Basic principles and applications of spin chemistry

(a brief review)

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Outline

- ❑ What is spin chemistry? Definition, history & introductory notes
- ❑ Radical pairs, radical pair reaction mechanism, spin correlation in a pair
- ❑ Methods of radical pair generation/detection of products
- ❑ CIDEP and CIDNP

I. What is spin chemistry?

An interdisciplinary field of chemistry and physics dealing with magnetic and spin effects in chemical reactions

Historical background

1900 Gomberg : Discovery of free radicals

1937 Hey and Walters: Role of free radicals in the solution reaction mechanisms

1944 Zavoisky: Discovery of EPR

1963 Fessenden and Schuler: Anomalous EPR intensities in irradiated CH_4 (**CIDEP**)

1967 Bargon et al.; Ward and Lowler: Anomalous NMR intensities in reacting systems **(CIDNP)**

1969 Closs; Captein and Oosterhoff: **Radical pair mechanism** proposed for explanation

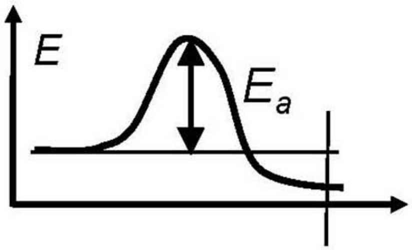
Range of phenomena

Magnetic field effects, chemically induced magnetic polarization, magnetic isotope effects, spin catalysis, quantum beats in radical pairs

In biology and medicine: animal magnetoreception, health hazards of environmental electromagnetic radiation

Chemical reactions are controlled by energy and angular momentum

- **Thermodynamic (ΔG) or kinetic (E_a) control**

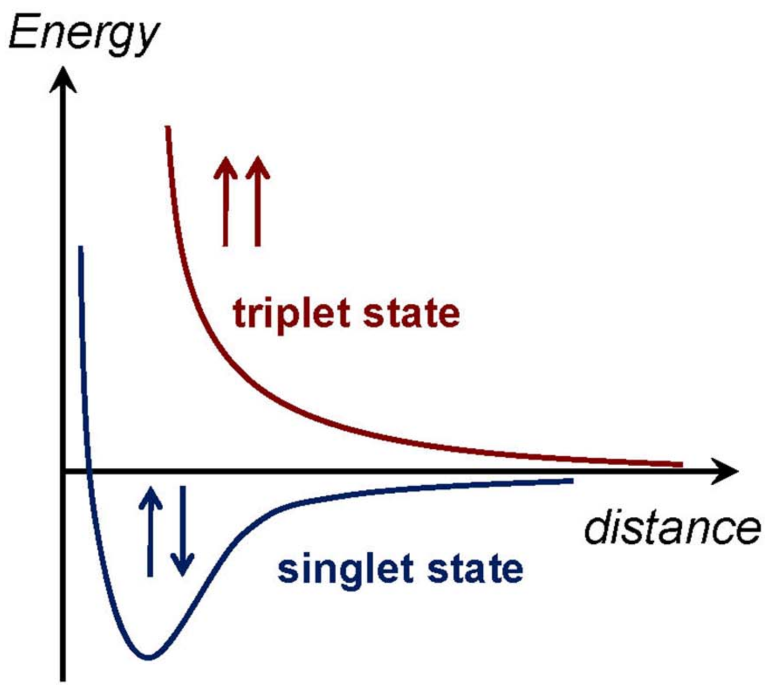


- **Chemical reactions are usually spin-conserving**

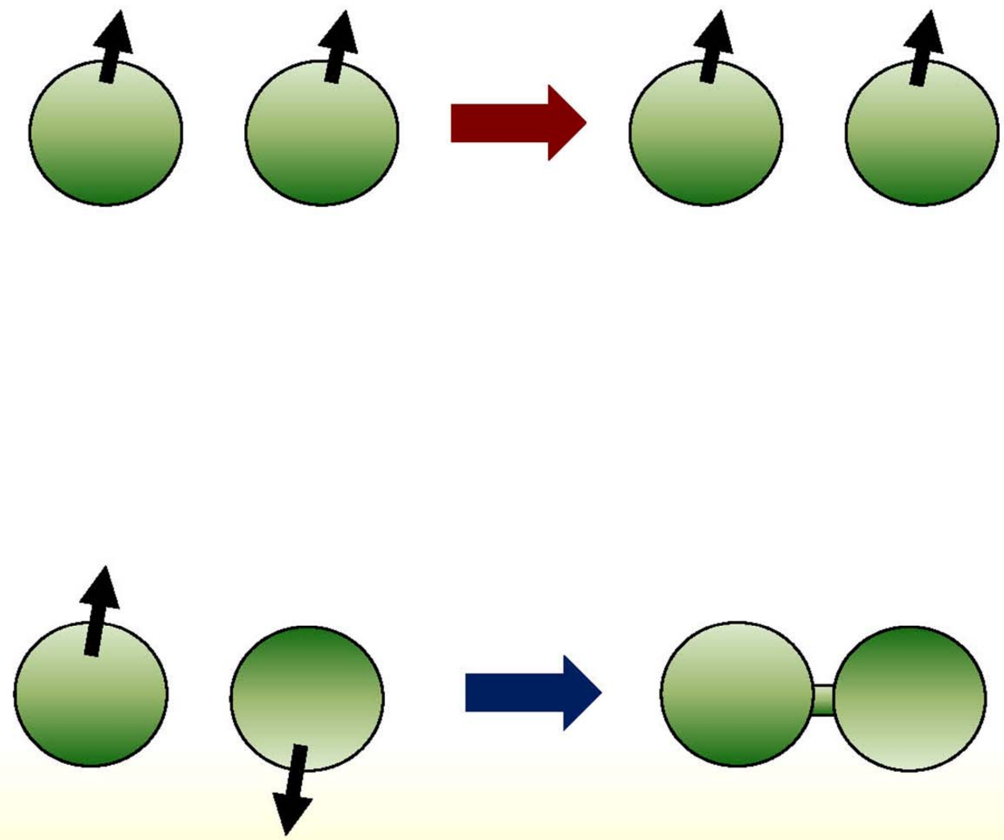
Basic principle:

$$\Sigma \vec{s}_i(\text{reactants}) = \Sigma \vec{s}_j(\text{products})$$

The reaction is controlled by spin state:



Recombination of two H atoms



"…one of the most mysterious problems in science – whether ordinary magnetic fields can exert an appreciable influence on chemical and biochemical reactions."

…Thermodynamic and kinetic effects of magnetic fields are very small.

<u>Thermal:</u> $kT = 2.5$ kJ/mole at 300K

<u>Chemical reactions</u>: $\Delta_r E \sim 10^2$ kJ/mole

<u>Magnetic field:</u> $E_B(kJ/mole) = -(\vec{\mu} \bullet \vec{B}) \sim \mu_B B \sim 10^{-2} \cdot B(T)$

$B_{HFC} \sim 10^{-3}\ T$ *300 MHz NMR: ~ 7 T*

"…Though negligibly small in terms of energy, magnetic interactions can play a key role in reaction mechanisms:

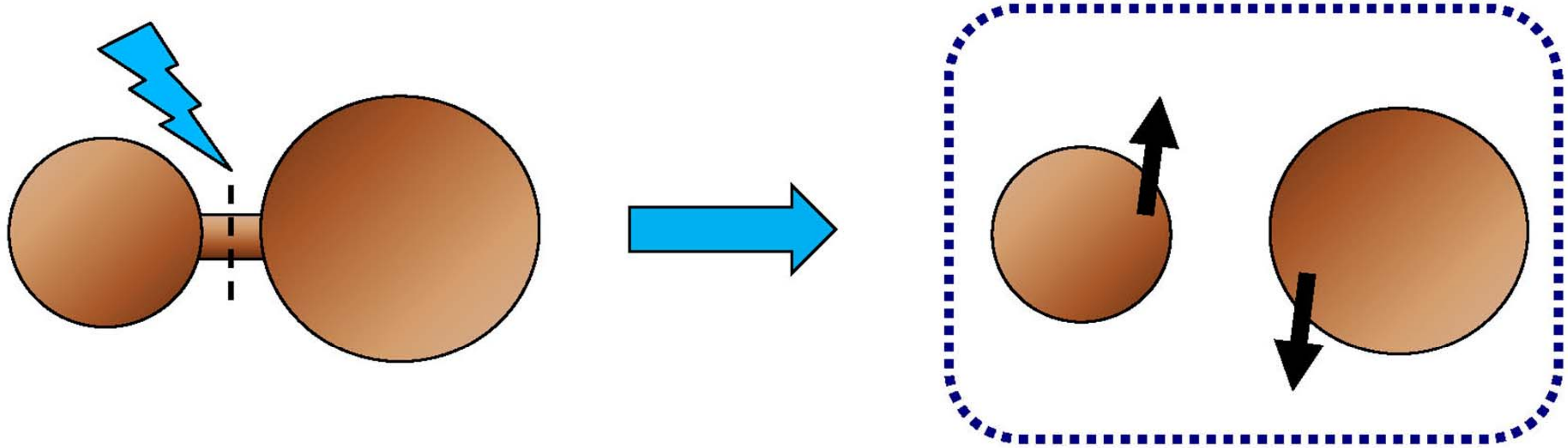
-by changing the spin multiplicity of pre-reactional state,

they allow switching between spin forbidden and spin-allowed reaction pathways"

Basic principle:

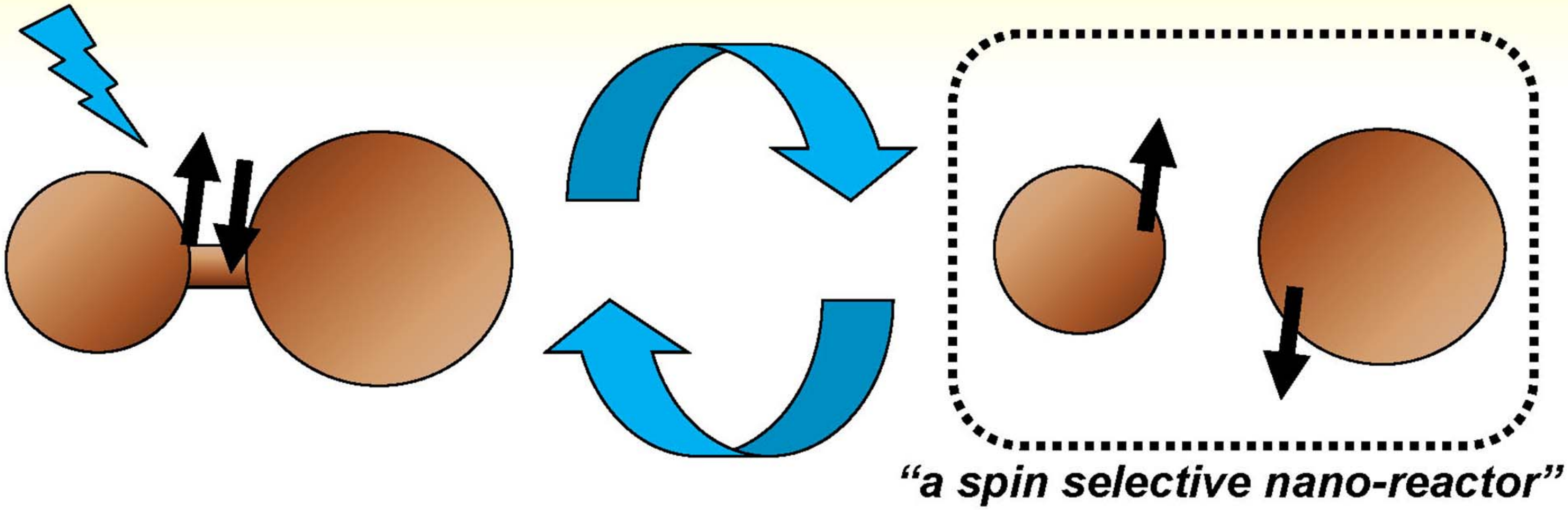
$$\Sigma\vec{s}_i(\text{reactants}) = \Sigma\vec{s}_j(\text{products})$$

- Radicals formed from diamagnetic precursors are created in ***pairs***
- The overall spin and multiplicity of radical pair is initially the same as that of its precursor ***(Spin correlation)***



Spin correlated radical pair

A radical pair is a chemical entity



A system of spins with a number of possible spin states

Spin evolution
Molecular/chemical dynamics

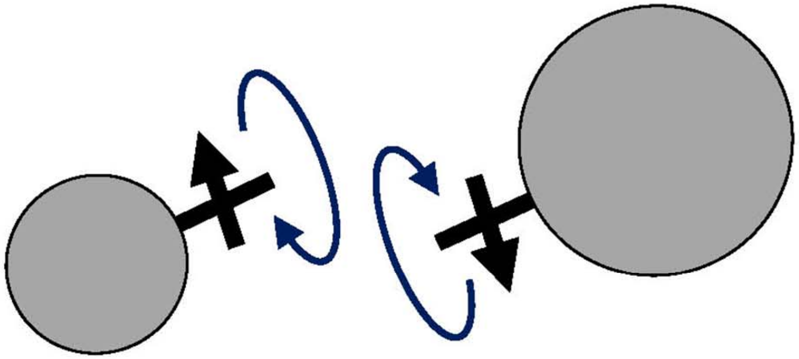
Spin allowed and spin-forbidden transformation pathways

a source of magnetic/spin effects

$$\Sigma \vec{s}_i(\text{reactants}) = \Sigma \vec{s}_j(\text{products})$$

How can the overall spin (multiplicity) of radical pair be changed?

- ❑ Constant or oscillating external magnetic field
- ❑ Presence of magnetic nuclei (hyperfine interaction)
- ❑ Paramagnetic relaxation: statistically **S:T** ratio is **1:3**
- ❑ Exchange interaction : modulating the efficiency of **S-T** mixing



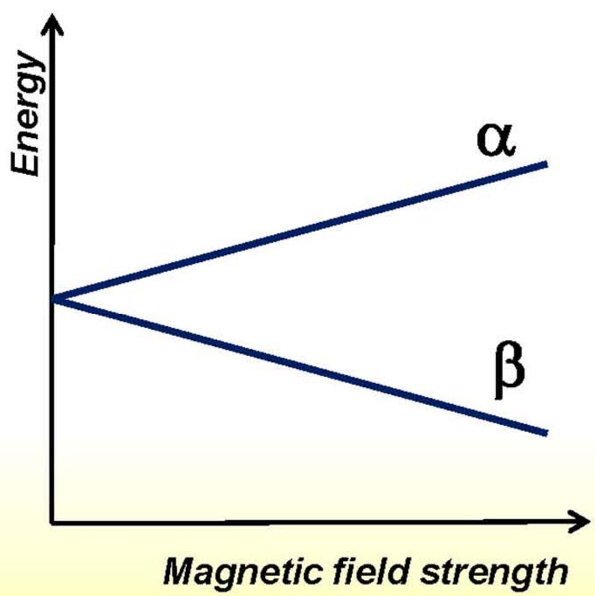
The motion of the two radical spins is controlled by local magnetic fields at each radical

Spin sublevels in magnetic field

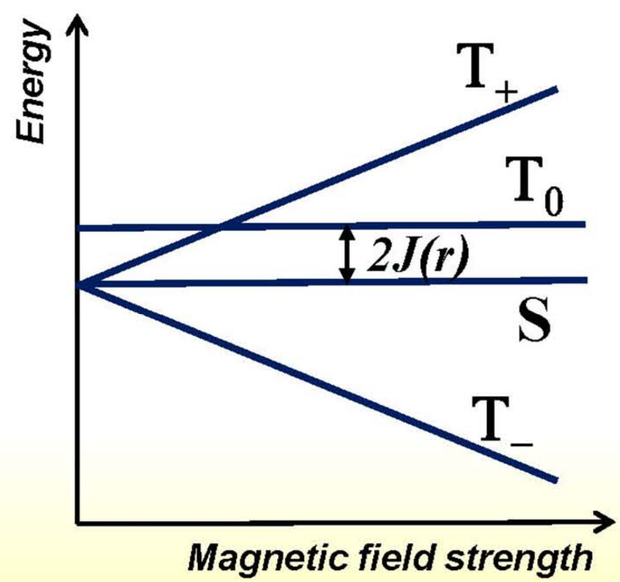
$$|\alpha\rangle = |\uparrow\rangle \qquad |S\rangle = \frac{1}{\sqrt{2}}\left(|\alpha\beta\rangle - |\beta\alpha\rangle\right) \qquad |T_-\rangle = |\beta\beta\rangle$$

$$|\beta\rangle = |\downarrow\rangle \qquad |T_0\rangle = \frac{1}{\sqrt{2}}\left(|\alpha\beta\rangle + |\beta\alpha\rangle\right) \qquad |T_+\rangle = |\alpha\alpha\rangle$$

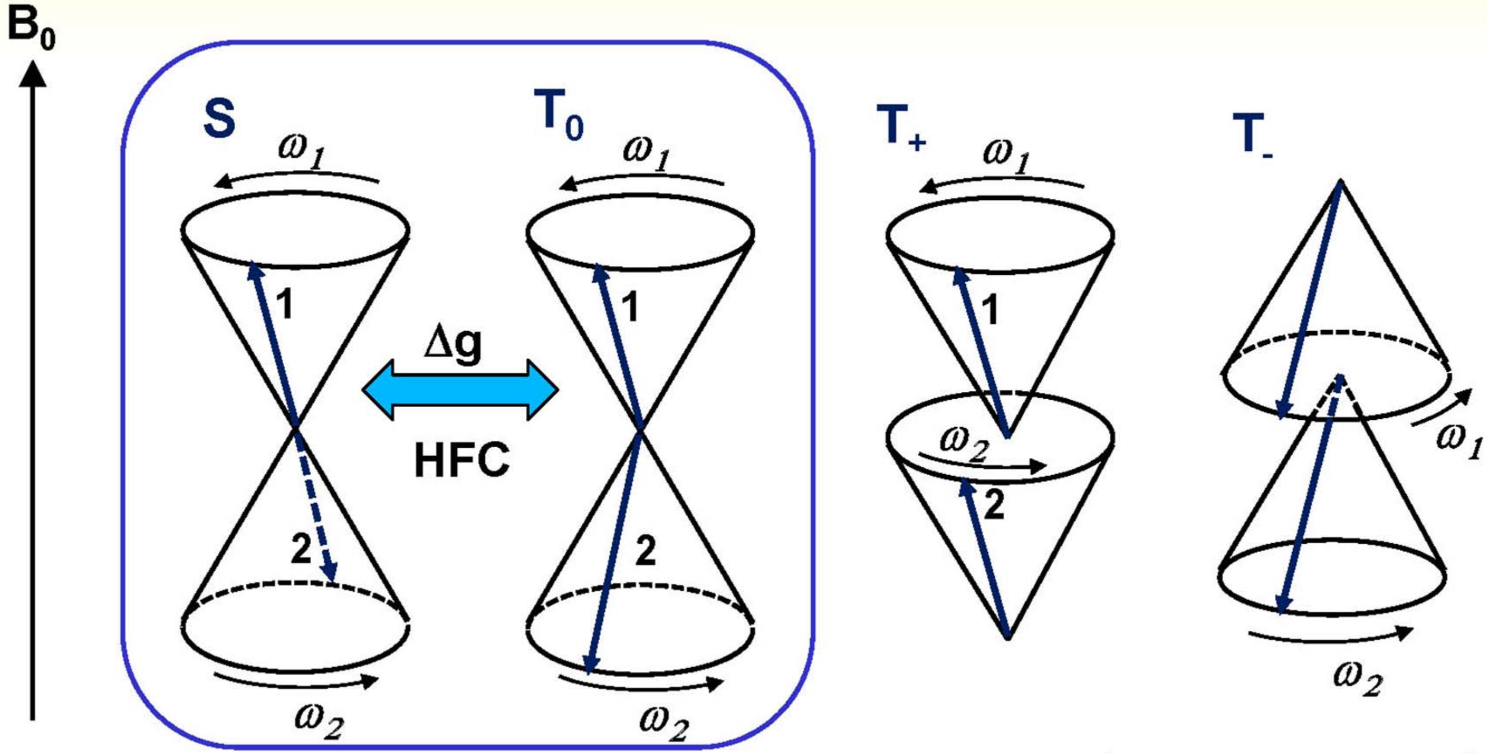
Single electron



Two coupled electrons



Spin state evolution in strong magnetic field



Larmor precession

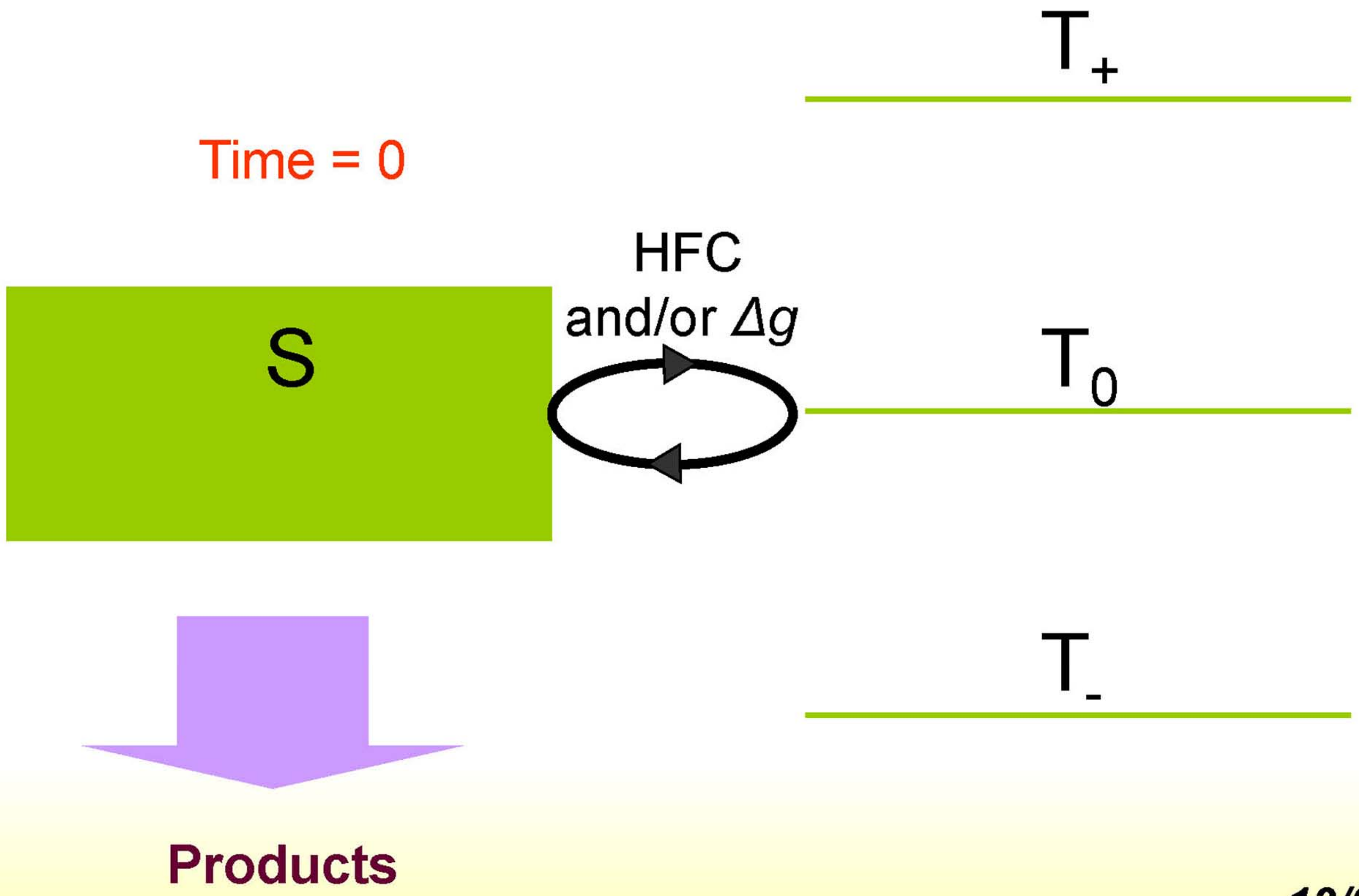
S-T_0 mixing

$$\omega_1 \neq \omega_2$$

$$\omega = \frac{g\mu_B B_{local}}{\hbar}$$

Spin evolution in a strong magnetic field

(quantum beats; time resolved magnetic field effect)



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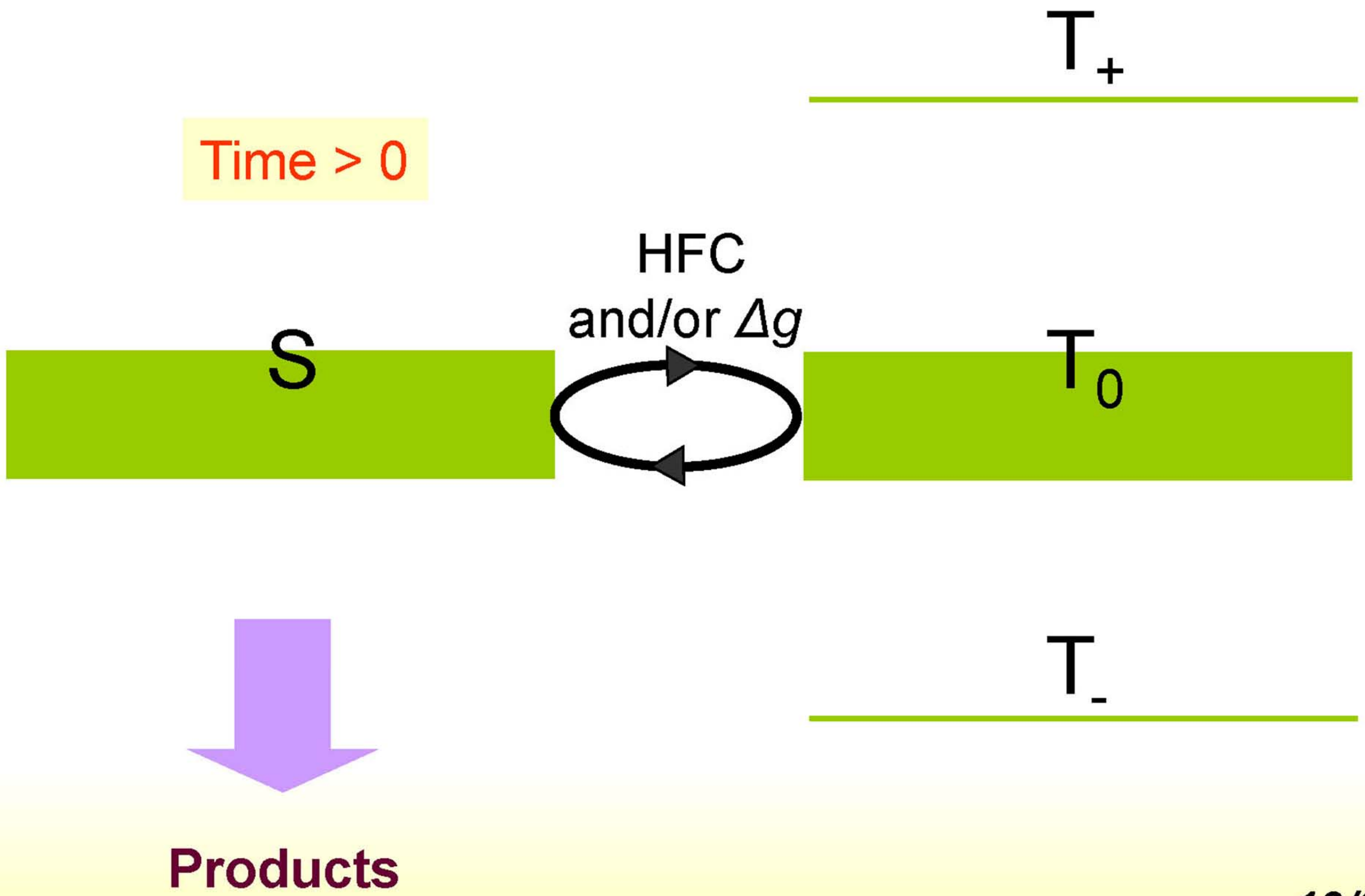

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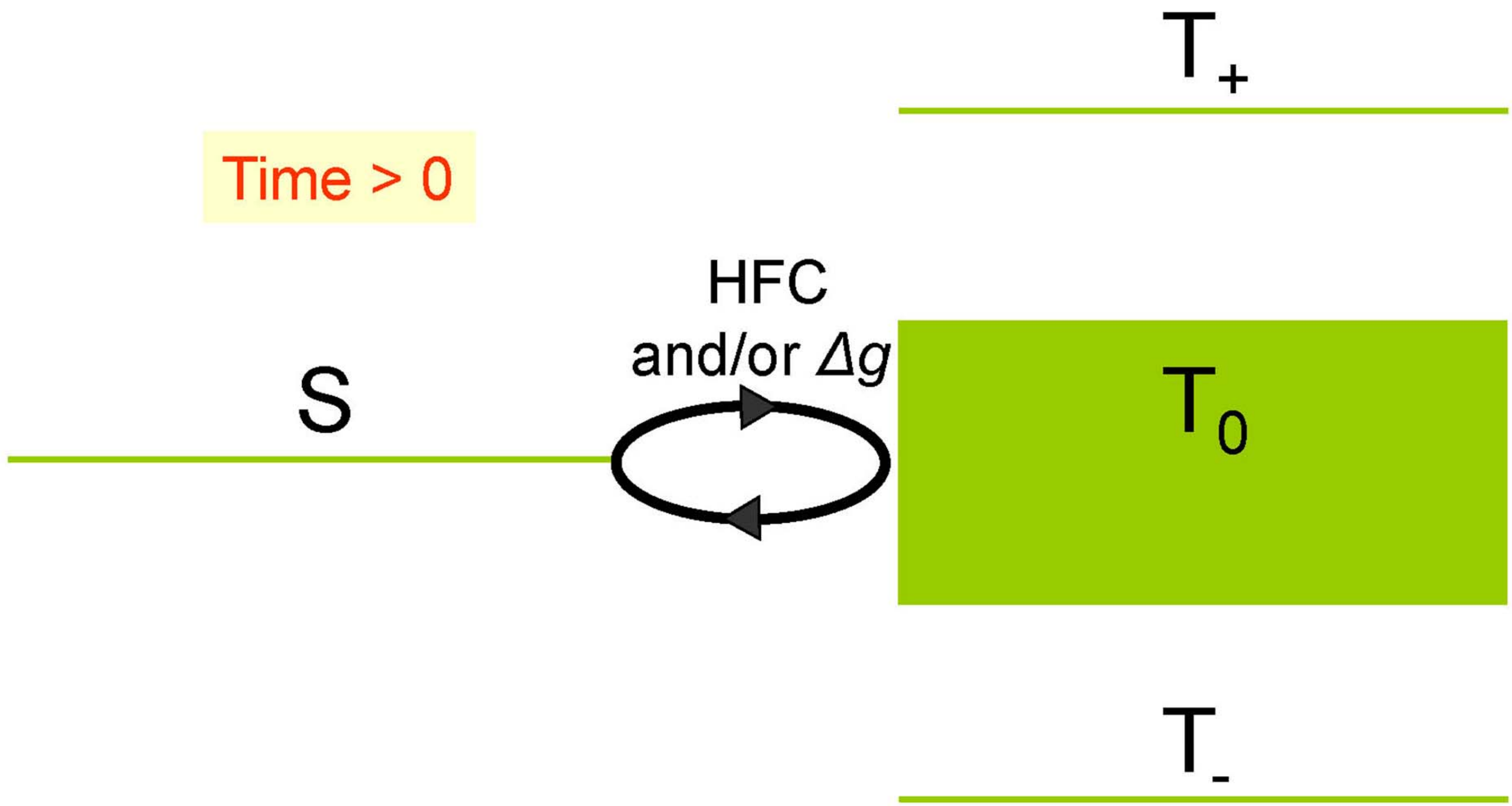
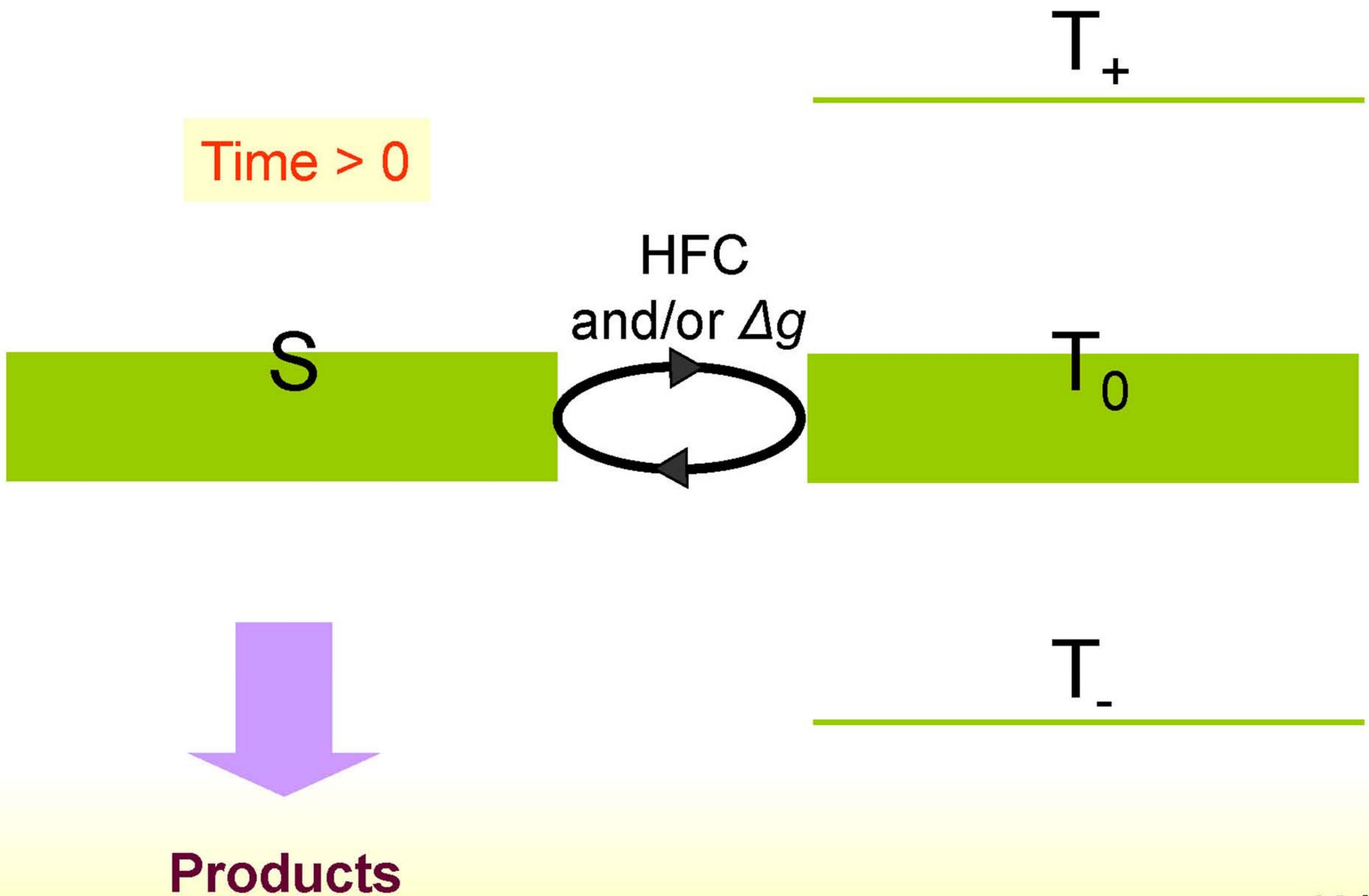


Products

Spin evolution in a strong magnetic field

(quantum beats; time resolved magnetic field effect)



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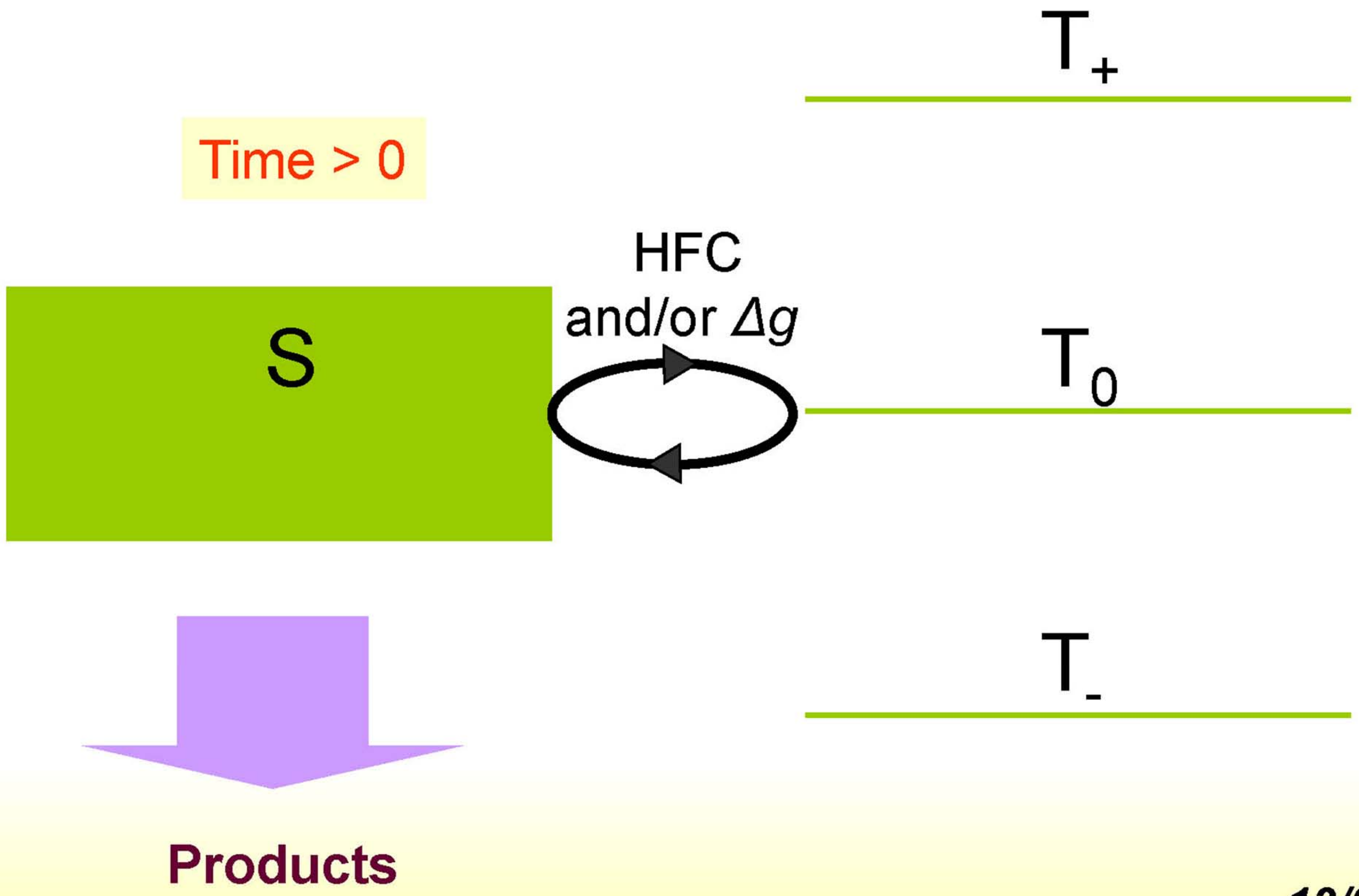

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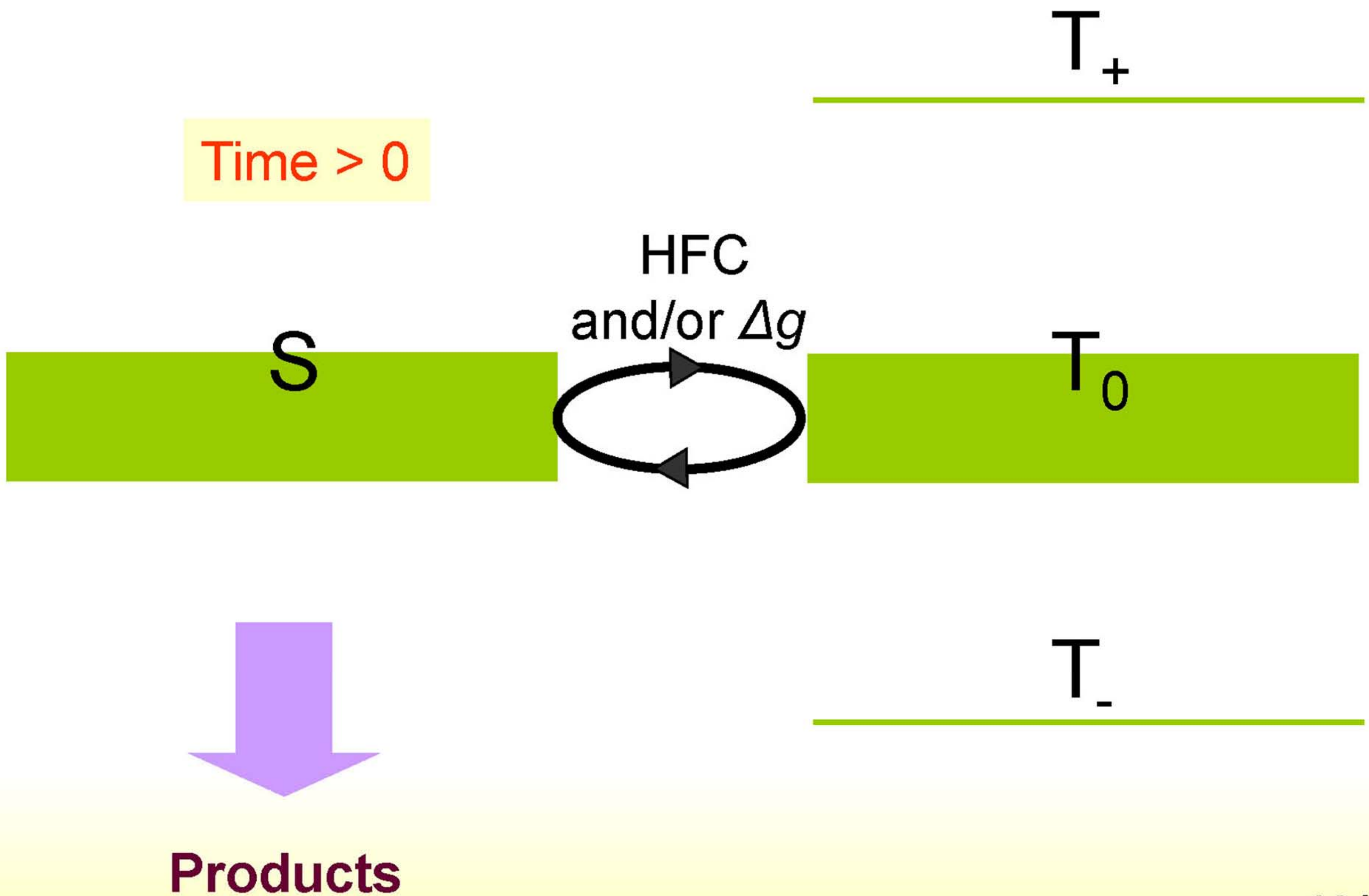

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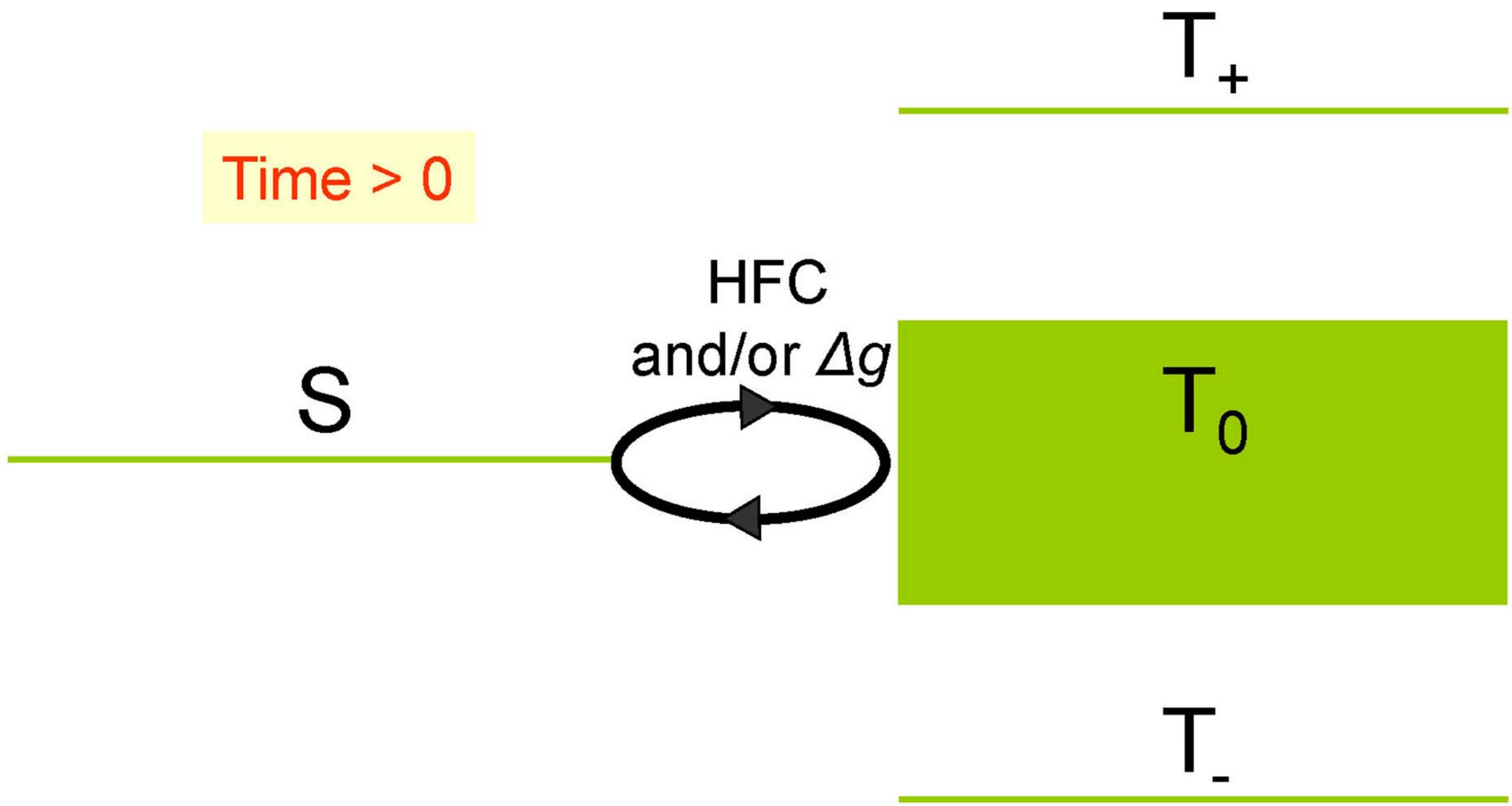

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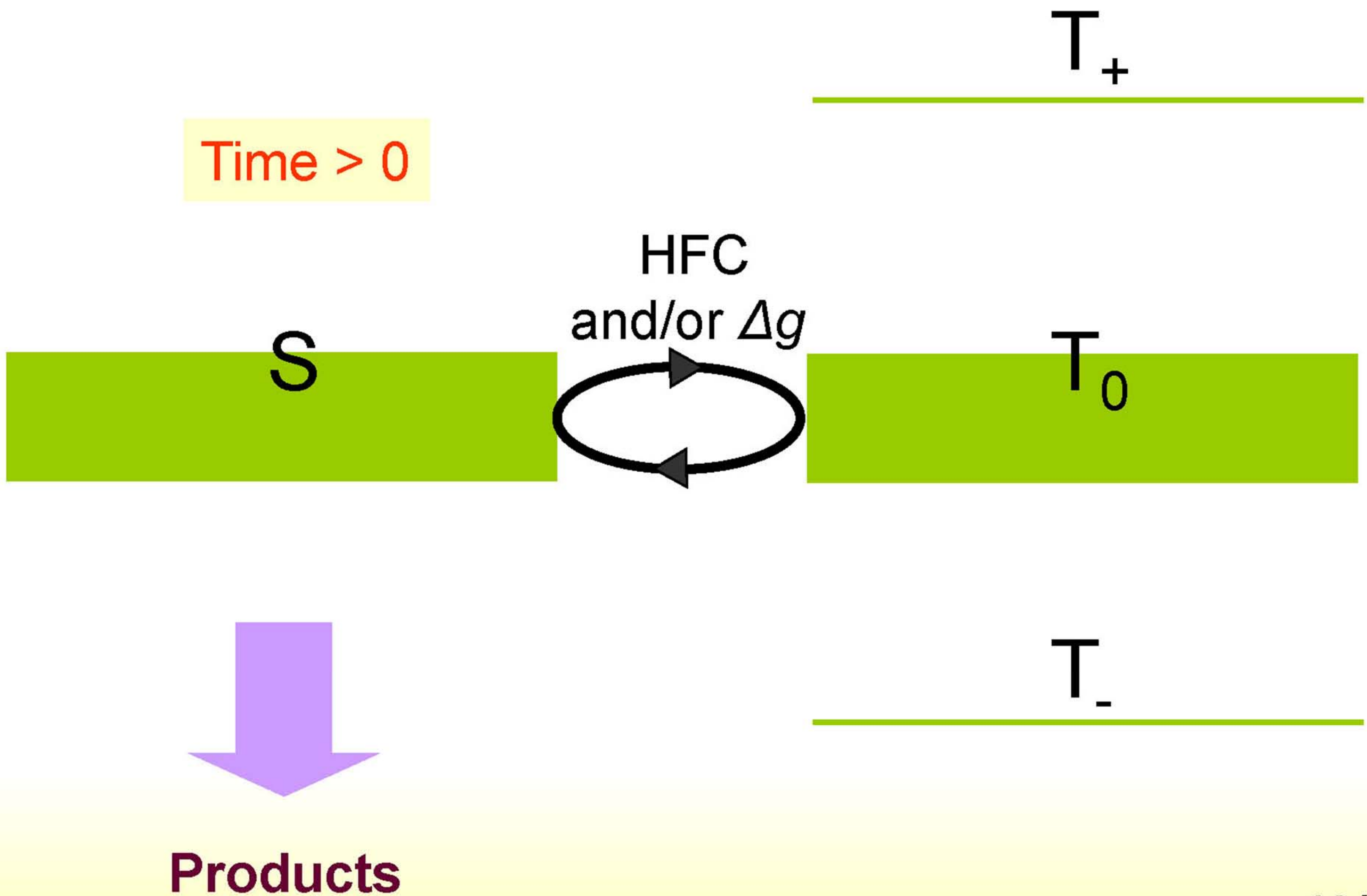

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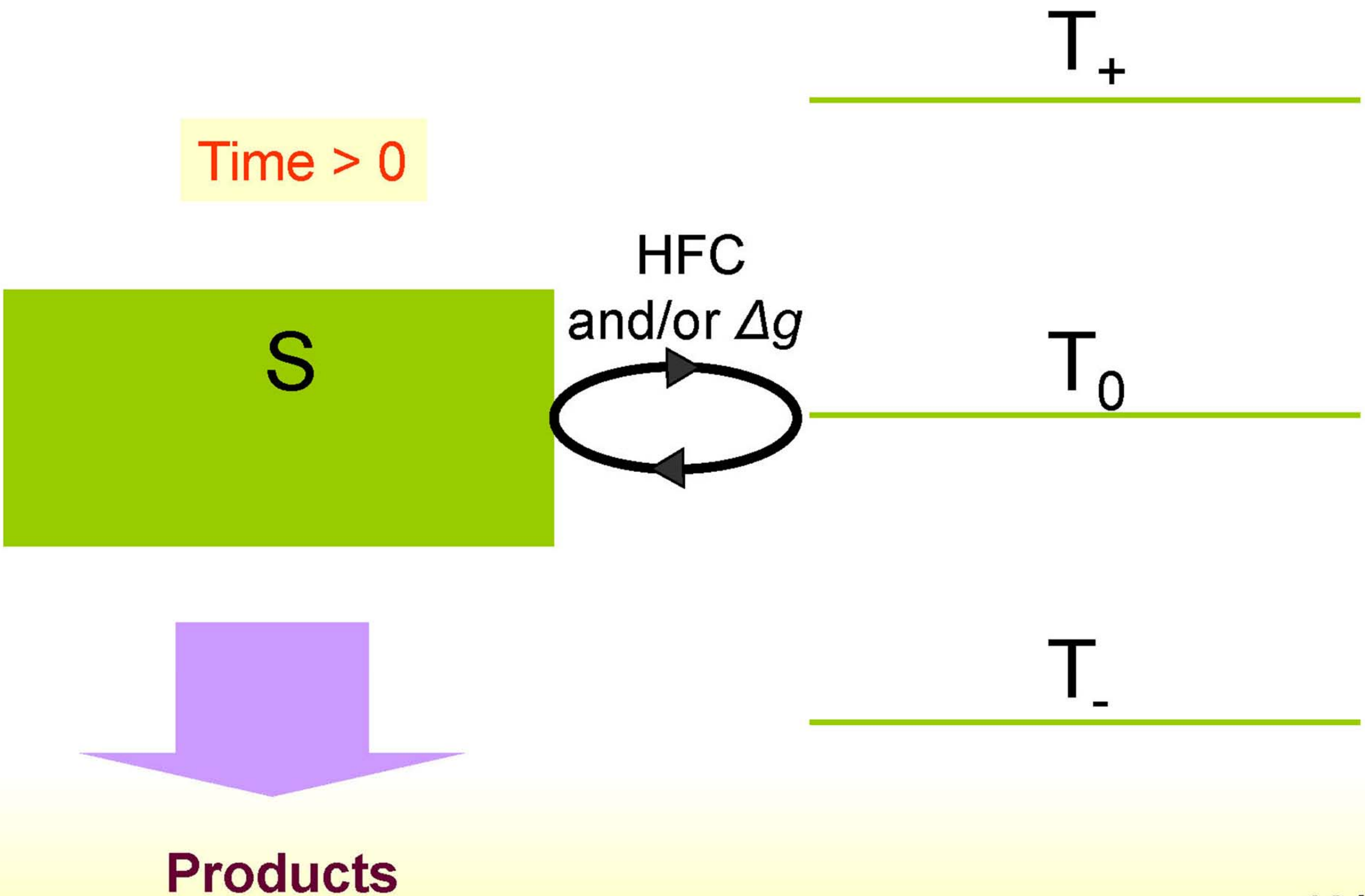
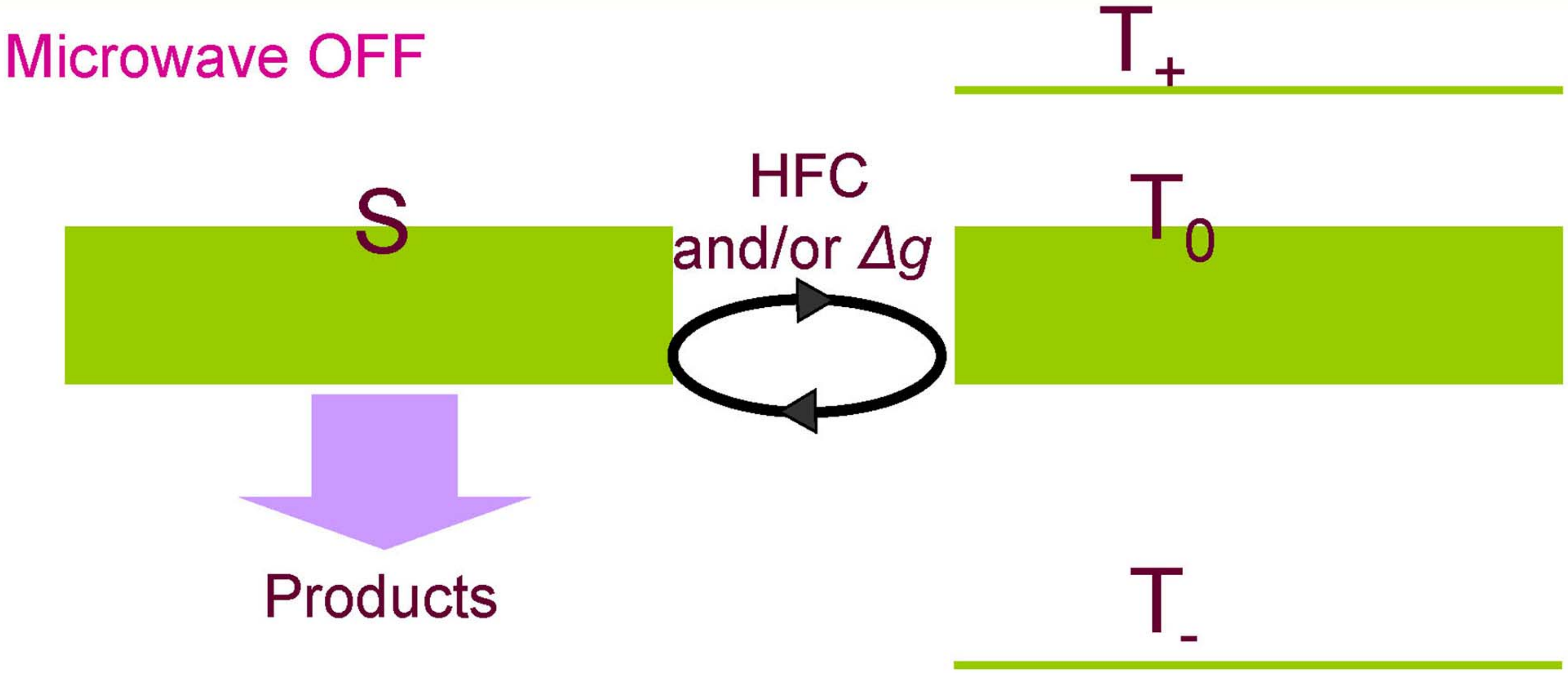


Reaction yield detected EPR:

direct detection of radical pairs



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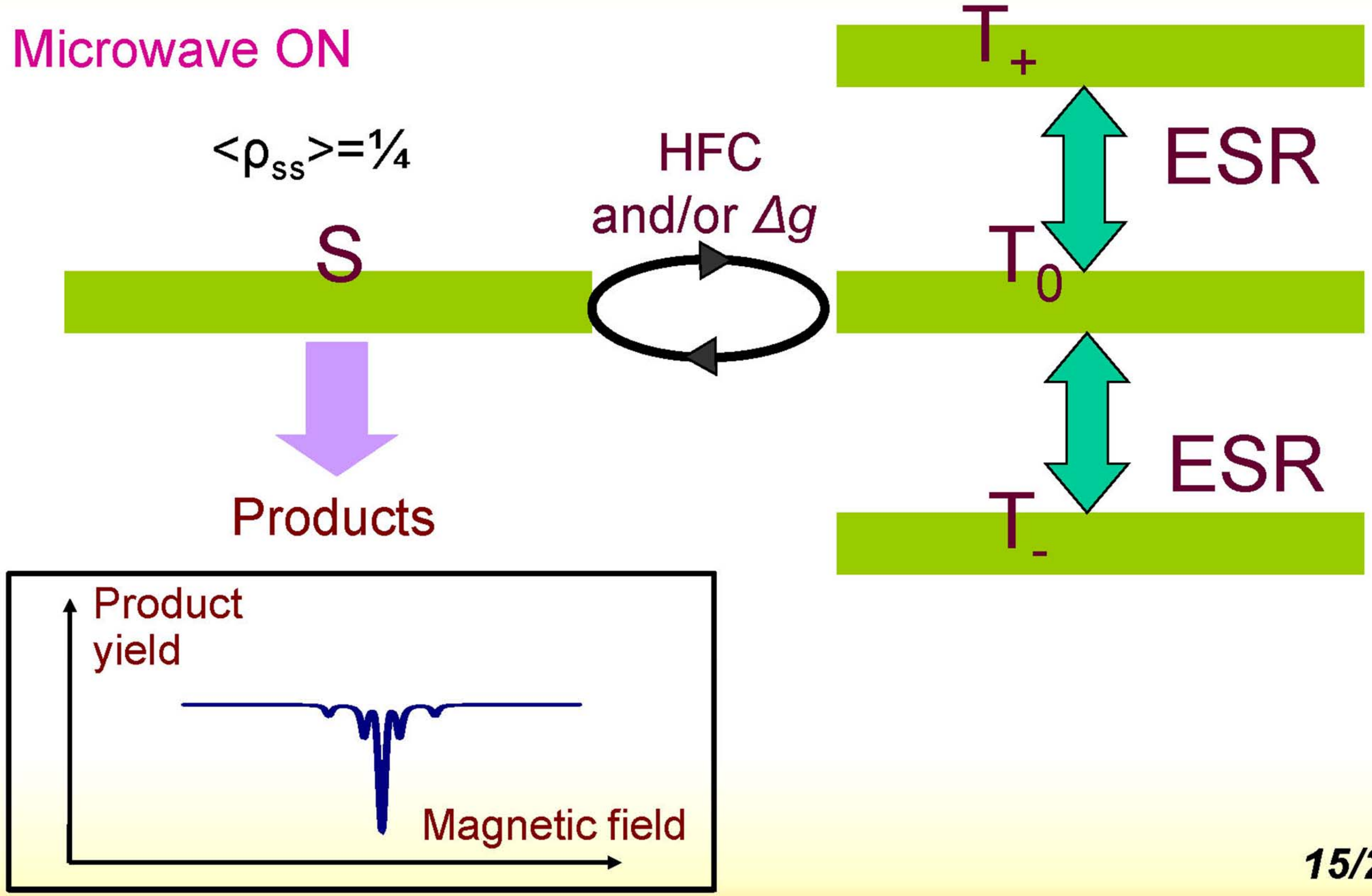


Spin state mixing in zero field

$$\hat{H}_{RP,J=0} = \mu_B(g_1\hat{\mathbf{S}}_1 \cdot \mathbf{B} + g_2\hat{\mathbf{S}}_2 \cdot \mathbf{B}) + \sum_i a_{i1}\hat{\mathbf{I}}_{i1} \cdot \hat{\mathbf{S}}_1 + \sum_i a_{i2}\hat{\mathbf{I}}_{i2} \cdot \hat{\mathbf{S}}_2$$

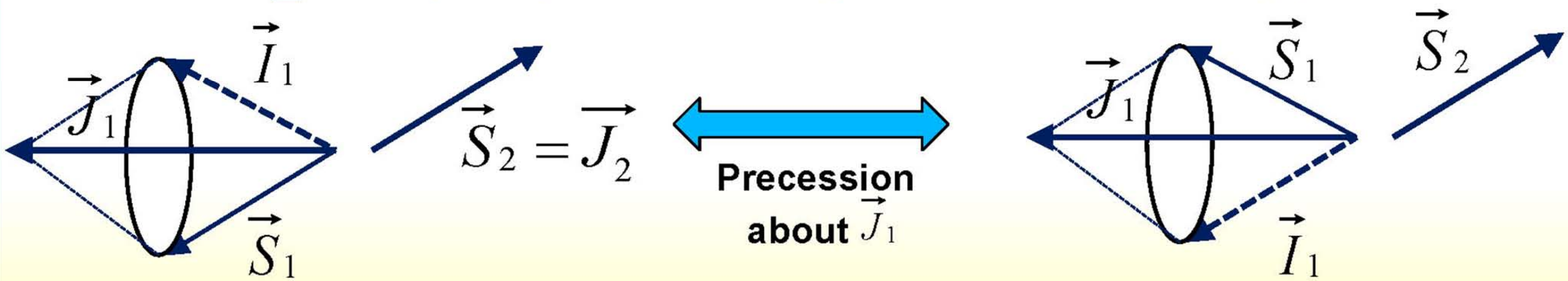
$$\langle T_0\varphi_N | H_{RP} | S, \varphi_N \rangle = \frac{1}{2}\left[\underbrace{\boxed{\cancel{\Delta g \mu_B B}}}_{\Delta g} + \underbrace{\boxed{\left(\sum_i a_{i1}m_{i1} - \sum_k a_{k2}m_{k2}\right)}}_{\text{HFC}} \right]$$

$$\langle T_{\pm 1}\varphi'_N | H_{RP} | S, \varphi_N \rangle = \frac{\mp a_i\sqrt{I_i(I_i+1) - m_i(m_i \pm 1)}}{\sqrt{8}}$$

where $\varphi_N = |m_{1i}, m_{2k}\rangle; \ \varphi'_N = |m_{1i} \mp 1, m_{2k}\rangle$

m_{1i} is a nuclear spin quantum number for nucleus i on radical 1

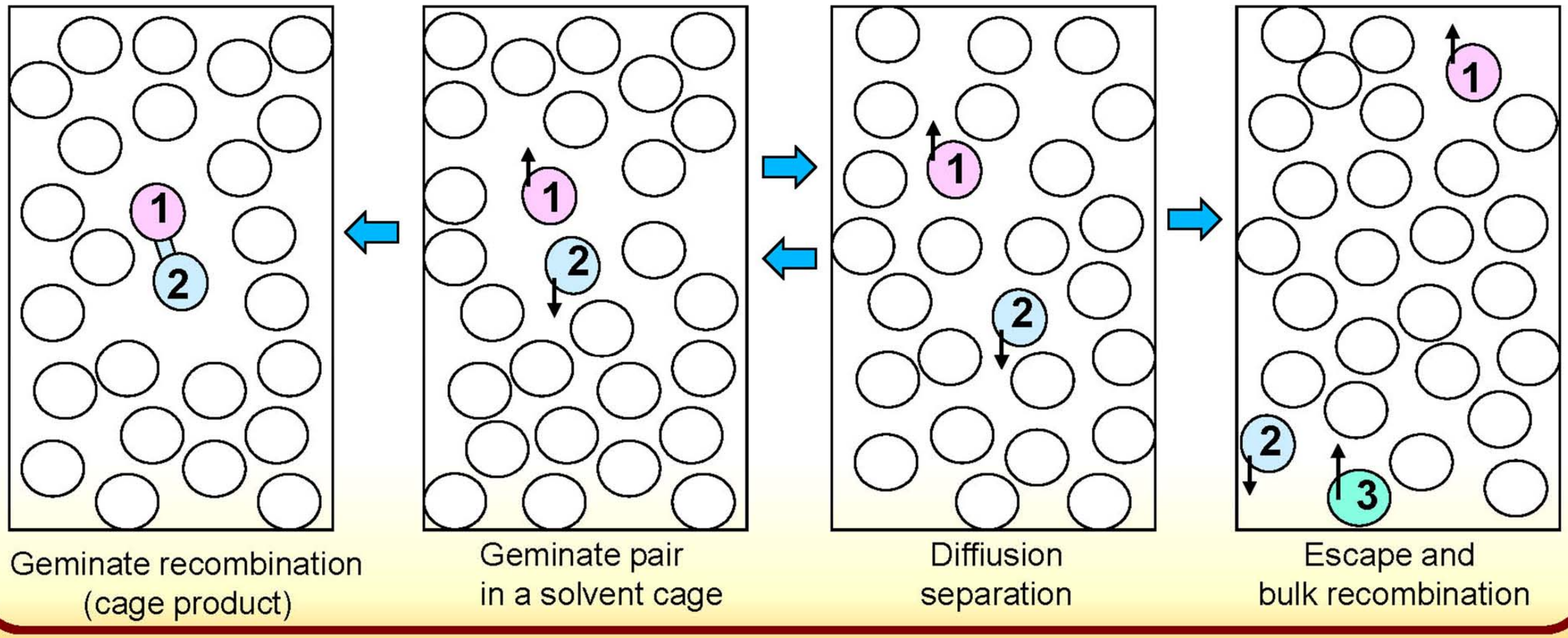
S-T$_{\pm}$ mixing in a pair with a single HFC in the radical (1):



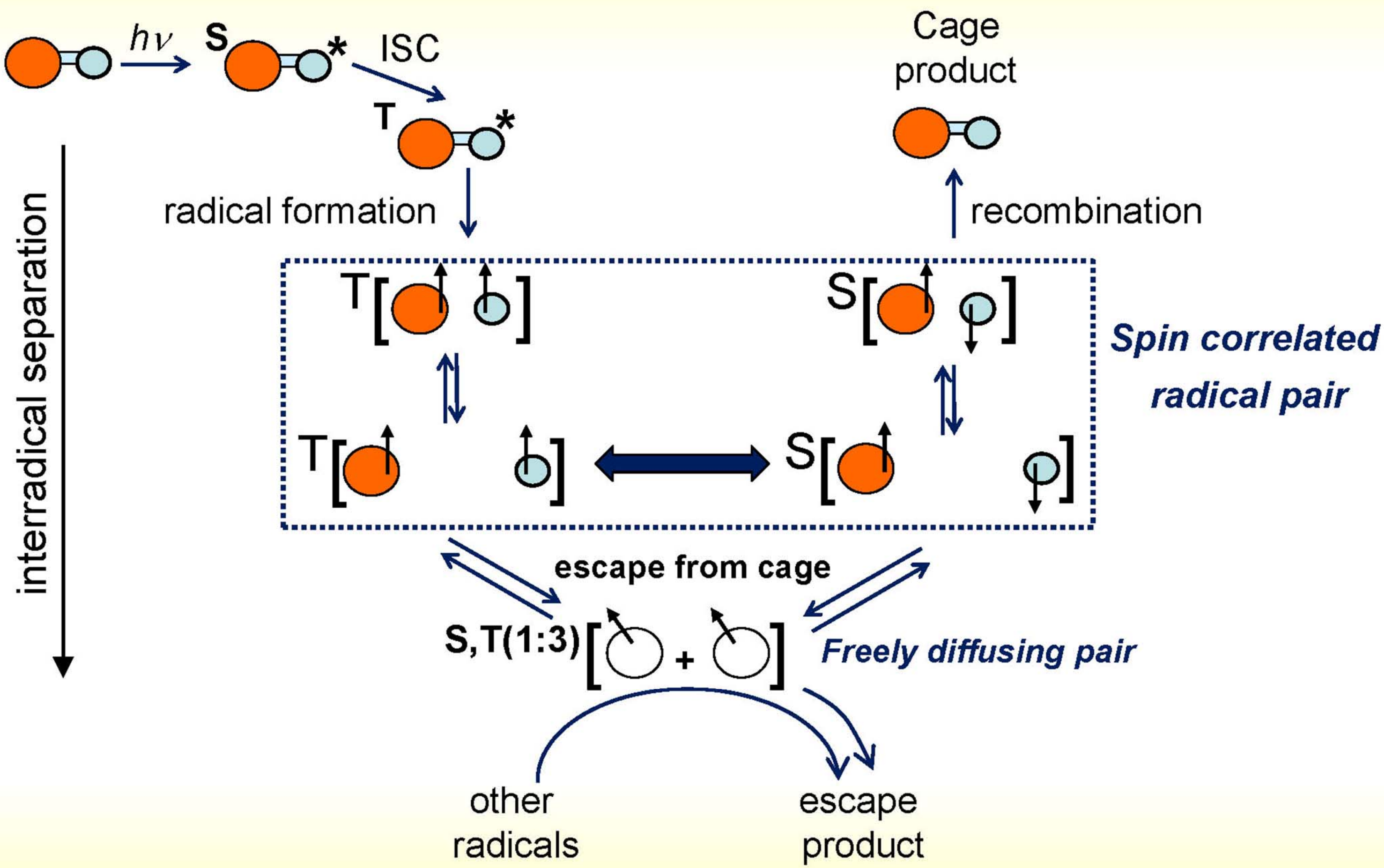
Nuclear and electron spins "flip" simultaneously

J.R. Woodward, Progress in Reaction Kinetics and Mechanism, 2002, vol. 27, 165-207

- Radical pair members are not bonded together
- Condensed phases restrict the radical movement relative to one another (cage effect)
- Diffusion and escape from the cage should be considered



A triplet-born radical pair: various fates in solution



J.R. Woodward, PRKM, 2002, vol. 27, 165-207

Methods of radical pair generation

To create radicals, it usually requires the input of external energy:

- ❑ **UV/visible light (photochemical generation)**

  photo-CIDNP – the most ubiquitous spin chemistry technique

  SNP, RYDMR, MARY, time resolved EPR

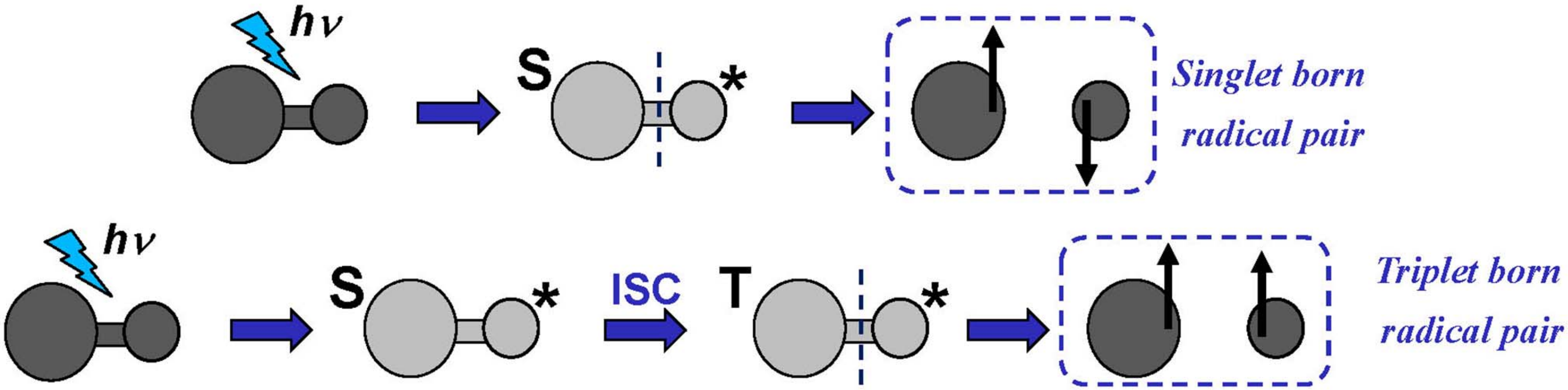
- ❑ **Ionizing irradiation (radiation chemistry)**

  radiofluorescence techniques: OD EPR, MARY, quantum beats spectroscopy;
  time resolved EPR

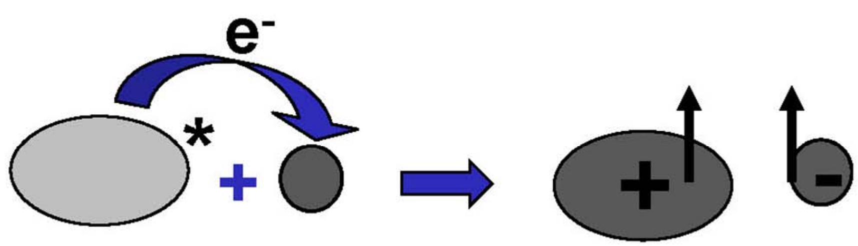
Photochemical generation:

- ❑ Absorbing molecules of photosensitizer in a "transparent" solvent => selective and uniform production of the excited solute molecules
- ❑ Decomposition/electron transfer of the excited state (S_1 or T_1) of the precursor
- ❑ Both singlet and triplet-born radical pairs (ISC mechanism)

Photochemical generation:



Homolytic bond cleavage => neutral radical pair



Photoinduced electron transfer => radical ion pair

Generation of radical pairs by ionizing radiation:

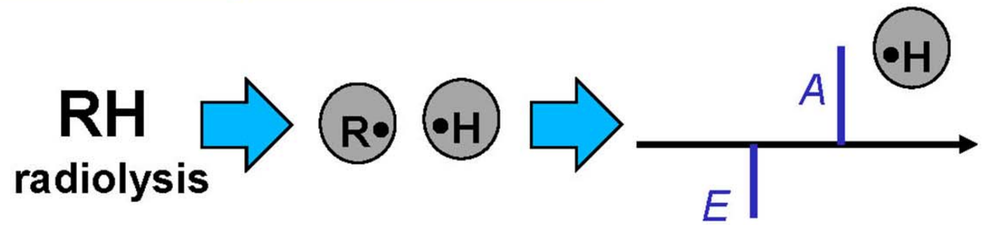
- an “overkill” method in terms of photon/particle energy
- each photon/particle produces many ionizations/excited states along its track
- the “bulk” solvent molecules are ionized/excited

Generation of radical pairs by ionizing radiation:

Time resolved EPR/pulse radiolysis ⇒ CIDEP

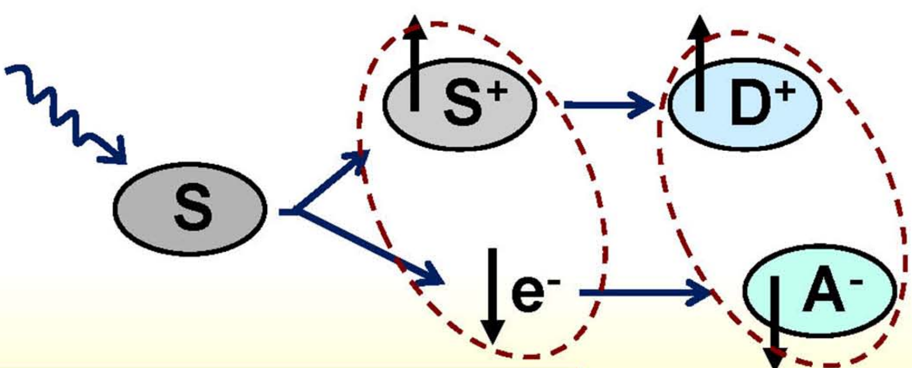
Diffusion radical pairs	*S-T_0 mixing (HFC, $g_1 \neq g_2$)*

exchange of spin polarizations induced by the exchange interaction

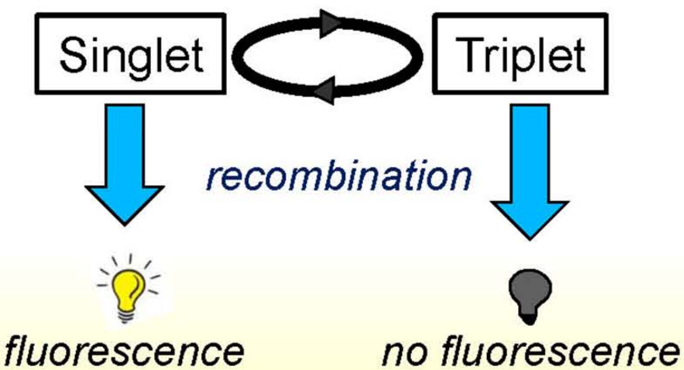


Fessenden and Schuler, 1963

Alkane solution radiofluorescence: singlet-born radical ion pairs



Brocklehurst et al., 1974



Chemically induced magnetic polarization (CIDEP and CIDNP)

Anomalous intensities of EPR and NMR spectral lines

- **Radicals** formed with non-equilibrium spin polarization
- **Short-lived** effect (microsecond timescale)
- More complex mechanism(s)
- Exchange interaction involved
- A mixture of **net (Δg)** and **multiplet (HFC)** polarization is observed

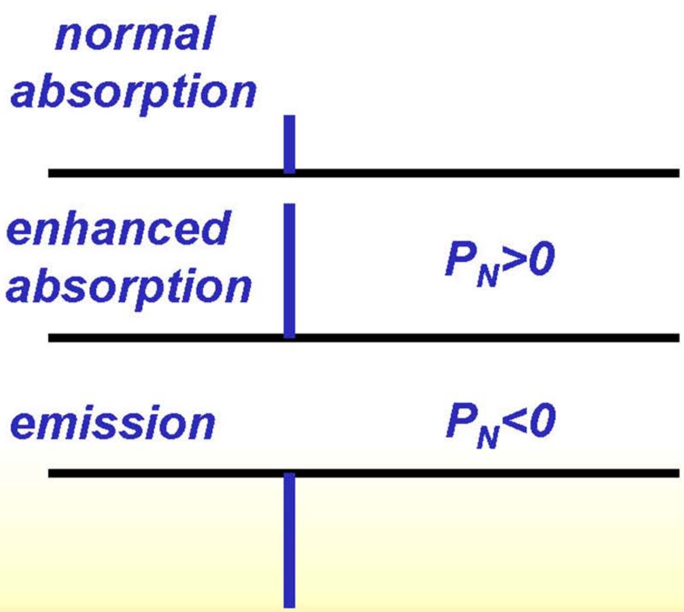
- **Stable products** formed with non-equilibrium **nuclear** spin polarization
- NMR relaxation timescale **(0.1-10s)**
- **S-T mixing** and **spin-selective recombination** => **sorting of nuclear spin states in the reaction products**

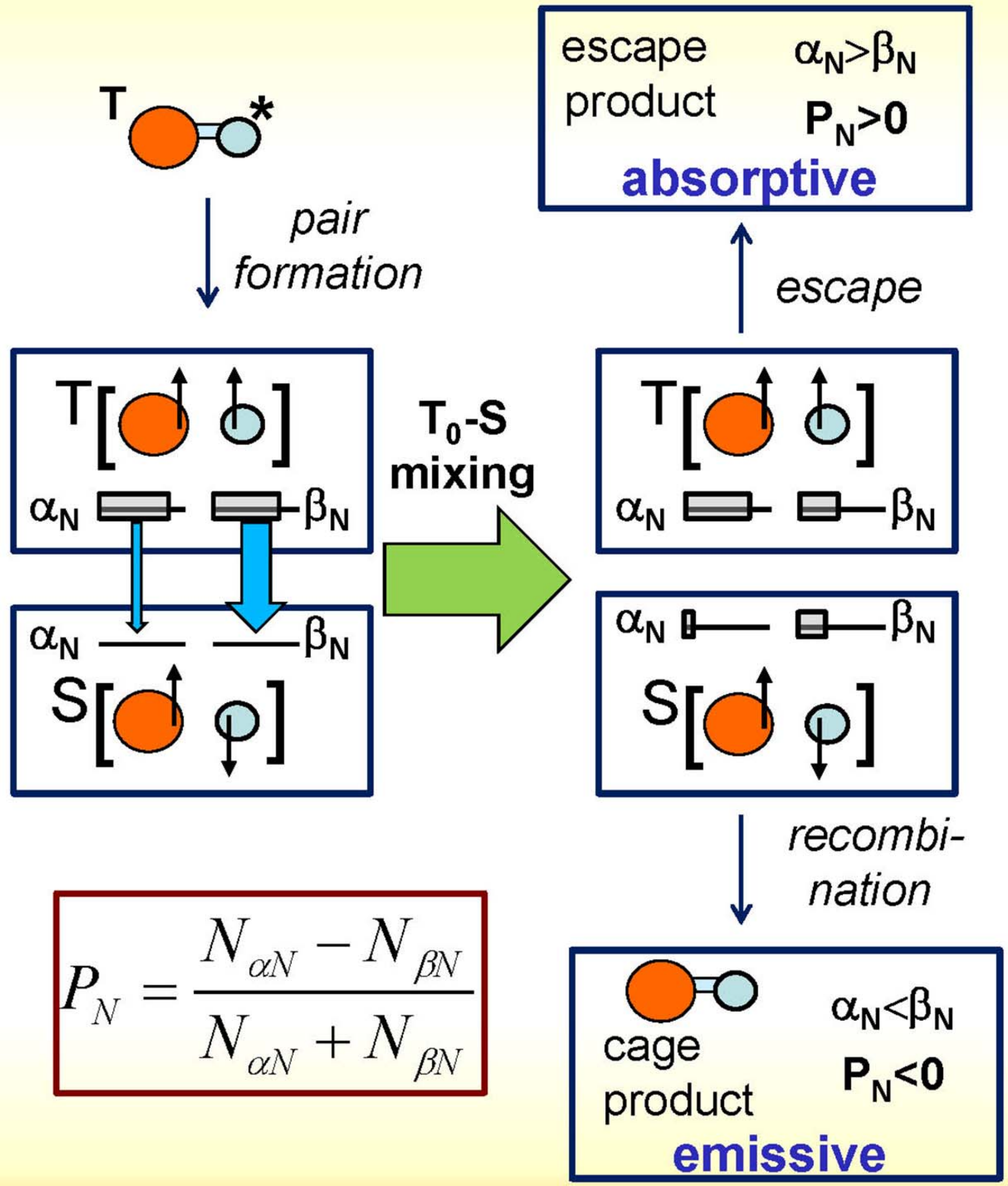
Generation of CIDNP in the cage/escape products

- Triplet –born radical pair
- Single positive HFC: I=1/2
- High magnetic field

α_N: I_z=+1/2 $B_{local} < B_0$

β_N: I_z=-1/2 $B_{local} > B_0$





$$P_N = \frac{N_{\alpha N} - N_{\beta N}}{N_{\alpha N} + N_{\beta N}}$$

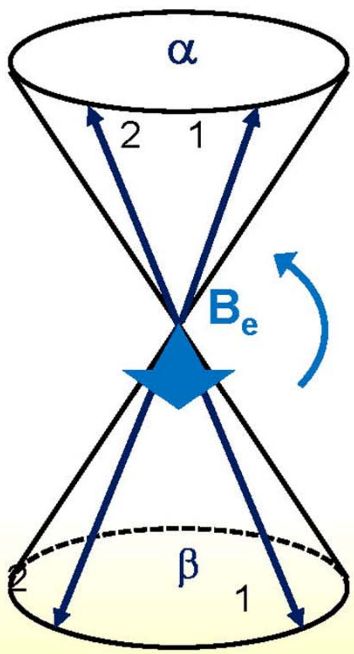
J.R. Woodward, PRKM, 2002, vol. 27, 165-207

CIDEP: a vector representation of the role of exchange interaction

$$\hat{\mathbf{H}}_{RP} = \mu_B(g_1\hat{\mathbf{S}}_1\cdot\mathbf{B} + g_2\hat{\mathbf{S}}_2\cdot\mathbf{B}) + a(\hat{\mathbf{I}}\cdot\hat{\mathbf{S}}_1) - J(\frac{1}{2} + \boxed{2(\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2)})$$

Exchange Hamiltonian $J(\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2)$ ***analogous in form*** *to HFC* $a(\hat{\mathbf{I}}\cdot\hat{\mathbf{S}}_1)$

$a(\hat{\mathbf{I}}\cdot\hat{\mathbf{S}}_1)$ <=> **interaction** of the magnetic field of the **nuclear** and **electron spin** with each other



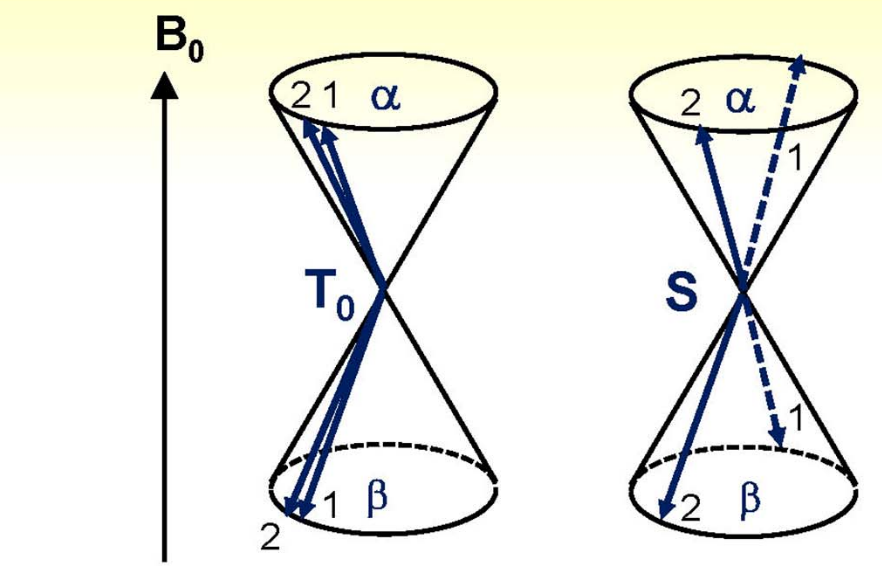
$J(\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2)$ <=> **mutual influence** of the magnetic fields of the **radical pair electron spins**

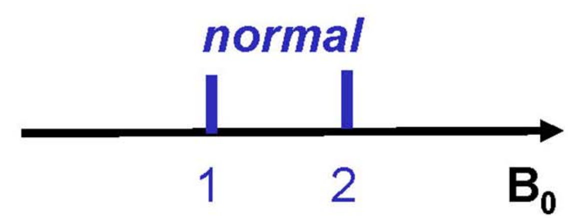
Precession of the electron spin vectors about each other <=> **rotation about the resultant axis**, $\mathbf{B}_e$

J.A. Syage, Chem.Phys. Lett. 1982 (91) 378-382

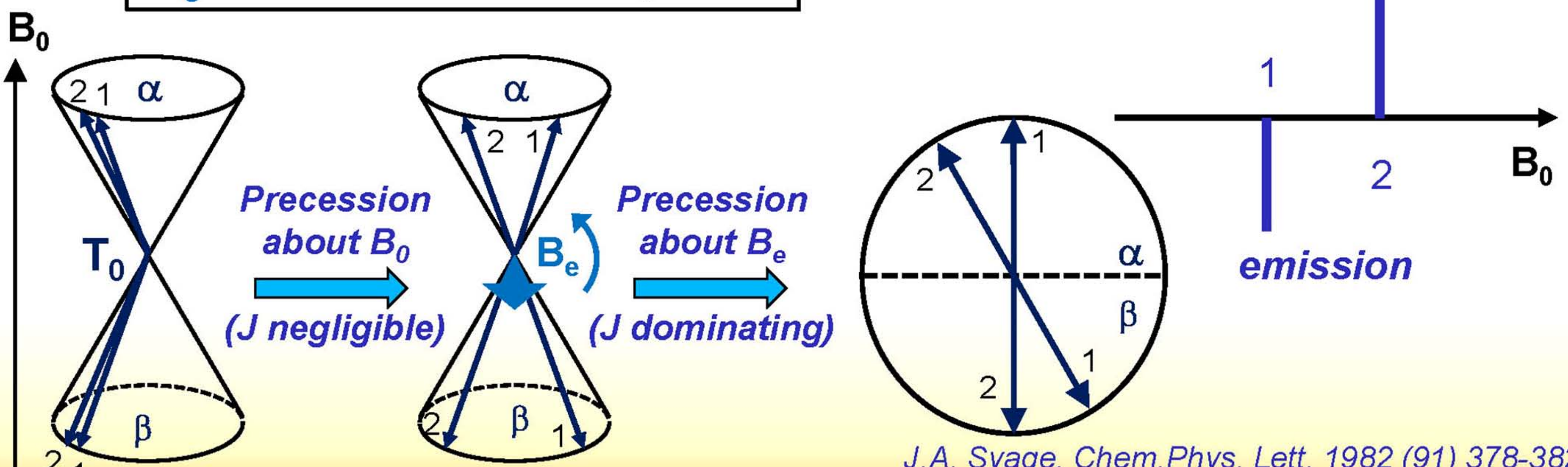
CIDEP: net polarisation

- Triplet –born radical pair
- No HFC
- $g_1 > g_2$
- $J = -|J|$





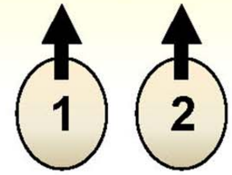
B_e is an effective exchange field

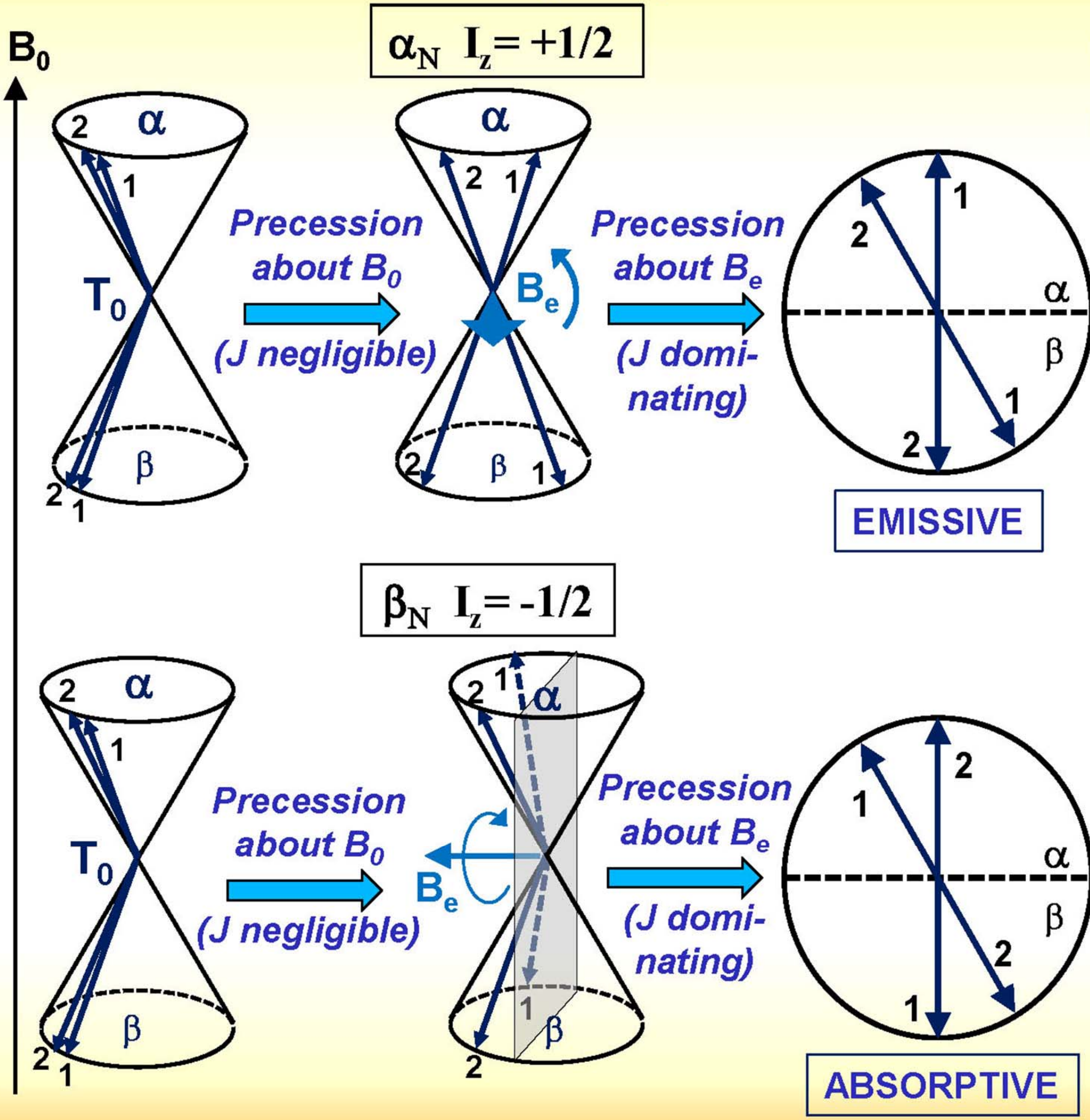


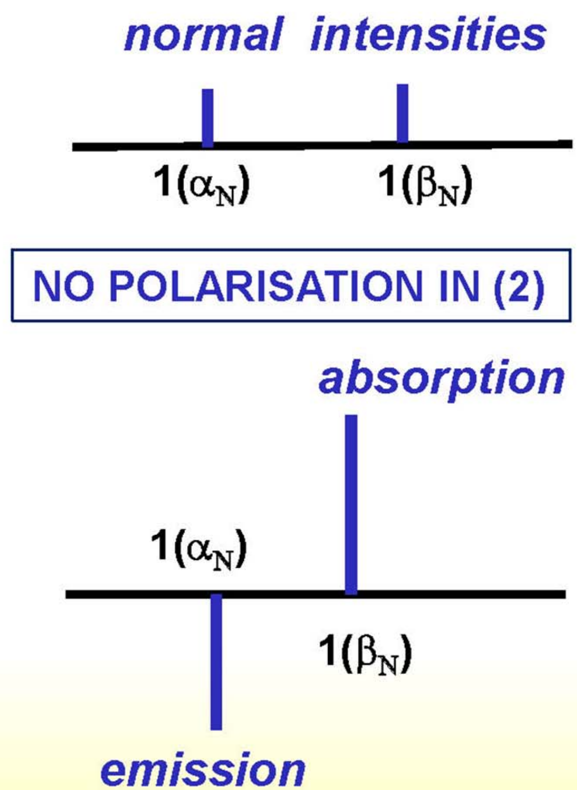
J.A. Syage, Chem.Phys. Lett. 1982 (91) 378-382
P.W. Atkins, Chem Phys. Lett. 1979 (66) 403-405

CIDEP: multiplet polarisation

- Triplet –born radical pair
- Single HFC in (1): I = ½
- $g_1=g_2$
- $J= -|J|$







References (what to read on spin chemistry)

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4. J.R. Woodward. Radical Pairs in Solution. //Progress in Reaction Kinetics and Mechanism, 2002, **27**, p. 65-207