Master equations for degenerate systems: electron radiative cascade in a Coulomb potential

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Abstract
We examine effects of degeneracy and its lifting for the problem of electron radiative cascade, described by master equations of the Lindblad form (quantum optical master equations). A weak external field approximation is used to study the resulting gradual transformation of cascade dynamics between degenerate and non-degenerate forms. Exploiting the spherical symmetry properties of the system (electron plus radiation field) we demonstrate significant difference between perturbations commuting with angular momentum and perturbations breaking the spherical symmetry, such as a homogeneous external field. We discuss the possibility and the general approach for reduction of the Lindblad master equations in the case of spectral degeneracy to the Pauli balance equations. This determines the appropriate choice of basis, as for example spherical or parabolic.

In recent years there has been important progress in the theoretical description of the dynamics of open quantum systems, i.e. systems which are interacting with another, high–dimensional system, usually called an environment, bath (of oscillators), thermal reservoir, etc. [1]. This activity has been stimulated in part by the rapidly developing field of quantum computing and information [2], in which processes leading to decoherence are very important. For our purposes here we note that radiative relaxation of an atomic system is an example of an open quantum system, in which quantized radiation plays the role of an environment [3].

Contrary to the unitary dynamics of closed systems, the evolution of open systems is non-unitary and cannot be described at the level of wave-function evolution, except, possibly, in the limit of a classical description of the environment. Such dynamics can be
described using the formalism of the density operator (see for example [4]). For an atomic system interacting with the electromagnetic field, the density operator is defined as

\[ \rho_e(t) = \text{Partial Trace}_{\text{over electromagnetic field states}} \left[ \Psi(\text{electron} \otimes \text{field}) \right] \left[ \Psi(\text{electron} \otimes \text{field}) \right]^\dagger. \]  

(1)

If the atomic state is not entangled with the state of the electromagnetic field the density operator describes a pure state, and the evolution of the atomic electron subsystem can be described by the Schrödinger equation.

Here we address the problem of spectral degeneracy (and its lifting by an external perturbation), in the spontaneous radiative decay of excited hydrogen-like atomic systems. We note that topics related to the dynamics of degenerate quantum systems have recently attracted attention in such fields as quantum control [5], decoherence [6], and quantum gate engineering utilizing non-abelian geometric phase [7].

The exact temporal evolution of \( \rho_e(t) \) is provided by the Kraus representation [8], or by the formalism of influence functional of Feynman and Vernon [9]. However these methods are not useful for physical problems such as radiative cascade, since in these methods the dynamics of the environment is still present in its full complexity. By first making the Born-Markov approximation, and then also the secular approximation, which are based on additional assumptions about the relaxation times of the bath (the electromagnetic field) and the system, one can obtain first-order differential equations in time for the density operator. For a minimal coupling Hamiltonian in dipole approximation the equations for \( \rho \) can be written in the form

\[ \frac{d}{dt} \rho_e = -i \hbar [H_e, \rho_e] + D\{\rho_e\}, \]

\[ \rho_e(t)\big|_{t=0} = \rho_0, \]

(2)

where \( \hat{H}_e \) is the electron Hamiltonian (strictly speaking \( \hat{H}_e \) incorporates the Lamb-shift contribution [10]). The dissipation superoperator \( D \) has the form

\[ D\{\rho_e\} = \sum_\xi \left( \tilde{L}_\xi \rho_e \tilde{L}_\xi^\dagger - \frac{1}{2} \tilde{L}_\xi^\dagger \tilde{L}_\xi - \frac{1}{2} \rho_e \tilde{L}_\xi^\dagger \tilde{L}_\xi \right), \]

(3)

where the Lindblad operators \( \tilde{L}_\xi \), associated with spontaneous photon emission at the given discrete frequency \( \omega_\xi \), are expressed as the following sum over pairs of atomic states \( |\gamma'\rangle \) and \( |\gamma\rangle \):

\[ \tilde{L}_\xi = \frac{4\omega_\xi}{3\hbar c} \sum_{\gamma', \gamma, E_\gamma > E_{\gamma'}} \delta(E_\gamma - E_{\gamma'} - \hbar \omega_\xi) |\gamma'\rangle \langle \gamma' | \tilde{r} |\gamma\rangle \langle \gamma| . \]

(4)
Particular frequencies in the set $\omega_\gamma$ correspond to some particular set of transitions $\gamma \rightarrow \gamma'$.

Equation (2)-(4) are usually called quantum optical master equations. Since they have the Lindblad form [11] they preserve trace and provide positive definite solutions for the density operator (for a review of the modern quantum optics formalism see for example [1, 12]).

The general scheme for calculating the radiative cascade line intensities and widths, angular correlations and polarization of emitted light is to calculate first the time evolution of the atomic density matrix using (2) and then calculate photon emission in a perturbative fashion within the Wigner-Weisskopf approximation. Some physical problems with this approach arise in the presence of additional spectral degeneracy, as with that due to the non-geometric dynamical symmetry of the hydrogen atom.

The first problem concerns the validity of equations (2)-(4) in the presence of small external perturbations, which may lift the degeneracy in $E_\gamma$. In this situation there may be close transition frequencies $\omega_\gamma \omega_\gamma'$ for which the characteristic oscillation time $|\omega_\gamma - \omega_\gamma'|^{-1}$ may be comparable with the relaxation time of the system, so that the secular (or rotating field) approximation is inapplicable. Such situations may be encountered in experiments where an external field is applied to an atom after selective electron capture into a highly excited Rydberg state [13]. Note that for large perturbations equations of the type (4) will again be valid, but now with distinct operators $L$ corresponding to partial sums of the terms in the degenerate case.

Another problem can be formulated as follows. Does degeneracy in energy lead to solutions of (1) which differ from the results of traditional approaches for radiative cascades, which (see below) are based on the Pauli master equations and the Seaton cascade matrix [14]? The Pauli master equations explicitly depend on the choice of basis set (in this case spherical or parabolic), and strictly speaking they are not applicable for the description of systems with degeneracy. One may inquire if there is a preferred basis set among the infinite number of possible basis sets in the space subtended by degenerate states.

These two problems are in fact closely related. When the Stark splitting between parabolic states is larger than the radiative line widths, the radiative cascade undergoes rearrangement from a degenerate basis to a parabolic basis. To solve these problems here we will use the technique of expansion in statistical tensors [15, 16] and the weak external field approximation described in [17].

If the spectrum of the system is not degenerate the sum in (4) reduces to only one term, and the equations for the diagonal elements of the density matrix decouple from the off-diagonal elements. As a result one arrives at the so-called Pauli master equations for the diagonal matrix elements of the density operator $b_\gamma = \langle \gamma | \rho | \gamma \rangle$, describing the populations of states as

$$\frac{d}{dt} b_\gamma = \sum_{\gamma' \neq \gamma} b_\gamma W_{\gamma, \gamma'} - b_\gamma \sum_{\gamma' \neq \gamma} W_{\gamma', \gamma},$$  

(5)
where the coefficients $W_{\gamma', \gamma} = \langle \gamma | L_{\gamma', \gamma} | \gamma' \rangle \langle \gamma' | L_{\gamma, \gamma'} | \gamma \rangle$ are radiative transition rates (the indices $\xi$ in the non-degenerate case correspond to a pair $\gamma, \gamma'$). The number of equations associated with (2) scales as $N^2$, while the number of equations in (5) increases only as $N$, where $N$ is the number of states in the problem. This explains why the Pauli master equations (5) underlie the main theoretical method utilized in atomic kinetics [18]. The problem associated with degeneracy is that the solution of equation (5), if it is applied to a degenerate system, generally does depend on the choice of basis set. For example, so-called branching ratios for a radiative cascade in a hydrogen-like ion calculated in this way in a spherical basis are different from those calculated in a parabolic basis [19], even though both bases are equivalent insofar as degeneracy is not lifted by an external field (or by fine structure interactions). While it has been argued that in some physical situations the parabolic basis set may provide better results [20] further justification would be needed.

It is important to note that the quantum optical master equations (2)-(4) are, in fact basis-independent, while their reduced form (5) is not. Thus, for the pure Coulomb spectrum of bound states energies $E_i$, where state energy is specified by the principal quantum number $n$, so that $s$ is specified by the pair $n, n'$, the Lindblad operators are determined as

$$\hat{L}_{n', n} = \frac{4 \omega_{n', n}}{3 \hbar c^2} \hat{P}_{n'} \hat{P}_n,$$

$$\hat{P}_n = \sum_{lm} |nlm\rangle \langle nlm| = \sum_{n_1, n_2, m, n_1 + n_2 + m = n} |n_1, n_2, m\rangle \langle n_1, n_2, m|,$$  

(6)

where the projection operators $\hat{P}_n$ are explicitly basis-independent. (The closed analytic form of these operators can be obtained as the residues of the Coulomb Green function singularities [21].) However the apparent structure of the solutions in these two bases is quite different. Consider the radiative decay from $n=2$ states. The $2s$ spherical state is metastable, while neither of the $n=2$ parabolic states are. Nevertheless, equations (2) and (6) correctly describe the metastability of the $2s$ state in both parabolic and spherical bases. This indicates that the off-diagonal part of the density operator in the parabolic basis, not included in (5) is very important for the correct description of cascade properties, such as the formation of the non-decaying $2s$ state as a proper linear combination of two parabolic states. Operators of the form $\sum_{\xi} \hat{L}_{n'} \hat{L}_{\gamma}$ in equation (3) are diagonal only in the spherical basis, and therefore in the parabolic basis non-diagonal matrix elements will be dynamically generated even if the initial density matrix has no non-diagonal matrix elements (the density matrix of a pure parabolic state, for example).

Let us discuss the removal of degeneracy in angular quantum number $l$, so that $\xi$ is now specified by the pair $nl, n'l'$. Consider the set of the Lindblad operators associated with the spherical basis
This equation is obtained from equation (2) assuming that $E_{nl_1} \neq E_{nl_2}$ for $l_1 \neq l_2$. Note that in this non-degenerate (in angular quantum number) case the summation index $i, j$ in equations (2)-(4) is changed from $n, n'$ to $nl, nl'$. (It is being supposed that degeneracy in $m$ remains.)

The last two terms in equation (3) cause radiative depopulation of excited states. If the same radial functions are used in (6) and (7) the sum $\hat{P}_n = \sum_{nl} \hat{P}_{nl}$, $\hat{P}_{nl} = \sum_m |nlm\rangle \langle nlm|$.

The first term in (3) describes the population of states as a result of radiative transitions from higher states, and this term is different for (6) and (7). First, there are non-diagonal ($l \neq l'$) matrix elements in (3) with (6), while there are no such terms with (7). Secondly, population rates depend on $l \neq l'$ off-diagonal elements of $\rho_e$ for (6), while only $l = l'$ terms are important if (7) is used. The off-diagonal elements determine the coherence between atomic states which can be observed in experiment [16].

The density operator for a statistical population is equal to the trace normalized identity operator in the space subtended by the set of degenerate states, so that spherical symmetry and the orthogonality of projection operators can be used to verify the validity of the Pauli master equation for this type of degeneracy. However this is not true for degeneracy associated with the dynamic symmetry of the atomic system. Let $\rho_0$ be a statistical distribution over the full set of degenerate states, so that at $t = 0$ the solution of (2) has the same form in both the spherical and parabolic basis – a block-diagonal matrix with equal coefficients for all states with the principal quantum number $n_0$. As the density operator evolves in time it will remain statistical in $m$-components, but it will not be statistical in wider degenerate subspaces (all states with the same principal quantum numbers). Therefore $\rho(t)$ will not be a statistical density operator in the parabolic basis.

From a physical point of view the spherical basis is more adequate for the description of the radiative cascade because spherical symmetry holds for the whole system – atom interacting with the radiation field - while the dynamical symmetry is applicable only for the isolated atom. This explains why most results on the properties of radiative cascades for H-like systems are obtained using Pauli master equations in a spherical basis [22].
Using the spherical symmetry of the dissipation superoperator $D$, equation (3), one may show that for arbitrary initial conditions the diagonal quantities $b_{\text{nl}}(t) = \sum \langle nlm | \rho_s(t) | nlm \rangle = \sum b_{\text{nl}}(t)$ obtained using (6) and (7) are equal, even though the populations of particular $m$ substates $b_{\text{nlm}}(t) = \langle nlm | \rho_s(t) | nlm \rangle$ obtained using (6) or (7), and the non-diagonal matrix elements between different $m$ components, are different. The inequality of these $b_{\text{nlm}}$ results in a change in the polarization and the angular distribution of the emitted photons. The equality of the $b_{\text{nl}}$ can be proved using a multipole expansion of the density operator in spherical tensor operators [4, 16] (see Appendix).

The spherical symmetry present in the unperturbed equations (2) allows an effective reduction of the full form of the master equations (2) to the simpler form of Pauli master equations for populations averaged over quantum number $m$ - i.e. quantities averaged over all possible Euler angles. This property of the system remains valid for perturbations commuting with angular momentum. Contrary to the spherical basis, the parabolic basis does not seem to have such properties – the additional symmetry due to commutation of the Runge-Lentz operator with the Hamiltonian is relevant only at the level of the Schroedinger equation without electron-field interaction, while spherical symmetry, applicable for the whole system (electron plus field), remains at the level of the master equations (2). As we will see below, a perturbation in the form of a homogeneous external field affects not only $b_{\text{nlm}}$ but also $b_{\text{nl}}$ and $b_n$, and the Pauli equations are not applicable (even for averaged values) for the description of such perturbations, until the external field is strong enough to completely lift the degeneracy, beyond the natural widths of the states involved in the radiative cascade.

Equations (6) and (7) provide two limiting cases – complete degeneracy in $l$ and complete lifting of degeneracy. To describe the intermediate case, we use the weak external field approximation [17].

The idea of the method is as follows. If a weak perturbation $V_e(t)$ to the Hamiltonian of the atomic system is added to the total Hamiltonian, then in first approximation the dissipation operator does not change. The perturbation $V_e(t)$ enters equations additively to the Hamiltonian:

$$\frac{d}{dt} \rho_s = -\frac{i}{\hbar} [H_e, \rho_s] - \frac{i}{\hbar} [V_e(t), \rho_s] + D\{\rho_s\}.$$  \hspace{1cm} (8)

If the system does not interact with the environment, equation (8) is equivalent to the Schrödinger equation for an atom with the Hamiltonian $H = H_e + V_e(t)$, so that the unitary part of the evolution of the atomic system is described by (8) exactly. The validity of (8) is achieved by imposing the perturbative requirement that $V_e$ is much smaller than $H_e$.

The degeneracy may be lifted in such a way that there are close transition frequencies, and the characteristic time of oscillations $|\omega_{ij} - \omega_{ij}'|$ may be of the order
of radiative transition times. In this case equations (6) and (7) are, strictly speaking, inapplicable for the determination of the superoperator $D$ in (2). However, the situation is correctly described by the combination of (6) and (8), where it is implied that $V_e$ is a perturbative operator, lifting the degeneracy. For example, if $V_e$ is a short-range potential, lifting degeneracy in the angular quantum number $l$, solutions of equations (2) with (7) would not be sensitive to the energy splitting, since $V_e$ commutes with the angular momentum operators. In contrast equations (6) and (8) demonstrate significant changes in the populations of $m$-components and coherences between some states with different $l$, even for small perturbations, comparable with radiative widths of states. In our numerical examples we introduce a lifting of degeneracy in the form of a perturbation $V_e(t)$, while the dissipation operator is taken in the unperturbed completely degenerate form (6). Numerical calculations demonstrate that, as degeneracy is lifted beyond the radiative widths of the transition states the solutions of (8) converge to those provided by (2) and (7).

We have made such calculations for a model radiative cascade problem – the relaxation of the excited 4p $m=0$ state of the H atom. The states 3s and 3d are considered as quasidegenerate. The splitting $\delta$ is introduced by $V_e(t) = \delta |3s\rangle \langle 3s|$. We vary the parameter $\delta$ and solve equations (8) using the form (6) for the Lindblad operators (as can be expected, using equations (8) and (7) one obtains solutions which are independent of the splitting). In Fig. 1 we show the population of the 2p $m=0$ magnetic substate as a function of time. Curve 1 correspond to calculations using the non-degenerate form (7), while curves 5 corresponds to the degenerate form (6) of the L operators, together with Eq. (3). Curves 2, 3 and 4, using (6) with (8), demonstrate how the effect of degeneracy is recovered as the splitting decreases. The considerable differences between the populations of $m$-substates in curves 1 and 5 are associated with the difference between the two forms of the Lindblad operators.

Next we take as perturbation a homogeneous external field

$$V_e(t) = \vec{F} \cdot \vec{r}.$$  \hspace{1cm} (9)

In this case the solutions of (8) describe the restructuring of the cascade from the limit of a degenerate (spherical) basis to the limit of a parabolic basis, as the intensity of the field increases.

In Fig. 2 and 3 we present results of calculation of the evolution of the fractional population of the levels $n=2$ and $n=3$ in an external electric field for various field intensities, small in comparison with the atomic field intensity, using equations (6), (8) and (9). The field-free fractional populations for $n=2$ and 3 are shown in the inset in Fig 2. In these calculations we neglected matrix elements of $\vec{F} \cdot \vec{r}$ between states with different principal quantum numbers. The initial condition for the density operator was taken to be a pure state, corresponding to a maximally elongated asymmetric parabolic state $n=4$, $n_1=3$, $n_2=0$, $m=0$. Field induced Stark splitting results in a noticeable change in the dynamics of state populations. For high enough field intensities the field dependence saturates and we obtain a result corresponding to that obtained from the
common Pauli master equations in the parabolic basis set. These effects are independent
of the choice of a spherical or parabolic basis set, since the Lindblad operators (6) are
basis invariant.

In conclusion, we have analyzed the effects of spectral degeneracy on the relaxation
of a system interacting with a bath (electromagnetic field). For a model of a radiative
cascade in the H atom, we observe significant dependence of the population of magnetic
substates on the particular form taken for the master equation. We also performed
calculations for radiative cascade in the presence of a homogeneous stationary external
field. The field is introduced as a perturbation in the master equations with degeneracy
(in l). We observed the rearrangement of the cascade from the low-field regime (spherical
symmetry suitable, and a spherical basis describes associated properties of the cascade) to
a strong-field regime (axial symmetry dominates). Populations of n – states, calculated
using equation (2) with the Lindblad operators in the form (7) are not sensitive to the
perturbations, which commute with the angular momentum operators. To correctly
describe a perturbation lifting degeneracy or mixing some close states in a system, one
has to express the Lindblad operators via projectors into subspaces subtended by those
close states.

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APPENDIX.

Spherical tensor operators

\[ T_{JM}^{nl_1, n_2l_2} = \sum_{m_1, m_2 = M} (-1)^{J-M} \langle l_1m_1, l_2m_2 | JM \rangle |n_1l_1m_1 \rangle \langle n_2l_2m_2 | \]

(A.1)

form a complete orthonormal basis in the Liouville space [4, 16]. We expand the density
operator as follows:

\[ \rho_c(t) = \sum_{n_1l_1, n_2l_2, J, M} \xi_{JM}^{n_1l_1, n_2l_2} (t) T_{JM}^{n_1l_1, n_2l_2} . \]  

(A.2)

The dissipative superoperator D in equation (2) is a scalar. The coefficients \( \xi_{JM}^{n_1l_1, n_2l_2} (t) \) decouple for different J, M, since \( D \{ T_{JM} \} \sim T_{JM} \), so that the time derivatives
of \( \xi_{JM}^{n_1l_1, n_2l_2} \) are only determined by coefficients \( \xi_{JM}^{n_1l_1, n_2l_2} \) with the same J, M. Since only
the monopole tensor has a non-zero trace,

\[ \sum_m \langle nlm | T_{JM}^{nl_1, n_2l_1} | nlm \rangle = \delta_{J,0} \delta_{M,0} , \]  

(A.3)
the populations $b_{nl} = \xi_{00}^{nl,nl}(t)$. As discussed in the text, the second and third terms of (3) are identical for both (6) and (7), so that the only difference between using (6) or (7) is associated with the contribution of the non-symmetric components \((l_1 \neq l'_1, l_2 \neq l'_2)\) of the first term in (3),

\[
\hat{P}_{n_{l_1}} \hat{P}_{n_{l_2}} T_{JM}^{n_{l_1}, n_{l_2}} \hat{P}_{n'_{l_1'}} \hat{P}_{n'_{l_2'}} \sim T_{JM}^{n_{l_1}, n_{l_2}} \begin{pmatrix} J & l_2' & l_2 \\ 1 & l_1' & l_1 \end{pmatrix},
\]

(A.4)

which are identically zero for \(J = 0\). So the difference between the Lindblad operators (6) and (7) affects only higher tensor components of the density operator.

References

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**Fig. 1.** Fractional population of the \((2p,m=0)\) state as a function of time. The cascade process starts from the state \((4p,m=0)\), so that the \((2p,m=0)\) state is populated via \(3s\) and \(3d\) states. To model the lifting of degeneracy between \(3s\) and \(3d\) we introduce a perturbation shifting the energy of the \(3s\) state by \(\delta = 2.0, 1.0, \text{ and } 0.5 \times 10^{-7} \text{ a.u.}\) (curves 2, 3 and 4 correspondingly). Curves 1 and 5 are obtained solving equation (2) using (7) and (6), respectively. Curves 2,3 and 4 are obtained solving (6) and (8) with \(V_e(t) = \delta |3s\rangle \langle 3s|\).

**Fig. 2.** Time dependence of the difference between the fractional population of the \(n=2\) state (calculated in a stationary electric field) and the field-free population. Curves 1, 2, 3 and 4 correspond to field intensities of 1, 2, 3 and 5 \(10^{-8} \text{ a.u.}\) correspondingly. The parabolic quantum numbers of the initial state are \(n = 4, \ n_1 = 3, \ n_2 = 0, \ m = 0\). The field-free fractional populations are shown in the inset for principal quantum numbers \(n = 2\) and \(n = 3\).

**Fig. 3.** The same as Fig. 3, for the \(n=3\) state.