PHYSICAL REVIEW A VOLUME 60, NUMBER 4 OCTOBER 1999

# Quasicontinuum modeling of photoassociation

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(Received 22 December 1998)

We analyze photoassociation theoretically by treating the dissociation continuum of a molecule as a quasicontinuum (QC) of discrete states. In this manner, free-bound transitions are reduced to a few-level problem. The correct continuum limit is deduced from an explicit analysis of the density of QC states. Besides giving the usual photoassociation rate, the QC model facilitates the analysis of the steady-state molecular yield. Moreover, complications such as velocity redistribution and line broadening due to atom-atom collisions may be treated basically in the same way as in connection with the customary two-level atom. Next we adapt the standard three-level quantum optics to describe free-bound-bound photoassociation for both continuous-wave and pulsed two-color excitation. For a quantum degenerate gas of atoms, a proper two-photon resonant scheme may transform atoms to ground state molecules with near-unit efficiency even in the presence of spontaneous losses from the intermediate state. [S1050-2947(99)08310-9]

PACS number(s): 34.50.Rk, 03.75.Fi

## I. INTRODUCTION

Theoretical descriptions of photoassociation first emerged as an early application of quantum mechanics, and are also among the first direct numerical computations in quantum mechanics. Coolidge *et al*. investigated the continuum of ultraviolet radiation emitted in the photodissociative transitions of the $H_2$ and $D_2$ molecules [1]. Also in the early days of quantum mechanics, Bose and Einstein predicted [2] that a gas of integer-spin particles cooled to a sufficiently low temperature would undergo a phase transition whereby its constituents would condense into the lowest available state of the center-of-mass motion. The evolution of lasers and the associated cooling and trapping techniques led first to the use of photoassociation as a high-precision tool in molecular spectroscopy [3], followed shortly thereafter by the observation of Bose-Einstein condensation (BEC) [4]. The primary connection between these two fields has been the utility of photoassociation for measuring atomic scattering lengths [5]. However, this connection is strengthened as of late by the suggestions that photoassociation might serve as a mechanism for producing a BEC of molecules from an atomic condensate [6,7].

The bulk of the theoretical work on photoassociation is founded on collision theory [8–10], and continues the numerical tradition of Refs. [1]. However, novel approaches have surfaced over the last few years. Photoassociation rates can be found by analyzing the equations of motion for the density matrix in the perturbative regime [11], or by solving the time-dependent Schrödinger equation [12].

We have taken yet another tack [7] by constraining the relative motion of the colliding atoms to a large but finite volume, so as to convert the continuum of dissociated molecular states into a quasicontinuum (QC). The correct physical results corresponding to the free-atom states are recovered no later than the end of a given calculation by taking the limit that the QC spacing tends to zero [13]. There are several advantages to such an approach beyond its nonperturbative nature. First and foremost, the QC model leads naturally to a few-level description, allowing one to bring the theoretical machinery of quantum optics and laser spectroscopy to bear on problems of photoassociation. Second, the average over the thermal energy distribution of the colliding atoms is performed trivially, and the density parameter for photoassociation is then unveiled to be essentially the same phase space density that governs BEC [7]. Third, a hierarchy is revealed for three-level free-bound-bound schemes, such that the Rabi frequency for the photoassociation color is negligibly small compared to that for the color driving the discrete molecular transition. Aside from facilitating analytical solutions, such a hierarchy renders coherent processes such as STIRAP [12] unimportant [7] in a nondegenerate gas.

The purpose of the present paper is twofold. We supplement our initial Rapid Communication [7] with details on the QC approach to photoassociation for one laser color, and add an analysis of two-color photoassociation. In the latter case we pay particular attention to potential ways of avoiding spontaneous-emission losses from an electronically excited intermediate molecular state. We suggest that resonant two-photon processes, as opposed to the two-step processes advocated earlier [6,14], might be the optimal way to reduce spontaneous-emission losses in a dense sample such as a condensate. Also, unlike in treatments based on collision theory, we may easily discuss pulsed excitation schemes. One of the practical advantages is that with pulses one may achieve higher intensities for the photoassociating laser than in the typical continuous-wave case. In an atomic sample that is not dense enough to be near-degenerate, increased intensity of the photoassociating laser turns out to be the key to reducing spontaneous-decay losses.

In Sec. II we introduce the QC approach in the model with one stable bound molecular state coupled by a laser to a dissociation continuum of a molecule. The emphasis is on the relations of this model to the prototype two-level system of quantum optics and laser spectroscopy. While we have stated the basic ideas before [7], here we add a wealth of detail so as to include, e.g., the counting of QC states, threshold law of photodissociation rate, atom-atom collisions, and the absence of coherent power broadening.

Section III presents an application of our QC approach to

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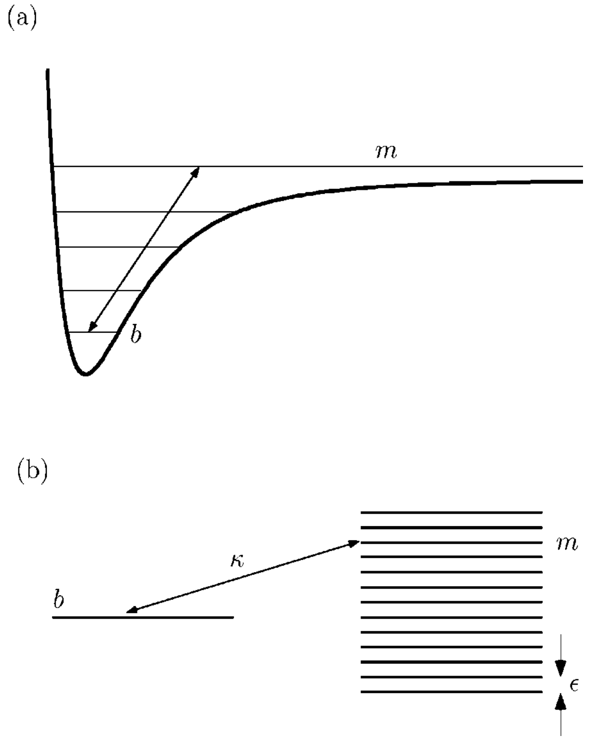

FIG. 1. (a) Scheme in which a laser drives transitions between a dissociated (quasicontinuum) state *m* and a (stable) bound molecular state *b*. (b) Quasicontinuum model of the same.

two-color free-bound-bound photoassociation. Although continuous-wave excitation may not be of immediate relevance in experiments, we analyze it in detail as an illustration of the pertinent concepts borrowed from laser spectroscopy, such as two-photon and two-step transitions. We then proceed to pulsed-laser excitation. The brief summary and concluding remarks in Sec. IV complete our paper.

## II. FREE-BOUND TRANSITIONS

In this section we consider photoassociation and photodissociation to and from a bound, stable molecular state. Although we know of no laser-based experiment on direct one-color photoassociation to a stable molecular state, one can envisage models in which this is possible at least in principle. We sketch such a situation in Fig. 1.

### A. Quasicontinuum (QC) model

As indicated in Fig. 1, we model the dissociation continuum of a molecule with a QC, an infinite number of states $|n\rangle$ between which there is an equal energy spacing $\hbar\varepsilon$. In our model the QC is also ''flat,'' so that the coupling matrix element between the bound state $|b\rangle$ and any QC state $|n\rangle$ equals the same constant $\hbar\kappa$. For dipole coupling to light we have the Rabi frequency $\kappa=dE/2\hbar$, where $E$ is the amplitude of the electric field and $d$ is the dipole matrix element between the bound state and any QC state. Within the rotating-wave approximation, the Hamiltonian of the system is

$$\frac{H}{\hbar}=\sum_{n=-\infty}^{\infty}\omega_n|n\rangle\langle n|-\sum_{n=-\infty}^{\infty}(\kappa|n\rangle\langle b|+\kappa^*|b\rangle\langle n|), \quad (1)$$

with $\omega_n=n\varepsilon$. The labeling of the QC states is chosen in such a way that the transition $|b\rangle\leftrightarrow|n=0\rangle$ is on optical resonance.

The state vector of the system is written

$$|\psi\rangle=b|b\rangle+\sum_n a_n|n\rangle, \quad (2)$$

where $b$ and $a_n$ are generally time-dependent amplitudes. Combining Eqs. (1) and (2), we have the time dependent Schrödinger equation

$$\dot{b}=i\kappa^*\sum_n a_n+b(0)\delta(t), \quad (3a)$$

$$\dot{a}_n=-i\omega_n a_n+i\kappa b+a_n(0)\delta(t). \quad (3b)$$

The delta functions together with the requirement that all amplitudes vanish for $t<0$ impose the initial conditions on the system at $t=0$.

The equations of motion (3) are solved using Fourier transform methods. Closed-form analytical solutions are obtained using the substitution for the self-energy

$$\sum_{n=-\infty}^{\infty}\frac{1}{\omega-n\varepsilon+i\eta}\simeq\frac{1}{\varepsilon}\int_{-\infty}^{\infty}dx\,\frac{1}{\omega-x+i\eta}=-\frac{i\pi}{\varepsilon}. \quad (4)$$

This is the crucial continuum limit that has to be taken in order to recover the free-atom results from the QC model. It is valid for times short enough that the discreteness of the QC states is unresolved, i.e., $t\lesssim\varepsilon^{-1}$. This fact has been confirmed with extensive numerical studies of the solutions to the Schrödinger equation [15]. At any rate, using Eq. (4), the Fourier solutions for the respective amplitudes are given as

$$b(t)=\frac{i}{2\pi}\int d\omega\, e^{-i\omega t}\left[\frac{1}{\omega+i\Gamma/2}\right]\times\left[\kappa^*\sum_n\frac{a_n(0)}{\omega-\omega_n+i\eta}+b(0)\right], \quad (5a)$$

$$a_n(t)=\frac{i}{2\pi}\int d\omega\, e^{-i\omega t}\left\{\left[\frac{\kappa}{(\omega-\omega_n+i\eta)(\omega+i\Gamma/2)}\right]\times\left[\kappa^*\sum_n\frac{a_n(0)}{\omega-\omega_n+i\eta}+b(0)\right]+\frac{a_n(0)}{\omega-\omega_n+i\eta}\right\}, \quad (5b)$$

where we have defined

$$\Gamma=\frac{2\pi|\kappa|^2}{\varepsilon}. \quad (6)$$

The terms $i\eta$, with $\eta=0+$, implement the requirement that the amplitudes vanish for $t<0$.

We begin with the analog of photodissociation, in which the system is initially in the bound state and finally in the QC. The initial conditions are $b(0)=1$ and $a_n(0)=0$. Evaluation of the integrals in Eqs. (5a) and (5b) gives the time-dependent amplitudes as

$$b(t)=e^{-\Gamma t/2}, \tag{7a}$$

$$a_n(t)=\frac{\kappa}{\omega_n-i\Gamma/2}\,(e^{-i\omega_n t}-e^{-\Gamma t/2}). \tag{7b}$$

The bound-state population is of course found to decay exponentially at the photodissociation rate $\Gamma$. Upon depletion of the bound state, $t\gg\Gamma^{-1}$, the population winds up in the QC, and has a Lorentzian profile with the half width at half maximum

$$\gamma=\Gamma/2. \tag{8}$$

In the continuum limit, one obtains a nonzero and finite value for the photodissociation rate by letting $\varepsilon\rightarrow 0$ and $|\kappa|^2\rightarrow 0$ in such a way that $\Gamma$ remains constant, the photodissociation rate as obtained from measurements or molecular-structure calculations for the given light intensity. In the continuum limit the time $\simeq\varepsilon^{-1}$ over which our approximation (4) remains valid automatically tends to infinity [16].

Moving on to photoassociation, the system is initially placed in the $m$th QC state, so that the initial conditions are $b(0)=0$ and $a_n(0)=\delta_{mn}$. Integrating the Fourier expressions (5) gives the time dependence of the respective amplitudes as

$$b(t)=\frac{\kappa^*}{\omega_m+i\gamma}(e^{-i\omega_m t}-e^{-\Gamma t/2}), \tag{9a}$$

$$a_{n\neq m}(t)=\frac{\gamma\varepsilon}{\pi}\left[\frac{e^{-\gamma t}}{(\omega_m+i\gamma)(\omega_n+i\gamma)}+\frac{e^{-i\omega_m t}}{\omega_{mn}(\omega_m+i\gamma)}-\frac{e^{-i\omega_n t}}{\omega_{mn}(\omega_n+i\gamma)}\right], \tag{9b}$$

$$a_m(t)=\frac{\gamma\varepsilon/\pi}{(\omega_m+i\gamma)^2}\{e^{-\gamma t}-[1+i(\omega_m+i\gamma)t]e^{-i\omega_m t}\}+e^{-i\omega_m t}, \tag{9c}$$

where we use the temporary definition $\omega_{mn}=\omega_m-\omega_n$.

Equation (9c) possesses a linear time dependence, and it appears that the population of the initially occupied state diverges for $t\rightarrow\infty$. However, our continuum limit (4) is valid only for $t\lesssim\varepsilon^{-1}$. The continuum-limit expressions have been compared with direct numerical solutions of the QC Schrödinger equations (3), and we find an agreement over such a timescale [15]. Again, this timescale tends to infinity in the limit $\varepsilon\rightarrow 0$.

### B. Equivalent two-level system

It should be clear from our preceding analysis that in the continuum limit the only effect of the light-induced coupling to the QC on the bound-state amplitude is exponential damping. This suggests that photoassociation may be modeled with a two-level system consisting of the initial state $|m\rangle$ and bound state $|b\rangle$, and that the attendant photodissociation is to be regarded simply as irreversible decay of the bound state to the (unobserved QC) states outside the two-level system $\{|m\rangle,|b\rangle\}$. Moreover, the solution of the QC model, Eqs. (9), have the feature that in the continuum limit ($\varepsilon\rightarrow 0$, $\kappa\rightarrow 0$) all light-induced perturbations vanish.

To study photoassociation, we therefore write a two-level model with the equations of motion

$$\dot{b}=-\gamma b+i\kappa a_m,\quad \dot{a}_m=-i\omega_m a_m+i\kappa^* b. \tag{10}$$

It is also understood that these equations are always to be solved perturbatively in the Rabi frequency $\kappa$, so that we write $\dot{a}_m=-i\omega_m a_m$. The solutions obtained in this way from Eq. (10) indeed agree with Eqs. (9a) and (9c) to lowest order in $\kappa$, i.e., they become exact in the continuum limit.

Whichever formalism we are using to study photoassociation, evidently after an initial transient that lasts a time of the order $\Gamma^{-1}$, atoms that were initially in the QC state $|m\rangle$ are transferred to the bound state $|b\rangle$ at the steady rate

$$R_m=\frac{2\gamma|\kappa|^2}{\omega_m^2+\gamma^2}=\frac{\gamma\Gamma\varepsilon/\pi}{\omega_m^2+\gamma^2}. \tag{11}$$

Since photodissociation removes molecules at the rate $\Gamma$, the equilibrium occupation probability of the state $|b\rangle$ is

$$|b(t=\infty)|^2=\frac{R_m}{\Gamma}=\frac{\gamma\varepsilon/\pi}{\omega_m^2+\gamma^2}. \tag{12}$$

The observation that a certain two-level system may be used to model photoassociation is the first of the two essential ingredients in our approach. The other one is also already implicit in Eq. (12), and will be discussed next.

### C. Multiple colliders

From the expression (12), the bound state population is proportional to the spacing of QC states $\varepsilon$. Hence, in the continuum limit with $\varepsilon\rightarrow 0$, the initial state $|m\rangle$ is not depleted at all, and the population of the bound state tends to zero. It seems as if photoassociation were impossible in the context of our QC model.

We make physical sense of this counterfactual result with two realizations. The first is that the limit of zero QC spacing corresponds to the limit of an infinite quantization volume. The second is that we have so far considered the relative motion of only two atoms in either the dissociated or bound state of a molecule. That photoassociation fails to occur should then come as no surprise, since two atoms do not collide at all in the limit of an infinite volume. This situation is remedied if we consider all the other $N-1\simeq N$ atoms as potential colliders while studying collisions experienced by any single ‘‘spectator’’ atom.

In the first steps of our argument, we continue to analyze a pair of atoms. As usual, we consider the relative coordinate only. In collisional calculations it is customary to treat different angular momenta $l$ separately. To prepare for explicit discussions, our QC should thus have angular momentum as a good quantum number. The frequency separation $\varepsilon$ of the QC model is essentially the inverse of the density of energy eigenstates. In order to work out photoassociation, we need the density of energy eigenstates for the two colliding atoms for a given angular momentum of the relative motion.

To facilitate our discussion, we quantize the continuum states by enclosing the relative motion of the atom pair in a spherical potential well with radius $R$, and use reflecting boundary conditions at the surface. Now, the interactions between the atoms change the continuum states and the density of energy eigenstates. For instance, the interactions pull some states down from the continuum, and make discrete molecular eigenstates out of them. However, if the interaction potential has a finite range, in the limit $R\to\infty$ its effect on the density of unbounded states is clearly negligible. All told, to study the density of states, we consider a free particle with reduced mass $\mu$.

The eigenstates of energy in a spherical box are well known, of the form

$$u_{nlm}(r,\theta,\phi)=K_{nlm}Y_m^l(\theta,\phi)j_l(kr). \tag{13}$$

Here $K_{nlm}$ is a normalization constant, $Y_m^l$ is a spherical harmonic, and $j_l$ is the spherical Bessel function of order $l$. Energy and wave number are related by $E=\hbar^2k^2/2\mu$. The reflecting boundary conditions give the quantization rule

$$k_{l,n}=\frac{j_{l,n}}{R}, \quad n=1,2,\ldots, \tag{14}$$

where $k_{l,n}$ are the possible wave numbers for fixed angular momentum $l$, and $j_{l,n}$ are the zeros of the spherical Bessel function. A study of the density of states reduces to counting these zeros.

Fortunately, good tools are available for the task. Reference [17] provides in Eqs. (9.3.39), (9.3.42), (9.5.22), (9.5.26), (10.4.94), and (10.4.105) an asymptotic expansion for $j_{l,n}$ which should be valid in the limit $n\to\infty$ uniformly for all $l=0,1,2,\ldots$ . We have implemented this formula, denote it by $j(l,n)$, numerically. By comparing the results from the asymptotic formula with the actual zeros of the spherical Bessel functions, we have found that $j(l,n)$ gives a very good approximation for $j_{l,n}$ even for $l=0$, $n=1$. The expression $j(l,n)$ is in practice exact for our purposes, for the studies of the limit $R\to\infty$.

Notwithstanding the restrictions on $l$ and $n$ in $j_{l,n}$, $j(l,n)$ is a continuous function of its variables. We therefore define the density of wavenumber eigenstates for a given angular momentum $l$ and a given wave number $k$ by finding a solution with $n>3/2$ to the equation $j(l,n)=kR$, and then write

$$D_l(k)=\frac{dn_l}{dk}\simeq\begin{cases}\dfrac{R}{j(l,n+1/2)-j(l,n-1/2)}, & n>3/2,\\ 0, & \text{otherwise.}\end{cases} \tag{15}$$

The key result from our numerical computations is that in the limit $R\to\infty$ this density of states is of the form

$$D_l(k)=\begin{cases}\dfrac{R}{\pi}\sqrt{1-\left(\dfrac{l}{kR}\right)^2}, & |l|\le kR,\\ 0, & \text{otherwise.}\end{cases} \tag{16}$$

Summing over all possible angular momenta, for large $R$ we find the total density of states

$$D(k)=\int_0^{kR}dl\,(2l+1)D_l(k)\simeq\frac{2k^2R^3}{3\pi}=\frac{k^2V}{2\pi^2}, \tag{17}$$

where $V=4\pi R^3/3$ is the volume of the sphere. The result is the same as the density of $k$ states obtained by quantizing free-particle motion in a cubic box. This is in accord with the standard assumption in quantum mechanics that, in the limit of infinite volume, the precise geometry of the quantization volume does not matter.

Let us again focus on $l$-wave collisions. Then we have $D_l(k)$ as the density of $k$ states,

$$\frac{dn_l}{d\varepsilon}=\frac{dn_l}{dk}\frac{dk}{d(E/\hbar)}=\frac{1}{v}D_l(k) \tag{18}$$

for the density of frequency eigenstates, and

$$\varepsilon_l=\frac{d\varepsilon}{dn_l}=\frac{v}{D_l(k)} \tag{19}$$

for the spacing of quasicontinuum levels.

The next step is to introduce all $N-1\simeq N$ colliders. We assume that each collider acts independently on our spectator atom, so that we simply multiply transition *probabilities* or transition *rates* due to one collider by the number of collision partners. The number of colliders comes with a subtlety, though. While we have $N$ atoms for the spectator to collide with, in an isotropic ensemble they are uniformly distributed over all available angular momentum states. The fraction of atoms available for $l$-wave collisions is therefore $(2l+1)D_l(k)/D(k)$. To obtain the total photoassociation rate for the spectator atom, we substitute Eq. (19) for the spacing of energy eigenstates in the one-collider rate (11), and multiply by $N(2l+1)D_l(k)/D(k)$.

The final phase of the derivation is to take the thermodynamic limit; $V\to\infty$ and $N\to\infty$, in such a way that the density of atoms $\rho=N/V$ stays constant. The spacing of levels with angular momentum $l$ and the fraction of atoms with angular momentum $l$ conspire to produce a nonzero, finite continuum limit for the photoassociation rate of a spectator atom in a gas with the density $\rho$. The rate is

$$R_m=2\pi(2l+1)\frac{\rho v}{k^2}\frac{\gamma\Gamma}{\omega_m^2+\gamma^2}. \tag{20}$$

We encapsulate our argument into the following prescription: For a given collisional angular momentum $l$, the continuum-limit photoassociation rate for an isotropic many-atom gas with density $\rho$ is obtained by multiplying the QC photoassociation rate for one collider by

$$f_l=(2l+1)\frac{2\pi^2\rho v}{\varepsilon k^2}. \tag{21}$$

The $\varepsilon$ in the denominator formally cancels the dependence of the one-atom photoassociation rate on the spacing of QC levels, leaving a factor that depends on atom density.

One might argue that the level density in wave number is simply $D(k)$ and the density of states in frequency is $D(k)/v$. This expression in fact agrees with the energy level density for free particles as quoted in virtually all statistical mechanics textbooks. Thus, the simplistic argument continues, the level spacing is $\varepsilon = v/D(k)$, which is to be inserted into Eq. (11). Finally, multiplying by *N*, taking into account that there are $2l+1$ angular momentum states for a given *l*, and going to the continuum limit, the result (20) is recovered.

Nonetheless, as neatly as this argument agrees with elementary textbook material and gives the right answer, we believe that it is in principle wrong. For instance, if the sample were not isotropic and some angular momentum eigenstates would occur more frequently than others, the rate of photoassociation could change. Yet nothing in our second type of argument would take this into account. We regard the right result from the simplistic reasoning as a pure accident.

In sum, we have shown how to circumvent the dilemma of the QC approach that the rate of photoassociation appears to vanish in the continuum limit. The foundation for our QC method is thus laid. In the remainder of the present Sec. II we basically just clean up the rough edges.

### D. Velocity distribution

Up to now, we have tacitly assumed that for any two colliders, the initial QC state $|m\rangle$ is the same. One sign of this assumption is the single collision velocity $v$ in Eq. (20). Of course, in a thermal gas the atom pairs do not all have the same collision velocity. Correspondingly, we next adopt a probability distribution over the QC states $P_m$, and average the photoassociation rate over the distribution of initial states:

$$R = \sum_m P_m R_m . \tag{22}$$

As an implementation of this idea, we average the rate (20) over the distribution of relative collision velocities in a thermal Maxwell-Boltzmann gas, which reads

$$f_0(v) = 4\pi \left( \frac{\mu}{2\pi k_B T} \right)^{3/2} v^2 e^{-\mu v^2/2k_B T}. \tag{23}$$

The task is to calculate

$$R = \int_0^\infty dv\, f_0(v) R(v), \tag{24}$$

where $R(v)$ is to be inferred from Eq. (20).

A few details must be attended to while carrying out the average. First, the resonance denominator in Eq. (20) contains the frequency $\omega_m$. That obviously stands for the detuning from optical resonance for a collision pair with the relative velocity $v$. Suppose that the laser is tuned so that two atoms with the collision velocity $v_0$ and the corresponding collision energy $\hbar\Delta = E(v_0) = \mu v_0^2/2$ above the continuum threshold are on optical resonance, then we have the replacement

$$\omega_m \rightarrow E(v)/\hbar - \Delta. \tag{25}$$

Second, and contrary to our flat-quasicontinuum model, the rate of photodissociation $\Gamma$ (and hence $\gamma = \Gamma/2$) depends on the relative velocity of the atoms after photodissociation. For instance, according to the Wigner threshold law, for *s*-wave processes $\Gamma \propto v$. This means that the coupling matrix elements $\kappa$ must similarly depend on the relative velocity of the incoming atoms. Without a full-blown (and difficult) exact QC or continuum analysis it is unclear how these dependences should be properly taken into account. Here we advocate the model that in the linewidths that depend on photodissociation one should use the values corresponding to the relative velocity of the atoms after photodissociation $v_0$:

$$\gamma = \gamma_0 \equiv \gamma(v_0). \tag{26}$$

On the other hand, the photodissociation rate $\Gamma$ in Eq. (11) is actually a placeholder for the square of the matrix element $|\kappa|^2$, and so we write in Eq. (20)

$$\Gamma = \Gamma(v) = \frac{v}{v_0} \Gamma_0 . \tag{27}$$

The second equality holds for (low-energy) *s*-wave processes, in which case $\Gamma_0$ is the photodissociation rate for the resonance velocity $v_0$. All told, for *s*-wave processes the rate to be averaged reads

$$R(v) = 2\pi \frac{\rho v^2}{v_0 k^2} \frac{\gamma_0 \Gamma_0}{[E(v)/\hbar - \Delta]^2 + \gamma_0^2}. \tag{28}$$

The integral in Eq. (24) may now be written down explicitly, and analyzed numerically for arbitrary values of the parameters. However, here we only consider the case when the linewidth due to photodissociation $\gamma_0$ is the smallest relevant frequency parameter in the problem. In particular, we assume that $\gamma_0 \ll k_B T/\hbar$. Then the resonance denominator in Eq. (28) in effect makes a delta function in energy that peaks with $E(v) = E(v_0)$, or a delta function in velocity that peaks at $v = v_0$. One simply has to convert the delta function in energy properly into a delta function in velocity, and carry out the integral. The result is

$$R = \rho \lambda_D^3 e^{-\hbar\Delta/k_B T} \Gamma_0 , \tag{29}$$

where

$$\lambda_D = \left( \frac{2\pi\hbar^2}{\mu k_B T} \right)^{1/2} \tag{30}$$

is the thermal de Broglie wavelength.

From Eqs. (28) and (29) it is easy to see that our QC results are in agreement with the standard scattering results [8], and with the latest analytical models [11,12] as well. The photoassociation density parameter $\rho\lambda_D^3$ is essentially the same density parameter as the phase space density for BEC [7]. In a way, the rest of the present paper consists of analysis of the role of the parameter $\rho\lambda_D^3$. The same parameter appears explicitly in, say, Ref. [11], but other authors do not seem to have realized the significance of this connection between photoassociation and BEC.

### E. Equilibrium

Given the rate *R* as in Eq. (29), namely, the probability per unit time at which any given atom participates in photoassociation, plus the fact that the photoassociated molecules also tend to break apart at the photodissociation rate $\Gamma_0$, we have an opportunity to discuss *equilibrium* photoassociation yield. For the time being we continue to assume that, photoassociation or no photoassociation, the velocity distribution of the atoms remains thermal, but allow for the depletion of the number of atoms remaining. Let us denote by $N_m$ the number of molecules in the sample and by $N$ the initial number of atoms, then the rate equation for molecule formation reads

$$\dot{N}_m = \frac{R}{2}(N - 2N_m) - \Gamma_0 N_m . \tag{31}$$

We have the factor $R/2$ instead of $R$ because $R$ is the probability per unit time that a given atom participates in photoassociation, and it double counts the rate at which molecules are formed. The equilibrium probability of photoassociation is given by

$$P = \frac{2N_m}{N} = \frac{R}{R+\Gamma_0} = \frac{\rho\lambda_D^3 e^{-\hbar\Delta/k_B T}}{1+\rho\lambda_D^3 e^{-\hbar\Delta/k_B T}}. \tag{32}$$

Within the present model, the equilibrium photoassociation yield is largely determined by the parameter $\rho\lambda_D^3$. This is basically the same phase phase density that dictates the absence or presence of the Bose-Einstein condensate. Put in another way, since the rate of photoassociation scales with the density as $\rho^2$ and the rate of the competing photodissociation as $\rho$, the equilibrium probability of photoassociation must involve a dimensionless parameter proportional to atom density—and this parameter just happens to be the phase space density that also governs BEC. We therefore anticipate that a near-unit yield is possible when photoassociating a condensate.

### F. Density matrix, power broadening, and collisions

One of the keys to our QC method is to treat the initial QC state and the bound state of the molecule as a two-level system irreversibly damped by the photodissociation of the molecules. So far we have discussed this two-level system in terms of probability amplitudes. However, in quantum optics and optical spectroscopy it is more customary to use the density matrix to describe the two-level system. In the presence of interactions between the two states and the rest of the universe, the two-level system need not remain in a pure state. Then something equivalent to a density matrix description is a must as a matter of principles. The density matrix formalism also conveys practical advantages, in that one may illustrate basic concepts and transparently add new phenomena to the model.

First consider an elementary two-level system consisting of the bound state and one QC state, $\{|b\rangle,|m\rangle\} \equiv \{|1\rangle,|2\rangle\}$, for one pair of atoms only. As before, this system is also effectively irreversibly coupled to the rest of the QC states at the rate $\Gamma_0$, so that the density matrix equations read

$$\dot{\rho}_{11} = -\Gamma_0\rho_{11} + i(\kappa^*\rho_{21} - \kappa\rho_{12}), \tag{33a}$$

$$\dot{\rho}_{21} = -(i\omega_m + \gamma_0)\rho_{21} - i\kappa(\rho_{22} - \rho_{11}), \tag{33b}$$

$$\dot{\rho}_{22} = -i(\kappa^*\rho_{21} - \kappa\rho_{12}). \tag{33c}$$

Concerning basic concepts, in the continuum limit the Rabi frequency $\kappa$ tends to zero while the photodissociation rate $\Gamma_0$ remains constant. Coherent transitions induced by light are thus much slower than the damping, and it is impossible to saturate or power-broaden this two-level system. That the physical system may nonetheless exhibit any distribution of the population between the two states has nothing to do with power broadening. Increasing the density of atoms enhances the molecular yield, but the time scale for coherent Rabi flopping remains unaffected.

In addition to illustrating the absence of coherent power broadening, the density matrix comes in handy for describing collisions phenomenologically. Hence, we complete our discussion of the two-level system with a rudimentary collision model that is already implicit in our preceding results. When it is all said and done, we assume that the relative velocity of the atoms tends to thermalize quickly.

Allowing for a distribution of atom-pair velocities, we have to make those density matrix elements that refer to atoms, all but $\rho_{11}$, functions of the relative velocity $v$. Moreover, we add several ingredients that are so far missing from our model. First, the molecules that get photodissociated do not vanish without a trace, but reemerge as atom pairs with some (normalized) distribution of relative velocity $\mathcal{L}(v)$. Second, collisions disrupt the coherence in photoassociation. We model this by adding a collisional broadening $\gamma_c$ to the linewidth of the transition $\gamma_0$. While at that, we also replace the resonance frequency with the same detuning factor as before, see Eq. (25). Third, collisions redistribute atoms between the velocities, so that there is some collision operator $K$ involved. Different collision models correspond to different collision operators. For the sake of illustration we write the explicit collision operator for strong collisions. By assumption, one such collision, which takes place at the rate $\Gamma_c$, is sufficient to restore the normalized thermal velocity distribution $f_0(v)$, Eq. (23). Fourth, as we are treating photodissociation separately and on a different footing from photoassociation, to avoid double-counting we have to drop all processes driven by the Rabi frequency whose effect would be to make atoms ($\rho_{22}$) from molecules ($\rho_{11}$), i.e., the $\rho_{11}$ term in Eq. (33b). Altogether, the two-level collisional model yields the integrodifferential equations

$$\dot{\rho}_{11} = -\Gamma_0\rho_{11} + i\int dv[\kappa^*(v)\rho_{21}(v) - \kappa(v)\rho_{12}(v)], \tag{34a}$$

$$\dot{\rho}_{21}(v) = -\{i[E(v)/\hbar - \Delta] + [\gamma_0 + \gamma_c]\}\rho_{21}(v) - i\kappa(v)\rho_{22}(v), \tag{34b}$$

$$\dot{\rho}_{22}(v) = \Gamma_0\mathcal{L}(v)\rho_{11} + \Gamma_c\left[f_0(v)\int dv'\rho_{22}(v') - \rho_{22}(v)\right] - i[\kappa^*(v)\rho_{21}(v) - \kappa(v)\rho_{12}(v)]. \tag{34c}$$

For an illustration of the implications of this model, we begin with the rate approximation. Whatever the justification might be, we just set $\dot{\rho}_{21}$ equal to zero in Eq. (34b), solve for $\rho_{21}=\rho_{12}^{*}$, and insert into the remaining equations. This gives the rate equations

$$\dot{\rho}_{11}=-\Gamma_0\rho_{11}+\int dv\frac{2(\gamma_0+\gamma_c)|\kappa(v)|^2}{[E(v)/\hbar-\Delta]^2+(\gamma_0+\gamma_c)^2}\,\rho_{22}(v), \tag{35a}$$

$$\dot{\rho}_{22}(v)=\Gamma_0\mathcal{L}(v)\rho_{11}+\Gamma_c\left[f_0(v)\int dv'\rho_{22}(v')-\rho_{22}(v)\right] -\frac{2(\gamma_0+\gamma_c)|\kappa(v)|^2}{[E(v)/\hbar-\Delta]^2+(\gamma_0+\gamma_c)^2}\,\rho_{22}(v). \tag{35b}$$

Next we assume that the total atom number for the dissociated system is $N$, and reinterpret the quantity $\rho_{11}\equiv P$ as the probability of photoassociation of any given spectator atom. Correspondingly, $\rho_{22}(v)\equiv f(v)$ is the probability density for atoms in a collision pair characterized by relative velocity $v$ that have not photoassociated. We also impose the normalization

$$\int dv\, f(v)=1-P. \tag{36}$$

Finally, as before we simply multiply the photoassociation rate for two atoms, the terms proportional to $|\kappa(v)|^2$ in Eqs. (35), by the factor (21). While there are in fact $(1-P)N$ atoms left, the normalization of the velocity distribution takes care of the factor $1-P$, so that our rate equations are

$$\dot{P}=-\Gamma_0 P+\int dv\frac{2f_l(\gamma_0+\gamma_c)|\kappa(v)|^2}{[E(v)/\hbar-\Delta]^2+(\gamma_0+\gamma_c)^2}\,f(v), \tag{37a}$$

$$\dot{f}(v)=\Gamma_0\mathcal{L}(v)P+\Gamma_c[(1-P)f_0(v)-f(v)] -\frac{2f_l(\gamma_0+\gamma_c)|\kappa(v)|^2}{[E(v)/\hbar-\Delta]^2+(\gamma_0+\gamma_c)^2}f(v). \tag{37b}$$

In the last step of our demonstration we assume that the rate of strong collisions $\Gamma_c$ is the largest rate occurring in Eqs. (37). In steady state we then approximately have

$$\Gamma_c[(1-P)f_0(v)-f(v)]=0 \tag{38}$$

or

$$f(v)=(1-P)f_0(v). \tag{39}$$

With this observation, we are back to the same mathematics that was already presented in Sec. II D. The only difference is that where we used to have the photodissociation linewidth $\gamma_0$, we now have the collision-broadened linewidth $\gamma=\gamma_0+\gamma_c$. If the collision broadened linewidth satisfies $\gamma\ll k_BT/\hbar$, the steady-state photoassociation yield is the same as before, Eq. (32).

It is easy to develop density matrix models with different levels of sophistication for various purposes. We will neither enter any general discussion of such models, nor even attempt a comprehensive analytical or numerical solution of our example case. We merely hope to have made two points.

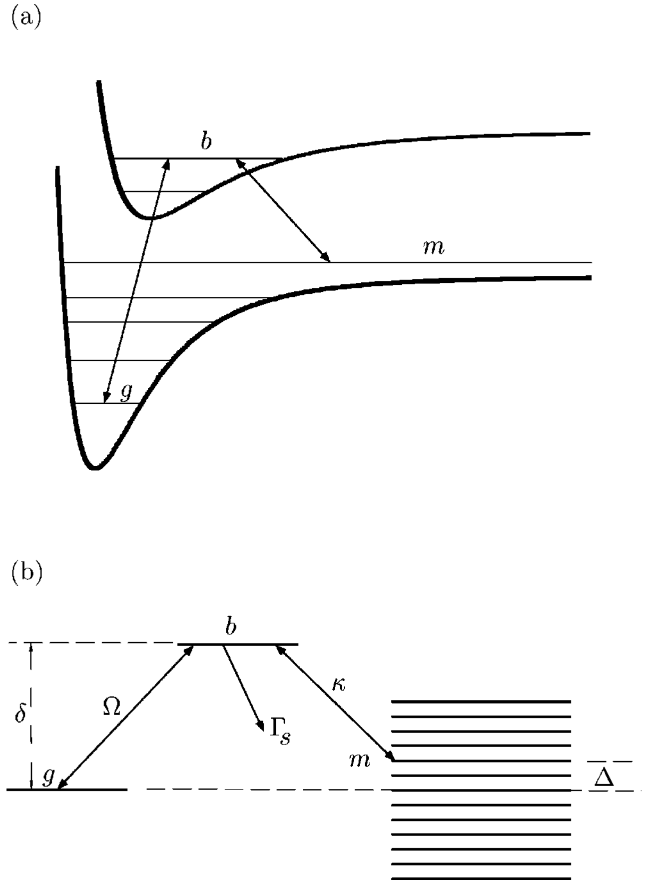

FIG. 2. (a) Scheme in which two lasers drive transitions between a dissociated (quasicontinuum) state *m*, an intermediate state *b*, and a stable bound molecular state *g*. (b) Quasicontinuum model of the same. As appropriate for a proper rotating frame, level energies are given by detunings and laser-driven couplings are independent of time.

First, as needed, one may devise density matrix treatments for the analysis of photoassociation in close analogy with the density matrix approaches that one sees in laser spectroscopy. Second, our particular model demonstrates that, given the right kind of collisions, the velocity distribution of collision pairs may well remain thermal in spite of photoassociation. The simple model of the preceding sections remains valid, provided one uses the collision broadened linewidth $\gamma=\gamma_0+\gamma_c$ in lieu of the photoassociation linewidth $\gamma_0$ in all the proper places. If the rethermalizing collisions are not fast enough, collision pairs with the resonance velocity $v_0$ are depleted. One may deal with this case, e.g., by solving Eqs. (37) numerically.

## III. ADDITION OF A SECOND COLOR

We now turn to the physical model depicted in Fig. 2(a), and to its QC counterpart sketched in Fig. 2(b). Two light frequencies are present, one of which drives photoassociation to a vibrational state within an electronically excited manifold, and the second that takes the excited molecules to another vibrational state in a stable electronic manifold. The motivation for such a scheme could be that the electronically excited molecule created in ordinary photoassociation is unstable, and decays spontaneously at the rate $\Gamma_s$ to either bound vibrational states or back to the dissociation continuum (radiative escape). We regard both of these outcomes as undesirable, and use the second laser to guide the molecule to the intended vibrational level. The goal is to put as many molecules as possible into the final stable state.

In the continuum limit precisely the same mathematics that led us to treat photoassociation using a two-level model now gives a three-level scheme that is implicit in Fig. 2(b). We again denote the initial QC state by $m$, the intermediate molecular state by $b$ (as in ''bound''), and introduce the final stable state as $g$ (''ground''). Two lasers with the frequencies $\omega_1$ and $\omega_2$ and Rabi frequencies $\kappa$, $\Omega$ drive transitions between the respective state pairs $\{|m\rangle,|b\rangle\}$ and $\{|b\rangle,|g\rangle\}$. In the rotating-wave approximation and in a suitable rotating frame, we have a Hamiltonian of the form

$$\frac{H_0}{\hbar}=-\Delta|g\rangle\langle g|+(\delta-\Delta)|b\rangle\langle b|-(\Omega|b\rangle\langle g|+\Omega^*|g\rangle\langle b|)$$
$$-(\kappa|b\rangle\langle m|+\kappa^*|m\rangle\langle b|). \tag{40}$$

Here

$$\delta=\omega_b-\omega_g-\omega_2, \tag{41a}$$

$$\Delta=\omega_m-\omega_g-(\omega_2-\omega_1) \tag{41b}$$

are the intermediate detuning that characterizes the degree of being off resonance in the transition between the two bound molecular states, and the two-photon detuning that stands for the total energy mismatch in the free-bound-bound molecular process. The slightly unusual appearance of the Hamiltonian is because here we have chosen the zero of energy in such a way that the energy of the state corresponding to the initial QC state $|m\rangle$ equals zero. We have assumed the $\Lambda$ configuration as in Fig. 2. Other types of three-level schemes, such as the cascade, can be accommodated with trivial changes in the notation.

In addition to the light-driven couplings, we have to consider both photodissociation taking place at the rate $\Gamma_0$, and the potentially harmful spontaneous transitions at the rate $\Gamma_s$. Since both of these mechanisms take the system outside of the three states under consideration, it is known from quantum optics and laser spectroscopy that such damping may be incorporated correctly by adding a piece with imaginary energy to the Hamiltonian $H_0$,

$$\frac{H_d}{\hbar}=-\frac{i}{2}(\Gamma_0+\Gamma_s)|b\rangle\langle b|. \tag{42}$$

Writing the state vector in the form

$$|\psi(t)\rangle=g(t)|g\rangle+b(t)|b\rangle+a_m(t)|m\rangle, \tag{43}$$

we thus have the time dependent Schrödinger equation

$$\dot{g}=i\Delta g+i\Omega^*b, \tag{44a}$$

$$\dot{b}=\left[i\delta-\frac{1}{2}(\Gamma_0+\Gamma_s)\right]b+i\Omega g+i\kappa a_m, \tag{44b}$$

$$\dot{a}_m=i\kappa^*b. \tag{44c}$$

As before, the coupling $\kappa$ to the QC vanishes in the limit $V\rightarrow\infty$. It follows immediately that $\kappa\ll\Omega$ holds for a large volume. This is exactly the result that prohibits the adiabatic condition from being satisfied [7] in a free-bound-bound STIRAP process [12]. Furthermore, while considering the state triplet $\{|g\rangle,|b\rangle,|m\rangle\}$, we should treat the free-bound coupling $\kappa$ as a perturbation. In practical terms, we simply adopt the reservoir approximation and set $a_m\equiv1$ in Eq. (44). In later sections, we apply these insights to obtain results for both continuous-wave and time dependent couplings.

### A. Dressed two-level system

Because we are going to treat transitions from the QC as perturbations, the basic system to be considered consists of the two bound states $|g\rangle$ and $|b\rangle$ and light with the detuning $\delta$ and Rabi frequency $\Omega$. The exact solution to this system is the familiar dressed atom [18]. For completeness, we briefly reiterate a few of the pertinent aspects.

Suppose first that the detuning is large, $|\delta|\gg|\Omega|$. In this case the dressed states $|+\rangle$ and $|-\rangle$ are close in character to the original states $|g\rangle$ and $|b\rangle$; say, $|+\rangle\simeq|g\rangle$ and $|-\rangle\simeq|b\rangle$. The dressed states are separated in frequency by an amount $\sim|\delta|$, and so coupling to the third state $|m\rangle$ will show two resonances [14] separated approximately by $|\delta|$. The resonance between states $|m\rangle$ and $|+\rangle$ is the two-photon resonance [19]. In a sense, the system makes its transition directly from the initial state $|m\rangle$ to the ground state $|g\rangle$. The other resonance, between states $|m\rangle$ and $|-\rangle$, corresponds to two-step processes. The image we have in mind is that the system primarily makes a transition from the state $|m\rangle$ to the bare state $|b\rangle$. Whatever population is found in the bare state $|g\rangle$ is there as a result of a second step, transitions between $|b\rangle$ and $|g\rangle$.

If only the state $|b\rangle$ is damped, the state that has predominantly the character of the stable state, $|+\rangle$, only decays because it has a small admixture of the unstable state $|b\rangle$. The decay rate is

$$\Gamma_+\simeq\frac{|\Omega|^2}{\delta^2}(\Gamma_0+\Gamma_s). \tag{45}$$

The other state $|-\rangle$ experiences the full force of damping at the rate $\Gamma_-\simeq\Gamma_0+\Gamma_s$. Of course, since the third state $|m\rangle$ is coupled directly to the bare state $|b\rangle$ only, the coupling strength to the dressed state $|+\rangle$ is similarly decreased, so that the matrix element from $|m\rangle$ to $|+\rangle$ is of the order $|\kappa\Omega/\delta|$.

In the contrary case $|\delta|\ll|\Omega|$, the dressed states $|\pm\rangle$, separated by $\simeq2|\Omega|$, are both near fifty-fifty admixtures of the bare states $|g\rangle$ and $|b\rangle$. Both of them are coupled to the QC state $|m\rangle$ with a comparable strength, and both of them also decay at a similar rate $\simeq(\Gamma_0+\Gamma_s)/2$ to states outside our three-level system.

### B. Continuous-wave transitions

In the continuous-wave case we find the steady state of Eqs. (44) with the additional simplifications that, by virtue of the continuum limit and the reservoir approximation, $\kappa\rightarrow0$ and $a_m\equiv1$. The result is a two-by-two set of linear equations, which may be solved trivially.

Instead of writing down the general solution, which is not particularly transparent, we go directly to the two special cases already mentioned in the preceding section on the dressed atom. First consider a large intermediate detuning, $|\delta|\gg|\Omega|,\Gamma_0,\Gamma_s$. If the detuning of the photoassociating laser is chosen in such a way that we are operating in the proximity of the two-photon resonance, $\Delta\simeq0$, the QC state $|m\rangle$ is near resonance with the dressed state $|+\rangle$ that has predominantly the character of the stable ground state $|g\rangle$. Hence, we take the two-photon detuning to be small. The populations of the two states are

$$|g|^2\simeq\frac{|\Omega|^2|\kappa|^2/\delta^2}{[\Delta+|\Omega|^2/\delta]^2+[(\Gamma_0+\Gamma_s)|\Omega|^2/2\delta^2]^2},\tag{46}$$

$$|b|^2\simeq\frac{\Delta^2|\kappa|^2/\delta^2}{[\Delta+|\Omega|^2/\delta]^2+[(\Gamma_0+\Gamma_s)|\Omega|^2/2\delta^2]^2}.\tag{47}$$

Both populations show the two-photon resonance shifted by the usual amount $-|\Omega^2|/\delta$ and broadened by the similarly expected spontaneous decay rate $(\Gamma_0+\Gamma_s)|\Omega|^2/\delta^2$. Besides, the expression for $|b|^2$ also displays the dark state: for $\Delta=0$ there should be *no* steady-state population at all in the intermediate state $|b\rangle$, and hence no harmful spontaneous leakage through the intermediate state.

In reality, the picture is not so rosy. First, one would usually photoassociate atoms from a range of energies, so that the two-photon resonance condition $\Delta=0$ cannot hold for all colliders. Second, as a result of phase perturbations due to, say, atom-atom collisions, the two-photon coherence that maintains the dark state tends to decay, and the dark state loses molecules. Third, even if the dark state were exact, when it is reached, photoassociation ceases as well. The fraction of atoms converted during the buildup of the dark state determines the final photoassociation yield. But, during this initial transient the intermediate state *is* populated, and it loses population to spontaneous emission.

The first two complications depend on experimental details, and we do not undertake any quantitative calculations. As a matter of fact, including collisional damping of the two-photon coherence would bring in the entire density matrix formalism, and substantially complicate the analysis.

The loss of atoms during the build-up of the dark state, though, is intrinsic to the physics, and we study it in some detail. We solve the Schrödinger equation (44) as a function of time, and find the total probability that leaked due to spontaneous emission losses from the intermediate state. For $\Delta=0$ we find

$$\int_0^\infty dt\,\Gamma_s|b(t)|^2=\frac{\Gamma_s}{\Gamma_0+\Gamma_s}\,\frac{|\kappa|^2}{|\Omega|^2}.\tag{48}$$

But Eq. (46) gives the corresponding steady-state probability of the ground state as

$$|g(t=\infty)|^2=\frac{|\kappa|^2}{|\Omega|^2},\tag{49}$$

so that the fraction $\Gamma_s/(\Gamma_0+\Gamma_s)$ of the atoms leaked out through the loss channel. The only way to improve on this (within the present assumptions) is to increase the intensity of the photoassociating laser, and thereby enhance the favorable branching.

Let us now take Eq. (46) at face value, ignoring spontaneous-emission leakage. Just as before, we may take the continuum limit and average over the thermal distribution of collider pairs. In so doing, with the assumption $a_m\equiv1$ we in effect ignore depletion of the atoms owing to photoassociation. Correspondingly, we regain basically the no-depletion version of the photoassociation yield of Eq. (32),

$$P=\rho\lambda_D^3e^{-\hbar(\Delta+|\Omega|^2/\delta)/k_BT}.\tag{50}$$

Here the physical mechanism leading to steady state involves coherent population trapping and is not simply the balance between photoassociation and photodissociation, but the quantitative result is very similar regardless.

We next take up the second dressed-atom case in which the auxiliary light between the discrete molecular states is tuned near resonance, $|\Omega|\gg|\delta|$. Then both dressed states have approximately a 1/2 admixture of the bare excited state $|b\rangle$, and are subject to nearly the full spontaneous-emission leakage. If there is any such leakage, all atoms will either wind up in bound molecular states as determined by branching ratios in spontaneous emission, or are lost to radiative escape. To make physical sense of the steady state of the continuous-wave case we therefore assume that there is no branching to spontaneous emission at all, $\Gamma_s=0$.

The two dressed states are separated by $2|\Omega|$, which we assume large, and so there are two separate resonances for photoassociation starting from a given QC state. We assume that the photoassociating laser is tuned close to resonance with the one that is higher up in frequency. Correspondingly, for the same photoassociating laser, the other dressed state is on resonance with atoms whose energies are about $2\hbar|\Omega|$ lower at the onset. If $2|\Omega|$ is large enough, this spurious resonance is below the continuum threshold and may be ignored. We take this to be the case, and only consider transitions to the dressed state higher in energy.

All told, with the assumptions that $|\Omega|\gg|\delta|$, $\Gamma_0$ and $\Delta\simeq|\Omega|$, the steady-state population of the stable molecular state is

$$|g|^2=\frac{(|\kappa|/2)^2}{(\Delta-|\Omega|)^2+(\gamma_0/2)^2}.\tag{51}$$

Just as twice before, we obtain the photoassociation yield in the assumed absence of atom depletion,

$$P=\frac{1}{2}\rho\lambda_D^3e^{-\hbar(\Delta-|\Omega|)/k_BT}.\tag{52}$$

The second resonance we have ignored carries half of the transition strength, accordingly we have lost a factor of 2 in the yield. Another way of thinking about the same factor of 2 is that the state pair $|g\rangle$ and $|b\rangle$ is saturated by the laser with a large Rabi frequency, and so only half of the atoms in this state pair are in the ground state $|g\rangle$.

### C. Transient excitation

Leaving the lasers on continuously is likely to lead to loss of atoms in the form of radiative escape and spontaneous transitions to unwanted vibrational states. Our three-level model also suggests that increasing the intensity of the photoassociating laser could improve the branching between photoassociation and spontaneous-emission loss. Both of these observations suggest that it might be advantageous to pulse the photoassociating laser. Accordingly, in this section we give examples of methods that could be used to treat pulsed excitation, and discuss a few generic results.

#### 1. Two-photon transitions

Given time dependent Rabi frequencies and a damping rate that also depends on time because the intensity of the photoassociating laser does, the Schrödinger equation (44) remains valid. However, for later convenience we change the overall zero of the energy, so that the matrix representing the Hamiltonian becomes

$$\frac{H_0}{\hbar}=\begin{pmatrix} 0 & -\Omega^*(t) & 0 \\ -\Omega(t) & \delta & -\kappa(t) \\ 0 & -\kappa^*(t) & \Delta \end{pmatrix}. \tag{53}$$

We seek to solve the time dependent response from this Hamiltonian using an adiabatic approximation valid in the limit when direct two-photon processes are the dominant mechanism for transfer of atoms from the QC to the ground state. Once more, we therefore have $|\delta|\gg|\Omega|,|\Delta|$. We apply a (time dependent) unitary transformation $U$ that makes the dressed states out of the two bound states, i.e., diagonalizes the two-by-two block on the upper left corner of the matrix in Eq. (53). This unitary matrix is

$$U(t)=\begin{pmatrix} 1 & -\dfrac{\Omega^*(t)}{\delta} & 0 \\ \dfrac{\Omega(t)}{\delta} & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}+O\left[\frac{1}{\delta^2}\right], \tag{54}$$

and the corresponding transformed Hamiltonian reads

$$\begin{aligned}\frac{\tilde{H}_0}{\hbar}&=i\frac{\partial U}{\partial t}U^\dagger+U\frac{H_0}{\hbar}U^\dagger\\ &=\begin{pmatrix} -\dfrac{|\Omega(t)|^2}{\delta} & 0 & -\dfrac{\kappa(t)\Omega^*(t)}{\delta} \\ 0 & \delta+\dfrac{|\Omega(t)|^2}{\delta} & -\kappa(t) \\ -\dfrac{\kappa^*(t)\Omega(t)}{\delta} & -\kappa^*(t) & \Delta \end{pmatrix}\\ &\quad+O\left[\frac{1}{\delta^2}\right].\end{aligned} \tag{55}$$

Here we have assumed that the time derivative of the Rabi frequency $\Omega(t)$ is formally zeroth order in $\delta$. This holds if $\Omega(t)$ changes little over the time $\delta^{-1}$.

At this point a digression on level shifts is due. The element $\tilde{H}_{11}$ in Eq. (55) is the same shift of the two-photon resonance that we already encountered in the preceding section on the continuous-wave response. This time, however, the level shift depends on time, which complicates the analysis. There is also another level shift present that we have so far not mentioned. Namely, because the photodissociation rate $\Gamma_0$ depends on the final continuum state, analogously to Kramers-Kronig relations it follows from causality that there must be an attendant shift of the continuum with respect to the state $|b\rangle$. This is akin to an imaginary part of the damping rate $\Gamma_0$, and is similarly proportional to the intensity of the photoassociating light. Both an *ab initio* theoretical analysis and an explicit measurement of this shift appear difficult, but as a rule of thumb one might expect that the shift is of the order of the photodissociation rate [20]. Finally, for the purpose of the argument, we have meticulously allowed the Rabi frequencies to be time dependent complex numbers. A time dependence of the form $e^{-i\xi t}$ obviously has precisely the same effect as a shift of the driving laser frequency by $\xi$.

The shift of the two-photon resonance, $-|\Omega|^2/\delta$, is proportional to $1/\delta$, and appears small within our approximations. However, it may be seen, e.g., from Eq. (46) that we may end up comparing this shift with a linewidth that is of the order $1/\delta^2$, and so the shift may be cause for concern. As it comes to the shift of the continuum with respect to the state $|b\rangle$, at the moment we believe that it may instead be considered as a shift of the level $|b\rangle$ with respect to the continuum, and therefore directly affects the intermediate detuning $\delta$ rather than the two-photon detuning $\Delta$. The change in the two-photon detuning enters via the shift $-|\Omega|^2/\delta$, and is second order in $1/\delta$. We have not, however, constructed a proof of this assertion. Hence, the possibility that the two-photon detuning might be affected even in the order $1/\delta^0$ is not ruled out.

In what follows, we simply ignore all time dependent level shifts. We have two potential justifications. First, we are going to assume short pulses of light. Obviously, a shift of the two-photon resonance smaller than the spectral width of the light pulse cannot have much physical effect. Alternatively, the driving pulses $\kappa(t)$ and/or $\Omega(t)$ may be chirped to cancel the level shifts. Since we are talking pulse widths of the order of the inverse of the photodissociation time and chirps of the order of photodissociation rate $\Gamma_0$, such chirping should not be much of a challenge to today's laser technology.

#### 2. Transition probabilities

As represented schematically in Fig. 3, we have three relevant pools of atoms: atoms available for photoassociation, atoms converted into stable ground state molecules, and atoms lost to radiative escape and branching to wrong molecular states. We denote the probabilities that an atom belongs to one of these pools by $P_a$, $P$, and $P_l$, respectively. As with our continuous-wave case, we assume that no other property of the pools changes with applied laser pulses except the numbers of atoms. For instance, each pulse leaves the remaining atoms available for photoassociation in the same (say, thermal) velocity distribution, and the two-photon co-

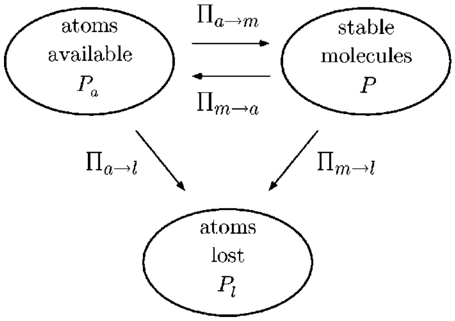

FIG. 3. Pictorial representation of various pools of atoms in the case of two-color excitation, also showing transition probabilities between the pools.

herences are assumed to decay away between successive pulses. Provided such a description is sufficient, a laser pulse causes transitions between the various pools with the probabilities $\Pi_{i\to j}$, where $i,j=a,m,l$. The probabilities $P_a, P, P_l$ evolve from pulse $n$ to pulse $n+1$ according to

$$P^{(n+1)}=(1-\Pi_{m\to a}-\Pi_{m\to l})P^{(n)}+P_a^{(n)}\Pi_{a\to m}, \tag{56a}$$

$$P_a^{(n+1)}=(1-\Pi_{a\to m}-\Pi_{a\to l})P_a^{(n)}+P^{(n)}\Pi_{m\to a}, \tag{56b}$$

$$P_l^{(n+1)}=P_l^{(n)}+P_a^{(n)}\Pi_{a\to l}+P^{(n)}\Pi_{m\to l}. \tag{56c}$$

The immediate task is to find the transition probabilities $\Pi_{i\to j}$. We proceed under the assumption that for a single pulse of light all of these probabilities are small. The practical implication is that while calculating, say, $\Pi_{a\to m}$, one may ignore depletion of the atoms.

We first turn to $\Pi_{a\to m}$. Using the Hamiltonian (55) and the familiar reservoir approximation that the population of the initial QC state remains a constant unity, i.e., $\psi=\{g,b,e^{-i\Delta t}\}$, we find a version of the Schrödinger equation

$$\dot{g}=\frac{i}{\delta}e^{-i\Delta t}\kappa^*(t)\Omega(t), \tag{57a}$$

$$\dot{b}=-i[\delta b+e^{-i\Delta t}\kappa(t)]. \tag{57b}$$

It should be noted that here the amplitudes $b$ and $g$ do not refer to the bare ground and bound states $|g\rangle$ and $|b\rangle$, but to the dresses states $|+\rangle$ and $|-\rangle$. However, with our assumption of large $\delta$, the ensuing difference in the final results is negligible.

We now proceed by imposing the adiabatic condition on the photoassociation color as well, i.e., we assume that $\kappa(t)$ changes little over the time $\delta^{-1}$. Recalling that $|\delta|\gg|\Delta|$, the bound state amplitude is then given by

$$b(t)=-e^{-i\Delta t}\kappa(t)/\delta. \tag{58}$$

In order to facilitate an easy analytical treatment, the shapes of the pulses are specified as

$$\kappa(t)=\kappa_0\exp[-|t|/\tau], \tag{59a}$$

$$\Omega(t)=\Omega_0\exp[-|t|/\tau]. \tag{59b}$$

The rate of photodissociation then varies in time as

$$\Gamma(t)=\Gamma_0\exp[-2|t|/\tau], \tag{60a}$$

$$\Gamma_0=2\pi|\kappa_0|^2/\varepsilon. \tag{60b}$$

The probability that an atom is photoassociated after the pulse is

$$\Pi_{a\to m}=2\left|\int_{-\infty}^{\infty}dt'\dot{g}(t')\right|^2=\frac{16\tau^2\Gamma_0\Omega_0^2\varepsilon}{\pi\delta^2(4+\Delta^2\tau^2)^2}, \tag{61}$$

where the factor 2 is because one process of photoassociation converts two atoms into a molecule. Again there seemingly is no photoassociation in the continuum limit. To include the contributions from all colliders, we multiply by the factor (21) as before, assuming $l=0$. In the process, we must divide the result by two in order to cancel the double-counting of collision pairs.

We must also contend with the velocity distribution of the atoms. To this end we first assume that the light pulse is so short that its spectral broadening covers all of the velocity distribution at once. In fact, in our argument we choose a pulse length $\tau$ such that $k_BT\tau/\hbar\simeq 1$. At microkelvin temperatures this allows for pulse durations of the order of microsecond, which is not particularly short in the standards of laser technology. The result is that in all of our expressions we may set $\Delta\tau\simeq 0$. Second, the use of Eq. (21) explicitly brings the collision velocity $v$ into the picture. We use the thermal velocity $u=\sqrt{k_BT/\mu}$ wherever the velocity $v$ appears. Third, we define the thermal frequency $\theta=k_BT/\hbar$, so that for our pulse duration $\tau$ we have $\tau\simeq 1/\theta$. The net result is

$$\Pi_{a\to m}\simeq\frac{\rho\lambda_D^3\Gamma_0\Omega_0^2}{2\sqrt{2\pi}\delta^2\theta}. \tag{62}$$

We next consider spontaneous-emission losses during photoassociation. Given that the excited molecular state decays spontaneously at the rate $\Gamma_s$, the corresponding population loss during one pulse in a transition from an initially occupied QC state to the ground state is

$$\Pi_{a\to l}=2\int_{-\infty}^{\infty}dt'\Gamma_s|b(t')|^2=\frac{\tau\Gamma_s\Gamma_0\varepsilon}{\pi\delta^2}. \tag{63}$$

Including the contributions from all colliders as before, we have

$$\Pi_{a\to l}\simeq\frac{\rho\lambda_D^3\Gamma_s\Gamma_0}{2\sqrt{2\pi}\delta^2}. \tag{64}$$

The probability for spontaneous decay now increases proportionally to the BEC phase space density of the gas. But, from Eqs. (62) and (64), we see that the fraction of population diverted to losses in spontaneous decay instead of ending up as ground state molecules is

$$\eta=\frac{\Pi_{a\to l}}{\Pi_{a\to l}+\Pi_{a\to m}}\simeq\frac{\Gamma_s\theta}{\Gamma_s\theta+\Omega_0^2}, \tag{65}$$

which is independent of atom density.

Once molecules begin to accumulate in the ground state, they may also be depleted through the reverse bound-bound-free transitions. Our next assignment is to consider the case where the ground state is initially occupied, and determine the population gone to photodissociation after one pulse. In our solution of the Schrödinger equation we simply keep $g=1$, and calculate the probability of photodissociation as the integral

$$\Pi_{m\rightarrow a}=\int dt|b(t)|^2\Gamma(t). \tag{66}$$

In this case, there is only one possible initial state, and therefore no need to consider any velocity distribution. Two atoms are released per pulse, but on the other hand the number of molecules is half the number of atoms. The implicit double counting therefore corrects itself, and the probability is

$$\Pi_{m\rightarrow a}=\frac{\Gamma_0\Omega_0^2}{2\delta^2\theta}. \tag{67}$$

Losses due to spontaneous emission also incur during photodissociation. The probability is

$$\Pi_{m\rightarrow l}=\frac{\Gamma_s\Omega_0^2}{\delta^2\theta}, \tag{68}$$

which is nothing but the usual scattering rate $\Gamma_s\Omega_0^2/\delta^2$ multiplied by the duration of the pulse.

From these expressions, the fraction of photodissociated population that is unavailable for recycling due to the losses to spontaneous decay is

$$\zeta=\frac{2\Gamma_s}{\Gamma_0+2\Gamma_s}. \tag{69}$$

This is almost the self-evident branching ratio. The extra factors of two are there because photodissociation rate depends on intensity, and thus on time.

### *3. Photoassociation yield*

One may study photoassociation yield as a function of the number of pulses by iterating Eqs. (56) numerically. However, instead of producing numerical data, we bring up a few qualitative points.

First suppose that there were no leakage due to spontaneous emission, $\Pi_{a\rightarrow l}=\Pi_{m\rightarrow l}=0$. Photoassociation yield may then be found as the invariant distribution (same for $n$ and $n+1$) of Eqs. (56). Using Eqs. (62) and (67), we have

$$P=\frac{\displaystyle\prod_{a\rightarrow m}}{\displaystyle\prod_{m\rightarrow a}+\prod_{a\rightarrow m}}\simeq\frac{\rho\lambda_D^3}{\sqrt{2\pi}+\rho\lambda_D^3}. \tag{70}$$

Conversion of a degenerate sample of atoms to ground state molecules with near-unit efficiency is possible in principle.

Next allow for nonzero spontaneous leakage. Technically, the pool $l$ is what is known as absorbing state for the Markov chain described by Eqs. (56). In physical terms, in the limit of large pulse number, all atoms are lost to spontaneous leakage. Nonetheless, let us consider the case of an ultradegenerate atomic sample, so that $\Pi_{a\rightarrow m}\gg\Pi_{m\rightarrow a},\Pi_{m\rightarrow l}$, and pulse numbers $n\ll1/\Pi_{m\rightarrow a},1/\Pi_{m\rightarrow l}$, so that we may ignore all transitions that break up ground-state molecules. Under these conditions a quasi-steady state valid for $1/(\Pi_{a\rightarrow m}+\Pi_{a\rightarrow l})\ll n\ll1/(\Pi_{m\rightarrow a}+\Pi_{m\rightarrow l})$ is found from Eqs. (56) as

$$P=\frac{\Pi_{a\rightarrow m}}{\Pi_{a\rightarrow m}+\Pi_{a\rightarrow l}}=1-\eta\simeq\frac{|\Omega_0|^2}{\Gamma_s\theta+|\Omega_0|^2}. \tag{71}$$

Branching between the transitions from atoms to molecules and from atoms to spontaneous-emission losses then determines the photoassociation yield. Interestingly enough, the yield may be adjusted by tuning the bound-bound Rabi frequency $\Omega_0$. Given microkelvin temperatures or lower, a Rabi frequency satisfying $\Omega_0\gg\Gamma_s,\theta\simeq k_BT/\hbar$ is nothing unusual in discrete atomic and molecular transitions. Efficient conversion of atoms into molecules is feasible for dense atomic samples in spite of spontaneous losses.

Conversely, suppose that the initial gas is nondegenerate, so that $\Pi_{m\rightarrow a}\gg\Pi_{a\rightarrow m},\Pi_{a\rightarrow l}$. For pulse numbers $n$ such that $1/(\Pi_{m\rightarrow a}+\Pi_{m\rightarrow l})\ll n\ll1/(\Pi_{a\rightarrow m}+\Pi_{a\rightarrow l})$, a quasisteady state still has $P_a\simeq1$, and so Eqs. (56) give

$$P\simeq\frac{\Pi_{a\rightarrow m}}{\Pi_{m\rightarrow a}+\Pi_{m\rightarrow l}}\ll\frac{\Pi_{m\rightarrow a}}{\Pi_{m\rightarrow a}+\Pi_{m\rightarrow l}}=1-\zeta\simeq\frac{\Gamma_0}{\Gamma_0+2\Gamma_s}. \tag{72}$$

Unless the gas is degenerate so that $\rho\lambda^3\gg1$, branching between photodissociation and spontaneous emission sets a limit on photoassociation yield.

Although the scaling in the first (approximate) equality in Eq. (72) actually is such that photoassociation yield is independent of intensity, at some level one will always meet with competition between spontaneous emission and light-induced transitions. The characteristic scale for the effects of light is the photodissociation rate $\Gamma_0$, which winds up being compared with the rate of spontaneous emission $\Gamma_s$. For a typical dipole transition in a molecule, it takes [8] a laser intensity of the order of 100 W/cm$^2$ to reach a photodissociation rate such that $\Gamma_0\sim\Gamma_s$.

## D. Discussion of two-color schemes

Our focus is on photoassociation of a highly degenerate atomic sample using two pulsed lasers. Spontaneous losses from the intermediate state always set the ultimate limit on photoassociation yield. Nonetheless, according to Eq. (71), the unwanted branching may be controlled by adjusting the parameters of the light that drives the *discrete* molecular transition. Highly efficient production of ground-state molecules appears possible in spite of losses to spontaneous emission.

Since the result of Eq. (71) is somewhat counterintuitive, we will reaffirm it using simple arguments. First, as is obvious from Eq. (58), the population of the bound state during the light pulse is of the order $|\kappa_0/\delta|^2$. This population will last a time of the order of the pulse duration $\tau$, and leads to spontaneous emission losses proportional to $P_s\sim|\kappa_0/\delta|^2\tau\Gamma_s$. On the other hand, according to the Hamiltonian of Eq. (55), the initial QC state is coupled to the ground state by the familiar two-photon Rabi frequency $|\kappa_0\Omega_0/\delta|$. In the continuum limit this is small, so that Rabi oscillations back and forth between the ground state and the QC state do not occur within our premises. Instead, the ground-state amplitude simply grows at a rate proportional to the Rabi frequency. At the end of the pulse the amplitude therefore is of the order $|\kappa_0 \Omega_0/\delta|\tau$. The probability that the system has made a transition to the ground state is the square of the latter $P_g \sim |\kappa_0 \Omega_0/\delta|^2 \tau^2$. The branching ratio between spontaneous emission and transitions to the ground state thus is

$$\frac{P_s}{P_g} \sim \frac{\Gamma_s}{|\Omega_0|^2 \tau}. \tag{73}$$

This may indeed be made arbitrarily small by increasing the Rabi frequency $|\Omega_0|$.

The reason for such advantageous branching is that, in the case of a two-photon resonance with an off-resonant intermediate state, the light-dressed ground state of the molecule acquires only a small admixture $\propto \Omega_0^2/\delta^2$ of the character of the excited state that is subject to spontaneous-emission losses. In addition, after the light pulse acting on the discrete transition has passed adiabatically, the dressed ground state has turned into the pure ground state again. This state of affairs is to be compared with the schemes considered previously [6,14], in which the intermediate state is also on resonance. The relevant dressed states are then fifty-fifty admixtures of the ground and intermediate states. In the normal course of affairs, after the light pulses the molecule will be left in this same admixture of ground and intermediate states. Half of the molecules will subsequently branch to spontaneous emission, and even more are lost if the pulses are long enough so that the molecules may decay substantially during the pulses.

In a continuous-wave experiment with an electronically excited intermediate state, the desired ground-state molecules would eventually be lost to spontaneous decay as they cycle back to the intermediate state. For this reason alone, we expect pulsed schemes to dominate in the experiments. Short pulses bring additional advantages. First, thanks to spectral broadening, it is possible to influence the entire thermal distribution of the atoms at once. Second, by adjusting the duty cycle, one may adjust the overall time scale of atom-molecule conversion. In this way, it might be possible to let the atoms thermalize between the pulses, and let the two-photon coherences decay away. Third, short pulses may be produced at much higher intensities than continuous-wave light. This is important in the case of a nondegenerate sample, when branching between spontaneous emission and photodissociation gives one, and possibly the dominant, limitation on photoassociation yield. By increasing the peak intensity, one may improve the yield.

## IV. CONCLUSIONS

We have presented a quasicontinuum model of free-bound transitions. The main achievement is that the model facilitates a treatment of photoassociation as a few-level problem analogous to the standard models in quantum optics and laser spectroscopy. The decades of experience accumulated in these disciplines is thus transferable to problems involving photoassociation. As first illustrations, we have discussed the absence of coherent power broadening, and sketched a two-level density matrix approach for the studies of the effects of atom-atom collisions on photoassociation.

As a further example of the few-level philosophy, we have addressed two-color photoassociation in a free-bound-bound scheme. Dressed states, dark state, two-photon resonance, and other standard paraphernalia of theoretical laser spectroscopy were found to bear on the problem. Our emphasis was on devising ways to avoid spontaneous-emission losses of atoms from the intermediate molecular state in two-color photoassociation. We have discussed the advantages of two-photon processes, as opposed to two-step processes, and of pulsed excitation. In a degenerate sample it is possible to achieve a near-unit photoassociation yield even in the presence of severe spontaneous losses from the intermediate-state, and the high intensity of pulsed lasers could improve photoassociation yield in a nondegenerate sample.

We have focused on theoretical concepts related to few-level modeling of QC systems, and have nonchalantly ignored experimental complications. For instance, we have assumed that the molecules stay around arbitrarily long, i.e., that they are trapped [21]. We have also taken the continuum limit for the atoms, even though in a tight enough trap the relative motion of two atoms should really be treated as a QC. Our theoretical machinery has its rough spots as well. As an example, we have used the Maxwell-Boltzmann velocity distribution while at the same time discussing degenerate gases.

The next logical step in our endeavor is to consider explicitly the quantum degeneracy of both the atoms and the molecules. Having already included these considerations into a description of one-color photoassociation in a Bose-Einstein condensate [22], we are currently working on the free-bound-bound analysis. From a theoretical viewpoint, the major change is that in a degenerate sample one winds up dealing with a transition *amplitude* that characterizes a (large) number of colliders, while here we add transition *probabilities*. Besides the Maxwell-Boltzmann statistics, the field theory approach we are currently developing could cure also the other ills we have mentioned in the preceding paragraph. Nonetheless, the quantum degenerate methods are still based on the QC picture. Our future progress should not supersede the present paper, but rather build on it.

## ACKNOWLEDGMENTS

Support from the NSF under Grant Nos. CHE-9612207 and PHY-9801888, and from NASA under Grant No. NAG8-1428, is gratefully acknowledged. We would also like to thank Edward Eyler, Phillip Gould, and William Stwalley for helpful discussions. M.M. would like to thank NASA's Connecticut Space Grant College Consortium for its generous support, as well as Marin Pichler and Steven Gensemer for sharing their insight into the experimental situation.

[1] A. S. Coolidge, H. M. James, and R. D. Present, J. Chem. Phys. **4**, 193 (1936); A. S. Coolidge and H. M. James, Phys. Rev. **55**, 184 (1939), and references therein.

[2] S. N. Bose, Z. Phys. **26**, 178 (1924); A. Einstein, Sitzungsber. K. Preuss. Akad. Wiss. **1925**, 3 (1925).

[3] P. D. Lett, K. Helmerson, W. D. Phillips, L. P. Ratliff, S. L. Ralston, and M. E. Wagshul, Phys. Rev. Lett. **71**, 2200 (1993); V. Bagnato, L. Marcassa, C. Tsao, Y. Wang, and J. Weiner, *ibid.* **70**, 3225 (1993); J. D. Miller, R. A. Cline, and D. J. Heinzen, *ibid.* **71**, 2204 (1993); D. Leonhardt and J. Weiner, Phys. Rev. A **52**, R4332 (1995); E. R. I. Abraham, N. W. M. Ritchie, W. I. McAlexander, and R. G. Hulet, J. Chem. Phys. **103**, 7773 (1995); H. Wang, P. L. Gould, and W. C. Stwalley, Phys. Rev. A **53**, R1216 (1996).

[4] M. H. Anderson, J. R. Ensher, M. R. Matthews, C. E. Wieman, and E. A. Cornell, Science **269**, 198 (1995); K. B. Davis, M.-O. Mewes, M. R. Andrews, N. J. van Druten, D. S. Durfee, D. M. Kurn, and W. Ketterle, Phys. Rev. Lett. **75**, 3969 (1995); C. C. Bradley, C. A. Sackett, and R. G. Hulet, *ibid.* **78**, 985 (1997); D. J. Han, R. H. Wynar, Ph. Courteille, and D. J. Heinzen, Phys. Rev. A **57**, R4114 (1998); U. Ernst, A. Marte, F. Schreck, J. Schuster, and G. Rempe, Europhys. Lett. **41**, 1 (1998); L. Vestergaard Hau, B. D. Busch, C. Liu, Z. Dutton, M. M. Burns, and J. A. Golovchenko, Phys. Rev. A **58**, R54 (1998).

[5] E. R. I. Abraham, W. I. McAlexander, C. A. Sackett, and R. G. Hulet, Phys. Rev. Lett. **74**, 1315 (1995); E. Tiesinga, C. J. Williams, P. S. Julienne, K. M. Jones, P. D. Lett, and W. D. Phillips, J. Res. Natl. Inst. Stand. Technol. **101**, 505 (1996); C. C. Tsai, R. S. Freeland, J. M. Vogels, H. M. J. M. Boesten, B. J. Verhaar, and D. J. Heinzen, Phys. Rev. Lett. **79**, 1245 (1997).

[6] P. S. Julienne, K. Burnett, Y. B. Band, and W. C. Stwalley, Phys. Rev. A **58**, R797 (1998).

[7] J. Javanainen and M. Mackie, Phys. Rev. A **58**, R789 (1998).

[8] H. R. Thorsheim, J. Weiner, and P. S. Julienne, Phys. Rev. Lett. **58**, 2420 (1987); R. Napolitano, J. Weiner, C. J. Williams, and P. S. Julienne, *ibid.* **73**, 1352 (1994).

[9] Y. B. Band and P. S. Julienne, Phys. Rev. A **51**, R4317 (1995).

[10] R. Côté and A. Dalgarno, Chem. Phys. Lett. **279**, 50 (1997).

[11] P. Pillet, A. Cruebellier, A. Bleton, O. Dulieu, P. Nosbaum, I. Mourachko, and F. Masnou-Seeuws, J. Phys. B **30**, 2801 (1997).

[12] A. Vardi, D. Abrashkevich, E. Frishman, and M. Shapiro, J. Chem. Phys. **107**, 6166 (1997).

[13] J. H. Eberly, J. J. Yeh, and C. M. Bowden, Chem. Phys. Lett. **86**, 76 (1982); P. W. Milonni *et al.*, Phys. Rev. A **28**, 32 (1983).

[14] J. L. Bohn and P. S. Julienne, Phys. Rev. A **54**, R4637 (1996).

[15] M. Mackie, Ph.D dissertation, University of Connecticut (1999).

[16] E. Kyrölä, J. Opt. Soc. Am. B **1**, 737 (1984); J. Javanainen and E. Kyrölä, Opt. Commun. **56**, 17 (1985); E. Kyrölä, J. Opt. Soc. Am. B **3**, 453 (1986).

[17] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1972).

[18] C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg, *Atom-Photon Interactions* (Wiley, New York, 1992).

[19] S. Stenholm, *Foundations of Laser Spectroscopy* (Wiley, New York, 1984); P. Meystre and M. Sargent, *Elements of Quantum Optics*, 2nd ed. (Springer, Berlin, 1991).

[20] J. Javanainen, J. Phys. B **16**, 1343 (1983); Opt. Commun. **46**, 175 (1983); Phys. Scr. **31**, 57 (1985).

[21] T. Takekoshi, B. M. Patterson, and R. J. Knize, Phys. Rev. Lett. **81**, 5105 (1998).

[22] J. Javanainen and M. Mackie, Phys. Rev. A **59**, R3186 (1999).