LASED: A Laser-Atom Interaction Simulator using Quantum Electrodynamics

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(Dated: March 30, 2022)

A laser-atom interaction simulator using quantum electrodynamics (LASED) is presented, which has been developed in the python programming language. LASED allows a user to calculate the time evolution of a laser-excited atomic system. The model allows for any laser polarization, a Gaussian laser beam profile, a rotation of the reference frame chosen to define the states, and an averaging over the Doppler profile of an atomic beam. Examples of simulations using LASED are presented for excitation of calcium from the 4P state to the 4P1 state, for excitation from the helium 3D2 state excited by electron impact to the 10P1 state, and for laser excitation of caesium via the D2 line.

I. INTRODUCTION

Laser-excitation of atoms is an essential physical process used in many experiments including spectroscopy [1, 2], trapping of atoms [3–6], and atomic interferometry [7]. To design experiments such as these, modelling of the dynamics of the laser-atom interaction with time is often required. The semi-classical approach to solving the equation of motions of these systems has been used extensively [8–10]. By contrast, a fully quantum-electro-dynamic (QED) treatment more accurately describes the interactions, particularly when the system is complex with many states involved in the interaction [11]. Deriving the equations of motion by hand and solving the QED laser-atom interaction is time-intensive, complex, and prone to mistakes. As an example, for transitions with hyperfine structure such as excitation of the Cs 6S1/2 state to the 6P3/2 state, a total of 48 individual substates are involved in the interaction. There are hence 2304 coupled differential equations that must be generated and solved simultaneously, to fully characterise the dynamics of the system. A computational method of generating and solving these equations is hence advantageous, so that the time evolution of the populations, optical coherences and the atomic coherences can be obtained.

This paper presents an open-source python package that solves this problem: a laser-atom interaction simulator using quantum electrodynamics (LASED). LASED allows a user to automatically set up a laser-atom system and generate all the equations of motion for that system, which can be printed out in LaTex. The package can be used to solve the dynamics of the complete system over a given time, outputting the evolution of all lower and upper state populations, their atomic coherences and all optical coherence terms that couple the states together. LASED can also model the system using laser beams that have different polarizations. It can model a rotation of the frame of reference of the system both prior to the interaction, as well as after the laser interaction has occurred. This rotation technique can often simplify the calculation, thereby reducing the time required for generating an output. LASED can further include integration over the Gaussian profile of the laser beam (assuming a TEM00 beam) and also allows integration over the Doppler profile of an atomic beam, should this be required for the experiment that is being modelled. The angular shape of the electron charge cloud for the excited and lower atomic states can also be modelled and plotted as the system evolves over time.

Other laser-atom interaction simulators exists such as presented in [12]. These simulators do not however include the atomic and optical coherences, which are necessary to fully characterise the interaction and the evolution of the laser-excited atom (both for the lower and upper states). LASED is designed to be easy-to-use and has comprehensive online documentation to aid users in creating the required laser-atom system they wish to model. This documentation also demonstrates how to run the simulations by solving examples of the differential equations automatically generated by LASED. [13].

In this paper the derivation of the general equations of motion which are adopted in LASED are briefly presented in section II. In section III the computational method for generating the coupled differential equations to solve the time evolution of the laser-atom system is discussed. This section also shows how averaging over the Gaussian and Doppler profiles is approximated, and it details how the reference frame is rotated. The method used to model a general polarization state of the laser is also described.

Section IV demonstrates the outcome from the model for three selected targets. In the first example excitation of Calcium from the ground 4S state to the 4P state is discussed, since this is one of the simplest systems that can be solved. These results are presented for both linear and elliptic excitation, and includes integration over both Doppler and Gaussian profiles. An example of the technique of rotating the frame of reference is then discussed, with the calcium target again used as an example. In the second example, laser excitation of helium initially excited by electron impact to a D-state is pre-
sent. This is a considerably more complex problem to solve, since the lower state is then in a coherent superposition of substrates due to the collision. Both the populations and atomic coherences are hence non-zero prior to laser excitation and these must be included as initial conditions. Finally, a discussion of laser excitation of the Cs atom from the ground state via the D₂ transition is presented for circular excitation, as would be used in a Magneto Optical Trap (MOT).

II. GENERAL EQUATIONS OF MOTION

The general equations of motion using the QED approach for atoms under the influence of continuous wave laser irradiation have been detailed in [11, 14–16], and so only a brief overview is presented here. The equations of motion are derived using the Heisenberg formulation, where the operators are chosen to evolve in time. The Hamiltonian of the laser-atom system is hence given by

\[ H = H_{\text{Atom}} + H_{\text{Field}} + H_{\text{Int}} \]  

where \( H_{\text{Atom}} \) describes the atom evolving freely over time, so that

\[ H_{\text{Atom}} = \sum_i \hbar \omega_i |i\rangle \langle i| \]  

where \( \hbar \omega_i \) is the energy of the \( i \)th level. The Hamiltonian for the field is

\[ H_{\text{Field}} = \sum_q \hbar \omega_q a_q^\dagger a_q \]  

where \( a_q^\dagger a_q \) are the creation and annihilation operators for the mode \( q \) of the field, with \( q \) representing both the wave vector and its polarization. The interaction Hamiltonian [17] is expressed in normal ordering [18] as

\[ H_{\text{Int}} = \hbar \sum_{q'q} g_{qq'} \sigma_{q'q'} e^{ik_{q'}z} + g_{q'q}^* a_{q'q}^\dagger e^{-ik_{q}z} \sigma_{q'q} \]  

where

\[ g_{qq'} = i \sqrt{\frac{\omega_{q'}}{2\epsilon_0 V}} \bar{e}_{q'} \cdot D_{q'q'} \]  

is a coupling coefficient between the mode of the laser field and the lower atomic state \( |q\rangle \) and upper state \( |q'\rangle \). \( V \) is the mode volume, \( D_{q'q'} \) is the dipole moment, and \( \bar{e}_{q'} \) is the polarization unit vector. The atomic operators are defined by the atomic states so that

\[ \sigma_{q'q} = |e\rangle \langle g| \]  

The atomic operators evolve over time using the Liouville equation [19]

\[ \frac{d\sigma_{q'q}}{dt} = -\frac{i}{\hbar} [\sigma_{q'q}, H] = -\frac{i}{\hbar} [\sigma_{q'q}, H_{\text{Atom}}] - \frac{i}{\hbar} [\sigma_{q'q}, H_{\text{Int}}]. \]  

\( H_{\text{Field}} \) does not contribute here as it commutes with the atomic operator. The first term in equation 7 can be simplified using the ortho-normality relations \( \langle e|e\rangle = \langle g|g\rangle = 1 \) and \( \langle e|g\rangle = \langle g|e\rangle = 0 \) so that

\[ -\frac{i}{\hbar} [\sigma_{e'g}, H_{\text{Atom}}] = -i(\omega_g - \omega_e) \langle e|g\rangle \]  

The second term in equation 7 can be expanded using equation 4 so that

\[ -\frac{i}{\hbar} [\sigma_{e'g}, H_{\text{Int}}] = -i \sum_{q'q} g_{q'q}^* a_{q'q}(t)^\dagger e^{-ik_{q'}z} \sigma_{e'g} + i \sum_{q'q} g_{q'q} a_{q'q}^\dagger e^{-ik_{q}z} \sigma_{e'g} \]  

As the time evolution of the annihilation and creation operators depends on the field coupling to the atomic states, an explicit function in time is required. For \( a_{q'}^\dagger \) this is given by

\[ a_{q'}^\dagger(t) = a_{q'}^\dagger(0) e^{i\omega_q t} + i \sum_{q''} g_{q'q''}^* a_{q''q'}(t)^\dagger e^{i\omega_{q''} t} + i \sum_{q''} g_{q'q''} a_{q''q'}^\dagger e^{-i\omega_{q''} t} \]  

with \( a_q^\dagger \) being given by the complex conjugate of this equation. In equation 10 the atomic operator can be removed from the integral using the Harmonic approximation [20]. When combined with equation 9, this then yields

\[ -\frac{i}{\hbar} [\sigma_{e'g}, H_{\text{Int}}] = -i \sum_{q'q''} g_{q'q''}^* a_{q''q'}(0)^\dagger e^{i\omega_{q''} t - k_{q''} z} \sigma_{e'g} + \sum_{q'q''} \left( g_{q'q''}^* g_{q'q''} \sigma_{q'q''} \right) \int_0^t e^{i(\omega_{q''} - k_{q''} z) t'} dt' \sigma_{e'g} - i \sum_{q'q''} g_{q'q''} a_{q''q'}(0)^\dagger e^{i\omega_{q''} t - k_{q''} z} \sigma_{g'q} \]  

When the laser frequency \( \omega_{q''} \) is close to the transition frequency \( \omega_{q''} - \omega_{q'} \) and for time periods much larger than the inverse of the oscillation frequency, the integrals in equation 11 can be approximated to \( \delta \) functions [18]. The time evolution of the atomic operator can hence be
written as

\[
\frac{d\hat{\sigma}_{eg}}{dt} = -i(\omega_g - \omega_e)\hat{\sigma}_{eg} - i\sum_{q' e'} g_{e' q'}^q a_{q'}^\dagger(0)e^{i(\omega_{e' t} - k_{q'} z)}\hat{\sigma}_{ee'}
+ i\sum_{q' g} g_{g' q'}^q a_{q'}^\dagger(0)e^{i(\omega_{e' t} - k_{q'} z)}\hat{\sigma}_{g' g}
- \sum_{q' g' e'} g_{e' q'}^q g_{g' q'}^q e_{q' g'}\hat{\sigma}_{e' e'}\pi\delta(\omega_{q'} - \omega_e + \omega_{g'}) .
\] (12)

Equation 12 contains rapidly oscillating terms at the frequency of the driving radiation. In many experiments these cannot be measured, and so the Rotating Wave Approximation (RWA) [20] is adopted. For a single mode continuous wave laser beam driving the transition, the RWA transforms the atomic operators into slowly varying operators \(\hat{\chi}_{eg}\), by setting

\[
\hat{\sigma}_{eg} = \hat{\chi}_{eg} e^{i(\omega_L t - k_L z)}
\] (13)
\[
\hat{\sigma}_{gg'} = \hat{\chi}_{gg'}
\] (14)
\[
\hat{\sigma}_{ee'} = \hat{\chi}_{ee'},
\] (15)

where \(\omega_L\) is the laser frequency and \(k_L\) is the associated wave vector. Equation 12 is hence transformed to slowly varying operators using equation 13. Expectation values are then taken, so that

\[
\langle \hat{\chi}_{eg} \rangle = -i(\omega_L - k_L z - \omega_{eg})\langle \hat{\chi}_{eg} \rangle
- i\sum_{Le'} g_{e' q'}^{L e} a_{L}^\dagger(0)\langle \hat{\chi}_{ee'} \rangle
+ i\sum_{Lg'} g_{e' g'}^{L g} a_{L}^\dagger(0)\langle \hat{\chi}_{g' g} \rangle
- \sum_{q' g' e'} g_{g' q'}^{L e} g_{e' g'}^{L g} \langle \hat{\chi}_{e' g'} \rangle\pi\delta(\omega_L - \omega_{e'} + \omega_{g'}) .
\] (16)

The slowly varying operators are directly related to the density matrix elements \(\rho_{eg}\) that are commonly used to describe the populations and coherences of an atomic system, since

\[
\langle \hat{\chi}_{eg} \rangle = \langle \psi|\langle g|\psi \rangle = \langle e|\langle \psi|\psi \rangle \rangle^* = (\rho_{eg})^* = \rho_{ge}.
\] (17)

The half-Rabi frequency is input to equation 16 using the relation [11]

\[
\Omega^L_{eg} = g_{eg} a_{L}^\dagger(0).
\] (18)

This is set to be real by an appropriate choice of phase [11].

The time evolution of \(\langle \hat{\chi}_{gg'} \rangle\) and \(\langle \hat{\chi}_{ee'} \rangle\) can be derived in an identical way to that of \(\langle \hat{\chi}_{eg} \rangle\) in equation 16. These can then be written in the density matrix formalism using equation 17. The general equations of motion for the populations, optical and atomic coherences as used in

\[
\rho_{gg'} = -i\Delta_{gg'}\rho_{gg'} + \sum_{q' e'} g_{g' e'}^q g_{e' q'}^q \pi\delta(\omega_q - \Delta_{e' e'})\rho_{e' e'}
+ \sum_{q' g} g_{g' q} g_{q' g}^q \pi\delta(\omega_q - \Delta_{e' g'})\rho_{e' e'}
\] (19)

\[
\rho_{ee'} = -i\Delta_{ee'}\rho_{ee'} + \sum_{Lg} \Omega^L_{e' g}\rho_{eg} - \sum_{Lg'} \Omega^L_{e' g'}\rho_{eg'}
- \sum_{q' g' e'} g_{g' q'}^q g_{e' g'}^{q*} \pi\delta(\omega_q - \Delta_{e' g'})\rho_{e' e'}
\] (20)

\[
\dot{\rho}_{ge} = -i\Delta_{L, eg}\rho_{ge} - i\sum_{L e'} \Omega^L_{e' g}\rho_{e' e'} + i\sum_{L g'} \Omega^L_{e' g'}\rho_{ge'}
- \sum_{q' g' e'} g_{g' q'}^q g_{e' g'}^{q*} \pi\delta(\omega_q - \Delta_{e' g'})\rho_{e' e'}
\] (21)

with \(\dot{\rho}_{eg}\) given by the complex conjugate of equation 21.

The populations of the states are derived by setting \(g = g'\) and \(e = e'\) in equations 19 and 20 respectively, whereas the atomic coherences are formulated by setting \(g \neq g'\) and \(e \neq e'\). Equation 21 is used to derive both the optical coherence terms generated directly by the laser, as well as the atomic coherences generated between upper and lower states. The term

\[
\Delta_{L, eg} = \omega_L - \frac{2\pi v_z}{\lambda_L} + \omega_e - \omega_g
\] (22)

is the detuning from resonance, where \(v_z\) is the velocity component of the atoms in the direction of the laser beam (which gives rise to the Doppler shift). \(\lambda_L\) is the wavelength of the laser mode \(L\) and the term \(\Delta_{eg} = \omega_e - \omega_g\). The half-Rabi frequency can be calculated in rad/s using the expression

\[
\Omega^q_{eg} = C^q_{eg} \Omega = C^q_{eg} \sqrt{\frac{3\lambda^3 L}{8\pi \hbar c \tau}}
\] (23)

where \(\tau\) is the lifetime of the transition, \(I_L\) is the laser intensity, and \(C^q_{eg}\) is a coupling coefficient given by [21]

\[
C^q_{eg} = (-1)^{n_F + n_{F'} + n_I + n_{I'} + n_L + n_S - m_F + 1}
\times \sqrt{(2F + 1)(2F' + 1)(2J + 1)(2J' + 1)(2L + 1)}
\times \left( F' \ 1 \ F' \ \begin{bmatrix} F & I & L \\ J & J' & S \end{bmatrix} \right) \begin{pmatrix} -m_F & q & m_{F'} \end{pmatrix}
\] (24)

where \(L, S, J, I,\) and \(F\) are the quantum numbers describing the upper state \(|e\rangle\) and their primed equivalents are
the quantum numbers describing the lower state \( |g\rangle \). \( q \) is set to be either +1, 0, or -1 for the laser polarization being right-hand circularly polarized (RHC), linearly polarized, or left-hand circularly polarized (LHC) respectively.

The triple summations in equations 19, 20, and 21 describe spontaneous emission. They produce decay of the atomic excitation even if there is no driving laser field. These terms can be calculated by relating them to the generalized decay rate given in [11]

\[
\Gamma_{eg'g} = \sum_{q} [g^q_{eg'}g^{q*}_{eg} \pi \delta(\omega_q - \Delta_{eg})] + g^q_{eg'g}g^{q*}_{eg} \pi \delta(\omega_q - \Delta_{eg})].
\] (25)

Equation 25 is then used to derive the decay rate between an excited substate \( |e\rangle \) to a lower state \( |g\rangle \) with

\[
\Gamma_{eg} = \Gamma_{eg'g} = 2 \sum_{q} |g^q_{eg}|^2 \pi \delta(\omega_q - \Delta_{eg}).
\] (26)

The total decay rate of state \( |e\rangle \) is then given by

\[
\Gamma_{e} = \sum_{g} \Gamma_{eg}.
\] (27)

The transition probability for spontaneous emission is proportional to the square of the dipole matrix element and so the decay constants \( \Gamma_{eg} \) can be calculated using

\[
\Gamma_{eg} = \frac{(\Omega_{eg})^2}{\sum_{g'}(\Omega_{eg'})^2} \Gamma_{e} = \frac{|C^g_{eg}|^2}{\tau \sum_{g'}|C^{g'}_{eg}|^2}
\] (28)

where the summation in the denominator is over all coupled ground states and \( \tau \) is the lifetime of the excited state. Here, \( q \) is the required polarization for the decay from \( |e\rangle \) to \( |g\rangle \).

The equations presented above are then used to compute the time evolution of the laser-atom system, as detailed in the next section.

**III. TIME EVOLUTION CALCULATIONS**

The process of setting up a laser-atom system and finding the solutions to the equations of motion is outlined in Fig. 1. LASED enables a user to define an atomic system by creating the states and substates of the atom that are coupled by the laser. Their relative energy separation, angular momenta, and the projection of the total angular momentum associated with each state is also input to the model as initial parameters. The substates are labelled as either an upper state \( |e\rangle \) or a lower state \( |g\rangle \).

The resonant transition laser wavelength between upper and lower states is defined as \( \lambda \). The user then enters the laser parameters by defining the laser polarization \( \mathbf{Q} \) and the intensity \( I \). The user then enters the laser parameters by defining the laser polarization \( Q \) and the intensity \( I \). This sets up the initial laser-atom system to be solved. The time steps \( t_i \) over which the simulation is run is also defined before the system evolves. At the initial time step \( t = t_0 \) the laser is turned on.

To solve the user-defined laser-atom system, equations 19, 20 and 21 are used to automatically generate the complete set of coupled differential equations which are solved numerically. LASED uses a matrix method by writing the equations in the form

\[
\dot{\rho} = A \rho(t)
\] (29)

where \( \rho \) is a column vector containing all the populations and coherences defined within the density matrix for the coupled system. The density matrix has \( n^2 \) elements, where \( n \) is the number of substates in the system. \( \rho \) is hence a column vector of \( n^2 \) elements. \( A \) is an \( n^2 \times n^2 \) coupling matrix that contains all of the coefficients of the interaction. This includes all half-Rabi frequencies generated from equation 23, the detuning terms and all decay constants. The matrix \( A \) can become very large, and so

![FIG. 1. The algorithm used in LASED to compute the time evolution of a laser-atom system. For details, see the text in section III.](image-url)
to reduce computation time equation 29 is solved by di-

agonalising the matrix and calculating the eigenvectors

and eigenvalues. The solution of $\rho$ using this technique

does not account for the population of the excited substate

and eigenvalues. The solution of

and eigenvalues. The solution of equation 29 is solved by di-

rection within $\rho$. The user hence must define the substate with a number that labels it, e.g. $|1\rangle$, $|2\rangle$, and $|3\rangle$ for a lower $P$-state with $m = -1, 0, +1$ respectively. The convention used throughout LASED is that the first element in the vector $\rho$ is the element $\rho_{11}$, which is the lower state population with the lowest projection of total angular momentum $-m_F$. The labelling continues until the excited substate population with the highest projection of total angular momentum $+m_F$ is set to be the $n^{th}$ substate. The vector would hence have the form: $[\rho_{11} \rho_{12} \ldots \rho_{1n}, \rho_{21} \rho_{22} \ldots \rho_{2n}, \rho_{n1} \rho_{n2} \ldots \rho_{nn}]$. The matrix $A$ is then populated using the coefficients generated using equations 19 to 21. These can be modified to give a set of equations with computable variables:

\[
\dot{\rho}_{gg''} = -\left(2i\Delta_{gg''} + \frac{1}{\tau_b}\right)\rho_{gg''} + i\Omega \sum_{q\epsilon} (C^g_{e\epsilon''} \rho_{ge} - C^g_{eg} \rho_{eg''}) + \frac{1}{\tau} \sum_{q\epsilon''} \gamma^q_{e\epsilon''}\rho_{e\epsilon''} + \gamma^{q'}_{e\epsilon''}\rho_{e\epsilon''}
\]

\[
\dot{\rho}_{ee''} = -\left(2i\Delta_{ee''} + \frac{1}{\tau} + \frac{1}{\tau_f}\right)\rho_{ee''} + i\Omega \sum_{qg} (C^{q}_{e\epsilon''g} \rho_{eg} - C^{q}_{eg} \rho_{e\epsilon''})
\]

\[
\dot{\rho}_{ge} = -i(\Delta^g_{eg} + \delta) + \frac{1}{2\tau} + \frac{1}{2\tau_f} + \frac{1}{2\tau_b}\rho_{ge} - i\Omega \sum_{q\epsilon''} C^q_{e\epsilon''}\rho_{e\epsilon''} + i\Omega \sum_{qg} C^q_{eg} \rho_{gg''}
\]

\[
\dot{\rho}_{ff''} = -\left(2i\Delta_{ff''} + \frac{1}{\tau} + \frac{1}{\tau_f}\right)\rho_{ff''} + i\Omega \sum_{qg} (C^{q}_{e\epsilon''g} \rho_{eg} - C^{q}_{eg} \rho_{e\epsilon''})
\]

The decay constants in $\dot{\rho}_{gg''}$ are contained in the term

\[
\gamma^{q}_{e\epsilon''} = \begin{cases} 
|C^{q}_{eg}C^{q'}_{g'g}|, & \text{if } e'' = e''' \\
\sum_{q\epsilon''} |C^{q}_{e\epsilon''g}C^{q'}_{e\epsilon''g'}|, & \text{if } e'' \neq e''' \text{ AND } \sum_{q\epsilon''} C^{q}_{e\epsilon''g}C^{q'}_{e\epsilon''g'} \neq 0.
\end{cases}
\]

where the sum over $q$ is the sum of all values over which spontaneous emission can occur: $+1, 0, -1$. The second case in equation 34 only appears when there is hyperfine splitting leading to vertical coherences [11].

The calculation of the generalized decay constants and their phase is shown in appendix B. The coupling coefficients are calculated using equation 5 and the maximum half-Rabi frequency $\Omega$ is calculated using equation 23. The detuning term is calculated using equation 22 as discussed in section II. The laser-atom system modelled using equations 31 to 33 are more general than the system modelled using equations 19 to 21 as these also include extra decay terms that describe the process of relaxation to states which are not directly coupled by the laser, as shown in Fig. 2. These include states that $|e\rangle$ and $|g\rangle$ may decay to that are not included in equations 19 to 21, as well as any non-radiative decay routes that may occur. The decay from a laser-excited state $|e\rangle$ to a non-coupled state $|f\rangle$ is modelled by the lifetime $\tau_f$ and the decay from a lower state $|g\rangle$ to a non-coupled state $|b\rangle$ is modelled by the lifetime $\tau_b$. Equation 33 also includes a detuning term $\delta$, which allows the user to add a constant detuning from resonance if required (e.g. for laser-cooling of atoms).

Whilst the matrix $A$ is being generated the equations of motion can be printed out in a numeric or symbolic format depending on the user’s preference. The Sympy package [22] is used to generate the symbolic equations, which can be output as LaTeX.

Once the matrix $A$ has been generated, the NumPy package [23] is used to diagonalise the matrix to form $D$. NumPy is also used to perform all matrix multiplication in LASED. The SciPy package [24] is used to generate

FIG. 2. The states of the atomic system used in LASED can also include states $|f\rangle$ and $|b\rangle$ which are not directly coupled by the laser as shown. For details, see the text.
the matrix of eigenvectors $V$ from $A$ and is also used in LASED to perform matrix exponentials and the inversion of matrices. For every element of the time array $t_i$, the column vector $\rho(t_i)$ of the laser-atom system is calculated numerically. Before looping over every element in $t_i$, $V^{-1}\rho(t_i)$ is calculated to save computation time. During the loop over $t_i$, the matrix exponential $e^{Dt}$ is calculated by taking the exponent of each diagonal element of $Dt$. Finally, $\rho(t)$ is calculated using equation 30. Once the time evolution is completed, the user can access any element of $\rho(t)$ for analysis, the data can be saved as a csv file, or it can be plotted.

A. Gaussian and Doppler Averaging

When a laser-atom system is modelled in LASED the default setting is that the spatial intensity profile of the laser beam is uniform. The user can however also specify a two-dimensional (2D) Gaussian laser beam profile, so as to emulate a TEM$_{00}$ mode [25]. For a Gaussian beam the intensity as a function of the radial distance from its beam axis $r$ is given by

$$I(r) = I_0 e^{-\frac{r^2}{\sigma^2}}$$ (35)

where $I_0$ is the intensity at the peak $r = 0$ and $\sigma$ is the radial distance equivalent to the 2D standard deviation. To obtain the total laser power $P_{\text{las}}$ as measured by a power meter, equation 35 is integrated so that

$$P_{\text{las}} = \int_{0}^{\infty} 2\pi r I_0 e^{-\frac{r^2}{\sigma^2}} dr = 2\pi \sigma^2 I_0$$ (36)

The intensity at any given radius is hence given by

$$I(r) = \frac{P_{\text{las}}}{2\pi \sigma^2} e^{-\frac{r^2}{\sigma^2}}.$$ (37)

from which the equivalent Rabi frequency can be generated. To model the effect of a Gaussian beam profile on the system, the beam profile is then divided into a series of radial rings with the populations and coherences generated for each ring then summed incoherently to obtain the total density matrix for the ensemble. LASED assumes that the atoms are uniformly distributed throughout the laser beam profile with a density given by $\rho_A$ and that the atoms are stationary during the interaction. Hence the number of atoms in any ring between $r$ and $r + \Delta r$ is given by

$$N_A^{\Delta r} = \rho_A(2\pi r \Delta r h)$$ (38)

where the laser beam is assumed to be parallel through the interaction region, which has a height along the laser beam of $h$. Equation 38 then provides a weighting term to calculate the total number of atoms in the interaction region, up to a given radius. The laser beam diameter is approximated as $6\sigma$ ($\pm 3\sigma$) and so the total number of atoms in the interaction volume is given by

$$N_{\text{total}}^{6\sigma} = \int_{0}^{3\sigma} 2\pi \rho_A hr dr = 9\pi \rho_A h \sigma^2$$ (39)

For $n_r$ equal rings and a beam diameter of $6\sigma$, the ring radius will be $\Delta r = 3\sigma/n_r$. The numerical calculation of the density matrix elements can then be calculated for averaging over the Gaussian laser profile, by performing a discrete sum of all $n_r$ rings and dividing by the total number of atoms:

$$\rho^{av}(I(r), t) = \frac{\sum_{j=0}^{n_r-1} (2j + 1) (\frac{9\sigma^2}{n_r^2}) \rho(I(r_j, r), t)}{9\sigma^2}$$

$$= \frac{1}{n_r} \sum_{j=0}^{n_r-1} (2j + 1) \rho(I(r_j, r), t)$$

$$= \frac{1}{n_r^2} \sum_{j=0}^{n_r-1} (2j + 1) \rho(\Omega(r_j, r), t).$$ (40)

The half-Rabi frequency is introduced in place of the intensity in equation 40 since this is what is required when combining equations 23 and 37. To model a Gaussian beam profile in LASED, the user must enter the number of rings $n_r$ as well as the 2D standard deviation of the beam profile $\sigma$ in millimetres. When performing the time evolution, an array of ring radii is created up to the maximum beam profile radius $3\sigma$. For each $r_j$ in the array, the time evolution of the laser-atom system is calculated and then averaged as given by equation 40.

LASED also includes a functionality to model the effect of the Doppler profile of atoms within the interaction region, as would occur in an atomic beam from an oven or gas jet. The Doppler profile of the atoms is input to the model as a detuning term $\delta$ in units of $10^9$ rad/s. For numerical purposes the Doppler profile is again split up into discrete values across the profile and the density matrix elements are calculated for each detuning term. The results are then averaged in a similar way to that adopted for representation of a TEM$_{00}$ laser beam. This Doppler averaging requires a weighting factor of the atoms given by [26]

$$F_{\text{Dopp}}(\delta) = \frac{1}{\sqrt{2\pi \Delta_{\text{Dopp}}^2}} e^{-\frac{\delta^2}{2\Delta_{\text{Dopp}}^2}}$$ (41)

where $\Delta_{\text{Dopp}}$ is the Doppler width. The averaged density matrix elements across the atomic Doppler profile are then given by

$$\rho^{av} = \sum_i \rho(\delta_i) F_{\text{Dopp}}(\delta_i) \Delta \delta_i$$

$$= \frac{1}{\sqrt{2\pi \Delta_{\text{Dopp}}^2}} \sum_i \rho(\delta_i) e^{-\frac{\delta_i^2}{2\Delta_{\text{Dopp}}^2}} \Delta \delta_i$$ (42)
where $\Delta \delta_i$ is the angular frequency spacing between the discrete detunings that are used to represent the Doppler profile. Hence, to model a Doppler profile using LASED the user must declare a value for the Doppler width and create an array which contains discrete detuning values. Equation 42 is then used to calculate the Doppler averaged density matrix elements for the system.

### B. Rotation of quantization reference frames

It is often advantageous to define an atomic system in a particular reference frame that makes the calculation easier, or that decreases the computation time. As an example, excitation by linearly polarized light can adopt a quantization z-axis (QA) along the direction of the electric field vector, so that the change in $m_F$ values between upper and lower substates is $\Delta m_F = 0$. An alternative and equally valid representation for linear excitation may choose the quantization axis along the direction of the laser beam, in which case simultaneous $\Delta m_F = \pm 1$ excitation occurs. In the former case for an S to P transition, this leads to $n = 4$ differential equations that must be solved. By contrast, in the latter case, nine equations must be generated and then solved. Both calculations lead to the same results and they can be related to each other using a suitable rotation from one frame to the other. Since the computational speed scales as $n^2$, choosing the QA along the electric field vector in this example hence produces results more than 5 times faster than when the QA is chosen along the beam.

An example where the rotation technique has been adopted to simplify the calculation can be found in [27], where electron excited mercury atoms in the $6^1P_1$ state were further excited by a laser beam to the $6^1D_2$ state using linearly polarized light. In this case the atomic system in the collision frame (QA along the direction of the electron beam) was first rotated into the laser frame along the electric field of the laser and the laser interaction was calculated in this new frame. The resulting atomic system was then rotated back to the collision frame to determine the evolved atomic structure in that frame. This required 36 differential equations to be solved for the laser interaction, compared to 64 equations that would need to be generated and solved simultaneously if the calculation had been carried out directly in the collision frame. A further advantage of moving to the laser frame was that the 12 equations for the populations and optical coherences decoupled from the 24 equations for the non-optical and atomic coherences, so that the matrix $A$ was block diagonal. This lead to a 5.7 fold increase in computational efficiency.

It is not however always possible to apply this technique, since there may be constraints on the system due to additional interactions. An example is found in [16, 28, 29], where an external magnetic $B$-field was imposed on the system. In these experiments the $B$-field direction was co-linear with the direction of the laser beam, and so the QA was chosen along this axis for excitation by both circular and linearly polarized laser beams, with the linear beam being considered as a superposition of right-hand and left-hand circularly polarized beams.

LASED can incorporate rotation between reference frames within its structure, so that these advantages can be exploited. The rotation is performed by rotating the density matrix for each atomic state using the Wigner rotation matrices [30], so that

$$\rho_{J,m,J'm'} = \sum_{\mu=-J}^{+J} \sum_{\mu'=-J}^{+J'} D^{J'}_{\mu \mu'}(\omega) \rho_{J,\mu,J'\mu'} D^{J}_{\mu' \mu}(\omega)$$

where $\rho_{J,\mu,J'\mu'}$ and $\rho_{J,m,J'm'}$ are the atomic state density matrix elements in the new and old reference frame respectively, $J$ is the total angular momentum of the state (which will be $F$ if there is non-zero isospin), $m$ is the projection of angular momentum onto the QA, and $\omega$ denotes the Euler angles for the rotation ($\alpha$, $\beta$, $\gamma$). In LASED, the Euler angles are defined as three angles of rotation performed in succession from Cartesian reference frame $Z$ to $Z''$, and then to a final $Z'''$. $\alpha$ then rotates around the z-axis, $\beta$ rotates around the new y'-axis, and $\gamma$ finally rotates around the new z'''-axis. The Wigner-D matrix is calculated using [31]

$$D^{J'}_{m'm}(\omega) = e^{-im'\alpha} d^{J'}_{m'm}(\beta) e^{-im\gamma}$$

where $d$ is determined using

$$d^{J'}_{m'm}(\beta) = \sqrt{(J+m')!(J-m')!(J+m)!(J-m)} \times \sum_{s=s_{\text{min}}}^{s_{\text{max}}} (-1)^{m'-m+s} (\cos^2 2J + m-m'-2s \sin^2 (m'-m+2s))$$

$$\frac{2sJ-J}{(J+m-s)!s!(m'-m+s)! (J-m'-s)!}$$

The summation over $s$ is constrained to $s_{\text{min}} = \max(0,m-m')$ and $s_{\text{max}} = \min(J+m,J-m')$ so that the factorials remain non-negative. Hence, if a rotation matrix is required to rotate a state with angular momentum $J$, it will be a square matrix of size $2J+1$. If required, LASED uses equation 43 to rotate any density matrix set up by the user to a new reference frame.

### C. Modelling different laser polarizations

In many experiments the laser beam interacting with the atoms is chosen to have either circular or linearly polarization. This makes the generation of the equations of motion and subsequent computation of the dynamics relatively straightforward, as discussed above. It is also important for LASED to model the interaction using a laser which has elliptic polarization, since this is the most general form for any beam. An elliptically polarized beam can be considered as one that has its E-field vector tracing out an ellipse, as shown in Fig. 3. The ellipse has major and minor axes, with the major axis being rotated
from the x-axis at an angle $\psi$ as shown. The direction of rotation of the $E$-field also must be defined to fully characterize the radiation.

Any elliptically polarized beam can be described as a superposition of right-hand and left-hand circular components with different complex amplitudes, the relative phase between the amplitudes producing the rotation of the major axis from the x-axis. These amplitudes then feed into the Rabi frequencies through equations 5 and 23. Since the QED model has been developed for the Rabi frequencies being real, it is necessary to first rotate the QA through the angle $\psi$ so that the new x-axis is aligned along the major axis of the ellipse. This rotation sets the relative phase to zero and so the elliptically polarized light can then described using two real amplitudes, as given by equation 46.

$$|P\rangle = \frac{1}{\sqrt{a_{-1}^2 + a_{+1}^2}} (a_{-1}|\sigma_{-1}\rangle + a_{+1}|\sigma_{+1}\rangle) \quad (46)$$

Here $|\sigma_{-1}\rangle$ and $|\sigma_{+1}\rangle$ are the LHC and RHC polarization unit vectors and $a_{-1}$ and $a_{+1}$ are real amplitudes. The computation then proceeds in the same way as described above, however two weighted Rabi frequencies are now required to describe the interaction. From equation 46 it follows that the half-Rabi frequency for elliptically polarized light in this frame is given by

$$\Omega_{\text{elliptic}} = \frac{1}{\sqrt{a_{-1}^2 + a_{+1}^2}} (a_{-1}\Omega_{-1} - a_{+1}\Omega_{+1}) \quad (47)$$

where the negative sign arises from the definition of the dipole moment in a circular basis. Once the interaction has been modelled in this frame, the QA can be rotated back into the original frame to calculate the final density matrix elements.

LASED uses the procedure detailed above to model excitation by elliptically polarized light, if this is required. The user can enter any polarization state into the model, however they must also include the normalisation factor to ensure the correct Rabi frequency is calculated. As an example, if the minor axis of the ellipse has $b = 0$, the ellipse represents linearly polarized light and so the half-Rabi frequency in this frame is represented by an equal weighting of the circular basis states. In this case $a_{-1} = a_{+1} = 1$ and so the normalisation factor to be input is $1/\sqrt{2}$.

D. Visualising the shape of the charge cloud

In LASED, the three dimensional angular shape of the charge cloud of an atomic state $|Jm\rangle$ can be visualised as given in [16, 32], using the expression

$$W(\theta, \phi, t) = \sum_{mm'} \rho_{mm'}(t) Y_{jm}(\theta, \phi) Y^*_{jm'}(\theta, \phi) \quad (48)$$

where $Y_{jm}$ are the spherical harmonics, $J$ is the total angular momentum and $m$ is the projection of $J$ onto the selected quantization axis. $\rho_{mm'}(t)$ is the time dependent density matrix element for the atomic state that is being visualised. In LASED, the user can generate the angular shape of the states $W(\theta, \phi, t)$ in the laser-atom system as the system evolves over time. Images of the charge cloud can then be created using any plotting package. These images can then be displayed sequentially as a function of time, using software that creates a video from the image sequence. The generated videos can be instructive to demonstrate how the states evolve under different experimental conditions. Examples of the generated charge clouds at different times for both the lower and upper states are shown in Fig. 6 in section IV.

IV. EXAMPLES FROM LASED MODELLING

In this section the features of LASED are presented using examples from different laser-atom systems. For each simulation, the time evolution of the populations of various atomic substates is presented. The sum of the populations of all substates is initially set to unity and so the populations directly represent the probability of a particular atom in the ensemble being in that substate at any given time. Additional examples and a guide showing how to install and use LASED can be found at [13].

A. Calcium S to P Excitation

The simplest system to simulate is from an S state to a P state and so as an example, laser excitation from the 4$^1$S$_0$ to the 4$^1$P$_1$ state in calcium is considered. A level diagram is shown in Fig. 4(a) for this transition. The
FIG. 4. (a) A level diagram for the $^4S_0$ to $^4P_1$ excitation of calcium using linearly polarized light, with the QA co-linear with the E-field of the laser beam so that $\Delta m_J = 0$. (b) The simulated time evolution of the population of substate $|3\rangle$, showing the effect of various simulation parameters, including a Doppler profile for the atomic beam and a Gaussian laser profile (see section IV A for details). (c) and (d) show the excited state populations using elliptically polarised light for different weightings $a_{-1}$ and $a_{+1}$. In this case the atom is described with the QA along the laser beam direction and so $|3\rangle$ remains unpopulated. All simulations used a laser intensity of 100 mW/mm².

lifetime and transition wavelength are taken from [33] and [34] respectively. In Fig. 4(b) the time evolution of the upper state population $\rho_{33}$ is presented under different conditions. These include a fixed laser detuning of $\delta = 300$ MHz, a Doppler atomic beam profile with $\Delta_{Dopp} = 300$ MHz, a Gaussian laser beam profile with $P_{las} = 100$ mW and $r_\sigma = 0.75$ mm, and when both Doppler and Gaussian averaging processes are included together. The simulation time was from 0 to 50 ns using 501 time steps. These simulations are in agreement with the calculations presented in [35].

Results for the same system with elliptically polarized light are shown in Fig. 4(c) and (d). In panel (c) the weightings are set to $a_{-1}/a_{+1} = 3.0$ whereas in panel (d) $a_{-1}/a_{+1} = 0.8$. As expected, the population of the $m_J = -1$ state is much larger in panel (c) due to the favoured $|\sigma^-\rangle$ weighting. By contrast in panel d) where the weighting for the $|\sigma^+\rangle$ basis state is higher, the $m_J = +1$ substate population dominates. The population of substate $m_J = 0$ is identically zero for the entire simulation as the laser cannot couple to state $|3\rangle$ in this frame with $\sigma^+$ and $\sigma^-$ polarization.

An example of using rotations in LASED can be seen in Fig. 5. To check that LASED is valid in all reference frames the calcium system described in Fig. 4(a) is once again considered. This system is now excited using linear-polarised light with the QA along the E-field of the laser, for a laser intensity of 100 mW/mm² and a detuning of 100MHz. The results from this simulation are shown in panel 5(a). Under these conditions four differential equations are required to describe the populations of states $|1\rangle$ and $|3\rangle$ as well as the optical coherences generated between them. An equally valid representation is to choose the QA along the direction of the laser beam. In this frame states $|2\rangle$ and $|4\rangle$ are excited using simultaneous $\sigma^-$ and $\sigma^+$ radiation. State $|3\rangle$ in this frame remains unpopulated. In this representation nine equations must be generated and solved. Three equations represent the populations of states $|1\rangle$, $|2\rangle$ and $|4\rangle$, four equations represent the optical coherences between them and two equations represent the atomic coherences generated between states $|2\rangle$ and $|4\rangle$.

The results from this calculation are shown in Fig. 5(b) for the populations $\rho_{11}$, $\rho_{22}$ and in Fig. 5(c) for the atomic coherence $\rho_{24}$. Note that $\text{Im}(\rho_{24}) = 0$ here due to the choice of axes in both reference frames. The results from this calculation are then rotated back to the reference frame where the QA is along the E-field of the laser in Fig. 5(d), which reproduces the results in Fig. 5(a) exactly. This shows that LASED produces the same result independent of the reference frame chosen, as long as the initial conditions are rotated before excitation.
B. $3^1D_2$ to $10^1P_1$ excitation in helium following electron impact

A more complex system to model using LASED is presented in this section, where laser excitation is from the $3^1D_2$ state to the $10^1P_1$ state. This transition is of interest as experiments are in preparation in Manchester to study this stepwise excitation process. Excitation to the $3^1D_2$ state is via electron collision and so the system is presented in the Natural frame $Z^{Nat}$, where the QA is set orthogonal to the scattering plane spanned by the ingoing electron momentum $k_0$ and the outgoing electron momentum $k_1$. The laser beam is then injected along the quantization axis and is linearly polarized along the incident beam direction, with an incident intensity of 1,500 mW/mm². The beam is set to be on-resonance with the transition at a vacuum wavelength of 899.75205 nm. In this frame, only the substates $m_J = -2, 0, +2$ are excited due to reflection symmetry in the scattering plane [38]. Since the laser beam is linearly polarised the interaction must be represented by simultaneous $\sigma^+$ and $\sigma^-$ excitation with equal weighting in this frame, as discussed above.

The substate populations and atomic coherences for the $3^1D_2$ state have been calculated for an incident energy of 40 eV and for a scattering angle of 45° by Igor Bray at Curtin University [36] using a Convergent Close Coupling theory. The excited $3^1D_2$ state decays to lower states $|b\rangle$ with a total lifetime of 15.7 ns. The upper $10^1P_1$ state decays to states $|f\rangle$ with a lifetime of 59.6 ns, whereas the lifetime for decay back to the $3^1D_2$-state is 80.7 μs [37]. The effect of including these decay routes is seen in Fig. 6, which shows the populations of both states on a logarithmic scale. The atomic coherences are not shown, however these are also calculated by LASED.

The decay routes to the states $|f\rangle$ and $|b\rangle$ leak both populations and atomic coherences away from the system. The population $\rho_{00}$ for the upper $10^1P_1$ state remains zero throughout the simulation, since the laser does not couple to this state in the Natural frame. The full calculation of the density matrices for the states then allows the charge clouds associated with each state to be modelled as a function of time, as discussed in section III D. Examples of these charge cloud models are shown at different times throughout the evolution of the system in Fig. 6, for both the $3^1D_2$ state and $10^1P_1$ state.

C. Caesium $D_2$-Line

LASED can also simulate the time evolution of systems with hyperfine structure, such as the caesium transition from the $6^2S_{1/2}$ state to the $6^2P_{3/2}$ state, commonly called the $D_2$-line. A level diagram for this system is shown in Fig. 7. In this example, the laser is on resonance between the $F' = 4$ and $F = 5$ states and is set to
have $\sigma^+$ polarization. The lifetime and wavelength of this transition are taken from [39] and [40] respectively. The hyperfine splittings for the upper and lower substates are taken from [41].

The time evolution of a subset of the populations in the caesium manifold described in Fig. 7 is shown in Fig. 8. This simulation was run with all ground states populated equally at $t = 0$ ns and with no atomic coherences in the initial state, as would be produced for atoms emitted from an atomic beam oven. Since the laser is tuned from the $F' = 4$ state, selection rules prohibit excitation from this state to the $F = 2$ state, which hence remains essentially unpopulated as shown in Fig. 8(c). The very small change in the population of these states as seen in panel (c) arises due to pumping from the $F' = 3$ state by the laser radiation red-detuned by 9,193 MHz. Selection rules allow the states $F = 3$ and $F = 4$ to be populated from the $F' = 4$ state, however since they are detuned from resonance by 251 MHz and 452.24 MHz respectively, they are excited with only a small probability as the interaction proceeds.

In panel (a) the population evolution over time of the $F' = 3$ ground state is shown. This is the lowest state in the system and is not coupled directly by the laser beam. Since the $F = 4$ and $F = 3$ states can however decay to this state via spontaneous emission, their population slowly increases with time as shown, until the substates reach a steady state at around 1500 ns. As the interaction progresses, the states to the left of figure 7 decrease in population since spontaneous emission feeds their population to the right, due to pumping with $\sigma^+$ radiation. This feeding to the right and subsequent decrease in population is seen in the substates of the $F = 3$ and $F = 4$ upper states in panels (d) and (e). Each of these states is effectively emptied within around 1500 ns.
FIG. 8. The time evolution of the populations of substates in the ground states (a) $F' = 3$, (b) $F' = 4$, the upper states (c) $F = 2$, (d) $F = 3$, (e) $F = 4$, and (f) $F = 5$ for the system described in Fig. 7. The laser is $\sigma^+$-polarised with an intensity of 50 mW/mm$^2$.

ns. By contrast, the populations of the $F = 5$, $m_F = +5$ and $F' = 4$, $m_{F'} = 4$ states shown in panels (b) and (f) are seen to rise steadily after the Rabi oscillations have decayed, which occurs at around 150 ns. The state populations rise quickly until they reach a steady state, after which their populations remain unchanged. This is a direct consequence of the system evolving towards the closed 2-level system between states $|16\rangle$ and $|48\rangle$. After this time the interaction can then be approximated to a 2-level system between these states, with spontaneous and stimulated emission from $|48\rangle$ always feeding back into state $|16\rangle$. This simplified system is often used to simulate laser interactions in atom cooling and trapping experiments in a Magneto Optical Trap (MOT).

LASED can easily simulate these large and complex systems and can generate all the equations of motion that are required. As noted above the computation time increases considerably as the number of states increases. As an example, simulation of the the calcium system in figure 4 required less than 1 second of computing time. The model for the D to P state transition in figure 6 took a few seconds to generate the data. By contrast, the caesium system required around 9,000 seconds of computing time to generate the results shown in Fig. 8.

V. CONCLUSION

LASED is an open source package available to researchers, that is written in the python programming language. The general equations of motion used in LASED have been described in this paper. LASED allows the
user to model different aspects of the interaction, including the Doppler profile of an atomic beam, the Gaussian profile of a TEM00 laser beam, an arbitrary polarization of the beam, any rotation between different frames of reference, and the angular shape of the atomic electron cloud. Examples of these techniques have been described here, using different atomic systems.

The purpose of LASED is to be a general, easy-to-use laser-atom system simulator which can be used for any atomic system excited by laser light. Later versions of the LASED library aim to extend its usefulness by including modelling of the interaction in magnetic fields, as well as including excitation by multiple laser beams. Computation times can be reduced by carefully considering the symmetry of the system and by eliminating equations that represent density matrix elements that remain zero throughout the simulation. To further extend the usefulness of LASED the authors have made this package freely accessible, so that other researchers can contribute to its development and further extend its functionality. The source code is hence available and can be edited at [42].

VI. ACKNOWLEDGEMENTS

We wish to thank the Engineering and Physical Sciences Research Council (EPSRC) for funding through grants R120272, R125924 and R126554. Manish Patel would like to thank the University of Manchester for providing a PhD scholarship to carry out this work.

Appendix A: Computing time

LASED aims to model an arbitrary atom-laser system as defined by the user. By designing LASED to be as general as possible, the computing time increases rapidly with the number of substates in the system. At the same time, LASED aims to be efficient and usable with low-powered machines on any operating system. The python language was hence chosen for its development as this is open source and can be run on a wide range of different platforms.

| n (Number of Energy Levels) | Execution Time (s) |
|-----------------------------|---------------------|
| 4                           | 0.833               |
| 6                           | 0.855               |
| 8                           | 2.50                |
| 24                          | 283                 |
| 36                          | 2270                |
| 48                          | 8570                |

TABLE I. A table to show execution times using LASED to simulate the time evolution of laser-atom systems with varying number of energy levels. 501 time steps were simulated from 0 to 500 ns with a laser intensity of 100 mW/mm², π-polarised light, and no Gaussian or Doppler averaging. For \( n \geq 24 \) the simulated systems have hyperfine structure.

To illustrate the computation time on a standard PC, table I shows the execution time for atomic systems that have different energy levels and substates. These computation times were obtained using an Intel i5-3320M CPU operating at 2.60 GHz using a Linux operating system with 8 GB of RAM.

Appendix B: Calculation of the generalized decay constant

The generalized decay constants need to be calculated directly when there are vertical coherences in a laser-atom system i.e. when there is hyperfine splitting, as shown in equation 34. For hyperfine splitting, the splitting between excited energy levels is small so \( \omega_{c'i'} \approx \omega_{c'g} \). Using equation 25 this approximation hence leads to

\[
\Gamma_{ege'g} = 2 \sum_q g^q_{e'g} g^q_{eg} \pi \delta(\omega_q - \Delta_{eg}) \quad (B1)
\]

and from equation 26 the magnitude of the generalized decay constant can be calculated by

\[
|\Gamma_{ege'g}| = \sqrt{\Gamma_{eg} \Gamma_{e'g}}. \quad (B2)
\]

The sign of the generalized decay constant is calculated by considering the coupling coefficients. The coupling coefficients are generally complex

\[
g^q_{e'g} = |g^q_{e'g}| e^{i\alpha} \quad (B3)
\]

\[
g^q_{eg} = |g^q_{eg}| e^{i\zeta} \quad (B4)
\]

and the half-Rabi frequency can be written in terms of phase and amplitude terms, so that

\[
\Omega^q_{e'g} = g^q_{e'g} \langle a_L(0) \rangle = |g^q_{e'g}| e^{i\alpha} \langle a_L(0) \rangle e^{i\beta} = |g^q_{e'g}| \langle a_L(0) \rangle e^{i(\alpha + \beta)} \quad (B5)
\]

and similarly

\[
\Omega^q_{eg} = |g^q_{eg}| \langle a_L(0) \rangle e^{i(\zeta + \beta)}. \quad (B6)
\]

Since the half-Rabi frequencies are defined here as being real, it follows that

\[
\alpha + \beta = n\pi \quad (B7)
\]

\[
\zeta + \beta = m\pi \quad (B8)
\]

where \( n \) and \( m \) are integers. If equation B7 is subtracted from B8 it is found that

\[
e^{i(n-m)\pi} = \begin{cases} +1, & \text{if } n - m \text{ even} \\ -1, & \text{if } n - m \text{ odd} \end{cases} \quad (B9)
\]

Hence if \( \Omega^q_{e'g} \) and \( \Omega^q_{eg} \) have the same sign then \((n-m)\) is even and if they have the opposite sign then \((n-m)\) is odd. This can be related to the calculated coupling coefficients using equation 23 so that

\[
\Gamma_{ege'g} = \begin{cases} +|\Gamma_{ege'g}|, & \text{if } C_{eg} C_{e'g} > 0 \\ -|\Gamma_{ege'g}|, & \text{if } C_{eg} C_{e'g} < 0 \end{cases} \quad (B10)
\]
