n)!n!} \hat{\rho}_{S_n} \hat{\rho}_{B_{N-n}} = 1$ , as it occurs in a grand-canonical ensemble [16, 21].

In the next to avoid a heavy formalism we will indicate  $S$  for the system and  $B$  for the bath without carrying further the particle number label  $n$  and  $N - n$ .

At this point, in order to reduce equation (1) only to the degrees of freedom of  $S$ , we integrate both sides of the equation w.r.t. the degrees of freedom of  $B$ , that is we calculate the trace over  $B$ :

$$i\hbar \frac{d\text{Tr}_B \hat{\rho}}{dt} = \text{Tr}_B [\hat{H}, \hat{\rho}]. \quad (4)$$

Due to additivity of the Lie bracket, the r.h.s of equation (4) becomes  $\text{Tr}_B [\hat{H}_n \otimes \mathbb{1}_B + \mathbb{1}_n \otimes \hat{H}_{N-n}, \hat{\rho}_n \otimes \hat{\rho}_B] = \text{Tr}_B [\hat{H}_n \otimes \mathbb{1}_B, \hat{\rho}_n \otimes \hat{\rho}_B] + \text{Tr}_B [\mathbb{1}_n \otimes \hat{H}_{N-n}, \hat{\rho}_n \otimes \hat{\rho}_B]$ .

We have:  $\text{Tr}_B [\hat{H}_n \otimes \mathbb{1}_B, \hat{\rho}_n \otimes \hat{\rho}_B] = [\hat{H}_n, \text{Tr}_B(\hat{\rho}_n \otimes \hat{\rho}_B)] = [\hat{H}_n, \hat{\rho}_n]$ . For the next term we have:  $\text{Tr}_B [\mathbb{1}_n \otimes \hat{H}_{N-n}, \hat{\rho}_n \otimes \hat{\rho}_B] = \text{Tr}_B(\hat{H}_{N-n} \hat{\rho}_B) \hat{\rho}_n - \hat{\rho}_n \text{Tr}_B(\hat{\rho}_B \hat{H}_{N-n})$ .

It can be noticed that  $\text{Tr}_B(\hat{H}_{N-n} \hat{\rho}_B)$  and  $\text{Tr}_B(\hat{\rho}_B \hat{H}_{N-n})$  are nothing else than the ensemble averaged energy of  $B$ , which we denote by  $\langle E_B \rangle$ . This quantity depends on the number of particles of  $S$  and  $B$  (i.e.  $n$  and  $N - n$ ). Here comes the crucial point of our modeling proposal, as explained below.  $\langle E_B(N - n) \rangle$  is an unknown function of the variable  $n$ , if we consider the situation of equilibrium between  $S$  and  $B$ , then we can reasonably expand the energy of  $B$  in Taylor series at the first order:

$$\langle E_B(N - n) \rangle = \langle E_B(N) \rangle + \left. \frac{\partial \langle E_B(N - n) \rangle}{\partial n} \right|_{n \ll N} n. \quad (5)$$

The term  $\langle E_B(N - n) \rangle$  is not known explicitly, the term  $\langle E_B(N) \rangle$  is not crucial since this is a constant that can be considered as the zero of the energy scale, instead  $-\left. \frac{\partial \langle E_B(N - n) \rangle}{\partial n} \right|_{n \ll N}$  is actually an explicitly known quantity that characterizes the thermodynamics of the system. It corresponds, by definition, to the chemical potential  $\mu$ , at constant entropy and volume for  $B$  (since we consider  $B$  in stationary equilibrium, see also [26]). It must be noticed, as expressed in the formalism above, that the expansion in  $n$  must not be seen as  $n \rightarrow 0$ , but as an expansion in the limit  $N \gg n$ , so that effectively  $n$  is negligible compared to  $N$ . This hypothesis implies that the effects of a variation of  $n$  on the physics of  $B$  is negligible, that is the macroscopic properties of  $B$  are determined as if  $B$  was a canonical ensemble with, effectively, a fixed number of particles  $N$  (see e.g. [21]). In practical terms, the validity of equation (5) strongly relies on considering a large  $B$  for which the variation of its macroscopic physical quantities, due to a variation of  $n$ , is negligible w.r.t. the numerical accuracy chosen for the calculations of physical quantities in the open system.

Moreover, the term  $-\left. \frac{\partial \langle E_B(N - n) \rangle}{\partial n} \right|_{n \ll N} n = \mu n$  must be interpreted within the framework of quantum statistical mechanics, that is,  $n$  in equation (5) must be considered as an operator,  $\hat{n}$ , which, at given thermodynamic conditions consistent with  $\mu$ , counts the number of particles of the corresponding quantum state of  $S$ . Next, we notice that while  $B$  is considered large enough so that the change of number of particles, from the physical point of view does not affect its properties (as it was at fixed number of particles), the same cannot be said for  $S$ . In fact, a change of number of particles carries sizable fluctuations in the statistical properties of  $S$  since

$\langle E_B(N-n) \rangle$  enters into equation (4) ‘acting on’  $\hat{\rho}_S$ . Thus for situations close to equilibrium equation (4) is reduced to:

$$i\hbar \frac{d\hat{\rho}_n}{dt} = [\hat{H}_n - \mu\hat{n}, \hat{\rho}_n] \quad (6)$$

and for the exact equilibrium with  $\frac{d\hat{\rho}_n}{dt} = 0$ , one would recover the grand canonical density matrix for  $S$ :  $\hat{\rho}_n = \frac{1}{Q_{GC_S}} e^{-\frac{1}{kT}(\hat{H}_n - \mu\hat{n})}$  as a solution, with  $Q_{GC_S} = \sum_{n=0}^{\infty} \text{Tr}_S[e^{-\frac{1}{kT}(\hat{H}_n - \mu\hat{n})}]$ . Note that equation (6) leads to a solution for  $\hat{\rho}_n$  that preserves the trace as:  $\sum_{n=0}^{\infty} (\text{Tr}_S \hat{\rho}_n) = 1$ .

The correspondence between classical and quantum statistical mechanics used above to expand  $\langle E_B(N-n) \rangle$  and write it in operator form is the main proposal of our model; it is inspired by the procedure usually used in literature to define statistical and thermodynamic quantities in quantum mechanics starting from the known classical case [21]. Once the model above is accepted, near equilibrium one may add any source of energy of (small) perturbation (e.g. particle current, heat, external fields) on the r.h.s. of equation (6). The meaning of ‘near equilibrium’ varies from system to system and problem to problem, a general criterion would be to consider perturbations that lead to a linear response with an input/perturbation of energy, with respect to the energy of equilibrium of the system, within a certain threshold, so that the physical hypothesis of ‘small perturbation’ holds (e.g. 10% of energy input/output, see e.g. [27]). The extended equation would then allow for a larger set of possibilities compared to the physical situations treatable by other approaches, e.g. the standard Lindblad equation.

### 3.2. Empirical derivation of $\hat{H} - \mu\hat{n}$ v.s. our first principles derivation

As anticipated above, an effective Hamiltonian similar to our result,  $\hat{H}_{GC} = \hat{H} - \mu\hat{n}$  was conjectured by Bogoljubov in the framework of superconductivity for open quantum systems. The argument used for advancing such a proposal is based on the physical intuition that the result obtained from the canonical ensemble can be carried over to the grand canonical ensemble by extending the canonical Hamiltonian with a term that regulates the variation of number of particles at the rate expressed by the chemical potential,  $\mu$ , as known from thermodynamics. That is, it seems reasonable to define a grand canonical effective Hamiltonian:  $\hat{H}_{GC} = \hat{H} - \mu\hat{n}$  so that for similarity to the canonical density matrix,  $\hat{\rho}_C = e^{-\beta\hat{H}}$ , one would obtain:  $\hat{\rho}_{GC} = e^{-\beta\hat{H}_{GC}} = e^{-\beta(\hat{H} - \mu\hat{n})}$ , that is the well known result of statistical mechanics regarding the grand canonical density matrix. It must be added that in literature the results of quantum statistical mechanics are derived through a formal similarity to the classical results, that is, the canonical or grand canonical density matrix are a formal extensions of the classical results to the Hilbert space (see e.g. [28] and references therein). In this sense, the Hamiltonian  $\hat{H}_{GC} = \hat{H} - \mu\hat{n}$ , in [9, 10], is based on an empirical formal extension of a classical result, it is not derived from a rigorous first principles equation of quantum mechanics (Von Neumann equation).

The approach shown here instead is not empirical in such sense, in fact we start from the Von Neumann equation, that is an equation that expresses the very nature of a quantum system, divide the system in an open system and a large reservoir, make physical hypothesis about the reservoir and integrate its degrees of freedom in the equation. The relevant consequence is that the chemical potential is not empirically ‘imposed’ *a priori*, but is formally obtained as a result of the integration of the reservoir (as the constant of the first order expansion in the number of particles for the system-reservoir coupling). This means that we do not impose the grand canonical density matrix as a constraints of our model, instead we verify that our



Hamiltonian automatically leads to the grand canonical density matrix as a natural solution of the Von Neumann equation for an open system in a stationary state.

In essence, our procedure embeds a formal justification of the empirical model of [9, 10]. Furthermore it clarifies that  $\hat{H} - \mu\hat{n}$  is a first order approximation within the system-reservoir coupling and the error is in the truncation terms of the Taylor series w.r.t. the number of particles of the open system.

It is important to notice that while, for technical reasons,  $\hat{H}_{GC} = \hat{H} - \mu\hat{n}$ , may be popular in fields such as theory of superconductivity, for quantum molecular simulations this Hamiltonian has not been considered yet, except in this work (see the next section). In fact in simulations, the variation of number of particles is implemented through a stochastic process within a Monte Carlo approach (see e.g. [29]), where particles are inserted or deleted according to the chemical potential. Instead,  $\hat{H}_{GC} = \hat{H} - \mu\hat{n}$ , as derived by us, allows for a fully dynamic picture, without the need of separating the purely dynamic part, generated by  $\hat{H}$ , with a stochastic part regulated by  $\mu$ . As a practical conclusion, one of the major advantage of the extended Hamiltonian is that it allows for the possibility of designing very efficient Molecular Dynamics algorithms for open systems [1, 12, 22].

#### 4. Example of a practical application: path integral molecular dynamics of open systems

The Path Integral formalism of Feynman can be used in molecular dynamics (MD) to account for the quantum delocalization in space of atoms/atomic nuclei (quantum nuclear effects). The essence of the idea (for the specific details see the [appendix](#) or appendix C and D of [11]) is that the quantum Hamiltonian of an atomic or molecular system can be mapped onto an effective classical Hamiltonian where the atoms in MD, or the nuclei in *ab initio* electronic structure calculations, are represented as ring polymers with beads connected via springs. The three dimensional fluctuation in space of such polymer rings describes the quantum atomic or nuclear delocalization in space. Moreover, the sampling of configurations in space, via classical trajectories produced by the MD, results in the statistical sampling of the corresponding atomic/nuclear quantum density matrix. As a consequence any physical quantity averaged over the MD trajectory corresponds to the quantum average of the quantity in question. Of specific interest for us is the Hamiltonian used for doing such simulation in the case of open systems that exchange energy and matter with a reservoir. In fact, in such simulations [30] the effective classical Hamiltonian contains an additional one-particle potential term that acts (mostly) at the border between the molecular system and the reservoir and regulates the system-reservoir exchange of particles. The system-reservoir exchange occurs in a way that the resulting statistics reproduces the Grand Canonical distribution at the (correct) chemical potential of the system, this latter corresponds approximately to the statistical average of the one-particle potential. In formal terms, the MD of the polymer rings (i.e. the effective classical simulation on which the quantum Hamiltonian has been mapped) contains the standard path integral Hamiltonian plus an additional, one-particle potential term:  $H_{PI} - \sum_{i=1}^n \phi_i(x)$ , with  $\langle \phi_i(x) \rangle \approx \mu$  and  $n$  the instantaneous number of particles in the system [31–34]. The corresponding MD simulation, as explained above, samples effectively the quantum, grand canonical, density matrix of the molecular system.

As a matter of fact the classical Hamiltonian  $H_{PI} - \sum_{i=1}^n \phi_i(x)$ , since it samples the grand canonical distribution, consistently maps on an effective classical problem the Hamiltonian of an open quantum system in equilibrium, that is, it effectively maps the Hamiltonian of equation (6)  $\hat{H}_n - \mu\hat{n}$  in the stationary case of equilibrium.

In the path integral MD the term,  $\sum_{i=1}^n \phi_i(x)$ , as underlined above, regulates the net number of particles that according to the statistical rate ( $\mu$ , the chemical potential) is allowed to enter into/exit from the system so that the statistics satisfies the grand canonical distribution of equilibrium, which, effectively, is the quantum grand canonical density matrix:  $\hat{\rho}_n = \frac{1}{Q_{\text{GC}_S}} e^{-\frac{1}{kT}(\hat{H}_n - \mu\hat{n})}$ . In a quantum view of the molecular system, the equivalent of the action of  $\sum_{i=1}^n \phi_i$  is the action of the operator  $\mu\hat{n}$ , i.e. counting the instantaneous number of particles of the system according to the rate  $\mu$  so that it satisfies the grand canonical density matrix at equilibrium (i.e.  $[\hat{H}_n - \mu\hat{n}, \hat{\rho}_n] = 0$ ). As a consequence, the effective classical Hamiltonian in the path integral MD,  $H_{\text{PI}} - \sum_{i=1}^n \phi_i(x)$ , when mapped back to the quantum Hamiltonian is physically consistent with the expression:  $\hat{H} - \mu\hat{n}$  of equation (6). Furthermore, since  $\langle \phi_i(x) \rangle \approx \mu$ , one has that  $\langle \sum_{i=1}^n \phi_i(x) \rangle \approx \mu\langle n \rangle$  and accordingly in quantum terms one would have that  $\langle \psi | \mu\hat{n} | \psi \rangle = \mu\langle n \rangle$ , which enforces the statistical correspondence between the classical operator used in path integral simulations of open systems and the quantum operator derived in this work. In essence, the result of this paper gives the needed conceptual legitimization to an otherwise purely empirical numerical approach. Until now, due to the lack of conceptual justification for the effective Hamiltonian used, the application of the open system approach to Path Integral Molecular Dynamics has often required a case-by-case numerical validation. The numerical validation was done running additional and rather expensive full quantum simulations of large systems [19, 20, 30, 35, 36]. The conceptual justification of the effective Hamiltonian shown in this paper implies that a specific case-by-case numerical validation is not required.

## 5. Conclusions

We have addressed the problem of system-reservoir exchange of energy and particles for quantum systems with the aim of deriving an effective Hamiltonian for molecular simulations. We start from the Von Neumann equation for the density matrix of the whole (large) system, and model it according to the partitioning of the total system in a system of  $n$  variable particles and a large stationary reservoir; furthermore we focus on the situation of equilibrium or near equilibrium. Next, by integrating out the degrees of freedom of the environment we obtain an equation for the density matrix of the subsystem of interest carrying terms of interaction with the environment/reservoir. The result is a  $n$ -hierarchy of equations for the density matrix of the system  $\hat{\rho}_n$ , where  $n$  is the number of particles governed by an effective Hamiltonian,  $\hat{H}_n - \mu\hat{n}$ .

Since  $n$  is a variable quantity it follows that each  $\hat{\rho}_n$  represents one of the possible statistical realizations; in the limit of stationary equilibrium we recover a known solution, that is the grand canonical density matrix as it would be expected for naturally fluctuating open system in equilibrium. The procedure employed for the derivation of the hierarchy of equations is similar to the procedure employed for a system of classical particles [16, 17]; such a procedure was used as a theoretical platform to design algorithms of (classical) molecular simulation [22]. We have pointed out that our derivation can be also considered as the explicit formal derivation of a result that was empirically conjectured within the field of superconductivity and that, in addition, now can be extended to the larger field of quantum molecular simulations. At numerical level, the theoretical model proposed here already gives sufficiently solid ground to computational methods for studying open molecular systems. In order to support such a claim we discussed how the model proposed here forms the theoretical basis of algorithms that are successfully used in Path Integral simulations of open molecular systems. In perspective, the proposed model can be used as a theoretical basis for *ab initio* simulations of open systems where molecules explicitly carry electrons. Existing algorithms for such systems are based



on empirical considerations only [1, 12]. This field, despite its potential relevance, is, in our view, still in its infancy and the search for a solid formal ground with the associated conceptual development of the subject is highly desired.

### Data availability statement

No new data were created or analysed in this study.

### Acknowledgment

This work was supported by the DFG Collaborative Research Center 1114 ‘Scaling Cascades in Complex Systems’, Project No.235221301, Projects C01 (L D S) ‘Adaptive coupling of scales in molecular dynamics and beyond to fluid dynamics’ and C10 ‘Numerical Analysis for nonlinear SPDE models of particle systems’ (A Dj). Further support by the DFG, Project No.DE 1140/11-1, ‘Grand Canonical Adaptive Resolution Simulation for Molecules with Electrons’ (L D S) is acknowledged.

### Appendix. Path integral formalism and its application in molecular dynamics

In this section, we report the basic information about the the path integral formalism within the framework of quantum statistical mechanics and its implementation in Molecular Dynamics to simulate quantum spatial delocalization in space of atoms of nuclei. A more complete treatment can be found in [37].

The starting point is the Hamiltonian of a single particle subject to a potential  $U$ :

$$\hat{H} = \frac{\hat{p}^2}{2m} + U(\hat{x}) = \hat{K} + \hat{U}, \quad (7)$$

with  $\hat{K}$  and  $\hat{U}$  the kinetic and potential energy operators, respectively, fulfilling the commutation relation:  $[\hat{K}, \hat{U}] \neq 0$ . The element in the space representation of the density matrix are written as:

$$\rho(x, x') = \langle x' | e^{-\beta\mathcal{H}} | x \rangle. \quad (8)$$

$\hat{K}$  and  $\hat{U}$  do not commute, thus to the aim of feasible calculation the Trotter theorem is used. For two non-commuting operators,  $A$  and  $B$ , the Trotter theorem reads:

$$e^{\lambda(\hat{A}+\hat{B})} = \lim_{P \rightarrow \infty} \left[ e^{\frac{\lambda\hat{A}}{2P}} e^{\frac{\lambda\hat{B}}{P}} e^{\frac{\lambda\hat{A}}{2P}} \right]^P, \quad (9)$$

where  $P$  is known as the ‘Trotter number’. The application of the theorem to the density matrix element gives:  $\rho(x, x') = \lim_{P \rightarrow \infty} \langle x' | [e^{-\frac{\beta\hat{U}}{2P}} e^{-\frac{\beta\hat{K}}{P}} e^{-\frac{\beta\hat{U}}{2P}}]^P | x \rangle$ . Next, let us define the operator  $\hat{\Omega} = e^{-\frac{\beta\hat{U}}{2P}} e^{-\frac{\beta\hat{K}}{P}} e^{-\frac{\beta\hat{U}}{2P}}$ , then :

$$\rho(x, x') = \lim_{P \rightarrow \infty} \langle x' | \hat{\Omega}^P | x \rangle = \lim_{P \rightarrow \infty} \langle x' | \overbrace{\hat{\Omega}\hat{\Omega}\hat{\Omega}\hat{\Omega}\dots\hat{\Omega}}^P | x \rangle. \quad (10)$$

$P - 1$  insertions of the identity operator,  $\hat{I} = \int dx |x\rangle \langle x|$ , between each  $\hat{\Omega}$  gives:

$$\rho(x, x') = \lim_{P \rightarrow \infty} \int dx_2 \dots dx_P \times \langle x' | \Omega | x_P \rangle \langle x_P | \Omega | x_{P-1} \rangle \langle x_{P-1} | \dots | x_2 \rangle \langle x_2 | \Omega | x \rangle. \quad (11)$$

As a consequence, the calculation of the matrix elements is simplified:

$$\langle x_{k+1} | \hat{\Omega} | x_k \rangle = \langle x_{k+1} | e^{-\frac{\beta \hat{U}}{2P}} e^{-\frac{\beta \hat{K}}{P}} e^{-\frac{\beta \hat{U}}{2P}} | x_k \rangle.$$

Since  $\hat{U}|x_k\rangle = U(x_k)$ , one has:  $\langle x_{k+1} | e^{-\frac{\beta \hat{U}}{2P}} e^{-\frac{\beta \hat{K}}{P}} e^{-\frac{\beta \hat{U}}{2P}} | x_k \rangle = e^{-\frac{\beta U(x_{k+1})}{2P}} \langle x_{k+1} | e^{-\frac{\beta \hat{K}}{P}} | x_k \rangle e^{-\frac{\beta U(x_k)}{2P}}$ .

Concerning the kinetic operator, one introduces the identity operator in momentum space:

$I = \int dp |p\rangle\langle p|$  and, since  $\hat{K}|p\rangle = \frac{p^2}{2m}$ , it follows:  $\langle x_{k+1} | e^{-\frac{\beta \hat{K}}{P}} | x_k \rangle = \int e^{-\frac{\beta p^2}{2mP}} \langle x_{k+1} | p\rangle\langle p | x_k \rangle dp$ . Furthermore, through the relation between the position and momentum eigenstate:  $\langle x | p \rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{\frac{ipx}{\hbar}}$  one obtains:

$$\langle x_{k+1} | e^{-\frac{\beta \hat{K}}{P}} | x_k \rangle = \frac{1}{2\pi\hbar} \int dp e^{\frac{ip(x_{k+1}-x_k)}{\hbar}} e^{-\frac{\beta p^2}{2mP}}, \quad (12)$$

whose integration delivers the following expression:  $\langle x_{k+1} | e^{-\frac{\beta \hat{K}}{P}} | x_k \rangle = \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{1/2} e^{-\frac{mP}{2\beta\hbar^2}(x_{k+1}-x_k)^2}$  and, by substituting in the expression of the density matrix, one obtains:

$$\begin{aligned} \rho(x, x') &= \lim_{P \rightarrow \infty} \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2} \int dx_2 \dots dx_P \\ &\times \exp\left(-\frac{1}{\hbar} \sum_{k=1}^P \left[ \frac{mP}{2\beta\hbar} (x_{k+1} - x_k)^2 + \frac{\beta\hbar}{2P} (U(x_{k+1}) + U(x_k)) \right]\right) \Bigg|_{x_1=x}^{x_{P+1}=x'}. \end{aligned} \quad (13)$$

The partition function of the system is calculated as the trace of the density matrix within a certain interval  $[0, L]$  (the linear size of the box containing the particle):

$$Z = \int_0^L dx \langle x | e^{-\beta \hat{H}} | x \rangle = \int_0^L dx \rho(x, x). \quad (14)$$

in explicit terms:

$$Z = \lim_{P \rightarrow \infty} \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2} \int_{D(L)} dx_1 \dots dx_P \times \exp\left(-\frac{1}{\hbar} \sum_{k=1}^P \left[ \frac{mP}{2\beta\hbar} (x_{k+1} - x_k)^2 + \frac{\beta\hbar}{P} U(x_k) \right]\right) \Bigg|_{x_1=x}^{x_{P+1}=x'}, \quad (15)$$

where  $D(L)$  are all the possible paths within  $[0, L]$ . If one expresses it as:

$$Z = \lim_{P \rightarrow \infty} \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2} \int_{D(L)} dx_1 \dots dx_P e^{-\beta H(x_1 \dots x_P)}$$

it can be concluded that the 'effective' Hamiltonian corresponds to:

$$H(x_1 \dots x_P) = \sum_{k=1}^P \left[ \frac{1}{2} m \omega_P^2 (x_{k+1} - x_k)^2 + \frac{1}{P} U(x_k) \right],$$

with  $\omega_P = \frac{\sqrt{P}}{\beta\hbar}$  and  $x_{P+1} = x_1$ . The result above corresponds (and it is known in literature as) the discretized path integral (quantum) representation of the partition function of a single particle. As a matter of fact, it can be seen as the partition function of a polymer ring with  $P$  beads

harmonically linked to each other via nearest neighbor connections, with  $\omega_P$  being the coupling strength. The extension  $N$  interacting particles is, in principle, not trivial since the statistics/symmetry (fermionic or bosonic) must be included. However, in first approximation, independently on whether the particles are fermions or bosons, the basic quantum effects of particle spatial delocalization do not need the introducing of the particle symmetry.

As a consequence, for a Hamiltonian of  $N$  particles in  $d$ -dimensions:  $\hat{H} = \sum_{i=1}^N \frac{\hat{p}_i^2}{2m} + U(\hat{\mathbf{r}}_1, \dots, \hat{\mathbf{r}}_N)$ , it follows that:

$$Z = \lim_{P \rightarrow \infty} \prod_{i=1}^N \left( \frac{m_i P}{2\pi\beta\hbar^2} \right)^{dP/2} \int \prod_{i=1}^N d\mathbf{r}_i^{(1)} \dots d\mathbf{r}_i^{(P)} \times \exp \left( - \sum_{k=1}^P \left[ \sum_{i=1}^N \frac{m_i P}{2\beta\hbar^2} \left( \mathbf{r}_i^{(k+1)} - \mathbf{r}_i^{(k)} \right)^2 + \frac{\beta}{P} U \left( \mathbf{r}_1^{(k)}, \dots, \mathbf{r}_N^{(k)} \right) \right] \right)_{\mathbf{r}_i^{(P+1)} = \mathbf{r}_i^{(1)}}. \quad (16)$$

A natural consequence of the formalism is that for two particles (atoms) in their bead representation, the atom-atom interaction implies that only the beads with the same index  $k$  do interact with each other. The density quantum density matrix (or the partition function) obtained above can be sampled using an effective fictitious dynamics as that produced by classical Molecular Dynamics, as reported in the subsection below.

#### A.1. Path integral formalism in molecular dynamics

The effective fictitious dynamics for MD simulations requires to have momenta associated to each particle (atom), which are not present in the effective ring polymer Hamiltonian. This problem can be solved by writing:  $\left( \frac{mP}{2\pi\beta\hbar^2} \right) = \int dp_1 \dots dp_P \left( -\beta \sum_{i=1}^P \frac{p_i^2}{2m'} \right)$  that is by artificially adding P-Gaussian integrals corresponding to fictitious momentum variables  $p_1, \dots, p_P$  where  $m' = \frac{mP}{(2\pi\hbar)^2}$ , is an arbitrary mass parameter. Here we want only to show the general idea so we can restrict our attention to a system of equivalent atoms, thus  $m_j = m_a$  for the  $j$ -atom and  $m'_j = m'$  for the fictitious mass. The extension to multi-atoms components is indeed straightforward. The partition function is written as:

$$Z = \lim_{P \rightarrow \infty} \int dp_1 \dots dp_P \int dx_1 \dots dx_P \times \exp \left( -\beta \sum_{k=1}^P \left[ \frac{p_k^2}{2m'} + \frac{1}{2} m_a \omega_P^2 (x_{k+1} - x_k)^2 + \frac{\beta\hbar}{P} U(x_k) \right] \right) \Bigg|_{x_1=x}^{x_{P+1}=x'}, \quad (17)$$

with the effective quantized Hamiltonian:  $\mathcal{H}_{PI} = \sum_{k=1}^P \left[ \frac{[p^{(k)}]^2}{2m'} + \frac{1}{2} m_a \omega_P^2 (x_{k+1} - x_k)^2 + \frac{1}{P} U(x_k) \right]$  to be used for the MD simulation.

In this way we have mapped the quantum problem on an effective sampling in space of interacting polymer rings via Molecular Dynamics, that is, while the dynamics is fictitious, the space sampling of the conformations is statistically equivalent to the quantum statistics of interacting atoms which are not rigid spheres but space-delocalized entities (the fluctuating shape of each ring).

#### ORCID iD

Luigi Delle Site  <https://orcid.org/0000-0001-8115-8261>

## References

- [1] Delle Site L 2018 Simulation of many-electron systems that exchange matter with the environment *Adv. Theory Simul.* **1** 1800056
- [2] Breuer H-P and Petruccione F 2002 *The Theory of Open Quantum Systems* (Oxford University Press)
- [3] Manzano D 2020 A short introduction to the Lindblad master equation *AIP Adv.* **10** 025106
- [4] Ramirez F, Dundas D, Sanchez C G, Scherlis D A and Todorov T N 2019 Driven liouville-von neumann equation for quantum transport and multiple-probe green's functions *J. Phys. Chem. C* **123** 12542
- [5] Prior J, Chin A W, Huelga S F and Plenio M B 2010 Efficient simulation of strong system-environment interactions *Phys. Rev. Lett.* **105** 050404
- [6] McCauley G, Cruikshank B, Bondar D I and Jacobs K 2020 Accurate lindblad-form master equation for weakly damped quantum systems across all regimes *npj Quantum Inf.* **6** 74
- [7] Horsfield A P, Bowler D R and Fisher A J 2004 Open-boundary ehrenfest molecular dynamics: towards a model of current induced heating in nanowires *J. Phys.: Condens. Matter.* **16** L65
- [8] Gemmer J, Michel M and Mahler G 2009 *Quantum thermodynamics (Lecture Notes in Physics)* (Springer)
- [9] Bogoljubov N N 1958 On a new method in the theory of superconductivity *Il Nuovo Cimento* **7** 794
- [10] Bruus H and Flensberg K 2004 *Many-Body Quantum Theory in Condensed Matter Physics: An Introduction* (Oxford University Press)
- [11] Delle Site L and Praprotnik M 2017 Molecular systems with open boundaries: theory and simulation *Phys. Rep.* **693** 1
- [12] Delle Site L 2018 Grand canonical adaptive resolution simulation for molecules with electrons: a theoretical framework based on physical consistency *Comput. Phys. Commun.* **222** 94
- [13] Levine I N 2000 *Quantum Chemistry* (Prentice Hall)
- [14] Duster A W, Wang C H, Garza C M, Miller D E and Lin H 2017 Adaptive quantum/molecular mechanics: what have we learned, where are we and where do we go from here? *WIREs Comput. Mol. Sci.* **7** e1310
- [15] Cortes-Huerto R, Praprotnik M, Kremer K and Delle Site L 2021 From adaptive resolution to molecular dynamics of open systems *Eur. J. Phys. B* **94** 189
- [16] Delle Site L and Klein R 2020 Liouville-type equation for the  $n$ -particle distribution function of an open system *J. Math. Phys.* **61** 083102
- [17] Klein R and Delle Site L 2022 Derivation of liouville-like equations for the  $n$ -state probability density of an open system with thermalized particle reservoirs and its link to molecular simulation *J. Phys. A: Math. Theor.* **55** 155002
- [18] Gholami A, Klein R and Delle Site L 2022 Simulation of a particle domain in a continuum, fluctuating hydrodynamics reservoir *Phys. Rev. Lett.* **129** 230603
- [19] Evangelakis A, Panahian Jand S and Delle Site L 2021 Path integral molecular dynamics of liquid water in a mean-field particle reservoir *ChemistryOpen* **11** e20210026
- [20] Panahian Jand S, Nourbakhsh Z and Delle Site L 2022 Nuclear quantum effects in fullerene-fullerene aggregation in water *Front. Chem.* **10** 1072665
- [21] Huang K 1986 *Statistical Mechanics* (Wiley)
- [22] Delle Site L, Krekeler C, Whittaker J, Agarwal A, Klein R and Höfling F 2019 Molecular dynamics of open systems: construction of a mean-field particle reservoir *Adv. Theory Simul.* **2** 1900014
- [23] Negele J and Orland H 1998 *Quantum Many-Particle Systems* (Westviewpress)
- [24] von Neumann J and Beyer R T 2018 *Mathematical Foundations of Quantum Mechanics* (Princeton University Press)
- [25] Schlosshauer M 2010 *Decoherence* (Springer series: The Frontiers Collection)
- [26] Ali M M, Huang W-M and Zhang W-M 2020 Quantum thermodynamics of single particle systems *Sci. Rep.* **10** 13500
- [27] Wang H, Schütte C, Ciccotti G and Delle Site L 2014 Exploring the conformational dynamics of alanine dipeptide in solution subjected to an external electric field: a nonequilibrium molecular dynamics simulation *J. Chem. Th. Comp.* **10** 1376
- [28] Mazenko G F 2000 *Equilibrium Statistical Mechanics* (Wiley)
- [29] Arnold A, Weigend F and Evers F 2007 Quantum chemistry calculations for molecules coupled to reservoirs: formalism, implementation and application to benzenedithiol *J. Chem. Phys.* **126** 174101

- [30] Agarwal A and Delle Site L 2015 Path integral molecular dynamics within the grand canonical-like adaptive resolution technique: simulation of liquid water *J. Chem. Phys.* **143** 094102
- [31] Wang H, Hartmann C, Schütte C and Delle Site L 2013 Grand-canonical-like molecular-dynamics simulations by using an adaptive-resolution technique *Phys. Rev. X* **3** 011018
- [32] Agarwal A, Wang H, Schütte C and Delle Site L 2014 Chemical potential of liquids and mixtures via adaptive resolution simulation *J. Chem. Phys.* **141** 034102
- [33] Agarwal A, Zhu J, Hartmann C, Wang H and Delle Site L 2015 Molecular dynamics in a grand ensemble: Bergmann-Lebowitz model and adaptive resolution simulation *New. J. Phys.* **17** 083042
- [34] Gholami A, Höfling F, Klein R and Delle Site L 2021 Thermodynamic relations at the coupling boundary in adaptive resolution simulations for open systems *Adv. Theory Simul.* **4** 2000303
- [35] Agarwal A and Delle Site L 2016 Grand-canonical adaptive resolution centroid molecular dynamics: implementation and application *Comput. Phys. Commun.* **206** 26
- [36] Agarwal A, Clementi C and Delle Site L 2017 Path integral-gc-adress simulation of a large hydrophobic solute in water: a tool to investigate the interplay between local microscopic structures and quantum delocalization of atoms in space *Chem. Phys. Phys. Chem.* **19** 13030
- [37] Tuckerman M E 2010 *Statistical Mechanics: Theory and Molecular Simulation* (Oxford University Press)