Atomic multipole relaxation rates near surfaces

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The spontaneous relaxation rates for an atom in free space and close to an absorbing surface are calculated to various orders of the electromagnetic multipole expansion. The spontaneous decay rates for dipole, quadrupole and octupole transitions are calculated in terms of their respective primitive electric multipole moments and the magnetic relaxation rate is calculated for the dipole and quadrupole transitions in terms of their respective primitive magnetic multipole moments. The theory of electromagnetic field quantization in magnetoelectric materials is used to derive general expressions for the decay rates in terms of the dyadic Green function. We focus on the decay rates in free space and near an infinite half space. For the decay of atoms near to an absorbing dielectric surface we find a hierarchy of scaling laws depending on the atom-surface distance z.

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I. INTRODUCTION

The spontaneous decay of an excited atom and the associated release of a photon into the environment is due to the interaction between the atom and the vacuum fluctuations of the electromagnetic field. It is a fundamental process that is of critical importance in the understanding of the dynamics of free atoms. It is, therefore, unsurprising that this process has been the subject of much study, some of which dates back almost to the beginnings of quantum mechanics itself [1]. The usual approach is to expand the atomic charge distribution into a sum of its multipole moments. The atom-field interaction is then considered to be dominated by the linear coupling between the vacuum field and the dipole component of the charge distribution. This approximation assumes the dipole-field interaction to be sufficiently large that the higher-order multipole terms can be neglected. Such atom-dipole calculations are a mainstay of quantum optics textbooks (e.g. [2, 3, 4, 5]). More recently, extensive work has been done on dipole interactions in more complex environments such as near absorbing surfaces [6, 7], near an absorbing microsphere [7, 8] and in a spherical microcavity [7].

In the past few years, there has been increasing experimental interest dipole-forbidden atomic transitions [9, 10]. In particular, there has been a large body of work exploring the use of such higher multipole moment transitions in atomic clocks, because the weak nature of these transitions leads to a narrow line width and hence a much better frequency standard [11]. Quadrupole transitions in ^{199}Hg$^+$ [12, 13] and $^{87/88}$Sr$^+$ [14, 15, 16] are frequently used and even the $^2F_{\frac{7}{2}} - {}^2S_{\frac{1}{2}}$ octupole transitions in ^{171}Yb$^+$ has been studied [17]. Although there have been some attempts to study the theory of quadrupole transitions [18], a complete understanding of the nature of higher-order multipole decays is still lacking.

The corresponding magnetic interaction between the atom and the vacuum fluctuations leads to a spontaneous change of the electronic spin state. With the recent rise in interest in the magnetic trapping and confinement of atoms for quantum control experiments and quantum information processing [19, 20, 21], these spin flips have become an increasingly important process. Atoms in specific Zeeman sublevels of their hyperfine ground state can be magnetically trapped. However, these states are subject to spin transitions which can take the atom from a trapped state to an anti-trapped state (i.e. the atom is actively expelled from the trap owing to the relative orientation of the magnetic field and atomic spin direction). This relaxation process is a limiting factor on the lifetime of trapped atoms and may place serious restrictions on experiments that require long trapping times such as those using a trapped atom as a fundamental qubit for quantum information processing. The dipole spin flip rate has been studied for a number of different environments, for example above conducting and superconducting surfaces [22, 23, 24, 25] and close to metal wires [26].

In this article, we present a general theory of higher multipole relaxation rates. The Green function method for the quantization of the electromagnetic field is briefly discussed in Sec. II. In Sec. III, the multipole expansion and the multipole interaction Hamiltonian are reviewed. In Sec. IV, the Heisenberg equation of motion are used to derive general expressions for the decay rates for various multipole orders from their respective interaction Hamiltonians. Finally in Secs. V and VI, the decay of atoms in free space and close to a planar dielectric surface are studied in detail. Some useful but lengthy calculations, in particular on rotational averaging of tensors, can be found in the Appendices.

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II. QUANTIZATION SCHEME

The electromagnetic field in an absorbing magnetoelectric medium can be quantized by expanding the electric field in terms of the dyadic Green function (the inverse of the Helmholtz operator) and a set of bosonic vector fields, which describe the collective excitations of the field and the absorbing matter (for reviews, see e.g. [27, 28]). The method begins with the classical Maxwell equations in frequency space. In the absence of free currents and charges these equations take the form

$$\boldsymbol{\nabla} \cdot \mathbf{B}(\mathbf{r}, \omega) = 0, \tag{1}$$

$$\boldsymbol{\nabla} \times \mathbf{E}(\mathbf{r}, \omega) - i\omega \mathbf{B}(\mathbf{r}, \omega) = \mathbf{0}, \tag{2}$$

$$\boldsymbol{\nabla} \cdot \mathbf{D}(\mathbf{r}, \omega) = 0, \tag{3}$$

$$\boldsymbol{\nabla} \times \mathbf{H}(\mathbf{r}, \omega) + i\omega \mathbf{D}(\mathbf{r}, \omega) = \mathbf{0}. \tag{4}$$

Maxwell's equations have to be supplemented by constitutive relations between the primary fields $\mathbf{E}(\mathbf{r}, \omega)$ and $\mathbf{B}(\mathbf{r}, \omega)$, and the derived fields $\mathbf{D}(\mathbf{r}, \omega)$ and $\mathbf{H}(\mathbf{r}, \omega)$, respectively, which can be written as

$$\mathbf{D}(\mathbf{r}, \omega) = \varepsilon_0 \mathbf{E}(\mathbf{r}, \omega) + \mathbf{P}(\mathbf{r}, \omega), \tag{5}$$

$$\mathbf{H}(\mathbf{r}, \omega) = \kappa_0 \mathbf{B}(\mathbf{r}, \omega) - \mathbf{M}(\mathbf{r}, \omega) \tag{6}$$

$[\kappa_0 = 1/\mu_0]$. The polarization field $\mathbf{P}(\mathbf{r}, \omega)$ and the magnetization field $\mathbf{M}(\mathbf{r}, \omega)$ are, in the linear-response approximation, related to the electric field and the magnetic induction by

$$\mathbf{P}(\mathbf{r}, \omega) = \varepsilon_0 \left[\varepsilon(\mathbf{r}, \omega) - 1 \right] \mathbf{E}(\mathbf{r}, \omega) + \mathbf{P}_{\mathrm{N}}(\mathbf{r}, \omega), \tag{7}$$

$$\mathbf{M}(\mathbf{r}, \omega) = \kappa_0 \left[1 - \kappa(\mathbf{r}, \omega) \right] \mathbf{B}(\mathbf{r}, \omega) - \mathbf{M}_{\mathrm{N}}(\mathbf{r}, \omega) \tag{8}$$

where $\varepsilon(\mathbf{r}, \omega)$ and $\kappa(\mathbf{r}, \omega) = 1/\mu(\mathbf{r}, \omega)$ are the dielectric permittivity and the (inverse) magnetic permeability, respectively.

Absorption in the medium is accounted for consistently by the addition of the noise polarization field $\mathbf{P}_{\mathrm{N}}(\mathbf{r}, \omega)$ and the noise magnetization field $\mathbf{M}_{\mathrm{N}}(\mathbf{r}, \omega)$. As a result of this, the (frequency components of the) electric field obey the inhomogeneous Helmholtz equation

$$\boldsymbol{\nabla} \times \kappa(\mathbf{r}, \omega) \boldsymbol{\nabla} \times \mathbf{E}(\mathbf{r}, \omega) - \frac{\omega^2}{c^2} \varepsilon(\mathbf{r}, \omega) \mathbf{E}(\mathbf{r}, \omega)$$
$$= i\omega\mu_0 \mathbf{j}_{\mathrm{N}}(\mathbf{r}, \omega) \tag{9}$$

with the noise current density

$$\mathbf{j}_{\mathrm{N}}(\mathbf{r}, \omega) = -i\omega \mathbf{P}_{\mathrm{N}}(\mathbf{r}, \omega) + \boldsymbol{\nabla} \times \mathbf{M}_{\mathrm{N}}(\mathbf{r}, \omega). \tag{10}$$

This equation can be formally solved using the Green tensor for the Helmholtz operator

$$\mathbf{E}(\mathbf{r}, \omega) = i\omega\mu_0 \int d^3 s \, \boldsymbol{G}(\mathbf{r}, \mathbf{s}, \omega) \cdot \mathbf{j}_{\mathrm{N}}(\mathbf{s}, \omega), \tag{11}$$

where the Green tensor $\boldsymbol{G}(\mathbf{r}, \mathbf{s}, \omega)$ has the property

$$\boldsymbol{\nabla} \times \kappa(\mathbf{r}, \omega) \boldsymbol{\nabla} \times \boldsymbol{G}(\mathbf{r}, \mathbf{s}, \omega) - \frac{\omega^2}{c^2} \varepsilon(\mathbf{r}, \omega) \boldsymbol{G}(\mathbf{r}, \mathbf{s}, \omega) = \boldsymbol{\delta}(\mathbf{r} - \mathbf{s}). \tag{12}$$

Quantization of the electromagnetic field is performed by decomposing the noise polarization and magnetization fields in terms of two sets of bosonic vector fields

$$\hat{\mathbf{P}}_{\mathrm{N}}(\mathbf{r}, \omega) = i\sqrt{\frac{\hbar\varepsilon_0}{\pi}\varepsilon''(\mathbf{r}, \omega)} \, \hat{\mathbf{f}}_e(\mathbf{r}, \omega), \tag{13}$$

$$\hat{\mathbf{M}}_{\mathrm{N}}(\mathbf{r}, \omega) = i\sqrt{\frac{\hbar\kappa_0}{\pi}\kappa''(\mathbf{r}, \omega)} \, \hat{\mathbf{f}}_m(\mathbf{r}, \omega), \tag{14}$$

and imposing canonical commutation relations for them $[\lambda, \lambda' = e, m]$

$$\left[\hat{\mathbf{f}}_\lambda(\mathbf{r}, \omega), \hat{\mathbf{f}}_{\lambda'}^\dagger(\mathbf{r}', \omega') \right] = \delta_{\lambda\lambda'} \boldsymbol{\delta}(\mathbf{r} - \mathbf{r}') \delta(\omega - \omega'). \tag{15}$$

Thus the frequency components of the quantized electric and magnetic field can be written as

$$\hat{\mathbf{E}}(\mathbf{r}, \omega) = \sum_{\lambda=e,m} \int d^3 s \, \boldsymbol{G}_\lambda(\mathbf{r}, \mathbf{s}, \omega) \cdot \hat{\mathbf{f}}_\lambda(\mathbf{s}, \omega), \tag{16}$$

and

$$\hat{\mathbf{B}}(\mathbf{r}, \omega) = \frac{1}{i\omega} \boldsymbol{\nabla} \times \hat{\mathbf{E}}(\mathbf{r}, \omega), \tag{17}$$

with the abbreviations

$$\boldsymbol{G}_e(\mathbf{r}, \mathbf{s}, \omega) = i\frac{\omega^2}{c^2} \sqrt{\frac{\hbar}{\pi\varepsilon_0}\varepsilon''(\mathbf{s}, \omega)} \boldsymbol{G}(\mathbf{r}, \mathbf{s}, \omega), \tag{18}$$

$$\boldsymbol{G}_m(\mathbf{r}, \mathbf{s}, \omega) = -i\frac{\omega}{c} \sqrt{\frac{\hbar}{\pi\varepsilon_0}\frac{\mu''(\mathbf{s}, \omega)}{|\mu(\mathbf{s}, \omega)|^2}} \left[\boldsymbol{G}(\mathbf{r}, \mathbf{s}, \omega) \times \overleftarrow{\boldsymbol{\nabla}}' \right]. \tag{19}$$

The total field operators read

$$\hat{\mathbf{E}}(\mathbf{r}) = \int_0^\infty d\omega \, \hat{\mathbf{E}}(\mathbf{r}, \omega) + \text{h.c.}, \tag{20}$$

$$\hat{\mathbf{B}}(\mathbf{r}) = \int_0^\infty d\omega \, \hat{\mathbf{B}}(\mathbf{r}, \omega) + \text{h.c..} \tag{21}$$

The bosonic operators $\hat{\mathbf{f}}_\lambda(\mathbf{s}, \omega)$ and $\hat{\mathbf{f}}_\lambda^\dagger(\mathbf{s}, \omega)$ describe collective excitations of the photonic modes and the absorbing medium and can be viewed as the generalization of the free-space photonic amplitude operators to arbitrary magnetoelectric media. The bilinear Hamiltonian

$$\hat{H}_F = \sum_{\lambda=e,m} \int d^3 r \int d\omega \, \hbar\omega \, \hat{\mathbf{f}}_\lambda^\dagger(\mathbf{r}, \omega) \cdot \hat{\mathbf{f}}_\lambda(\mathbf{r}, \omega) \tag{22}$$

can be used to generate the time-dependent Maxwell equations from the Heisenberg equations of motion for the displacement field and the magnetic field.

III. MULTIPOLAR-COUPLING HAMILTONIAN AND THE MULTIPOLE EXPANSION

The macroscopic interaction between light and matter is commonly described using the multipolar coupling. In

this picture, the matter is described in terms of a polarization field, which is a result of displaced charges within the material, and a magnetization field, which is a result of charge currents within the material. The interaction terms take the form of linear couplings with the polarization field interacting solely with the external electric field and the magnetization field interacting solely with the external magnetic field.

The Hamiltonian for a globally neutral system of point particles of mass m_α and charge q_α in the presence of an external electromagnetic field, whose centre of mass is at rest, has three contributions describing the medium-assisted quantized electromagnetic field, the free motion of the charged particles and the particle-field interaction, respectively [28, 29],

$$\hat{H} = \hat{H}_F + \hat{H}_A + \hat{H}_{\text{int}}, \qquad (23)$$

with

$$\hat{H}_A = \sum_\alpha \frac{\hat{\mathbf{p}}_\alpha^2}{2m_a} + \frac{1}{2\varepsilon_0} \int d^3r \, \hat{\mathbf{P}}_A^2(\mathbf{r}), \qquad (24)$$

$$\hat{H}_{\text{int}} = -\int d^3r \, \hat{\mathbf{P}}_A(\mathbf{r}) \cdot \hat{\mathbf{E}}(\mathbf{r}) - \int d^3r \, \hat{\mathbf{M}}_A(\mathbf{r}) \cdot \hat{\mathbf{B}}(\mathbf{r}), \qquad (25)$$

and $\hat{H}_F$ given by Eq. (22). Note here that diamagnetism, which is quadratic in the magnetic field, is not considered. Furthermore, since the centre of mass of the charge distribution is assumed to be stationary, the velocity dependent Röntgen term vanishes. By considering the divergence of the polarization field and the curl of the magnetization in terms of displaced point charges and charge currents respectively, the polarization and magnetization fields can be written in integral representation as (see Appendix A)

$$\hat{\mathbf{P}}_A(\mathbf{r}) = \sum_\alpha q_\alpha \int_0^1 ds \, \delta \left[\mathbf{r} - \hat{\mathbf{r}}_A - s(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \right] (\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A), \qquad (26)$$

$$\hat{\mathbf{M}}_A(\mathbf{r}) = \sum_\alpha \frac{q_\alpha}{2m_\alpha} \int_0^1 ds \, s \, \delta \left[\mathbf{r} - \hat{\mathbf{r}}_A - s(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \right]$$
$$\times \left[(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \times \hat{\mathbf{p}}_\alpha - \hat{\mathbf{p}}_\alpha \times (\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \right]$$
$$+ \sum_\alpha \gamma_\alpha \hat{\mathbf{S}}_\alpha \delta \left(\mathbf{r} - \hat{\mathbf{r}}_\alpha \right). \qquad (27)$$

Here $\hat{\mathbf{S}}_\alpha$ is the spin operator for particle α located at $\hat{\mathbf{r}}_\alpha$, $\hat{\mathbf{p}}_\alpha$ is the canonical momentum of the particle relative to the atomic centre of mass and γ_α is the gyromagnetic ratio of the particle (for an electron: $\gamma_e = -eg_e/(2m_e)$ with the electron g-factor $g_e \simeq 2$). Hence, the electric and magnetic terms in the interaction Hamiltonian become

$$\hat{H}_{\text{int}}^{(E)} = -\int d^3r \sum_\alpha q_\alpha \int_0^1 ds \, \delta \left[\mathbf{r} - \hat{\mathbf{r}}_A - s(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \right]$$
$$\times (\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \cdot \hat{\mathbf{E}}(\mathbf{r}), \qquad (28)$$

$$\hat{H}_{\text{int}}^{(B)} = -\int d^3r \sum_\alpha \frac{q_\alpha}{2m_\alpha} \int_0^1 ds \, s \, \delta \left[\mathbf{r} - \hat{\mathbf{r}}_A - s(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \right]$$
$$\times \left[(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \times \hat{\mathbf{p}}_\alpha - \hat{\mathbf{p}}_\alpha \times (\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \right] \cdot \hat{\mathbf{B}}(\mathbf{r})$$
$$- \int d^3r \sum_\alpha \gamma_\alpha \hat{\mathbf{S}}_\alpha \delta \left(\mathbf{r} - \hat{\mathbf{r}}_\alpha \right) \cdot \hat{\mathbf{B}}(\mathbf{r}). \qquad (29)$$

A. Electric multipole expansion

The interaction Hamiltonians (28) and (29) are difficult to handle and some simplifications are necessary to proceed. The usual approach is to expand the polarization and magnetization fields in terms of their multipole moments. The procedure is outlined here. More information on the both the classical and quantum multipole expansion can be found in Refs. [30, 31, 32].

Consider first the electric term of the interaction Hamiltonian (28). The δ-function can be expanded about the point $\mathbf{r} = \hat{\mathbf{r}}_A$

$$\hat{H}_{\text{int}}^{(E)} = -\sum_\alpha q_\alpha \int d^3r \int_0^1 ds (\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \cdot \hat{\mathbf{E}}(\mathbf{r})$$
$$\times \left\{ \delta(\mathbf{r} - \hat{\mathbf{r}}_A) - s(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \cdot \boldsymbol{\nabla} \delta(\mathbf{r} - \hat{\mathbf{r}}_A) \right.$$
$$\left. + \frac{s^2}{2!} [(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \cdot \boldsymbol{\nabla}]^2 \delta(\mathbf{r} - \hat{\mathbf{r}}_A) + O[(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A)^3] \right\}. \qquad (30)$$

Both integrals can now be performed. The spatial integral is evaluated by integration by parts on the derivatives of the δ-function. As the vector $(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A)$ is not a function of the spatial variable $\mathbf{r}$, the derivatives act only on the electric field. Thus the expansion becomes

$$\hat{H}_{\text{int}}^{(E)} = -\sum_\alpha q_\alpha (\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \cdot \hat{\mathbf{E}}(\hat{\mathbf{r}}_A)$$
$$- \frac{1}{2!} \sum_\alpha q_\alpha [(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \otimes (\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A)] \bullet [\boldsymbol{\nabla} \otimes \hat{\mathbf{E}}(\mathbf{r})]|_{\mathbf{r}=\hat{\mathbf{r}}_A}$$
$$- \frac{1}{3!} \sum_\alpha q_\alpha [(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \otimes (\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \otimes (\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A)]$$
$$\bullet [\boldsymbol{\nabla} \otimes \boldsymbol{\nabla} \otimes \hat{\mathbf{E}}(\mathbf{r})]|_{\mathbf{r}=\hat{\mathbf{r}}_A} + \mathcal{O} \left[(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A)^4 \right], \qquad (31)$$

where the symbol $\bullet$ denotes the Hadamard product ($\mathbf{A} \bullet \mathbf{B} = A_{i_1 \ldots i_n} B_{i_1 \ldots i_n}$). Equation (31) can be written in a simpler form by defining multipole moment (tensor) operators. The primitive electric dipole, quadrupole and octupole moment operators are defined as

$$\hat{\mathbf{d}} = \sum_\alpha q_\alpha (\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A), \qquad (32)$$

$$\hat{\mathbf{d}}^{(4)} = \frac{1}{2!} \sum_\alpha q_\alpha (\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \otimes (\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A), \qquad (33)$$

$$\hat{\mathbf{d}}^{(8)} = \frac{1}{3!} \sum_\alpha q_\alpha (\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \otimes (\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \otimes (\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A), \qquad (34)$$

respectively. Note here that the multipole moments are defined as in Refs. [4, 32] with the coefficients of the Taylor expansion absorbed into the definition of the moment. As a result, the electric multipole interaction Hamiltonian can be written as

$$
\hat{H}_{\text{int}}^{(E)} = -\hat{\mathbf{d}} \cdot \hat{\mathbf{E}}(\hat{\mathbf{r}}_A) - \hat{\mathbf{d}}^{(4)} \bullet [\boldsymbol{\nabla} \otimes \hat{\mathbf{E}}(\mathbf{r})]\mid_{\mathbf{r}=\hat{\mathbf{r}}_A}
$$
$$
- \hat{\mathbf{d}}^{(8)} \bullet [\boldsymbol{\nabla} \otimes \boldsymbol{\nabla} \otimes \hat{\mathbf{E}}(\mathbf{r})]\mid_{\mathbf{r}=\hat{\mathbf{r}}_A} + \mathcal{O}\left[(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A)^4\right].
\tag{35}
$$

B. Magnetic multipole expansion

A similar expansion can be performed for the magnetic term of the interaction Hamiltonian (29). Once again the δ-function can be expanded about the point $\mathbf{r} = \hat{\mathbf{r}}_A$. Performing the integrals as before and defining the primitive magnetic dipole and quadrupole moments as

$$
\hat{\mathbf{m}} = \frac{1}{2!}\sum_\alpha \left[q_\alpha(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \times \hat{\mathbf{p}}_\alpha + 2\gamma_\alpha \hat{\mathbf{S}}_\alpha\right]
\tag{36}
$$

$$
\hat{\mathbf{m}}^{(4)} = \frac{1}{3!}\sum_\alpha \frac{q_\alpha}{m_\alpha}\bigg\{ [(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \times \hat{\mathbf{p}}_\alpha] \otimes (\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A)
$$
$$
+ \left((\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \otimes [(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \times \hat{\mathbf{p}}_\alpha]\right)^T\bigg\}
$$
$$
+ \sum_\alpha (\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A) \otimes \gamma_\alpha \hat{\mathbf{S}}_\alpha,
\tag{37}
$$

respectively, leads to a magnetic multipole interaction Hamiltonian of the form

$$
\hat{H}_{\text{int}}^{(B)} = -\hat{\mathbf{m}} \cdot \hat{\mathbf{B}}(\hat{\mathbf{r}}_A) - \hat{\mathbf{m}}^{(4)} \bullet [\boldsymbol{\nabla} \otimes \hat{\mathbf{B}}(\mathbf{r})]\mid_{\mathbf{r}=\hat{\mathbf{r}}_A}
$$
$$
- \mathcal{O}\left[(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A)^3\right].
\tag{38}
$$

IV. ATOMIC EQUATIONS OF MOTION

The dynamics of atoms subject to electric dipole interaction with the medium-assisted electromagnetic field has been studied extensively in the literature [6, 7, 8]. More recently, atoms subject to electric quadrupole interactions [18] and magnetic dipole interactions [23, 24, 25, 26] have been considered. In order to analyse the effect of higher-order multipole interactions on the atomic decay rates, we derive the equation of motion for an atom subject to a single, specific higher-order interaction. We develop the Heisenberg equation of motion for general multipoles and derive a general expression for multipole driven relaxation rates. It is assumed that each transition is driven by a single multipole interaction term and hence each multipole order can be studied independently.

Beginning with Eq. (23), the microscopic multipolar-

coupling Hamiltonian can be written as

$$
\hat{H} = \sum_{\lambda=e,m}\int d^3r \int d\omega \, \hbar\omega \, \hat{\mathbf{f}}_\lambda^\dagger(\mathbf{r},\omega) \cdot \hat{\mathbf{f}}_\lambda(\mathbf{r},\omega)
$$
$$
+ \sum_i \hbar\omega_i \hat{\sigma}_{ii} + \hat{H}_{\text{int}}.
\tag{39}
$$

Here $\hat{\sigma}_{ii} = |i\rangle\langle i|$ are the projection operators onto the energy eigenstates $|i\rangle$, with energies $\hbar\omega_i$, of the atomic Hamiltonian. We define an operator $\hat{\mathcal{Q}}^{\mathbf{r}}$ that corresponds to the (differential) operator acting on the electric field in the relevant term of the multipole expansion [e.g. for the electric dipole $\hat{\mathcal{Q}}^{\mathbf{r}} = (\hat{\mathbf{d}}\cdot)$, for the electric quadrupole $\hat{\mathcal{Q}}^{\mathbf{r}} = (\hat{\mathbf{d}}^{(4)} \bullet \boldsymbol{\nabla}_{\mathbf{r}}\otimes)$, etc]. Furthermore, we can rewrite the interaction Hamiltonian as

$$
\hat{H}_{\text{int}} = \hat{\mathcal{Q}}^{\mathbf{r}}\hat{\mathbf{E}}(\mathbf{r})\mid_{\mathbf{r}\mathbf{r}_A}
$$
$$
= -\left(\sum_i \hat{\sigma}_{ii}\right)\hat{\mathcal{Q}}^{\mathbf{r}}\left(\sum_j \hat{\sigma}_{jj}\right)\hat{\mathbf{E}}(\mathbf{r})\mid_{\mathbf{r}=\mathbf{r}_A}
$$
$$
= -\sum_{ij}\mathcal{Q}_{ij}^{\mathbf{r}}\hat{\sigma}_{ij}\hat{\mathbf{E}}(\mathbf{r})\mid_{\mathbf{r}=\mathbf{r}_A},
\tag{40}
$$

where the electric field is given by Eqs. (16) and (20), and the completeness relation $\sum_i \hat{\sigma}_{ii} = \hat{1}$ has been used to rewrite the expression in terms of the atomic flip operators $\hat{\sigma}_{ij} = |i\rangle\langle j|$. The Heisenberg equations of motion for the atomic flip operators and the bosonic field operators are thus

$$
\dot{\hat{\mathbf{f}}}_\lambda(\mathbf{r},\omega) = -i\omega\hat{\mathbf{f}}_\lambda(\mathbf{r},\omega) - i\sum_{ij}\boldsymbol{g}_{\lambda,ij}^*(\mathbf{r}',\mathbf{r},\omega)\hat{\sigma}_{ij}
\tag{41}
$$

and

$$
\dot{\hat{\sigma}}_{ij} = i\omega_{ij}\hat{\sigma}_{ij} - i\sum_{\lambda=e,m}\sum_k \int d^3s \int d\omega
$$
$$
[\boldsymbol{g}_{\lambda,jk}(\mathbf{r},\mathbf{s},\omega)\hat{\sigma}_{ik} - \boldsymbol{g}_{\lambda,ki}(\mathbf{r},\mathbf{s},\omega)\hat{\sigma}_{kj}] \cdot \hat{\mathbf{f}}_\lambda(\mathbf{s},\omega) + \text{h.c.}
\tag{42}
$$

where the coupling tensors $\boldsymbol{g}_{\lambda,ij}(\mathbf{r},\mathbf{r}',\omega)$ are defined by

$$
\boldsymbol{g}_{\lambda,ij}(\mathbf{r},\mathbf{r}',\omega) = \frac{1}{i\hbar}\mathcal{Q}_{ij}^{\mathbf{r}}\boldsymbol{G}_\lambda(\mathbf{r},\mathbf{r}',\omega)|_{\mathbf{r}=\mathbf{r}_A}.
\tag{43}
$$

Our goal is to study the dynamics of the atom under the influence of an external field, hence the next step is to remove the electromagnetic degrees of freedom. This is done by solving the equation of motion for the field (41) and substituting the solution into the equation of motion of the atom (42). Equation (41) can be solved in the Markov approximation which assumes that atom to be memoryless and hence not affected by previous field states. Writing the atomic operator as a slowly varying envelope function and a term oscillating with the atomic transition frequency, $\hat{\sigma}_{ij} = \tilde{\hat{\sigma}}_{ij}e^{i\omega_{ij}t}$, Eq. (41) can be integrated to give

$$
\hat{\mathbf{f}}_\lambda(\mathbf{r},\omega) = e^{-i\omega t}\hat{\mathbf{f}}_\lambda^{\text{free}}(\mathbf{r},\omega) + \sum_{ij}\boldsymbol{g}_{\lambda,ij}^*(\mathbf{r}',\mathbf{r},\omega)\zeta(\omega-\omega_{ij})\hat{\sigma}_{ij}
\tag{44}
$$

where $\zeta(\omega - \omega_{ij})$ is defined as

$$\zeta(\omega - \omega_{ij}) = \frac{1 - e^{i(\omega - \omega_{ij})t}}{(\omega - \omega_{ij})}. \qquad (45)$$

Note here the imaginary part of this function is sharply peaked around $\omega = \omega_{ij}$ and hence for large values of t the function $\zeta(\omega - \omega_{ij})$ can be replaced by $\pi\delta(\omega - \omega_{ij})$.

Thus, in the long time limit, $\zeta(\omega - \omega_{ij})$ becomes

$$\zeta(\omega - \omega_{ij}) = \mathcal{P}\frac{1}{(\omega - \omega_{ij})} + i\pi\delta(\omega - \omega_{ij}) \qquad (46)$$

with $\mathcal{P}$ denoting the principal value. Resubstituting the expression for the field into the equation of motion for the atom gives

$$\dot{\hat{\sigma}}_{ij} = i\omega_{ij}\hat{\sigma}_{ij} - i\sum_{\lambda=e,m}\sum_{k}\int d^3s\int d\omega e^{-i\omega t}\left[\boldsymbol{g}_{\lambda,jk}(\mathbf{r},\mathbf{s},\omega)\hat{\sigma}_{ik} - \boldsymbol{g}_{\lambda,ki}(\mathbf{r},\mathbf{s},\omega)\hat{\sigma}_{kj}\right]\cdot\hat{\mathbf{f}}_\lambda^{\text{free}}(\mathbf{s},\omega)$$

$$- i\sum_{\lambda=e,m}\sum_{k,p,q}\int d^3s\int d\omega\left[\boldsymbol{g}_{\lambda,jk}(\mathbf{r},\mathbf{s},\omega)\hat{\sigma}_{ik} - \boldsymbol{g}_{\lambda,ki}(\mathbf{r},\mathbf{s},\omega)\hat{\sigma}_{kj}\right]\cdot\boldsymbol{g}_{\lambda,pq}^*(\mathbf{r}',\mathbf{s},\omega)\zeta(\omega - \omega_{pq})\hat{\sigma}_{pq}. \qquad (47)$$

The first term in Eq. (47) corresponds to the free motion of the atom, the second to the interaction of the atom with the free external field. The third term corresponds to an atom self interaction mediated by the medium-assisted electromagnetic field. It is this term that leads to spontaneous relaxation processes.

State populations are described by the projection operator $\hat{\sigma}_{ii}$. Since the free motion of a projection operator on to a state is static the first term in Eq. (47) vanishes. If there is no external field then the second term also vanishes. Thus Eq. (47), after some rearranging, becomes

$$\dot{\hat{\sigma}}_{ii} = i\sum_{\lambda=e,m}\sum_{k,q}\int d^3s\int d\omega$$

$$\left[\boldsymbol{g}_{\lambda,ki}(\mathbf{r},\mathbf{s},\omega)\cdot\boldsymbol{g}_{\lambda,iq}^*(\mathbf{r}',\mathbf{s},\omega)\hat{\sigma}_{kq}\zeta(\omega - \omega_{iq})\right.$$

$$\left. - \boldsymbol{g}_{\lambda,ik}(\mathbf{r},\mathbf{s},\omega)\cdot\boldsymbol{g}_{\lambda,kq}^*(\mathbf{r}',\mathbf{s},\omega)\hat{\sigma}_{iq}\zeta(\omega - \omega_{kq})\right]. \qquad (48)$$

The problem can be simplified by studying only the two relevant atomic levels that are involved in the transition. Since the multipole moment matrix element contained in $\mathcal{Q}_{ij}^{\mathbf{r}}$ vanishes for paired indices, $\boldsymbol{g}_{ii}(\mathbf{r},\mathbf{s},\omega)$ vanishes and the evolution of the excited state (here labelled as 2) can be reduced to

$$\dot{\hat{\sigma}}_{22} = i\sum_{\lambda=e,m}\int d^3s\int d\omega$$

$$\left[\boldsymbol{g}_{\lambda,12}(\mathbf{r},\mathbf{s},\omega)\cdot\boldsymbol{g}_{\lambda,21}^*(\mathbf{r}',\mathbf{s},\omega)\hat{\sigma}_{11}\zeta(\omega - \omega_{21})\right.$$

$$\left. - \boldsymbol{g}_{\lambda,21}(\mathbf{r},\mathbf{s},\omega)\cdot\boldsymbol{g}_{\lambda,12}^*(\mathbf{r}',\mathbf{s},\omega)\hat{\sigma}_{22}\zeta(\omega - \omega_{12})\right]. \qquad (49)$$

The state labelled 1 indicates the ground state. Solving

this equation for the excited-state population gives

$$\hat{\sigma}_{22}(t) = e^{-i(\Omega - i\Gamma)t}\left[\hat{\sigma}_{22}(0) + i\sum_{\lambda=e,m}\int_0^t dt'\int d^3s\int d\omega\right.$$

$$\left. \times \boldsymbol{g}_{\lambda,12}(\mathbf{r},\mathbf{s},\omega)\cdot\boldsymbol{g}_{\lambda,21}^*(\mathbf{r}',\mathbf{s},\omega)\hat{\sigma}_{11}(t')\zeta(\omega - \omega_{21})\right]. \qquad (50)$$

The relaxation rate appears as an exponential decay factor in the free evolution of the excited-state projection operator and is given by

$$\Gamma = \sum_{\lambda=e,m}\int d^3s\int d\omega\,\boldsymbol{g}_{\lambda,21}(\mathbf{r},\mathbf{s},\omega)\cdot\boldsymbol{g}_{\lambda,12}^*(\mathbf{r}',\mathbf{s},\omega)$$

$$\times\text{Im}\zeta(\omega - \omega_{21}). \qquad (51)$$

Expanding the coupling tensors $\boldsymbol{g}_{\lambda,ij}(\mathbf{r},\mathbf{s},\omega)$, replacing $\text{Im}\left[\zeta(\omega - \omega_{21})\right]$ with a delta function, and using the integral relation for the Green functions,

$$\sum_{\lambda=e,m}\int d^3s\,\boldsymbol{G}_\lambda(\mathbf{r},\mathbf{s},\omega)\cdot\boldsymbol{G}_\lambda^*(\mathbf{s},\mathbf{r}',\omega)$$

$$= \frac{\hbar\omega^2}{\pi c^2\varepsilon_0}\text{Im}\,\boldsymbol{G}(\mathbf{r},\mathbf{r}',\omega), \qquad (52)$$

the final expression for the decay rate is found to be

$$\Gamma = \lim_{\mathbf{r},\mathbf{r}'\to\mathbf{r}_A}\frac{\omega_{21}^2}{\hbar c^2\varepsilon_0}\mathcal{Q}_{21}^{\mathbf{r}}\text{Im}\,\boldsymbol{G}(\mathbf{r},\mathbf{r}',\omega_{21})\mathcal{Q}_{12}^{\mathbf{r}'}. \qquad (53)$$

Equation (53) is a general result and hence true for all multipole orders. In order to obtain any relaxation rate one only needs to determine the form of the differential operator $\mathcal{Q}_{ij}^{\mathbf{r}}$ for the relevant order, which itself can be easily found from the multipole expansions (35) and (38) of the electromagnetic field. Together with the definition

of the multipole differential operator $\mathcal{Q}_{ij}^{\mathbf{r}}$, Eq. (53) constitutes the main result of this article. Note that this can equivalently be written as

$$\Gamma = \lim_{\mathbf{r},\mathbf{r}'\to\mathbf{r}_A} \frac{\omega_{21}^2}{\hbar c^2\varepsilon_0} \mathrm{Tr}\left[\left(\mathcal{Q}_{12}^{\mathbf{r}'}\otimes\mathcal{Q}_{21}^{\mathbf{r}}\right)\mathrm{Im}\,\boldsymbol{G}(\mathbf{r},\mathbf{r}',\omega_{21})\right],$$

(54)

where care has to be taken when carrying out the derivatives. This form will turn out to be useful later on when we consider unorientated ensembles of atoms.

Substituting in the relevant expressions for $\mathcal{Q}_{ij}^{\mathbf{r}}$ the decay rates for various multipole order can be found:

$$\Gamma = \frac{\omega_{21}^2}{\hbar c^2\varepsilon_0}\mathbf{d}_{21}\cdot\mathrm{Im}\,\boldsymbol{G}(\mathbf{r}_A,\mathbf{r}_A,\omega_{21})\cdot\mathbf{d}_{12}\,,$$

(55)

$$\Gamma = \lim_{\mathbf{r},\mathbf{r}'\to\mathbf{r}_A}\frac{\omega_{21}^2}{\hbar c^2\varepsilon_0}\mathbf{d}_{21}^{(4)}\bullet\boldsymbol{\nabla}\otimes\mathrm{Im}\,\boldsymbol{G}(\mathbf{r},\mathbf{r}',\omega_{21})\otimes\overleftarrow{\boldsymbol{\nabla}}'\bullet\mathbf{d}_{12}^{(4)}\,,$$

(56)

$$\Gamma = \lim_{\mathbf{r},\mathbf{r}'\to\mathbf{r}_A}\frac{\omega^2}{\hbar c^2\varepsilon_0}\times$$
$$\mathbf{d}_{21}^{(8)}\bullet(\boldsymbol{\nabla}\otimes\boldsymbol{\nabla})\otimes\mathrm{Im}\,\boldsymbol{G}(\mathbf{r},\mathbf{r}',\omega_{21})\otimes\left(\overleftarrow{\boldsymbol{\nabla}}'\otimes\overleftarrow{\boldsymbol{\nabla}}'\right)\bullet\mathbf{d}_{12}^{(8)}\,,$$

(57)

$$\Gamma = \lim_{\mathbf{r},\mathbf{r}'\to\mathbf{r}_A}\frac{\mu_0}{\hbar}\mathbf{m}_{21}\cdot\boldsymbol{\nabla}\times\mathrm{Im}\,\boldsymbol{G}(\mathbf{r},\mathbf{r}',\omega_{21})\times\overleftarrow{\boldsymbol{\nabla}}'\cdot\mathbf{m}_{12}\,,$$

(58)

$$\Gamma = \lim_{\mathbf{r},\mathbf{r}'\to\mathbf{r}_A}\frac{\mu_0}{\hbar}\times$$
$$\mathbf{m}_{21}^{(4)}\bullet\boldsymbol{\nabla}\otimes\left[\boldsymbol{\nabla}\times\mathrm{Im}\,\boldsymbol{G}(\mathbf{r},\mathbf{r}',\omega_{21})\times\overleftarrow{\boldsymbol{\nabla}}'\right]\otimes\overleftarrow{\boldsymbol{\nabla}}'\bullet\mathbf{m}_{12}^{(4)}\,.$$

(59)

In these expressions, Eqs. (55)—(57) are the electric dipole, quadrupole, and octupole transition rates, respectively, and Eqs. (58) and (59) the magnetic dipole and quadrupole transition rates.

V. MULTIPOLE DECAY RATES IN FREE SPACE

The expressions for the spontaneous decay and magnetic spin flip rates in Eqs. (55)—(59) are valid for any environment with the geometry of the system contained in the, as yet unspecified, Green function. Calculating rates for different environments requires knowledge of the specific Green function for that system. For complicated geometries its calculation can be highly involved, but in some simple cases it is analytically known. In this section, the Green function for free space is used to calculate the vacuum decay rates. In the next section, the Green function for an infinite half space will be used to calculate the decay rates of atoms near an absorbing dielectric surface.

The Green function for free space, in component form, is given by

$$G_{\alpha\beta}^{(0)}(\mathbf{r},\mathbf{r}',\omega) = \left(\partial_\alpha^{\mathbf{r}}\partial_\beta^{\mathbf{r}} + q^2\delta_{\alpha\beta}\right)\frac{e^{iq|\mathbf{r}-\mathbf{r}'|}}{4\pi q^2|\mathbf{r}-\mathbf{r}'|},$$

(60)

where $q = \omega/c$ is the wave number and the greek indices run over the Cartesian coordinates x, y and z.

1. Electric dipole decay rate

Extensive work has been done on the dipole transition [6, 7, 8]. For completeness the result is stated here. The spontaneous decay rate for an electric dipole transition is given in component form by

$$\Gamma = \lim_{\mathbf{r},\mathbf{r}'\to\mathbf{r}_A}\frac{\omega^2}{\hbar c^2\varepsilon_0}d_\alpha d_\beta\mathrm{Im}\,G_{\alpha\beta}(\mathbf{r},\mathbf{r}',\omega).$$

(61)

Here the state indices have been dropped for clarity (hence $\omega_{12} = \omega_{21} = \omega$ and $\mathbf{d}_{12} = \mathbf{d}_{21} = \mathbf{d}$). From Eq. (60), the imaginary part of the free space Green function in the coincidence limit $\mathbf{r}\to\mathbf{r}'$ is found to be

$$\mathrm{Im}\,G_{\alpha\beta}^{(0)}(\mathbf{r}_A,\mathbf{r}_A,\omega) = \frac{\omega}{6\pi c}\delta_{\alpha\beta}.$$

(62)

Hence the free space dipole spontaneous decay rate is given by the well known formula

$$\Gamma_0 = \frac{\omega^3}{6\pi\hbar c^3\varepsilon_0}d_\alpha d_\alpha.$$

(63)

2. Electric quadrupole decay rate

The quadrupole spontaneous decay rate in component form is given by

$$\Gamma = \lim_{\mathbf{r},\mathbf{r}'\to\mathbf{r}_A}\frac{\omega^2}{\hbar c^2\varepsilon_0}d_{\alpha\beta}^{(4)}d_{\gamma\delta}^{(4)}\partial_\alpha\partial_\gamma'\mathrm{Im}\,G_{\beta\delta}(\mathbf{r},\mathbf{r}',\omega).$$

(64)

Once again the state indices have been dropped for clarity. The double derivatives of the imaginary part of the free space Green function for coincident spatial variables are easily found. Note that the both the Green function and $d_{\alpha\beta}^{(4)}$ are symmetric in their respective indices. Using these symmetries it is possible to show that the only non-vanishing terms are those with paired indices in the outer product of the two quadrupole moment vectors (sometimes referred to as the quadrupole polarizability tensor). After collecting terms, the quadrupole spontaneous decay rate in free space is found to be

$$\Gamma_0 = \frac{\omega^5}{20\pi\hbar c^5\varepsilon_0}\left\{d_{\alpha\beta}^{(4)}d_{\alpha\beta}^{(4)} - \frac{1}{3}d_{\alpha\alpha}^{(4)}d_{\beta\beta}^{(4)}\right\}.$$

(65)

Note here that the primitive moments have been used. In certain circumstances (e.g. when the external field is divergence free), the quadrupole moment tensor can be made traceless [30, 31]. In these cases the second term in Eq. (65) vanishes. This returns the result which is consistent with Ref. [18] where the traceless quadrupole moment tensor is used. However, traceless moments are not valid for all physical situations (for example, if there are other sources in the external field) and hence must be used with care. In contrast, the primitive moments are always valid and hence the full form of Eq. (65) is true for all physical situations.

3. Electric octupole decay rate

The octupole spontaneous decay rate in component form is given by

$$\Gamma = \lim_{\mathbf{r},\mathbf{r}'\to\mathbf{r}_A} \frac{\omega^2}{\hbar c^2 \varepsilon_0} d^{(8)}_{\alpha\beta\gamma} d^{(8)}_{\delta\eta\zeta} \partial_\alpha \partial_\beta \partial'_\delta \partial'_\eta \mathrm{Im}\, G_{\gamma\zeta}(\mathbf{r},\mathbf{r}',\omega).$$
(66)

The derivatives of the imaginary part of this function for coincident spatial variables are again easily found. Here $d^{(4)}_{\alpha\beta\gamma}$ is symmetric in all its indices. Thus, again, all non-vanishing terms have paired indices in the octupole polarizability tensor. Hence the octupole spontaneous decay rate in free space can be written as

$$\Gamma_0 = \frac{2\omega^7}{105\pi\hbar c^7 \varepsilon_0}\left\{ d^{(8)}_{\alpha\beta\gamma} d^{(8)}_{\alpha\beta\gamma} - \frac{1}{4} d^{(8)}_{\alpha\alpha\gamma} d^{(8)}_{\beta\beta\gamma} \right\}.$$
(67)

As for the quadrupole decay rate, the primitive octupole moments have been used. In certain circumstances trace constraints cause the second term in Eq. (67) to vanish. Note that for successive multipole orders the free space decay rates change by a factor proportional to $\omega^2 R^2/c^2$ where R is the characteristic length of the charge distribution of the atom.

4. Magnetic dipole decay rate

Let us now turn to magnetic transitions. The calculations are slightly more involved due to the presence of the spatial derivatives acting upon the Green tensor. In component form the magnetic dipole transition rate is given by

$$\Gamma = \lim_{\mathbf{r},\mathbf{r}'\to\mathbf{r}_A} \frac{\mu_0}{\hbar} m_\alpha m_\mu \varepsilon_{\alpha\beta\gamma}\varepsilon_{\mu\nu\lambda} \partial_\beta \partial'_\nu \mathrm{Im}\, G_{\gamma\lambda}(\mathbf{r},\mathbf{r}',\omega).$$
(68)

Calculating the derivatives one finds that the double curl of the Green function in the coincidence limit is

$$\lim_{\mathbf{r},\mathbf{r}'\to\mathbf{r}_A} \varepsilon_{\alpha\beta\gamma}\varepsilon_{\mu\nu\lambda} \partial_\beta \partial'_\nu \mathrm{Im}\, G^{(0)}_{\gamma\lambda}(\mathbf{r},\mathbf{r}',\omega) = \frac{\omega^3}{6\pi c^3}\delta_{\alpha\beta}. \quad (69)$$

Hence the magnetic dipole spin flip rate is given by

$$\Gamma_0 = \frac{\mu_0 \omega^3}{6\pi\hbar c^3} m_\alpha m_\alpha.$$
(70)

This is consistent with previous calculations based on dyadic Green functions [26] as well as on employing Fermi's Golden Rule [33].

5. Magnetic quadrupole decay rate

Finally, we calculate the quadrupole moment spin flip rate. The notable complication at this order, compared to that of the electric quadrupole moment, is that the primitive magnetic quadrupole moment is not symmetric in its indices. In component form the quadrupole spin flip rate is given by

$$\Gamma = \lim_{\mathbf{r},\mathbf{r}'\to\mathbf{r}_A} \frac{\mu_0}{\hbar} m^{(4)}_{\alpha\beta} m^{(4)}_{\lambda\mu} \varepsilon_{\beta\gamma\delta}\varepsilon_{\mu\nu\sigma}$$
$$\times \partial_\alpha \partial_\gamma \partial'_\nu \partial'_\lambda \mathrm{Im}\, G_{\delta\sigma}(\mathbf{r},\mathbf{r}',\omega). \quad (71)$$

Computing the derivatives one finds the magnetic quadrupole decay rate in free space to be

$$\Gamma_0 = \frac{\mu_0 \omega^5}{15\pi\hbar c^5}\left\{ m^{(4)}_{\alpha\beta} m^{(4)}_{\alpha\beta} - \frac{1}{4}\left(m^{(4)}_{\alpha\beta} m^{(4)}_{\beta\alpha} + m^{(4)}_{\alpha\alpha} m^{(4)}_{\beta\beta} \right) \right\}.$$
(72)

As with the electric decay rates, successive magnetic multipole orders change by a factor proportional to $\omega^2 R^2/c^2$. From the above recipe, multipole decay rates of even higher order can be easily derived, if needed.

VI. MULTIPOLE DECAY RATES NEAR ABSORBING SURFACES

In this section the decay rates of atoms near an absorbing surface are calculated. We shall consider surfaces that are not bianisotropic (i.e. no cross-responses between electric and magnetic degrees of freedom). Note also that diamagnetic materials are excluded from this consideration as diamagnetism is an inherently nonlinear process. Furthermore, we are interested in atoms that are subject to either an electric or magnetic interaction. Thus there are in principle four possible combinations of electric/magnetic atoms interacting with electric/magnetic surfaces. However, the work involved can be reduced when one considers the duality properties of the electric and magnetic fields. It was Silberstein [34] who first suggested the existence of symmetries in Maxwell's equations under exchange of the electric and magnetic fields. This idea was further developed in Refs. [35, 36], and the concept has been more formally established recently in Refs. [37, 38] in the context of macroscopic QED. It has been shown that under global exchange of the two fields various QED quantities, in particular relaxation rates, remain unchanged.

Hence, in order to calculate the magnetic relaxation rate for an atom above a purely magnetic surface one would only need to calculate the electric relaxation rate for an atom near a purely electric surface and apply the global transformations $\varepsilon \to \mu$ and $\hat{\mathbf{d}} \to -\hat{\mathbf{m}}/c$. Similarly, in order to find the electric relaxation rate of an atom above a purely magnetic surface one only needs to calculate the magnetic relaxation rate for an atom near a purely electric surface and then apply the same global transformation. In light of this duality, we will only calculate two of the four combinations and then deduce the other two from duality. We shall formally calculate the interaction of atoms above a purely electric surface since it is these systems, owing to the dominant strength of electric interactions, that are of most practical interest.

In the following, we envisage a medium that is infinitely extended along the (x,y)-directions and layered in the z direction such that

$$\varepsilon(\mathbf{r}, \omega) = \begin{cases} 1, & z > 0 \\ \varepsilon(\omega), & z < 0 \end{cases} \tag{73}$$

that is, an absorbing dielectric material of permittivity $\varepsilon(\omega)$ occupying the lower half space with a single interface to free space at $z = 0$. The Green function can be split into three parts,

$$\begin{aligned} &\mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) \\ &= \begin{cases} \mathbf{G}^{bulk}(\mathbf{r}, \mathbf{r}', \omega) + \mathbf{R}(\mathbf{r}, \mathbf{r}', \omega), & z, z' > 0 \text{ or } z, z' < 0 \\ \mathbf{T}(\mathbf{r}, \mathbf{r}', \omega), & \text{otherwise} \end{cases} \end{aligned} \tag{74}$$

where $\mathbf{T}(\mathbf{r}, \mathbf{r}', \omega)$ is the Green function for waves transmitted through the interface, $\mathbf{R}(\mathbf{r}, \mathbf{r}', \omega)$ is the Green function for waves reflected at the interface and $\mathbf{G}^{bulk}(\mathbf{r}, \mathbf{r}', \omega)$ is the Green function for a infinitely homogeneous, isotropic (bulk) medium of permittivity equal to that of the layer where the spatial variables are located. From the general expression for the decay rate (53) it is clear that the Green function has to be evaluated in the limit of coinciding spatial arguments. Hence, the transmission part $\mathbf{T}(\mathbf{r}, \mathbf{r}', \omega)$ does not play any role. Furthermore, since the atom is located in free space above the dielectric surface, the bulk contribution reduces to the free-space Green function (60). Hence the decay rate of an atom close to an absorbing surface can be decomposed into the free space decay rate and a reflective correction owing to the presence of the surface

$$\Gamma = \Gamma_0 + \Gamma^{(S)}. \tag{75}$$

The reflective part of the Green function can be written as the partial Fourier transform of its components

$$\mathbf{R}(\mathbf{r}, \mathbf{r}', \omega) = \int \frac{d^2 k_{\parallel}}{(2\pi)^2} \mathbf{R}(\mathbf{k}_{\parallel}, z, z'\omega) e^{i\mathbf{k}_{\parallel} \cdot (\mathbf{r}_{\parallel} - \mathbf{r}'_{\parallel})} \tag{76}$$

where $\mathbf{r}_{\parallel} = (x, y, 0)$ and $\mathbf{k}_{\parallel} = (k_x, k_y, 0)$ are vectors restricted to the (x, y)-plane parallel to the dielectric interface, and $k_{\parallel} = |\mathbf{k}_{\parallel}|$. The Green tensor components for a dielectric material in this specific geometry are listed in Appendix B. The symbols r^{TM} and r^{TE} denote the Fresnel coefficients for TM and TE waves

$$r^{TM} = \frac{\varepsilon(\omega)\beta_{z>0} - \beta_{z<0}}{\varepsilon(\omega)\beta_{z>0} + \beta_{z<0}}, \quad r^{TE} = \frac{\beta_{z>0} - \beta_{z<0}}{\beta_{z>0} + \beta_{z<0}}, \tag{77}$$

with

$$\beta_{z<0} = \sqrt{q^2 \varepsilon(\omega) - k_{\parallel}^2}, \quad \beta_{z>0} = \sqrt{q^2 - k_{\parallel}^2}, \tag{78}$$

where $\text{Im}\beta_{z \lessgtr 0} > 0$ and $q = \omega/c$. The generic form of the Green function does not lend itself to analytical investigations. However, in certain regimes it is possible to simplify the expression greatly. Here we consider the two limiting cases of near-field and far-field regimes.

A. Near field

For a purely dielectric material the near-field approximation assumes that the atom-surface distance is less than the effective transition wavelength, thus $z|\sqrt{\varepsilon(\omega)}|\omega/c \ll 1$ and hence $q^2, q^2|\varepsilon(\omega)| \ll k_{\parallel}^2$. Thus it is possible to expand the expressions for $\beta_{z<0}$ and $\beta_{z>0}$ about $q^2/k_{\parallel}^2\varepsilon(\omega)$ and $q^2/k_{\parallel}^2$, respectively. As a result,

$$\begin{aligned} \beta_{z<0} &\approx ik_{\parallel} \left\{ 1 - \frac{q^2}{2k_{\parallel}^2}\varepsilon(\omega) + \mathcal{O}\left(\frac{q^4}{k_{\parallel}^4}\varepsilon(\omega)^2 \right) \right\}, \\ \beta_{z>0} &\approx ik_{\parallel} \left\{ 1 - \frac{q^2}{2k_{\parallel}^2} + \mathcal{O}\left(\frac{q^4}{k_{\parallel}^4} \right) \right\}. \end{aligned} \tag{79}$$

By considering only the leading order terms in these expansions, we can find the leading order correction to the decay rates associated with electric transitions. Thus,

$$\beta_{z<0}, \beta_{z>0} \to ik_{\parallel}, \quad r^{TM} \to \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 1}, \quad r^{TE} \to 0, \tag{80}$$

and hence the reflective part of the Green function, in the near-field approximation, to leading order is

$$\begin{aligned} &\mathbf{R}(\mathbf{k}_{\parallel}, z, z'\omega) \approx \\ &\frac{1}{2q^2} \left[\frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 1} \right] e^{-k_{\parallel}(|z| + |z'|)} \begin{pmatrix} \frac{k_x^2}{k_{\parallel}} & \frac{k_x k_y}{k_{\parallel}} & -ik_x \\ \frac{k_x k_y}{k_{\parallel}} & \frac{k_y^2}{k_{\parallel}} & -ik_y \\ ik_x & ik_y & k_{\parallel} \end{pmatrix}. \end{aligned} \tag{81}$$

For magnetic transitions near purely dielectric bodies, to leading order in $\beta_{z<0}$ and $\beta_{z>0}$ there is no correction to the decay rate. In this case, it is necessary to include the next-to-leading order terms in $\beta_{z<0}$ and $\beta_{z>0}$,

$$\beta_{z<0} = ik_{\parallel} - i\frac{q^2}{2k_{\parallel}}\varepsilon(\omega), \quad \beta_{z>0} = ik_{\parallel} - i\frac{q^2}{2k_{\parallel}}. \tag{82}$$

Evaluating the double curl $[\mathbf{\nabla} \times \mathbf{R}(\mathbf{k}_{\parallel}, z, z'\omega) \times \mathbf{\nabla}]$, expanding all occurrences of $\beta_{z<0}$ and $\beta_{z>0}$ as above and neglecting terms of order $\mathcal{O}\left(q^4/k_{\parallel}^2\right)$ one finds that terms proportional to r^{TM} vanish. Only terms proportional to r^{TE} remain which itself can be approximated as

$$r^{TE} = \frac{\beta_{z>0} - \beta_{z<0}}{\beta_{z>0} + \beta_{z<0}} \approx \frac{q^2}{4k_{\parallel}^2}[\varepsilon(\omega) - 1]. \tag{83}$$

Hence, the double curl of the reflective part of the Green function, in the near field approximation, to next-to-leading order is

$$\begin{aligned} &\left[\mathbf{\nabla} \times \mathbf{R}(\mathbf{k}_{\parallel}, z, z'\omega) \times \mathbf{\nabla} \right] \approx \\ &\frac{q^2}{8k_{\parallel}^3}[\varepsilon(\omega) - 1] e^{-k_{\parallel}(|z| + |z'|)} \begin{pmatrix} k_x^2 & k_x k_y & -ik_x k_{\parallel} \\ k_x k_y & k_y^2 & -ik_y k_{\parallel} \\ ik_x k_{\parallel} & ik_y k_{\parallel} & k_{\parallel}^2 \end{pmatrix}. \end{aligned} \tag{84}$$

Equation (81) will be used, together with Eqs. (55)—(57), to find the transition rates associated with electric transitions of an atom above a purely dielectric surface and Eq. (84) will be used, together with Eqs. (58) and (59), to calculate the corresponding transition rates associated with magnetic transitions.

1. Electric multipole transitions

In the following, we specify our general near-field results to the electric dipole, quadrupole and octupole transitions. We start by recalling the well-known results for electric-dipole transitions. Upon using Eq. (61), the reflective correction to the spontaneous dipole decay rate is found to be [39, 40, 41]

$$\Gamma^{(S)} = \frac{1}{16\pi\hbar\varepsilon_0 z^3}\frac{\varepsilon''(\omega)}{|\varepsilon(\omega)+1|^2}\left\{d_x^2+d_y^2+2d_z^2\right\}. \quad (85)$$

Although this is a general result, in many cases such detail is not necessary. The above result assumes knowledge of the individual components of the dipole moment vector, and hence the orientation of the dipole moment.

For a free atom ensemble the dipole moment orientation of each individual atom is generally unknown. For sufficiently large ensembles of atoms, or for cases where the dipole orientation is unknown, it is possible to rotationally average the tensor formed by the outer product of the two dipole moment vectors (previously referred to as a polarizability tensor) that appears in the alternative form (54) over the sphere to obtain an expression for the decay rate that is isotropic with respect to the dipole moment orientation. The method used for the rotational averaging involves contracting the polarizability tensor with an averaging tensor (see Appendix C),

$$d_i^{\text{iso}}d_j^{\text{iso}} = I_{ij}^{\alpha\beta}d_\alpha d_\beta. \quad (86)$$

Hence the spontaneous dipole decay rate becomes

$$\Gamma_{\text{iso}} = \frac{\omega^2}{\hbar c^2\varepsilon_0}I_{ij}^{\alpha\beta}d_\alpha d_\beta\text{Im}\,G_{ij}(\mathbf{r}_A,\mathbf{r}_A,\omega). \quad (87)$$

The rank-2 averaging tensor is

$$I_{ij}^{\alpha\beta} = \frac{1}{3}\delta_{\alpha\beta}\delta_{ij}, \quad (88)$$

which leads to a decay rate of

$$\Gamma_{\text{iso}} = \frac{\omega^2}{3\hbar c^2\varepsilon_0}d_\alpha d_\alpha\,\text{Im}\,G_{ii}(\mathbf{r}_A,\mathbf{r}_A,\omega). \quad (89)$$

Note that the free-space decay rate is unchanged since the free-space Green function for coincident spatial variables is already spherically symmetric. The reflective correction to the decay rate thus becomes

$$\begin{aligned}\Gamma_{\text{iso}}^{(S)} &= \frac{1}{12\pi\hbar\varepsilon_0 z^3}\frac{\varepsilon''(\omega)}{|\varepsilon(\omega)+1|^2}d_\alpha d_\alpha \\ &= \frac{\varepsilon''(\omega)}{2|\varepsilon(\omega)+1|^2}\left(\frac{c}{\omega z}\right)^3\Gamma_0,\end{aligned} \quad (90)$$

where Γ_0 is the dipole spontaneous decay rate (63) in free space.

Similar considerations lead to the decay rates associated with higher-order electric multipole transitions. The reflective correction to the quadrupole spontaneous decay is given by [recall Eq. (64)]

$$\begin{aligned}\Gamma^{(S)} &= \lim_{\mathbf{r},\mathbf{r}'\to\mathbf{r}_A}\frac{\omega^2}{\hbar c^2\varepsilon_0}d_{\alpha\beta}^{(4)}d_{\gamma\delta}^{(4)} \\ &\times \partial_\alpha\partial_\gamma'\text{Im}\left[\int\frac{d^2 k_\parallel}{(2\pi)^2}R_{\beta\delta}(\mathbf{k}_\parallel,z,z'\omega)e^{i\mathbf{k}_\parallel\cdot(\mathbf{r}_\parallel-\mathbf{r}_\parallel')}\right].\end{aligned} \quad (91)$$

Remembering that the quadrupole moment tensor is symmetric in its indices gives a reflective correction to the quadrupole decay rate of

$$\Gamma^{(S)} = \frac{3}{64\pi\hbar\varepsilon_0 z^5}\frac{\varepsilon''(\omega)}{|\varepsilon(\omega)+1|^2}\left\{A_{\alpha\beta\gamma\delta}d_{\alpha\beta}^{(4)}d_{\gamma\delta}^{(4)}\right\}, \quad (92)$$

where the term in curly brackets is a sum over the quadrupole moment tensor components. The coefficients $A_{\alpha\beta\gamma\delta}$ for the non-vanishing tensor components are given in Table I. We can again rotationally average over the

$d_{\alpha\beta}^{(4)}d_{\gamma\delta}^{(4)}$	$A_{\alpha\beta\gamma\delta}$	$d_{\alpha\beta}^{(4)}d_{\gamma\delta}^{(4)}$	$A_{\alpha\beta\gamma\delta}$	$d_{\alpha\beta}^{(4)}d_{\gamma\delta}^{(4)}$	$A_{\alpha\beta\gamma\delta}$
$d_{xx}^{(4)}d_{xx}^{(4)}$	3	$d_{yy}^{(4)}d_{yy}^{(4)}$	3	$d_{zz}^{(4)}d_{zz}^{(4)}$	8
$d_{xy}^{(4)}d_{xy}^{(4)}$	1	$d_{yz}^{(4)}d_{yz}^{(4)}$	4	$d_{zx}^{(4)}d_{zx}^{(4)}$	4
$d_{xy}^{(4)}d_{yx}^{(4)}$	1	$d_{yz}^{(4)}d_{zy}^{(4)}$	4	$d_{zx}^{(4)}d_{xz}^{(4)}$	4
$d_{yx}^{(4)}d_{xy}^{(4)}$	1	$d_{zy}^{(4)}d_{yz}^{(4)}$	4	$d_{xz}^{(4)}d_{zx}^{(4)}$	4
$d_{yx}^{(4)}d_{yx}^{(4)}$	1	$d_{zy}^{(4)}d_{zy}^{(4)}$	4	$d_{zx}^{(4)}d_{zx}^{(4)}$	4
$d_{xx}^{(4)}d_{yy}^{(4)}$	1	$d_{yy}^{(4)}d_{zz}^{(4)}$	-4	$d_{zz}^{(4)}d_{xx}^{(4)}$	-4
$d_{yy}^{(4)}d_{xx}^{(4)}$	1	$d_{zz}^{(4)}d_{yy}^{(4)}$	-4	$d_{xx}^{(4)}d_{zz}^{(4)}$	-4

TABLE I: Table of coefficients for the quadrupole spontaneous decay rate of an atom close to an absorbing surface.

quadrupole polarizability tensor to obtain an isotropic expression for the decay rate of an unorientated ensemble

$$\Gamma_{\text{iso}} = \lim_{\mathbf{r},\mathbf{r}'\to\mathbf{r}_A}\frac{\omega^2}{\hbar c^2\varepsilon_0}d_{ij}^{(4)\text{iso}}d_{km}^{(4)\text{iso}}\partial_i\partial_k'\text{Im}\,G_{jm}(\mathbf{r},\mathbf{r}',\omega), \quad (93)$$

with

$$d_{ij}^{(4)\text{iso}}d_{km}^{(4)\text{iso}} = I_{ijkm}^{\alpha\beta\gamma\delta}d_{\alpha\beta}^{(4)}d_{\gamma\delta}^{(4)}. \quad (94)$$

The full expression for $I_{ijkm}^{\alpha\beta\gamma\delta}$ is given in Appendix C. We thus find a reflective correction to the spherically averaged quadrupole decay rate of

$$\begin{aligned}\Gamma_{\text{iso}}^{(S)} &= \frac{3}{10\pi\hbar\varepsilon_0 z^5}\frac{\varepsilon''(\omega)}{|\varepsilon(\omega)+1|^2}\left\{d_{\alpha\beta}^{(4)}d_{\alpha\beta}^{(4)}-\frac{1}{3}d_{\alpha\alpha}^{(4)}d_{\beta\beta}^{(4)}\right\} \\ &= 6\frac{\varepsilon''(\omega)}{|\varepsilon(\omega)+1|^2}\left(\frac{c}{\omega z}\right)^5\Gamma_0,\end{aligned} \quad (95)$$

where Γ_0 is the quadrupole spontaneous decay rate (65) in free space.

The same procedure can be repeated for the electric octupole transition whose decay rate is given by [cf. Eq. (66)]

$$\Gamma^{(S)} = \lim_{\mathbf{r},\mathbf{r}'\to\mathbf{r}_A} \frac{\omega^2}{\hbar c^2 \varepsilon_0} d^{(8)}_{\alpha\beta\gamma} d^{(8)}_{\delta\eta\zeta} \partial_\alpha \partial_\beta \partial'_\delta \partial'_\eta$$
$$\times \mathrm{Im}\left[\int \frac{d^2 k_\parallel}{(2\pi)^2} R_{\gamma\zeta}(\mathbf{k}_\parallel, z, z'\omega) e^{i\mathbf{k}_\parallel\cdot(\mathbf{r}_\parallel - \mathbf{r}'_\parallel)}\right]. \tag{96}$$

By the same token, the reflective correction to the octupole decay rate is

$$\Gamma^{(S)} = \frac{45}{256\pi\varepsilon_0 z^7} \frac{\varepsilon''(\omega)}{|\varepsilon(\omega)+1|^2} \left\{ A_{\alpha\beta\gamma\delta\mu\nu} d^{(8)}_{\alpha\beta\gamma} d^{(8)}_{\delta\mu\nu} \right\}, \tag{97}$$

with coefficients $A_{\alpha\beta\gamma\delta\mu\nu}$ given in Table II. Note that the coefficients are unchanged under all index permutations of the octupole moment tensor and by the commutation of the two tensors. For unorientated ensembles the decay rate becomes

$d^{(8)}_{\alpha\beta\gamma} d^{(8)}_{\delta\mu\nu}$	$A^{(8)}_{\alpha\beta\gamma\delta\mu\nu}$	$d^{(8)}_{\alpha\beta\gamma} d^{(8)}_{\delta\mu\nu}$	$A^{(8)}_{\alpha\beta\gamma\delta\mu\nu}$
$d^{(8)}_{xxx} d^{(8)}_{xxx}$	5	$d^{(8)}_{xzz} d^{(8)}_{xxx} + perm.$	-6
$d^{(8)}_{yyy} d^{(8)}_{yyy}$	5	$d^{(8)}_{yxx} d^{(8)}_{yyy} + perm.$	1
$d^{(8)}_{zzz} d^{(8)}_{zzz}$	16	$d^{(8)}_{yzz} d^{(8)}_{yyy} + perm.$	-6
$d^{(8)}_{xxy} d^{(8)}_{xxy} + perm.$	1	$d^{(8)}_{zxx} d^{(8)}_{zzz} + perm.$	-8
$d^{(8)}_{xxz} d^{(8)}_{xxz} + perm.$	6	$d^{(8)}_{zyy} d^{(8)}_{zzz} + perm.$	-8
$d^{(8)}_{yyx} d^{(8)}_{yyx} + perm.$	1	$d^{(8)}_{xyy} d^{(8)}_{xzz} + perm.$	-2
$d^{(8)}_{yyz} d^{(8)}_{yyz} + perm.$	6	$d^{(8)}_{yzz} d^{(8)}_{yxx} + perm.$	-2
$d^{(8)}_{zzx} d^{(8)}_{zzx} + perm.$	8	$d^{(8)}_{zxx} d^{(8)}_{zyy} + perm.$	2
$d^{(8)}_{zzy} d^{(8)}_{zzy} + perm.$	8	$d^{(8)}_{xyz} d^{(8)}_{xyz} + perm.$	2
$d^{(8)}_{xyy} d^{(8)}_{xxx} + perm.$	1		

TABLE II: Table of coefficients for the octupole spontaneous decay rate of an atom close to an absorbing surface.

rate becomes

$$\Gamma = \lim_{\mathbf{r},\mathbf{r}'\to\mathbf{r}_A} \frac{\omega^2}{\hbar c^2 \varepsilon_0} d^{(8)iso}_{ijk} d^{(8)iso}_{pqr} \partial_i \partial_j \partial'_p \partial'_q \mathrm{Im}\, G_{kr}(\mathbf{r}, \mathbf{r}', \omega), \tag{98}$$

with

$$d^{(8)iso}_{ijk} d^{(8)iso}_{pqr} = I^{\alpha\beta\gamma\delta\eta\zeta}_{ijkpqr} d^{(8)}_{\alpha\beta\gamma} d^{(8)}_{\delta\eta\zeta}. \tag{99}$$

The full expression for $I^{\alpha\beta\gamma\delta\eta\zeta}_{ijkpqr}$ is given in Appendix C. The reflective correction thus becomes

$$\Gamma^{(S)}_{\mathrm{iso}} = \frac{9}{7\pi\hbar\varepsilon_0 z^5} \frac{\varepsilon''(\omega)}{|\varepsilon(\omega)+1|^2} \left\{ d^{(8)}_{\alpha\beta\gamma} d^{(8)}_{\alpha\beta\gamma} - \frac{1}{4} d^{(8)}_{\alpha\alpha\gamma} d^{(8)}_{\beta\beta\gamma} \right\}$$
$$= \frac{135}{2} \frac{\varepsilon''(\omega)}{|\varepsilon(\omega)+1|^2} \left(\frac{c}{\omega z}\right)^7 \Gamma_0, \tag{100}$$

where Γ_0 is the octupole spontaneous decay rate (67) in free space.

Equations (90), (95) and (100) reveal that with increasing order of the electric multipole, the near-field scaling law of the relevant spontaneous decay rates change by a factor proportional to R^2/z^2 where R is the characteristic charge separation length of the atom and z is the atom-surface distance.

2. Magnetic multipole transitions

We complete this study of near-field decay rates by investigating magnetic multipole transitions. Magnetic dipole transitions in the presence of dielectric materials have been intensively studied previously [22, 23], and their results are presented here for completeness. The reflective correction to the magnetic dipole transition rate is given by [recall Eq. (68)]

$$\Gamma^{(S)} = \lim_{\mathbf{r},\mathbf{r}'\to\mathbf{r}_A} \frac{\mu_0}{\hbar} m_\alpha m_\beta$$
$$\times \mathrm{Im}\left[\int \frac{d^2 k_\parallel}{(2\pi)^2} \left[\boldsymbol{\nabla} \times \boldsymbol{R}(\mathbf{k}_\parallel, z, z'\omega) \times \boldsymbol{\nabla}\right]_{\alpha\beta} e^{i\mathbf{k}_\parallel\cdot(\mathbf{r}_\parallel - \mathbf{r}'_\parallel)}\right] \tag{101}$$

which, after inserting the expressions for the Green tensor, leads to

$$\Gamma^{(S)} = \frac{\mu_0\omega^2}{64\pi\hbar c^2 z} \varepsilon''(\omega)\{m_x^2 + m_y^2 + 2m_z^2\}. \tag{102}$$

This is consistent with parts of the results in Refs. [22, 23], corresponding to spin flip rates for an atom above a metallic film in the case of large skin depth and film thickness.

In the case of electric multipole transitions, it made sense to consider unoriented atomic ensembles and to define rotationally averaged spontaneous decay rates. In principle the same averaging process could be performed here. However, the result would not be physically meaningful since the atomic spin is quantized about a specific quantization axis and hence cannot have an arbitrary direction. Furthermore, in most practical situations the spins of an ensemble of atoms are aligned by external magnetic fields and hence assume a particular orientation. Thus the rotationally averaged quantity is only of academic interest and hence its calculation is renounced.

Finally, the reflective contribution to the magnetic quadrupole decay rate is given by [recall Eq. (71)]

$$\Gamma^{(S)} = \lim_{\mathbf{r},\mathbf{r}'\to\mathbf{r}_A} \frac{\mu_0}{\hbar} m^{(4)}_{\alpha\beta} m^{(4)}_{\gamma\delta} \partial_\alpha \partial'_\gamma$$
$$\times \mathrm{Im}\left[\int \frac{d^2 k_\parallel}{(2\pi)^2} \left[\boldsymbol{\nabla} \times \boldsymbol{R}(\mathbf{k}_\parallel, z, z'\omega) \times \boldsymbol{\nabla}\right]_{\beta\delta} e^{i\mathbf{k}_\parallel\cdot(\mathbf{r}_\parallel - \mathbf{r}'_\parallel)}\right] \tag{103}$$

which, in the near-field limit, can be written as

$$\Gamma^{(S)} = \frac{\mu_0\omega^2}{512\pi\hbar c^2 z^3} \varepsilon''(\omega)\{A_{\alpha\beta\gamma\delta} m^{(4)}_{\alpha\beta} m^{(4)}_{\gamma\delta}\}. \tag{104}$$

The coefficients for the non-vanishing components of the tensor $A_{\alpha\beta\gamma\delta}$ are given in Table I with the obvious interchange $d_{ij} \leftrightarrow m_{ij}$. Note here that the coefficients are the same as those for the electric quadrupole decay rate, because they are properties of the geometry of the system and hence come from the Green function. For the same reason as given for the dipole case rotational averaging is not performed. As with the spontaneous decay rates, the magnetic transition rates also change by a factor proportional to R^2/z^2.

B. Far field

In the far-field limit one assumes that the distance to the surface z is large compared to the effective transition wavelength and thus $z|\sqrt{\varepsilon(\omega)}|\omega/c \gg 1$. In that limit one can apply the method of stationary phase to compute the first-order contribution to the Fourier integral (76). The integral can be split into contributions from propagating waves ($k_\parallel \leq q$) and evanescent waves ($k_\parallel > q$), the latter of which can be neglected in the far field. The propagating part consists of a product of an amplitude function with a sinusoidal waveform whose frequency is modulated by a further function with one stationary point in the range of integration. At the stationary point $k_\parallel = 0$ we have

$$\beta_{z<0} = q\sqrt{\varepsilon(\omega)}, \quad \beta_{z>0} = q, \tag{105}$$

and therefore

$$r^{TE} \mapsto \frac{1 - \sqrt{\varepsilon(\omega)}}{1 + \sqrt{\varepsilon(\omega)}}, \quad r^{TM} \mapsto -r^{TE}. \tag{106}$$

Thus, in the far-field limit, the reflective part of the Green function becomes

$$\mathbf{R}(\mathbf{k}_\parallel, z, z'\omega) = \frac{i}{2q}r^{TE}e^{i\sqrt{q^2-k_\parallel^2}(|z|+|z'|)}\mathrm{diag}(1, 1, 0). \tag{107}$$

Analogously, the double curl of the reflective part of the Green function in the far-field limit is found to be

$$\left[\boldsymbol{\nabla} \times \mathbf{R}(\mathbf{k}_\parallel, z, z'\omega) \times \boldsymbol{\nabla}\right]$$
$$= \frac{iq}{2}r^{TE}e^{i\sqrt{q^2-k_\parallel^2}(|z|+|z'|)}\mathrm{diag}(1, 1, 0). \tag{108}$$

1. Electric multipole transition rates

The reflective corrections to the far-field electric dipole, quadrupole and octupole transition rates are given by Eqs. (61), (64) and (66), respectively. By performing the inverse Fourier transform over $k_\parallel$ for each component and taking the limit as $\mathbf{r}, \mathbf{r}' \to \mathbf{r}_A$, the reflective correction to the spontaneous decay rates associated with dipole

transitions is found to be

$$\Gamma^{(S)} = \frac{\omega^2}{8\pi\hbar c^2\varepsilon_0 z}|r^{TE}|\sin\left(\frac{2\omega z}{c} + \arg r^{TE}\right)\{d_x^2 + d_y^2\}. \tag{109}$$

Note here that r^{TE} is the approximated coefficient given by Eq. (106). Similar considerations lead to the far-field contributions to the decay rate associated with electric quadrupole transitions,

$$\Gamma^{(S)} = -\frac{\omega^4}{8\pi\hbar c^4\varepsilon_0 z}|r^{TE}|\sin\left(\frac{2\omega z}{c} + \arg r^{TE}\right)$$
$$\times \left\{d_{zx}^{(4)}d_{zx}^{(4)} + d_{zy}^{(4)}d_{zy}^{(4)}\right\} \tag{110}$$

and octupole transitions,

$$\Gamma^{(S)} = \frac{\omega^6}{8\pi\hbar c^6\varepsilon_0 z}|r^{TE}|\sin\left(\frac{2\omega z}{c} + \arg r^{TE}\right)$$
$$\times \left\{d_{zzx}^{(8)}d_{zzx}^{(8)} + d_{zzy}^{(8)}d_{zzy}^{(8)}\right\}, \tag{111}$$

respectively.

As with the near-field decay rates these results can be rotationally averaged using the appropriate rotational averaging tensors. For an unorientated ensemble of atoms the lth electric multipole decay rate becomes

$$\Gamma_{\mathrm{iso}}^{(S)} = (-1)^{l+1}\frac{\Gamma_0}{2}|r^{TE}|\sin\left(\frac{2\omega z}{c} + \arg r^{TE}\right)\left(\frac{c}{\omega z}\right), \tag{112}$$

where Γ_0 is the respective spontaneous decay rate in free space (63), (65) or (67) for dipole, quadrupole or octupole transitions, respectively. We see that successive multipole orders change by a factor proportional to $\omega^2 R^2/c^2$, just as the free space ones do.

2. Magnetic multipole transition rates

The reflective corrections to the transition rates associated with magnetic dipole or quadrupole transitions is given by Eqs. (68) and (71), respectively. By performing the inverse Fourier transform and taking the limit as $\mathbf{r}, \mathbf{r} \to \mathbf{r}_A$, the reflective correction to the dipole spin flip rate is found to be

$$\Gamma^{(S)} = -\frac{\mu_0\omega^2}{8\pi\hbar c^2 z}|r^{TE}|\sin\left(\frac{2\omega z}{c} + \arg r^{TE}\right)\{m_x^2 + m_y^2\}, \tag{113}$$

and for the quadrupole rate one finds analogously

$$\Gamma^{(S)} = \frac{\mu_0\omega^4}{8\pi\hbar c^4 z}|r^{TE}|\sin\left(\frac{2\omega z}{c} + \arg r^{TE}\right)$$
$$\times \left\{m_{zx}^{(4)}m_{zx}^{(4)} + m_{zy}^{(4)}m_{zy}^{(4)}\right\}. \tag{114}$$

As with the near-field transition rates the presence of a fixed quantization axis prevents rotational averaging. Once again we see that successive multipole orders change by a factor proportional to $\omega^2 R^2/c^2$.

In the far-field regime, both the electric and magnetic multipole rates show a $1/z$-behaviour. This is to be expected as the far fields created by all multipoles have the same distance scaling.

C. Magnetic surfaces

From the reflective correction for atoms above a dielectric surface, the reflective correction for atoms above magnetically active surfaces can be found using the duality of the electric and magnetic fields by applying the transformation $\varepsilon \leftrightarrow \mu$ and $\hat{\mathbf{d}} \to -\hat{\mathbf{m}}/c$ or $\hat{\mathbf{m}} \to c\hat{\mathbf{d}}$. For example, the near-field reflective correction to the dipole spin flip rate for an atom above a magnetic surface can be found from Eq. (85) as

$$\Gamma^{(S)} = \frac{\mu_0}{16\pi\hbar z^3} \frac{\mu''(\omega)}{|\mu(\omega)+1|^2} \left\{ m_x^2 + m_y^2 + 2m_z^2 \right\}. \quad (115)$$

Similarly, the near-field reflective correction to the dipole spontaneous decay rate can be found from Eq. (102) as

$$\Gamma^{(S)} = \frac{\omega^2}{64\pi\hbar\varepsilon_0 c^2 z} \mu''(\omega)\{d_x^2 + d_y^2 + 2d_z^2\}. \quad (116)$$

All other results convert in an identical fashion.

VII. SUMMARY

Using the theory of electromagnetic field quantization in absorbing magnetoelectric materials, the spontaneous decay and spin flip rates for the first few multipole orders have been calculated. In the calculations the primitive moments, as opposed to the traceless moments, have been used since the primitive moments are applicable to all physical situations whereas the traceless moments are only applicable where the external field obeys the Laplace equation and hence is divergence free. The decay rates for an atom in free space are given by Eqs. (63), (65), (67), (70) and (72), respectively.

When considering an atom in the prescence of an absorbing surface, the free-space decay rate is modified by a reflective correction which is a result of wave reflection from the surface. In the near-field limit, because of absorption by the surface, there are extra degrees of freedom to which the atom can decay. The atom can lose energy non-radiatively to the surface and hence the final state phase space is larger and hence the decay rate is increased. The calculation shows that the reflective correction is a complicated function of the multipole orientation but there is also an inverse dependence on the atom-surface distance z. The z-dependencies of the dominant order in the reflective correction for the different multipole decay rates are given in Table III.

Note that there is a clear hierarchy, with the power law dependence of z reducing by 2 with each successive

surface	electric		magnetic	
atom	electric	magnetic	electric	magnetic
dipole	z^{-3}	z^{-1}	z^{-1}	z^{-3}
quadrupole	z^{-5}	z^{-3}	z^{-3}	z^{-5}
octupole	z^{-7}			z^{-7}

TABLE III: Distance dependence of near-field multipole transition rates.

multipole order. It is clear from the structure of the multipole expansion that this trend will continue to higher order multipole moments.

In the far field the reflective correction is inversely dependent on the atom-surface distance to all orders of the multipole expansion and hence the far fields created by all multipoles follow the same distance scaling law. The other aspect of the far field result is the sinusoidal nature of the reflective correction with the atom-surface distance. This is caused by interference of virtual electromagnetic waves reflected from the surface.

VIII.   ACKNOWLEDGEMENTS

APPENDIX A: S-INTEGRAL PARAMETRIZATION OF THE POLARIZATION AND MAGNETIZATION FIELDS

A common parametrization for the polarization and magnetization fields involves re-writing the polarization and magnetization fields as an integral over and auxiliary parameter s. The derivations of these parametrizations are briefly reviewed here. More information can be found in Refs. [3, 32, 42].

A collection of α point charges located at $\mathbf{r}_\alpha$ can be described by the charge distribution

$$\hat{\rho}(\mathbf{r}) = \sum_\alpha q_\alpha \delta(\mathbf{r} - \hat{\mathbf{r}}_\alpha). \quad (A1)$$

In most cases, it is convenient to describe the system of charges by a coarse-grained distribution

$$\hat{\rho}_A(\mathbf{r}) = \left(\sum_\alpha q_\alpha \right) \delta(\mathbf{r} - \hat{\mathbf{r}}_A). \quad (A2)$$

The difference between the actual charge distribution (A1) and its coarse-grained average defines the atomic polarization field via the implicit relation

$$\boldsymbol{\nabla} \cdot \hat{\mathbf{P}}_A(\mathbf{r}) = -\hat{\rho}(\mathbf{r}) + \hat{\rho}_A(\mathbf{r}). \quad (A3)$$

Fourier transforming with respect to the spatial variable **r** gives

$$i\mathbf{k} \cdot \tilde{\hat{\mathbf{P}}}_A(\mathbf{k}) = \sum_\alpha q_\alpha e^{-i\mathbf{k}\cdot\hat{\mathbf{r}}_A}\left[1 - e^{-i\mathbf{k}\cdot(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A)}\right]. \quad (A4)$$

This expression can be re-written in terms of an integral over an auxiliary parameter s

$$\tilde{\hat{\mathbf{P}}}_A(\mathbf{k}) = \sum_\alpha q_\alpha e^{-i\mathbf{k}\cdot\hat{\mathbf{r}}_A}\int_0^1 ds(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A)e^{-i\mathbf{k}\cdot(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A)s}. \quad (A5)$$

Performing the inverse Fourier transform gives the parametrized expression for the polarization field

$$\hat{\mathbf{P}}_A(\mathbf{r}) = \sum_\alpha q_\alpha \int_0^1 ds(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A)\delta\left[\mathbf{r} - \hat{\mathbf{r}}_A - s(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A)\right]. \quad (A6)$$

The magnetization field is generated by currents within the material and hence is related to the rate of change of the distribution of charges. Differentiating Eqn. (A3) with respect to time and applying the continuity equation $\dot{\hat{\rho}} + \boldsymbol{\nabla}\cdot\hat{\mathbf{j}} = 0$ gives

$$\boldsymbol{\nabla}\cdot\left[\hat{\mathbf{j}}(\mathbf{r}) - \hat{\mathbf{j}}_A(\mathbf{r}) - \dot{\hat{\mathbf{P}}}_A(\mathbf{r})\right] = 0. \quad (A7)$$

The quantity $\hat{\mathbf{j}}(\mathbf{r}) - \hat{\mathbf{j}}_A(\mathbf{r}) - \dot{\hat{\mathbf{P}}}_A(\mathbf{r})$ is known as the magnetization current. Since this represents a divergence free quantity it can be written as the curl of another vector field, the atomic magnetization $\hat{\mathbf{M}}_A(\mathbf{r})$

$$\boldsymbol{\nabla}\times\hat{\mathbf{M}}_A(\mathbf{r}) = \hat{\mathbf{j}}(\mathbf{r}) - \hat{\mathbf{j}}_A(\mathbf{r}) - \dot{\hat{\mathbf{P}}}_A(\mathbf{r}). \quad (A8)$$

For globally neutral ensembles of charges at rest, $\hat{\mathbf{j}}_A(\mathbf{r})$ vanishes. The remaining two terms in Eqn. (A7) are Fourier transformed with respect to **r**. Substituting in the parametrized expression for the polarization field, performing the time differentiation and taking into account the spin contribution to $\hat{\mathbf{j}}(\mathbf{r})$ gives

$$i\mathbf{k}\times\tilde{\hat{\mathbf{M}}}_A(\mathbf{k}) = \sum_\alpha q_\alpha\dot{\hat{\mathbf{r}}}_\alpha e^{-i\mathbf{k}\cdot\hat{\mathbf{r}}_\alpha}$$

$$-\sum_\alpha q_\alpha\int_0^1 ds\dot{\hat{\mathbf{r}}}_\alpha e^{-i\mathbf{k}\cdot[\hat{\mathbf{r}}_A + s(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A)]}$$

$$-\sum_\alpha q_\alpha\int_0^1 dss(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A)(-i\mathbf{k}\cdot\dot{\hat{\mathbf{r}}}_\alpha)e^{-i\mathbf{k}\cdot[\hat{\mathbf{r}}_A + s(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A)]}$$

$$+\sum_\alpha i\mathbf{k}\times\gamma_\alpha\hat{\mathbf{S}}e^{i\mathbf{k}\cdot\hat{\mathbf{r}}}. \quad (A9)$$

Integrating the second term on the rhs by parts and applying the vector identity $\mathbf{A}\times(\mathbf{B}\times\mathbf{C}) = \mathbf{B}(\mathbf{A}\cdot\mathbf{C}) - \mathbf{C}(\mathbf{A}\cdot\mathbf{B})$ to the remaining terms gives

$$\tilde{\hat{\mathbf{M}}}_A(\mathbf{k}) = \sum_\alpha q_\alpha\int_0^1 ds\, s\left[(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A)\times\dot{\hat{\mathbf{r}}}_\alpha\right]$$

$$\times e^{-i\mathbf{k}\cdot[\hat{\mathbf{r}}_A + s(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A)]}$$

$$+\sum_\alpha \gamma_\alpha\hat{\mathbf{S}}e^{i\mathbf{k}\cdot\hat{\mathbf{r}}_\alpha}. \quad (A10)$$

The final step is to perform the inverse Fourier transform to give the parametrized expression for the atomic magnetization field as

$$\hat{\mathbf{M}}_A(\mathbf{r}) = \sum_\alpha q_\alpha\int_0^1 ds\, s\left[(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A)\times\dot{\hat{\mathbf{r}}}_\alpha\right]$$

$$\times \delta\left[\mathbf{r} - \hat{\mathbf{r}}_A - s(\hat{\mathbf{r}}_\alpha - \hat{\mathbf{r}}_A)\right]$$

$$+\sum_\alpha\gamma_\alpha\hat{\mathbf{S}}_\alpha\delta\left(\mathbf{r} - \hat{\mathbf{r}}_\alpha\right). \quad (A11)$$

Note here that the physical variables have been used. For a Hamiltonian, the canonical momenta have to be introduced instead of the physical velocities.

APPENDIX B: GREEN FUNCTION FOR A PLANAR DIELECTRIC INTERFACE

The reflective part of the Green function in terms of the partial Fourier transform of its components is derived in Ref. [43], the result of which is quoted here. Given that

$$R_{\alpha\beta}(\mathbf{r},\mathbf{r}',\omega) = \int\frac{d^2 k_\parallel}{(2\pi)^2}R_{\alpha\beta}(\mathbf{k}_\parallel, z, z'\omega)e^{i\mathbf{k}_\parallel\cdot(\mathbf{r}_\parallel - \mathbf{r}'_\parallel)}, \quad (B1)$$

with $\mathbf{r}_\parallel = (x, y, 0)$ and $\mathbf{k}_\parallel = (k_x, k_y, 0)$, which are vectors restricted to the (x, y)-plane, and $k_\parallel = |\mathbf{k}_\parallel|$, the components for the reflective part of the Green function for an infinitely extended planar dielectric material, which fills the lower half space $z < 0$, are given by

$$R_{xx} = \frac{-i}{2\beta_{z>0}}e^{i\beta_{z>0}(|z|+|z'|)}\left[\frac{r^{TM}}{q^2}\beta_{z>0}^2\frac{k_x^2}{k_\parallel^2} - r^{TE}\frac{k_y^2}{k_\parallel^2}\right], \quad (B2)$$

$$R_{yy} = R_{xx}(k_x \leftrightarrow k_y) \quad (B3)$$

$$R_{zz} = \frac{i}{2\beta_{z>0}}e^{i\beta_{z>0}(|z|+|z'|)}\left[\frac{r^{TM}}{q^2}k_\parallel^2\right], \quad (B4)$$

$$R_{xy} = R_{yx}$$

$$= \frac{-i}{2\beta_{z>0}}e^{i\beta_{z>0}(|z|+|z'|)}\left[\frac{r^{TM}}{q^2}\beta_{z>0}^2\frac{k_x k_y}{k_\parallel^2} + r^{TE}\frac{k_x k_y}{k_\parallel^2}\right], \quad (B5)$$

$$R_{xz} = \frac{-i}{2\beta_{z>0}}e^{i\beta_{z>0}(|z|+|z'|)}\left[\frac{r^{TM}}{q^2}\beta_{z>0}k_x\right] = -R_{zx}, \quad (B6)$$

$$R_{yz} = \frac{-i}{2\beta_{z>0}}e^{i\beta_{z>0}(|z|+|z'|)}\left[\frac{r^{TM}}{q^2}\beta_{z>0}k_y\right] = -R_{zy}. \quad (B7)$$

The functions r^{TM} and r^{TE} are the Fresnel coefficients for TM and TE waves

$$r^{TM} = \frac{\varepsilon(\omega)\beta_{z>0} - \beta_{z<0}}{\varepsilon(\omega)\beta_{z>0} + \beta_{z<0}}, \quad r^{TE} = \frac{\beta_{z>0} - \beta_{z<0}}{\beta_{z>0} + \beta_{z<0}} \quad (B8)$$

with

$$\beta_{z<0} = \sqrt{q^2\varepsilon(\omega) - k_\parallel^2}, \quad \beta_{z>0} = \sqrt{q^2 - k_\parallel^2} \qquad \text{(B9)}$$

and $q = \omega/c$.

APPENDIX C: ROTATIONAL AVERAGING OF TENSORS

In many cases physical systems are isotropic in nature but not explicitly isotropic in their mathematical description. Substantial simplification can be achieved by averaging of tensorial quantities over the sphere. The description of the following method follows closely the arguments in Ref. [44].

Contraction of a tensor with a rotation matrix whose components are the cosines of an angle will rotate the coordinate system of the tensor by that angle

$$T_{i_1 \cdots i_n} = I_{i_1 \cdots i_n}^{\alpha_1 \cdots \alpha_n} T_{\alpha_1 \cdots \alpha_n}. \qquad \text{(C1)}$$

By integrating the rotation matrices over the Euler angles and dividing by the spherical area the rotational average can be found

$$\langle I_{i_1 \cdots i_n}^{\alpha_1 \cdots \alpha_n} \rangle = \frac{1}{8\pi^2} \int_0^{2\pi} d\psi \int_0^{2\pi} d\phi \int_0^\pi \sin\theta \, d\theta \, I_{i_1 \cdots i_n}^{\alpha_1 \cdots \alpha_n}, \qquad \text{(C2)}$$

with

$$T_{i_1 \cdots i_n}^{iso} = \langle I_{i_1 \cdots i_n}^{\alpha_1 \cdots \alpha_n} \rangle T_{\alpha_1 \cdots \alpha_n}. \qquad \text{(C3)}$$

This is cumbersome even for tensors of low rank. A simpler method is to contract the tensor with an 'averaging tensor'. Owing to its spherical symmetry, any averaging tensor of rank n can be written as a sum of the basic linearly independent rank-n isomers which in turn can be constructed from the two fundamental isotropic tensors in three dimensions; the Kronecker delta δ_{ij} and the Levi-Civita symbol ε_{ijk}. Consider a Cartesian frame of reference in three dimensions $\mathbb{V}$ with a set of basic rank-n isomers $\boldsymbol{f}^{(n)}$ where the initial non-isotropic tensor lies and a Cartesian frame of reference $\mathbb{U}$ with a set of basic rank-n isomers $\boldsymbol{g}^{(n)}$ in which the rotationally averaged tensor lies. The averaging tensor $\boldsymbol{I}^{(n)}$ is a rank-$2n$ tensor that maps between the two spaces, $\boldsymbol{I} : \mathbb{V} \to \mathbb{U}$, such that

$$\boldsymbol{g}^n = \boldsymbol{I}^{(n)} \cdot \boldsymbol{f}^n. \qquad \text{(C4)}$$

Furthermore,

$$\boldsymbol{I}^{(n)} = \boldsymbol{g}^n \cdot \mathbf{M} \cdot \boldsymbol{f}^n, \qquad \text{(C5)}$$

where $\mathbf{M}$ is a matrix of coefficients. Since the isomers for each rank are known all that is required is to determine $\mathbf{I}^{(n)}$ is to find $\mathbf{M}$. Combining Eqs. (C4) and (C5) yields

$$\boldsymbol{g}^n = \boldsymbol{g}^n \cdot \mathbf{M} \cdot (\boldsymbol{f}^n \cdot \boldsymbol{f}^n),$$
$$(\boldsymbol{g}^n \cdot \boldsymbol{g}^n) = (\boldsymbol{g}^n \cdot \boldsymbol{g}^n) \cdot \mathbf{M} \cdot (\boldsymbol{f}^n \cdot \boldsymbol{f}^n). \qquad \text{(C6)}$$

Note that the coordinates of $\mathbb{V}$ and $\mathbb{U}$ are both Cartesian (merely rotated with respect to each other), hence the isomers for the two spaces have the same form and magnitude

$$(\boldsymbol{g}^n \cdot \boldsymbol{g}^n) = (\boldsymbol{f}^n \cdot \boldsymbol{f}^n) = \mathbf{S}^{(n)}, \qquad \text{(C7)}$$

where $\mathbf{S}^{(n)}$ is a matrix formed from all possible contractions of each isomer in the set. Thus

$$\mathbf{S}^{(n)} = \mathbf{S}^{(n)} \cdot \mathbf{M} \cdot \mathbf{S}^{(n)} \Rightarrow \mathbf{M} = \left(\mathbf{S}^{(n)}\right)^{-1}. \qquad \text{(C8)}$$

Hence, $\mathbf{I}^{(n)}$ can be determined purely from the isomers.

The rank-2 averaging tensor, used in the rotational averaging of the dipole decay rate, is constructed from the single rank-2 isomer $f^{(2)} = \delta_{\alpha\beta}$, hence $\mathbf{S}^{(2)}$ is a single number

$$\mathbf{S}^{(2)} = f^{(2)} f^{(2)} = \delta_{\alpha\beta} \delta_{\alpha\beta} = 3, \qquad \text{(C9)}$$

$\mathbf{M} = 1/3$ and thus

$$I_{ij}^{\alpha\beta} = \frac{1}{3} \delta_{ij} \delta_{\alpha\beta}. \qquad \text{(C10)}$$

As a non-trivial example we calculate the averaging tensor for a rank-4 tensor used in the rotational averaging of the quadrupole decay rate. The rank-4 isomers are

$$f_1^{(4)} = \delta_{\alpha\beta}\delta_{\mu\nu}, \quad f_2^{(4)} = \delta_{\alpha\mu}\delta_{\beta\nu}, \quad f_3^{(4)} = \delta_{\alpha\nu}\delta_{\beta\mu}. \quad \text{(C11)}$$

The elements of $\mathbf{S}^{(4)}$ are

$$S_{ij}^{(4)} = f_i^{(4)} f_j^{(4)}, \qquad \text{(C12)}$$

so for example

$$S_{11}^{(4)} = f_1^{(4)} f_1^{(4)} = \delta_{\alpha\beta}\delta_{\mu\nu}\delta_{\alpha\beta}\delta_{\mu\nu} = 9,$$
$$S_{12}^{(4)} = f_1^{(4)} f_2^{(4)} = \delta_{\alpha\beta}\delta_{\mu\nu}\delta_{\alpha\mu}\delta_{\beta\nu} = 3. \qquad \text{(C13)}$$

Hence,

$$\mathbf{S}^{(4)} = \begin{pmatrix} 9 & 3 & 3 \\ 3 & 9 & 3 \\ 3 & 3 & 9 \end{pmatrix} \Rightarrow \mathbf{M} = \frac{1}{30} \begin{pmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{pmatrix}, \qquad \text{(C14)}$$

so that we can write the rank-4 averaging tensor as

$$I_{ijkm}^{\alpha\beta\mu\nu} = \frac{1}{30} \begin{pmatrix} \delta_{ij}\delta_{km} \\ \delta_{ik}\delta_{jm} \\ \delta_{im}\delta_{jk} \end{pmatrix}^T \begin{pmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{pmatrix} \begin{pmatrix} \delta_{\alpha\beta}\delta_{\mu\nu} \\ \delta_{\alpha\mu}\delta_{\beta\nu} \\ \delta_{\alpha\nu}\delta_{\beta\mu} \end{pmatrix}. \qquad \text{(C15)}$$

Finally, using the above method, the rank-6 rotational averaging tensor, used in the calculation of the octupole spontaneous decay rate, is given below.

$$I_{ijkpqr}^{\alpha\beta\gamma\delta\eta\zeta} = \frac{1}{210}
\begin{pmatrix}
\delta_{ij}\delta_{kp}\delta_{qr} \\
\delta_{ij}\delta_{kq}\delta_{pr} \\
\delta_{ij}\delta_{kr}\delta_{pq} \\
\delta_{ik}\delta_{jp}\delta_{qr} \\
\delta_{ik}\delta_{jq}\delta_{pr} \\
\delta_{ik}\delta_{jr}\delta_{pq} \\
\delta_{ip}\delta_{jk}\delta_{qr} \\
\delta_{ip}\delta_{jq}\delta_{kr} \\
\delta_{ip}\delta_{jr}\delta_{kq} \\
\delta_{iq}\delta_{jk}\delta_{pr} \\
\delta_{iq}\delta_{jp}\delta_{kr} \\
\delta_{iq}\delta_{jr}\delta_{kp} \\
\delta_{ir}\delta_{jk}\delta_{pq} \\
\delta_{ir}\delta_{jp}\delta_{kq} \\
\delta_{ir}\delta_{jq}\delta_{kp}
\end{pmatrix}^{T}
\begin{pmatrix}
16 & -5 & -5 & -5 & 2 & 2 & -5 & 2 & 2 & 2 & 2 & -5 & 2 & 2 & -5 \\
-5 & 16 & -5 & 2 & -5 & 2 & 2 & 2 & -5 & -5 & 2 & 2 & 2 & -5 & 2 \\
-5 & -5 & 16 & 2 & 2 & -5 & 2 & -5 & 2 & 2 & -5 & 2 & -5 & 2 & 2 \\
-5 & 2 & 2 & 16 & -5 & -5 & -5 & 2 & 2 & 2 & -5 & 2 & 2 & -5 & 2 \\
2 & -5 & 2 & -5 & 16 & -5 & 2 & -5 & 2 & -5 & 2 & 2 & 2 & 2 & -5 \\
2 & 2 & -5 & -5 & -5 & 16 & 2 & 2 & -5 & 2 & 2 & -5 & -5 & 2 & 2 \\
-5 & 2 & 2 & -5 & 2 & 2 & 16 & -5 & -5 & -5 & 2 & 2 & -5 & 2 & 2 \\
2 & 2 & -5 & 2 & -5 & 2 & -5 & 16 & -5 & 2 & -5 & 2 & 2 & 2 & -5 \\
2 & -5 & 2 & 2 & 2 & -5 & -5 & -5 & 16 & 2 & 2 & -5 & 2 & -5 & 2 \\
2 & -5 & 2 & 2 & -5 & 2 & -5 & 2 & 2 & 16 & -5 & -5 & -5 & 2 & 2 \\
2 & 2 & -5 & -5 & 2 & 2 & 2 & -5 & 2 & -5 & 16 & -5 & 2 & -5 & 2 \\
-5 & 2 & 2 & 2 & 2 & -5 & 2 & 2 & -5 & -5 & -5 & 16 & 2 & 2 & -5 \\
2 & 2 & -5 & 2 & 2 & -5 & -5 & 2 & 2 & -5 & 2 & 2 & 16 & -5 & -5 \\
2 & -5 & 2 & -5 & 2 & 2 & 2 & 2 & -5 & 2 & -5 & 2 & -5 & 16 & -5 \\
-5 & 2 & 2 & 2 & -5 & 2 & 2 & -5 & 2 & 2 & 2 & -5 & -5 & -5 & 16
\end{pmatrix}
\begin{pmatrix}
\delta_{\alpha\beta}\delta_{\gamma\delta}\delta_{\eta\zeta} \\
\delta_{\alpha\beta}\delta_{\gamma\eta}\delta_{\delta\zeta} \\
\delta_{\alpha\beta}\delta_{\gamma\zeta}\delta_{\delta\eta} \\
\delta_{\alpha\gamma}\delta_{\beta\delta}\delta_{\eta\zeta} \\
\delta_{\alpha\gamma}\delta_{\beta\eta}\delta_{\delta\zeta} \\
\delta_{\alpha\gamma}\delta_{\beta\zeta}\delta_{\delta\eta} \\
\delta_{\alpha\delta}\delta_{\beta\gamma}\delta_{\eta\zeta} \\
\delta_{\alpha\delta}\delta_{\beta\eta}\delta_{\gamma\zeta} \\
\delta_{\alpha\delta}\delta_{\beta\zeta}\delta_{\gamma\eta} \\
\delta_{\alpha\eta}\delta_{\beta\gamma}\delta_{\delta\zeta} \\
\delta_{\alpha\eta}\delta_{\beta\delta}\delta_{\gamma\zeta} \\
\delta_{\alpha\eta}\delta_{\beta\zeta}\delta_{\gamma\delta} \\
\delta_{\alpha\zeta}\delta_{\beta\gamma}\delta_{\delta\eta} \\
\delta_{\alpha\zeta}\delta_{\beta\delta}\delta_{\gamma\eta} \\
\delta_{\alpha\zeta}\delta_{\beta\eta}\delta_{\gamma\delta}
\end{pmatrix}.$$

(C16)

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