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Probability of photoassociation from a quasicontinuum approach

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We examine photoassociation by using a quasicontinuum to describe the colliding atoms. The quasicontinuum system is analyzed using methods adapted from the theory of laser spectroscopy and quantum optics, and a continuum limit is then taken. In a degenerate gas the equilibrium probability of photoassociation may be close to unity. In the continuum limit, for a thermal atomic sample, the stimulated Raman adiabatic passage (STIRAP) mechanism cannot be employed to eliminate unwanted spontaneous transitions.
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At the lowest temperatures reached by laser cooling and evaporative cooling, the range of thermal energies of atoms translates into a range of frequencies that is narrower than a typical atomic linewidth. An optical transition that combines two thermal atoms into a molecule, i.e., a laser-induced transition from the continuum of the relative motion of two atoms to a bound vibrational state of a molecule, may therefore exhibit a narrow resonance. In photoassociation (PA) spectroscopy these resonances are utilized to measure positions of vibrational levels of diatomic molecules [1]. The results include improved determinations of molecular potential surfaces [2], *s*-wave scattering lengths [3], and dipole matrix elements for *atomic* transitions [4]. PA is also a potential method to create cold molecules in a predetermined internal state [5–7].

In addition to its utility, PA is also an interesting theoretical challenge, in that it is a case of *free-bound* transitions. As is appropriate for free initial states, past analyses of PA are often based on collision theory [1,6,8,9]. Other theoretical approaches include direct integration of the Schrödinger equation for the colliding atomic wave packets [7] and a perturbative treatment within the density-matrix formalism [10]. In this paper, we take yet another tack. We assume that the colliding atoms are confined to a finite volume. This converts the continuum of the dissociated states of the molecule into a quasicontinuum (QC). We analyze the QC system, and finally take the continuum limit by letting the quantization volume go to infinity [11]. We first study PA, including a simple model for rethermalizing collisions between the atoms. The result surprisingly suggests that the equilibrium yield of PA may approach unity in systems near or at quantum degeneracy, such as in Bose-Einstein condensates in alkali-metal vapors [12]. Second, we put forth that, unlike in discrete-level atomic systems, in PA the stimulated Raman adiabatic passage (STIRAP) process [13] is unlikely to provide relief to the problem of unwanted spontaneous emissions.

The QC consists of discrete energy eigenstates. Much of the understanding of, and insights into, few-level systems that has evolved in laser spectroscopy and quantum optics [14] may thus be transferred to problems of PA. One could achieve a similar discretization by utilizing normalizable wave packets along the lines of Ref. [7]. However, to complete an analysis of this type, one has to construct an ensemble of wave packets to represent a thermal gas and then average over the ensemble. Within our QC method the required average follows trivially from statistical mechanics.

We first model the case in which PA takes place directly to a stable bound state of the molecule. The applied light is then the only mechanism for transitions to and from the bound state. The bound state $|b\rangle$, whose energy we set equal to zero, is coupled with a QC of states $|n\rangle$ with evenly spaced eigenfrequencies $\omega_n = n\epsilon$. For the time being the QC is assumed to be flat; i.e., the coupling matrix element between $|b\rangle$ and $|n\rangle$ $\kappa_n \equiv \kappa$ is taken to be the same for all $n = 0, \pm 1, \pm 2, \ldots$. For photodissociation (PD) and PA the coupling would normally be due to dipole interactions of the atoms with a laser field. Within the rotating-wave approximation we have $\kappa = dE/2\hbar$, where E is the amplitude of the electric field and d is the (assumedly) constant dipole matrix element between the bound state and the QC states. The choice of the QC state $n=0$ is such that the transition $|b\rangle \rightarrow |0\rangle$ is on optical resonance.

The Hamiltonian for this system is

$$\frac{H}{\hbar} = \sum_n |n\rangle \omega_n \langle n| - \sum_n (\kappa |n\rangle\langle b| + \kappa^* |b\rangle\langle n|). \qquad (1)$$

Writing the state vector as $|\psi\rangle = b|b\rangle + \Sigma_n a_n |n\rangle$, we find the time-dependent Schrödinger equation

$$\dot{b} = i\kappa^* \sum_n a_n, \quad \dot{a}_n = -i\omega_n a_n + i\kappa b. \qquad (2)$$

We use Fourier transforms to solve these differential equations with constant coefficients. For the solution, a self-energy is needed. Here we resort to a continuum approximation,

$$\Sigma(\omega) = |\kappa|^2 \sum_{n=-\infty}^{\infty} \frac{1}{\omega - \omega_n + i\eta} \simeq |\kappa|^2 \int dn \, \frac{1}{\omega - n\epsilon + i\eta} = \frac{\pi |\kappa|^2}{\epsilon}, \qquad (3)$$

with $\eta = 0+$. The continuum approximation (3) is valid as long as one considers times short enough that the discreteness of the QC states is not resolved, $t \sim \omega^{-1} \lesssim \epsilon^{-1}$. We have verified this with extensive numerical studies of the Schrödinger equation.

With the continuum approximation, Eqs. (2) are easy to solve. We first model PD; the system starts in the bound state and winds up in the QC. The initial conditions are $b(0)=1$, $a_n(0)=0$. The result is a simple exponential decay of the bound-state population to the QC at the PD rate $\Gamma=2\pi|\kappa|^2/\epsilon$.

Let us pause for a crucial mathematical remark. One sees from Eqs. (2) that the QC state amplitudes a_n respond to the time evolution of the bound-state amplitude b, and that the changes in a_n then couple back to b. It may be easily shown that, within the continuum approximation (3), the *only* effect of such back action of the bound-state amplitude on itself via the QC is exponential damping, $\dot{b}=-\gamma b+\cdots$, with $\gamma\equiv\Gamma/2$. A roughly equivalent way of stating this is that once the system has made a transition from the bound state to the QC, it will not return to the bound state. This is because the phases of the amplitudes of the QC states are such that, up to times of the order $t\sim\epsilon^{-1}$, transitions back to the bound state interfere destructively.

The continuum limit of the QC model is effected by letting the spacing of QC levels go to zero, $\epsilon\to 0$. Obviously, for a given laser tuning and intensity one should retain a PD rate Γ that is in agreement with, say, measurements or molecular-structure calculations. We achieve this by setting $\epsilon\to 0$ and $|\kappa|^2\to 0$ in such a way that $\Gamma=2\pi|\kappa|^2/\epsilon$ remains constant. With the continuum limit the time over which our continuum approximation (3) is valid, $\simeq\epsilon^{-1}$, automatically tends to infinity [15].

Of course, it is well known that exponential decay follows when a discrete state is coupled to a true (and flat) continuum. Until now, the two main purposes of our discussion have been to demonstrate that the same behavior emerges for a QC, and to derive the quantitative connection between a QC and a continuum.

We now move on to a model of PA. Suppose that the system starts out in the QC state $|m\rangle$; $b(0)=0$, $a_n(0)=\delta_{mn}$. Once the system has made a transition to the bound state, subsequent interactions between the bound state and the QC states simply amount to a damping of the bound state. Our key realization is that the states $|b\rangle$ and $|m\rangle$ thus behave as a two-level system with the Rabi frequency κ, albeit not as a closed one; the population of the bound state decays at the rate Γ to the QC states that for the purpose of the two-level system $\{|b\rangle, |m\rangle\}$ are unobservable.

This minor complication is easy to take into account in the familiar analysis of two-level systems. We find the rate of transitions $|m\rangle\to|b\rangle$, which we write, using the relation $\Gamma=2\pi|\kappa|^2/\epsilon$, as

$$R_m=\frac{2|\kappa|^2\gamma}{\omega_m^2+\gamma^2}=\frac{\gamma\Gamma\epsilon/\pi}{\omega_m^2+\gamma^2}. \tag{4}$$

Over the relevant time scale Γ^{-1}, the depletion of the initial state is proportional to ϵ. The balancing PD removes probability out of the state $|b\rangle$ at the rate Γ, so that the population of the bound state $P=R_m/\Gamma$ is also proportional to ϵ. In the continuum limit, $\epsilon\to 0$, the initial state $|m\rangle$ is not depleted at all, and the population of the bound state tends to *zero*. We have seemingly banished PA. The resolution of this dilemma is sought next.

To begin with, we set up a link between our QC model and collision physics. First, we need a QC for two atoms. Second, in collisions it is customary to consider partial waves one by one, so that our QC should have angular momentum l as a good quantum number. We achieve both ends by quantizing the relative motion of two colliding atoms in a spherical potential well with radius R, using reflecting boundary conditions at the surface.

Finding and counting the eigenstates of a free particle in the well is a straightforward exercise, which we discuss in detail elsewhere [16]. The level spacing ϵ indeed tends to zero in the limit $R\to\infty$, and so does the PA rate. At this point, though, we may see why such a seemingly bizarre behavior is as it should be. We are discussing *exactly* two atoms. When the volume holding the atoms tends to infinity, atom density tends to zero and collisions must cease.

To regain a finite PA rate with increasing radius R of the quantization volume, we evidently must increase the number of colliders N in such a way that the density $\rho=3\pi N/4R^3$ remains constant. We thus multiply the rate R_m for the transition $|m\rangle\to|b\rangle$ obtained for one collider, by N. Second, in an isotropic ensemble only a fraction of the atoms is actually in the given angular-momentum state l, so that we must adjust the density in a manner that depends on both l and R. All told, it turns out that in the continuum limit the one-pair rate R_m should be multiplied by the factor

$$F_l=2\pi^2(2l+1)\,\frac{\rho v}{k^2}\times\frac{1}{\epsilon}. \tag{5}$$

Here, the wave number k encodes the collision energy $E=\hbar^2k^2/2\mu$, with μ being the reduced mass and $v=\hbar k/\mu$ the collision velocity. The rate of PA for the given angular momentum is

$$\mathcal{R}_m=F_l\,R_m=\frac{\gamma\Gamma}{\omega_m^2+\gamma^2}\times 2\pi(2l+1)\,\frac{\rho v}{k^2}. \tag{6}$$

Our Eq. (6) is in complete agreement with earlier results from collision theory. Equations (1) and (3) of Ref. [8] provide a particularly transparent comparison.

For the sake of argument, we next introduce three experimental assumptions. First, we assume that atoms and molecules alike are trapped. Under such conditions, PD of the bound state redistributes the atoms over the QC states. The molecules do not stay in the state doublet $|b\rangle$, $|m\rangle$, and one might as well allow a probability distribution P_m of colliding atom pairs over the QC states $|m\rangle$ to begin with [17]. Second, we take the trap to be big enough that the actual discreteness of the center-of-mass states may be ignored [18]. Third, we assume that, whether as a result of atom-atom collisions or, say, laser cooling, the atoms rethermalize on a time scale τ_c that is short compared to the time it takes to cycle an atom through PA and PD.

Two significant consequences arise from the third assumption. First, the coherent interaction between the states $|m\rangle$ and $|b\rangle$ is interrupted by collisions, which leads to collision broadening. The usual modeling in spectroscopy directs us to replace the linewidth γ in Eq. (6) (but *not* the factor Γ) by a collision broadened linewidth $\gamma_c\simeq\gamma+\tau_c^{-1}$. Second, the system presents the same QC occupation prob-

abilities P_m with and without the laser field, except that, with the laser on, these probabilities should be reduced by the factor $(1-P)$ if a substantial fraction P of the atoms wind up as molecules in the bound state. Overall, we model the evolution of the occupation probability of the bound state P with the simple rate equation

$$\dot{P}=\mathcal{R}(1-P)-\Gamma P, \tag{7a}$$

$$\mathcal{R}=\sum_m \mathcal{R}_m P_m . \tag{7b}$$

The time scale for a PA $\rightarrow$ PD cycle is seen to be the longer of $\mathcal{R}^{-1}$ and Γ^{-1}. Our technical assumption about the collision time is valid if either $\mathcal{R}\tau_c \lesssim 1$ or $\Gamma\tau_c \lesssim 1$. This may always be achieved by choosing a low enough laser intensity.

It basically remains to clean up the notation. First, suppose that the laser is tuned so that a bound state and a state with the energy $\hbar\Delta$ above the continuum threshold are on resonance. The PA rate depends on the resonant continuum state, so we have to use the appropriate value for the PD rate Γ. Second, as in Eq. (7b), we average over the distribution of the relative energies of the colliding atoms. We adopt the Maxwell-Boltzmann distribution at temperature T. We also make the assumption that $\gamma_c \ll k_B T/\hbar$. Then, a Lorentzian resonance line with width γ_c effectively acts as a δ function in energy in the sum (7b). For the s wave $(l=0)$ we find

$$\mathcal{R}=\rho\lambda_D^3\, e^{-\hbar\Delta/k_B T}\,\Gamma, \tag{8}$$

where $\lambda_D=(2\pi\hbar^2/\mu k_B T)^{1/2}$ is the conventional thermal de Broglie wavelength, albeit for the reduced mass $\mu=m/2$ instead of the atom mass m. The steady-state occupation probability of the bound state is

$$P=\frac{\rho\lambda_D^3\, e^{-\hbar\Delta/k_B T}}{1+\rho\lambda_D^3\, e^{-\hbar\Delta/k_B T}}. \tag{9}$$

In a degenerate atomic sample with $\rho\lambda_D^3 \gtrsim 1$, the PA probability may approach unity. The results do not depend critically on the technical assumption that $\gamma_c \ll k_B T/\hbar$; except for a factor of the order of unity, Eq. (8) remains valid all the way to the optimal overlap between the velocity distribution and the PA resonance that occurs with $\hbar\Delta \simeq \hbar\gamma_c \simeq k_B T$.

Of course, we have resorted to a classical counting of atomic states and to the Maxwell-Boltzmann velocity distribution, so that in the limit of a degenerate gas the functional form of Eq. (9) must be taken with a grain of salt. We believe, though, that the qualitative features of our results survive a full quantum degenerate analysis. Generally speaking, the PA rate scales with atom density as ρ^2 and the competing PD rate as ρ, so that the equilibrium PA yield must involve a dimensionless parameter made of atom density. In our example the density parameters for PA yield and atom degeneracy are essentially the same. The degree of degeneracy in itself is unlikely to change this state of affairs.

In a practical experiment one usually photoassociates ground-state atoms into electronically excited molecules. The latter decay spontaneously to both bound vibrational states of lower-lying electronic manifolds and to a wide band of energies in the continuum of the relative motion of two atoms. Next, we investigate within our QC model a scheme that has been suggested [7] as a means of keeping spontaneous emission in check.

For background, first consider an ordinary discrete three-level atom $\{|m\rangle,|b\rangle,|f\rangle\}$, with the Rabi frequencies $\kappa(t)$ and $\Omega(t)$ driving the respective transitions $|m\rangle\rightarrow|b\rangle$ and $|b\rangle\rightarrow|f\rangle$. The idea of STIRAP goes as follows [13]. Suppose that the transition $|m\rangle\rightarrow|f\rangle$ is on exact two-photon resonance, upon which one can always make one atom-field dressed state as a linear combination of the states $|m\rangle$ and $|f\rangle$ without involving the state $|b\rangle$. If one adjusts the time evolution of the Rabi frequencies in such a way that first $\Omega(t) \gg \kappa(t)$ and at later times $\kappa(t) \gg \Omega(t)$ (''counterintuitive pulse order''), for $t\rightarrow-\infty$ this dressed state coincides with the atomic state $|m\rangle$ and for $t\rightarrow\infty$ it coincides with the state $|f\rangle$. If the dressed state evolves from $|m\rangle$ to $|f\rangle$ adiabatically, an atom starting in the state $|m\rangle$ will end up in the state $|f\rangle$ without ever visiting the intermediate state $|b\rangle$.

In the case of a molecule, one picks a stable vibrational state $|f\rangle$ from the electronic ground state and sets up a coherent, two-photon resonant process $|m\rangle\rightarrow|b\rangle\rightarrow|f\rangle$ by adding another laser with Rabi frequency Ω between the states $|b\rangle$ and $|f\rangle$. The suggestion in Ref. [7] is to utilize STIRAP in such free-bound-bound processes to bypass the intermediate state troubled by spontaneous decay.

Within our QC method, we may similarly discuss the system of two discrete states $|f\rangle$ and $|b\rangle$ and a QC of states $|m\rangle$. As before, from the point of view of the three-level system that ensues for each fixed $|m\rangle$, the sole effect of the QC is to make a sink for the population of the intermediate state $|b\rangle$. Spontaneous transitions to states that are not included in our QC model simply add to the rate at which the system leaks out of the three active states via the intermediate state.

The problem with free-bound-bound STIRAP is now obvious. In the continuum limit the Rabi frequency of the $|b\rangle\rightarrow|m\rangle$ transition tends to zero, $\kappa\propto\sqrt{\epsilon}\rightarrow 0$. It is therefore impossible to effect the reversal of the relative sizes of Ω and κ required for STIRAP. Though STIRAP clearly occurs with properly timed atomic wave packets and laser pulses as in Ref. [7], we believe that, in a gas whose density operator is diagonal in the energy representation (such as a thermal gas), it is washed away by the requisite average over the ensemble of colliding wave packets. The trademark signatures of STIRAP, such as optimal population transfer with counterintuitive pulse order, will probably be absent in PA [18].

Even though the three-level scheme $|m\rangle\rightarrow|b\rangle\rightarrow|f\rangle$ cannot directly draw from STIRAP, it may be beneficial for other reasons [16]. For instance, the molecules are guided into a selected stable state $|f\rangle$. Overall, though, we wonder if eventually a direct two-level transition *down in energy* from the continuum to a vibrational state of the ground-state electronic manifold might be a viable option for creating cold molecules in a specific state. Such schemes may require inconvenient wavelengths and suffer from unfavorable transition matrix elements. However, once cold molecules can be trapped, spurious spontaneous branching may be a more serious problem than a low PA rate.

The one general caveat about the relation between molecular processes and QC models has to do with our assump-

tion that the QC is flat. In reality the rate of PD varies depending on where in the PD continuum the laser deposits the atoms. As long as the detuning-dependent rate $\Gamma(\Delta)$ is much smaller than its scale of variation with the detuning Δ, the same kind of exponential damping of the bound state as in the case of a flat continuum may be expected [19]. However, along with the PA rate come frequency shifts of the QC relative to the discrete states coherently coupled to it. Such shifts are proportional to laser intensity, by rule of thumb of the order of Γ, but their precise values depend on the shape of the entire continuum [19]. The shifts are difficult to calculate, and difficult to measure. One should always bear in mind that in PA both transition rates *and* level energies depend on laser intensity.

As it comes to the fundamentals, such as PA rate in the free-bound scheme, our model agrees with the earlier collision work. However, the density parameter $\rho\lambda_D^3$ does not seem to have been unveiled before. Besides, we can easily go, and have gone, further than collision theory analyses do. We have incorporated a transfer of atoms to and *from* the bound state, plus a simple model of rethermalizing collisions between the atoms, and thus obtained an *equilibrium* probability of PA (9). We may also treat [16] coherent transient schemes [7] without conceptual difficulty.

Whether our observations are helpful in eventual experiments remains to be seen, but we hope to have made a methodological point anyway: We have developed a framework for PA that enables one to draw from all of the understanding and insights that have accumulated over decades of laser spectroscopy and quantum optics. The results suggest that at atom densities approaching quantum degeneracy, near-unit PA efficiencies may be reached. Detailed many-body analyses with proper inclusion of photon recoil, propagation of light through the sample, etc., remain to be carried out. Nonetheless, we speculate that even in steady state, PA may convert a Bose-Einstein condensate of cold atoms into a Bose-Einstein condensate of diatomic molecules.

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