Comment on "Quasicontinuum modeling of photoassociation"

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(Received 6 December 1999; published 4 January 2002)

We maintain that the reservations against the use of stimulated Raman adiabatic photoassociation in a nondegenerate gas, expressed by Mackie and Javanainen in a recent manuscript [Phys. Rev. A **60**, 3174 (1999)], do not account for the coherence induced by the photoassociating laser. The authors treat the problem of two-color stimulated photoassociation using a set of decoupled three-mode problems, each containing a box eigenstate and the two bound states. We argue that such decomposition is not justified, since in the limit of a very large box all three-mode problems are, in fact, coherently coupled. The three-mode condition can only be met with a set of wave packets whose bandwidth matches the spectral width of the photoassociating pulse. Using this basis set, we show that by the authors' own formalism; stimulated Raman photoassociation is a viable process in the thermal ensemble.

DOI: 10.1103/PhysRevA.65.027401 PACS number(s): 34.50.Rk

A recent article by Mackie and Javanainen [1] provides the details of a previously published theoretical analysis of photoassociation [2]. The authors use box quantization to depict the dissociation continuum. Starting with one bound state coupled to the quasicontinuum, they obtain the following equations of motion for the population amplitudes,

$$\dot{b} = i\kappa^* \sum_n a_n + b(0)\,\delta(t), \tag{1a}$$

$$\dot{a}_n = -i\omega_n a_n + i\kappa b + a_n(0)\,\delta(t), \tag{1b}$$

where b is the bound state amplitude, a_n are the quasicontinuum amplitudes, $\omega_n = n\varepsilon$ (ε being the spacing between the quasicontinuum states) is the energy of the nth box state, and κ (assumed to be independent of n, i.e., "flat continuum") is the bound-free coupling. Fourier transform methods are used to obtain the closed-form solutions

$$b(t) = \frac{i}{2\pi}\int d\omega \exp(-i\omega t)\left[\frac{1}{\omega + i\Gamma/2}\right] \times \left[\kappa^* \sum_n \frac{a_n(0)}{\omega - \omega_n + i\eta} + b(0)\right], \tag{3a}$$

$$a_n(t) = \frac{i}{2\pi}\int d\omega \exp(-i\omega t)\left\{\left[\frac{\kappa}{(\omega - \omega_n + i\eta)(\omega + i\Gamma/2)}\right] \times \left[\kappa^* \sum_n \frac{a_n(0)}{\omega - \omega_n + i\eta} + b(0)\right] + \frac{a_n(0)}{\omega - \omega_n + i\eta}\right\}, \tag{3b}$$

where $\Gamma = 2\pi|\kappa|^2/\varepsilon$ is the photodissociation rate. The authors rightly point out that at the continuum limit the number of continuum states coupled to the bound state increases to the same extent that the bound-free coupling decreases, resulting in a finite photodissociation rate. They then proceed to treat the reverse process of photoassociation, using the initial conditions

$$b(0) = 0, \quad a_n = \delta_{mn}, \tag{4}$$

which on substitution into Eq. (3a), result in the following dynamics for the bound-state amplitude:

$$b(t) = \frac{\kappa^*}{\omega_m + i\Gamma/2}[\exp(-i\omega_m t) - \exp(-\Gamma t/2)]. \tag{5}$$

By taking the continuum limit of this expression ($\epsilon \to 0$, $|\kappa|^2 \to 0$) the authors conclude that "the only effect of the light-induced coupling to the quasicontinuum on the bound-state amplitude is exponential damping," thereby dismissing the possibility of photoassociation. Consequently, they construct a damped two-level model that is supposed to correctly describe photoassociation. Generalizing their argumentation to a two-level system, coupled to a quasicontinuum, they claim that "as before, the coupling κ to the quasicontinuum vanishes in the limit $V \to \infty$ (where V is the box volume). It follows immediately that $\kappa \ll \Omega$ (Ω is the Rabi frequency for the transition between the two bound states) holds for a large volume. This is exactly the result that prohibits the adiabatic condition from being satisfied in a free-bound-bound stimulated adiabatic Raman passage (STIRAP) process [3]." Moreover "we should treat the free-bound coupling κ as a perturbation."

A basic assumption of box quantization is that the results of any such model should be completely independent of the box size or the particular basis set chosen to represent the continuum. Yet the results of Ref. [1] seem to be highly dependent on both. To illustrate this point, we consider a different set of continuum states, composed of superpositions of box eigenstates, or wave packets

$$\phi_m(t=0) = \sum_n a_{m,n}(0)\,\psi_n, \tag{6}$$

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where ψ_n are the box eigenstates. The photoassociation amplitude from ϕ_m at time t is given as

$$b_m(t)=\kappa^*\sum_n \frac{1}{\omega_n+i\Gamma/2}[a_{m,n}(0)\exp(-i\omega_n t) - \exp(-\Gamma t/2)]. \quad (7)$$

It is evident that the first associative term on the r.h.s. of Eq. (7) would couple more continuum levels to the bound state as the continuum limit is approached, thereby compensating for the reduction in the coupling of any single box state to the bound manifold. The number of terms in the sum

$$\sum_n \frac{1}{\omega_n+i\Gamma/2}a_{m,n}(0)\exp(-i\omega_n t) \quad (8)$$

increases at the continuum limit as $1/\varepsilon$, while their amplitudes scale down as $1/\sqrt{\varepsilon}$ to maintain normalization. Therefore, this sum increases as $1/\sqrt{\varepsilon}$. As the authors point out, the continuum limit is obtained by taking ε and κ to zero while maintaining a fixed $|\kappa|^2/\varepsilon$ ratio. Thus, by the authors own methodology, the first term on the r.h.s. of Eq. (7) converges to a nonzero (and not necessarily small) finite value at any given time. The ensemble yield is calculated by taking the bundle of wave packets $\{\phi_n\}_{n=1,N}$ and summing over association *probabilities* rather than amplitudes, as the authors suggest (and as indeed is appropriate for a thermal ensemble):

$$P_{mol}(t)=\sum_m |b_m(t)|^2. \quad (9)$$

Clearly, at any given time a certain fraction of the packets would have a good overlap with the bound state and this fraction would only depend on the *density* of particles (number of packets per box length) rather than on the particular choice of wave-packet parameters, leading to a fixed and finite photoassociation rate. This is the approach we have used in Ref. [3]. It is a manifestation of the fact that a certain fraction of the particles confined in the box, proportional to the pair density, do collide at any given instant. The free-bound transition amplitude for these colliding pairs is significant, and STIRAP is possible.

The apparent dependence of the viability of STIRAP on the choice of basis set is puzzling. According to Mackie and Javanainen, who use a basis-set of box eigenstates, STIRAP cannot be carried out due to the incompatibility of the free-bound rate and the bound-bound rate [1,2]. On the other hand, using a set of wave packets as we did, STIRAP is alive and well, at least for the subset of colliding particles [3]. Moreover, it appears that the choice of the wave-packet bandwidth (a box eigenstate is in fact, an infinitely narrow packet in energy domain) would affect the outcome of the calculation. Yet, the results could not possibly depend on the basis set.

The formalism of Mackie and Javanainen decomposes the problem of photoassociation in a thermal ensemble, into a set of three-mode problems (or two-mode problems in the one-color case). The total efficiency is obtained as appropriate, by incoherent summation over probabilities. However, the three-mode approximation works poorly for box eigenstates. Starting with the entire population in one such state, back dissociation would populate many neighboring states from which association can take place. Thus, all the three-mode problems are in fact, coherently coupled.

On the other hand, choosing a basis set of wave packets with the same spectral width as that of the photoassociating pulse, back dissociation would take place predominantly into the initial packet and the three-mode approximation would be justified. Two-color photoassociation in the thermal ensemble can thus be described to a very good approximation, by a set of decoupled three-mode problems, each containing a wave packet and the two-bound states. Moreover, the requirement for a three-mode description sets the correct wave-packet width. Any choice other than the bandwidth of the photoassociating laser pulse (including a box eigenstate), would invalidate the three-mode approximation. This is not to say that other basis sets are less correct. However, if they are to be used, incoherent summation over the three-mode problems [1,2] is not justified.

A simple analogy should make this point starkly clear. The $N\times N$ Hamiltonian, whose elements in one basis are

$$H_{ij}=\frac{1}{\sqrt{N-1}}\begin{pmatrix} 0 & 1 & \dots & 1 \\ 1 & 0 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 1 & 0 & \dots & 0 \end{pmatrix} \quad (10)$$

has $N-2$ zero eigenvalues, and two eigenvalues of ± 1. No time scale of order $(N-1)^{-1/2}$ is actually involved. And it is both entirely valid, and very convenient, to diagonalize H_{ij} by a change of basis.

To summarize, while the initial thermal density operator may be diagonal in eigenstates of energy [i.e., the initial conditions of Eq. (4) are as legitimate as others], the Hamiltonian used to propagate these states certainly is not. The authors' formalism does not allow for the coherence produced by the laser pulse. On the other hand, the choice of wave packets with energy width matching the pulse bandwidth, naturally reflects this coherence and (to a good approximation) diagonalizes the Hamiltonian. As this choice indicates that STIRAP is possible in a nondegenerate gas, to the extent that a thermal collision is possible, we conclude that the viability of adiabatic stimulated Raman photoassociation is not affected by the findings of Mackie and Javanainen. This simple analytical point is empirically confirmed by a recent experiment [4], clearly demonstrating coherent Raman resonances in the photoassociation of thermal cesium atoms.

All said, we acknowledge the importance of Bose stimulated collisions in allowing near-unity photoassociation efficiencies when the STIRAP process takes place in a quantum degenerate gas [5]. The collisional STIRAP process in the thermal ensemble, is essentially limited to the fraction of atoms colliding during the pulse time. Consequently, the photoassociation yield in a μK thermal ensemble of Na atoms was predicted to be 6×10^{-6} per 20-ns pulse [3]. This is

significantly different from the ''conventional'' STIRAP process involving three internal bound states, which offers nearly complete population transfer. In conducting free-bound-bound STIRAP starting with an atomic Bose-Einstein condensate, the three-level picture may be restored and the process efficiency dramatically increased.

This work was supported by the National Science Foundation through a grant for the Institute for Theoretical Atomic and Molecular Physics at Harvard University and Smithsonian Astrophysical Observatory.

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