VI. Coherent Control

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Quantum mechanics, though a probabilistic theory, gives a "deterministic" answer to the question of how the present determines the future. In essence, in order to predict future probabilities, we need to (numerically) propagate the time dependent Schrödinger equation from the present to the future. The field of *Quantum Control* deals with an important modification of this task, namely, it asks – given a wave function in the present, what dynamics (e.g. the Hamiltonian) guarantees a desired outcome ("objective") in the future?

In practice one can modify the Hamiltonian by introducing external fields (e.g. laser light). It is then possible to reach the objective in a "trial-and-error" fashion: to guess a Hamiltonian, propagate the initial wave function to the future, compare the result with the desirable objective, and correct the guess for the Hamiltonian until satisfactory agreement with the objective is reached.

A systematic way of executing this procedure is the sub-field called *Optimal Control*

This trial-and-error method is very time consuming, requiring the repeated solution of the time dependent Schrödinger equation. When the explicit time-dependent terms in the Hamiltonian merely serve to prepare a state which then evolves in the absence of an external field, or when its explicit time dependence can be treated adiabatically, there exists a much more elegant method, called *Coherent Control* (**CC**) which necessitates the solution of the (time-independent) Schrödinger equation, and this only once. Moreover, in that case, the CC solution allows for the simultaneous exploration of other possible future outcomes (and not just a single "desirable" objective) resulting from different preparations of the initial wave function.

VI.1 The Principles of Coherent Control

When discussing photodissociation we have seen that much of the difficulty in controlling future events arises from the generation of entangled states, leading to many possible future outcomes. We now show how to overcome this difficulty and disentangle material states, thus giving rise to just one, pre-chosen, future outcome.

VI.1 The Principles of Coherent Control

When discussing photodissociation we have seen that much of the difficulty in controlling future events arises from the generation of entangled states, leading to many possible future outcomes. We now show how to overcome this difficulty and disentangle material states, thus giving rise to just one, pre-chosen, future outcome.

We consider a photodissociation process of the type,

$$ABC \xrightarrow{\hbar\omega} ABC^* \rightarrow \left\{ \begin{array}{cccl} A & + & BC, & q=1 \\ B & + & AC, & q=2 \\ C & + & AB, & q=3 \end{array} \right. .$$

under the action of a light field of the form

$$\mathbf{E}(t) = \hat{\epsilon}\varepsilon(t) = \hat{\epsilon} \int d\omega \epsilon(\omega) \exp(-i\omega t).$$

If there is only one $|E_1\rangle$ "precursor" state,

$$b_{E,\mathrm{n}}(t) = \frac{-1}{i\hbar}\langle E, n^-|\mathrm{d}|E_1\rangle \int_{-\infty}^{t} dt'\varepsilon(t')b_1(t')e^{i(\omega_{E,1}-\omega_a)t'},$$

and the branching ratio to observe different final states is given at all times as

$$\frac{P_{E,n}(t)}{P_{E,m}(t)} = \left|\frac{b_{E,n}(t)}{b_{E,m}(t)}\right|^2 = \left|\frac{\langle E, n^-|\mathrm{d}|E_1\rangle}{\langle E, m^-|\mathrm{d}|E_1\rangle}\right|^2$$

and no control over this quantity via manipulation of laser fields appears possible.

This argument motivates the idea

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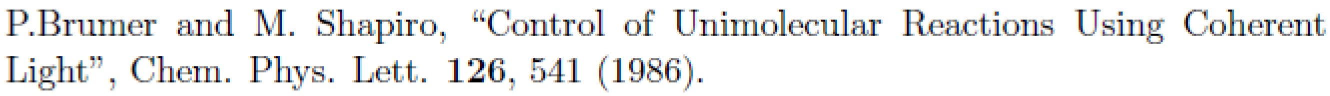

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This argument motivates the idea that the way to control photodissociation is to use more than one “precursor” state, or in greater generality, to use multiple excitation pathways to the same continuum state. We thus first extend the treatment of the previous lectures to the photodissociation of initial non-stationary *superposition* states,

$$|\,\chi(t)\,\rangle = \sum_i b_i(t)|E_i\rangle e^{-iE_i t/\hbar} \; .$$

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$$|\,\chi(t)\,\rangle = \sum_i b_i(t)|E_i\rangle e^{-iE_it/\hbar} \;.$$

Numerous experimental techniques can be used to create the $\chi(t)$ state. Whatever the method of preparation, the amplitude and phase of $b_i(t)$ and matrix elements connecting $|\,E_i\,\rangle$ to the continuum are functions of the experimentally controllable preparation and excitation lasers parameters.

With $\chi(t)$ as the initial state the system wave function can be expanded as,

$$|\,\Psi(t)\,\rangle = \sum_i b_i(t)e^{-iE_it/\hbar}|\,E_i\,\rangle + \sum_{n,q}\int dE b_{E,n,q}(t)e^{-iEt/\hbar}|\,E,n,q^-\,\rangle\ .$$

Assuming that the field does not directly couple the $|\,E_i\,\rangle$ bound states (because e.g., its Fourier components are far off resonance with respect to the $\omega_{i,j} \equiv (E_i - E_j)/\hbar$ transition frequencies), we obtain a set of equations identical to the ODE obtained previously

$$\begin{aligned} \dot{b}_j(t) &= \frac{i}{\hbar}\int dE\sum_{n,q}\varepsilon(t)e^{-i\omega_{E,j}t}\langle\,E_j\,|\hat{\epsilon}\cdot\mathbf{d}|\,E,n,q^-\,\rangle b_{E,\mathrm{n},q}(t)\ , \\ \dot{b}_{E,n,q} &= \frac{i}{\hbar}\sum_i\langle E,n,q^-|\hat{\epsilon}\cdot\mathbf{d}|E_i\rangle\varepsilon(t)e^{i\omega_{E,i}t}b_i(t)\ ,\ \text{all}\ \ E,n,q\ . \end{aligned}$$

Solving the second equation for the continuum coefficients we obtain

$$b_{E,\mathrm{n},q}(t) = \frac{i}{\hbar}\sum_i \langle E, n, q^- | \hat{\epsilon}\cdot \mathbf{d} | E_i \rangle \int_0^t dt' \varepsilon(t') e^{i\omega_{E,i} t'} b_i(t') \ .$$

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As a result, the photodissociation probability is given by

$$P_n^{(q)}(E) = |b_{E,\mathbf{n},q}(\infty)|^2 =$$

$$\frac{1}{\hbar^2}\left|\sum_i \langle E,n,q^-|\hat{\epsilon}\cdot\mathbf{d}|E_i\rangle \int_0^\infty dt\varepsilon(t)e^{i\omega_{E,i}t}b_i(t)\right|^2 \ .$$

Note that it is no longer possible to factor out the pulse parameters from the above expression. We say that the light fields have been “entangled” with the material system.

VI.2. Weak field bichromatic control

In the *weak field limit* we can assume that the initial coefficients do not get significantly depleted by the photodissociating pulse and equate $b_i(t) \approx b_i(0) \equiv b_i$ to obtain that

$$P_n^{(q)}(E) = \left| \sum_i b_i \langle E, n, q^- | \hat{\epsilon} \cdot \mathbf{d} | E_i \rangle \int_0^\infty dt \varepsilon(t) e^{i\omega_{E,i} t} \right|^2$$

$$= \left(\frac{2\pi}{\hbar} \right)^2 \left| \sum_i b_i \langle E, n, q^- | \hat{\epsilon} \cdot \mathbf{d} | E_i \rangle \epsilon(\omega_{E,i}) \right|^2 .$$

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$$= \left(\frac{2\pi}{\hbar} \right)^2 \left| \sum_i b_i \langle E, n, q^- | \hat{\epsilon} \cdot \mathbf{d} | E_i \rangle \epsilon(\omega_{E,i}) \right|^2 .$$

Thus, the probability to produce at infinite time a free state $| E, n, q; 0 \rangle$ involves *multiple interfering pathways*. In each pathway a different on-resonance $\epsilon(\omega_{E,i})$ Fourier component of the laser pulse connects a different precursor state $| E_i \rangle$ to the same continuum state $| E, n, q^- \rangle$.

By changing the amplitude and phase of these Fourier components (i.e., by "shaping" the pulse) we can affect the nature and magnitude of the interference between all the pathways. Since this interference is affected also by the $\langle E, n, q^{-}|\hat{\epsilon}\cdot\mathbf{d}|E_i\rangle$ complex matrix elements, it is possible to induce destructive interference in one fragment channel and constructive interference in another, thereby achieving the desired channel *selectivity*.

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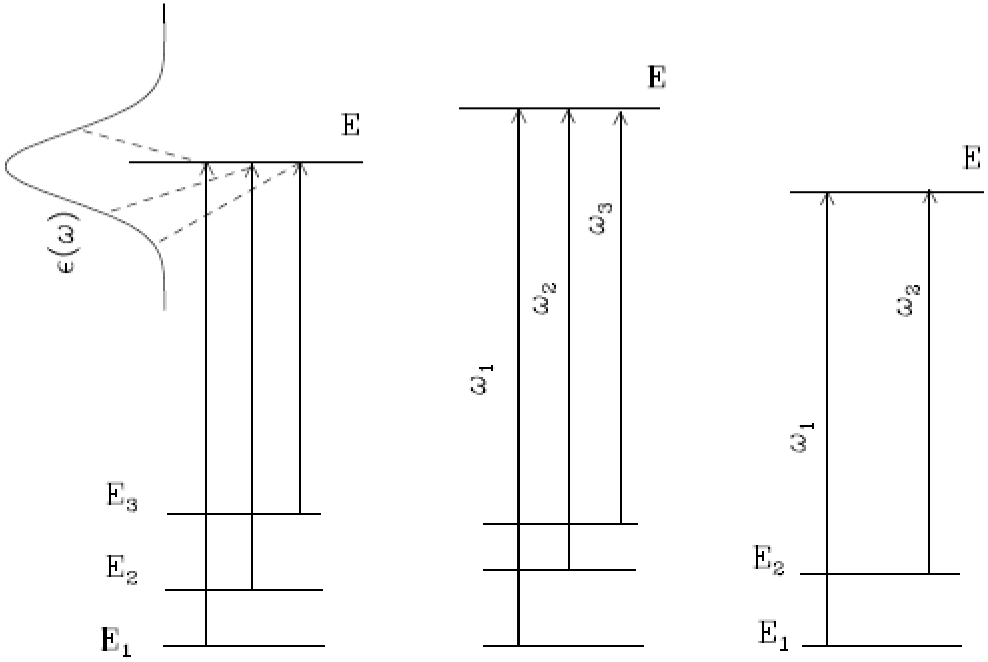

Of particular interest is the probability of being in a *complete* subspace of states, denoted by the label q, given as,

$$P_q(E) = \sum_m P_{m,q}(E) = \sum_m |b_{E,m,q}|^2 \ ,$$

i.e.,
$$P_q(E) = (2\pi/\hbar)^2 \sum_{i,j=1}^{N} [b_i b_j^* \epsilon(\omega_{E,i}) \epsilon^*(\omega_{E,j})] \mathrm{d}_q(ji) \ ,$$

where
$$\mathrm{d}_q(ji) = \sum_n \langle E_j | \hat{\epsilon} \cdot \mathbf{d} | E, n, q^- \rangle \langle E, n, q^- | \hat{\epsilon} \cdot \mathbf{d} | E_i \rangle .$$

The branching ratio between two channels at energy E, $R_{q,q'}(E)$, which we control below, is then,

$$R_{q,q'}(E) = P_q(E)/P_{q'}(E) \ .$$

Analyzing the structure of $P_q(E)$ we see that the diagonal terms $(i = j)$ give the standard probability, at energy E, of photodissociation out of a bound state $|E_j\rangle$ to produce a product in channel q. The off-diagonal terms $(i \neq j)$ correspond to interference terms between these photodissociation routes. These interference terms describe the constructive enhancement, or destructive cancellation of product formation in subspace q.

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The probability expression we obtained is important *in practice* because the interference terms have coefficients $[b_i b_j^* \epsilon(\omega_{E,i})\epsilon^*(\omega_{E,j})]$ whose magnitude and sign depend upon *experimentally controllable* parameters. Thus the experimentalist can manipulate laboratory parameters and, in doing so, alter the interference term and hence control the reaction product yield.

The probability expression displays another important feature: The entire control map, i.e. $P_q(E)$ or $R_{q,q'}(E)$ as a function of the control parameters, is a function of only the $\mathrm{d}_q(ji)$ molecular parameters. As a consequence, the experimentalist need only determine these few parameters in order to produce the entire control map. This statement constitutes the weak field version of "Adaptive Feedback Control".

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Experimentally attaining control by this scenario requires a light source containing N frequencies $\omega_i, (i = 1...N)$. Both pulsed excitation with a source whose frequency width encompasses these frequencies, as well as excitation with N Continuous Wave (CW) lasers of frequencies $\omega_i = \omega_{E,i}$, $(i = 1...N)$ are possible approaches.

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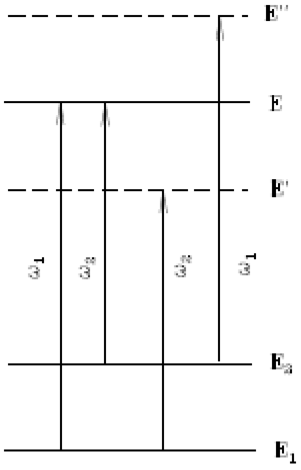

Let us consider two parallel CW fields of frequencies ω_1 and ω_2 incident on a molecule and tune the ω_1 and ω_2 frequencies such that, $\omega_2 - \omega_1 = (E_1 - E_2)/\hbar$, we have that $P_q(E)$ at energy $E = E_1 + \hbar\omega_1 = E_2 + \hbar\omega_2$, only has two contributions, corresponding to the excitations shown on the left hand side of the Figure.

$P_q(E = E_1 + \hbar\omega_1)$ is given[3] by,

$$P_q(E) = P_q(11) + P_q(22) + P_q(12)$$

where $$P_q(ii) = \left(\frac{2\pi}{\hbar}\right)^2 |b_i|^2 |\epsilon(\omega_i)|^2 \mathrm{d}_q(ii)\ , \quad i = 1, 2,$$

and $$P_q(12) = \left(\frac{2\pi}{\hbar}\right)^2 2R_e\ b_1 b_2^* \epsilon(\omega_1)\epsilon(\omega_2) e^{i(\phi_2 - \phi_1)} \mathrm{d}_q(12)$$

where $\phi_i \equiv \phi(\omega_i)$.

Defining

$$
\begin{aligned}
x &= \frac{|\epsilon(\omega_2)b_2|}{|\epsilon(\omega_1)b_1|} \quad , \quad \xi_{1,2} = arg(b_1) - arg(b_2) \ , \\
\mathrm{d}_q(ij) &= |\mathrm{d}_q(ij)| \exp(i\alpha_q(ij)) \ , \quad \phi_{1,2} = \phi_1 - \phi_2 \ ,
\end{aligned}
$$

with $\alpha_q(ij)$ termed the “material phase”, we have that

$$P_q(E) = |\mathrm{d}_q(11)| + x^2|\mathrm{d}_q(22)| + 2x\cos(\phi_{1,2} + \xi_{1,2} + \alpha_q(12))|\mathrm{d}_q(12)|.$$

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The branching ratio, $R_{q,q'}(E) \equiv P_q(E)/P_{q'}(E)$, is given as,

$$R_{q,q'}(E) = \frac{|\mathrm{d}_q(11)| + x^2|\mathrm{d}_q(22)| + 2x\cos(\phi_{1,2} + \xi_{1,2} + \alpha_q(12))|\mathrm{d}_q(12)|}{|\mathrm{d}_{q'}(11)| + x^2|\mathrm{d}_{q'}(22)| + 2x\cos(\phi_{1,2} + \xi_{1,2} + \alpha_{q'}(12))|\mathrm{d}_{q'}(12)|} \ ,$$

Varying $\phi_{1,2}$ or x, changes the interference term and thus gives us control over the dissociation probabilities. These changes may be accomplished either by varying the coefficients of the initial superposition state, $\{b_j\}$, or by changing the intensity and relative phases of the dissociation lasers.

VI.3 Controllability

We now ask the question, what is the best we can do concerning the control of the population of an entire subspace using just two frequency "knobs"? Considering just two subspaces q and q', each containing many n channels, it is clear that in order to maximize the probability in one q subspace we must *minimize* the probability in the other q' subspace.

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Since the above expression has two positive (P_{11} and P_{22}) terms the minimum is attained by making the interference term as negative as possible and this is attained when

$$\cos\left[\phi_{1,2} + \xi_{1,2} + \alpha_{q'}(12)\right] = -1 \ ,$$

namely when $\phi_{1,2} + \xi_{1,2} = \pi - \alpha_{q'}(12)$.

With this condition we obtain that

$$P_{q'}^{min}(E) = |\mathrm{d}_{q'}(11)| + x^2|\mathrm{d}_{q'}(22)| - 2x|\mathrm{d}_{q'}(12)|.$$

Equating $P_{q'}^{min}(E) = 0.$ The equation has a solution provided that the discriminant vanishes, i.e., that

$$|\mathrm{d}_{q'}(12)|^2 = |\mathrm{d}_{q'}(11)||\mathrm{d}_{q'}(22)|.$$

The above condition is fulfilled identically when the q' space contains only one n channel. In that case we can get *perfect* control and there is one x value

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$$x^{min} = |\mathrm{d}_{q'}(12)/\mathrm{d}_{q'}(22)|$$

which guarantees that $P_{q'}^{min}(E) = 0.$ In all other cases we know by the Schwarz inequality that

$$|\mathrm{d}_{q'}(12)|^2 < |\mathrm{d}_{q'}(11)||\mathrm{d}_{q'}(22)|,$$

and $P_{q'}^{min}(E) \geq 0$, i.e., perfect control is unattainable in general. The situation becomes progressively worse as the number of n channels in each q manifold increases because

$$\left|\mathrm{d}_q(12)\right| = \left|\sum_n \langle E_1|\hat{\epsilon}\cdot\mathbf{d}|E,n,q^-\rangle\langle E,n,q^-|\hat{\epsilon}\cdot\mathbf{d}|\,E_2\,\rangle\right|$$

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VI.3.a. A Numerical Example

As an example of this approach we consider control over the relative probability of forming ${}^2P_{3/2}$ vs. ${}^2P_{1/2}$ atomic iodine, denoted I and I*, in the dissociation of methyl iodide in the regime of 266 nm,

$$\mathrm{CH_3 + I^*(^2}P_{1/2}) \leftarrow \mathrm{CH_3I} \rightarrow \mathrm{CH_3 + I(^2}P_{3/2})\ .$$

This reaction is an example of electronic branching of photodissociation products. The results reported below are for a non-rotating two-dimensional collinear model in which the H_3 center-of-mass, the C and the I atoms are assumed to lie on a line.

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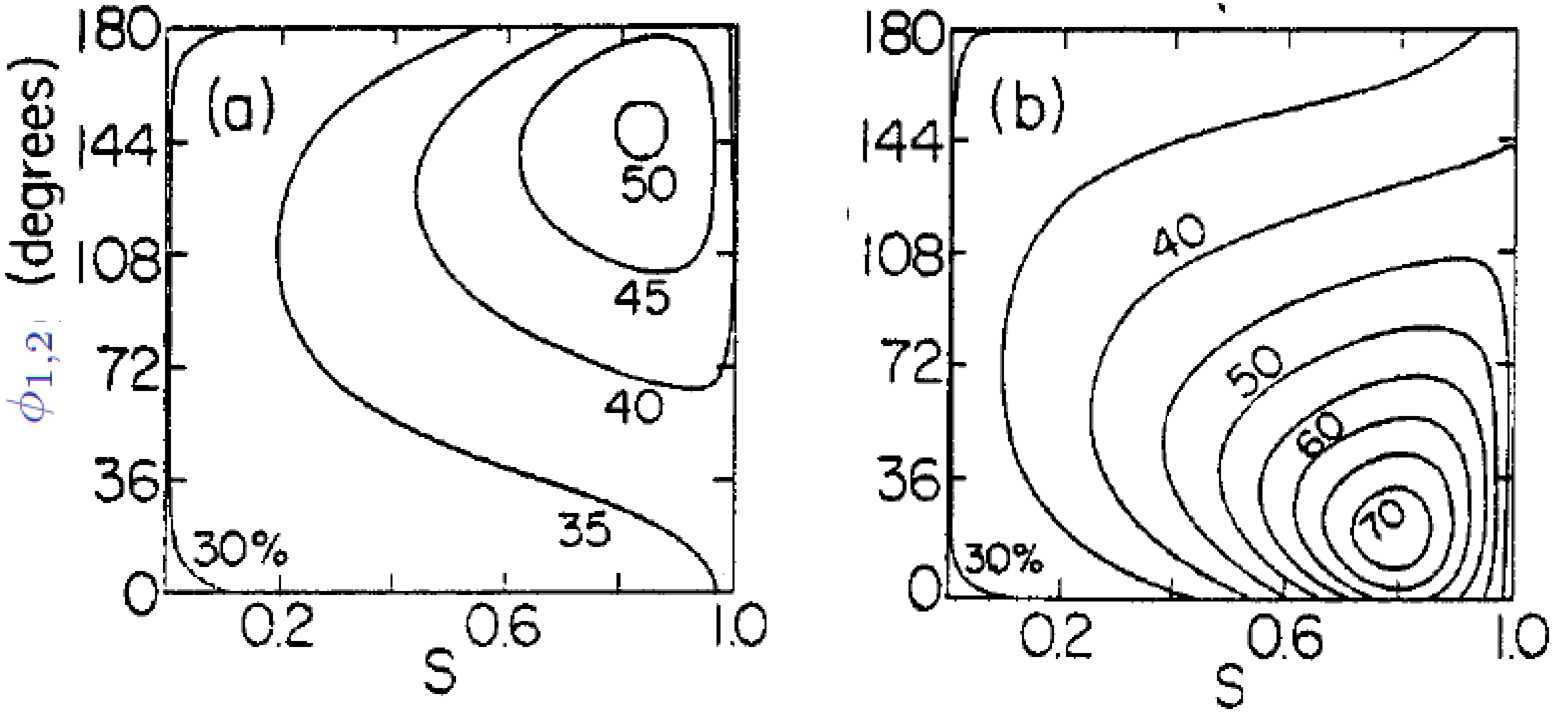

Contour plot of the yield of CH_3 +I from the photodissociation CH_3I from a superposition of states at $\omega_1 = 37593.9\text{cm}^{-1}$. (a) $|\chi(0)\rangle = a_1|E_1\rangle + a_2|E_2\rangle$,

(b) $|\chi(0)\rangle = a_1|E_1\rangle + a_3|E_3\rangle$

VI.4 Energy Averaging and Satellite Contributions

In general, experiments measure energy averaged quantities such as

$$P_q = \int dE\ P_q(E)\ , \qquad R_{q,q'} = P_q/P_{q'}\ ,$$

since products are not distinguished on the basis of total energy. As such, it is necessary to compute photodissociation to all energies.

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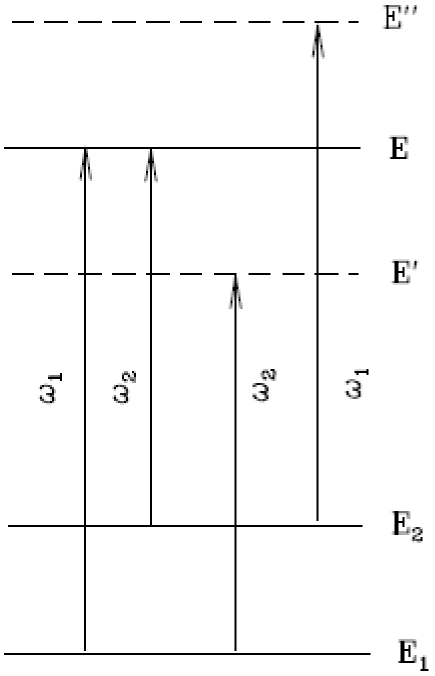
For the case considered : two states irradiated with two CW fields of frequencies ω_1 and ω_2, $P_q(E)$ is nonzero at three energies: $E = E_1 + \hbar\omega_1 = E_2 + \hbar\omega_2,$

$E' = E_1 + \hbar\omega_2,$ and $E'' = E_2 + \hbar\omega_1.$



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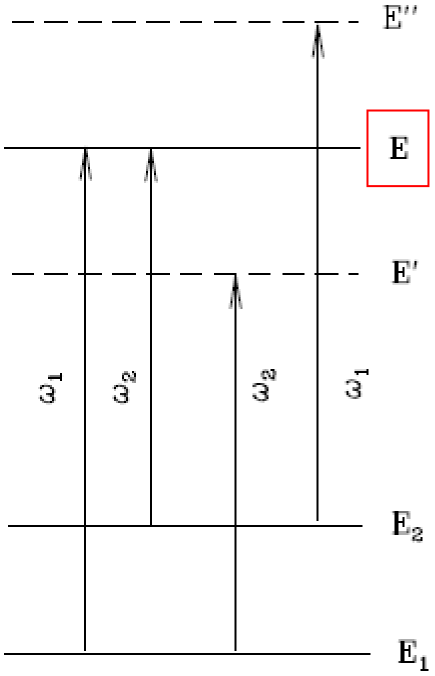

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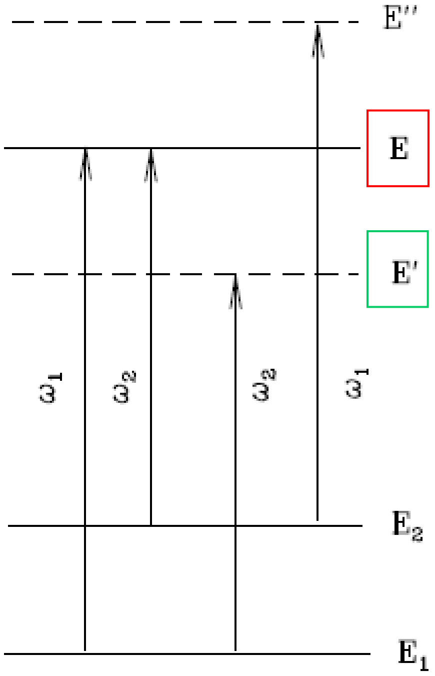

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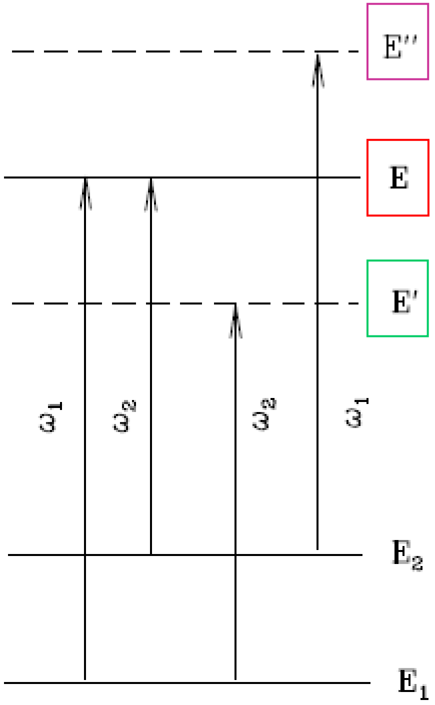


$$P_q(E = E_1 + \hbar\omega_1 = E_2 + \hbar\omega_2) =$$

$$\left(\frac{2\pi}{\hbar}\right)^2 |b_1\epsilon(\omega_1)|^2 \mathrm{d}_q(11) + \left(\frac{2\pi}{\hbar}\right)^2 |b_2\epsilon(\omega_2)|^2 \mathrm{d}_q(22) \; + \left(\frac{2\pi}{\hbar}\right)^2 2R_e\; b_1 b_2^* \epsilon(\omega_1)\epsilon(\omega_2) e^{i(\phi_2-\phi_1)} \mathrm{d}_q(12)$$

controllable

$$P_q(E' = E_1 + \hbar\omega_2) \quad = \quad \left(\frac{2\pi}{\hbar}\right)^2 |b_1\epsilon(\omega_2)|^2 \mathrm{d}_q(11) \; ,$$

uncontrollable

$$P_q(E'' = E_2 + \hbar\omega_1) \quad = \quad \left(\frac{2\pi}{\hbar}\right)^2 |b_2\epsilon(\omega_1)|^2 \mathrm{d}_q(22).$$

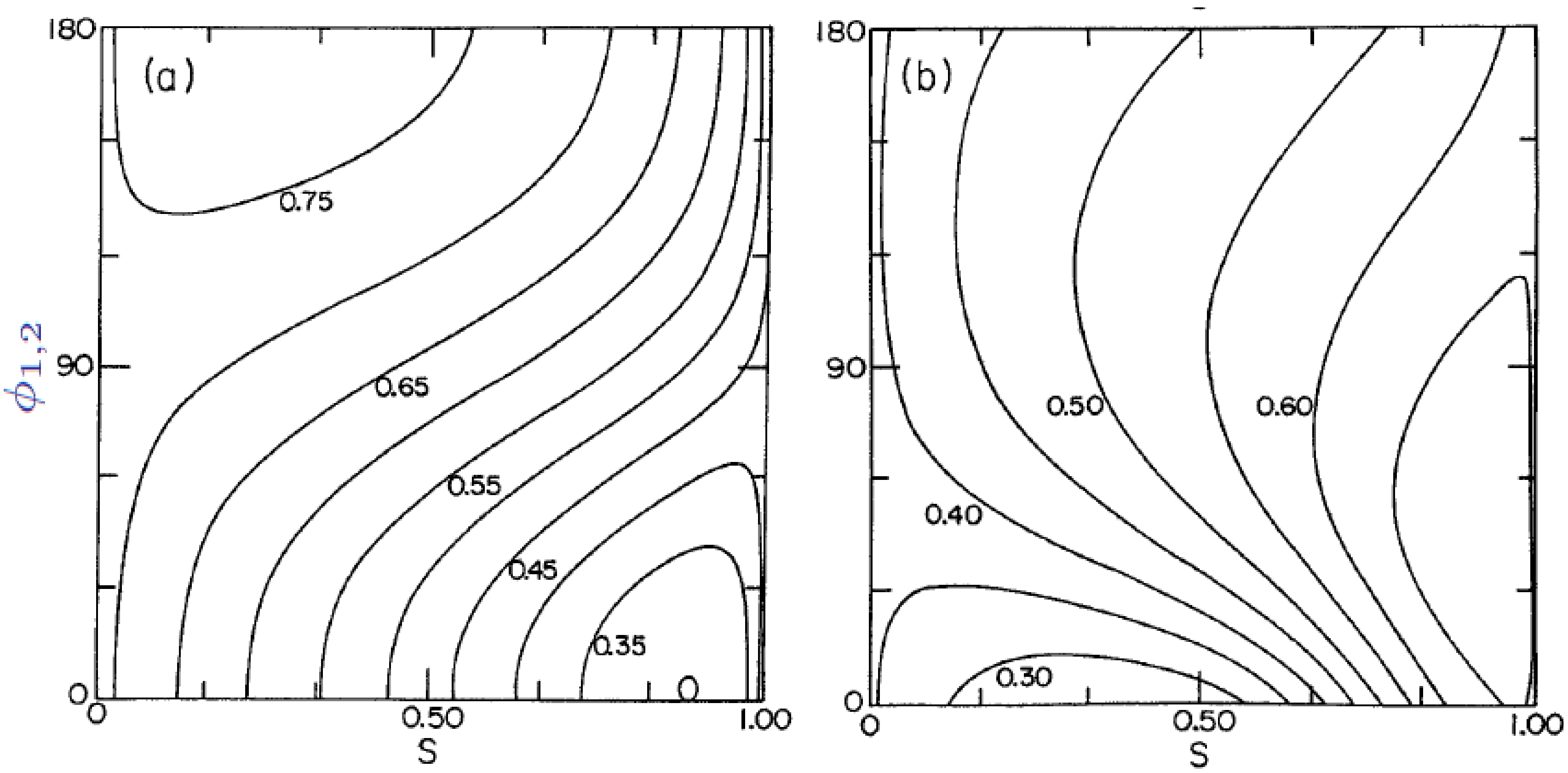
uncontrollable

Thus, the overall P_q for $N = 2$ is given by,

"satellites"

$$P_q = \boxed{P_q(E = E_1 + \hbar\omega_1)} + P_q(E' = E_1 + \hbar\omega_2) + P_q(E'' = E_2 + \hbar\omega_1)\; .$$

The latter two terms correspond to traditional photodissociation and are *uncontrollable*.



Contour plot of the yield of I* (i.e. fraction of I* as product) in the photodissociation of CH_3I starting from an $M-$averaged initial state.

(a) $\omega_1 = 39,639$ cm^{-1}, (b) $\omega_1 = 42,367$ cm^{-1}.

In both cases $\omega_2 = (E_1 - E_2)/\hbar + \omega_1$

We note that there is no interference between terms of different energies. This is a general principle which plays a role in all control scenarios. The reason for it is that products of terms of different energies contain oscillatory $\exp[i(E_1 - E_2)t/\hbar]$ term which average out to zero with time.

VI.5. Control of the direction of electronic motion: current without voltage!

(G. Kurizki, M. Shapiro, P. Brumer, Phys. Rev. B, **39**, 3435 (1989)).

As another application of the above formulation we now discuss a scenario in which we interfere a one-photon process with a two-photon process in order to control the directionality of electronic currents in semiconductors and other environments. This scenario is of extreme importance as it relates both to the frequency comb measurements and the diagnostics of attosecond pulses, but its discovery in 1989

In this scenario we irradiate the material system by two fields, $2R_e\epsilon_1\, e^{-i\omega_1 t - i\phi_1}$, inducing a *one-photon* transition, and $2R_e\epsilon_2\, e^{-i\omega_2 t - i\phi_2}$, where $\omega_2 = \omega_1/2$, inducing a *two-photon* transition.

Given an initial $|\mathbf{k}_v\rangle$ semi-conductor valence-band state, and that both processes are in resonance with transitions to $|\mathbf{k}_c\rangle$ conduction-band states, the probability-density in the conduction-band, $P(\mathbf{k}_c)$, is given as the square of the sum of one-photon and two-photon amplitudes. Explicitly,

$$P(\mathbf{k}_c) = |f(\mathbf{k}_c)|^2$$

with $$f(\mathbf{k}_c) \propto \epsilon_1 p_{c,v} e^{-i\phi_1} + \epsilon_2^2 d_{c,v} e^{-2i\phi_2}$$

where $$p_{c,v} \equiv \langle\, \mathbf{k}_c \,|\mathrm{p}|\, \mathbf{k}_v \,\rangle \ , \ d_{c,v} \equiv \sum_i \frac{p_{c,i} p_{i,v}}{\hbar\omega_2 - E_i} \ ,$$

with $$p_{i,v} \equiv \langle\, \mathbf{k}_i \,|\mathrm{p}|\, \mathbf{k}_v \,\rangle \ p_{c,i} \equiv \langle\, \mathbf{k}_c \,|\mathrm{p}|\, \mathbf{k}_i \,\rangle \ ,$$

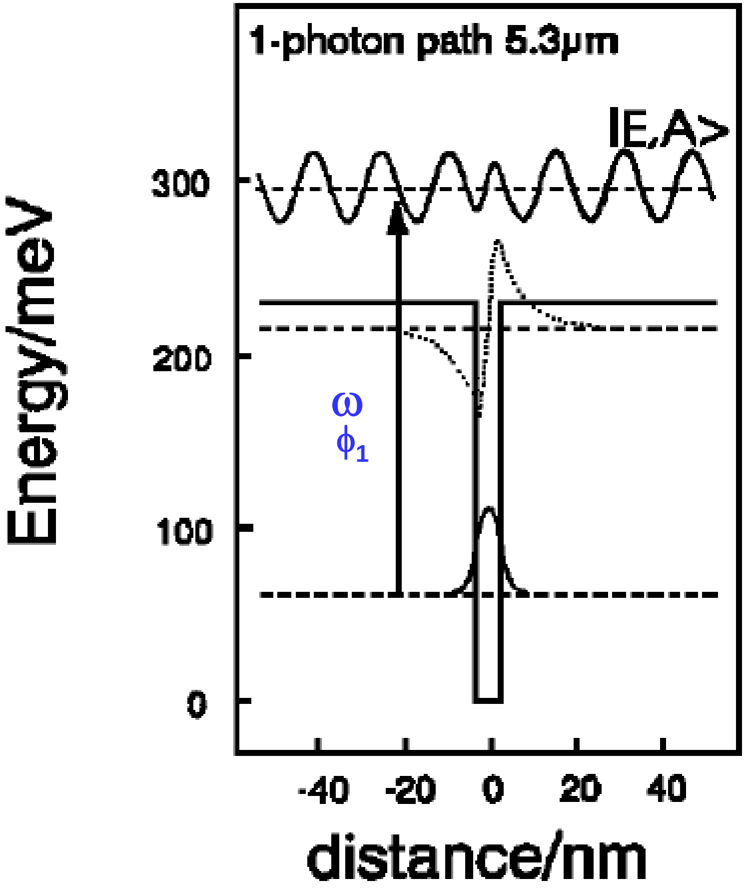
being the momentum matrix elements between the initial/final state and all intermediate states $|\,\mathbf{k}_i\,\rangle$ of energy E_i.

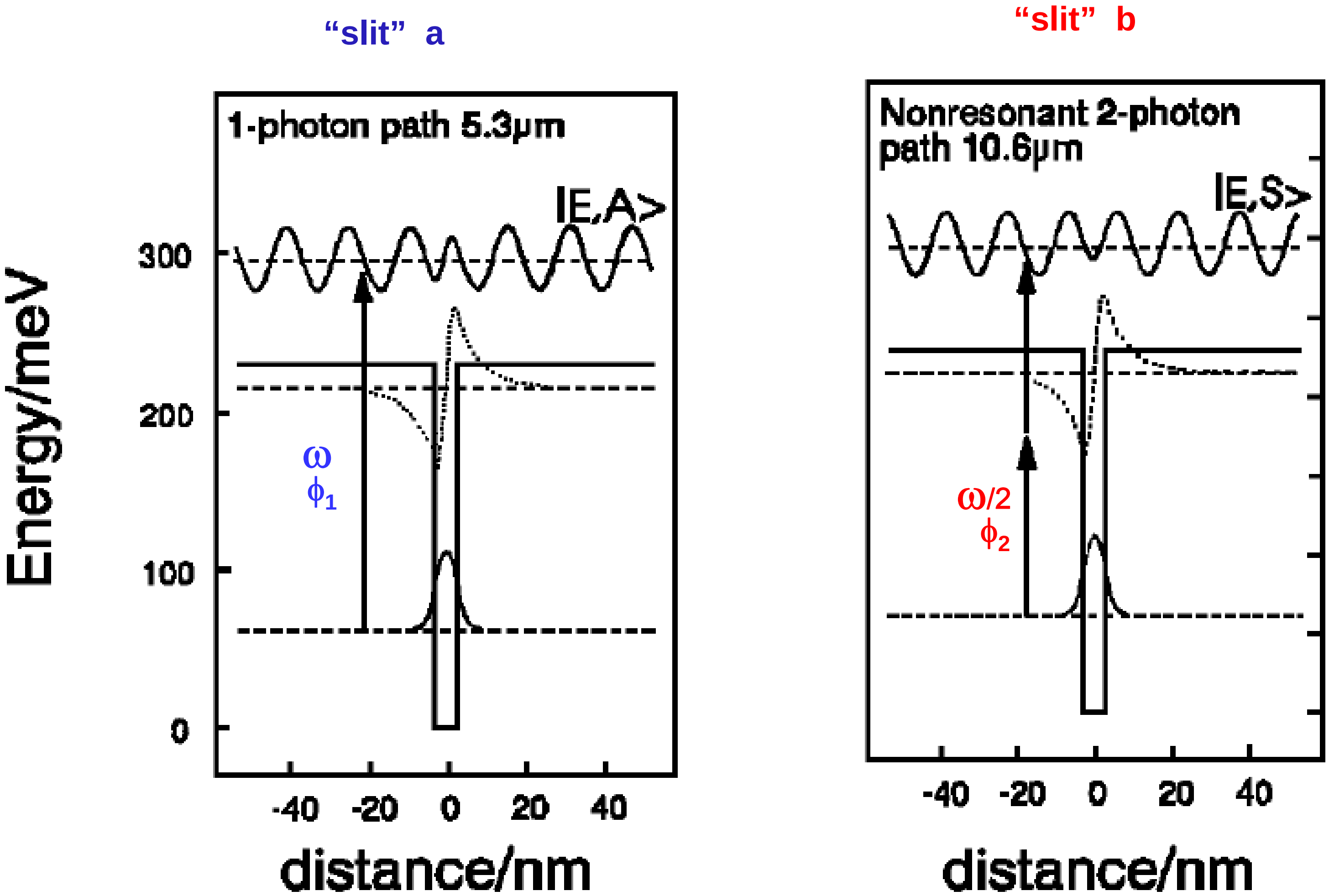
Squaring and separating out $P_{non} \equiv \left|\epsilon_1 p_{cv}\right|^2 + \left|\epsilon_2^2 d_{cv}\right|^2$, the non-interfering sum of one-photon and two-photon probabilities, from the interference term, $2R_e\left\{\epsilon_1^* p_{cv}^* \epsilon_2^2 d_{cv} e^{i[\phi_1 - 2i\phi_2]}\right\}$, i.e., twice the real part of the product of the one-photon and two-photon amplitudes, we can write $P(\mathbf{k}_c)$ as,

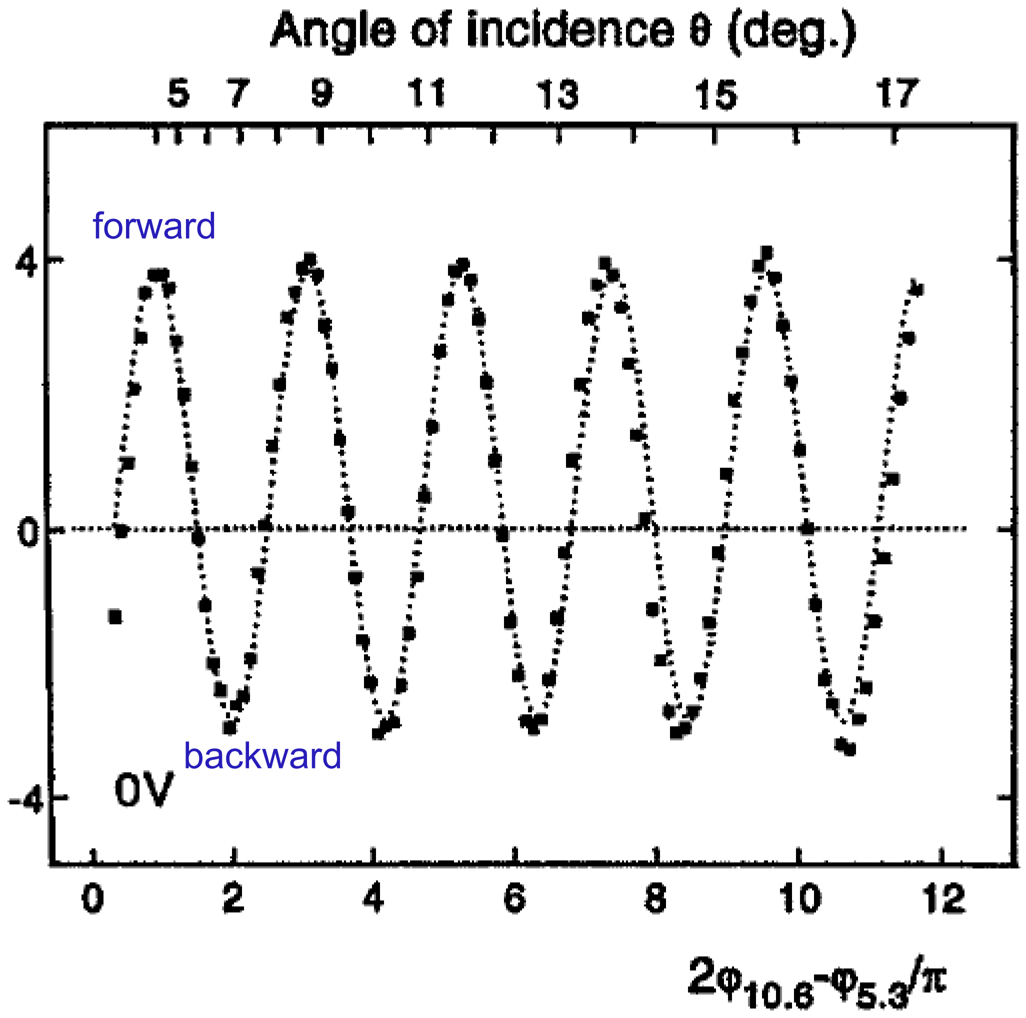
$$P(\mathbf{k}_c) \propto P_{non} + P_{int}\ \cos\left(\alpha(1,2) + \phi_1 - 2\phi_2\right)$$

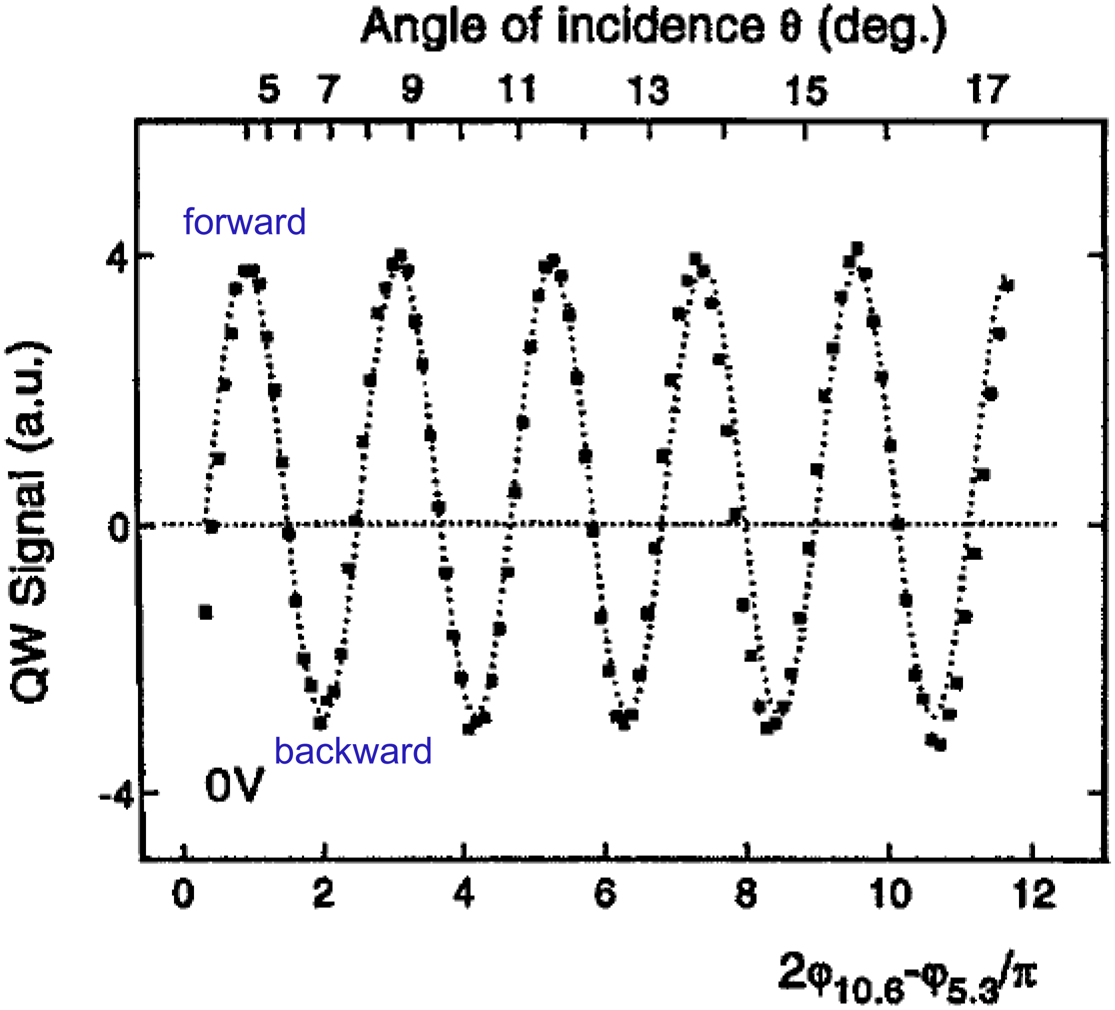
where $P_{int} \equiv \left|\epsilon_1 \epsilon_2^2 p_{c,v} d_{c,v}\right|$, with $\alpha(1,2)$ denoting the "material" phase of the $p_{cv}^* d_{cv}$ product.

We see that we can control the sign of the interference term and hence whether the interference be constructive or destructive, by varying $\phi_1 - 2\phi_2$.


1-photon path 5.3μm
|E,A>
ω
ϕ_1
Energy/meV
300
200
100
0
-40
-20
0
20
40
distance/nm

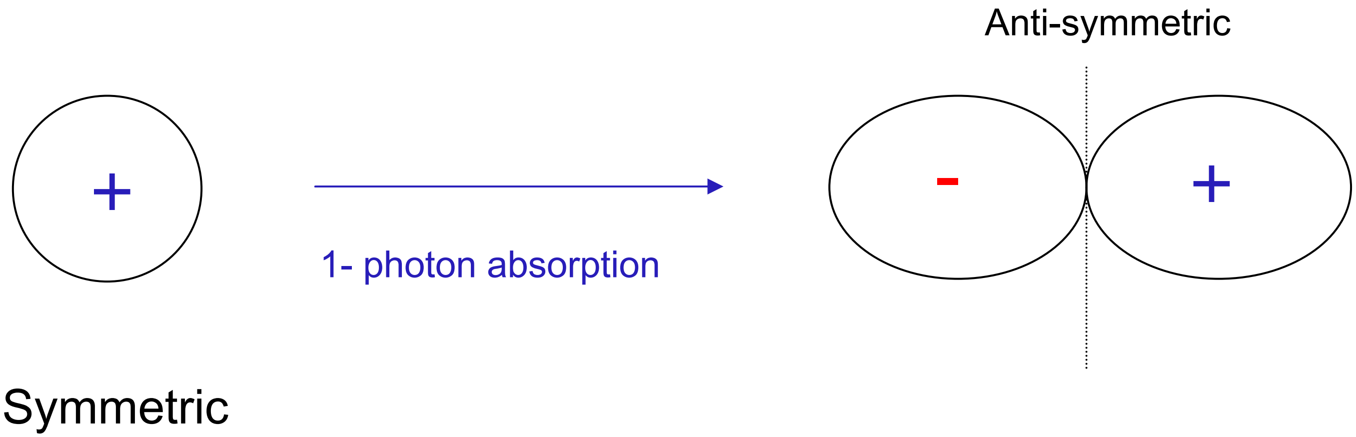

"slit" a
"slit" b
1-photon path 5.3μm
Nonresonant 2-photon path 10.6μm
|E,A>
|E,S>
ω
ϕ_1
ω/2
ϕ_2
Energy/meV
300
200
100
0
-40
-20
0
20
40
distance/nm
-40
-20
0
20
40
distance/nm


Angle of incidence θ (deg.)
5
7
9
11
13
15
17
forward
4
0
-4
0V
backward
0
2
4
6
8
10
12
2φ10.6-φ5.3/π



Experiment: E. Dupont, P.B. Corkum, H.C. Liu, M. Buchanan, and Z.R. Wasilewski, Phys. Rev. Lett. **74**, 3596 (1995)

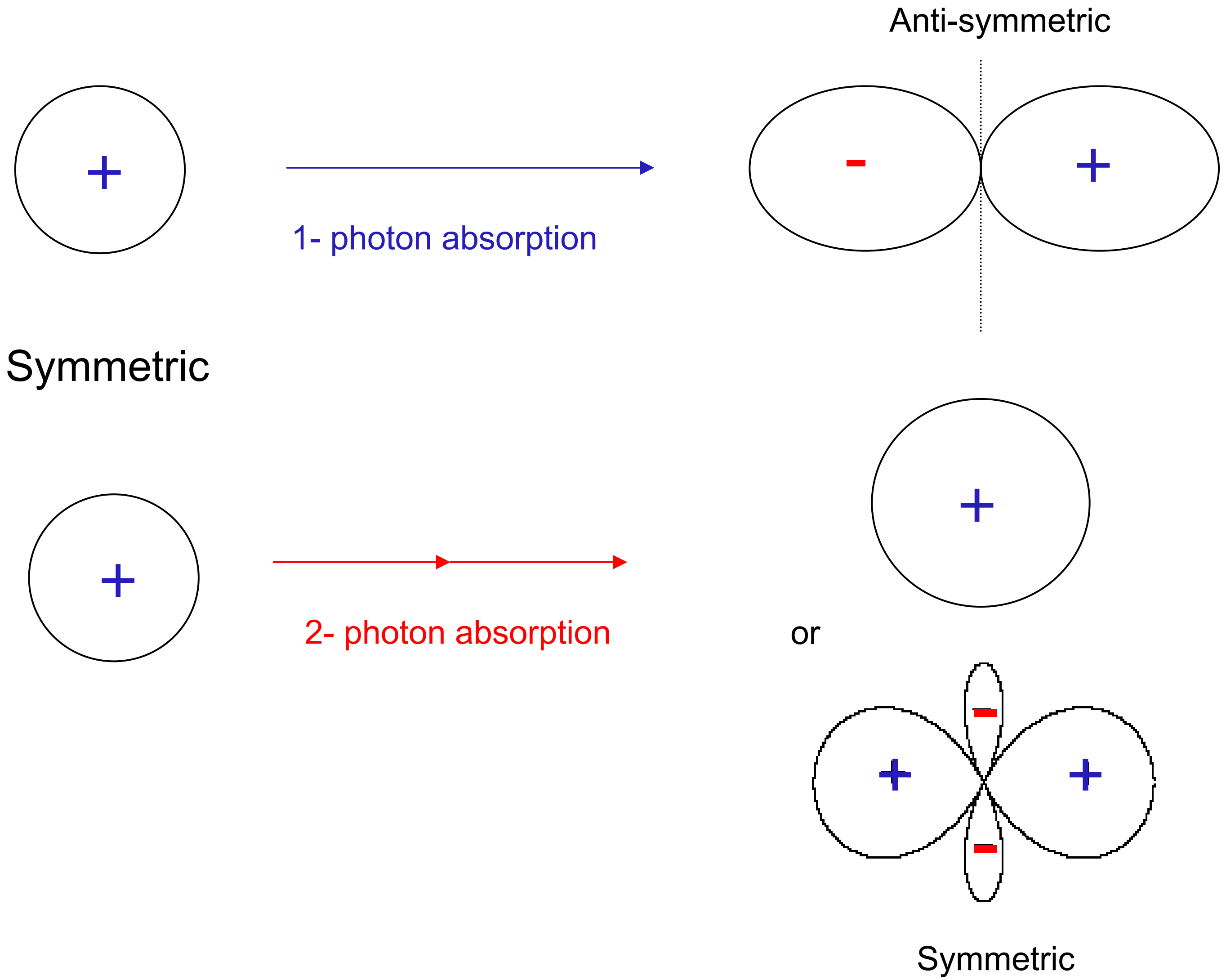
How is the DC created?



Anti-symmetric

1- photon absorption

Symmetric



Anti-symmetric

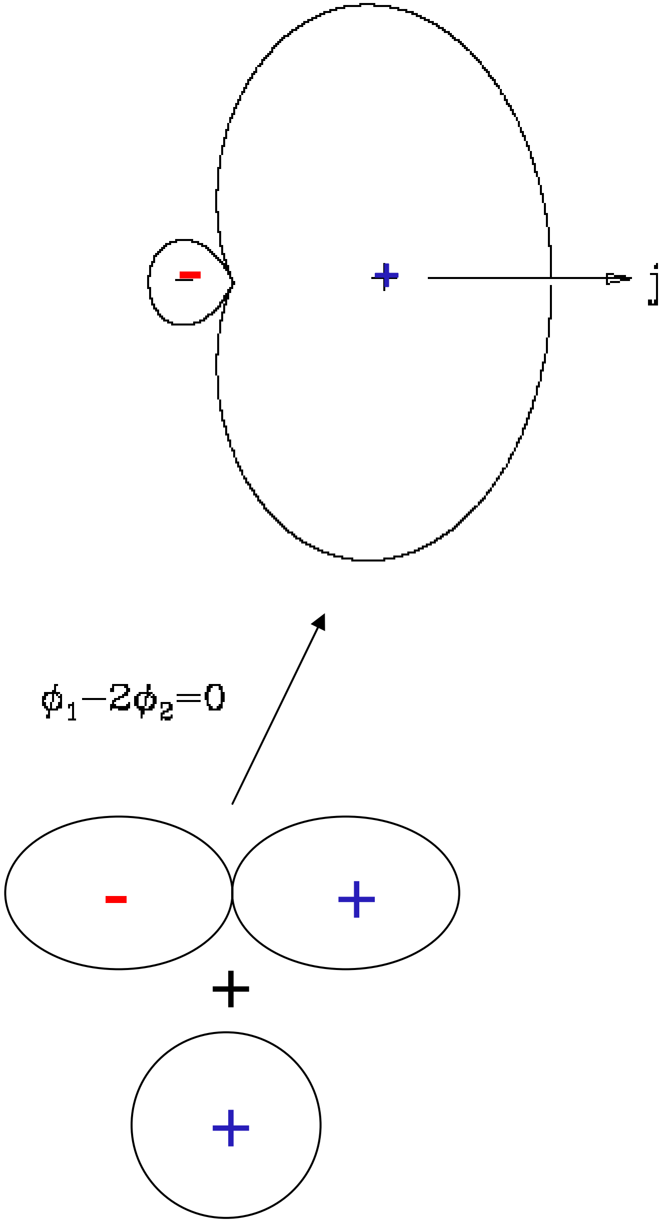
1- photon absorption

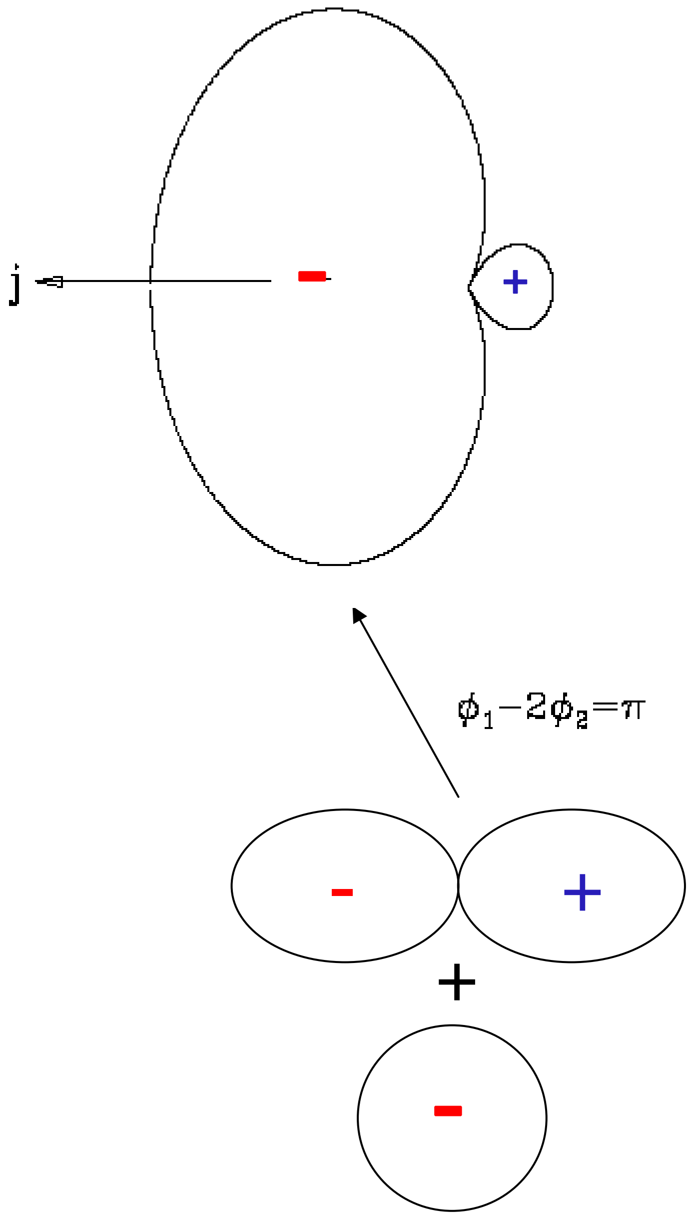
Symmetric

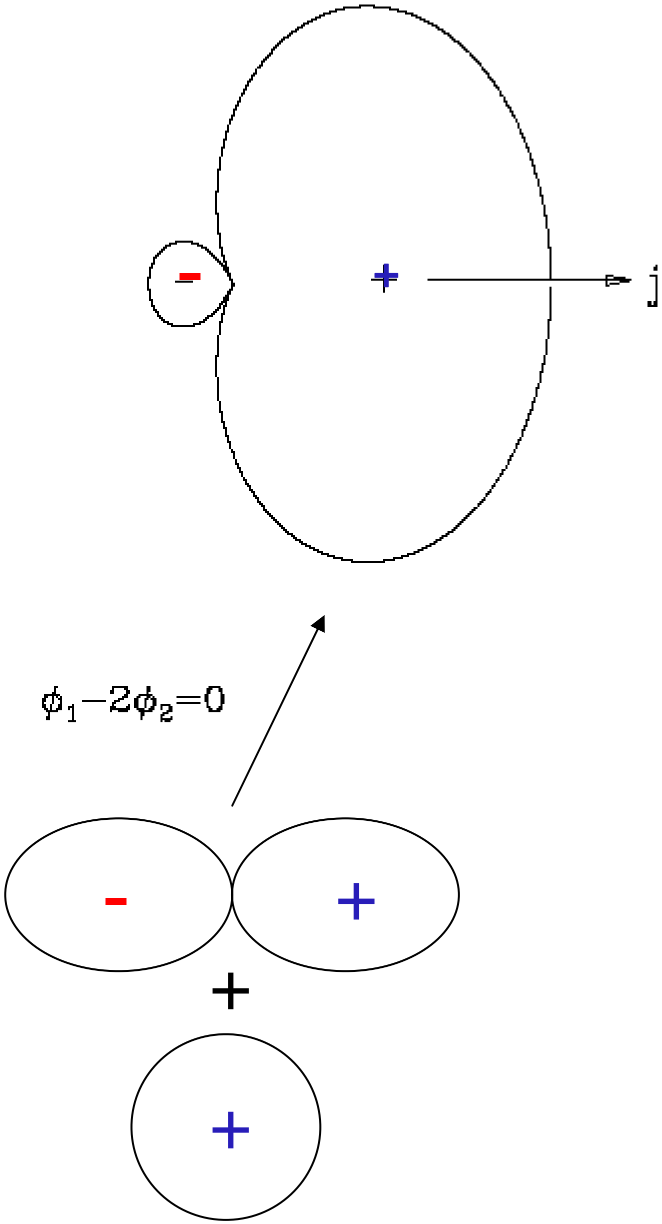
2- photon absorption

or

Symmetric


-
+
j
φ1−2φ2=0
-
+
+
+

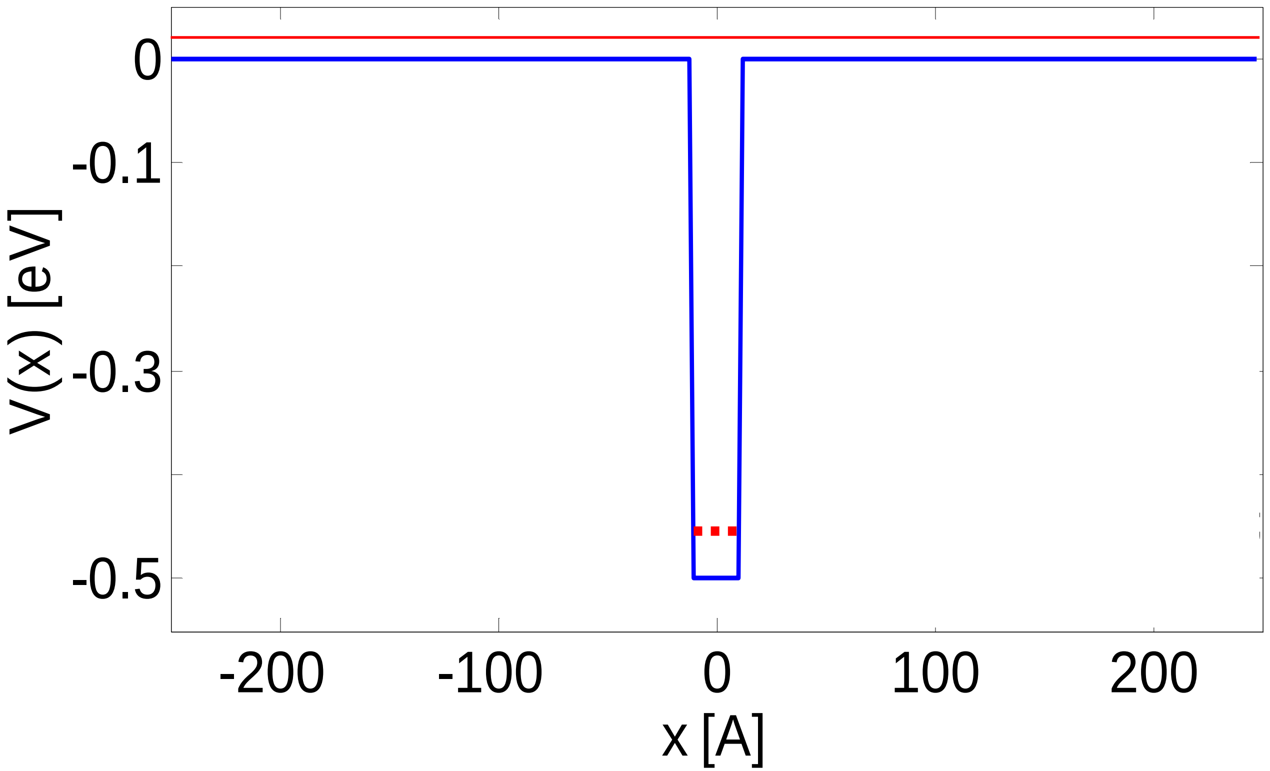

j
-
+
$\phi_1-2\phi_2=\pi$
-
+
+
-


-
+
j
$\phi_1-2\phi_2=0$
-
+
+
+

We see that a phase difference that results in the interference being constructive in the forward direction leads to destructive interference in the backward direction, and *vice versa*. Depending on the $\phi_1 - 2\phi_2$ *relative phase* the injection rates into the $|\pm k_c\rangle$ states can be different, resulting in the generation of a DC electric current, $j_c \propto \int \mathbf{k}_c P_{\mathbf{k}_c} d\mathbf{k}_c \neq 0$ ($j_v \neq j_c$), in the conduction (valence) band of the semiconductor.

A new twist: creating DC and AC currents in nanowires

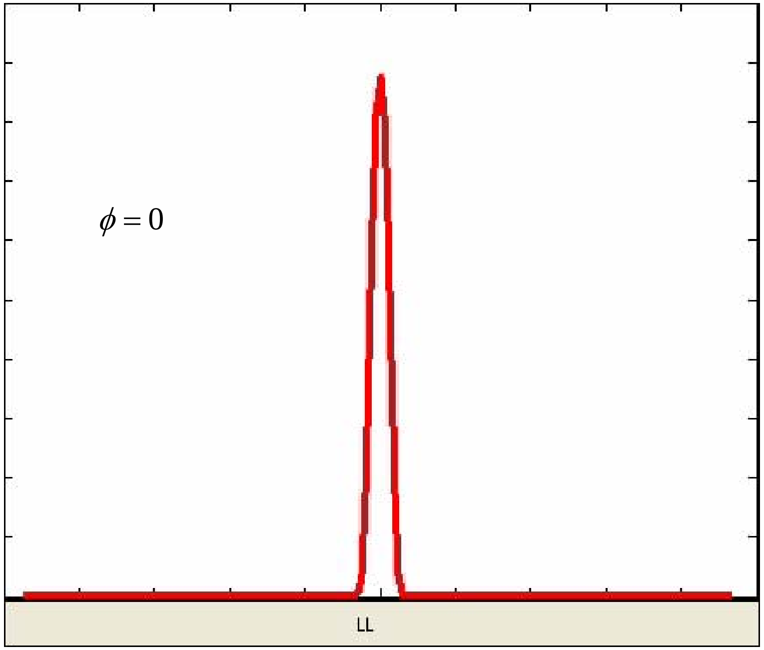
I. Franco, P. Brumer, MS, PRL **99**, 126802 (2007)

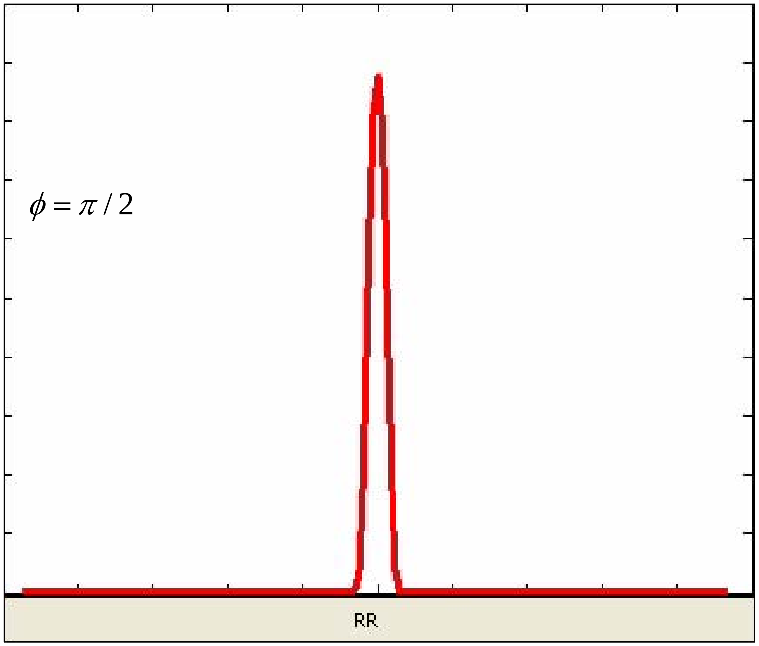


$$V(x) = \begin{cases} 0 & |\mathrm{x}| > 0.1\ \mathrm{nm} \\ -0.5\ \mathrm{eV} & |\mathrm{x}| < 0.1\ \mathrm{nm} \end{cases}$$

$$U(x,t) = x\left[\sin\left(\omega t\right) + \sin\left(2\omega t + \varphi\right)\right] f(t)$$

$$f(t) = e^{-(t/\lambda)^2}$$

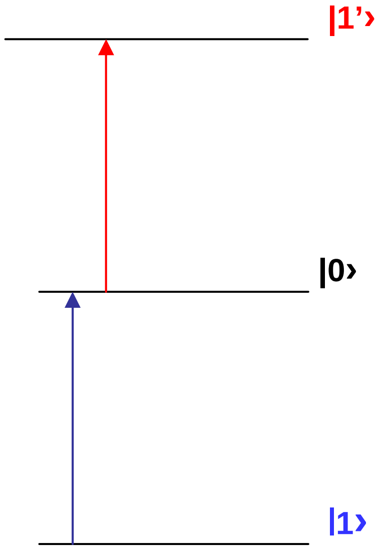




$$\dot{\psi} = -iH\psi$$

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) + U(x,t)$$

Adiabatic passage

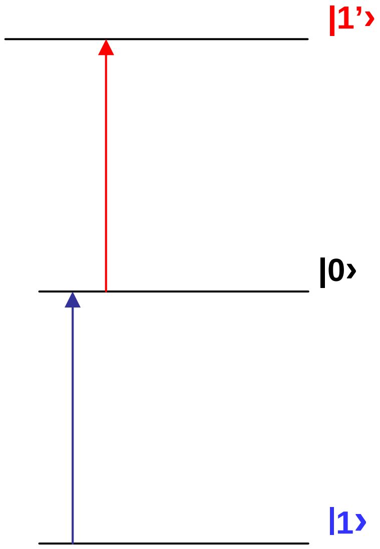


3 states adiabatic passage

K. Bergmann et al.
Rev. Mod. Phys., 70, 1003 (1998).

VI.6. Bound state controllability

Adiabatic passage

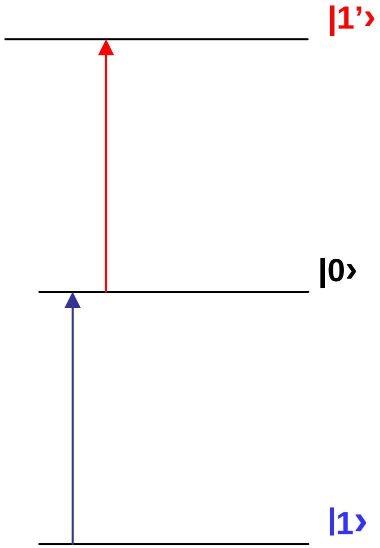


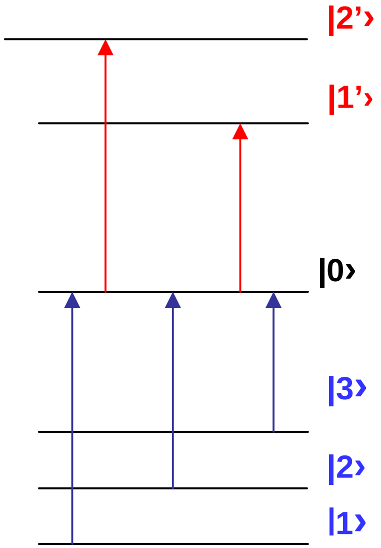
3 states adiabatic passage

K. Bergmann et al.
Rev. Mod. Phys., 70, 1003 (1998).

VI.6. Bound state controllability

Adiabatic passage





3 states adiabatic passage

A new feature:

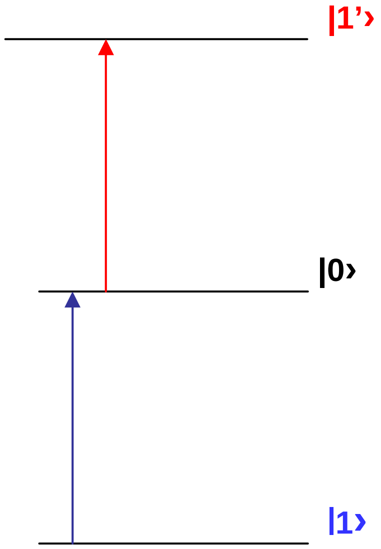
**wave packet-to-wave packet
adiabatic passage via a single state**

**K. Bergmann et al.
Rev. Mod. Phys., 70, 1003 (1998).**

**P. Kral, I. Thanopoulos and M.S.,
Rev. Mod. Phys., 79, 53 (2007).**

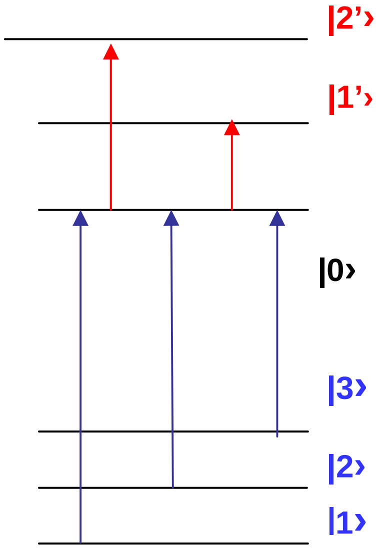
VI.6. Bound state controllability

Adiabatic passage



3 states adiabatic passage

K. Bergmann et al.
Rev. Mod. Phys., 70, 1003 (1998).



Another solution:

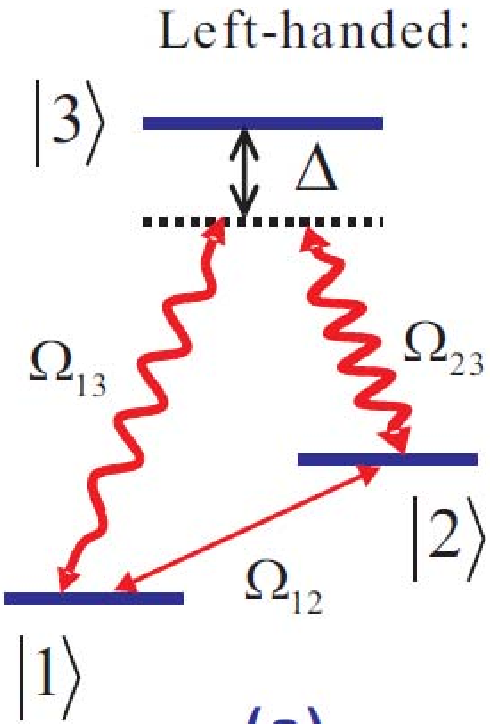
Proof of the non-uniqueness
Of the strong field solutions

“Loop” adiabatic passage

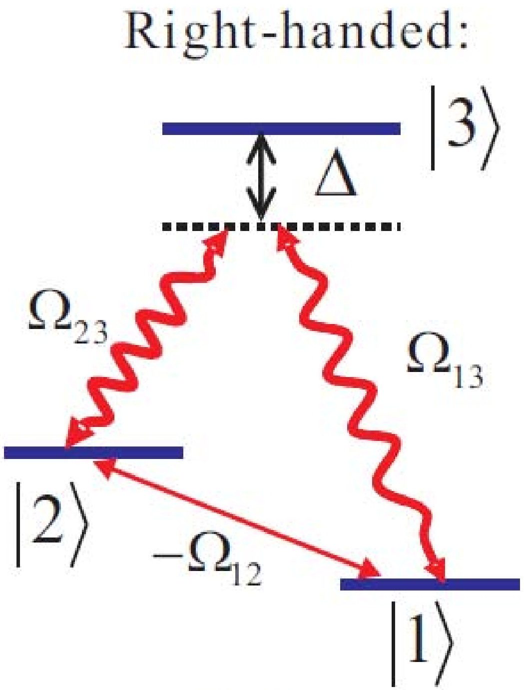
P. Král and M. Shapiro, Phys. Rev. Lett. **87**, 183002 (2001)

P. Král, I. Thanopoulos, M. Shapiro, and D. Cohen, Phys. Rev. Lett. **90**, 033001 (2003).

I. Thanopulos, P. Král, and M. Shapiro, J. Chem. Phys. **119**, 5105 (2003)



(a)



(b)

VI.7 Coherent Control beyond the weak field limit

Beyond the weak field limit one can no longer neglect the variation in the initial coefficients during the pulse. By substituting the solution of the continuum coefficients into the equation for the bound coefficients we obtain,

$$\frac{db_j(t)}{dt} = -\frac{1}{\hbar^2}\sum_i \sum_{n,q} \varepsilon(t) \int_0^t dt' \varepsilon(t') e^{i(E_j t - E_i t')/\hbar}$$

$$\int dE e^{-iE(t-t')/\hbar} \langle\, E_j \,|\hat{\epsilon}\cdot \mathrm{d}|\, E, n, q^- \,\rangle \langle E, n, q^- |\hat{\epsilon}\cdot \mathrm{d}| E_i \rangle b_i(t') \ .$$

VI.7 Coherent Control beyond the weak field limit

Beyond the weak field limit one can no longer neglect the variation in the initial coefficients during the pulse. By substituting the solution of the continuum coefficients into the equation for the bound coefficients we obtain,

$$\begin{aligned}\frac{db_j(t)}{dt} = -\frac{1}{\hbar^2}\sum_i \sum_{n,q} \varepsilon(t)\int_0^t dt'\varepsilon(t')e^{i(E_j t - E_i t')/\hbar} \\ \int dE e^{-iE(t-t')/\hbar}\langle\, E_j\, |\hat{\epsilon}\cdot \mathbf{d}|\, E, n, q^-\,\rangle\langle E, n, q^-|\hat{\epsilon}\cdot \mathbf{d}|E_i\rangle b_i(t')\ .\end{aligned}$$

Assuming that $\langle\, E_j\, |\hat{\epsilon}\cdot \mathbf{d}|\, E, n, q^-\,\rangle$ varies slowly with E we can use the so-called Slowly Varying Continuum Approximation (SVCA) to replace it by its value at some representative energy $\bar{E}$:

$$\langle\, E_j\, |\hat{\epsilon}\cdot \mathbf{d}|\, E, n, q^-\,\rangle \approx \langle\, E_j\, |\hat{\epsilon}\cdot \mathbf{d}|\, \bar{E}, n, q^-\,\rangle\ .$$

With this approximation, the last integral becomes

$$\int dEe^{-iE(t-t')/\hbar}\langle\, E_j\,|\hat{\epsilon}\cdot\mathbf{d}|\,E,n,q^-\,\rangle\langle E,n,q^-|\hat{\epsilon}\cdot\mathbf{d}|E_i\rangle \approx$$

$$\langle\, E_j\,|\hat{\epsilon}\cdot\mathbf{d}|\,\bar{E},n,q^-\,\rangle\langle\bar{E},\mathbf{n},q^-|\hat{\epsilon}\cdot\mathbf{d}|E_i\rangle\int dEe^{-iE(t-t')/\hbar} =$$

$$2\pi\hbar\langle\, E_j\,|\hat{\epsilon}\cdot\mathbf{d}|\,\bar{E},n,q^-\,\rangle\langle\bar{E},\mathbf{n},q^-|\hat{\epsilon}\cdot\mathbf{d}|E_i\rangle\delta(t-t')\ .$$

,

With this approximation, the last integral becomes

$$\int dE e^{-iE(t-t')/\hbar} \langle E_j | \hat{\epsilon} \cdot \mathbf{d} | E, n, q^- \rangle \langle E, n, q^- | \hat{\epsilon} \cdot \mathbf{d} | E_i \rangle \approx$$

$$\langle E_j | \hat{\epsilon} \cdot \mathbf{d} | \bar{E}, n, q^- \rangle \langle \bar{E}, \mathbf{n}, q^- | \hat{\epsilon} \cdot \mathbf{d} | E_i \rangle \int dE e^{-iE(t-t')/\hbar} =$$

$$2\pi\hbar \langle E_j | \hat{\epsilon} \cdot \mathbf{d} | \bar{E}, n, q^- \rangle \langle \bar{E}, \mathbf{n}, q^- | \hat{\epsilon} \cdot \mathbf{d} | E_i \rangle \delta(t-t') \ .$$

Using this equation and the identity $\int_0^t dt' \delta(t-t') = 1/2$, we obtain that,

$$\frac{d}{dt} b_j(t) = -\sum_i \varepsilon(t)^2 e^{i\omega_{j,i}t} \Gamma_{j,i}(\bar{E}) b_i(t)$$

where $\Gamma_{j,i}(\bar{E})$ are elements of the "width" matrix $\Gamma(\bar{E})$,

$$\Gamma_{j,i}(\bar{E}) \equiv \frac{\pi}{\hbar} \sum_q \langle E_j | \hat{\epsilon} \cdot \mathbf{d} \left\{ \sum_n | \bar{E}, n, q^- \rangle \langle \bar{E}, n, q^- | \right\} \hat{\epsilon} \cdot \mathbf{d} | E_i \rangle \equiv \sum_q \Gamma_{j,i}^{(q)}(\bar{E}) \ ,$$

where $\Gamma_{j,i}^{(q)}(\bar{E})$ are the *partial* width matrix elements,

$$\Gamma_{j,i}^{(q)}(\bar{E}) \equiv \frac{\pi}{\hbar} \sum_n \langle E_j | \hat{\epsilon} \cdot \mathbf{d} | \bar{E}, n, q^- \rangle \langle \bar{E}, n, q^- | \ \hat{\epsilon} \cdot \mathbf{d} | E_i \rangle \ .$$

It is clear that the $\omega_{j,i}$ are the most important Fourier components of $|\varepsilon(t)|^2$.

We now consider a pulse composed of discrete Fourier components of the form,

$$\epsilon(\omega) = \sum_i \varepsilon_i \delta(\omega - \omega_{E,i}) + \varepsilon_i^* \delta(\omega + \omega_{E,i}) \ .$$

As a function of time this pulse is a discrete sum of Continuous Waves (CW)

$$\varepsilon(t) = \sum_i \varepsilon_i \exp(-i\omega_i t) + c.c. \ ,$$

whose intensity is given by

$$\varepsilon(t)^2 \equiv \sum_{i'i} [I_{i',i} \exp(-i(\omega_{i'} - \omega_i)t) + J_{i',i} \exp[-i(\omega_{i'} + \omega_i)t] + c.c.]$$

where

$$I_{i',i} = \varepsilon_{i'} \varepsilon_i^* \ , \qquad J_{i',i} = \varepsilon_{i'} \varepsilon_i$$

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where

$$I_{i',i} = \varepsilon_{i'} \varepsilon_i^* \ , \qquad J_{i',i} = \varepsilon_{i'} \varepsilon_i$$

Setting $\omega_i = \omega_{E,i} = (E - E_i)/\hbar$ and neglecting the very fast Fourier components of $|\varepsilon(t)|^2$ associated with $J_{i',i}$, we have that

$$\frac{d}{dt}b_j(t) = -\sum_i \sum_{i',i''} \{ I_{i',i''} \exp[i(\omega_{j,i} - (\omega_{i'} - \omega_{i''})t] +$$

$$I^*_{i',i''} \exp[i(\omega_{j,i} + (\omega_{i'} + \omega_{i''})t] \} \, \Gamma_{j,i}(\bar{E}) b_i(t)$$

Keeping just those terms for which $\omega_{j,i} - (\omega_{i'} + \omega_{i''}) = 0$ or $\omega_{j,i} + (\omega_{i'} + \omega_{i''}) = 0$, i.e., $i' = j$ and $i'' = i$, we have that

$$\frac{d}{dt}b_j(t) = -\sum_i I_{j,i} \Gamma_{j,i}(\bar{E}) b_i(t)$$

$$\frac{d}{dt}b_j(t) = -\sum_{i}\sum_{i',i''}\{I_{i',i''}\exp[i(\omega_{j,i} - (\omega_{i'} - \omega_{i''})t] + I^*_{i',i''}\exp[i(\omega_{j,i} + (\omega_{i'} + \omega_{i''})t]\}\,\Gamma_{j,i}(\bar{E})b_i(t)$$

Keeping just those terms for which $\omega_{j,i} - (\omega_{i'} + \omega_{i''}) = 0$ or $\omega_{j,i} + (\omega_{i'} + \omega_{i''}) = 0$, i.e., $i' = j$ and $i'' = i$, we have that

$$\frac{d}{dt}b_j(t) = -\sum_{i} I_{j,i}\Gamma_{j,i}(\bar{E})b_i(t)$$

By eliminating the continuum we have obtained a discrete number of coupled differential equations. The results can then be used to obtain the photodissociation probability. In addition to the diagonal $\Gamma_{i,i}$ terms, which describe the decay of each bound state to the continuum, the off diagonal $\Gamma_{j,i}$ terms allow for laser-induced population transfer between the bound states, in what amounts to a stimulated resonance Raman process via the continuum.

Thus, a strong pulse whose power spectrum encompasses the $\omega_{j,i}$ component, would, even if operating on a single precursor $|E_i\rangle$ state, give rise in a short time to the formation of a superposition of $|E_j\rangle$ states (i.e., the $|\chi(t)\rangle$ state of Bichromatic control). Pulse shaping thus acts not only to modify the photo-excitation to the continuum, but also to modify the composition of the of the precursor $|\chi(t)\rangle$ state.

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VI.7 Resonantly Enhanced Two-Photon Association

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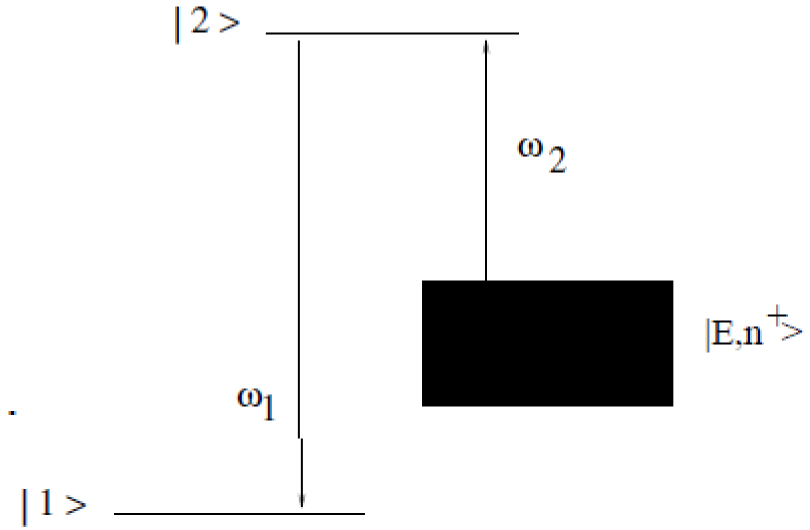
VI.7 Resonantly Enhanced Two-Photon Association



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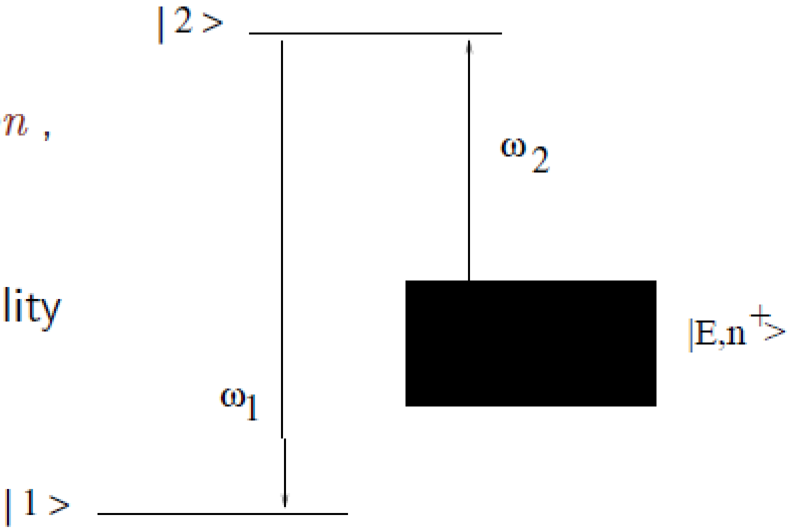
VI.7 Resonantly Enhanced Two-Photon Association



Resonantly enhanced two photon *association*, is depicted schematically in the Figure.

The significance stems from the possibility of using it to form ultra-cold molecules.

Those laser cooling schemes that work for atoms tend to fail for molecules, mainly due to the presence of many near-resonance lines.

Rather than cooling warm molecules one can try to *synthesize* cold molecules by associating cold atoms. The molecules thus formed are expected to maintain the translational temperature of the recombining atoms, because the center-of-mass motion remains unchanged in the association process (save for the little momentum imparted by the photon) .

Rather than cooling warm molecules one can try to *synthesize* cold molecules by associating cold atoms. The molecules thus formed are expected to maintain the translational temperature of the recombining atoms, because the center-of-mass motion remains unchanged in the association process (save for the little momentum imparted by the photon) . This idea was first proposed by Julienne et al. who envisioned a multi-step association, first involving the continuum-to-bound excitation of translational continuum states of cold trapped atoms to an excited vibrational level in an excited electronic molecular state. This step was followed by a bound-bound spontaneous emission to the ground electronic state.

An undesirable feature of this scheme is that the spontaneous nature of the second step allows the molecules to end up in a large range of vibrational levels. As a consequence, the use of *stimulated* emission discussed below, is preferable because it allows population transfer to a particular final molecular state of interest.

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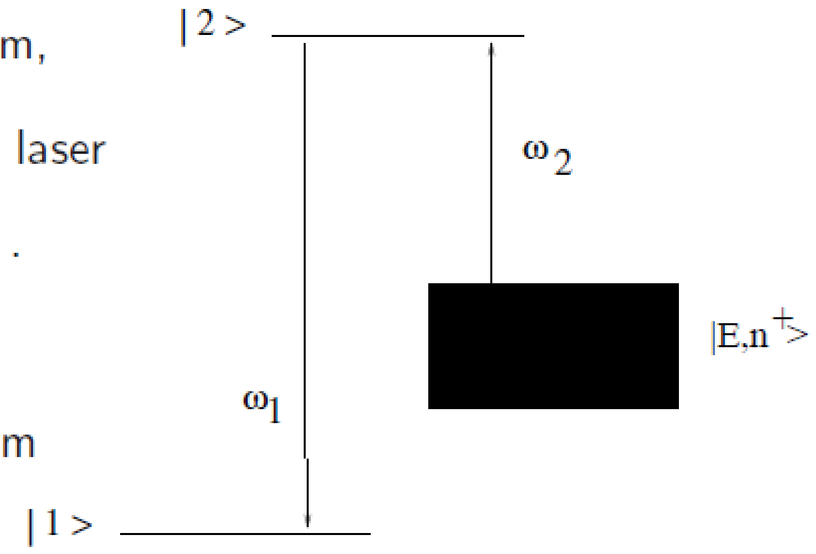
VI.7.a Theory of Photo-Association of a Coherent Wave Packet

In photoassociation the initial state is the scattering state and the goal is to transfer the population to the final *bound* state $|E_1\rangle$. We therefore consider a pair of colliding atoms described by scattering states $|E, n^+\rangle$ with n incorporating the quantum indices specifying the electronic states of the separated atoms and E being the total collision energy. The plus notation signifies, in contrast with the minus states that were previously used to describe dissociation processes, that the *initial* state of the fragments is known.

We focus attention on a Λ-type system, subjected to the combined action of two laser pulses of central frequencies ω_1 and ω_2 .

Here ω_2 is in near-resonance with the transition from the $|\,E, n^+\rangle$ continuum to an intermediate bound state $|\,E_2\,\rangle$ and ω_1 is in near-resonance with the transition from $|\,E_2\,\rangle$ to $|\,E_1\,\rangle$.



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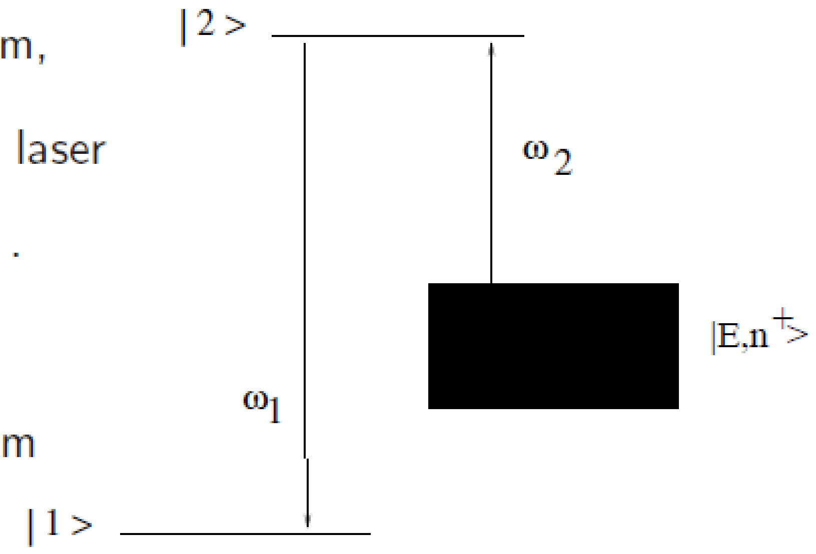

We then solve the Schrödinger equation by expanding the total wave function as before, with the notable exception that here the *incoming* solutions $|\, E, n^- \rangle$ are replaced by the outgoing solutions $|\, E, n^+ \rangle$,

$$
|\,\Psi(t)\,\rangle = b_1(t)|\,E_1\,\rangle e^{-iE_1t/\hbar} + b_2(t)(t)|\,E_2\,\rangle e^{-iE_2t/\hbar} + \\
\sum_n \int dE b_{E,\mathrm{n}}(t)|\,E, n^+\,\rangle e^{-iEt/\hbar} \; .
$$

We obtain a set of first-order differential equations, which is now of the form

$$
\begin{aligned}
&\tfrac{d}{dt} b_1(t) = i\Omega_1^*(t)e^{-i\Delta_1 t} b_2(t) \; , \\
&\tfrac{d}{dt} b_2(t) = i\Omega_1(t)e^{i\Delta_1 t} b_1(t) + i \textstyle\int dE \sum_{\mathrm{n}} \Omega_{2,E,\mathrm{n}}(t)e^{-i\Delta_E t} b_{E,\mathrm{n}}(t) \; , \\
&\tfrac{d}{dt} b_{E,\mathrm{n}} = i\Omega_{2,E,\mathrm{n}}^*(t)e^{i\Delta_E t} b_2(t)(t) \; , \qquad\qquad \text{for all } E \text{ and } n \; ,
\end{aligned}
$$

where

$$
\begin{aligned}
\Omega_1(t) &\equiv \langle\psi_2|\mathbf{d}_1 \cdot \hat{\epsilon}_1 \mid E_1\rangle\varepsilon_1(t)/\hbar \; , \\
\Omega_{2,E,\mathrm{n}}(t) &\equiv \langle\psi_2|\mathbf{d}_2 \cdot \hat{\epsilon}_2|\,E, n^+\,\rangle\varepsilon(t)/\hbar \; , \\
\Delta_1 &\equiv (E_2 - E_1)/\hbar - \omega_1, \\
\Delta_E &\equiv (E - E_2)/\hbar - \omega_2.
\end{aligned}
$$

Contrary to photo-dissociation, in photo-association, the continuum is initially populated. Therefore, the formal solution of the continuum coefficients is,

$$b_{E,\mathrm{n}}(t) = b_{E,\mathrm{n}}(t=0) + i\int_0^t dt'\Omega^*_{2,E,\mathrm{n}}(t')e^{i\Delta_E t'}b_2(t') \ .$$

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Substituting this solution into the equation for $b_2(t)$ gives

$$\tfrac{d}{dt} b_2(t) = i\Omega_1(t) e^{i\Delta_1 t} b_1(t) + i \textstyle\sum_{\mathrm{n}} \int dE \Omega_{2,E,\mathrm{n}}(t) e^{-i\Delta_E t} b_{E,\mathrm{n}}(0)$$
$$- \textstyle\sum_{\mathrm{n}} \int dE \int_0^t dt' \Omega_{2,E,\mathrm{n}}(t) \Omega^*_{2,E,\mathrm{n}}(t') \exp\left[-i\Delta_E (t-t')\right] b_2(t') \ .$$

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$$\tfrac{d}{dt}b_2(t) = i\Omega_1(t)e^{i\Delta_1 t}b_1(t) + i\textstyle\sum_\mathrm{n}\int dE\Omega_{2,E,\mathrm{n}}(t)e^{-i\Delta_E t}b_{E,\mathrm{n}}(0)$$
$$-\textstyle\sum_\mathrm{n}\int dE\int_0^t dt'\Omega_{2,E,\mathrm{n}}(t)\Omega^*_{2,E,\mathrm{n}}(t')\exp\left[-i\Delta_E(t-t')\right]b_2(t') \ .$$

When the molecular continuum is unstructured we can invoke the SVCA and replace the energy-dependent bound-continuum dipole matrix-elements by their value at the pulse center, given (in the Λ configuration) as $E_L = E_2 - \hbar\omega_2$.

This is the case, for example, for Na$_2$ at threshold energies, where the bound-continuum dipole matrix-elements vary with energy by less than 1% over a typical nsec-pulse bandwidth. Within the SVCA we obtain

$$\frac{db_2(t)}{dt} = i\Omega_1(t)e^{i\Delta_1 t}b_1(t) - \Gamma_2(t)b_2(t) + iF(t) \ ,$$

where $\quad F(t) \equiv \varepsilon(t)\bar{\mathrm{d}}_2(t)/\hbar \ ,$

$$\bar{\mathrm{d}}_2(t) \equiv \sum_{\mathbf{n}} \int dE \langle \psi_2 | \mathbf{d}_2 \cdot \hat{\epsilon}_2 | \, E, n^+ \rangle e^{-i\Delta_E t} b_{E,\mathbf{n}}(0) \ .$$

$\Gamma_2(t)$ of the above is defined (in analogy to the CW case) as,

$$\Gamma_2(t) \equiv (\pi/\hbar)\varepsilon_2^2(t) \sum_n \langle \, E_j \, | \hat{\epsilon}_2 \cdot \mathbf{d}_2 | \, \bar{E}, n^+ \, \rangle \langle \, \bar{E}, n^+ \, | \, \hat{\epsilon}_2 \cdot \mathbf{d}_2 | E_i \rangle \ .$$

The first-order differential equations can be expressed in matrix notation as

$$\frac{d}{dt}\underline{\mathsf{c}} = i\underline{\underline{\mathsf{H}}}(t) \cdot \underline{\mathsf{c}}(t) + i\underline{\mathsf{f}} \ ,$$

where $\underline{\mathsf{f}}$ and $\underline{\mathsf{c}}$ are column vectors defined as, $\underline{\mathsf{f}}(t) = (0, F(t))$,
$\underline{\mathsf{c}} \equiv (e^{i\Delta_1 t}b_1, b_2(t))$, and

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The “*net association rate*” $R(t)$ is the rate of population-change in the bound manifold, given by $\frac{d}{dt}(|b_1|^2 + |b_2(t)|^2)$. It can be written as,

$$\begin{gathered} R(t) = \tfrac{d}{dt}\left(|b_1|^2 + |b_2(t)|^2\right) = \tfrac{d}{dt}|\underline{c}|^2 = \underline{c}^\dagger \cdot \left(\tfrac{d}{dt}\underline{c}\right) + \left(\tfrac{d}{dt}\underline{c}^\dagger\right) \cdot \underline{c} = \\ i\left\{\underline{c}^\dagger \cdot (\underline{\underline{H}}(t) - \underline{\underline{H}}(t)^\dagger) \cdot \underline{c} + \underline{c}^\dagger \cdot \underline{f} - \underline{f}^\dagger \cdot \underline{c}\right\} = \\ 2I_m[F^*(t)b_2(t)] - 2\Gamma_2(t)|b_2(t)|^2\ . \end{gathered}$$

The first term in represents the association rate,

$$R_{rec}(t) \equiv 2I_m[F^*(t)b_2(t)] \ ,$$

and the second term is the back-dissociation rate,

As expected, the net association rate is the difference between the association rate and the back-dissociation rates.

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We can solve these differential equations adiabatically by diagonalizing the $\underline{\underline{\mathsf{H}}}(t)$ matrix,

$$\underline{\underline{\mathsf{U}}}^{\mathsf{T}}(t) \cdot \underline{\underline{\mathsf{H}}}(t) \cdot \underline{\underline{\mathsf{U}}}(t) = \underline{\underline{\lambda}}(t),$$

where $\underline{\underline{\mathsf{U}}}^{\mathsf{T}}$ is the transpose of $\underline{\underline{\mathsf{U}}}$.

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Operating with $\underline{\underline{\mathsf{U}}}^{\mathsf{T}}$ and defining $\underline{\mathrm{a}}(t) \equiv \underline{\underline{\mathsf{U}}}^{\mathsf{T}}(t) \cdot \underline{\mathrm{c}}$, we obtain that

$$\underline{\dot{\mathrm{a}}} = (i\underline{\underline{\lambda}}(t) + \underline{\underline{\mathrm{A}}}) \cdot \underline{\mathrm{a}} + i\underline{\mathrm{g}} \ ,$$

where $\underline{\underline{\mathsf{A}}} \equiv \left(d\underline{\underline{\mathsf{U}}}^{\mathsf{T}}/dt \right) \cdot \underline{\underline{\mathsf{U}}}$ is the non-adiabatic coupling matrix.

$\underline{\mathrm{g}}$ is a column ("source") vector whose transpose is given as

$$\underline{\mathrm{g}}^{\mathsf{T}}(t) = \Big(F(t)U_{1,2}(t), F(t)U_{2,2}(t) \Big) = \Big(F(t)\sin\theta(t), F(t)\cos\theta(t) \Big) \; .$$

When $\underline{\underline{\mathsf{A}}}$ is neglected (the adiabatic approximation) we obtain that

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$$\dot{\underline{\mathrm{a}}} = i\underline{\underline{\lambda}}(t)\cdot\underline{\mathrm{a}}(t) + i\underline{\mathrm{g}}(t) \quad .$$

In the association process the initial conditions are such that

$$\underline{\mathrm{a}}(t=0) = 0 \ ,$$

so that the adiabatic solutions are

$$\underline{\mathrm{a}}(t) = \underline{\underline{\mathrm{v}}}(t)\cdot\underline{\mathrm{q}}(t) \ ,$$

where $\underline{\underline{\mathrm{v}}}(t) = \exp\left(i\int_0^t \underline{\underline{\lambda}}(t')dt'\right)$, and $\underline{\mathrm{q}}(t) = i\int_0^t \underline{\underline{\mathrm{v}}}^{-1}(t')\cdot\underline{\mathrm{g}}(t')dt'$.

The $b_1(t)$ and $b_2(t)$ coefficients are thus given in the adiabatic approximation as,

$$\begin{aligned} b_1(t) = \ & i\left\{\cos\theta(t)\int_0^t dt' e^{i\int_{t'}^t \lambda_1(t'')dt''} F(t')\sin\theta(t')\right. \\ & \left. -\sin\theta(t)\int_0^t dt' e^{i\int_{t'}^t \lambda_2(t'')dt''} F(t')\cos\theta(t')\right\} e^{-i\Delta_1 t}\ , \\ b_2(t) = \ & i\left\{\sin\theta(t)\int_0^t dt' e^{i\int_{t'}^t \lambda_1(t'')dt''} F(t')\sin\theta(t')\right. \\ & \left. +\cos\theta(t)\int_0^t dt' e^{i\int_{t'}^t \lambda_2(t'')dt''} F(t')\cos\theta(t')\right\}\ . \end{aligned}$$

Given $b_2(t)$, the (channel-specific) continuum coefficients $b_{E,\mathrm{n}}(t)$ can then be readily obtained.

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& -\sin\theta(t)\int_0^t dt' e^{i\int_{t'}^{t}\lambda_2(t'')dt''}F(t')\cos\theta(t')\Big\}\, e^{-i\Delta_1 t}\,, \\
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\end{aligned}
$$

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It is clear that the source term $F(t)$ is linearly proportional to the pulse amplitude. On the other hand, since $\Omega_2 > 0$ and $t' < t$, the $\exp\left(-\int_{t'}^{t}\Gamma_2(t'')dt''\right)$ factor (describing dissociation back to the continuum) decays exponentially with increasing intensity. Thus, merely increasing the laser power does not necessarily increase the association yield. There exists some optimal intensity, beyond which the association probability decreases.

As an example of this formulation we consider pulsed photo-association of a coherent wave packet of cold Na atoms. The colliding atoms are described by an (energetically narrow) normalized Gaussian packet of $J=0$ radial waves:

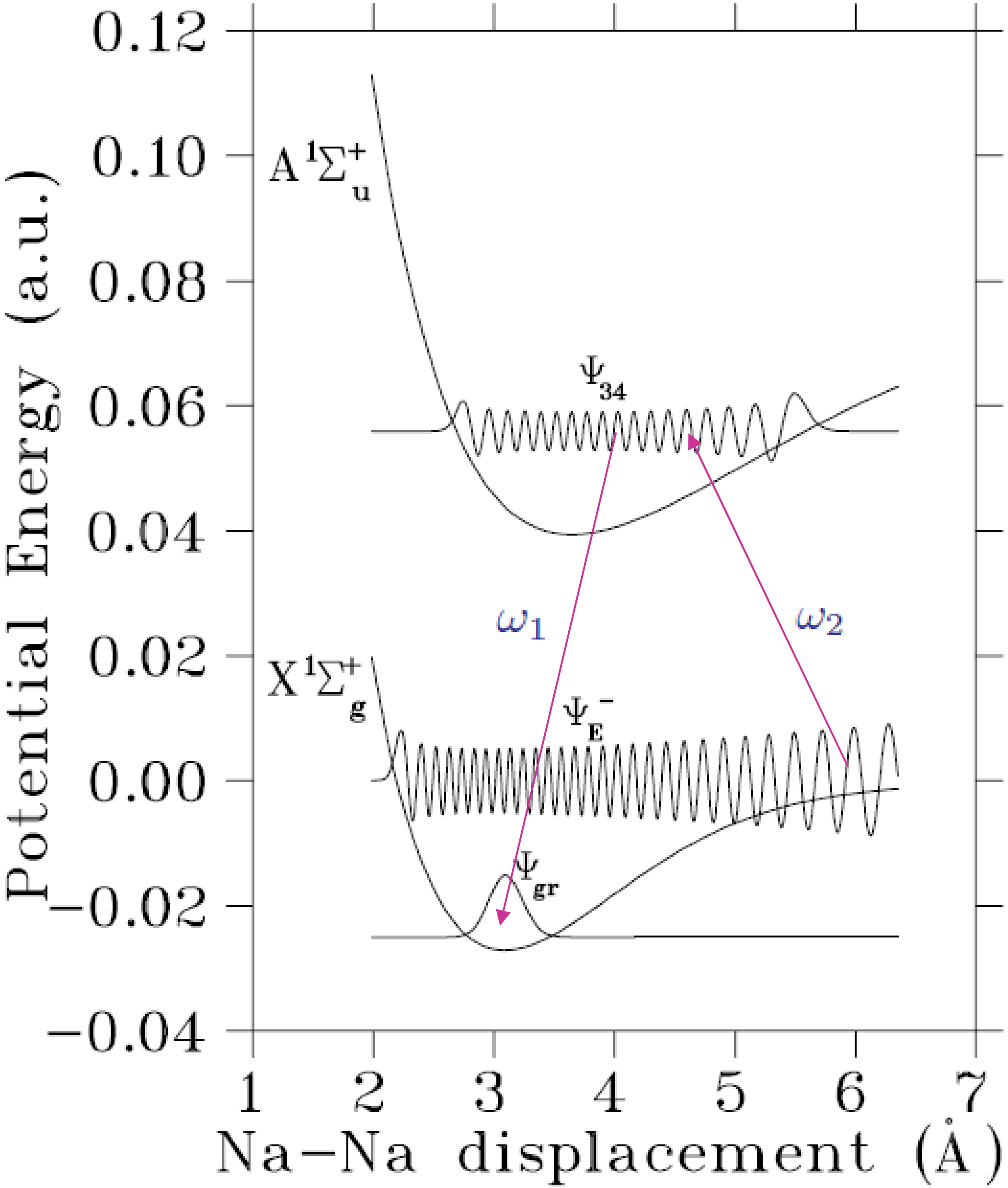
$$|\,\Psi(t=0)\,\rangle = \int dE\; b_E(t=0)|\,E, 3s+3s\,\rangle \quad ,$$

where $|\,E, 3s+3s\,\rangle$ are the translational Na-Na s-waves with the atoms in the 3s state, and b_E at time zero is taken as

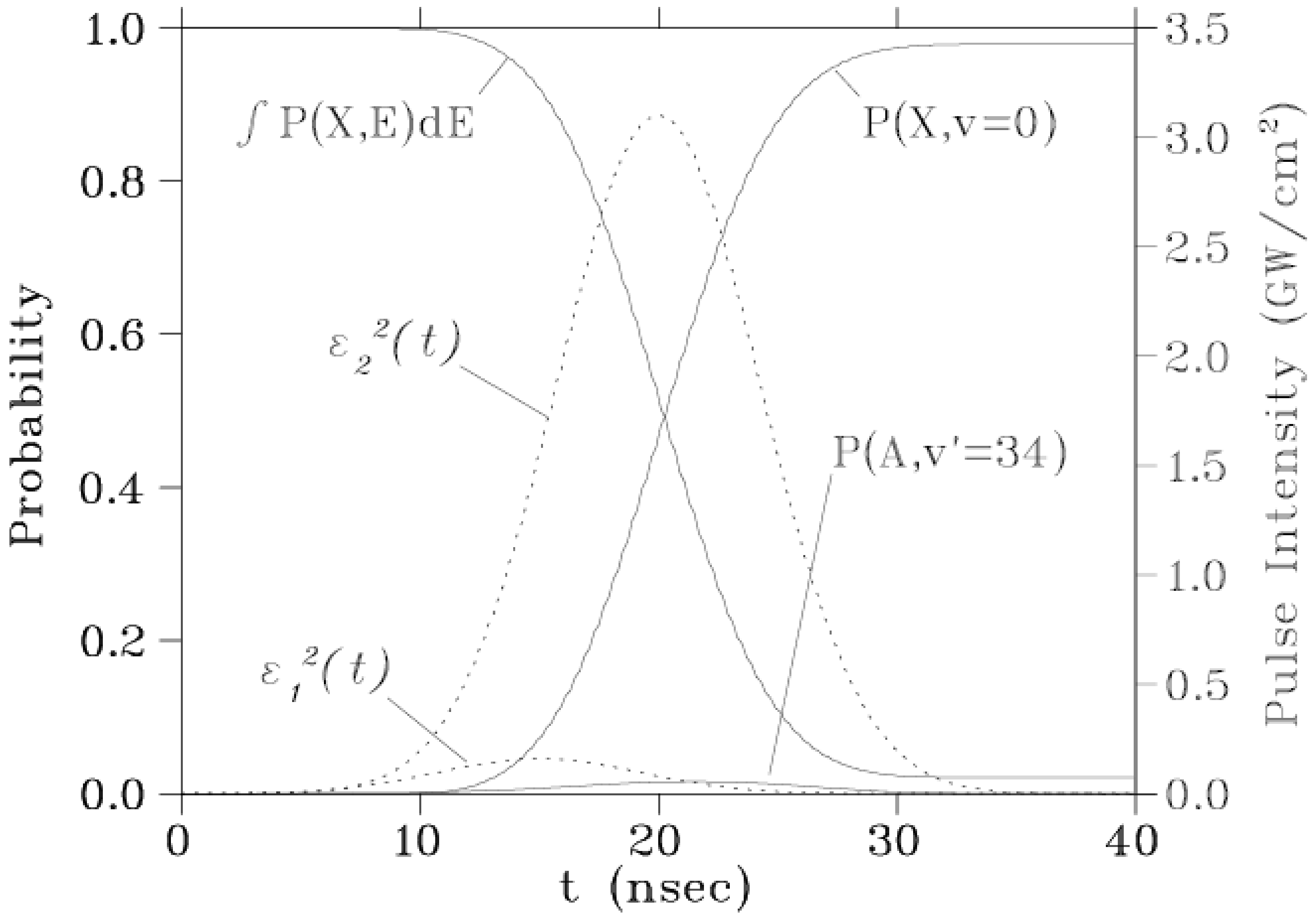
$$b_E(t=0) = (\delta_E^2\pi)^{-1/4}\exp\left\{-(E-E_{col})^2/2\delta_E^2 + i\Delta_E t_0\right\} \quad .$$

Here, t_0 denotes the instant of maximum overlap of the Na+Na wave packet with the $|\,E_2\,\rangle$ state. In the simulations, E_{col} , the mean collision energy, varies between $E_{col} = 0.00695 - 0.0695\mathrm{cm}^{-1} \approx 0.01K - 0.1K$ and the wave packet widths, δ_E , vary over the range $\delta_E = 10^{-4} - 10^{-3}\mathrm{cm}^{-1}$.

State $|E_1\rangle$ is chosen as the $(X^1\Sigma_g^+, v=0, J=0)$ state and $|E_2\rangle$ as $(A^1\Sigma_u^+, v'=34, J=1)$



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



Thus, the combined effect of the two laser pulses is the transfer of population from the continuum to the ground vib-rotational state $(X^1\Sigma_g^+, v = 0, J = 0)$, with the bound $(A^1\Sigma_u^+, v' = 34, J = 1)$ state acting as an intermediate state. The "counter-intuitive" scheme where the "dump" pulse $\varepsilon_1(t)$ is applied *before* the $\varepsilon_2(t)$ "pump" pulse eliminates spontaneous emission losses

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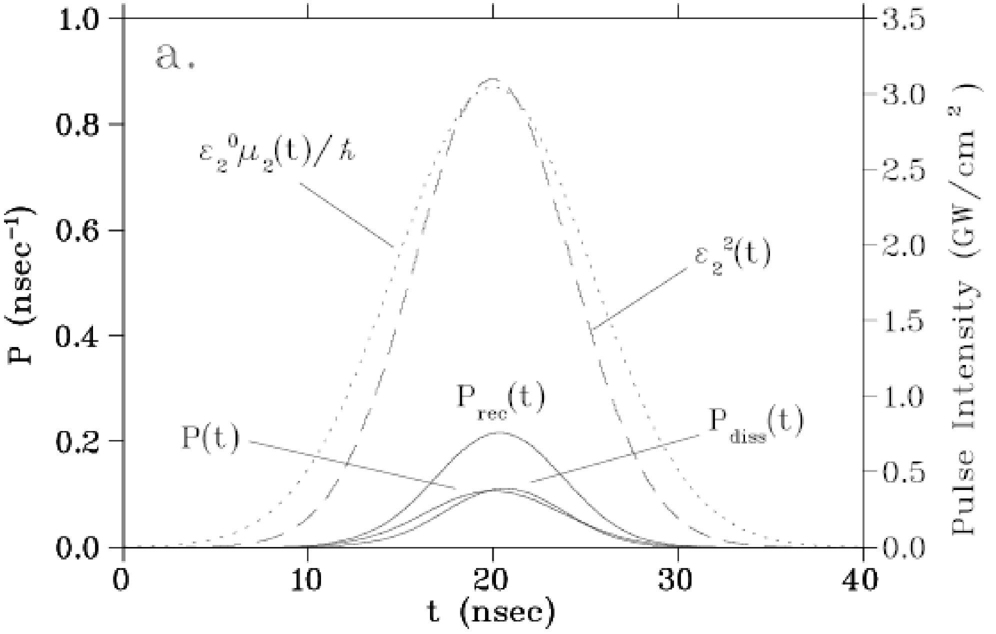
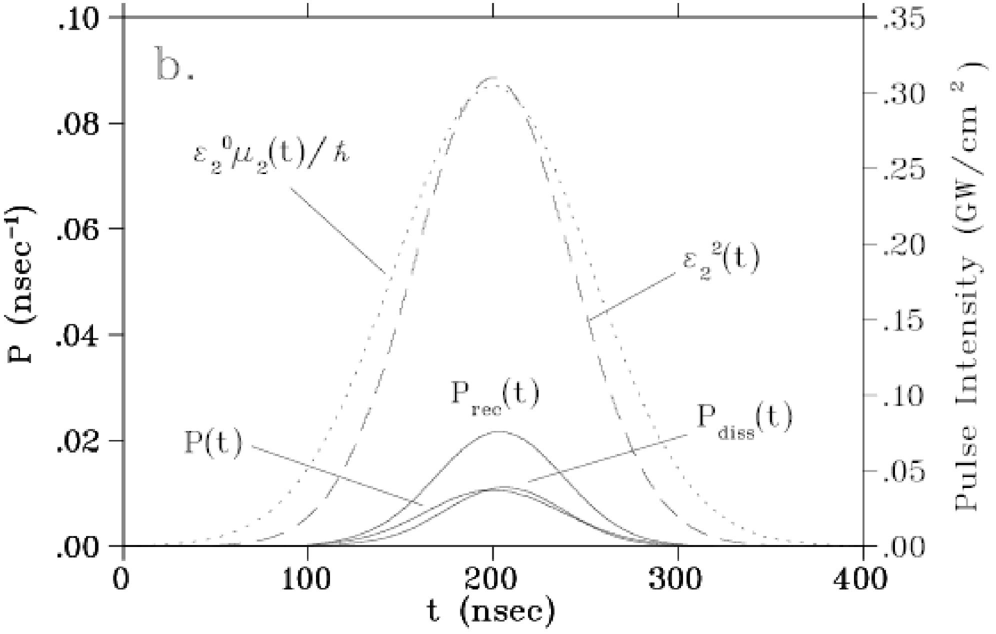
The appearance of an imaginary Rabi frequency, such as $i\Gamma_2(t)$, which is due to the presence of a continuum, may change the range of validity of the adiabatic approximation. A "large area" ($\int \Omega dt$) pulses no longer guarantees that we can neglect the non-adiabatic coupling matrix $\underline{\underline{\mathsf{A}}}$. Despite this fact, we show below that with the proper choice of pulse parameters, an effective "dark state" can be formed.


a.
$\varepsilon_2{}^0\mu_2(t)/\hbar$
$\varepsilon_2{}^2(t)$
$P_{rec}(t)$
$P(t)$
$P_{diss}(t)$
P (nsec^{-1})
0.0
0.2
0.4
0.6
0.8
1.0
Pulse Intensity (GW/cm^2)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
t (nsec)
0
10
20
30
40


b.
$\varepsilon_2{}^0\mu_2(t)/\hbar$
$\varepsilon_2{}^2(t)$
$P_{rec}(t)$
$P(t)$
$P_{diss}(t)$
P (nsec^{-1})
.00
.02
.04
.06
.08
.10
Pulse Intensity (GW/cm^2)
.00
.05
.10
.15
.20
.25
.30
.35
t (nsec)
0
100
200
300
400

Rates of association, (P_{rec}) back-dissociation (P_{diss}) and total molecule-formation (P) in the "counter-intuitive" scheme. Dashed lines - pulse intensity profile, dotted lines - effective Rabi frequency.

(**a**) Initial wave packet width of $\delta_E = 10^{-3}$ cm^{-1} . Other pulse parameters as in the previous Figure. (**b**) The same dynamics scaled by $s = 10$: Initial wave packet width of $\delta_E = 10^{-4}$ cm^{-1} ; durations of both pulse - 85 nsec; pump (dump) pulse peaking at $t_0 = 200$ (150) nsec. Peak intensity of the dump (pump) pulse - 1.6×10^6 W/cm^2 (3.1×10^8 W/cm^2). From Ref. [5].

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

Both pannels appear identical, though in pannel b the abscissa is scaled up by a factor of 10 and the ordinate is scaled down by a factor of 10.

The scaling behavior demonstrated here is due to the existence of exact scaling relations. This scaling is obtained when the initial wave packet-width and the pulse intensities are scaled down as

$$\delta_E \rightarrow \frac{\delta_E}{s}\,, \quad \varepsilon_1^0 \rightarrow \frac{\varepsilon_1^0}{s}\,, \quad \varepsilon_2^0 \rightarrow \frac{\varepsilon_2^0}{\sqrt{s}}\,,$$

and the pulse durations are scaled up as $\Delta t_{1,2} \rightarrow \Delta t_{1,2} s$.

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It follows from the definition of $F(t)$ that under these transformations

$$F(t) \to \bar{F}_2(t) = \frac{F(t/s)}{s}\ ; \frac{\Omega_{1,2}(t/s)}{s}\ ,$$

and the set of ODE becomes

$$\frac{d\underline{\mathsf{c}}'}{dt/s} = i\underline{\underline{\mathsf{H}}}(t)(t/s)\cdot\underline{\mathsf{c}}' + i\underline{\mathsf{f}}(t/s)\ \ ,$$

where $\underline{\mathsf{c}}'$ denotes the vector of solutions of the scaled equations. Thus, the scaled coefficients at time t are identical to the un-scaled coefficients at times t/s .

One of the results of the above scaling relations is that the pulses' durations can be made longer and their intensities concomitantly scaled down, without changing the final population-transfer yields. As noted above, lengthening of the pulses is beneficial because it causes more atoms to recombine within a given pulse.

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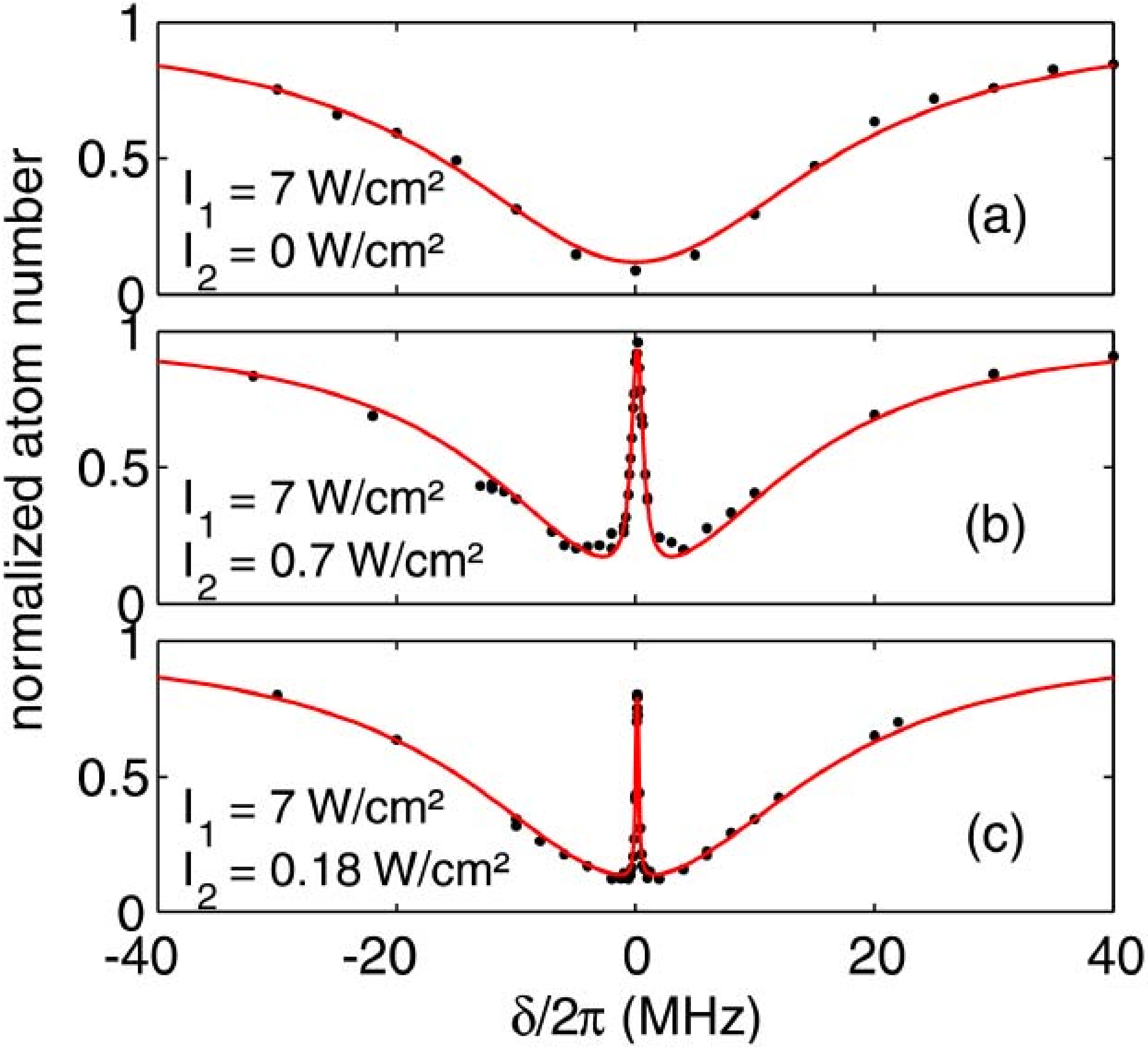
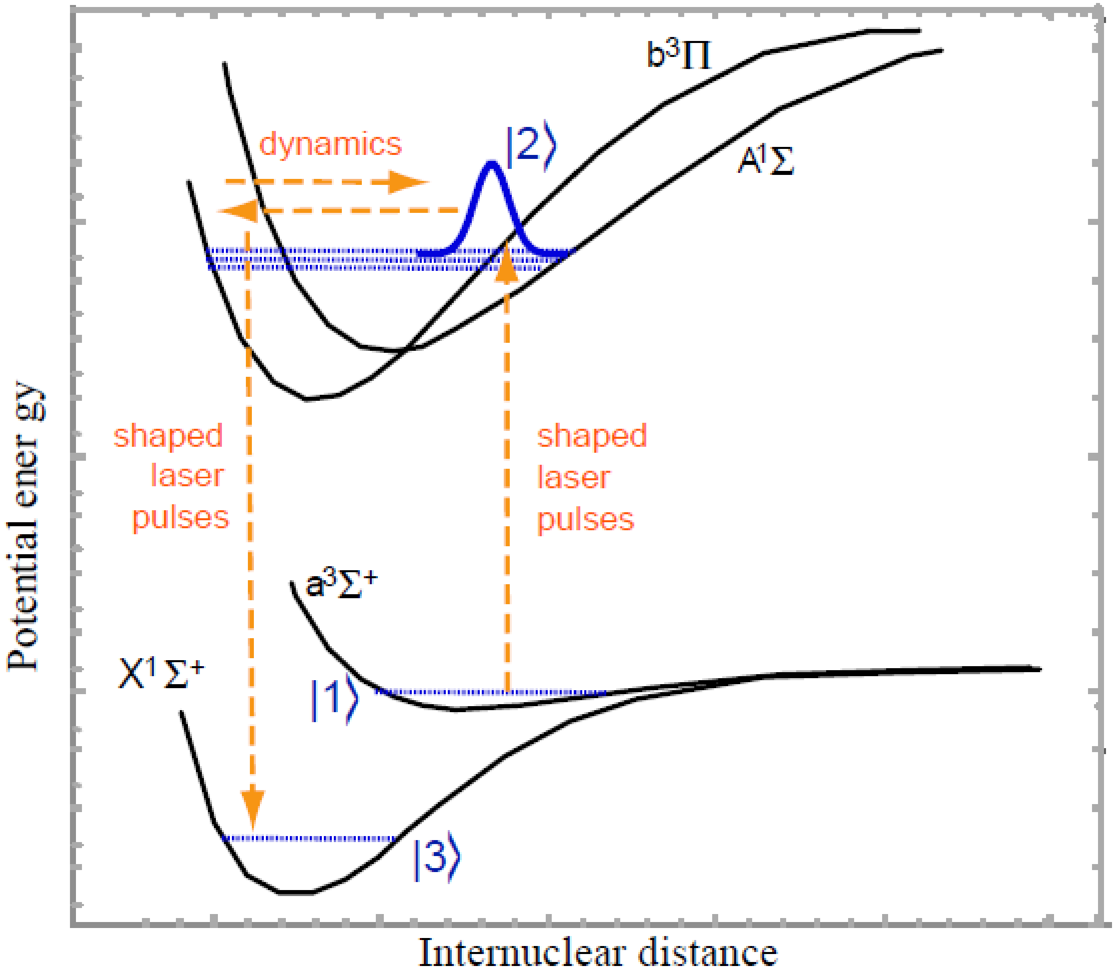
There is a range of pulse parameters (such as the pulse area, $\Omega_{2,E_L}\Delta t_2$) that maximizes the association yield for a *fixed* initial wave packet. For both the "intuitive" and the "counter-intuitive" schemes there is a clear maximum at a specific pulse area; merely increasing the pulse intensity does not lead to an improved association yield. We can attribute this behavior to the fact that the association rate [R_{rec}], increases linearly with increasing pulse intensity, whereas dissociation rate [R_{diss}] increases exponentially with the intensity.

Experimental confirmations of photoassociation via two photon transition as discussed above have been obtained. Evidence that counter-intuitive pulse ordering might result in large photo-association cross-sections as suggested above has also been presented. Of especial significance is the experiment of Winkler et al. where a dark state such as the one predicted above has been observed in the photoassociation of Rb BEC to form Rb_2 BEC. As shown in the Figure as the intensity of the dump laser is lowered a dark state causing the system to "decouple" from the laser fields is seen to be formed. .



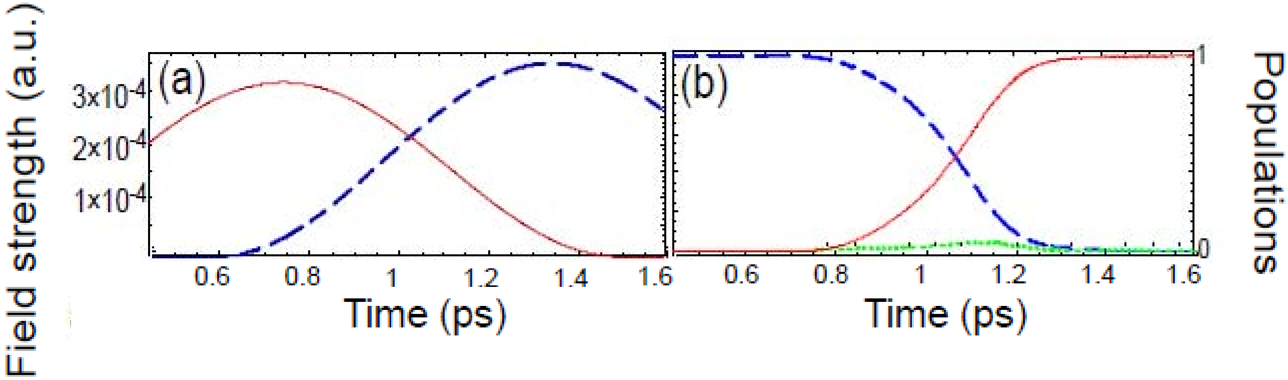
Formation of dark state in photoassociation of Rb BEC. Taken from

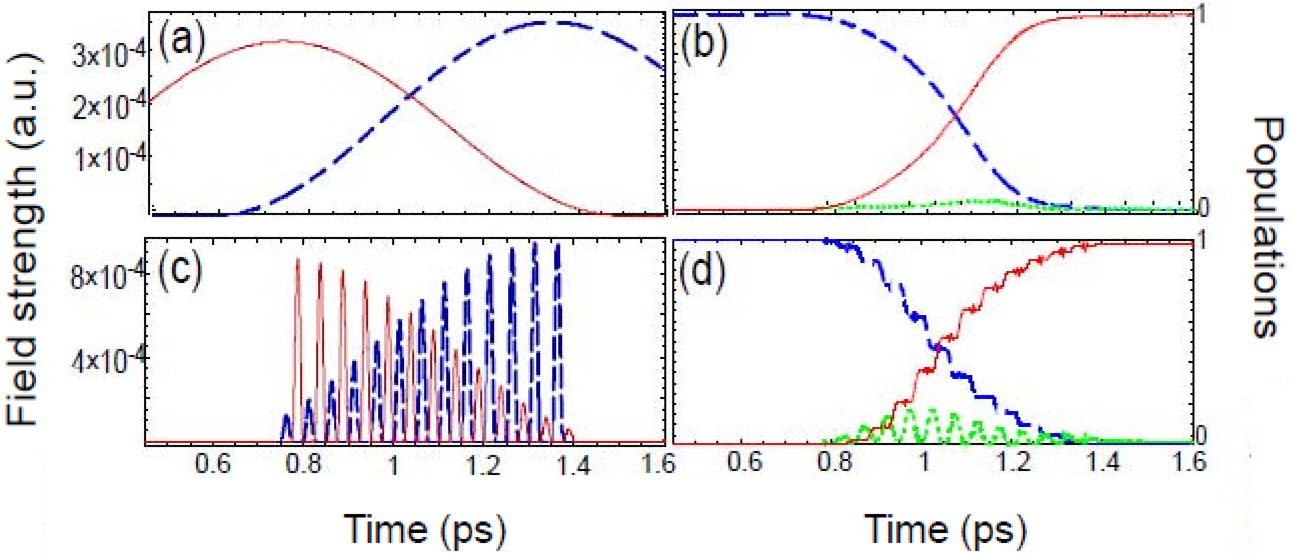
K. Winkler, G. Thalhammer, M. Theis, H. Ritsch, R. Grimm, and
J. Hecker Denschlag, Phys. Rev. Lett. **95**, 063202 (2005).

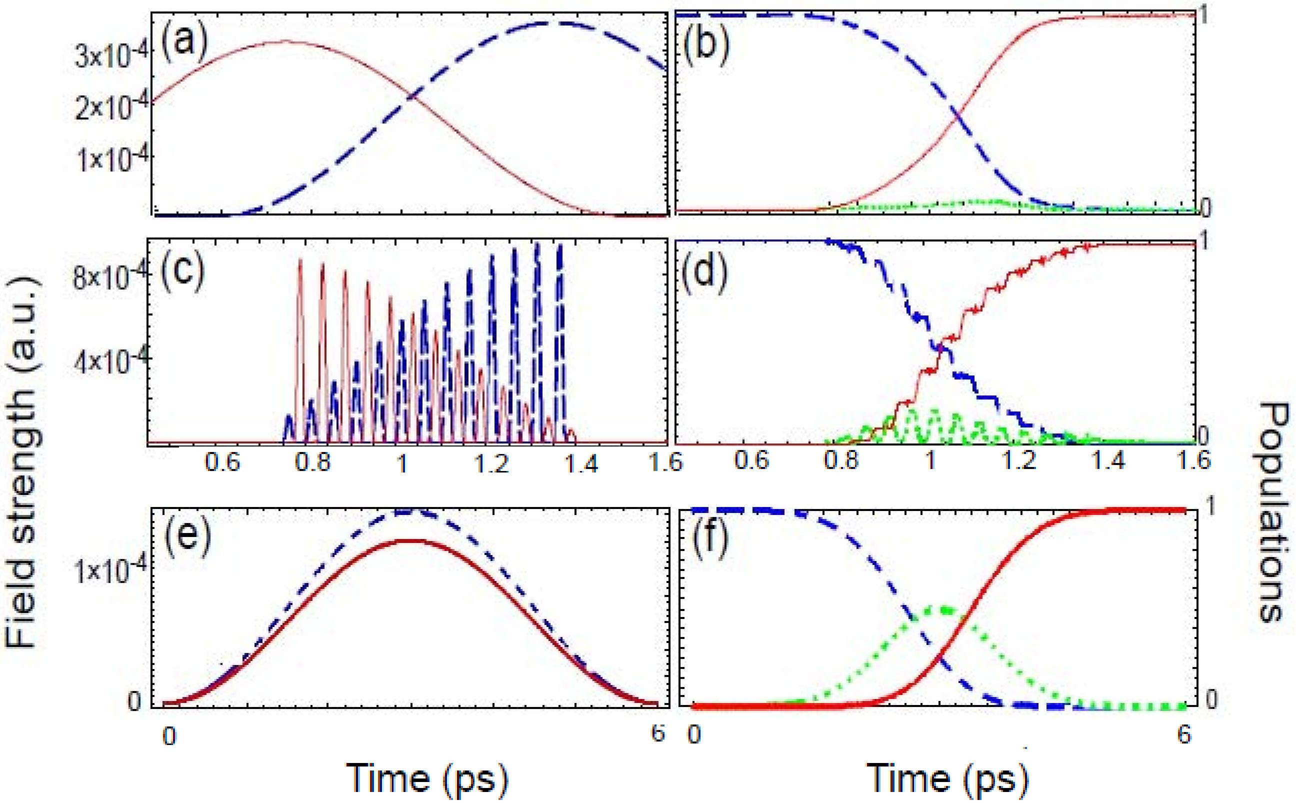


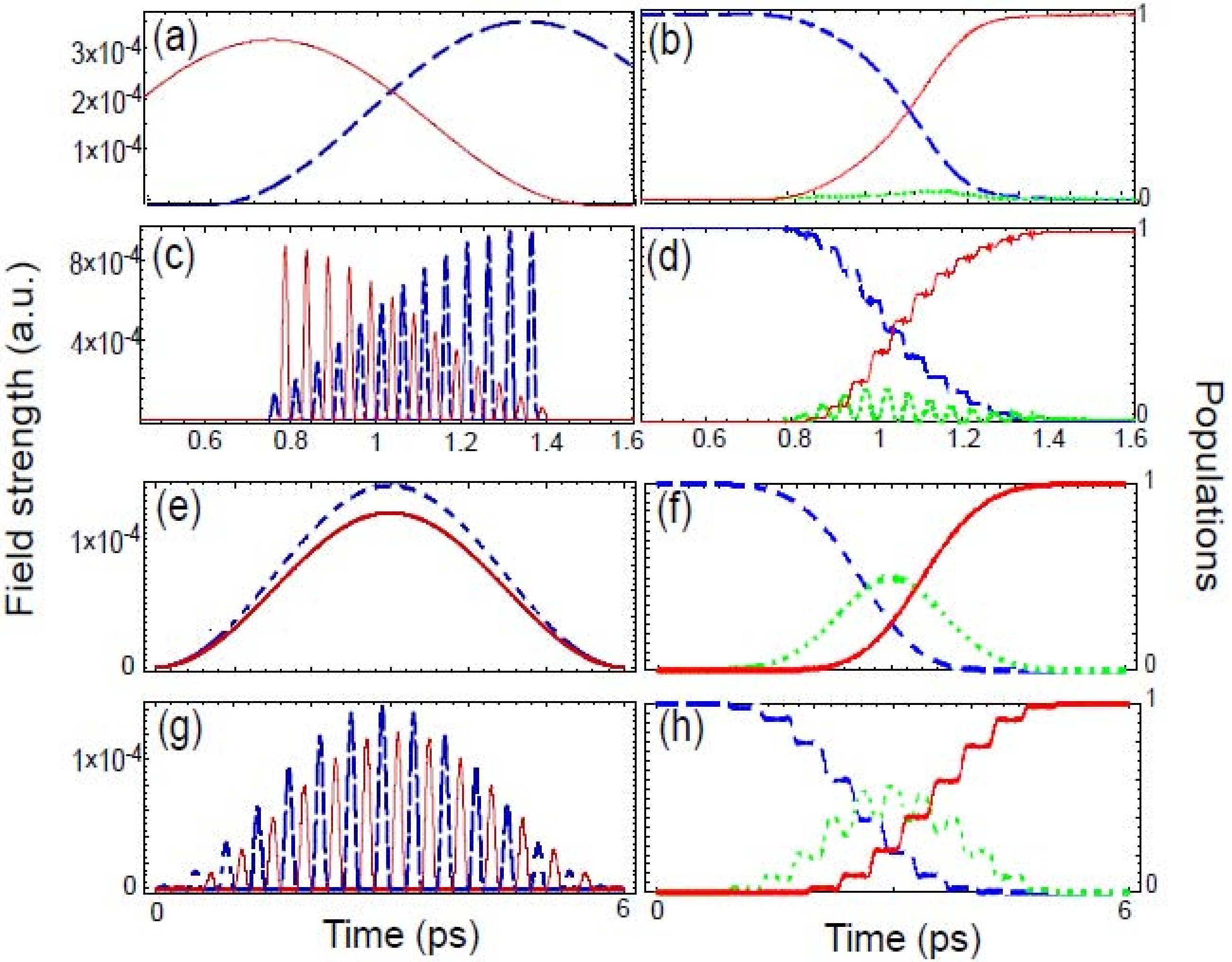
KRb potentials and Piecewise Adiabatic Passage Ref. [8]

Evgeny A. Shapiro, Avi Pe'er, Jun Ye, Moshe Shapiro, Phys. Rev. Lett. in press .

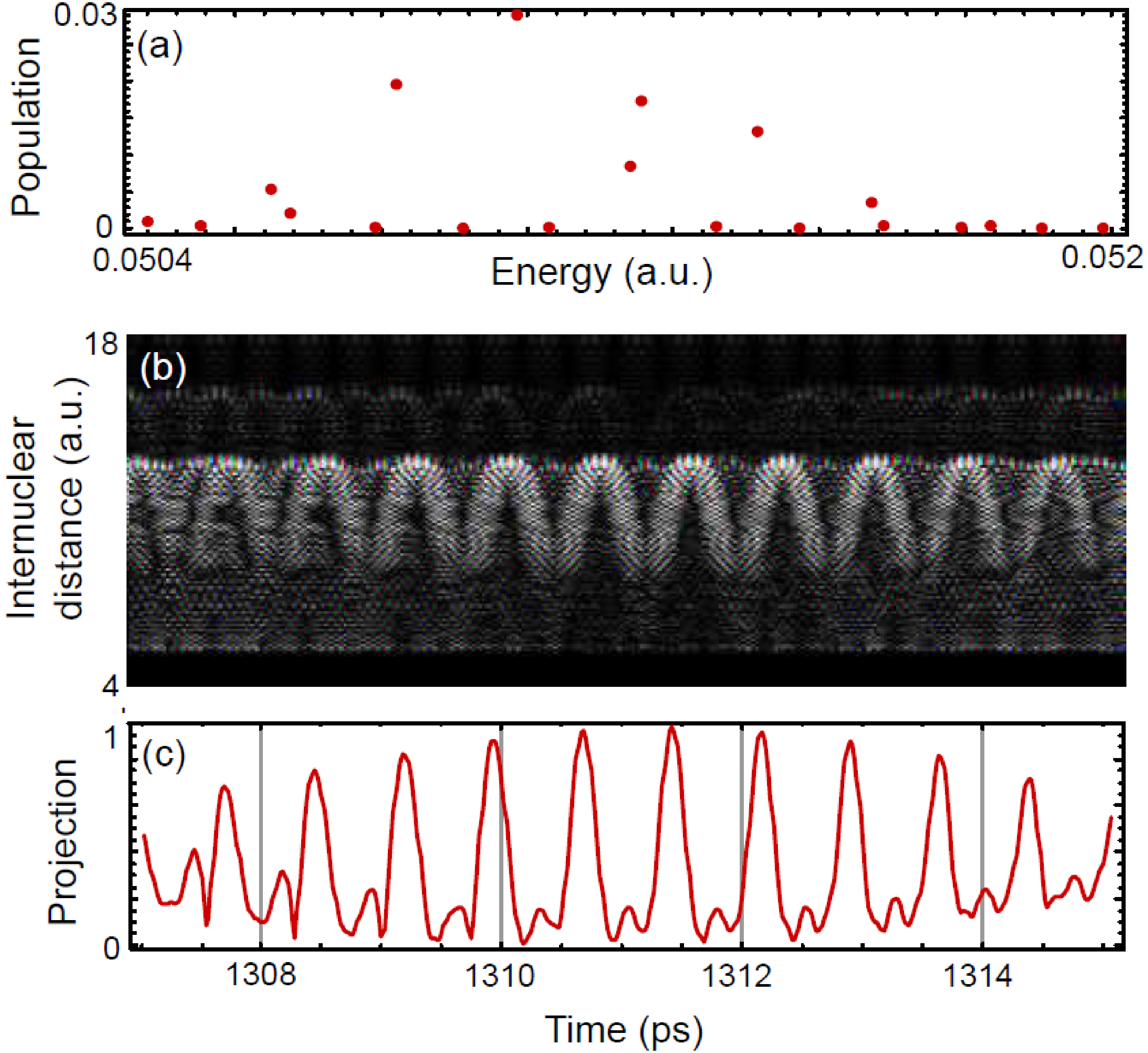

Field strength (a.u.)
(a)
3x10-4
2x10-4
1x10-4
0.6
0.8
1
1.2
1.4
1.6
Time (ps)
(b)
1
0
0.6
0.8
1
1.2
1.4
1.6
Time (ps)
Populations


(a)
(b)
(c)
(d)
Field strength (a.u.)
3x10-4
2x10-4
1x10-4
8x10-4
4x10-4
Populations
1
0
1
0
0.6
0.8
1
1.2
1.4
1.6
0.6
0.8
1
1.2
1.4
1.6
Time (ps)
Time (ps)


(a)
(b)
(c)
(d)
(e)
(f)
3x10-4
2x10-4
1x10-4
8x10-4
4x10-4
1x10-4
0
1
0
1
0
1
0
0.6
0.8
1
1.2
1.4
1.6
0.6
0.8
1
1.2
1.4
1.6
0
6
0
6
Field strength (a.u.)
Populations
Time (ps)
Time (ps)



Two types of PAP processes: (a,c,e,g) - the pulse sequences; dashed blue - the pump, firm red - the dump. (b,d,f,h) - the populations ($|b_i(t)|^2$); dashed blue - $i = 1$, dotted green - $i = 2$, firm red - $i = 3$. (a,b,c,d):


(a)
Population
0.03
0
0.0504
0.052
Energy (a.u.)
(b)
Internuclear distance (a.u.)
18
4
(c)
Projection
1
0
1308
1310
1312
1314
Time (ps)

(a): Populations of $A^1\Sigma$-$b^3\Pi$ states following a single pump pulse;

(b): Quantum carpet showing the evolution of the $b^3\Pi$ component of the $b^3\Pi$-$A^1\Sigma$ wave packet. Amplitude of the wave function a each point is shown by brightness, its phase by color

(c): Correlation of the time-dependent excited state with that immediately after excitation. Time is measured relative to the beginning of the pump pulse.

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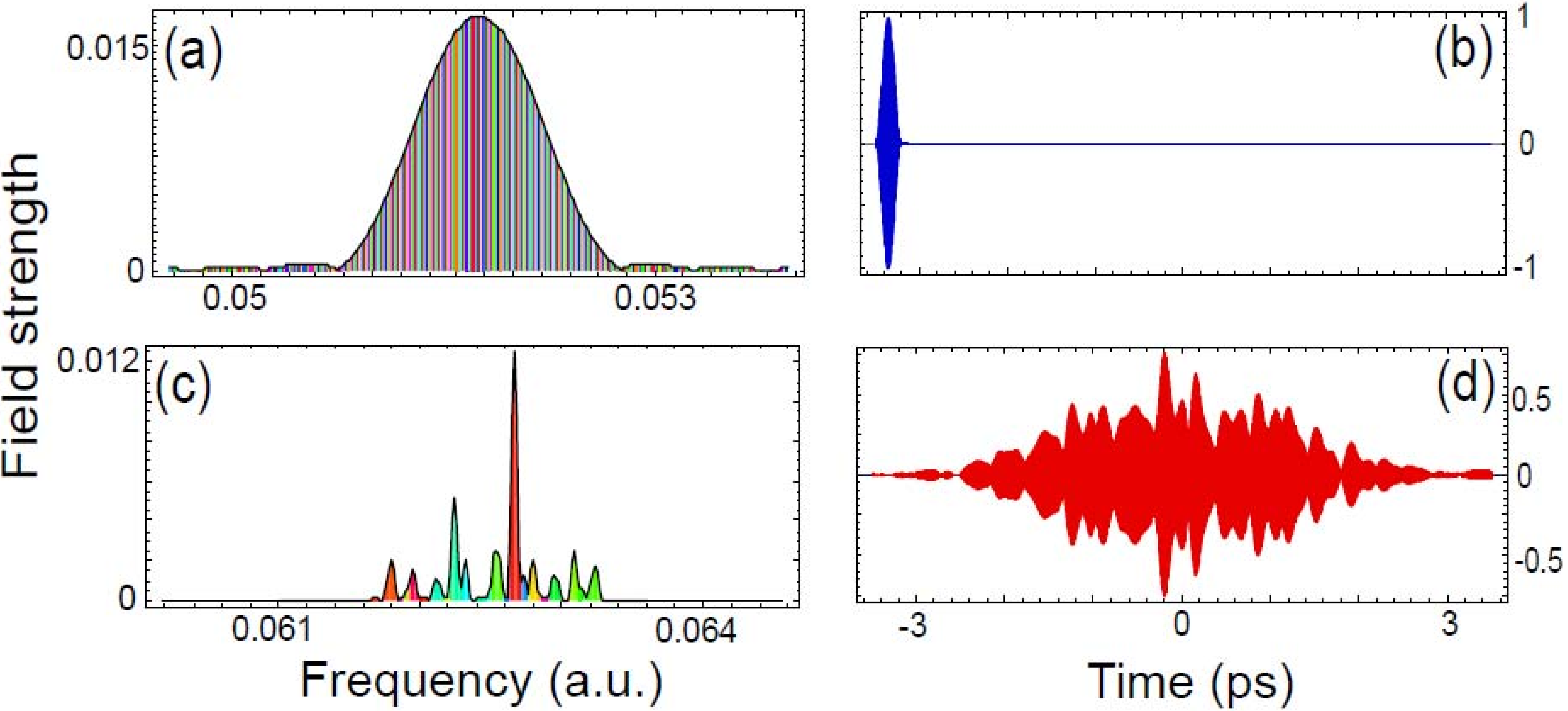
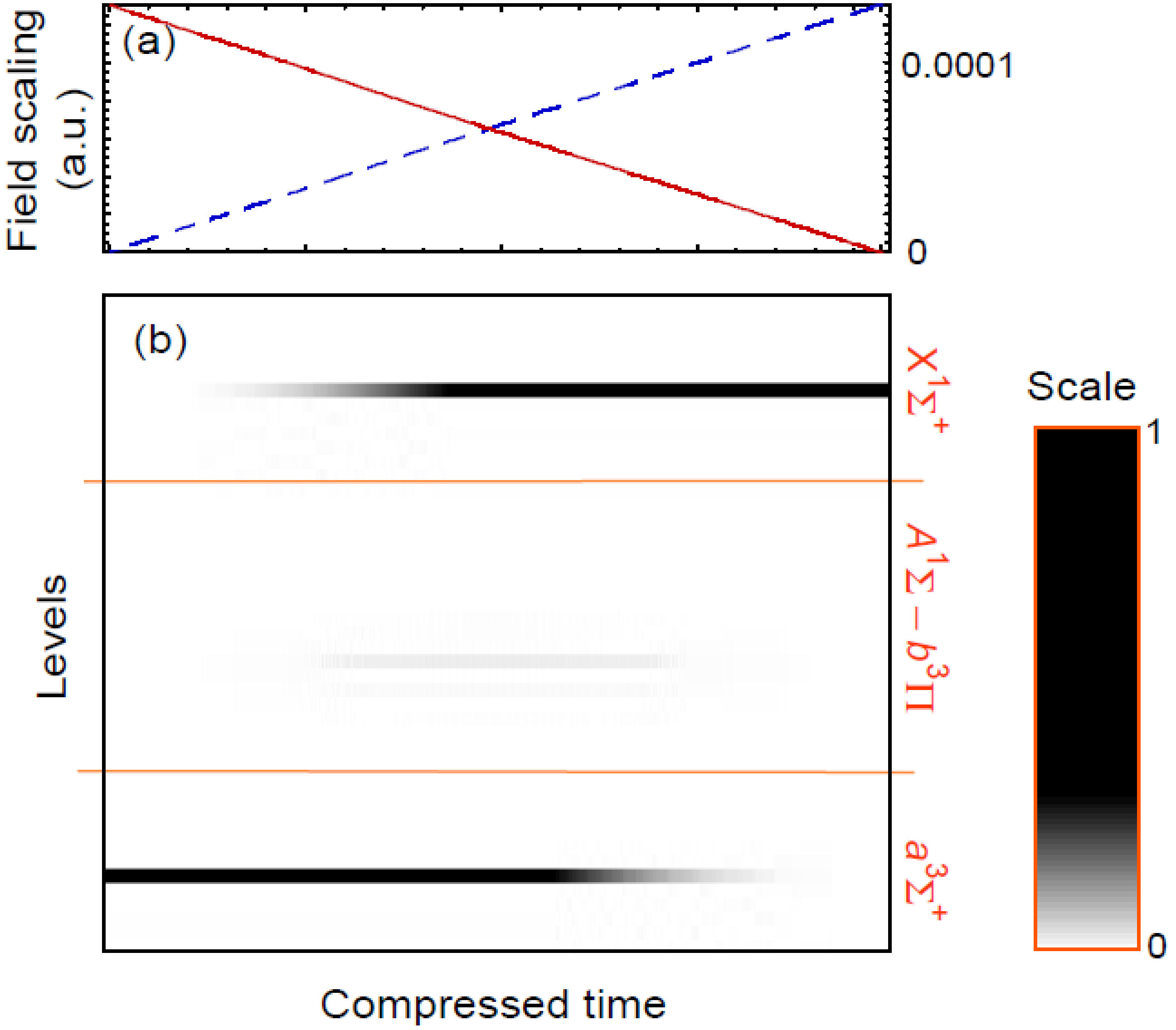
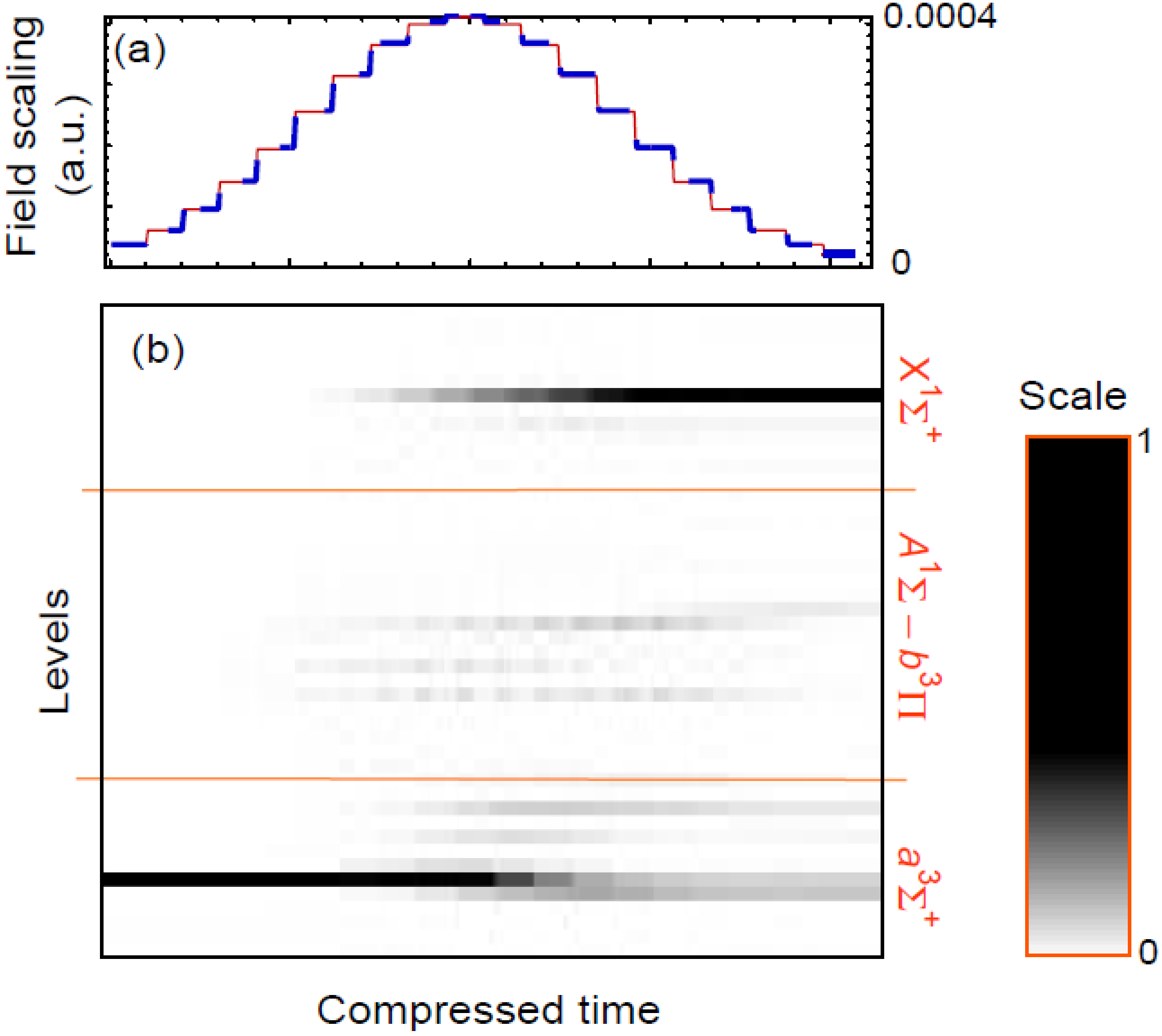


Spectrum (a,c) and time-dependant field (b,d) of the pump (a,b), and dump (c,d) pulses. The phase of the spectral components in Panels (a,c) is shown by color.



Dynamics of the STIRAP-like PAP in KRb. (a): Envelopes of the pump (dashed blue) and dump (red) pulses. (b): Population dynamics of all the levels in the system.


(a)
Field scaling (a.u.)
0.0004
0
(b)
Levels
$X^1\Sigma^+$
$A^1\Sigma-b^3\Pi$
$a^3\Sigma^+$
Scale
1
0
Compressed time

References

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