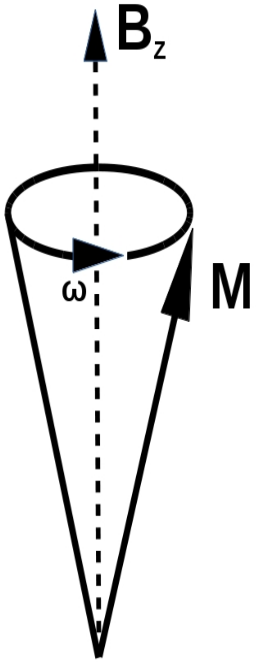
Spins precess about external field

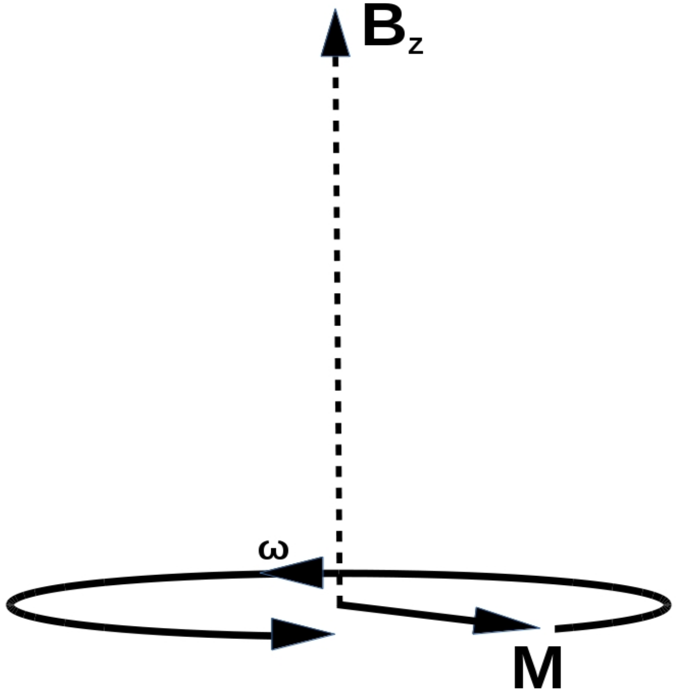


B : External magnetic field

M : Electronic magnetic moment

ω : Precession frequency

Flip spins by $\frac{\pi}{2}$



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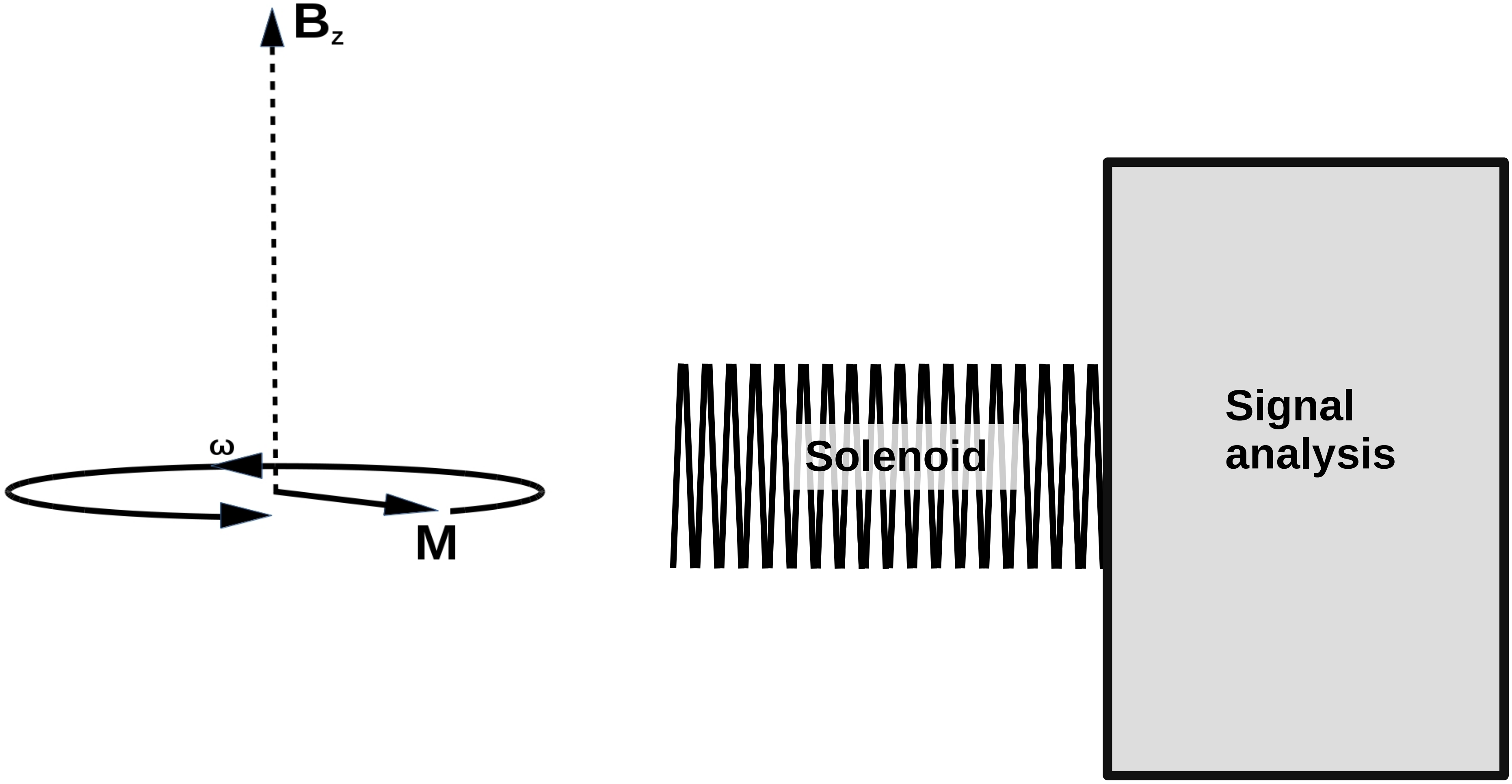
Measure induced current



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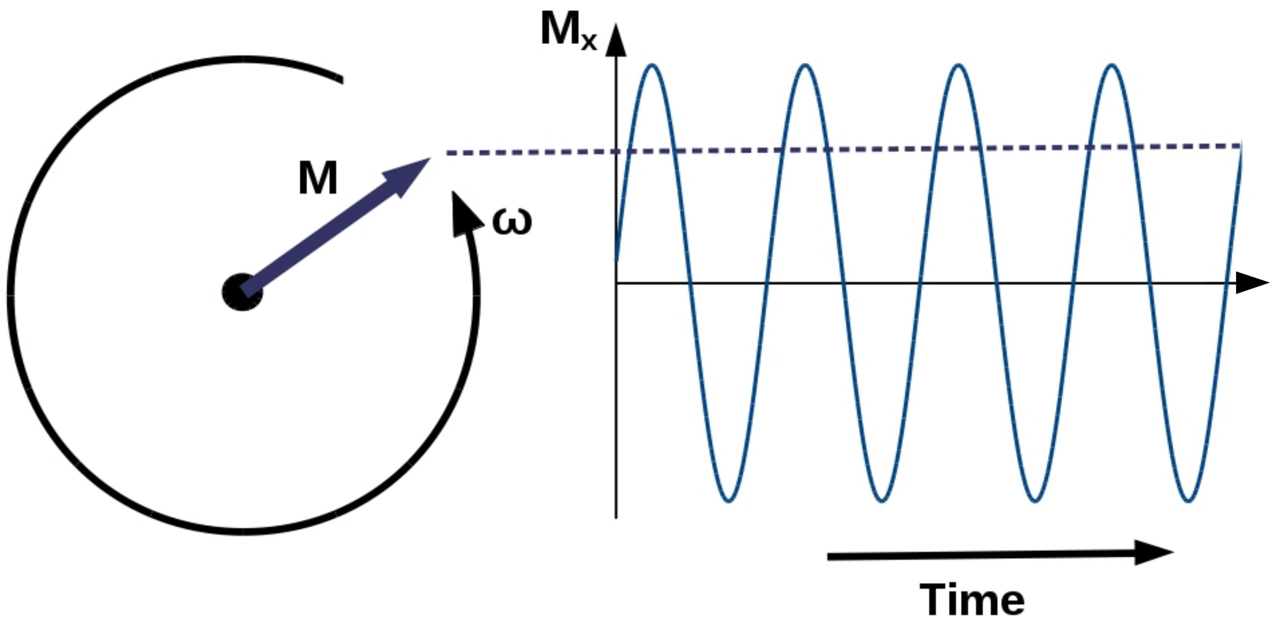
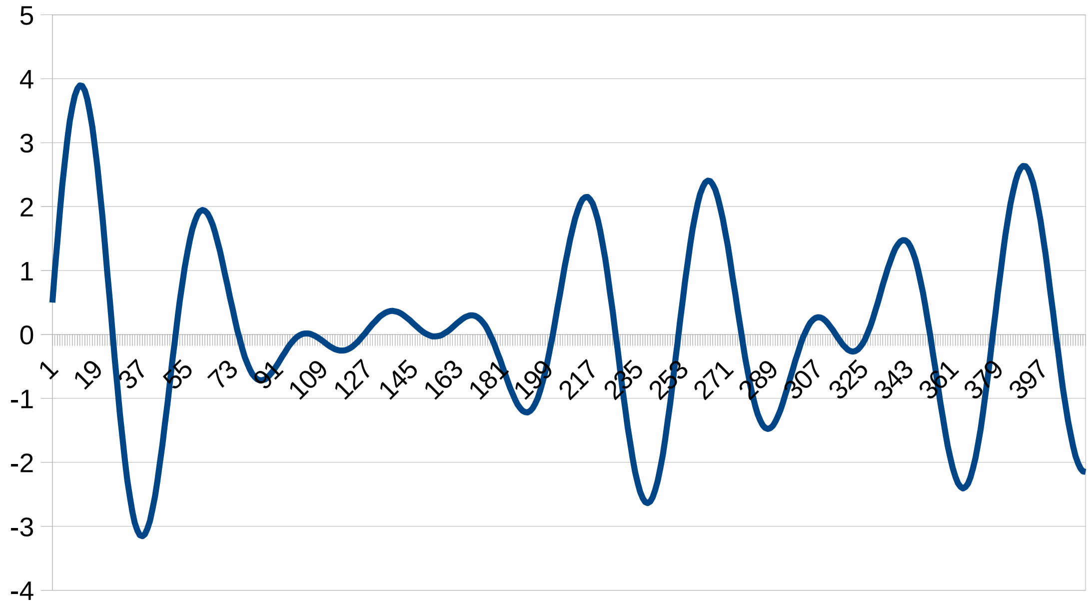


- The oscillating magnetization results in an electron motive force, and hence a current in the solenoid.
- The rate of oscillation of the EMF, and current, is determined from the Larmour frequency.

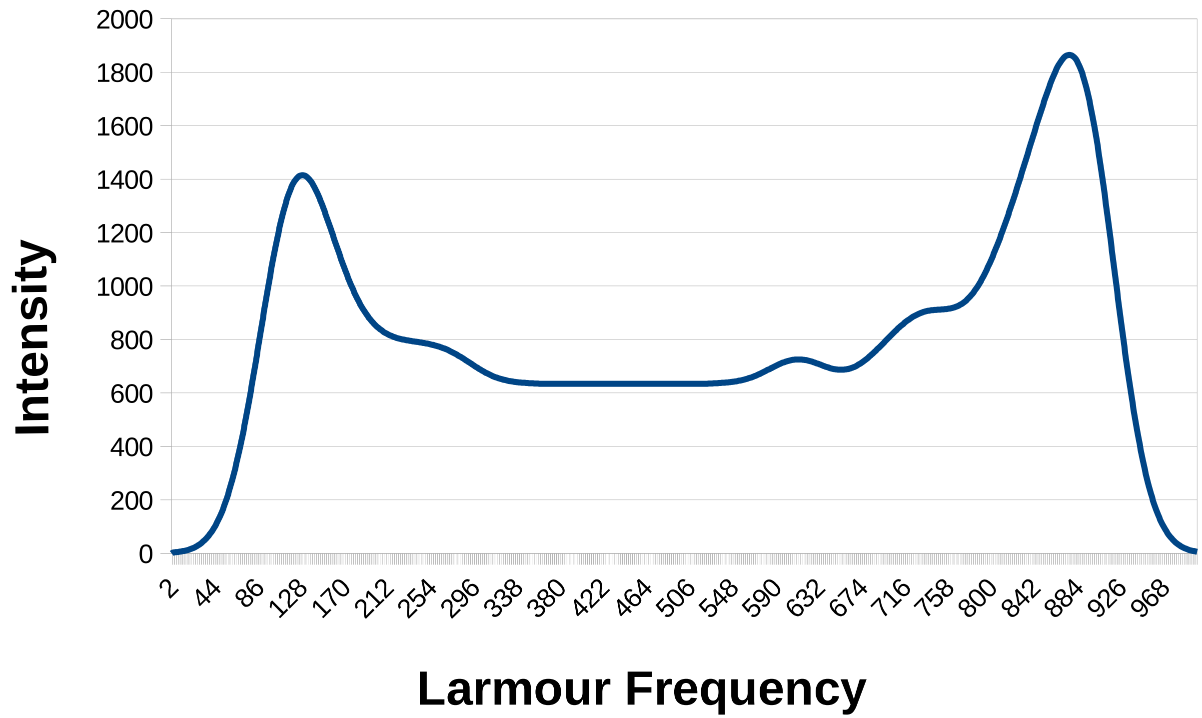
Measure induced current



- Collect information for entire system at once; every molecular orientation is included.

$$s(t) = \sum_l a_l exp[(i\Omega_l - \lambda_l)t],$$

Computationally generated EPR plot



Arbitrary Units

- Fourier transform signal to get contributions from individual orientations:

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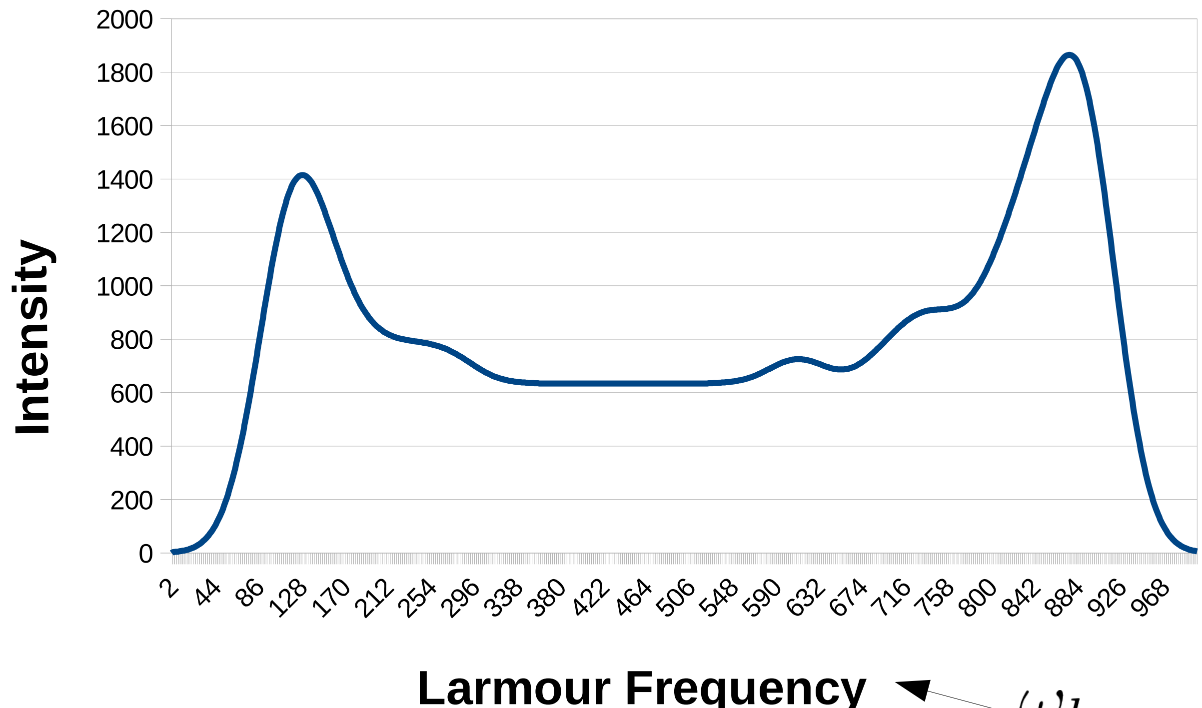
Computationally generated EPR plot

(a_l)



ω_l

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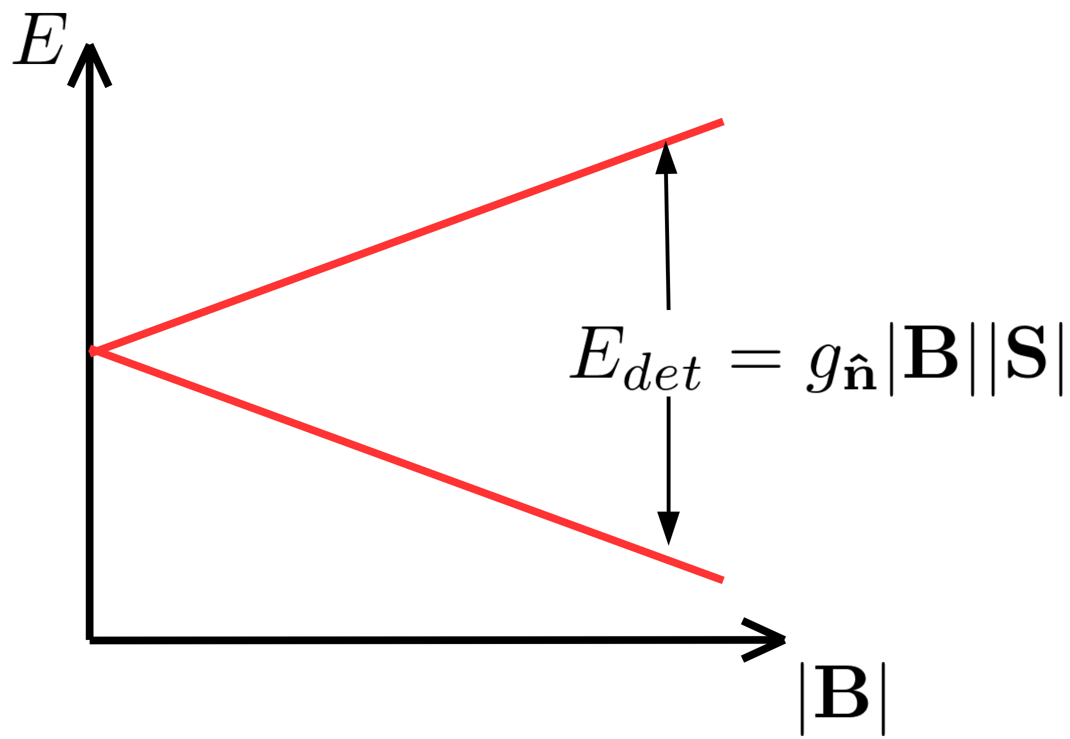
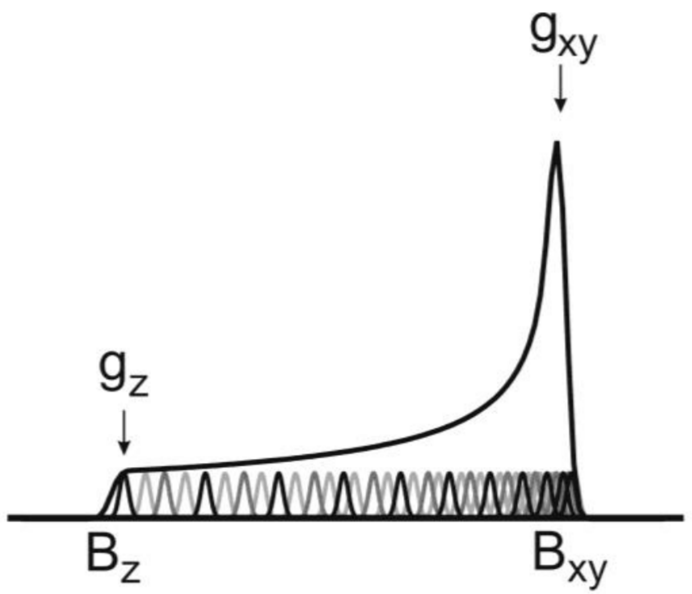


- Detect one frequency, vary **|B|**.
- g_n determines the field strength at which the signal is detected.

Experimentalists do a field sweep



E. Duin, Electron Paramagnetic Resonance Theory Lecture notes.

Density matrix approach

- Define how the system evolves in time:

$$\rho(t) = U(t)\rho(0)U^{\dagger}(t)$$

- Determine this evolution from the Hamiltonian:

$$e^{i\hat{H}t} = U(t) \quad \xrightarrow[\textbf{basis restriction}]{} \quad e^{i[\sum_{uv} B_u g_{uv} \sigma_v]t} = U(t)$$

- Restriction of basis causes errors in systems with low lying spin states and strong spin-orbit coupling.

Time evolution

- Red square correspond to “forbidden” mixing of different spin multiplets.

$$e^{i[H]t} = U(t) = \begin{bmatrix} [\mathbf{U}(t)]_{00} & [\mathbf{U}(t)]_{01} & [\mathbf{U}(t)]_{02} & \cdots \\ [\mathbf{U}(t)]_{10} & [\mathbf{U}(t)]_{11} & [\mathbf{U}(t)]_{12} & \cdots \\ [\mathbf{U}(t)]_{20} & [\mathbf{U}(t)]_{21} & [\mathbf{U}(t)]_{22} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{bmatrix}$$

These forbidden transitions are inherently impossible to describe with a g-tensor, as it is constructed from a single multiplet.

Time evolution

- Ehrenfest theorem:

$$\frac{d}{dt}\langle\hat{A}\rangle = \frac{1}{i\hbar}\langle[\hat{A},\hat{H}]\rangle + \left\langle\frac{\partial\hat{A}}{\partial t}\right\rangle,$$

Operator of interest

Hamiltonian

- Use eigenfunctions of non-relativistic Hamiltonian as the basis for representation of time evolution.
  - Will enable use to distinguish contributions from inter and intra molecular transitions.

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b) Do non-relativistic CASSCF followed by relativistic FCI.

- Hamiltonian is now diagonal, but information contribution from forbidden transitions is lost.
- Simplifies construction of time reversal operator.

Method

2) Build density matrix and time evolution operator.

- Density matrix is straightforward...

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Method

2b) Rotate spin of density matrix into xy plane.

$$V(\pi/2)\rho_z V^\dagger(\pi/2) = \rho_x$$

Method

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3d) The FFT coefficients are the intensity coefficients for your spectra.

Method

4a) Repeat the procedure for different orientations of the molecule.

4b) I don’t want to rotate the molecule, so instead I rotate the magnetic field; must rebuild time evolution.

4c) Add results all into the same array, and plot it like a histogram.

4d) Include weights to account for different populations of different orientations.

Problems!

- Evolution of non-linear terms in Hamiltonian.
- Population of states.
- Simulation of spin flip pulse.
- Decoherence times.
- Measurement of signal? What is thrown out?
- Magnetic field sweeps if Zeeman splitting is non-linear.

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Operator of interest

Hamiltonian

Problem?

- Time variation of RF pulse.
- Find out how Gaunt terms are calculated.

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Ensemble density matrix

- Populate states according to Boltzman distribution:

$$\rho_{ens} = \sum_{i}^{N} w_i \rho_i = \sum_{i}^{N} w_i |\Psi_i\rangle\langle\Psi_i|$$

$$w_i = \frac{e^{-i\frac{E_i}{kT}}}{\sum_j^N e^{-i\frac{E_i}{kT}}}$$

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- We choose N based on how many excited states we want to include.

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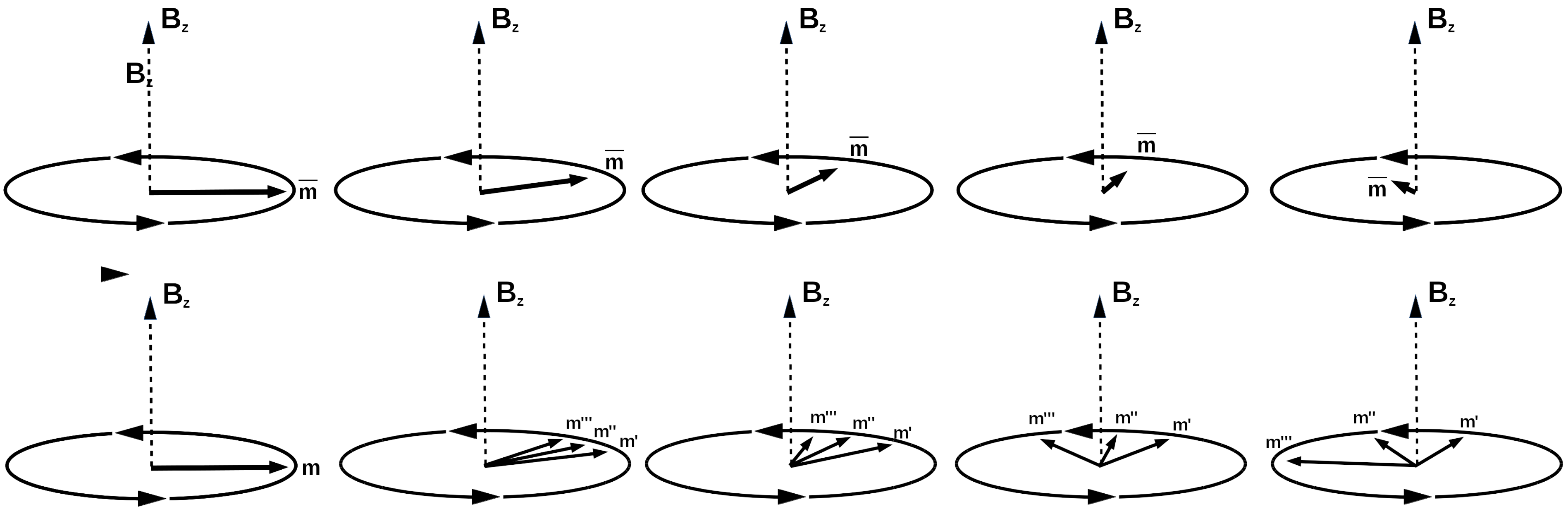
- Must rebuild density for every orientation of **B**.

Spin decoherence!



- Dephasing of spins causes signal to decay
- Anisotropic spin-orbit contributes to this.
- Can potential simulate this; just add to FFT array.

Problems!

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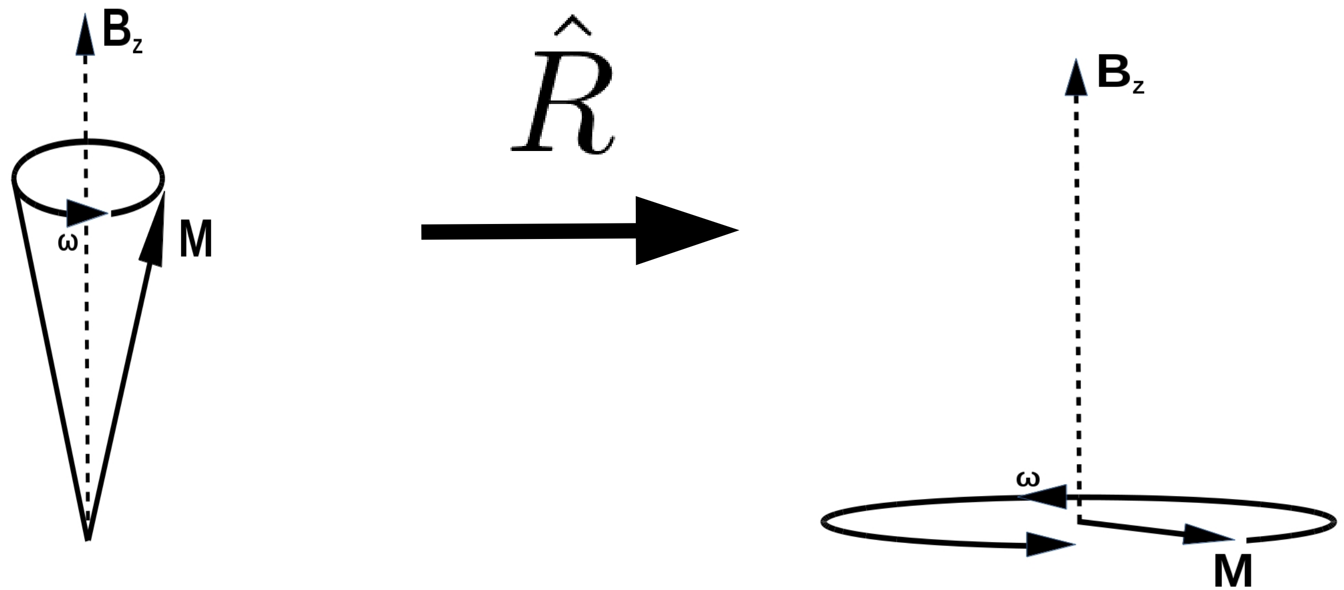
Spin rotation pulse

- We want to rotate a rotating spin:



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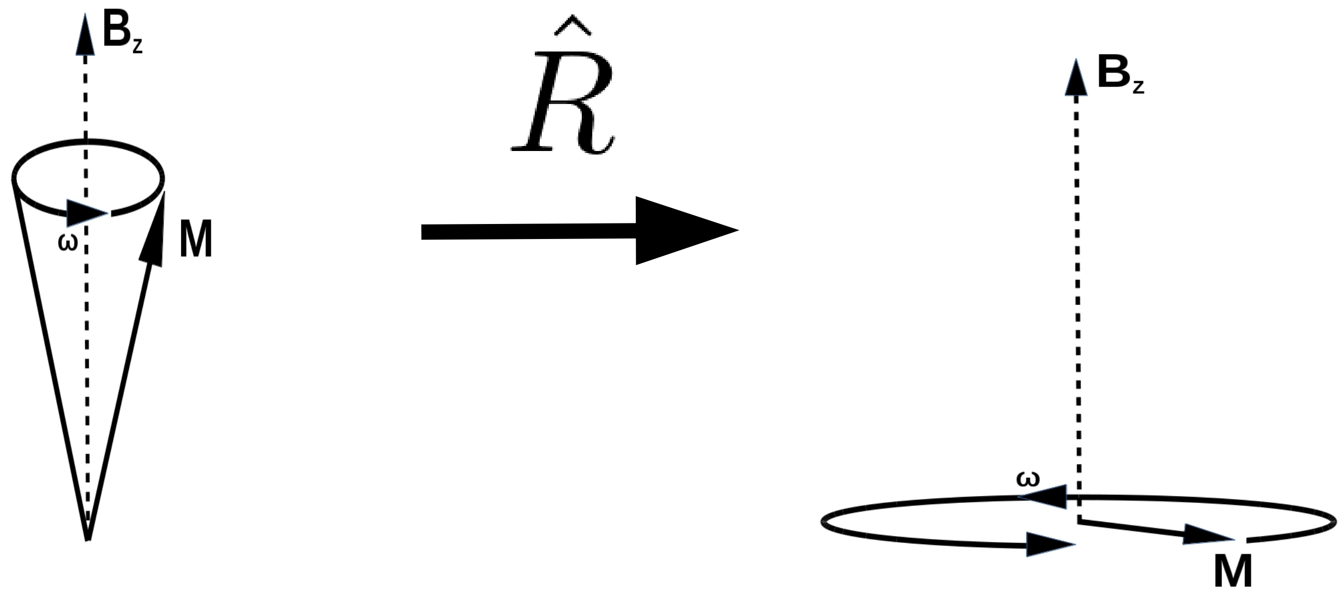

- Maintain rotation about z-axis, whilst also rotating about y (or x).

Spin rotation pulse

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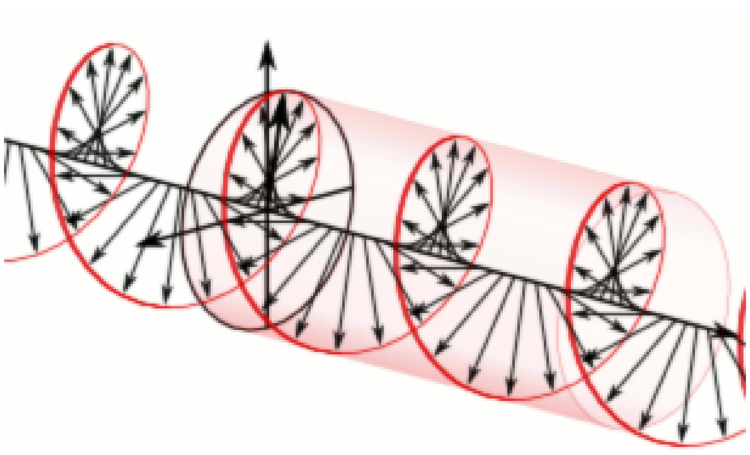
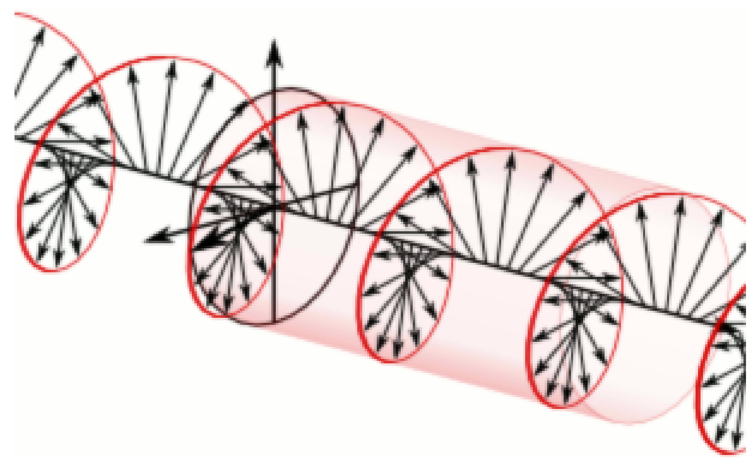
- An planar polarized pulse is the sum of two circularly polarized ones:





GIFS: Wikipedia Commons

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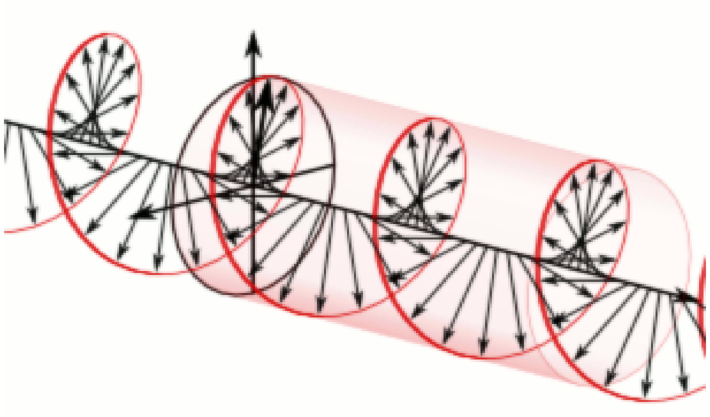

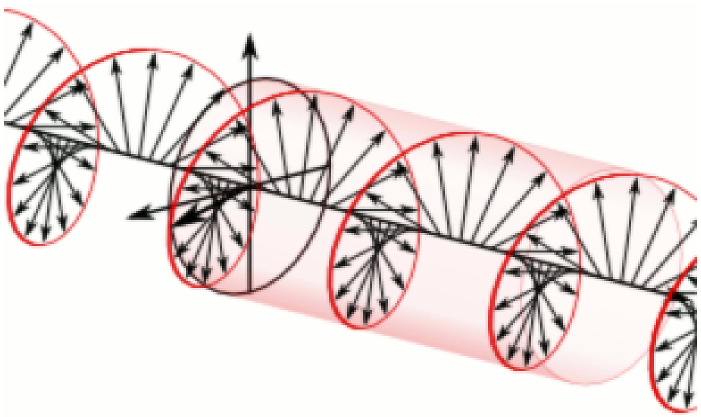

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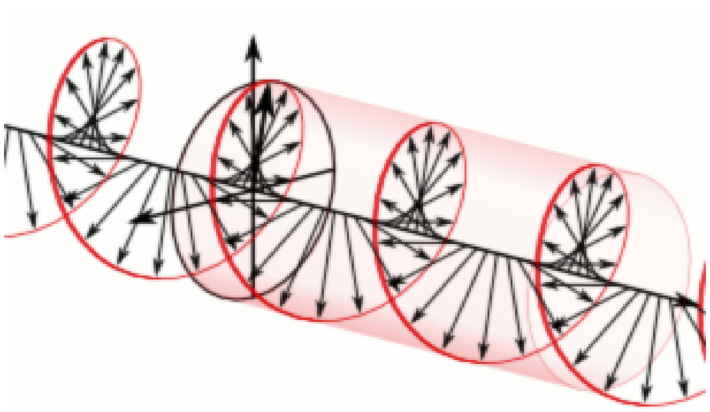

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GIFS: Wikipedia Commons

Spin rotation pulse

- **Problem ! :** Doesn't work if spin-orbit coupling is strong.
- Must use Ehrenfest to generate the spin-rotation operator, and simulate spin rotation:

$$\frac{d}{dt}\langle\hat{A}\rangle = \frac{1}{i\hbar}\langle[\hat{A},\hat{H}]\rangle + \left\langle\frac{\partial\hat{A}}{\partial t}\right\rangle,$$

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- Will need to find the length, amplitude etc., of rotation pulse used in an experiment in order to simulate it.

- Errors can arise due to a phase offset between the electron moment and the RF pulse.

Problems!

- Evolution of non-linear terms in Hamiltonian.
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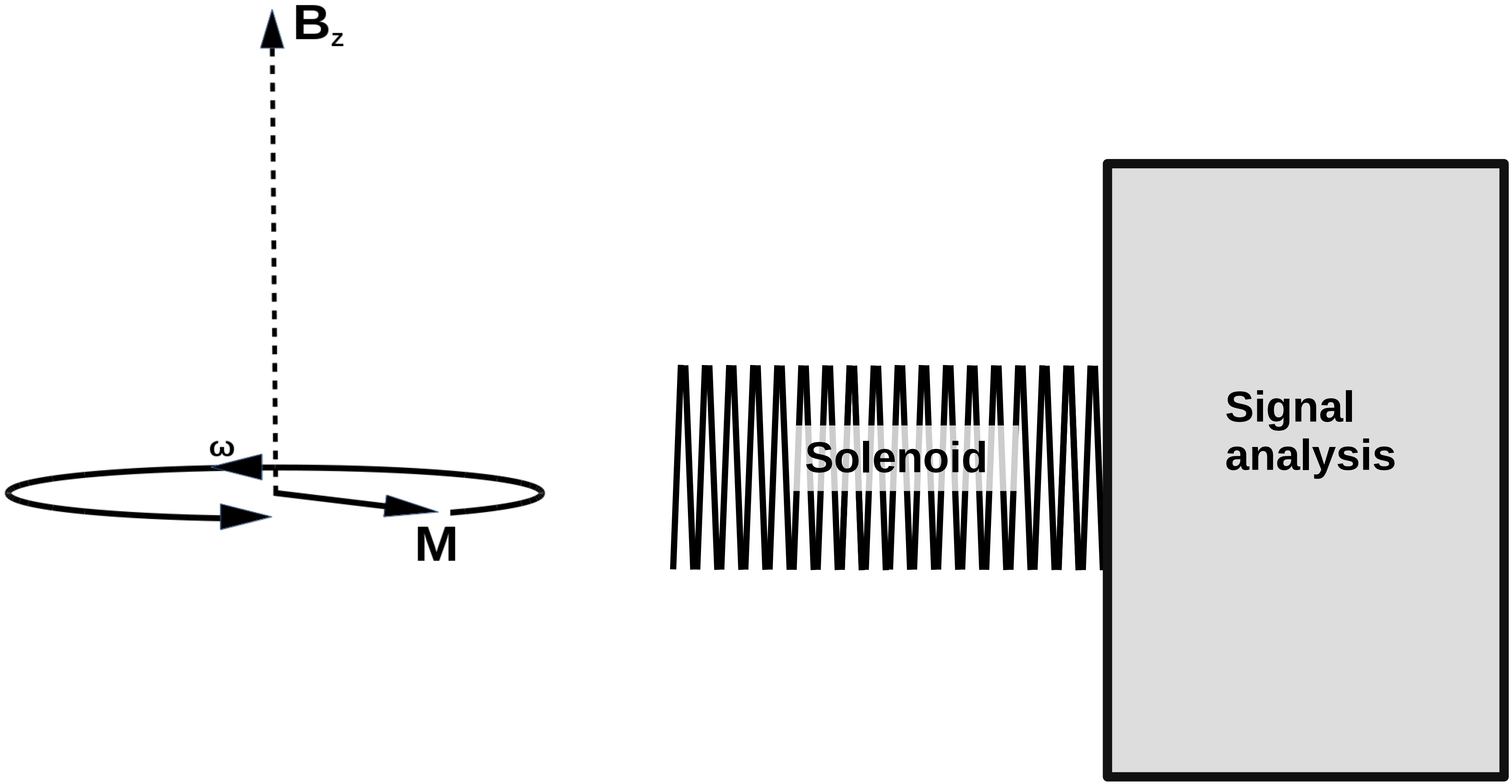
- Simulation of spin flip pulse.
- **Measurement of signal? What is thrown out?**
- Magnetic field sweeps if Zeeman splitting is non-linear.

Measure induced current



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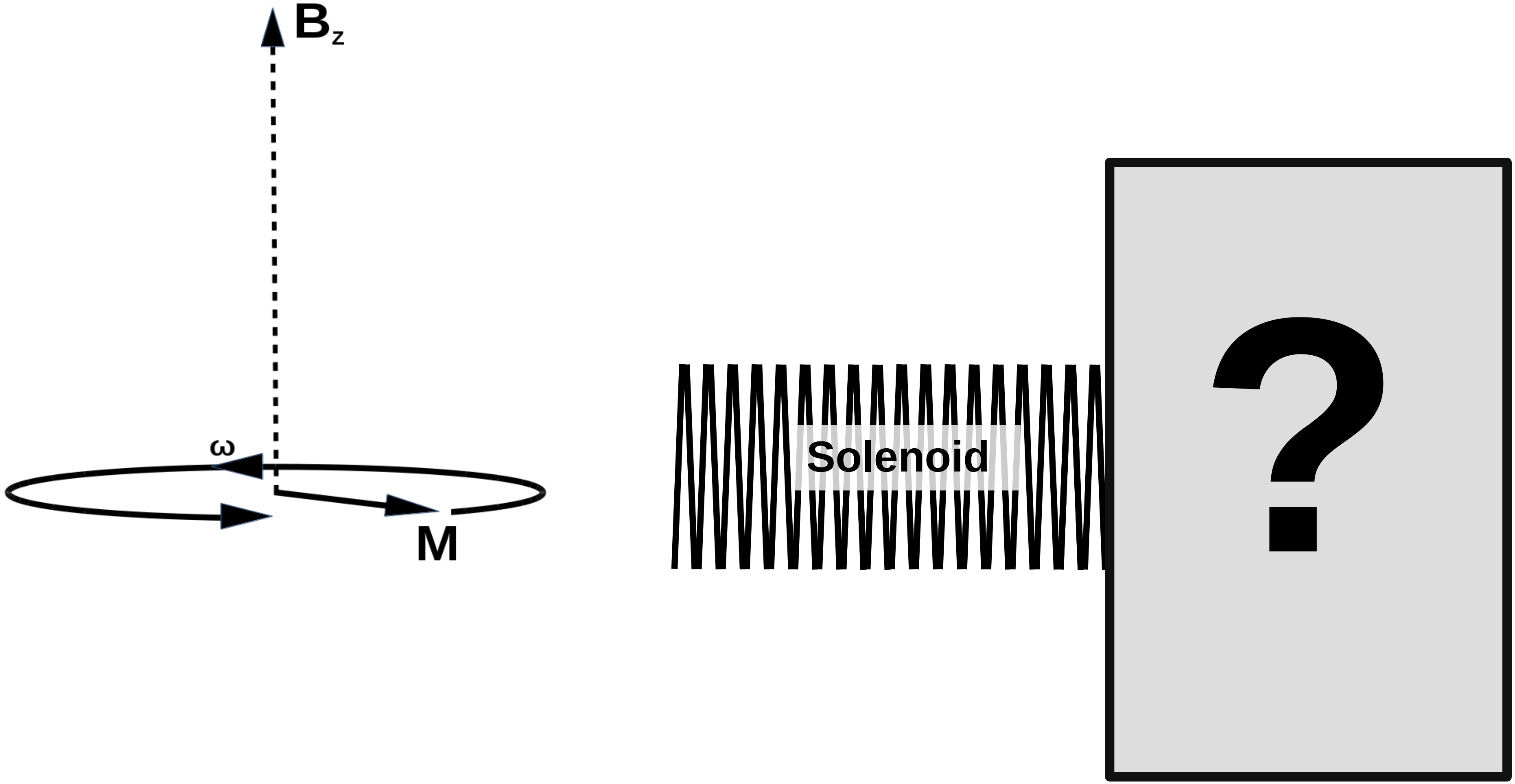

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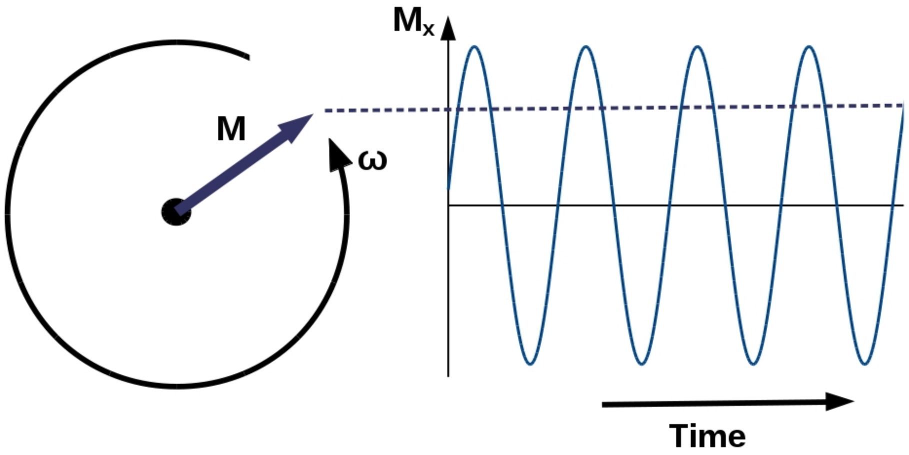

- A complex signal, but we only ever hear about the real part......I'm calculating it, and just throwing it out.
- Signal processing in EPR machines is very complicated; fluctuations in the current in the solenoid are so tiny even that is not straightforward.

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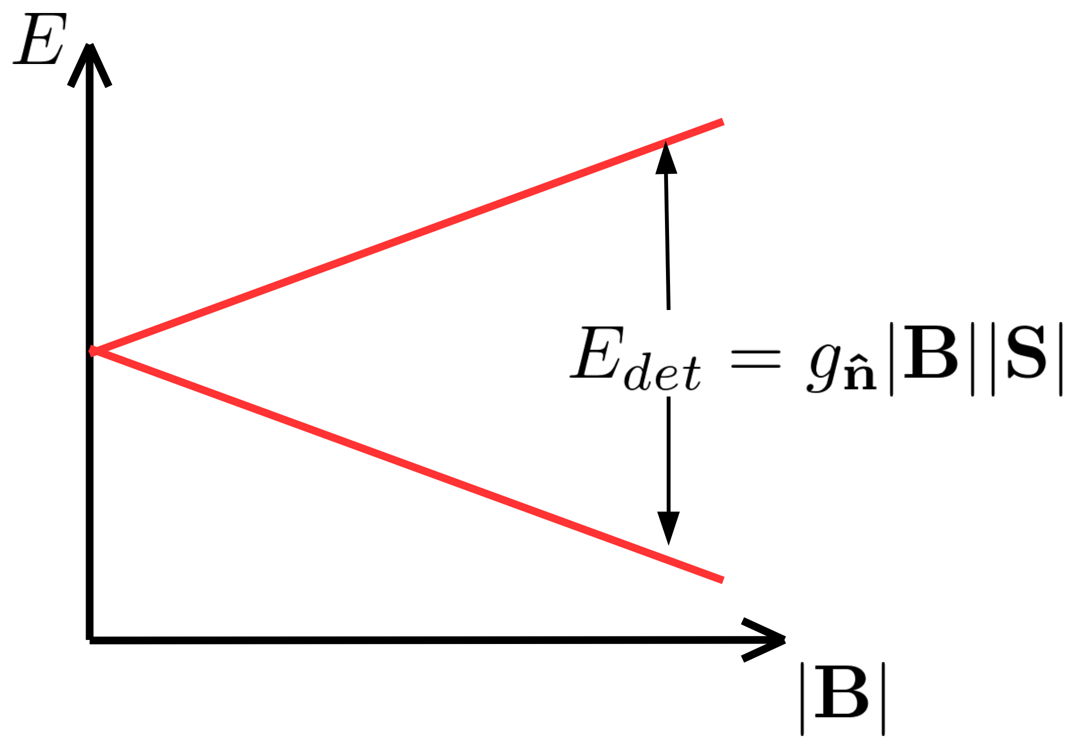
- **Magnetic field sweeps if Zeeman splitting is non-linear.**

Linear Zeeman Splitting



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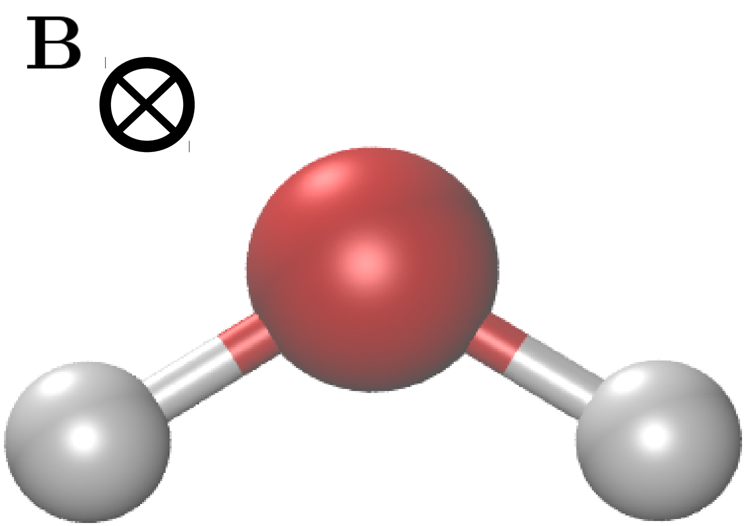
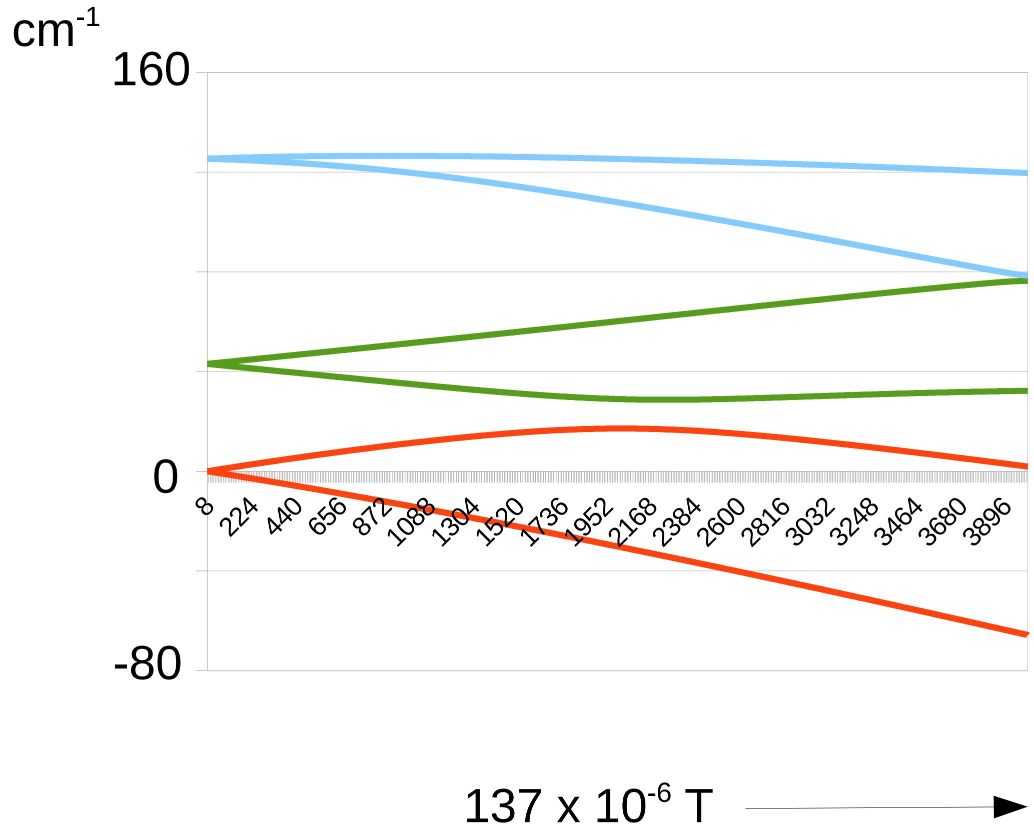
Non-linear Zeeman splitting



IrH$_2$



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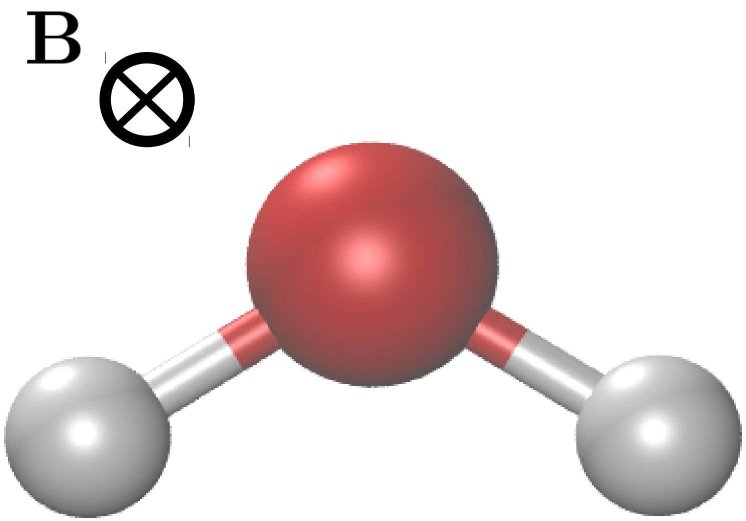
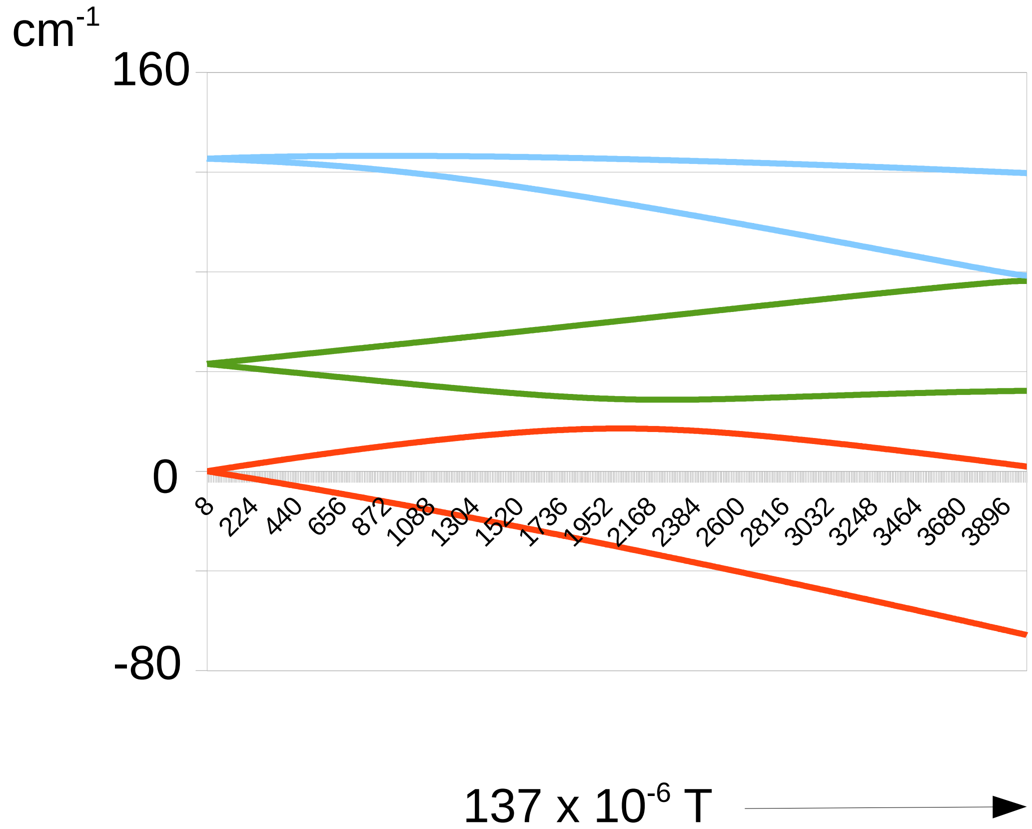


IrH_2



- Must reconstruct density matrix and redo populations for all orientations of magnetic field.
- Need to thoroughly check the units......

Hyperfine tensors

- Need hyperfines; most systems of interest involve either hydrogen, or some nucleus with spin.
- Working on relativistic CASPT2; goal is to used resulting states to calculate hyperfines.
- XMS-CASPT2; involves coupling of multiple states.
- XMS reference space would need to include all states which could influence ground state.
- Transformation of states could prove problematic as operator for describing magnetic field and operators used in determining correlation do not commute.

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- Working on relativistic XMS-CASPT2; goal is to used resulting states to calculate hyperfines.
- XMS-CASPT2; involves coupling of multiple states.
- Potential difficulties transforming in CASPT2 basis; at least XMS reference space would need to include all states which could influence ground state.
- Need to understand relationship between electron correlation (relativistic) and magnetic fields.

Tasks

- Get more things to converge