Atomic and Molecular Physics Report

$\boxed{\text{Coherent Transfer of Population}}$

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Introduction: In this article we will review the process of coherent transfer of population among atoms and molecules. Different phenomena are described by this method of transfer of population from one state to another. For example, a state which is prepared in initial state $|i\rangle$ evolves into some other state under the action of some time-varying Hamiltonian. To realize this process in an experiment, we mainly use lasers to transfer the population of one state to the desired state.

But the efficiency of this transfer, i.e. what percentage of the original state is being transferred, can be increased if we use two lasers to couple three states instead of one laser linking between two states. Below we discuss the two-state transfer method, its drawbacks, and the modified method, i.e. the three-state-two laser system in detail, we talk about the theory of this and explain its experimental procedure. We know that symmetry forbids different transitions from one state to another state directly (e.g. transition of an electron in the hydrogen atom). But we can realize those transitions by involving an extra intermediate state in this process, i.e. three state transfer methods.

Theoretical Discussions:

Two state One laser setup: Our goal is to transfer the population of one state to two other states by some intermediate process. By population, we mean the probability of finding the system in our desired state. Say, initially our state was in a state $|1\rangle$ ($\psi(0) = |1\rangle$). Essentially this transfer can be performed by three methods, 1) Adiabatic transfer 2) Incoherent excitation, and 3) Coherent Excitation.

1) **Incoherent excitation:** If we use an incoherent laser pulse to transfer population we get a time-dependent differential equation:

$$\frac{dP(t)}{dt} = \frac{\alpha I(t)}{2} - \alpha I(t)P(t)$$

. Here $P(t)$ is the probability of population transfer from $|1\rangle$ to $|2\rangle$. This equation quantifies a constant population transfer due to the applied laser pulse and an opposite transfer from the final to the initial state again driven by this laser. The solution of this equation simply reads:

$$P(t) = \frac{1}{2}(1 - e^{-\alpha \int_{-\infty}^{t} I(t')dt'}) \tag{1}$$

So, at $t \to \infty$, $P(t) = \frac{1}{2}$. We can see that at the end of the process, only half of the population gets transferred to our desired state which we would like to improve. To do that we use a coherent light pulse.

Coherent Excitation : In the case of coherent excitation, we need to describe the evolution of the probability amplitudes instead of probability as in the case of incoherent excitation. Because in the incoherent case, the interference was averaged out. In this case, the evolution is described by the Schrodinger equation, $i\bar{h}\partial_t |\psi\rangle = H |\psi\rangle$.

The process of coherent radiative transfer is described by a slow-varying enveloping pulse. That is if we apply a pulse $E(t) = A(t)e^{i\omega t}$ where $A(t)$ is a slowly varying amplitude of the pulse then we observe Rabi oscillation.

For a Time-varying Hamiltonian $H = (E_1 |1\rangle \langle 1| + E_2 |2\rangle \langle 2|) + [A(e^{i\omega t} + e^{-i\omega t} |1\rangle \langle 2| + \text{h.c}]$, by rotating the basis $|1\rangle \to |1'\rangle = e^{i\omega t} |1\rangle ; |2\rangle \to |2'\rangle = |2\rangle$and taking rotating wave approximation we find can rewrite the Hamiltonian as $H' = E_1 |1\rangle \langle 1| + E_2 |2\rangle \langle 2| + A[|1'\rangle \langle 2'| + |2'\rangle \langle 1'|]$.

If any state is written as $|\psi\rangle = c_1 |1'\rangle + c_2 |2'\rangle$ with initial conditions $c_1(0) = 0, c_2(0) = 0$ (these are called dressed states), we will get by solving the dressed Hamiltonian, $|c_1(t)|^2 = 1 - \frac{A^2}{\Omega^2} \sin(\Omega t)^2$ and $|c_2(t)|^2 = \frac{A^2}{\Omega^2} \sin(\Omega t)^2$. Here $\Omega = \sqrt{A^2 + (\frac{\omega - E_{12}}{2})^2}$ is called the Rabi frequency, ω is the driving frequency, and $E_{12} = E_1 - E_2$ is the energy gap. In case of resonance, $\omega = E_{12}$, so Rabi frequency simply is A. Even though this was for constant A, for slowly varying pulse we can consider the same equation from Rabi frequency.

In our case of slowly-varying enveloped electromagnetic pulse with amplitude $E(t)$, we get $\Omega = \frac{\mu E(t)}{\hbar}$ where μ is the transition dipole moment component along the direction of the electric field which we have taken to be polarized. Also, for this time-dependent pulse, Ωt will surely be replaced by $\int_i^t \Omega(t')dt'$ where i stands for the initial time.

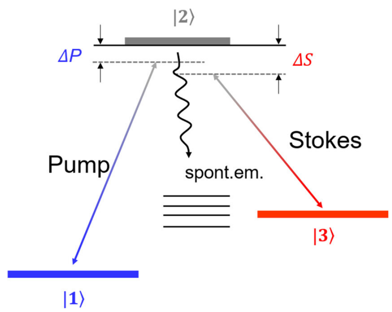
So, we can see that with coherent excitation the population oscillates between the two states. At resonance, we obtain maximum efficiency, but we never transfer the population from one state to another as we wish to do.

Adiabatic transfer: We don't achieve our goal completely using the last two methods. So, to increase the efficiency of population transfer we can use the adiabatic transfer method. In this process, we use coherent pulses, the frequency of which varies slowly about the resonance frequency. This way we get better results.

[Figure to be put here]

Having looked at the different processes of population transfer from one state to another state directly we understand their drawbacks. Below we discuss the three state transfer methods.

Population transfer for three state systems: The most widespread method used in this case is 'SEP' (Stimulated emission Pumping). A three-state transfer process in which we aim to transfer population from $|1\rangle$ to $|3\rangle$ with intermediate state $|2\rangle$ includes a pump laser (P) which couples $|1\rangle$ and $|2\rangle$ and a stokes laser (S) which couples $|2\rangle$ and $|3\rangle$. In the SEP process first P is activated which transfers 50% of the population for $|1\rangle$ to $|2\rangle$ and that when acted upon by S decays to $|3\rangle$. Though this process is easy, it's not very efficient, so discuss a new process.



Instead of applying P and then S, we use S to couple $|2\rangle$ and $|3\rangle$ and then use P to couple $|1\rangle$ and $|2\rangle$. This way, the population is directly transferred to $|3\rangle$ state. Below we discuss this in a little more detail:

For this two pulse case, the Hamiltonian is $H = H_0 + H_1$ where $H_0 = E_1 |1\rangle\langle 1| + E_2 |2\rangle\langle 2| + E_3 |3\rangle\langle 3|$ where E_i's are the energies of the states. Now, $H_1 = \Omega_P(t)(e^{i\omega_1 t} + e^{i\omega_2 t}) |1\rangle\langle 2| + \Omega_S(t(e^{i\omega_2 t} + e^{i\omega_2 t}) |3\rangle\langle 2| +$h.c where ω_1, ω_2 are frequencies of P and S respectively. Under a basis rotation, $|1'\rangle = e^{-iE_1 t}|1\rangle, |2'\rangle = e^{-i(E_1+\omega_1)t}|2\rangle, |3'\rangle = e^{-i(E_1+\omega_1-\omega_2)t}|3\rangle$.

With rotating wave approximation we obtain the Hamiltonian to be:

$$\text{H=} \begin{pmatrix} 0 & \Omega_P(t) & 0 \\ \Omega_P(t) & 2\Delta_P & \Omega_S(t) \\ 0 & \Omega_S(t) & 2(\Delta_P - \Delta_S) \end{pmatrix}$$

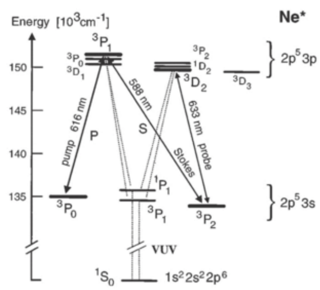
The eigenstates of this Hamiltonian are:
$|a^+\rangle = \sin(\theta)\sin(\phi)|1\rangle + \cos(\phi)|2\rangle + \cos(\theta)\sin(\phi)|3\rangle, |a^-\rangle = \sin(\theta)\cos(\phi)|1\rangle - \sin(\phi)|2\rangle + \cos(\theta)\cos(\phi)|3\rangle, |a^0\rangle = \cos(\theta)|1\rangle - \sin(\theta)|3\rangle$.

Here $\tan(\theta) = \frac{\Omega_P(t)}{\Omega_S(t)}$ and $\tan(2\phi) = \frac{\sqrt{\Omega_p^2+\Omega_S^2}}{\Delta_P}$, $\Delta_S = (E_2 - E_1)/\bar{h} - \omega_1, \Delta_P = (E_2 - E_3)/\bar{h} - \omega_2$ are detuning of P, S frequencies (ω_1, ω_2) from the transition frequencies to the intermediate states. These states are called 'dressed states' and their eigenvalues are $\omega^\pm = \Delta_P \pm \sqrt{\Delta_P^2 + \Omega_P^2 + \Omega_S^2}, \omega^0 = 0$.

In the rotating wave approximation, we neglect the terms with frequencies $2\omega_{1,2}$ from the Hamiltonian, because the most important frequency components are close to resonance.

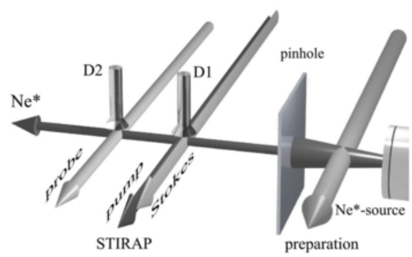
The system $|\psi\rangle$ is initially in the state $|1\rangle$ and starts evolving under this STIRAP process. We want the state to be $|3\rangle$ after a long time and avoid the state having any overlap with $|2\rangle$ because the population can leak from there. So, we want the state to be $|a^0\rangle$. For this to be $|1\rangle$ at early times. $\frac{\Omega_P}{\Omega_S}$ has to be zero, i.e. we need to turn on the Stokes laser before the Pump laser. At intermediate times these two have overlap which does the population transfer by coupling $|1\rangle$ with $|3\rangle$. Then we switch off S followed by P resulting in the state being $|3\rangle$. But we need to know whether or not these couplings are sufficient enough to make the state flow along $|a^0\rangle$ adiabatically. The coupling needs to be sufficiently strong, i.e. if the Rabi frequencies are too small then the actual state $|\psi\rangle$ will process around $|a^0\rangle$ (dressed state), hence the transfer process loses maximum efficiency.

Discussion about Experimental setup of the Three-level system: Having discussed the theory behind this method, we now talk about the experimental setup. To apply S and P one after another in the way we have discussed above, in the experiment we just spatially displace the S and P pulses and let the beam of molecules (those we want a population transfer of) pass through the two pulses. Below we discuss this in detail for a beam of metastable neon (Ne*).



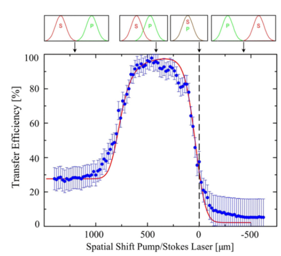
Experimental Arrangement: A beam of Ne* atoms is discharged from a source and boosted into a vacuum tube. Neon's electronic configuration $(2p^5 3s)$ gives rise to two metastable states. $^3P_0$ and $^3P_2$. These two states are of even parity. These states are connected with the levels of $2p^5 3p$. So, the state $2p^5 3p$ $(^3P_1)$ is used as the intermediate state of the experiment. Now a preparation laser removes one of the metastable states by optical pumping. The $^3P_0$ atoms along with other ground-state atoms move through a collimating slit and enter the STIRAP zone. The stokes and pump laser (which are perpendicular to the motion of these atoms) are spatially displaced in order to get the required Ω_P, Ω_S behavior that we had discussed. As discussed, in the region where P and S overlap, the population transfer occurs, here $^3P_0$ atoms are transferred to $^3P_2$ state along the $|a^0\rangle$ dressed state.

To detect the population transfer, the 'vuv' (vacuum-ultraviolet, $74nm$) radiation that is emitted due to the decay of ${}^3P_1$ (intermediate state) to the ground state. Monitoring this radiation using a channeltron, we find the population of the intermediate state. After passing through the S,P laser zones a probe laser is used to excite the atoms in ${}^3P_2$ state and subsequently measure the population in this state by measuring the radiation emitted from the decay of this excited state to the ground state.



The population transfer depends on the pump laser frequency as found in the theory (Stokes frequency is kept slightly off-resonance). As pump frequency is tuned, at some point maximum population transfer occurs and we see a dark resonance in the channeltron which measures intermediate state population, that is the state is completely in the $|a^0\rangle$ dressed state.

Confirimg STIRAP signature: Though we observe a population transfer, we need to confirm that this is due to the STIRAP mechanism, and for that, we need to check how the efficiency varies as a function of the overlap between two lasers.



In the figure above we see the transfer efficiency as a function of the overlap of P and S lasers. There is 25% efficiency when there is no overlap, almost unity when the overlap is described in the theory. The efficiency decreases lower than 25% for complete overlap and becomes zero when the stokes laser lags behind the pump laser. This indicates that the population transfer is happening due to the STIRAP process.

A generalization: ladder system: Like the delayed interaction with states in the Λ-type configuration, we can consider population transfer for a ladder system, i.e transfer via a sequence of intermediate states, say from $|1\rangle$ to $|N\rangle$ via $|2\rangle, ..., |N-1\rangle$. Similarly as before we can first couple $|N\rangle - |N-1\rangle, |N-2\rangle - |N-3\rangle, ..., |3\rangle - |2\rangle$ by Stokes lasers and then $|1\rangle - |2\rangle, |3\rangle - |4\rangle, ..., |N-2\rangle - |N-1\rangle$ by pump lasers. The stokes lasers can be applied simultaneously followed by the pump laser. In this way, the even states contain very little population while the odd states have some transient population. It is found numerically, that instead if we first couple $|N\rangle - |N-1\rangle$ by S and $|1\rangle - |2\rangle$ by P followed by the coupling of other states, we achieve better transfer, i.e. no intermediate state contain any significant population.

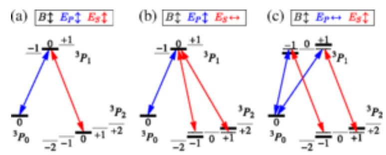
Adiabatic following: Adiabatic following is the process of the state $|\psi\rangle$ following the dressed state $|a^0\rangle$, which requires sufficient coupling between the states, otherwise the state will precess around the dressed state and population will lose due to decay. For this the non-adiabatic coupling $\langle a^{\pm}| |\dot{a}^0\rangle$ must be small compared to $|\omega^{\pm} - \omega^0| = \bar{\Omega}$, or $\mod \dot{\theta} << |\omega^{\pm} - \omega^0|$ from the dressed state equations. If this condition is satisfied, we obtain an adiabatic following and hence good efficiency. By taking the average this can also be written as $\langle \dot{\theta}_{av} \rangle = \frac{\pi}{2\delta t}$, where δ is the period of overlap of P and S. From numerical simulations it is found that $\bar{\Omega}\delta >> 10$. It is found that for a beam pulse of Gaussian shape, the efficiency is highest when the pulse delay is equal to the pulse width. When there is complete overlap between the pulses, $\dot{\theta} = 0$. As there is overlap with states $|a^+\rangle, |a^-\rangle$, population is lost due to decay and we observe about 25% efficiency. However, when the pulse delay is very big, $\max \theta$ occurs when the radiative coupling is relatively weak. So, for optimum delay, the 'mixing angle' $\bar{\Omega} = \frac{\pi}{4}$.

Like continuous lasers, we can use pulsed lasers. We see that lasers with a width of nanosecond order and energy of 1mJ order work well for the STIRAP process. For lasers with even shorter widths, the rate of change of the mixing angle is very fast and so are harder to use in the laboratory for adiabatic following. But coherent transfer using tightly focused Picosecond lasers has been realized in laboratories for atomic systems.

Discussion on population transfer in multilevel system: We talked about coherent population transfer in ladder systems earlier. Here, we discuss the multi-level systems, i.e. when we have many degenerate states (or nearly degenerate) and we want to transfer the population from one of the states to another one. Level splitting due to fine and hyperfine interaction, Zeeman splitting or high level density implies that the lasers may couple states other than the three states that we want to couple. However, we can consider breaking the degeneracy using an external magnetic field, which is done for Ne* atoms.

The coupling obeys the optical selection rule in the presence of this external magnetic field. When both the Stokes and Pulse lasers are polarized along B, $\Delta m = 0$, i.e. only $m = 0$ states of ${}^3P_0, {}^3P_1, {}^3P_2$ are coupled together. If any of the two lasers are parallel and the other is perpendicular, then four or more states can be coupled, and when none of them are parallel, all nine states are coupled as the selection rule allows that.

We derived our result for the case when the detuning of two lasers matched exactly. In experiments, we find that when the detunings are off of each other, the population transfer is not maximum efficiency, in this case, the population transfer is due to spontaneous emission due to the pulse laser. When all the states are allowed to interact, we again see efficient population transfer along the $\Delta_P = \Delta_S$ line.



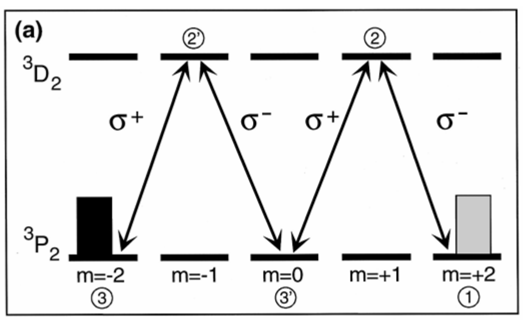
Now we observe the transfer efficiency dependence on the strength of the magnetic field. When one of the fields is parallel and five states are coupled, the frequency of S is fixed to one of the intermediate states, and the frequency of P is varied. Now when $\vec{B} = 0$ the degeneracy of the three systems is not broken, hence transfer efficiency is high. When the field strength is about $3G$, there is no population transfer. For higher magnetic field strength, population transfer happens to one of the states of $m = \pm 1$.

When the magnetic field is zero, the evolution of the five bare states are same as the three-state system with degeneracy of the five states seen at early and late times when the lasers are turned off. When the magnetic field is non-zero, degeneracy is broken into two subsets with one having two states and another with three states. Due to the lasers' coupling, these degeneracies are broken and one state of the two initially degenerate states crosses states from the other degenerate set when the Rabi frequency exceeds the Zeeman detuning. At the crossing point, P introduces coupling. When the splitting of the two sets is small, the crossing happens before P is acted, and the state crosses the transfer path as well, which is the energy of the transfer path ($|a^0\rangle$ in the three-level case). Hence, coherent population transfer can not happen. However, if the strength of the magnetic field is sufficiently high, the crossing state doesn't cross the transfer path and so the energy of the state remains zero or very small at later times allowing coherent population transfer to occur. For an even higher magnetic field, the crossing is entirely removed, and the coherent transfer happens as before. However, we can transfer the population for the intermediate magnetic field by setting the laser frequency a little off the resonance.

Coherent Momentum Transfer: With coherent population transfer, dissipation free momentum exchange between the radiation field and the atoms also takes place. In the STIRAP process when the atoms pass through the radiation field and absorb a photon, along with the energy of the photon it also absorbs its momentum. Spontaneous emission of photons by this excited atom results in a randomly distributed recoil. As this emission process is dissipative, we see a broadening of the distribution of the deflection angle.

Now if there are multiple photons involved between multiple states, we get a similar a 5×5 Hamiltionian after taking rwa. The condition of adiabatic following is having a zero eignevalue at all times, i.e. $\det(H(t)) = 2\Delta_{1,3}\det(H_4(t)) - \Omega^2_{2',3}\det(H_3(t)) = 0$.

Here, H_4, H_3 are minors of the actual Hamiltonian. Δs are detuning for corresponding levels. The second term corresponds to the three-level case, for which there exists a zero eigenvalue dressed state when two-photon resonance is there. Hence if four-photon resonance is established and $\Delta_{1,3} = 0$, there exists a zero eigenvalue dressed state, i.e. adiabatic following happens. The intermediate $2, 2'$ states have negligible population. However, the $m = 0$ state has about 30% population in intermediate times. But after a long time almost all the population is transfered to $m = 2$ state.



Continuum Transfer: Similar to the three-level discrete state, we can consider the transfer process through continuum levels. It is shown that in the case of transfer mediated by autoionizing states, coherent effects are important. However, the continuum transfer is limited by the Stark shift of the bounded states. But we can counter those shifts by adding an extra laser or by using chirped pulse lasers to maintain the two-photon resonance.

Summary and conclusion: In this report about coherent population transfer using different methods, e.g. we have discussed the two-state transfer and the three-level STIRAP process. Also, we have talked about other mechanisms like transfer in ladder systems, multilevel transfer, etc. We have discussed its relation with other coherent phenomena. And lastly, we discussed in brief about continuous transfer processes.

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