



# Non-unitary master equation for the internal state of ions traversing solids

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## Abstract

We present a new method describing the time development of the internal state of fast highly charged ions subject to collisions and to spontaneous radiative decay during transport through solids. Our method describes both the build-up of coherences and the decoherence of the open quantum system due to the interaction with its environment. The dynamics of the reduced density matrix is governed by a Lindblad master equation that can be solved by Monte Carlo sampling techniques. In practice, the standard Lindblad equation can be of limited value because it describes strictly unitary time transformations of the reduced density matrix. We have developed a generalized non-unitary Lindblad form (and its Monte Carlo implementation) for the evolution in finite subspaces in which the coupling to the complement is taken into account. We use the radiative decay of a free hydrogenic atom in vacuum as a simple test case. We present an application for  $\text{Kr}^{35+}$  ions traversing carbon foils with varying thickness and compare our results with experiments.

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## 1. Introduction

The open quantum system (OQS) approach in atomic physics provides a useful theoretical framework describing the time evolution of atomic electronic states interacting with a large environment. The passage of an ion through solids provides an

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example of the interaction of an OQS (the internal state of the ion) with a large environment (the solid and the electromagnetic field).

Difficulties in calculating the time evolution of OQSs have their source in the high dimensionality of the problem. Approximate solutions are commonly accomplished by transforming the governing master equation for the reduced density matrix of the system of interest to a Lindblad form [1–4], which can be solved using a quantum trajectory Monte Carlo (QTMC) method [1,2,5]. Depending on the physical system to be described the reduction to the Lindblad form is not unique and is still an open problem. We have recently introduced a formalism for this reduction that accounts for both the build-up of coherences and decoherence of internal states of the ion during its passage through a solid [5]. We applied our approach to the transmission of  $\text{Kr}^{35+}$  ions through carbon foils. Differences between theory and experiments were observed for thick foils. In this work we present an extension of our previous formalism which can account for previously observed discrepancies.

One of the major features of the Lindblad formalism is the unitarity of the evolution of the explicitly described system. This feature is of limited value when dealing with a high dimensional state space typical for atomic collisions in solids. For example, during the transmission the ion is excited to high-lying states including the continuum (ionization), which cannot be completely represented within any realistic basis size. From this point of view it seems desirable to find a new approach that describes not only the dynamics within a finite Hilbert space but also the flow of probability to its complement (which is not explicitly represented). Specifically, the goal is to treat explicitly the low-lying states of the ion while implicitly accounting for the flow of probability towards highly excited bound states and continuum states in the complement. This is the purpose of this work. Atomic units will be used unless otherwise stated.

## 2. Unitary open quantum system approach

In this section we briefly review our previous formalism (a more detailed description can be

found in [5]). Consider a system of interest with Hamiltonian  $H_S$  interacting with a reservoir  $H_R$  through an interaction  $V_{SR}$ . The time evolution of the density matrix  $\rho(t)$  of the entire interacting system is given by the Liouville–von Neumann equation,  $d\rho(t)/dt = -i[H_S + H_R + V_{SR}, \rho(t)]$ . Since the calculation of the time evolution of the entire system is out of reach for interacting systems with a large number of degrees of freedom, a simpler OQS approach is usually adopted. Within this formalism, a master equation is derived for the density matrix of the system of interest by tracing out all degrees of freedom of the reservoir, i.e.  $\sigma(t) = \text{Tr}_R[\rho(t)]$ . In our previous work [5] a Lindblad master equation  $d\sigma(t)/dt = -i[H_S, \sigma(t)] + R\sigma(t)$  with

$$R\sigma(t) = -\frac{1}{2V} \sum_{\vec{k}} \left( \left[ S^\dagger(\vec{k})S(\vec{k}), \sigma(t) \right]_+ - 2S(\vec{k})\sigma(t)S^\dagger(\vec{k}) \right) \quad (1)$$

was adopted, where  $R$  represents a relaxation operator describing the interaction of the system with the reservoir involving a sum containing the transition operator  $S(\vec{k})$  representing transitions between states of  $S$  due to the coupling with the reservoir determined by  $V_{SR}$ . Details of  $S(\vec{k})$  will be discussed below. We solve the Lindblad equation by a QTMC method by evaluating  $\sigma(t)$  as an average over quantum trajectories  $|\Psi^\eta(t)\rangle$ ,

$$\sigma(t) = \frac{1}{N_{\text{traj}}} \sum_{\eta=1}^{N_{\text{traj}}} |\Psi^\eta(t)\rangle \langle \Psi^\eta(t)|, \quad (2)$$

with the number of quantum trajectories  $N_{\text{traj}}$  controlling the statistical uncertainty and  $\eta$  labeling different stochastic realizations.  $|\Psi^\eta(t)\rangle$  is obtained by  $|\Psi^\eta(t)\rangle = U^\eta(t,0)|\Psi(0)\rangle$ , where the time evolution operator  $U^\eta(t,0)$  is constructed as a product of continuous time evolution operators and discontinuous jump operators as

$$U_{\text{cont}}^\eta(t, t_n) \prod_{j=1}^n U_{\text{jump}}^\eta(\vec{k}_j, t_j) U_{\text{cont}}^\eta(t_j, t_{j-1}).$$

$U_{\text{jump}}^\eta(\vec{k}_j, t_j)$  is directly proportional to  $S(\vec{k}_j)$  while  $U_{\text{cont}}^\eta(t_j, t_{j-1}) \propto \exp[-iH_{\text{eff}}(t_j - t_{j-1})]$ , with the non-Hermitian effective Hamiltonian

$$H_{\text{eff}} = H_S - \frac{i}{2}\Gamma = H_S - \frac{i}{2V} \sum_{\vec{k}} S^\dagger(\vec{k})S(\vec{k}). \quad (3)$$

The jump times  $t_j$  and the parameters  $\vec{k}_j$  are chosen at random such that the Monte Carlo solution (2) converges to the solution of the original Lindblad equation (1) in the limit of an infinite number of realizations.

### 3. Non-unitary extension

Eq. (1) corresponds to a unitary mapping of the Hilbert space onto itself preserving positive definiteness. One of its virtues is that  $d\text{Tr}_S[\sigma(t)]/dt = 0$ . For realistic high-dimensional systems which include continuum states, this virtue is of limited value. Only a subspace  $\mathbb{P}$  of the Hilbert space  $\mathbb{H}_S$  can be represented in a numerical simulation by a truncated basis. The subspace  $\mathbb{P}$  is coupled to its complement  $\mathbb{Q}$  by  $V_{\text{SR}}$ . The flow of probability from  $\mathbb{P}$  into  $\mathbb{Q}$  is therefore not an artifact but real for any computationally feasible truncated basis set. The point to be noted is that  $\mathbb{Q}$  refers to a subspace of the system Hilbert space, not to the environment. It is therefore an acceptable approximation to account for a flow from  $\mathbb{P}$  into  $\mathbb{Q}$  while neglecting the back coupling from  $\mathbb{Q}$  to  $\mathbb{P}$ . The consequence is the violation of unitarity within  $\mathbb{P} \subset \mathbb{H}_S$ .

Suppose that one would like to lift the restriction  $d\text{Tr}_S[\sigma(t)]/dt = 0$  and to develop a new master equation that accounts for the probability flow from  $\mathbb{P}$  into  $\mathbb{Q}$  in an OQS. The most natural extension consists of a ‘generalized’ Lindblad equation in which we replace the relaxation superoperator by

$$R\sigma(t) = -\frac{1}{2V} \sum_{\vec{k}} \left( \left[ P^{\mathbb{P}} S^\dagger(\vec{k}) S(\vec{k}) P^{\mathbb{P}}, \sigma(t) \right]_+ - 2S^{\mathbb{P}}(\vec{k}) \sigma(t) S^{\mathbb{P}\dagger}(\vec{k}) \right), \quad (4)$$

where  $S$  is defined in the entire Hilbert space  $\mathbb{H}_S$  while  $S^{\mathbb{P}}$  is the submatrix of  $S$  mapping  $\mathbb{P}$  onto itself. That is,  $S^{\mathbb{P}} = P^{\mathbb{P}} S P^{\mathbb{P}}$ , where  $P^{\mathbb{P}} = \sum_{\alpha \in \mathbb{P}} |\alpha\rangle\langle\alpha|$  is the projector operator onto the subspace  $\mathbb{P}$ . This gives rise to the decomposition

$$\Gamma^{\mathbb{P}\mathbb{P}} = \frac{1}{V} \sum_{\vec{k}} S^{\mathbb{P}\dagger}(\vec{k}) S^{\mathbb{P}}(\vec{k}) = \frac{1}{V} \sum_{\vec{k}} \Gamma^{\mathbb{P}\mathbb{P}}(\vec{k}), \quad (5)$$

$$\Gamma^{\mathbb{P}} = \frac{1}{V} \sum_{\vec{k}} P^{\mathbb{P}} S^\dagger(\vec{k}) S(\vec{k}) P^{\mathbb{P}} = \frac{1}{V} \sum_{\vec{k}} \Gamma^{\mathbb{P}}(\vec{k}), \quad (6)$$

where the former (Eq. (5)) describes decay within  $\mathbb{P}$  while the latter (Eq. (6)) also includes decay from  $\mathbb{P}$  to  $\mathbb{Q}$ . In other words, (6) involves the submatrix  $S^{\mathbb{P}\mathbb{Q}}(\vec{k})$  mapping  $\mathbb{P}$  onto  $\mathbb{Q}$ . In the QTMC algorithm the generalized jump operator using  $S^{\mathbb{P}}(\vec{k}_j)$  remains unchanged while the continuous flow operator becomes

$$\begin{aligned} |\Psi^n(t_j)\rangle &= \|\Psi^n(t_{j-1})\| e^{-iH_{\text{eff}}^{\mathbb{P}}(t_j-t_{j-1})} |\Psi^n(t_{j-1})\rangle \\ &\times \left\| e^{-iH_{\text{eff}}^{\mathbb{P}\mathbb{P}}(t_j-t_{j-1})} |\Psi^n(t_{j-1})\rangle \right\|^{-1}. \end{aligned} \quad (7)$$

In Eq. (7) the norm of the wavefunction is not preserved in contrast to the operators used in the standard Monte Carlo method for solving the Lindblad equation. The non-hermitian effective Hamiltonians are  $H_{\text{eff}}^{\mathbb{P}} = H_S - \frac{i}{2} \Gamma^{\mathbb{P}}$  and  $H_{\text{eff}}^{\mathbb{P}\mathbb{P}} = H_S - \frac{i}{2} \Gamma^{\mathbb{P}\mathbb{P}}$ .

### 4. Application to radiative decay

In this section we test our new approach for a problem that can be solved exactly: the multilevel time evolution of an excited hydrogenic ion subject to spontaneous radiative decay. Subsequently, we proceed to apply our method to the more challenging case of an ion in a collisional environment.

Consider a highly charged hydrogenic ion,  $\text{Kr}^{35+}$ , in vacuum. Since radiative decay is an exothermic process, the Hilbert space  $\mathbb{H}_S$  necessary for a full representation of all possible states is finite, and is delimited by the initial state (Fig. 1(a)). In our test case (Fig. 1(b)) we divide the Hilbert space into a subspace  $\mathbb{P}$  consisting of the  $n = (3,4)$  levels and a complement  $\mathbb{Q}$  ( $n = (1,2)$ ). For this example there exists only ‘loss’ of probability from  $\mathbb{P}$  into  $\mathbb{Q}$  but no ‘back coupling’. The unperturbed Hamiltonian of the system including relativistic corrections and the Lamb-shift is

$$H_S = -\nabla_r^2/2 - Z_p/r + \Delta H_{\text{rel}} + \Delta H_{\text{Lamb}}. \quad (8)$$

The matrix elements of the transition operator  $S$  for the radiative decay are  $S_{\alpha\beta}(\mathfrak{I}) = \frac{2}{\sqrt{3c^3}} \omega_{\beta\alpha}^{3/2} \langle\alpha|r_{\mathfrak{I}}|\beta\rangle \theta(\omega_{\beta\alpha})$ , where the index  $\mathfrak{I}$  indicates

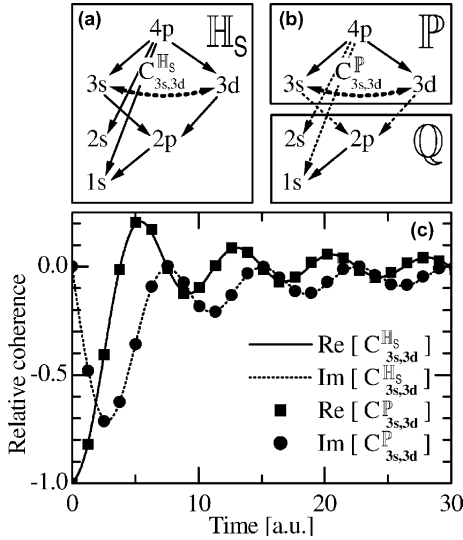


Fig. 1.  $\text{Kr}^{35+}$  ion in vacuum under the influence of radiative decay only. (a) Full Hilbert space  $\mathbb{H}_S$  with the initial state  $4p$ . (b) Decomposition into subspace  $\mathbb{P}$  and complement  $\mathbb{Q}$ . (c) Comparison for the real and imaginary parts of the relative coherence  $C_{\alpha\beta}(t) = \sigma_{\alpha\beta}(t)/\sqrt{\sigma_{\alpha\alpha}(t)\sigma_{\beta\beta}(t)}$  between the  $3s_{3/2}$  and the  $3d_{3/2}$  states calculated exactly for the entire Hilbert space  $\mathbb{H}_S$  and with the non-unitary QTMC within subspace  $\mathbb{P}$ .

the polarization of the emitted photon. The near-perfect agreement between the exact result for the relative coherence and the one calculated with our method employing the split into the  $\mathbb{P}$  and  $\mathbb{Q}$  spaces in Fig. 1(c) demonstrates the validity of the non-unitary approach. Clearly this level of agreement is, in part, due to the fact that the back coupling from  $\mathbb{Q}$  to  $\mathbb{P}$ , which is neglected in our approach, vanishes exactly in this problem.

## 5. Application to collisions

Consider now the passage of a  $\text{Kr}^{35+}$  ion through a carbon foil. In this case, the system Hamiltonian is given by Eq. (8) plus the wake field induced by the projectile ion. The environment consists of the electromagnetic field and the target solid, which can be decomposed into two components. One consists of the ionic cores of the target atoms screened by the surrounding electrons. The interaction with ionic cores will lead to phonon

excitations in the solid. Secondly, the projectile electron interacts with the target electrons leading to single-particle-single-hole and collective (plasmon) excitations of the quasi-free electron gas. The matrix elements of the transition operator  $S(\vec{k})$  are in both cases proportional to  $\langle\alpha|e^{-i\vec{k}\cdot\vec{r}}|\beta\rangle$  in Born approximation.

For this problem we decompose the Hilbert space representing the internal state of the ion into a finite subspace  $\mathbb{P}$  consisting of all bound states with  $n \leq 4$  and the complement  $\mathbb{Q}$  containing the excited states  $n > 4$  and the continuum. The summation in Eq. (6) extending over the entire Hilbert space of hydrogenic eigenstates including the continuum involves an infinite number of states and hence poses a major hurdle. We bypass this hurdle by applying a closure approximation for the calculation of  $\Gamma^{\mathbb{P}}(\vec{k})$ . Our calculations can be compared with experiments performed at GANIL [6] directing beams of  $\text{Kr}^{35+}$  ions with velocity  $v_p = 47$  a.u. onto thin self-supporting amorphous carbon foils. Varying the foil thickness between 3 and 220  $\mu\text{g}/\text{cm}^2$  (i.e.  $\sim 0.01$ – $1$   $\mu\text{m}$ ) allows to study ion transport from near-single-collision regime to the multiple-collision regime. The relative intensities of emitted Balmer  $\alpha$  lines are depicted in Fig. 2 giving a measure of the relative population of the corresponding electronic states of the projectile during the time evolution. The improved agreement with experiment achieved with the present simulation demonstrates the importance of the probability

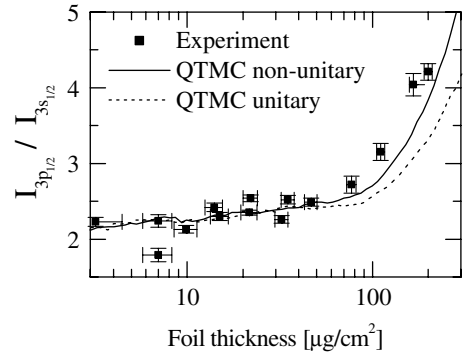


Fig. 2. Relative line emission intensities  $I_{3p_{1/2}}/I_{3s_{1/2}}$  resulting from the transmission of a  $\text{Kr}^{35+}(1s)$  ion through amorphous carbon at a velocity of 47 a.u. as a function of target thickness.

flow from  $\mathbb{P}$  to  $\mathbb{Q}$  and thus the need for a non-unitary treatment of the problem.

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