A master equation for strongly interacting dipoles

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Abstract
We consider a pair of dipoles such as Rydberg atoms for which direct electrostatic dipole–dipole interactions may be significantly larger than the coupling to transverse radiation. We derive a master equation using the Coulomb gauge, which naturally enables us to include the inter-dipole Coulomb energy within the system Hamiltonian rather than the interaction. In contrast, the standard master equation for a two-dipole system, which depends entirely on well-known gauge-invariant $S$-matrix elements, is usually derived using the multipolar gauge, wherein there is no explicit inter-dipole Coulomb interaction. We show using a generalised arbitrary-gauge light-matter Hamiltonian that this master equation is obtained in other gauges only if the inter-dipole Coulomb interaction is kept within the interaction Hamiltonian rather than the unperturbed part as in our derivation. Thus, our master equation depends on different $S$-matrix elements, which give separation-dependent corrections to the standard matrix elements describing resonant energy transfer and collective decay. The two master equations coincide in the large separation limit where static couplings are negligible. We provide an application of our master equation by finding separation-dependent corrections to the natural emission spectrum of the two-dipole system.

1. Introduction

Dipole–dipole interactions are central to several important effects in atomic and molecular physics. Early studies by Eisenschitz, London and Förster [1, 2] treated dipolar interactions as perturbative effects arising from direct electrostatic coupling. Molecular quantum electrodynamics (QED) extends these treatments by incorporating retardation effects due to finite signal propagation. As was first shown by Casimir and Polder [3], a striking retardation effect occurs at large separations $R/\lambda \gg 1$ where the $R^{-6}$ dependence of the dispersion energy is increasingly replaced by an $R^{-7}$ dependence.

In order to study the dynamics of systems of interacting dipoles open quantum systems theory has proven useful [4]. The master equation formalism can be used to obtain dynamical information about state populations and coherences, and to obtain fluorescence spectra [5–8]. As will be confirmed in this work, the standard second-order Born–Markov-secular master equation describing two dipoles within a common radiation reservoir depends entirely on well-known QED matrix elements. These matrix elements describe dipole–dipole coupling and decay with retardation effects included. This master equation is obtained by treating the direct electrostatic coupling between the dipoles as a perturbation along with the coupling to transverse radiation. However, it is clear that if the former is sufficiently strong this approach may not be justified, in analogy with the case of externally imposed interactions [9]. Here we consider a system of free dipoles strongly coupled by dipole–dipole interactions. Our focus is on discerning the full dependence of the physics on the inter-dipole separation. We also delineate how microscopic gauge-freedom effects the ensuing master equation derivation.

An important class of systems strongly coupled by dipole–dipole interactions are Rydberg atoms, which have been of interest for some time [10]. In recent years dipole–dipole interactions of Ryberg atoms have been the subject of numerous experimental and theoretical works [11–23]. Recently the first experimental confirmation of Förster resonant energy transfer was demonstrated using two Rydberg atoms separated by 15 $\mu$m [14]. This
type of resonant energy transfer is an important mechanism within photosynthesis, whose quantum nature is of continued interest within open quantum systems theory [24]. Dipole–dipole interactions of Rydberg atoms also offer promising means of implementing quantum gates in which adjacent Rydberg states are treated as effective two-level systems and dipolar interactions are tuned with the use of lasers [21].

Such adjacent Rydberg states are typically separated by microwave transitions, which for small enough separations can be matched or even exceeded by the electrostatic dipole–dipole interaction strength divided by \( h \). Thus, a novel regime of strong electrostatic coupling occurs, in which the usual weak-coupling theory is expected to break down. A reapportioning of the Hamiltonian is necessary in order to identify a genuinely weak system–reservoir interaction, which can then constitute the starting point for perturbation theory. More specifically, we include the direct inter-dipole Coulomb energy within the unperturbed part of the Hamiltonian and only treat the coupling to transverse radiation as a weak perturbation. The master equation we derive exhibits a different dependence on the inter–dipole separation, and this has important consequences for the predicted physics. The rates of collective decay and resonant energy transfer are altered, as are the properties of the light emitted by the system.

There are five sections in this paper. We begin in section 2 by reviewing the standard one and two dipole master equations in the Born–Markov and secular approximations. We show how the standard two-dipole master equation can be obtained for various choices of gauge for the microscopic Hamiltonian. Our purpose is to clearly identify limitations in the standard derivation, which is usually always performed using the multipolar Hamiltonian [4]. This concrete form of the Hamiltonian is the form obtained by choosing the multipolar gauge, also known as the Poincaré gauge [25]. In section 3 we derive an alternative master equation describing the two-dipole system, which only reduces to the standard result in the limit of vanishing direct electrostatic coupling between the dipoles. This occurs in the limit of large separation. In section 4 we solve the master equation derived in section 3 and compare the solution with that of the standard master equation. We also obtain corrections to the emission spectrum of the two-dipole system. Finally in section 5 we summarise our findings. We assume natural units \( \hbar = \varepsilon = c = 1 \) throughout.

2. Gauge-invariant master equations

2.1. Single-dipole Hamiltonian and master equation

Here we identify sufficient conditions in order that the same master equation can be obtained from different microscopic Hamiltonians. This will be important when it comes to deriving the two-dipole master equation in the following sections. Let us consider a single dipole within the electromagnetic bath, and assume that there are only two relevant states \( |g\rangle, |e\rangle \) of the dipole separated by energy \( \omega_0 = \omega_e - \omega_g \). Associated raising and lowering operators are defined by \( \sigma^+ = |e\rangle \langle g| \) and \( \sigma^- = |g\rangle \langle e| \). The electromagnetic bath is described by creation and annihilation operators \( a^\dagger_{k\lambda}, a_{k\lambda} \) for a single photon with momentum \( k \) and polarisation \( \lambda \). The photon frequency is denoted \( \omega_k = |k| \).

The energy of the dipole-field system is given by a Hamiltonian of the form \( H = H_0 + V \), where

\[
H_0 = \omega_0 \sigma^+ \sigma^- + \sum_{k\lambda} \omega_k a^\dagger_{k\lambda} a_{k\lambda},
\]

defines the free (unperturbed) Hamiltonian and \( V \) denotes the interaction Hamiltonian. Gauge-freedom within the microscopic description results in the freedom to choose a number of possible interaction Hamiltonians. We define the generalised–gauge transformation [26]

\[
R_{(a_{(1)})} = \exp \left[ \mathbf{d} \cdot \mathbf{A}_{(a_{(1)})} (0) \right], \quad \mathbf{A}_{(a_{(1)})} (\mathbf{x}) = \sum_{k\lambda} \left( \frac{1}{2\omega_k L^2} \right)^{1/2} \alpha_{k\lambda} \mathbf{e}_{k\lambda} e^{i \mathbf{k} \cdot \mathbf{x}} + \mathrm{h.c.}
\]

In this expression the \( \alpha_{k\lambda} \) are real and dimensionless, the \( \mathbf{e}_{k\lambda}, \lambda = 1, 2 \) are mutually orthogonal polarisation unit vectors, which are both orthogonal to \( \mathbf{k}, L^2 \) is the volume of the assumed fictitious quantisation cavity, and \( \mathbf{d} \) denotes the dipole moment operator. By making the two-level approximation after having transformed the Coulomb gauge Hamiltonian using the unitary operator \( R_{(a_{(1)})} \) we obtain the Hamiltonian \( \hat{H} = \hat{H}_0 + V \) where [26]

\[
V = \left[ \sum_{k\lambda} \alpha_{k\lambda} \right] \sigma^+ \left( \hat{a}_{k\lambda}^\dagger \hat{a}_{k\lambda} + \hat{a}_{k\lambda} \hat{a}_{k\lambda}^\dagger \right) + \text{h.c.} + V^{(2)}
\]

\[
V^{(2)} = \sum_{k\lambda} \frac{1}{2L^3} \alpha_{k\lambda}^2 |\mathbf{e}_{k\lambda} \cdot \mathbf{d}|^2 + \frac{e^2}{2m} \hat{\lambda}(0)^2.
\]
The term $V^{(2)}$ is a self-energy term, which does not act within the two-level dipole Hilbert space and which depends on the field

$$\tilde{A}(x) = \sum_{k,l} \left( \frac{1}{2\omega L^2} \right)^{\frac{1}{2}} (1 - \alpha_k) a_{kl} e^{ik\cdot x} + \text{H.c.}$$

(5)

The coupling constant $g_{k\lambda}$ and the (real) coefficients $u_k^{\pm}$ are defined as

$$S_{k\lambda} = -i \left( \frac{\omega_0}{2L^2} \right)^{\frac{1}{2}} e_{k\lambda} \cdot d, \quad u_k^\pm = (1 - \alpha_k) \left( \frac{\omega_0}{\omega_k} \right)^{1/2} \pm \alpha_k \left( \frac{\omega_k}{\omega_0} \right)^{1/2}$$

(6)

where $d$ and $\omega_0$ denote the two-level transition dipole moment and transition frequency, respectively. The real numbers $\alpha_k$ can be chosen arbitrarily. Choosing $\alpha_k = 0$ yields the Coulomb-gauge Hamiltonian while choosing $\alpha_k = 1$ yields the multipolar-gauge Hamiltonian. Letting $\alpha_k = 1$ in equation (2) yields the well-known Power–Zienau–Woolley (PZW) transformation that relates the Coulomb and multipolar gauges. While the relation between the Coulomb and multipolar gauge has been discussed extensively [27–31], the PZW transformation is in fact a special case of a broader class of unitary gauge-fixing transformations [31–33]. More generally still, the freedom to choose the $\alpha_k$ within the canonical transformation (2) implies redundancy within our mathematical description and is henceforth referred to as generalised gauge–freedom. A third special case of equation (3) is afforded by making the choice $\alpha_k = \omega_0/(\omega_0 + \omega_k)$, which specifies a symmetric mixture of Coulomb and multipolar couplings. This representation has proved useful in both photo-detection theory [31, 34] and open quantum systems theory [26], because within this representation $u_k^+ = 0$. The counter-rotating terms in the linear dipole-field interaction term $V = V^{(0)}$ are thereby eliminated without use of the rotating-wave approximation.

Given the above arbitrary generalised-gauge description, it is clear that arbitrary matrix elements $M_{\beta}(t) = \langle f | M(t) | i \rangle$ between eigenstates $|f\rangle$ and $|i\rangle$ of $H_0$ will not be the same when the evolution of the operator $M$ is determined by different total Hamiltonians $H$ and $H'$, that have been obtained by making different choices of $\alpha_k$ in equation (3). In contrast on-energy-shell QED $S$-matrix elements are necessarily the same for two interaction Hamiltonians $V$ and $V'$, constrained such that the corresponding total Hamiltonians are related by a unitary transformation $e^{iT}$ as [25, 28, 35]

$$H = H_0 + V, \quad H' = e^{iT}He^{-iT} = H_0 + V'.$$

(7)

For gauge-invariance to hold the unperturbed Hamiltonian $H_0$ must be identified as the same operator before and after the transformation by $e^{iT}$. Note however, that the unperturbed Hamiltonian $H_0$ given in equation (1) does not commute with the unitary transformation $R(\alpha_k)$ given in equation (2) meaning that this $H_0$ represents a different physical observable depending on the choice of interaction. Despite this, $S$-matrix elements based on the partition $H = H_0 + V$ are invariant, because $H_0$ in equation (1) does not explicitly depend on the $\alpha_k$ and is therefore the same for each different choice of generalised-gauge.

Having determined the conditions under which QED matrix elements are gauge-invariant we now turn our attention to deriving a master equation describing the two-level dipole within the radiation field. The conventional derivation of the second order quantum optical master equation, as found in [36] for example, does not at any point involve self-energy contributions due to the $V^{(2)}$ term within the interaction $V$. In general however, this term does contribute to dipole level-shifts, as is shown in appendix A.1. In the general case that the temperature of the radiation field is arbitrary, the self-energy contributions from $V^{(2)}$ can be incorporated into the master equation by defining the Hamiltonian

$$\tilde{H}_d = (\omega_0 + \delta_0^{(2)} - \delta_0^{(2)} \sigma^+ \sigma^-),$$

(8)

where the excited and ground state self-energy shifts are defined as

$$\delta_0^{(2)} = \text{tr}(V|n\rangle\langle n| \otimes \rho_0^{(S)}) - \text{tr}(V^{(2)}|n\rangle\langle n| \otimes \rho_0^{(S)}),$$

(9)

in which $n = e.g$ and $\rho_0^{(S)}(\beta) = e^{-\beta \sum_k \omega_k a_k^{\dagger} a_k}/\text{tr}(e^{-\beta \sum_k \omega_k a_k^{\dagger} a_k})$ with $\beta$ the inverse temperature of the radiation field. Since $V^{(2)}$ is gauge-dependent we cannot include the self-energy shifts within the unperturbed Hamiltonian $H_0$ without ruining the gauge-invariance of any $S$-matrix elements obtained using the unperturbed states. Instead we replace the free system Hamiltonian in the usual Born–Markov master equation with the shifted Hamiltonian $\tilde{H}_d$ directly to obtain the second order master equation

$$\dot{\rho} = -i[\tilde{H}_d, \rho] - e^{-iH_d t} \int_0^\infty ds \text{tr}[V(t), [V(t - s), \rho(t) \otimes \rho_0^{(S)}]] e^{iH_d s}.$$  

(10)

This master equation automatically includes the level shifts due to $V^{(2)}$ within the unitary evolution part, but the rest of the master equation is expressed in terms of the original partition $H = H_0 + V$. Using this partition where $H_0$ and $V$ are given in equations (1) and (3) respectively, equation (10) yields the $\alpha_k$-independent result
where the continuum limit for wavevectors \( \mathbf{k} \) has been applied and \( N_k = 1/(e^{\hbar k} - 1) \). Further details of the calculations leading to the final result for \( \Delta \) in equation (12) are given in appendix A.1. We note that for \( N_k = 0 \) we have
\[
\Delta = \omega_0 - \omega_k = \langle 0, e \vert V(0, e) \rangle + \sum_{k, \lambda} \frac{|\langle 0, e \vert V(0, \mathbf{k}, \lambda, g) \rangle|^2}{\omega_0 - \omega_k} - \langle 0, g \vert V(0, g) \rangle + \sum_{k, \lambda} \frac{|\langle 0, g \vert V(0, \mathbf{k}, \lambda, e) \rangle|^2}{\omega_0 + \omega_k}.
\]
(13)

The \( \alpha_k \)-independence (generalised gauge-invariance) of the master equation (11) can be understood by noting that the spontaneous emission rate \( \gamma \) and level-shift \( \Delta \) in equation (13) are gauge-invariant QED matrix elements that can be obtained directly using second order perturbation theory.

In summary, we have shown that the master equation obtained from different, unitarily equivalent microscopic Hamiltonians is the same provided it depends only on \( \omega_0 \) and \( \omega_0 \)-independence terms. We give a general derivation of the standard two-dipole master equation, in which the gauge freedom within the microscopic Hamiltonian is left open throughout. This reveals limitations within the conventional derivation using the multipolar gauge. To begin we define the two-dipole generalised PZW gauge transformation by [26, 34]
\[
R_{(\alpha k)} := \exp \left( i \sum_{\mu=1}^{2} d_\mu \cdot A_{(\alpha k)}(\mathbf{R}_\mu) \right)
\]
(14)
where \( d_\mu \) denotes the dipole moment operator of the \( \mu \)-th dipole. We now transform the dipole approximated Coulomb gauge Hamiltonian using \( R_{(\alpha k)} \) and afterwards make the two-level approximation for each dipole. This implies that \( d_\mu = d(\sigma_\mu^+ + \sigma_\mu^-) \), and that the Hamiltonian can be written \( H = H_0 + V \) with
\[
H_0 = \sum_{\mu=1}^{2} \omega_0 \sigma_\mu^+ \sigma_\mu^- + \sum_{k, \lambda} \omega_k a_{k, \lambda}^+ a_{k, \lambda}
\]
(15)
and
\[
V = \sum_{k, \lambda} \frac{2}{\alpha_k^2} \left( u_{k, \lambda}^+ a_{k, \lambda}^+ e^{-i \mathbf{k} \cdot \mathbf{R}_0} + u_{k, \lambda}^- a_{k, \lambda} e^{i \mathbf{k} \cdot \mathbf{R}_0} + \text{h.c.} \right) + V_{(\alpha k)}^{(2)} + C_{(\alpha k)}.
\]
(16)
Analogously to the single-dipole case the first term in equation (16) defines a linear dipole-field interaction component while the term \( V_{(\alpha k)}^{(2)} \) consists of self-energy contributions for each dipole and the radiation field;
\[
V_{(\alpha k)}^{(2)} = \sum_{k, \lambda} \frac{1}{3} \alpha_k^2 \left( |\mathbf{k} \cdot \mathbf{d}|^2 + \sum_{\mu} \frac{e^2}{2m} \mathbf{A}(\mathbf{R}_\mu)^2 \right),
\]
(17)
where \( m \) is the dipole mass. Due to the two-level approximation the first term in (17) is proportional to the identity, while the second term is a radiation self-energy term. The field \( \mathbf{A} \) is defined as in the single-dipole case by equation (5). The final term in equation (16) \( C_{(\alpha k)} \) has no analogue in the single-dipole Hamiltonian. This
term gives a static Coulomb-like interaction between the dipoles, which is independent of the field;

\[ C_{(α_k)} = \sum_{kk} \frac{\alpha_k^2}{L^2} (\sigma^\mu_k - 1) |e_k \lambda \cdot d|^2 e^{ikk} \sigma^\mu_k \sigma^\mu_k, \]

(18)

where \( \sigma^\mu_k = \sigma^\mu_k + \sigma^\mu_k \). In the Coulomb gauge (\( α_k = 0 \)) the term \( C_{(α_k)} \) reduces to the usual dipole–dipole Coulomb interaction. In the multipolar gauge \( C_{(α_k)} \) vanishes, and the interaction in equation (16) therefore reduces to a sum of interaction terms for each dipole.

It is important to note that as in the single-dipole case \( R_{(α_1)} \) does not commute with \( H_0 \) given in equation (15) implying that \( H_0 \) represents a different physical observable for each choice of \( α_k \). More generally, since \( R_{(α_k)} \) is a non-local transformation, which mixes material and transverse field degrees of freedom, the canonical material and field operators are different for each choice of \( α_k \). This implies that the master equation for the dipoles will generally be different for each choice of \( α_k \). We can, however, obtain a gauge-invariant result by ensuring that the master equation depends only on gauge-invariant S-matrix elements. These matrix elements are gauge-invariant despite the implicit difference in the material and field degrees of freedom within each generalised gauge. Usually the two-dipole master equation is derived using the specific choice \( α_k = 1 \) (multipolar gauge) for which the direct Coulomb-like coupling \( C_{(α_k)} \) vanishes identically. To obtain the same master equation for any other choice of \( α_k \), we must include \( C_{(α_k)} \) within the interaction Hamiltonian \( V \). The reason is that \( H_0 \) must be identified as the same operator for each choice of \( α_k \) in order that the gauge-invariance of the associated S-matrix holds.

We now proceed with a direct demonstration that the standard two-dipole master equation can indeed be obtained for any other choice of \( α_k \). Provided \( C_{(α_k)} \) is kept within the interaction Hamiltonian \( V \). To do this we substitute the interaction Hamiltonian in equation (16) into the second order Born–Markov master equation in the interaction picture with respect to \( H_0 \); which is given by

\[ \dot{ρ}_I(t) = -itr\{V_I(t), \rho_I(t) \otimes \rho_{F0}^eq\} - \int_0^\infty ds \ tr\{V_I(t), [V_I(t - s), \rho_I(t) \otimes \rho_{F0}^eq]\}, \]

(19)

where \( V_I(t) \) denotes the interaction Hamiltonian in the interaction picture and \( ρ_I(t) \) denotes the interaction picture state of the two dipoles. We retain contributions up to order \( e^2 \) and perform a further secular approximation, which neglects terms oscillating with twice the transition frequency \( ω_0 \). Transforming back to the Schrödinger picture and including the single-dipole self-energy contributions as in equation (10), we arrive after lengthy but straightforward manipulations at the final \( e^2 \)-independent result

\[
\dot{ρ} = -iω_0 \sum_{μν} [\sigma^μ, \sigma^ν, ρ] - i\Delta_{12} \sum_{μν} [\sigma^μ, \sigma^ν, ρ] + \sum_{μ, ν} \gamma_{μν}(N + 1)\left[\frac{σ_μ \rho σ_ν - \frac{1}{2} (σ_μ σ_ν \rho)}{2}\right]
\]

(20)

This equation is identical in form to the standard two-dipole master equation, which can be found in [4] for example. The decay rates \( \gamma_{μν} \) are given by

\[
\gamma_{μν} = γ, \quad \gamma_{12} = 2π \sum_{kλ} \langle 0, g, g \rangle V[k, λ, g, g] \langle k, λ, g, g \rangle V[0, g, g] δ(ω_0 - ω_k) = d_i d_j τ_{ij}(ω_0, R),
\]

(21)

where

\[
τ_{ij}(ω_0, R) = \frac{ω_0^2}{2π} \left( δ_{ij} - \hat{R}_i \hat{R}_j \sin ω_0 R \right) - \frac{3ω_0 R}{(ω_0 R)^2} \sin ω_0 R \left( \frac{ω_0 R}{(ω_0 R)^2} \right). \]

(22)

In equation (21) and throughout we denote spatial components with Latin indices and adopt the convention that repeated Latin indices are summed. The quantity \( \gamma_{12} \) denoted an \( R \)-dependent collective decay rate. The third equality in equation (21) wherein \( \gamma_{12} \) has been expressed as a matrix element involving \( V \) makes the reason for the \( α_k \)-independence of this rate clear. We now turn our attention to the master equation shifts \( Δ = \tilde{ω}_0 - ω_0 \) and \( Δ_{12} \). The single-dipole shift \( Δ \) includes all self-energy contributions, which have been dealt with in the same way as for the single-dipole master equation (see equation (10)). The shift \( Δ \) is therefore as in equation (12). Details of the calculation of the joint shift \( Δ_{12} \) are given in appendix A.2 with the final result being

\[
Δ_{12} = \sum_n \sqrt{\frac{\langle f | V[n] | n \rangle}{ω_i - ω_n}} \frac{ω_0^2}{ω_0^2 - ω_i^2} = \int \frac{d^3k}{(2π)^3} \sum_{λ} |e_i(\vec{k}) \cdot d|^2 e^{i\vec{k} \cdot \vec{R}} \frac{ω_0^2}{ω_0^2 - ω_i^2} = d_i d_j V_{ij}(ω_0, R),
\]

(23)
where \( |f\rangle = |g, e, 0\rangle \) and \(|n\rangle\) are eigenstates of \( H_0 \) and

\[
V_{ij}(\omega_0, R) = -\frac{\omega_0^2}{4\pi} \left( (\delta_{ij} - \hat{R}_i \hat{R}_j) \frac{\cos \omega_0 R}{\omega_0 R} - (\delta_{ij} - 3\hat{R}_i \hat{R}_j) \left[ \frac{\sin \omega_0 R}{(\omega_0 R)^2} \right] \right). \tag{24}
\]

As indicated by the second equality in equation (23) \( \Delta_{12} \) is nothing but the well-known gauge-invariant QED matrix-element describing resonant energy-transfer.

We have therefore obtained the standard result, equation (20), without ever making a concrete choice for the \( \alpha_k \). In order that the standard result is obtained the direct Coulomb-like interaction \( C_{(0)} \) must be kept within the interaction Hamiltonian \( V \). This ensures that for all \( \alpha_k \) the unperturbed Hamiltonian \( H_0 \) is that is used in conventional derivations wherein \( \alpha_k = 1 \). The \( S \)-matrix elements involving \( C_{(0)} \) that appear as coefficients in the master equation are then \( \alpha_k \)-independent and are the same as those obtained in the conventional derivation. Our derivation makes it clear that when \( C_{(0)} \) is sufficiently strong compared with the linear dipole-field coupling term, its inclusion within the interaction Hamiltonian rather than \( H_0 \) may be ill-justified. The standard master equation may therefore be inaccurate in such regimes. This fact is obscured within conventional derivations that use the multipolar gauge \( \alpha_k = 1 \), because in this gauge \( C_{(0)} \) vanishes identically. However, one typically already assumes weak-coupling to the radiation field in the multipolar gauge, and this leads to the standard master equation (20). If instead we adopt the Coulomb gauge \( \alpha_k = 0 \) we obtain the static dipole–dipole interaction \( C_{(0)} = \alpha R_{\parallel}^2 \), where in the mode continuum limit

\[
C = \frac{d_i d_j}{4\pi R^3} (\delta_{ij} - 3\hat{R}_i \hat{R}_j). \tag{25}
\]

This quantity coincides with the near-field limit of the resonant energy transfer element \( \Delta_{12} \) given in equation (23). In the near-field regime \( R/\lambda \ll 1 \), \( C_{(0)} \) may be too strong to be kept within the purportedly weak perturbation \( V \) and the standard master equation, which only results when one treats \( C_{(0)} \) as a weak perturbation, should then break down. This will be discussed in more detail in the following section.

### 3. Corrections to the standard master equation

#### 3.1. Derivation of an alternative master equation

In the near-field regime \( R/\lambda \ll 1 \) the rate of spontaneous emission into the transverse field is much smaller than the direct dipolar coupling; \( C/\gamma \gg 1 \). Moreover, for a system of closely spaced Rydberg atoms, the electrostatic Coulomb interaction may be such that \( C \sim \omega_0 \). For example, given a Rydberg state with principal quantum number \( n = 50 \) we can estimate the maximum associated dipole moment as \((3/2)n^2a_0 \approx 10^{-26} \) Cm where \( a_0 \) is the Bohr radius and \( e \) the electronic charge. For a 1 μm separation, which is approximately equal to \( 10n^2a_0 \), the electrostatic dipole interaction \( C/\omega_0 \sim 1 \) for \( \omega_0 \) corresponding to a microwave frequency. In such situations it is not clear that the Coulomb interaction can be included within the perturbation \( V \) with the coupling to the transverse field. In the multipolar gauge where no direct Coulomb interaction is explicit the same physical interaction is mediated by the low frequency transverse modes, which must be handled carefully. A procedure which separates out these modes should ultimately result in a separation of the Coulomb interaction, which is of course already explicit within the Coulomb gauge. We remark that when considering realistic Rydberg atomic systems within the strong dipole–dipole coupling regime the validity of the two-level model should also be considered. However, moving beyond the two-level approximation is beyond the scope of this paper. Our aim is to consider general atomic, molecular and condensed matter systems strongly-coupled by dipole–dipole interactions for which two-level models are typically used [4, 37, 38]. Retaining the two-level model for each dipole allows us to succinctly compare with existing literature and thereby determine the relative difference produced by our non-perturbative treatment of dipole–dipole interactions.

In the Coulomb gauge the interaction Hamiltonian \( V \) coupling to the transverse radiation field is

\[
V = \frac{2}{\omega_0} \sum_{\mu=1}^{2} \sigma_{\mu} \cdot A(R_{\mu}) + \frac{e^2}{2m} A(R_{\mu})^2 \tag{26}
\]

with \( \sigma_{\mu} = -i(\sigma_{\mu}^\dagger - \sigma_{\mu}) \) and

\[
A(x) = \sum_{k\lambda} \sqrt{\frac{1}{2\omega_k L^3}} e_{ki} \sigma_{k\lambda}^\dagger e^{-i k \cdot x} + \text{H.c.} \tag{27}
\]
The contribution of the transverse field to $\Delta_{12}$ in equation (21) is found using equation (26) to be

$$
\Delta_{12} = \sum_{n} \langle 0, e, g | V[n] | n | V[0, g, e] \rangle_{\omega_0 - \omega_n}
= -\frac{\omega_0 d d_i}{4 \pi} \left( (\delta_{ij} - \hat{R}_i \hat{R}_j) \frac{\cos \omega_0 R}{\omega_0 R} - (\delta_{ij} - 3 \hat{R}_i \hat{R}_j) \left( \sin \omega_0 R \left( \frac{1}{(\omega_0 R)^2} - \frac{1 - \cos \omega_0 R}{(\omega_0 R)^3} \right) \right) \right)
= \Delta_{12} - C.
$$

(28)

When the contribution $C = \langle 0, e, g | C_{(0)} | 0, g, e \rangle$ resulting from the direct Coulomb interaction is added to $\Delta_{12}$ the fully retarded result $\Delta_{12}$ is obtained. The two matrix elements $\Delta_{12}$ and $\Delta_{12}$ therefore only differ in their near-field components, which vary as $R^{-3}$ and which we denote by $\Delta^{nf}_{12}$ and $\Delta^{nf}_{12}$, respectively. According to equations (23) and (28) the components $\Delta^{nf}_{12}$ and $\Delta^{nf}_{12}$ dominate at low frequencies $\omega_0$. Since $\Delta_{12}$ is evaluated at resonance $\omega_k = \omega_0$, it follows that within the multipolar-gauge the low $\omega_k$ modes within the system-reservoir coupling give rise to a strong dipole–dipole interaction in the form of $\Delta^{nf}_{12} \approx C$. In such regimes the multipolar interaction Hamiltonian cannot be classed as a weak perturbation. On the other hand, the matrix element $\Delta_{12}$ is obtained using the Coulomb gauge interaction in equation (26), and is such that $\Delta_{12}^{nf} = \Delta_{12}^{nf} - C \approx 0$. Within the Coulomb gauge the interaction equivalent to the low frequency part of the multipolar gauge system-reservoir coupling is a direct dipole–dipole Coulomb interaction $C_{(0)}$. This appears explicitly in the Hamiltonian, but has not been included within equation (26), which therefore represents a genuinely weak perturbation.

The collective decay rate $\gamma_12$, as given in equation (21), does not involve the direct Coulomb interaction $C_{(0)}$ in any way, and can be obtained from the transverse field interaction in equation (26) or from the multipolar interaction. Crucially, in the near-field regime $R / \lambda_0 \ll 1$ the terms $\gamma_1$, $\gamma_12$ and $\Delta_{12}$, which result from the interaction in equation (26), are several orders of magnitude smaller than the direct electrostatic coupling $C$. Motivated by the discussion above, we include the Coulomb interaction within the unperturbed Hamiltonian, but continue to treat the interaction with the transverse field as a weak perturbation. This gives rise to a master equation depending on different $S$-matrix elements.

The unperturbed Hamiltonian $H_0 = H_d + H_F$ is defined by

$$
H_d = \sum_{\mu=1}^{2} \omega_0 \sigma_{\mu}^{d} \sigma_{\mu}^{d} + C \sigma_1^{d} \sigma_2^{d}, \quad H_F = \sum_{k\lambda} \omega_k a_{k\lambda}^{d} a_{k\lambda}^{d},
$$

(29)

where $C \in \mathbb{R}$ is given by equation (25). The corresponding interaction Hamiltonian is then given in equation (26). We begin by diagonalising $H_d$ as

$$
H_d = \sum_{n=1}^{4} \epsilon_n | \epsilon_n \rangle \langle \epsilon_n |,
$$

(30)

where

$$
\epsilon_1 = \omega_0 - \eta, \quad \epsilon_2 = \omega_0 - C, \quad \epsilon_3 = \omega_0 + C, \quad \epsilon_4 = \omega_0 + \eta,
$$

(31)

and

$$
|\epsilon_1\rangle = \frac{1}{\sqrt{C^2 + (\omega_0 + \eta)^2}} (|\omega_0 + \eta\rangle |g, g\rangle - C |e, e\rangle), \quad |\epsilon_2\rangle = \frac{1}{\sqrt{2}} (|e, g\rangle - |g, e\rangle),
$$

$$
|\epsilon_3\rangle = \frac{1}{\sqrt{2}} (|e, g\rangle + |g, e\rangle), \quad |\epsilon_4\rangle = \frac{1}{\sqrt{C^2 + (\omega_0 - \eta)^2}} (C |e, e\rangle - |\omega_0 - \eta\rangle |g, g\rangle),
$$

(32)

with $\eta = \sqrt{\omega_0^2 + C^2}$. Next we move into the interaction picture with respect to $H_0$ and substitute the interaction picture Hamiltonian into equation (19). Moving back into the Schrödinger picture we eventually obtain

$$
\dot{\rho} = -i[H_d, \rho] + \sum_{\zeta, \zeta' = \pm 1} \sum_{\mu, \nu = 1}^{2} \left[ \Gamma_{\mu\nu}^{(1)} (A_{\mu\nu} \rho A_{\nu\mu}^{†} - A_{\nu\mu}^{†} A_{\mu\nu} \rho) + \text{h.c.} \right].
$$

(33)

Here, $\omega_1 = \eta - C$ and $\omega_2 = \eta + C$, while $A_{(n-\zeta)} = A_{\nu\mu}^{†}$ and $A_{\mu\nu} \equiv A_{\mu\nu}$ $(n = 1, 2)$ with

$$
A_{11} = a |\epsilon_1\rangle \langle \epsilon_1 | + b |\epsilon_2\rangle \langle \epsilon_2 |, \quad A_{12} = c |\epsilon_1\rangle \langle \epsilon_2 | - d |\epsilon_2\rangle \langle \epsilon_1 |,
$$

$$
A_{21} = a |\epsilon_1\rangle \langle \epsilon_2 | + b |\epsilon_2\rangle \langle \epsilon_1 |, \quad A_{22} = c |\epsilon_2\rangle \langle \epsilon_2 | + d |\epsilon_1\rangle \langle \epsilon_1 |,
$$

(34)
\[ a = \frac{\omega_0 + \eta - C}{\sqrt{2(C^2 + [\omega_0 + \eta]^2)}}, \quad b = \frac{\omega_0 - \eta - C}{\sqrt{2(C^2 + [\omega_0 - \eta]^2)}}, \]
\[ c = \frac{\omega_0 + \eta + C}{\sqrt{2(C^2 + [\omega_0 + \eta]^2)}}, \quad d = \frac{-\omega_0 + \eta + C}{\sqrt{2(C^2 + [\omega_0 - \eta]^2)}}. \quad (35) \]

The coefficients \( \Gamma_{\mu\nu}(\omega) \) are defined by
\[ \Gamma_{\mu\nu}(\omega) = \omega_d^2 d_d^i \int_0^\infty ds \ e^{i\omega s} \langle A_{\mu}(R_{\mu}, s)A_{\nu}(R_{\nu}, 0) \rangle_{\beta}, \quad (36) \]

where \( A_{\mu}(x, t) \) denotes the field \( A(x) \) in equation (27) once transformed into the interaction picture, and \( \langle \cdot \rangle_{\beta} \) denotes the average with respect to the radiation thermal state at temperature \( \beta^{-1} \). The \( \Gamma_{\mu\nu}(\omega) \) are symmetric \( \Gamma_{\mu\nu}(\omega) = \Gamma_{\nu\mu}(\omega) \) and can be written
\[ \Gamma_{\mu\nu}(\omega) = \frac{1}{2} \gamma_{\mu\nu}(\omega) + iS_{\mu\nu}(\omega), \quad (37) \]

where
\[ \gamma_{\mu\nu}(\omega) = (1 + N) \frac{\gamma}{\omega_0}, \quad \gamma_{12}(\omega) = (1 + N) d_d^i \int_0^\infty ds \ e^{i\omega s} \langle A_{1}(R_{1}, s)A_{2}(R_{2}, 0) \rangle_{\beta}, \]
\[ S_{\mu\nu}(\omega) = \frac{\gamma}{2\pi} \int_0^\infty d\omega_k \frac{\omega_k}{\omega_0} \left[ \frac{1 + N_k}{\omega - \omega_k} + \frac{N_k}{\omega + \omega_k} \right], \]
\[ S_{12}(\omega) = \frac{d_d^i d_d^j}{2\pi} \int_0^\infty d\omega_k \tau_{\alpha}(\omega_k, R) \frac{\omega_k^2}{\omega_k^2} \left[ \frac{1 + N_k}{\omega - \omega_k} + \frac{N_k}{\omega + \omega_k} \right]. \quad (38) \]

The frequency integrals in equation (38) are to be understood as principal values. The decay rates \( \gamma_{\mu\nu}(\omega) \) in equation (38) coincide with those found in the standard master equation (20) when evaluated at \( \omega_0 \) though are here evaluated at the frequencies \( \omega_{1,2} \). The quantities \( S_{\mu\nu} \) are related to the shifts \( \Delta \) and \( \Delta_{12} \), defined in equations (12) and (23) respectively, by
\[ \Delta = S_{\mu\nu}(\omega_0) - S_{\mu\nu}(-\omega_0), \quad \Delta_{12} - C = \Delta_{12} = S_{12}(\omega_0) + S_{12}(-\omega_0). \quad (39) \]

In deriving equation (33) we have not yet performed a secular approximation, in contrast to the derivation of equation (20). However, naïvely applying a secular approximation that neglects off-diagonal terms for which \( \zeta = \zeta' \) in the summand in equation (35) would not be appropriate, because this would eliminate terms that are resonant in the limit \( C \to 0 \). Instead we perform a partial secular approximation which eliminates off-diagonal terms for which \( \zeta \) and \( \zeta' \) have opposite sign. These terms remain far off-resonance for all values of \( C \). The resulting master equation is given by
\[ \dot{\rho} = -\frac{i}{\hbar} [H_{\mu\nu}, \rho] + \sum_{\zeta, \zeta'} \sum_{n, m, n'} \left[ \Gamma_{\mu\nu}(\zeta)(A_{\nu\zeta} A_{\mu\zeta'} + A_{\mu\zeta'} A_{\nu\zeta}) + \Gamma_{\mu\nu}(-\zeta)(A_{\nu\zeta} A_{\mu\zeta'} - A_{\mu\zeta'} A_{\nu\zeta}) + \text{h.c.} \right]. \quad (40) \]

We are now in a position to compare our master equation (40) with the usual result in (20). In the limit \( C \to 0 \) we have \( \eta \to \omega_0 \) so that \( \omega_{1,2} \to \omega_0 \). The rates and shifts in equation (38) are then evaluated at \( \omega_0 \) within equation (40). Also, the Hamiltonian \( H_{\mu\nu} \) tends to the bare Hamiltonian \( \omega_0 (\sigma_1^{+} \sigma_1^{-} + \sigma_2^{+} \sigma_2^{-}) \), and furthermore we have that
\[ \sum_{\zeta = \omega_{1,2}} A_{\mu\zeta} \to \sigma_{\mu}^{-}. \quad (41) \]

Thus, taking the limit \( C \to 0 \) in equation (40) one recovers equation (20) with \( \Delta_{12} \) replaced by \( \Delta_{12} \) given in equation (28). However, since \( \Delta_{12} \to \Delta_{12} \) when \( C \to 0 \), equations (40) and (20) coincide in this limit. For finite \( C \), equation (40) offers separation-dependent corrections to the usual master equation and is the main result of this section.

### 3.2. Discussion: gauge-invariance of the new master equation

It is important to note that while our master equation (40) is generally different to the usual gauge-invariant result (equation (20)) there is no cause for concern regarding the issue of gauge-invariance. As we have shown the standard master equation can be obtained when \( \omega_{1,2} \to \omega_0 \) provided one uses a partitioning of the Hamiltonian in the form \( H = H_0 + V_{\text{usual}} \) where \( H_0 \) is given by equation (15) and
\[ V_{\text{usual}} = \sum_{\mu=1}^{2} \omega_0 \sigma_{\mu} \cdot A(R_{\mu}) + \sum_{\mu=1}^{2} \frac{e^2}{2m} A(R_{\mu})^2 + C(0). \] (42)

Our master equation (40) has also been obtained by choosing \( \alpha_k = 0 \), but our derivation makes use of the different partitioning \( H = H_0 + V \) where \( H_0 \) is defined as in equation (29) and \( V = V_{\text{usual}} - C(0) \) is defined as in equation (26). The two different partitionings of the same Hamiltonian yield two different second order master equations.

As we have shown the standard Born–Markov-secular master equation (20) can be obtained for any other choice of \( \alpha_k \) provided that the unperturbed Hamiltonian is always defined as in equation (15). Similarly a full secular approximation of our master equation (40) can also be obtained for any other choice of \( \alpha_k \) provided the unperturbed Hamiltonian is always defined as in equation (29). We note further that the secular approximation is well justified within the near-field regime of interest \( R \ll \lambda_0 \). Let us consider for example the multipolar gauge obtained by choosing \( \alpha_k = 1 \). In order to achieve the appropriate partitioning of the multipolar Hamiltonian for derivation of our master equation one must add \( C(0) \) to the usual multipolar unperturbed Hamiltonian \( H_0 \) given in equation (15), and simultaneously subtract \( C(0) \) from the usual multipolar interaction Hamiltonian. Using this repartitioning of the multipolar Hamiltonian the Born–Markov-secular master equation is found to coincide with our master equation (40) once a full secular approximation is performed within the latter. This derivation is however, more cumbersome than the Coulomb gauge derivation. Since the Coulomb energy is naturally explicit within the Coulomb gauge, the latter is the most natural gauge to choose for the purpose of including the relatively strong static interaction within the unperturbed Hamiltonian.

Any difference between the master equation (40) and the corresponding partially-secular result found using \( \alpha_k \neq 0 \) is contained entirely within non-secular contributions. These contributions are negligible within the regime of interest \( R \ll \lambda_0 \) and have only been retained within equation (40) to facilitate comparison with the standard result equation (20). Moreover, in the far-field regime \( R \gg \lambda_0 \) the master equations (20) and (40) coincide, so the master equation (40) is also gauge-invariant within this regime.

### 4. Solutions and emission spectrum

#### 4.1. Solutions

For large inter-dipole separations \( R \gg \lambda \) the master equations (20) and (40) coincide and they therefore yield identical physical predictions. However, in the near-zone \( R \ll \lambda_0 \) the master equations generally exhibit significant differences. To compare the two sets of predictions we assume a vacuum field \( N = 0 \) and consider the experimental situation in which the system is prepared in the symmetric state \( |\psi_s\rangle \). This state is a simultaneous eigenstate of the dipole Hamiltonian \( \omega_0 (\sigma_1^0 \sigma_1^0 + \sigma_2^0 \sigma_2^0) \) appearing in the standard master equation (20), and of the Hamiltonian \( H_f \) appearing in our master equation (40). Experimentally, one expects to find that the system initially prepared in the state \( |\psi_s\rangle \) decays into the stationary state. Theoretically, different stationary states are predicted by the two master equations (20) and (40), and the rates of decay into these respective stationary states are also different. Figures 1 and 2 compare the symmetric and stationary state populations found using master equations (20) and (40) when the system starts in the symmetric eigenstate \( |\psi_s\rangle \). For small separations the ground and symmetric state populations obtained from our master equation (40) crossover earlier, which indicates more rapid symmetric state decay than is predicted by equation (20) (see figure 1). This gives rise to the different starting values at \( R = r_c \) of the curves depicted in figure 2. For larger separations the solutions converge and become indistinguishable for all times.

The different behaviour in figures 1 and 2 can be understood by looking at a few relevant quantities. The matrix element of the combined dipole moment between ground and symmetric eigenstates is found to be

\[ d_{11} = \langle \psi_s | d_1 + d_3 | \psi_s \rangle = 2ad, \] (43)

which is different to the usual transition dipole moment \( \langle \psi_s | d_1 + d_3 | \psi_g \rangle = \sqrt{2}d \). Since \( a \to 1/\sqrt{2} \) as \( C \to 0 \), the dipole moment \( d_{11} \) reduces to \( \sqrt{2}d \) when \( R \to \infty \). As \( R \) decreases, however, \( d_{11} \) becomes increasingly large compared with \( \sqrt{2}d \). This is consistent with the more rapid decay observed in figure 1. A more complete explanation of this behaviour can be obtained by calculating the rate of decay of the symmetric state into the vacuum, which we denote \( \gamma_r \). Using Fermi’s golden rule, and the eigenstates given in equation (32), we obtain

\[ \gamma_r(\omega_2) = 2e^2 [\gamma_{\mu \mu}(\omega_2) + \gamma_{12}(\omega_2)]_{N=0}. \] (44)

Only when \( C \to 0 \), such that \( \omega_2 = \eta + C \to \omega_0 \) and \( c \to 1/\sqrt{2} \), does this decay rate reduce to that obtained when using the bare eigenstates \( |i, f\rangle \), \( (i, j = e, g) \), which is

\[ \gamma_{r,0} = \gamma + \gamma_{12}(\omega_0), \] (45)

where \( \gamma_{12}(\omega_0) \) is given in equation (21). As shown in figure 3, for sufficiently small \( R \) the decay rate \( \gamma_r(\omega_2) \) is significantly larger than \( \gamma_{r,0} \).
In contrast to the decay behaviour of the symmetric state, the predictions of the master equations (20) and (40) are the same if the system is assumed to be prepared in the anti-symmetric state $\psi_2$, which like $\psi_3$ is a simultaneous eigenstate of $\sum \sigma_i^+ + \sum \sigma_i^-$ and $H_d$. Both master equations predict that the population of the state $\psi_2$ remains stationary, i.e., that it is a completely dark state. This can be understood by noting that the collective dipole moment associated with the anti-symmetric to stationary state transition vanishes when either stationary state, $\psi_1$ or $\psi_3$, is used. Finally, the predicted behaviour by our master equation (40) of the standard stationary state $\psi_1$ is illustrated in figure 4. For an initial state $\psi_3$ the population $p_{ss}(t)$ of the state...
\[ \gamma_s(\omega) \]
\[ \frac{\gamma_s}{\gamma} \]

Figure 3. Comparison of the symmetric state decay rates \( \gamma_s \) (from our master equation) and \( \gamma_s,0 \) (from the standard master equation) as functions of separation \( R \). All parameters are chosen as in figure 1.

![Graph of symmetric state decay rates](image)

| \( R \) |
|------------------|
| 10r_a            |
| 100r_a           |

\[ \gamma_s(\omega) \]
\[ \frac{\gamma_s}{\gamma} \]

4.2. Emission spectrum

In this section we apply our master equation (40) to calculate the emission spectrum of the two-dipole system initially prepared in the symmetric state \( |g, g\rangle \). This provides a means by which to test experimentally whether our predictions are closer to measured values than the standard approach. The spectrum of radiation is defined according to the quantum theory of photodetection by [39, 40].

![Graph of population as a function of separation](image)

| \( R \) |
|------------------|
| 10r_a            |
| 100r_a           |

\[ \langle g, g\rangle \] at a given time \( t \), is identical to that predicted by equation (20) only for sufficiently large \( R \) whereby \( |\epsilon_1\rangle \approx |g, g\rangle \).

![Figure 4. Population](image)

Figure 4. The population of the state \( |g, g\rangle \) found using equation (40) is plotted as a function of separation \( R \) for various times. All remaining parameters are as in figure 1. The dashed lines give the corresponding populations found using equation (20), which are insensitive to variations in \( R \) over the range considered. For large \( R \) the two sets of solutions agree. In particular, the steady state population \( \rho_{gg}(\infty) = |\langle g, g\rangle \rangle^2 \) is equal to unity only for sufficiently large \( R \).
where for simplicity we assume that the field is in the vacuum state. Since the master equations (20) and (40) yield different predictions for this experimentally measurable quantity, an experiment could be used to test which master equation is the most accurate.

The detector is located at position \( \mathbf{x} \) with \( x \gg R \), so that only the radiative component \( E_{r,\text{rad}} \) of the electric source field, which varies as \( |x - R_x|^{-1} \), need be used. This is the only part of the field responsible for irreversibly carrying energy away from the sources. The positive and negative frequency components of the radiation source field are given within both rotating-wave and Markov approximations by

\[
E^{(\pm)}_{r,\text{rad}}(t, \mathbf{x}) = \sum_{\mu=1}^{2} \frac{\omega_0^2}{4\pi} (\delta_{ij} - \hat{n}_{\mu}(t_{\mu})) \frac{1}{t_{\mu}} \sigma^\mp(t_{\mu}),
\]

where \( r_\mu = x - R_\mu \), and \( t_{\mu} = t - r_{\mu} \) is the retarded time associated with the \( \mu \)'th source. For \( x \gg R \) we have to a very good approximation that \( r_1 = r_2 = r \), where \( r \) is the relative vector from \( x \) to the midpoint of \( R_1 \) and \( R_2 \).

Substituting equation (47) into equation (46) within this approximation yields

\[
s(\omega) = \mu \omega_0^4 \int_0^\infty dt \int_0^\infty dt' e^{-i\omega(t-t')} \left( \sum_{\mu=1}^{2} \sigma^\mu(t) \sigma^\mu(t') \right),
\]

where

\[
\mu = \left[ \frac{1}{4\pi} \left( \delta_{ij} - \hat{n}_{\mu}(t_{\mu}) \right) \frac{1}{t_{\mu}} \right]^T.
\]

To begin with, let us use the standard master equation (20) to find the required two-time correlation function. Assuming that the system is initially prepared in the symmetric state \( |s_3\rangle \), using the standard master equation (20) together with the method of calculation given in appendix A.3 we obtain the two-time correlation function

\[
\sum_{\mu,\mu'=1}^{2} \langle \sigma^\mu(t) \sigma^{\mu'}(t') \rangle = 2e^{\gamma_{0,0}(t+t')} e^{i(\omega_0 + \Delta_{12})(t-t')},
\]

where \( \gamma_{0,0} \) and \( \Delta_{12} \) are given in equations (45) and (21), respectively. By direct integration of equation (50) one obtains the corresponding Lorentzian spectrum

\[
s_0(\omega) = \frac{2\omega_0^4 \mu}{(\gamma_{0,0}/2)^2 + (\omega - [\omega_0 + \Delta_{12}]/2)^2}.
\]

Let us now turn our attention to the spectrum obtained from our new master equation (40). We have seen that the solutions of equations (40) and (20) differ only in the near field regime \( R \ll \lambda \). For sufficiently small \( R \) we have that \( \omega_0 \sim C \), and the frequency difference \( \omega_2 - \omega_1 = 2C \sim 2\omega_0 \) is large. In this situation we can perform a full secular approximation within equation (40) to obtain the master equation

\[
\dot{\rho} = -i[H_d, \rho] + D(\rho),
\]

with

\[
H_d = H_d + \sum_{\omega=\pm\omega_{12}, \mu,\mu'=1}^{2} S_{\mu\mu'}(\omega) A^\dagger_{\mu\omega} A_{\mu'\omega},
\]

and

\[
D(\rho) = \sum_{\omega=\pm\omega_{12}, \mu,\mu'=1}^{2} \gamma_{\mu\mu'}(\omega) \left[ A_{\mu\omega} \rho A^\dagger_{\mu'\omega} - \frac{1}{2} \{ A^\dagger_{\mu'\omega} A_{\mu\omega}, \rho \} \right].
\]

Solving this secular master equation allows us to obtain a simple expression for the emission spectrum.

The correlation function in equation (46) defines the radiation intensity when it is evaluated at \( t = t' \). Naively calculating the quantity \( \sum_{\omega=\pm\omega_{12}, \mu,\mu'=1}^{2} \langle \sigma^\mu(t) \sigma^{\mu'}(t) \rangle \), taken in the stationary state \( |c_3\rangle \) yields a non-zero stationary intensity, because \( |c_3\rangle \) is a superposition involving both \( |g, g\rangle \) and the doubly excited bare state \( |e, e\rangle \). A non-zero radiation intensity even in the stationary state is clearly non-physical. However, a more careful analysis recognises that when the radiation source fields are to be used in conjunction with equation (40) the optical approximations used in their derivation should be applied in the interaction picture defined in terms of the dressed Hamiltonian \( H_d \), given in equation (30). One then obtains the source field.
spectrum then yields the Lorentzian spectrum Full details of the calculation of the spectrum in equation is the shifted symmetric to ground transition frequency. Integration of equation where we have again assumed that (equation ) operators are denoted (equation ) transition frequencies associated with this basis are denoted (equation ) correlation functions intensity is therefore seen to vanish in the stationary limit as required physically. According to equation the annihilation (creation) radiation source field is now associated with lowering (raising) operators in the dressed basis (equation ) rather than in the bare basis (equation ), (equation ). Substitution of equation (equation ) into equation (equation ) yields

\[
E^{(t)}_{\text{rad},i}(t, x) = \sum_{i=1}^{2} \sum_{n<m} \int_{-\infty}^{\infty} \left( e^{n} - e^{-n} \right) \left( \sigma_{\mu,nm}^+ \sigma_{\mu,nm}^- \right) d\mu \int_{0}^{\infty} \left( e^{\mu} - e^{-\mu} \right) \left( \sigma_{\mu,nm}^+ \sigma_{\mu,nm}^- \right) d\mu,
\]

where (equation ) in which (equation ) denotes the (equation ) th matrix element of (equation ) in the basis (equation ). The transition frequencies associated with this basis are denoted (equation ) and the raising and lowering operators are denoted (equation ), (equation ). The derivation of equation (equation ) is given in appendix A.4. According to equation (equation ) the annihilation (creation) radiation source is now associated with lowering (raising) operators in the dressed basis (equation ) rather than in the bare basis (equation ), (equation ), (equation ). Substitution of equation (equation ) into equation (equation ) yields

\[
s(\omega) = \mu \int_{0}^{\infty} dt \int_{0}^{\infty} dt' \sum_{i=1}^{2} \sum_{n<m} \int_{-\infty}^{\infty} \left( e^{n} - e^{-n} \right) \left( \sigma_{\mu,nm}^+ \sigma_{\mu,nm}^- \right) d\mu \int_{0}^{\infty} \left( e^{\mu} - e^{-\mu} \right) \left( \sigma_{\mu,nm}^+ \sigma_{\mu,nm}^- \right) d\mu,
\]

where we have again assumed that (equation ). Unlike the correlation function in equation (equation ), when (equation ) the correlation functions (equation ) vanish in the stationary (ground) state (equation ). The radiation intensity is therefore seen to vanish in the stationary limit as required physically.

Taken in the symmetric state (equation ) the only non-zero two-time correlation function that contributes to equation (equation ) is found to be

\[
C_{33}(t, t') = \langle \theta_{31}(t) \theta_{31}(t') \rangle = e^{-c^2(\gamma_{01}(\omega_0^3 + \gamma_{01}(\omega_0^3))(t-t')^2} e^{i\omega_0 (t-t')},
\]

where

\[
\tilde{\omega}_0 = \omega_2 + 2(S_{pp}(-\omega_1)[b^2 - a^2] + S_{12}(-\omega_1)[b^2 + a^2])
+ c^2[S_{pp}(-\omega_2) - S_{pp}(-\omega_2) + S_{12}(\omega_2) - S_{12}(\omega_2)]
\]

is the shifted symmetric to ground transition frequency. Integration of equation (equation ) according to equation (equation ) then yields the Lorentzian spectrum

\[
s(\omega) = \frac{2\mu(\omega_2)^2}{(\gamma_0(\omega_2)^2 + (\omega - \omega_2)^2)}.
\]

Full details of the calculation of the spectrum in equation (equation ) are given in appendix A.4. In the limit of large separation (equation ) 0, which implies that (equation ) (equation ) and (equation ) 1/\( \gamma_0 \). As a result (equation ) for large (equation ) and the predicted spectra coincide. On the other hand, for sufficiently small (equation ) the spectrum (equation ) again offers separation-dependent corrections to the standard result (equation ) .

The two spectra (equation ) and (equation ) are compared in figures 5 and 6. As their relative widths are proportional to the rates, they are given in equations (equation ) and (equation ), respectively. These quantities have been plotted already in figure 3. The relative heights of the spectral peaks are (equation ) and (equation ) respectively, which are plotted in figure 7. This figure shows that the peak heights in the spectra begin to diverge as (equation ) decreases. At a
separation of $15r_a$, where $r_a = n^2a_0$, $n = 50$ is a characteristic Rydberg atomic radius, the peak value of $s(\omega)$ is around two times larger than the peak value of $s_0(\omega)$ for the parameters chosen here. The positions of the peaks are $\tilde{\omega}_0 + \Delta_2$ and $\tilde{\omega}_2$, respectively, and these are plotted in figure 8. The ultra-violet cut-off chosen for the calculation of the single-dipole shift components corresponds to the inverse dipole radius wavelength, namely $2\pi c / r_a$. This value is chosen for consistency with the electric dipole approximation that we have used throughout. For small $R$ the spectrum $s(\omega)$ is blue-shifted relative to $s_0(\omega)$. Figure 8 shows that the ratio of peak positions approaches a constant value around two for very small $R$. These differences could in principle be detected in an experiment. At a separation of $20r_a$, which is roughly 2.5 $\mu$m, for instance, the difference in shifted frequencies $\tilde{\omega}_2 - \tilde{\omega}_0 - \Delta_2$ is around 1 GHz for the parameters chosen in figure 1. This is similar in magnitude to the Lamb-shift in atomic hydrogen.
5. Conclusions

In this paper we have derived a partially secular master equation valid for arbitrarily separated dipoles within a common radiation field at arbitrary temperature. The equation is intended for the modelling of dipolar systems in which static dipole–dipole interactions are strong compared with the coupling to transverse radiation. This situation can arise in systems of Rydberg atoms and other molecular systems [10–23, 41–44].

We have shown that the standard gauge-invariant two-dipole master equation can only be derived in gauges other than the multipolar gauge if the direct inter-dipole Coulomb energy is included within the interaction Hamiltonian rather than the unperturbed part. Our arbitrary gauge approach makes a particular limitation of this method clear. Specifically, the usual approach can only be justified when the direct Coulomb interaction is weak along with the coupling to transverse radiation. In situations in which this is not the case our master equation, which is based on a repartitioning of the Hamiltonian into unperturbed and interaction parts, yields significant corrections to previous results. In addition to corrections to the decay of the excited states of the system, we have found corrections to the natural emission spectrum of the initially excited system. In principle, spectroscopy could be used to determine which predictions are closer to the measured values. A possible extension of our result would be to include an external driving Hamiltonian that represents coherent irradiation. The techniques employed here could then be used to calculate the fluorescence spectrum of the driven system.

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Appendix

A.1. Self-energy contributions and the Gauge-invariance of the single dipole-shift

Here we determine the contribution of self-energy terms to dipole level-shifts and demonstrate that the single-dipole transition shift is gauge-invariant. The self-energy term $V^{(2)}$ is given in equation (4). The shifts arising from this term are divergent in the mode continuum limit $\omega_{k} \to \infty$, but this divergence is not unexpected within the non-relativistic dipole approximated treatment. It is typically handled through the introduction of an ultra-violet cut-off. In the treatment of the Lamb-shift in atomic hydrogen the Coulomb gauge self-energy $V^{(2)}$ with $\alpha_{x} = 0$ is independent of the atomic electron levels and is therefore ignored within the calculation of the measurable shift [35]. In the multipolar gauge $V^{(2)}$ represents a polarisation self-energy term and when its contribution is combined with the remaining contribution to the shift coming from the linear part of the

\[\omega_{\text{shift}} = \omega_{0} + \Delta \omega \]

Figure 8. The positions of the peaks in the spectra $s(\omega)$ and $s_{0}(\omega)$ as functions of the separation $R$. We have chosen all remaining parameters as in figure 4. The upper subplot shows the ratio of the two peak positions over the same range of values of $R$, while the lower subplot shows the difference in peak positions over the same range of values of $R$. 

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multipolar interaction Hamiltonian one obtains the same result as the Coulomb gauge treatment. In all cases mass renormalisation must also be performed to obtain the correct shift.

In the Coulomb gauge $V^{(2)}$ does not contribute to the master equation transition shift of the two-level dipole, which is the difference between excited and ground state shifts. This is independent of whether the two-level approximation has been made. However, even within the Coulomb gauge it is important to note that one must generally account for all self-energy contributions when explicitly verifying that quantities are gauge-invariant. In particular, to verify that the ground and excited level-shifts are separately gauge-invariant, the contributions $(n^{|V^{(2)}|}m^{|V^{(2)}|})$, $n = e, g$ must be taken into account.

Using the Hamiltonian in equation (3), the standard Born-Markov master equation has form given in equation (11), in which the decay rate $\gamma$ is independent of $\alpha_k$. In this equation, the transition shift can be expressed as the difference between excited and ground state shifts as $\Delta = \delta_e - \delta_g$ where

$$
\delta_e = \int d^3k \sum_k \left| \Delta_\nu(k) \cdot \mathbf{d} \right|^2 \frac{\epsilon^2}{2m} \omega_k \left( \frac{u_k^{g2}N_k}{\omega_k + \omega_0} - \frac{u_k^{e2}[1 + N_k]}{\omega_k + \omega_0} \right),
$$

$$
\delta_g = \int d^3k \sum_k \left| \Delta_\nu(k) \cdot \mathbf{d} \right|^2 \frac{\epsilon^2}{2m} \omega_k \left( \frac{u_k^{e2}N_k}{\omega_k - \omega_0} - \frac{u_k^{g2}[1 + N_k]}{\omega_k - \omega_0} \right),
$$

are $\alpha_k$-dependent. This $\alpha_k$-dependence is due to the lack of any contribution from the self-energy term $V^{(2)}$ in equation (60).

The $\alpha_k$-dependence within the master equation is eliminated when one accounts for the self-energy contributions and the effect of the two-level approximation, recalling that the latter was made after the transformation $R_{\alpha_k}$ was performed. More specifically it is possible to demonstrate that the single dipole master equation (10) is $\alpha_k$-independent, and that it coincides with equation (11). First we note that we can continue to express the second line in equation (10) in terms of the original partition $H = H_0 + V$. Thus, provided $H_0$ is kept the same for each choice of the $\alpha$ the dissipative part of the master equation is $\alpha_k$-independent. It remains to show that when one adds the shift contributions $\delta^{(1)}_{\alpha_k}$ coming from the second line in equation (10) to the corresponding self-energy contribution in equation (9) one obtains gauge-invariant total shifts. To this end let us first consider the Coulomb gauge $\alpha_k = 0$. The total excited and ground state shifts are

$$
\delta^e_{\text{CG}} = \delta^{(1)}_{\text{CG}} + \delta^{(2)}_{\text{CG}}, \quad \delta^g_{\text{CG}} = \delta^{(1)}_{\text{CG}} + \delta^{(2)}_{\text{CG}}.
$$

The components $\delta^{(1)}_{\text{CG}}$ are obtained by setting $\alpha_k = 0$ in equation (60), while the remaining component

$$
\delta^{(2)}_{\text{CG}} = \frac{\epsilon^2}{2m} \int d^3k \sum_k \left| \Delta_\nu(k) \right|^2 \frac{1 + 2N_k}{2\pi^2\omega_k}
$$

is the Coulomb gauge self-energy shift due to the $A^2$ part of the Coulomb gauge interaction Hamiltonian. Since this term is independent of the dipole, the shift $\delta^{(2)}_{\text{CG}}$ is the same for the ground and excited levels. The single-dipole transition shift $\Delta$ given in equation (12) in the main text can be expressed in terms of Coulomb gauge shifts as

$$
\Delta = \delta^e_{\text{CG}} - \delta^g_{\text{CG}} = \delta^{(1)}_{\text{CG}} - \delta^{(1)}_{\text{CG}}.
$$

More generally, for arbitrary $\alpha_k$ the total ground and excited state level shifts are denoted $\delta_{e,g}$. In what follows we will show that

$$
\delta_e - \delta_{\text{CG}} = \delta^{(1)}_{e,\text{CG}}
$$

and

$$
\delta_g - \delta_{\text{CG}} = \delta^{(1)}_{g,\text{CG}},
$$

from which it follows using equation (63) that $\delta_e - \delta_g = \Delta$ for all choices of $\alpha_k$.

In order to show that equations (64a) and (64b) hold we must carefully account for the two-level approximation, which was performed after the gauge transformation $R_{\alpha_k}$. Let us consider a general shift of the $m$'th level of the dipole with the form

$$
\bar{\omega}_m = \omega_m + \sum_n \omega_{mn} \mathbf{v} \cdot \mathbf{d}_{mn},
$$

where $\mathbf{v}$ is arbitrary. If we restrict ourselves to two levels $e$ and $g$, and if $m = e$ in the above, then the sum includes only one other level $n = g$, so we get for the shift

$$
\sum_n \omega_{mn} \mathbf{v} \cdot \mathbf{d}_{mn} = - \omega_{eg} \mathbf{v} \cdot \mathbf{d}_{eg}.
$$
where \( \omega_0 := \omega_{eg} = -\omega_{ge} \) and \( d := d_{eg} = d_{ge}^* \). If instead \( m = g \) then the shift is
\[
\sum_n \omega_n |v \cdot d_n|^2 = +\omega_0 |v \cdot d|^2.
\]
(67)
The shift is clearly different in the \( m = e \) and \( m = g \) cases when considering a two-level system. However, for an infinite-dimensional dipole the shift is independent of \( m \) being given by
\[
\sum_n \omega_n |v \cdot d_n|^2 = \frac{e^2}{2m} |v|^2,
\]
(68)
where we have made use of the identity
\[
\sum_n \omega_n d_n d_n^* = \frac{i e^2}{2m} (m| [p_1, r_j]| m) = \delta_0 \frac{e^2}{2m}.
\]
(69)
The difference between the finite and infinite-dimensional cases arises because the proof of equation (69) rests directly on the CCR algebra \([\tau_n, p_i] = i \delta_{ni}\), which can only be supported in infinite-dimensions. When the algebra is truncated to \( su(2) \), the same shift comes out level-dependent. Since the gauge transformation \( R_{(\alpha)} \) is made on the infinite-dimensional dipole it is necessary to employ equation (68) in order to exhibit gauge-invariance of the shifts. Thus, in order to get the correct level-shifts within the two-level approximation, when dealing with the excited level shift \( m = e \) we use equations (66) and (68), which imply
\[
\omega_0 |v \cdot d|^2 = -\frac{e^2}{2m} |v|^2,
\]
(70)
but when dealing with the ground level shift \( m = g \) we use equations (67) and (68), which imply
\[
\omega_0 |v \cdot d|^2 = \frac{e^2}{2m} |v|^2.
\]
(71)

We now proceed to verify that equations (64a) and (64b) hold. The complete shifts \( \delta_{e,g} \) are obtained by taking the shifts in equation (60) and adding their respective self-energy contributions. Subtracting \( \delta^{(2)}_{e} \) in equation (62) from \( \delta_e \) and subsequently using equation (70), which is appropriate for the excited state shift, we obtain
\[
\delta_e - \delta_{e}^{(2)} = \int d^4k \sum_{\lambda} \frac{|e_{\lambda}(k) \cdot d|^2}{2(2\pi)^3} \times \left( \alpha_k^2 - \alpha_k(\alpha_k - 2)[1 + 2N_k] \frac{\omega_0}{\omega_k} + \omega_0 \left( \frac{u_k^2 N_k}{\omega_k + \omega_0} - \frac{u_k^2 [1 + N_k]}{\omega_k - \omega_0} \right) \right)
\]
(72)
Using equation (6) we express the bracket within the integrand in this expression in terms of \( \alpha_k \). The part independent of \( N_k \) is
\[
\alpha_k^2 - \alpha_k(\alpha_k - 2) \frac{\omega_0}{\omega_k} - \frac{\omega_0}{\omega_k - \omega_0} \left( 1 - \alpha_k \right)^2 \frac{\omega_0}{\omega_k} + \frac{\omega_0}{\omega_k} \left( \frac{u_k^2 N_k}{\omega_k + \omega_0} - \frac{u_k^2 [1 + N_k]}{\omega_k - \omega_0} \right)
\]
(73)
In this expression we identify the coefficient of \( \alpha_k^2 \) as
\[
1 - \frac{\omega_0}{\omega_k - \omega_0} \left( \frac{\omega_0}{\omega_k} + \frac{\omega_0}{\omega_k} \right) = 1 - \frac{\omega_0}{\omega_k} \frac{\omega_0}{\omega_k} = 0,
\]
(74)
and the coefficient of \( 2\alpha_k \) as
\[
\frac{\omega_0}{\omega_k} \left( 1 - \frac{\omega_0}{\omega_k} \right) = \frac{\omega_0}{\omega_k} - \frac{\omega_0}{\omega_k} \frac{\omega_k}{\omega_k - \omega_0} = 0.
\]
(75)
Thus, equation (73) is \( \alpha_k \)-independent. The remaining part is
\[
\frac{\omega_0}{\omega_k (\omega_0 - \omega_k)}.
\]
(76)
The \( N_k \)-dependent parts of \( \delta_e - \delta_{e}^{(2)} \) can be dealt with in a similar manner. The coefficient of \( \alpha_k^2 \) in the \( N_k \)-dependent part of the bracket within the integrand of the expression for \( \delta_e - \delta_{e}^{(2)} \) is
The integral is regularised by introducing a convergence factor $E$.

Evaluating the angular integral and polarisation summation yields

$$
\Delta_{ij} = \int \frac{d^3k}{(2\pi)^3} \sum_{\lambda} |e_{ij}(k) \cdot d|^2 e^{i\vec{k}\cdot\vec{R}} \left( \alpha_{ij}^2 - 1 - \frac{\omega_0}{\omega_k + \omega_0} \right) \left( \frac{u_{ij}^2}{\omega_k + \omega_0} + \frac{u_{ij}^2}{\omega_k - \omega_0} \right).
$$

Using equation (6) all $\alpha_{ij}$-dependence can be shown to vanish in the same way as with the single-dipole shifts dealt with in appendix A.1. The final result is

$$
\Delta_{ij} = \frac{\omega_k}{\omega_0 - \omega_k}.
$$

Evaluating the angular integral and polarisation summation yields

$$
\Delta_{ij} = \frac{1}{\pi} \int_0^\infty d\omega_k \, d\omega_j \, \tau_{ij} \left( \frac{\omega_k}{\omega_0 - \omega_k} \right).
$$

The integral is regularised by introducing a convergence factor $e^{-\omega_0}$ under the integral, and finally taking the limit $\epsilon \to 0^+$. We substitute $\tau_{ij}$ given in equation (22) into equation (83) and evaluate the resulting integrals term by term. The integral arising from the first part of $\tau_{ij}$ is

$$
\lim_{\epsilon \to 0^+} \int_0^\infty d\omega_k \, \omega_k^4 e^{-\omega_0} \frac{\sin \omega_k R}{\omega_0 - \omega_k} = \frac{1}{2 \epsilon} \int_{-\infty}^\infty d\omega_k \, \frac{\omega_k^4 e^{-\omega_0}}{\omega_0^2 - \omega_k^2}.
$$
We now make the substitution $z = \omega_R R$, and make a suitable choice of contour $C$ such that by the residue theorem we obtain

$$\frac{1}{2iR^2 e^{-\theta}} \int_C dz \frac{z^3 e^{i\theta} - R}{(\omega_R)^2 - z^2} = -\frac{\omega_R^2}{2} \cos \omega_R R. \quad (87)$$

Thus, the part of the shift $\Delta_{12}$ arising from the first part $(R^{-1})$ component of $\tau_{ij}$ is

$$-\frac{\omega_R^2}{4\pi R} (\delta_{ij} - \hat{\mathbf{R}} \hat{\mathbf{R}}) d_i d_j \cos \omega_R R, \quad (88)$$

which we recognise as the $R^{-1}$ component of $\Delta_{12}$ in equation (21). The remaining parts of equation (85) can be evaluated in a similar way, which yields the final result given in equation (21).

**A.3. Method of calculation of the spectrum**

We denote the dynamical map governing evolution of the reduced density matrix by $F(t, t')$, which is such that $F(t, t') \rho(t') = \rho(t)$. A general two-time correlation function for arbitrary system observables $O$ and $O'$ can be written [36]

$$\langle O(t) O'(t') \rangle = \text{tr}(OF(t, t') O'F(t') \rho). \quad (89)$$

We define the super-operator $\Lambda$ by $\rho(t) = \Lambda \rho(t)$ using the master equation (equation (20) or equation (40)). Since $\Lambda$ is time-independent, from the initial condition $F(0, 0) \equiv I$ we obtain the general solution $F(t, t') = e^{\Lambda(t-t')}$. For convenience we write $F(t(0)) = F(t)$, so that $F(t, t') = F(t - t')$.

In order to calculate the two-time correlation functions we first find a concrete representation of the maps $\Lambda$ and $F(t)$. For this purpose we introduce a basis of operators denoted $\{x_i: i = 1, \ldots, 16\}$, which is closed under Hermitian conjugation. The trace defines an inner product $\langle O, O' \rangle = \text{tr}(O'O)$ with respect to which the basis $x_i$ is assumed to be orthonormal. We identify two resolutions of unity as $\sum_i \text{tr}(x_i^\dagger \cdot x_i) = I \equiv \sum_i \text{tr}(x_i \cdot x_i)^\dagger$, which imply that any operator $O$ can be expressed as $O = \sum_i \text{tr}(x_i^\dagger O)x_i = \sum_i \text{tr}(O x_i)x_i^\dagger$. Expressing both sides of the equation $F(t) = \Lambda F(t)$ in the basis $x_i$ yields the relation

$$\hat{F}_j(t) = \sum_i \Lambda_{ij} F_k(t), \quad (90)$$

where

$$F_j(t) = \text{tr}[x_j^\dagger F(t)x_j], \quad \Lambda_{ij} = \text{tr}[x_i^\dagger \Lambda x_j]. \quad (91)$$

Equation (90) can be written in the matrix form $\mathbf{F} = \mathbf{A} \mathbf{F}(t)$ whose solution is expressible in the matrix exponential form $F(t) = e^{\Lambda t}$. A general two-time correlation function of system operators can then be expressed using equation (89) as

$$\langle O(t) O'(t') \rangle = \sum_{ijkl} \text{tr}(O_{ij} x_k^\dagger x_l^\dagger F_{ij}(t - t') \text{tr}(x_i^\dagger x_j) x_k x_l F_{il}(t') \text{tr}(x_i^\dagger \rho)) = \mathbf{O}^\dagger \mathbf{F}(t - t') \mathbf{O} \mathbf{F}(t') \rho, \quad (92)$$

where $O_{ij} = \text{tr}(O_{ij})$, $\rho_{ij} = \text{tr}(x_i^\dagger \rho)$ and $\rho_{ij}^\dagger = \text{tr}(x_j^\dagger O' x_i)$. Choosing the basis $\{x_i\}$ to be the operators obtained by taking the outer products of the bare states $|n, m\rangle$, $\langle n, m | c, g\rangle$, the above machinery can be used to obtain the correlation function (50).

**A.4. Derivation of spectrum associated with the new master equation**

The mode expansion for the transverse field canonical momentum $\Pi_T$ is

$$\Pi_T(t, x) = -i \sum_{l=1}^6 \frac{\omega_{kl}}{2L^2} e_{kl}^\dagger a_{kl}^\dagger(t) e^{ikx} + \text{h.c.} \quad (93)$$

This operator represents a different physical observable for each choice of $\alpha_{kl}$, because it does not commute with the generalised gauge transformation $R_{[n]}$. Similarly the photonic operators $a_{kl}$ are implicitly different for each choice of $\alpha_{kl}$. In the multipolar gauge the field canonical momentum coincides with the total electric field away from the sources; $\Pi_T(x) = -E(x)$, $x = R_j$. The positive frequency (annihilation) and negative frequency (creation) components of the electric field are therefore defined for $x = R_j$ by

$$E^{(+)}(t, x) = i \sum_{l=1}^6 \frac{\omega_{kl}}{2L^2} e_{kl}^\dagger a_{kl}^\dagger(t) e^{ikx}, \quad E^{(-)}(t, x) = E^{(+)}(t, x)^\dagger, \quad (93)$$

where $a_{kl}$ is the photon annihilation operator within the multipolar gauge. For a system of two dipoles the integrated Heisenberg equation for the multipolar photon annihilation operator yields the source component
Performing the angular integration and polarisation summation, and retaining only the radiative transition and is given by equation (46) then yields the spectrum in equation (59).

\[ a_{k\lambda}(t) = \sqrt{\frac{2\omega_k}{2\rho}} \sum_{\mu=1}^{2} e^{-i\delta_{\mu}} \int_0^\infty dt' e^{-i\omega(t-t')} \mathbf{e}_{k\lambda} \cdot \mathbf{d}_\mu(t'). \]  
\[ (95) \]

Since the dipole moment operators \( \mathbf{d}_\mu \) commute with the transformation \( R_{\mu\alpha} \) they represent the same physical observable for each choice of \( \alpha \). This implies that equation (95) can be expressed in terms of Coulomb gauge raising and lowering operators \( \sigma^\pm_\mu \) in the two-level approximation, despite the implicit difference between these operators and their counterparts defined within the multipolar gauge. We subsequently express the Coulomb gauge operators \( \sigma^\pm_\mu \) in the dressed basis \( \{|\epsilon_n\rangle\} \) to obtain

\[ a_{k\lambda}(t) = \sqrt{\frac{2\omega_k}{2\rho}} \sum_{\mu=1}^{2} e^{-i\delta_{\mu}} \int_0^\infty dt' e^{-i\omega(t-t')} \sigma_{\mu,mm}^{\pm} \theta_{mm}(t'), \]
\[ (96) \]

where \( \sigma_{\mu,mm} = \sigma^+_\mu \sigma^-_{\mu,mm} + \sigma^-_\mu \sigma^+_{\mu,mm} \), \( \epsilon_{nm} = \epsilon_n - \epsilon_m \), and \( \theta_{mm} = \langle \epsilon_n | \epsilon_m \rangle \). We now perform a rotating-wave approximation, which eliminates terms that are rapidly oscillating within the interaction picture defined by the dressed Hamiltonian \( \hat{H}_d \) given in equation (30). Substitution of the resulting expression into equation (94) yields in the mode continuum limit

\[ E_{E}^{(\perp)}(t, x) = i \int d^4k \sum_{\lambda} \frac{\omega_k}{2(2\pi)^3} e_{\lambda}(k) [e_{\lambda}(k) \cdot d] \sum_{\mu=1}^{2} e^{-i\delta_{\mu}} \int_0^\infty dt' e^{-i\omega(t-t')} e^{i\omega_{\mu}t'} \sigma_{\mu,mm}^{\pm} \theta_{mn}(t'), \]
\[ (97) \]

where \( \bar{\theta}_{mn}(t') \) denotes the operator \( \theta_{mn}(t') \) transformed into the interaction picture with respect to \( \hat{H}_d \) and \( r_\mu = x - R_\mu \). Performing the angular integration and polarisation summation, and retaining only the radiative component yields

\[ E_{E}^{(\perp)}(t, x) = \frac{i}{4\pi} \sum_{\mu=1}^{2} \sum_{n<m} (\delta_{\mu} - \bar{\delta}_{\mu,mm}) d_{\mu} \int_0^\infty d\omega_k \int_0^\infty dt' \frac{\sin(\omega_{\mu}t')}{\omega_{\mu}} e^{-i\omega(t-t')} e^{i\omega_{\mu}t'} \sigma_{\mu,mm} \theta_{mn}(t'), \]
\[ (98) \]

Finally, using the Markov approximation

\[ \int_0^\infty d\omega_k \int_{-\infty}^{\infty} f(\epsilon_{nm}) \left[ e^{i\omega_{\mu}t'} \delta(t'-(t+\rho)) \delta(t'-(t+\rho)) \right] \approx 2\pi f(\epsilon_{nm}) e^{i\omega_{\mu}t'} [\delta(t'-(t+\rho)) \delta(t'-(t+\rho))], \]
\[ (99) \]

valid for a suitably behaved function \( f \), we obtain the final result equation (55) given in the main text.

To calculate the spectrum according to our master equation (40) we choose the basis of operators \( \{x_\mu\} \) used within the general method laid out in appendix A.3 as that obtained by taking the outer-products of the basis states \( \{|\epsilon_n\rangle\} \) given in equation (32). Using equation (92) we define the array of correlation functions

\[ C_{nm}(t, t') = \langle x_\mu^*(t') x_\mu(t) \rangle |_{\theta_3} = \langle \mathbf{F}(t-t') X_m \mathbf{F}(t') \rangle |_{up}, \]
\[ (100) \]

where \( p \) is restricted to values such that \( x_p \) is diagonal, and where the matrix \( X_m \) has elements \( (X_m)_{\mu k} = \text{tr}(x_p^* x_m x_k) \). Taken in the symmetric state \( \theta_{33} \) the correlations appearing in equation (56) are all elements of the array \( C_{nm}(t, t') \), which is given by equation (100) with \( x_p = \theta_{33} \). We choose a labelling whereby the \( x_i \) are given by

\[ x_1 = |\epsilon_1\rangle \langle \epsilon_1|, \quad i = 1, \ldots, 4, \]
\[ x_2 = |\epsilon_2\rangle \langle \epsilon_{-4}|, \quad i = 5, \ldots, 8, \]
\[ x_3 = |\epsilon_3\rangle \langle \epsilon_{-8}|, \quad i = 9, \ldots, 12, \]
\[ x_4 = |\epsilon_4\rangle \langle \epsilon_{-12}|, \quad i = 13, \ldots, 16. \]
\[ (101) \]

In this case the only non-zero off-diagonal element of \( C_{nm}(t, t') \) is \( C_{33}(t, t') \) where \( x_3 = \theta_{11} \) and \( x_{13} = \theta_{33} \). Furthermore the diagonal elements \( C_{nm}(t, t') \) are zero unless \( n \) is odd. It follows that the only non-vanishing correlations in equation (56) are \( C_{33}(t, t') \) and \( C_{77}(t, t') \). Moreover, since \( \sum_{\mu=1}^{2} \sigma_{\mu,3} \sigma_{\mu,23} = 0 \) only the term involving \( C_{33}(t, t') \) contributes. This term describes correlations associated with the symmetric to ground state transition and is given by equation (57) in the main text. Integration of this correlation function according to equation (46) then yields the spectrum in equation (59).

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