

That's all very well in practice, but does it work in theory?

When we have the TeachSpin exhibition trailer 'Food Truck for the Physics Mind' up and running for a campus visit, we typically are simultaneously operating three distinct spectroscopy experiments. There's our Diode-Laser Spectroscopy experiment, driving optical transitions at 780 nm (frequency 384 THz) in Rb vapor. There's our pulsed/cw-NMR experiment, causing proton spin-flip transitions, in a field near 0.5 Tesla, using a frequency near 21 MHz. Thirdly, there's the Optical Pumping apparatus, using light at 795 nm to make possible the detection of radio-frequency transitions in ground-state atoms of Rb vapor. So these three pieces of apparatus run perfectly well *in practice*; this Newsletter will make clear to you that it's nearly a miracle that two of these techniques can be made to work at all *in theory*.



Left, David at Optical Pumping; center, Matt at Diode Laser Spectroscopy; right, Cassie at pulsed/cw NMR

Each of these three techniques only works when a certain 'Bohr condition' is satisfied, requiring that the frequency of oscillation of an external perturbation match an energy-level separation:

$$f_{ext} = (E_{upper} - E_{lower})/h$$

There is a further 'selection rule' requirement, that the polarization of the perturbing electric or magnetic field should have the right relationship with the eigenfunctions of the two participating states.

But there is a third requirement, often overlooked, involving the populations of the two participating states. That's because any perturbation which will drive systems from state A to state B will equally well drive them from state B to state A. So a perturbation will tend to equalize the populations of two states (if they start with unequal populations); but if the two states start with equal populations, the perturbation will have no detectable effect on the system.

Finally, there is the practical issue of whether the result we get from perturbing the system is technically possible to detect. In this newsletter, we'll look quantitatively into these issues.

The easy case: Optical Spectroscopy

The transitions we drive in 'Diode-Laser Spectroscopy' are fully-allowed electric-dipole transitions between the $S_{1/2}$ ground state and the $P_{3/2}$ excited state of rubidium (Rb) atoms, freely flying about in vacuum inside an optical cell. We perturb

the ground-state atoms with a 780-nm laser beam, tuned to match the required Bohr condition; the electric field of the linearly-polarized laser beam is what excites the atoms. And in this experiment, we rarely think of the population condition, since it is 'satisfied automatically'. The energy levels involved are separated by about 2 eV in energy, while the sample of vapor-phase atoms is in equilibrium with a cell-wall temperature of (say) 45 °C or 318 K. In the $k_B \cdot T$ sense, that temperature is 'worth' about 0.03 eV. Hence the Boltzmann ratio for (excited-state population)/(ground-state population) is

$$\frac{N_{upper}}{N_{lower}} = \exp\left(-\frac{\Delta E}{k_B T}\right) \cong \exp\left(-\frac{2 \text{ eV}}{0.03 \text{ eV}}\right) \cong 10^{-30}$$

Essentially, all the atoms are in their ground state.

And how many ground-state atoms are involved? At our chosen temperature, the vapor pressure of Rb is about 3.3×10^{-4} Pascals; using the ideal-gas law, we get a number density of atoms n/V given by

$$\frac{n}{V} = \frac{p}{k_B T} \cong \frac{3.3 \times 10^{-4} \text{ N/m}^2}{4.1 \times 10^{-21} \text{ N}\cdot\text{m}} \approx 0.8 \times 10^{17} / \text{m}^3$$

For a laser beam of typical transverse size about 1 mm \times 2 mm, and a cell length of 25 mm, we get a sample volume of about 50 mm³; so using the number density computed above, we conclude there are about 4×10^9 Rb atoms present in the laser beam.

How much energy is absorbed if we laser-excite all those atoms? Each such absorption removes from the laser beam an energy of $h \cdot f = 2.5 \times 10^{-19}$ J, so the energy cost of exciting all the atoms is 1.0×10^{-9} J. That

nanoJoule of energy sounds small, but if we imagine all these atoms being excited in 25 ns, and then decaying spontaneously within a mean lifetime of 26 ns more, we see that we might repeat this energy transaction about every 50 ns. This represents an energy-per-unit-time, or power absorption, of about 0.02 Watts or 20 mW. That is to say, we could imagine sending in a 100-mW laser beam, and having only 80 mW of that beam emerge, while 20 mW of light is the steady-state fluorescent emission of the excited atoms decaying back to the ground state. It is very easy to detect so large a fractional absorption of the incident beam, and it is also easy to detect (part of) the fluorescent light continually emerging from the illuminated sample.

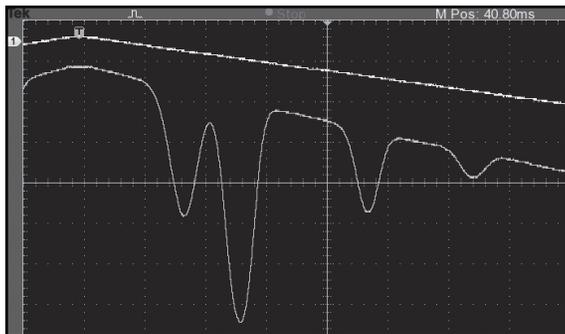


Fig. 1: Light transmission of Rb vapor as a function of laser frequency, for a scan over about 8 GHz of optical frequency, centered near 384,000 GHz.

A harder case: Proton NMR (nuclear magnetic resonance)

One picture of proton NMR comes from imagining the two allowed spin states of a spin-1/2 proton in a static magnetic field. In TeachSpin's PS2 NMR apparatus, a field of about 0.5 Tesla (5000 gauss) makes the energy separation of those two states equal to $h \cdot 21$ MHz. Then a radio-frequency magnetic field (of that frequency, and of direction perpendicular to the static field) can drive the fully-allowed magnetic-dipole transition between the two levels. That takes care of the Bohr condition, and the selection rules, applicable in this case.

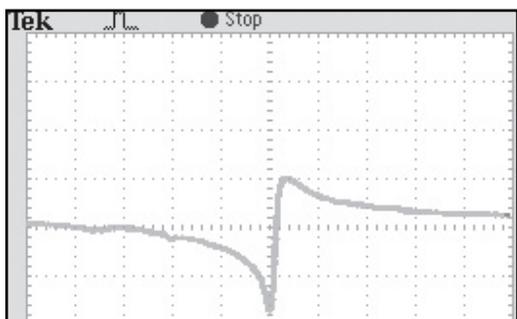


Fig. 2: NMR signal for light mineral oil, as a function of field for a scan over about 63 μ T of field near 499.6 mT, for fixed frequency of 21.27095 MHz, using the 'cw' mode of TeachSpin's PS2 pulsed/cw spectrometer.

How many protons are involved here? A typical sample (of water, or mineral oil) might have approximate size $(3 \text{ mm})^3$ or a volume of about $3 \times 10^{-8} \text{ m}^3$. For water's density of 10^3 kg/m^3 , the

sample mass is about $3 \times 10^{-5} \text{ kg}$. For water at 18 g/mole, there are about 0.002 moles of water present; each H_2O molecule offers us two active protons, so there are about 3×10^{21} protons in our sample. (Note the vastly larger proton count, compared to the paltry number of Rb atoms in the vapor-phase optical sample.)

To compute the amount of energy absorbed in driving this spin transition, we must recognize that we have the entirely opposite limiting case of the Boltzmann factor for these two states, compared to the previous case of an optical transition. With an energy separation that is now vastly *smaller* than $k_B T$, the two states involved in NMR are very close to the fatal limit of being equally populated. We can work out their small population difference, using a series expansion of the Boltzmann factor:

$$N_{up} \cong \frac{N}{2} \left(1 - \frac{\Delta E}{k_B T} \right) ; N_{dn} \cong \frac{N}{2} \left(1 + \frac{\Delta E}{k_B T} \right) ,$$

so the population difference is the much smaller number

$$\delta N \equiv N_{dn} - N_{up} \approx N \frac{\Delta E}{k_B T} = (3 \times 10^{21}) \frac{1.4 \times 10^{-26} \text{ J}}{4 \times 10^{-21} \text{ J}} \approx 5 \times 10^{15} .$$

Hence the best we might do is to excite these 5×10^{15} protons by energy $h f \approx 1.4 \times 10^{-26} \text{ J}$, which represents an energy uptake by the sample of $7 \times 10^{-11} \text{ J}$, or 70 pJ. Not only is this smaller than the corresponding energy uptake in the optical case; the 'cycle time' is also much longer, as in this case the excited-state protons relax back to equilibrium on a timescale of milliseconds or even whole seconds, not mere nanoseconds. Yet so advanced are radio-frequency detection methods that an absorption of 70 pJ each second, or 70 pW of power, is readily detectable.

Note that we had a much larger number-density in our (liquid) sample, and a much higher sample 'count'; so even after taking the Boltzmann factor into account, we still had a population difference bigger by 10^6 than in the optical case. That's the NMR advantage of being able to use a condensed-matter, rather than a vapor-phase, sample. But we do pay a penalty for using the much lower-frequency excitation, as the photons that are absorbed in the transition are of much lower energy.

The worst of both worlds: Optical Pumping

In TeachSpin's 'Optical Pumping' apparatus, the transitions we excite are those connecting adjacent Zeeman sub-levels in the ground state of rubidium, driven in atoms of a vapor-phase sample of Rb in an optical cell. That level separation can be 'tuned' by changing the local value of the static magnetic field, and we'll imagine picking a field strength such that adjacent sub-levels are separated in energy by $h \cdot 37.7 \text{ kHz}$. Then transitions can be driven using a perturbing transverse magnetic field, oscillating at 37.7 kHz (a number picked merely because it is just 10^{-10} of the optical frequency of the light that's doing the magic 'pumping' of the atoms). Thus we've satisfied both the Bohr condition, and the selection rules, for this magnetic-dipole transition.

The number of atoms involved is again small. We assume a sample volume, illuminated by the (non-laser) light, that's 10 mm square by 25 mm long, so the volume

is $2.5 \times 10^{-6} \text{ m}^3$. Using the same number density as before (appropriate to Rb at 45°C) of $0.8 \times 10^{17}/\text{m}^3$, we get the number of atoms involved as 2.0×10^{11} .

And now we take a real beating from the Boltzmann factor, with an even smaller ΔE than in the case of proton NMR. The population difference between the lower and the upper state is given by

$$\delta N = N \frac{\Delta E}{k_B T} \approx (2.0 \times 10^{11}) \frac{2.5 \times 10^{-29} \text{ J}}{4.1 \times 10^{-21} \text{ J}} = (2.0 \times 10^{11})(6 \times 10^{-9}) \approx 12 \times 10^2$$

so that there are only about 1200 excess atoms in the lower state. Driving all these atoms to the upper state would involve the absorption of 1200 quanta, each of the very low energy $h\nu \approx 2.5 \times 10^{-29} \text{ J}$, for a total energy uptake of about $3 \times 10^{-26} \text{ J}$. Supposing that this can be repeated once per average ‘pumping time’ of perhaps 20 ms, we get a truly tiny average energy-exchange rate near $1.5 \times 10^{-24} \text{ W}$.

It’s easy to see the basic reasons for this discouraging result: we have, as in optical spectroscopy, the problem of a tiny number-density of atoms in a vapor-phase sample; and we also have, even more so than in the NMR case, the problem of truly tiny energy-per-photon of the perturbing radiation.

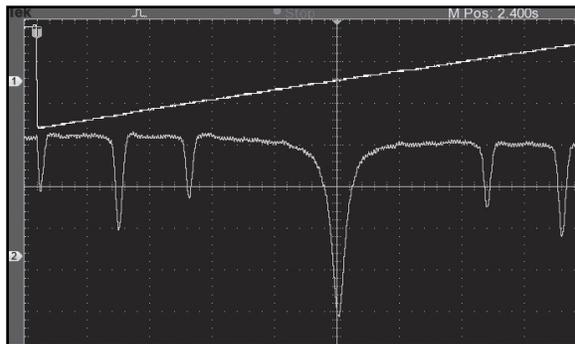


Fig. 3: Light transmission through pumped Rb vapor as a function of longitudinal magnetic field, for perturbing frequency 40.0 kHz; the scan extends from -11 to + 11 μT of field strength

Comparison

The table below shows some comparative numbers for the three cases of spectroscopy we have considered. The most telling number is found in the rightmost column, giving the average rate of energy exchange that we’ve computed in our three cases. In the optical-spectroscopy case, we see we might imagine a steady-state of order 10^{-2} W of light coming from the atomic sample. In the case of proton NMR, the rate of energy exchange is much smaller, of order 10^{-10} W . But in the case of optical pumping, we suffer the double penalty of having *both* a very low-density sample, and of using very low-energy photons, and above we’ve seen the computed energy-exchange rate of order 10^{-24} W . By the comparisons we have modelled above, it seems that transitions in optical pumping are *22 orders of magnitude(!)* harder to detect than those in diode-laser spectroscopy.

Case	f , in Hz	ΔE	N	δN	$\Delta E \cdot \delta N$	timescale	‘power’
Opt. spec.	384×10^{12}	$2.5 \times 10^{-19} \text{ J}$	4×10^9	4×10^9	$10 \times 10^{-10} \text{ J}$	50 ns	$20 \times 10^{-3} \text{ W}$
p-NMR	21×10^6	$1.4 \times 10^{-26} \text{ J}$	3×10^{21}	5×10^{15}	$7 \times 10^{-11} \text{ J}$	$\approx 1 \text{ s}$	$70 \times 10^{-12} \text{ W}$
Op. pump.	37.7×10^3	$2.5 \times 10^{-29} \text{ J}$	2×10^{11}	1200	$3 \times 10^{-26} \text{ J}$	20 ms	$1.5 \times 10^{-24} \text{ W}$

Comparing the three experimental cases numerically. We give f , the frequency of the driven transition, and ΔE , the quantum of energy involved; N , the number of objects in the sample, and δN , the population difference between the levels; $\Delta E \cdot \delta N$, the possible energy absorption, and the timescale on which it can be repeated; and finally the average ‘power’, or rate of energy exchange, involved in steady-state operation.

Yet users of our Optical Pumping apparatus will easily detect these radio-frequency transitions, in real time, with very good signal-to-noise ratio, without needing any fancy averaging schemes. What’s the magic method that makes up for all those daunting orders of magnitude?

There are actually two separate ‘tricks’ in optical pumping, both accomplished by using *light* to pump the atoms. First of all, the pumping light is made to be circularly polarized, and optical selection rules ensure that this can establish a markedly *non-thermal* population distribution among the ground-state sub-levels. In one limiting case, such light might fully empty one, and fully fill the other, of a pair of levels. That removes the terrible Boltzmann factor of (6×10^{-9}) we saw penalizing us above.

Next, in an actual optical-pumping experiment, we choose *not* to detect the tiny amount of radio-frequency energy directly absorbed by the sample, but instead detect the transition indirectly. Because of the pumping mechanism, an absorption of one quantum of r.f. energy will cause an atomic transition that permits, on average, about one more photon of light to be absorbed out of the pumping beam. Then we choose to detect the resulting decrease in *light* transmission, each photon of which light (in our example) has 10^{10} times more energy than the r.f. quantum involved. That trick gives us a ‘leverage’ of size 10^{10} in our favor.

Together these two factors can make optical pumping about 10^{18} times easier (i.e. more detectable) than indicated by our computation tabulated above. This lifts this effect out of the realm of an impossible experiment to one that can be readily conducted on a table-top by undergraduates. So now you can see why theory agrees that these three experiments really are feasible in practice. Or, as we sometimes say in the lab here at TeachSpin: “If it happens, it must be possible.”



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Inside:

We compare three kinds of spectroscopy, showing how one of them needs to be rescued from *impossibility*.

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TeachSpin has played a central role in the creation of the Advanced Laboratory Physics Association (ALPhA), the NSF-sponsored BFY conferences, and the Jonathan F. Reichert Foundation. It is seeking a physicist who shares this mission of advanced laboratory education. We are certainly interested in physicists considering a “second career” with our unusual company.

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If you would like to make a difference in experimental physics education in the world, this might just be the opportunity for you to realize that goal. Contact us at JFReichert@teachspin.com.

❖*Invitation*❖

Come visit us at TeachSpin’s exhibition trailer, the “Food Truck for the Physics Mind”, on the show floor at the APS March meeting in Denver, open to view March 2, 3, & 4.