Cavity-controlled ultracold chemistry

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Ultracold ground-state molecules can be formed from ultracold atoms via photoassociation followed by a spontaneous emission process. Typically, the molecular products are distributed over a range of final states. Here, we propose to use an optical cavity with high cooperativity to selectively enhance the population of a pre-determined final state by controlling the spontaneous emission. During this process, a photon will be emitted into the cavity mode. Detection of this photon heralds a single reaction. We discuss the efficiency and the dynamics of cavity-assisted molecule formation in the frame of realistic parameters that can be achieved in current ultracold-atom setups. In particular, we consider the production of Rb$_2$ molecules in the $a^3\Sigma_u$ triplet ground state. Moreover, when working with more than two atoms in the cavity, collective enhancement effects in chemistry should be observable.

INTRODUCTION

In recent years, the control and manipulation of ultracold atomic samples has enabled studies of chemical reactions in the ultracold regime. Here, the internal and external quantum states of the collision partners can be very well controlled, allowing for precise studies of reactions and observations of possible quantum interference effects. Furthermore, it might be possible to gain absolute control over chemical reactions (reviews: [1, 2]). In ultracold chemistry, one important reaction type is photoassociation where laser light can fuse together colliding atoms into a well-defined excited molecular bound state [3, 4]. Typically, the excited molecule can decay spontaneously into a number of ro-vibrational levels in the electronic ground state.

Here, we propose a way to control the chemical reaction. For this, we combine concepts of cavity quantum electrodynamics (CQED) in an high-finesse optical cavity with ultracold molecule formation. We make use of the fact that strong confinement of the electromagnetic field modes around a molecule can control its spontaneous emission and thus its final quantum state. Our scheme is related to previous proposals for a molecular matter-wave amplifier in an optical cavity [5] or for coupling atoms to broadband photonic crystal waveguides [6].

Strong-light matter coupling with molecules is a recent hot topic, even outside the field of ultracold temperatures. Applications range from quantum information processing to the modification of chemical reaction landscapes. In these contexts, coherent coupling of single dye molecules [7] and ensembles of polymers [8] to a cavity have recently been observed.

So far, high-finesse optical microcavities have been very successfully used for single cold atoms (for a review, see e.g., [9]). The strong confinement of the electromagnetic field in such cavities enables fast coherent transfer of atomic excitation into the cavity mode before the atom can decay by spontaneous emission. Instead, the cavity photon is emitted into a single external mode with high probability while the atom is prepared in a desired ground state. Important applications include deterministic single-photon sources [10].

Introducing micro-cavities technologies to the realm of ultracold chemistry will enable us to control and instantly detect single reactions with a high efficiency. Furthermore, it will allow for a detailed study of the dynamics and statistics of reactions, in particular where collective effects come into play.

The implementation of cavity quantum electrodynamics concepts with molecules is even more challenging than for atoms: Due to the lack of closed electronic transitions in molecules and due to Franck-Condon factors which are in general small, smaller cavity mode volumes than for atoms are required to reach the regime of high cooperativity. Nevertheless, recent advances in cavity design and fabrication (e.g., fiber-based microcavities [11]) have enabled much smaller mode volumes, higher coupling strengths and better integrability compared to traditional cavities formed by bulky mirrors. Therefore, CQED technologies can now be applied to ultracold chemistry.

After presenting the basic scheme for cavity-chemistry, we estimate realistic parameters for an experimental setup with ultracold rubidium atoms. Afterwards, we simulate the reaction dynamics and efficiency for a square-shaped photoassociation pulse. Finally, we discuss collective effects when several molecules are produced.

SINGLE-MOLECULE SCHEME

We start out by presenting a somewhat simplified version of the cavity-controlled photoassociation scheme. We consider an unbound atom pair $|i\rangle$ which is trapped by an optical dipole trap in between the cavity mirrors. A bound state $|e\rangle$ of the electronically excited molecular potential (asymptotically, e.g., $S+P$) is excited from $|i\rangle$ by a photoassociation (PA) laser with Rabi frequency
The laser illuminates the atoms from the open side of the cavity, see Fig. 1(a). The cavity couples two unbound ground state atoms, denoted as $|i\rangle$, to a bound excited molecular state $|e\rangle$ with Rabi frequency $\Omega$, see also (b). The cavity couples this state at rate $2g$ to a molecular ground state $|g\rangle$, see also (c). Alternatively, the molecule can decay to other states at rate $\Gamma$. (c) After an electronically excited molecule $|e\rangle$ has been formed, the excitation oscillates ($2g$) between the molecule and the cavity mode. (d) Either the excited molecule decays ($\Gamma$), or the cavity photon ($2\kappa$). In the latter case, the molecule is left in a predetermined ground state level $|g\rangle$ and the photon can be detected with high efficiency outside the cavity.

When driving the $|i\rangle \leftrightarrow |e\rangle$ transition for a single atom pair with the PA laser, at most one electronic or photonic excitation can be brought into the system at a time. We can then model the system effectively by five quantum states denoted by $|m,n\rangle$, where $m$ denotes the atomic/molecular quantum state and $n$ the cavity photon number, see Fig. 1 Further more, we assume tight confinement in the Lamb-Dicke regime ($\hbar\omega_{\text{trap}} \gg E_{\text{recoil}}$), and therefore, we need not consider the external motion of the particles.

The couplings, detunings and decay rates of the five states are shown in Fig. 2. The PA laser field (frequency $\omega_{\text{L}}$) couples the asymptotic two-atom state $|i,0\rangle$ and the excited molecular state $|e,0\rangle$ with Rabi frequency $\Omega$ and detuning $\Delta_1 = \omega_{\text{ge}} - \omega_{\text{L}} - \omega_{ji}$. The $|e,0\rangle$-state is coupled coherently at rate $2g$ to the state $|g,1\rangle$, which can decay to $|g,0\rangle$ at rate $2\kappa$. The two-photon detuning $\Delta_2 = \omega_{\text{ce}} - \omega_{\text{L}} - \omega_{ji}$ is the frequency mismatch between emitted photon and cavity frequency. The $|e,0\rangle$-state can also decay spontaneously at rates $\Gamma_i$ and $\Gamma_h$ to the states $|g,0\rangle$ and $|h,0\rangle$, respectively ($\Gamma = \Gamma_i + \Gamma_h$). Here, $|g,0\rangle$ represents the desired final state, while $|h,0\rangle$ represents all other possible states.

The Hamiltonian of the coherently-coupled sub-system $|i,0\rangle, |e,0\rangle, |g,1\rangle$ in a frame rotating with the laser frequency reads in the rotating-wave approximation

$$\hat{H} = \hbar \Delta_1 |e,0\rangle \langle e,0| + \hbar \Delta_2 |g,1\rangle \langle g,1| + \hbar \omega_{\text{L}} |e,0\rangle \langle i,0| + \hbar \omega_{\text{ge}} |e,0\rangle \langle e,0| + \hbar c.$$

To take into account the molecular and cavity decay processes, we solve the corresponding master equation in Lindblad form (see Appendix). The system is initialized in $|i,0\rangle$ at $t = 0$. The goal is to transfer the popula-
tion from this state as fast, efficiently and coherently as possible to the state $|g,0\rangle$ of the ground state molecule. We therefore define the efficiency $\eta$ of the scheme by the probability to produce a ground-state molecule $|g,0\rangle$ via cavity decay,

$$\eta = 2\kappa \int_{t=0}^{\infty} \rho_{g|g_1}(t) dt,$$

where $\rho_{g|g_1}(t)$ is the population of the $|g,1\rangle$ state.

We can derive an analytical expression for $\eta$ in the weak-driving limit, $(\Omega \ll \Gamma, g^2/\kappa)$, as we will later see, exhibits optimal achievable efficiency for time-independent control parameters. In the weak-driving limit, the coherent couplings of the laser $\Omega$ and the cavity $g$ slowly keep populating the spontaneously decaying states $|e,0\rangle$ and $|g,1\rangle$. As a result, a quasi-steady superposition state $|D\rangle$ forms, which slowly decays in an exponential manner. As derived in the appendix, $|D\rangle \approx |i,0\rangle + \frac{\Omega}{2g^2 + \Gamma (\kappa - i\Delta_2)}[(i\kappa + \Delta_2)|e,0\rangle - g|g,1\rangle],$

where $\rho_{ij}$ are components of the density matrix $\rho_{wd} = |D\rangle \langle D|$. The efficiency $\eta_{wd}$ is maximal on two-photon resonance, $\Delta_2 = 0$. The decay rate takes place through the small populations in $|e,0\rangle$ and $|g,1\rangle$ which decay via $\Gamma$ and $\kappa$, respectively. This yields the transfer efficiency,

$$\eta_{wd} = \frac{2\kappa \rho_{g|g_1}}{2\kappa \rho_{g|g_1} + \Gamma_{d|e} \rho_{e|0}} = \frac{2C}{2C + 1 + (\Delta_2/\kappa)^2},$$

where $\rho_{jj}$ are components of the density matrix $\rho_{wd} = |D\rangle \langle D|$. The efficiency $\eta_{wd}$ is maximal on two-photon resonance, $\Delta_2 = 0$, which we consider from now on. One can also interpret $\eta_{wd}$ as the ratio of cavity-induced decay rate $\Gamma_{\kappa} = 2g^2/\kappa$ of $|e,0\rangle$ (via green arrows in Fig. 2) and the total decay rate $\Gamma_{\kappa} + \Gamma$ of $|e,0\rangle$ (for $\Delta_2 = 0$). To obtain significant cavity-stimulated photoassociation, i.e., a large fraction in the $|g,0\rangle$ state, we therefore aim at $C \gg 1$. For example, a moderate cooperativity $C \gtrsim 5$ will already result in an efficiency of $\eta_{wd} > 0.9$ for producing the chosen molecular quantum state.

As already mentioned the weak-driving limit gives optimal results in terms of transfer efficiency. This can be made plausible as follows. For vanishing $\Delta_2$ and $\kappa$, the states $|i,0\rangle, |e,0\rangle, |g,1\rangle$ form a $\Lambda$-system which exhibits a dark state $|D\rangle \propto 2g|i,0\rangle + \Omega|g,1\rangle$. This state is long-lived with no spontaneous decay via $\Gamma$, because $|e,0\rangle$ is not populated. If we now allow for a small but finite $\kappa \ll g^2/\Gamma$ to populate the desired final state $|g,0\rangle$, the dark state $|D\rangle$ will become a little bit lossy due to population of $|e,0\rangle$ ($\propto \kappa^2$, see eq. (1)) and subsequent decay via $\Gamma$. These unwanted losses, however, are much smaller than the wanted decay flux from $|g,1\rangle \rightarrow |g,0\rangle$ which is proportional to $\kappa$. In addition, in the weak driving limit, $\Omega \rightarrow 0$, the dark state $|D\rangle$ mainly consists of state $|i,0\rangle$.

Since this is precisely the initially prepared state the weak driving limit is optimal for efficient transfer from $|i,0\rangle$ to the molecular state $|g,0\rangle$.

### Realistic experimental parameters

Compared to a single atom, a molecule often exhibits a reduced dipole matrix element of the electronic transition and thus a reduced coupling strength $g$ and cooperativity $C$. The reduction is to first approximation determined by the Franck-Condon factor $f_{FC} = \Gamma_2/\Gamma$ for the specific ro-vibrational transition in a molecule,

$$g = g_{\text{max}} \sqrt{f_{FC}} \quad \text{and} \quad C = C_{\text{max}} f_{FC},$$

where the coupling strength and cooperativity for a closed two-level system ($f_{FC} = 1$) are given by

$$g_{\text{max}} = d_{el} \sqrt{\frac{\omega_{ge}}{2\hbar \epsilon_0 V}} \quad \text{and} \quad C_{\text{max}} = \frac{g_{\text{max}}^2}{\kappa \Gamma},$$

respectively. Here, $V$ is the volume of the cavity mode and $d_{el}$ the dipole moment of the electronic molecular $|g\rangle \leftrightarrow |e\rangle$ transition with frequency $\omega_{ge}$ (for a CQED review, we refer the reader to e.g., [12]). In a diatomic molecule, $d_{el}$ depends in general on the internuclear distance $R$, and the decay rate $\Gamma$ is about 2 times larger as compared to an atomic excited state (due to a Dicke superradiance effect [14]). In a rubidium dimer (Rb$_2$), there are strong transitions between ro-vibrational states $\nu^\prime$ of the shallow well of the $(1)^3\Pi_u$ potential (which asymptotically correlates to the atomic states $5S_{1/2}$ + $5P_{1/2}$) and the states $\nu^\prime\nu$ of the $a^3\Sigma_u$ potential ($5S_{1/2}$ + $5S_{1/2}$). In particular, the transition $\nu^\prime = 8 \rightarrow \nu^\prime\nu = 0$ at a wavelength of 744 nm has the largest $f_{FC,\text{max}} = 0.37$, see [15]. Apart from the transition dipole moment and Franck-Condon factor, the coupling strength $g$ depends also on the mode volume as $g \propto 1/\sqrt{V}$, thus $V$ should be minimized. For the fundamental TEM$_{10}$ mode of a Fabry-Perot resonator, $V = \pi w_0^2 L/4$, where $L$ is the cavity length and $w_0$ the mode waist. Similar as in [16], we consider the dipole trap beams to enter from the side without being clipped by the mirror substrates, which puts a lower limit on $L$. The mode waist $w_0$ is typically limited by the numerical aperture of the in-/outcoupling optics. According to Eq. [3] in order to maximise $C$, $\kappa$ should be minimized. However, as we will discuss in the next section a small $\kappa$ might lead to unacceptably long transfer times. Furthermore, the transmission through the mirror coatings should dominate over unavoidable absorption and scattering losses in the coatings. In table [1] we give an example for realistic CQED parameters for the above mentioned molecular transition in Rb$_2$. For those parameters, an efficiency of $\eta_{wd} > 0.9$ could be achieved for vibrational transitions with $f_{FC} \gtrsim 0.05$.

### System dynamics

Ideally, the transfer from the atom pair $|i,0\rangle$ to the molecular state $|g,0\rangle$ should be efficient and fast. In the
TABLE I. Example of a set of realistic CQED parameters. The parameters $g_{\text{max}}$, $\Gamma$, $C_{\text{max}}$ are derived for the transitions between vibrational states of the (1)$^3\Pi_g$ and $a^3\Sigma_u$ potentials in Rb. Here, $d_1 \approx 3 \times 10^{-29}$ C·m, see \cite{6, 17}.

| Parameter | Symbol | Value |
|-----------|--------|-------|
| Cavity length | $L$ | $280 \mu$m |
| Cavity mode waist | $w_0$ | $4.8 \mu$m |
| Cavity finesse | $\mathcal{F}$ | $5 \times 10^4$ |
| Coupling strength for $f_{\text{FC}} = 1$ | $g_{\text{max}}$ | $2\pi \times 80$ MHz |
| Cavity field decay rate | $\kappa$ | $2\pi \times 5.4$ MHz |
| Excited state decay rate | $\Gamma$ | $2\pi \times 12$ MHz |
| Cooperativity for $f_{\text{FC}} = 1$ | $C_{\text{max}}$ | 100 |
| Max. Franck-Condon factor | $f_{\text{FC, max}}$ | 0.37 |

The parameters $g_{\text{max}}, \Gamma, C_{\text{max}}$ are derived for the transitions between vibrational states of the $(1)^3\Pi_g$ and $a^3\Sigma_u$ potentials in Rb. Here, $d_1 \approx 3 \times 10^{-29}$ C·m, see \cite{6, 17}.

weak driving limit the transfer efficiency is nearly optimal but can be very slow as the transfer time is $\propto \kappa^{-1}$. In fact, it can be shown that the transfer rate, which is the exponential decay rate of $|D\rangle$, is given by

$$R_{\text{wed}} = \frac{\Omega^2}{\Gamma(2C + 1)} \approx \frac{\kappa^2}{2g^2},$$

if $\Delta_1 = 0$. Clearly, too slow a transfer can be problematic for many reasons, e.g. when the transfer time is on the order of the particle lifetime in the trap.

We therefore now consider the limit of strong driving where a very short $\pi$-pulse quasi instantaneously transfers the population from $|i, 0\rangle$ to $|e, 0\rangle$ at $t = 0$. From there, it partially decays into $|g, 0\rangle$ via the cavity mode but it also partially decays via $\Gamma$ into $|h, 0\rangle$. The efficiency $\eta_\pi$ of the short-pulse scheme is then reduced as compared to $\eta_{\text{wed}}$ of the weak-driving limit,

$$\eta_\pi = \frac{2\kappa}{2\kappa + \Gamma} \eta_{\text{wed}},$$

where we set $\omega_c = \omega_{ge}$. Besides the decay, the dynamics exhibit a damped oscillation of the population between $|e, 0\rangle$ and $|g, 1\rangle$. The oscillation can be understood as a beat of the two eigenstates

$$|B_\pm\rangle \approx \frac{1}{\sqrt{2}}(|e, 0\rangle \pm |g, 1\rangle)$$

of the coupled system, which are populated at $t = 0$ by the $\pi$-pulse as an equal superposition state. In order for $\eta_\pi$ to reach the weak-driving efficiency $\eta_{\text{wed}}$, we need $\kappa \gg \Gamma$, according to eq. (5). However, for a large $\eta_{\text{wed}}$ we need $\kappa \ll g^2/\Gamma$. Both conditions can be simultaneously met only when $g \gg \Gamma$ \cite{18}. According to our parameters in table I and even when using a relatively large Franck-Condon factor of $f_{\text{FC}} > 0.3$, this condition is not easily reached. Assuming a more typical $f_{\text{FC}} = 0.1$, we obtain $\eta_\pi \approx 0.77$ compared to $\eta_{\text{wed}} \approx 0.95$. Therefore, in general, the infinitely short excitation pulse does not seem to be ideal for the transfer.

Therefore, the question arises, how quickly the optical pumping can be done without substantial loss of efficiency compared to the weak-driving limit? To answer this question, we investigate how the transfer efficiency to the ground state $|g, 0\rangle$ can be optimized when employing a resonant square pulse of duration $t_p$ and Rabi frequency $\Omega$ \cite{19}.

For this, we solve the time-dependent master equation of the five-level system numerically. In Fig. 3 some examples of the time-dependent populations are plotted. For $\Omega = \kappa/2$, we almost reach the weak-driving efficiencies $\eta_{\text{wed}} = \frac{2\kappa}{\Gamma} (\text{for } C = 10 \text{ (C = 1), respectively. Using } \Gamma = 2\pi \times 12 \text{ MHz, one reaches 95% of the respective asymptotic value within } t \approx 3 \mu s (t \approx 0.5 \mu s). \text{ For a higher Rabi frequency (here, } \Omega = 3\kappa), \text{ the transfer works faster but the efficiency is already significantly reduced.}$

In order to carry out an optimization, we determine the highest Rabi frequency $\Omega$ and shortest pulse duration $t_p$ for which the inefficiency $1 - \eta$ does not increase by more than a factor $1 + \varepsilon$ compared to the weak-driving limit. In Fig. 4 the inefficiency, pulse duration and the Rabi frequency are plotted for $\varepsilon = 0.1$, assuming $g_{\text{max}} = 2\pi \times 80$ MHz (see table I). We compare four different values of $f_{\text{FC}}$ and corresponding $g = g_{\text{max}}\sqrt{f_{\text{FC}}}$. For larger $\kappa$ and smaller $f_{\text{FC}}$, shorter pulses with higher Rabi frequencies can be used, while the inefficiency increases (because $C$ decreases). For $\kappa/2\pi \lesssim 10$ MHz, the Rabi frequency and the pulse duration roughly scale as $\Omega \approx \kappa$ and $t_p \propto f_{\text{FC}}/\kappa^2$. For larger values of $\kappa$, $\Omega$ diverges and $t_p$ vanishes (the condition for $t_p \rightarrow 0$ is derived in the appendix). For example, if an efficiency of $\eta = 0.97$
COLLECTIVE EFFECTS

So far, we have only considered the coupling of a single molecule to the cavity mode. However, in a typical experiment, there can be up to $N \approx 10^3$ atom pairs or molecules that couple simultaneously to the cavity mode (see Appendix). Coherence can build up among the molecules which modifies their spontaneous emission, thus they should not be treated as independent, giving rise to effects like Dicke-superradiance [14].

is desired on a transition with $f_{FC} = 0.1$, we require $\kappa = 2\pi \times 3\text{ MHz}$, see Fig. 4(a). For this, we obtain $t_p = 4 \times 10^{-5}\text{ s}$ and $\Omega = 2\pi \times 3\text{ MHz}$, see Fig. 4(b).

CONCLUSIONS AND OUTLOOK

In summary, we have shown that ultracold molecule formation in a well-defined quantum state can be strongly enhanced by an optical cavity. We have estimated that preparation of a molecule in certain quantum states can be efficient ($>90\%$) for transitions with moderate Franck-Condon factors ($f_{FC} \gtrsim 0.05$) in medium high finesse cavities ($F \approx 5 \times 10^4$). In contrast to existing coherent two-photon schemes for photoassociation of ultracold molecules, our scheme can be regarded as a method to pump (cool) molecules into a desired (ground) state since...
the necessary dissipation is already built in via the cavity losses. Moreover, the photons dissipated into a single spatial mode can be detected with high efficiency.

The scheme could potentially be extended to cascaded reactions, e.g., \( A \rightarrow B^* \rightarrow C^* \rightarrow D \), where \( B^* \) is, e.g., produced in a collision. Here, one could use the cavity to observe and control the spontaneous transition between \( B^* \rightarrow C^* \).

Finally, the coupling of several atom pairs or molecules to the cavity will give rise to interesting collective effects for reactions, which have not been discussed or demonstrated yet. The collective enhancement of the rate and efficiency of molecule formation would be the basis for “superradiant chemistry”.

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APPENDIX

Master equation

In order to take into account the incoherent decay processes of the excited molecular state and the cavity photon, we use a master equation in Lindblad form,

\[
\frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}] + 2\kappa D[\hat{a}, \hat{\rho}] + \Gamma_2 D[\hat{g}](\hat{e}, \hat{\rho}) + \Gamma_4 D[\hat{g}](\hat{e}, \hat{\rho}) - \frac{1}{2} \hat{b} \hat{b} \hat{\rho} - \frac{1}{2} \hat{\rho} \hat{b} \hat{b},
\]

where \( D[\hat{b}, \hat{\rho}] = \hat{b} \rho \hat{b}^\dagger - \frac{1}{2} \hat{b}^\dagger \hat{b} \hat{\rho} - \frac{1}{2} \hat{\rho} \hat{b} \hat{b}. \)

Here, \( \hat{\rho} \) denotes the density operator and \( \hat{a} \) is the annihilation operator of the cavity field.

Efficiency in the weak-driving limit

In the limit of weak driving \( (\Omega < \Gamma, \gamma^2 / \kappa) \), we can derive an analytical expression for the efficiency \( \eta_{\text{wd}} \), Eq. (2). It is given by the ratio of the decay rates from \( |g, 1 \rangle \) and \( |e, 0 \rangle \) in “quasi steady-state”:

\[
\eta_{\text{wd}} = \frac{2\kappa \rho_{g21}^{ss}}{2\kappa \rho_{g21}^{ss} + \Gamma \rho_{g00}^{ss}} = \left[ 1 + \frac{\Gamma \rho_{g21}^{ss}}{2\kappa \rho_{g00}^{ss}} \right]^{-1}.
\]

Here, \( \rho_{g21}^{ss} \) and \( \rho_{g00}^{ss} \) are components of the steady-state density matrix \( \rho^{ss} \) which we calculate as follows. We formally close the system in Fig. 2 by introducing an artificial “repump” rate \( \zeta \) from the states \( |g, 0 \rangle \) and \( |h, 0 \rangle \) back to state \( |i, 0 \rangle \), which can be, in principle, arbitrarily slow \( (\zeta \rightarrow 0) \). It turns out, however, that the population ratio \( \rho_{g00}^{ss} / \rho_{g21}^{ss} \) is independent of \( \zeta \), turning the system effectively into a three-level system, since the populations of the levels \( |g, 0 \rangle \) and \( |h, 0 \rangle \) are not relevant. The solution for the density matrix \( \rho^{ss} = |D^{ss}\rangle\langle D^{ss}| \) in the weak-driving regime is, to first order in \( \Omega \),

\[
|D^{ss}\rangle \approx |i, 0 \rangle + \Omega \frac{(ik + \Delta_2)|e, 0 \rangle - g|g, 1 \rangle}{2g^2 + (\Gamma - 2i\Delta_1)(\kappa - i\Delta_2)}.
\]

If the system is open, i.e. \( \zeta = 0 \), this state slowly decays exponentially, which can be described by

\[
|D\rangle = \exp \left\{ -\frac{R_{\text{wd}}}{2} t \right\} |D_{ss}\rangle,
\]

where \( R_{\text{wd}} \) is given, for \( \Delta_1 = \Delta_2 = 0 \), by eqn. (4).

Condition for \( \pi \)-pulses

For a chosen \( \varepsilon \), infinitely short \( \pi \)-pulses (as discussed before) are efficient enough if

\[
(1 - \eta_{\pi}) \leq (1 + \varepsilon)(1 - \eta_{\text{wd}}).
\]

Using eqns. (2) and (5), this is equivalent to the following condition

\[
\frac{\kappa}{\Gamma} \geq \sqrt{\frac{g^2}{\varepsilon \Gamma^2} + \frac{1}{16} - \frac{1}{4}},
\]

which can be approximated by \( \kappa \gtrsim g / \sqrt{\varepsilon} \) for \( g \gg \Gamma \sqrt{\varepsilon} \).

Number of atom pairs

The estimated number of pairs \( N \approx 10^3 \) in the optical cavity for typical experimental conditions corresponds to a thermal cloud of approx. \( 10^6 \) atoms with diameter \( 2\sigma \approx 40 \mu m \) in a three-dimensional cubic optical lattice with laser wavelength \( \lambda_{\text{latt}} \approx 1 \mu m \), which overlaps with the fundamental cavity mode with waist \( w_0 \approx 5 \mu m \).

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It turns out, that for a given $g$ the optimal $\eta_\pi$ is reached for $\kappa = g \gg \Gamma$.

We note that there are more efficient schemes than using resonant square laser pulses to transfer electronic excitation into the cavity. Some of them are based on vacuum stimulated rapid adiabatic passages [20, 21] and use specially designed laser pulses $\Omega(t)$ to transfer the system adiabatically from $|i,0\rangle$ to $|g,0\rangle$ without populating the excited state $|e,0\rangle$, i.e. by keeping it in a dark state. Those schemes are, however, beyond the scope of the present work.

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