Ab-initio theory of nuclear spin flip processes
within NV center of diamond
via orbital degrees of freedom

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experimental *theoretical model*

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Why DFT?

ab-initio package

DFT is conventionally used for: <u>electronic structure</u>

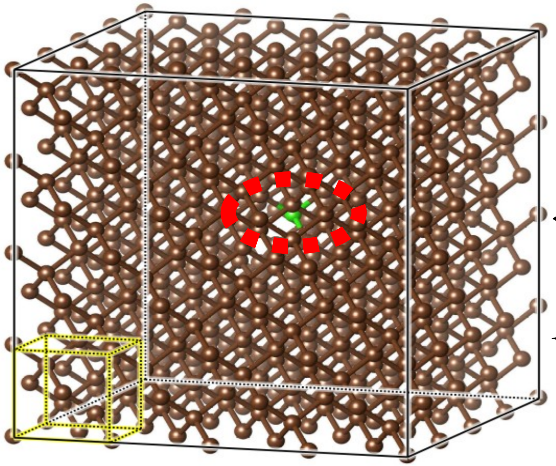
simulate defects in ~100-1000-atom *supercells to get:*

☞ **Formation** energies

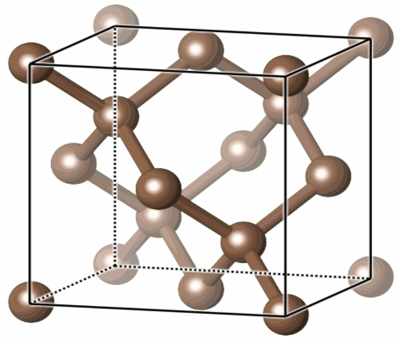
☞ **Optical** excitations *(~0.1 eV precision – HSE06 hybrid functional)*

☞ **Electron-phonon** coupling *(vibronic sideband for optical centers)*

DFT: *density functional theory* – simulate the electronic structure on HPC supercomputers



← *512-atom supercell with* NV *inside*



← *diamond Bravais lattice (8-atom supercell)*

Why DFT?

ab-initio package

DFT is conventionally used for: <u>electronic structure</u>

simulate defects in ~100-1000-atom *supercells to get:* "hidden" properties of qubits

☞ **Formation** energies

☞ **Optical** excitations *(~0.1 eV precision – HSE06 hybrid functional)*

☞ **Electron-phonon** coupling *(vibronic sideband for optical centers)*

☞ **Spin-phonon** relaxation

☞ **Spin-orbit** matrix elements: $\lambda \mathbf{LS}$ *(λ up to ~20% precision)*

☞ **Spin-spin** interaction: **ZFS** (*Zero field splitting*) *magnetic dipole-dipole:* $\mathbf{SDS}$

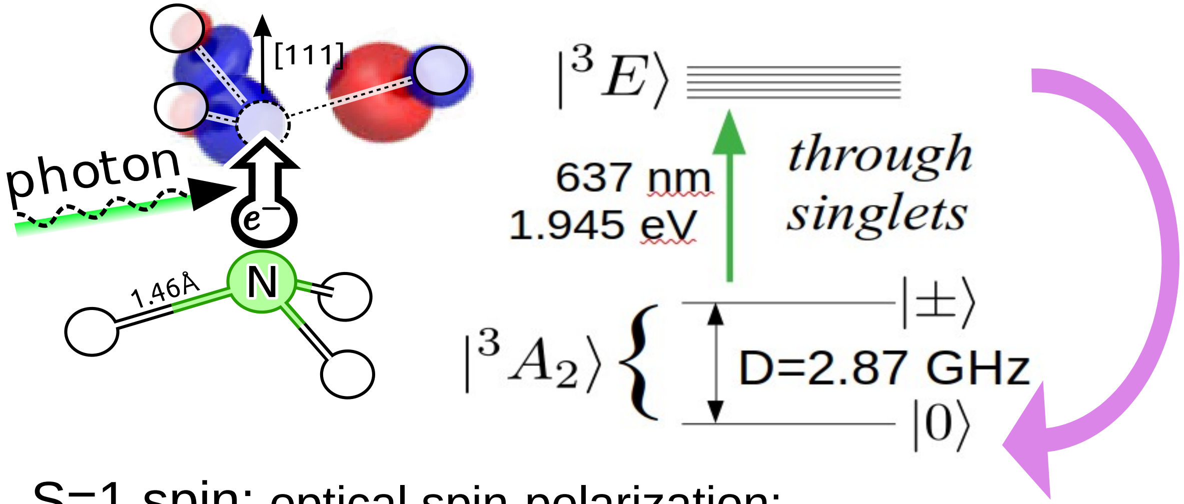
☞ **Hyperfine** interaction: *electronic + nuclear spin dipole-dipole:* $\mathbf{SAI}$

☞ **Nuclear quadrupolar** interaction: $\mathbf{IQI}$

aim: *determine unconventional (spin) parameters inaccessible by experiments*

<u>This talk</u>: Predict motion of ^{14}**N nuclear spin** during **optical cycles**

Introduction: *qubit* $|0\rangle$ *initialization for NV –* ***electronic spin***

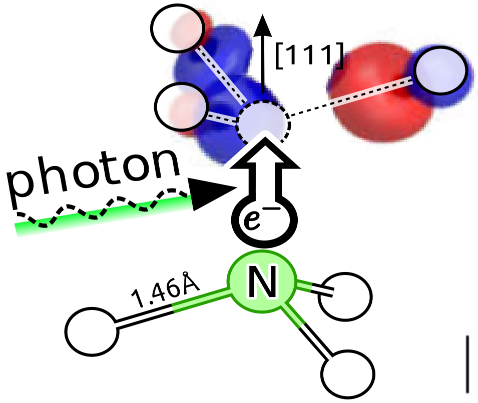


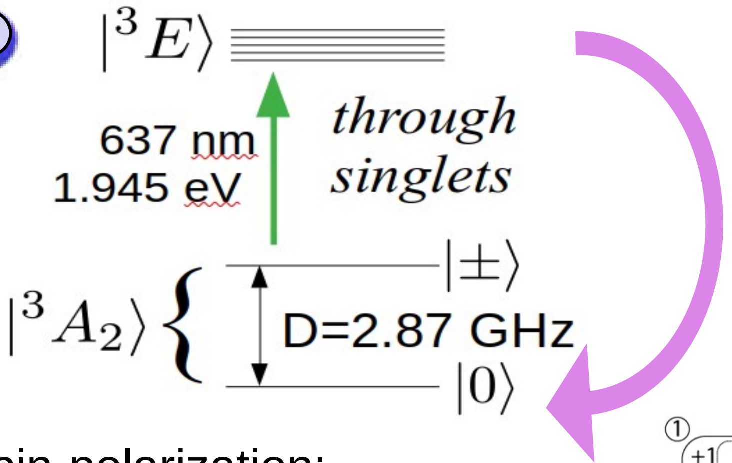
S=1 spin: optical spin-polarization:
ms=0 is preferentially populated
over ms=±1
upon exposure to green light

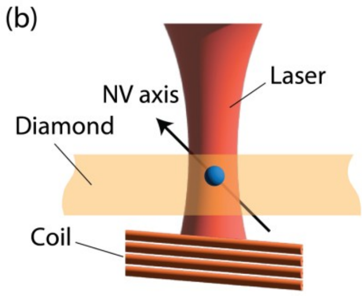
G. Thiering, A. Gali, Phys. Rev. B **96**, 081115(R) (2017)
G. Thiering, A. Gali, Phys. Rev. B **98**, 085207 (2018)
M. L. Goldman, … Phys. Rev. Lett. **114**, 145502 (2015)
… *and many other studies*

Introduction: *qubit* $|0\rangle$ *initialization for NV –* ^{14}N ***nuclear spin***

This talk: Predict relaxation of ^{14}N nuclear spin during optical cycles



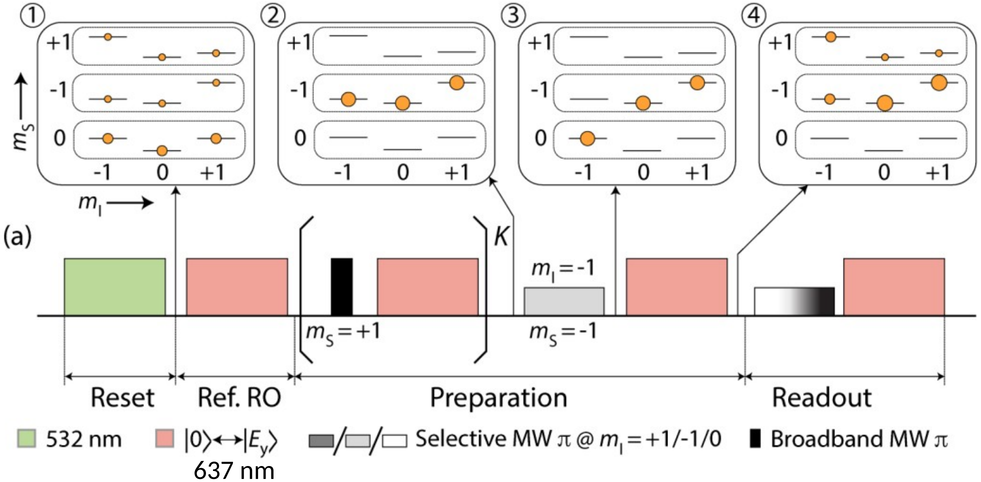




^{14}N nuclear spin can be **initialized** too:
hyperpolarization

quantum memory
long T_1 time: seconds, hours
T_2 time ~ ms

Preparation and readout of ^{14}N spins:



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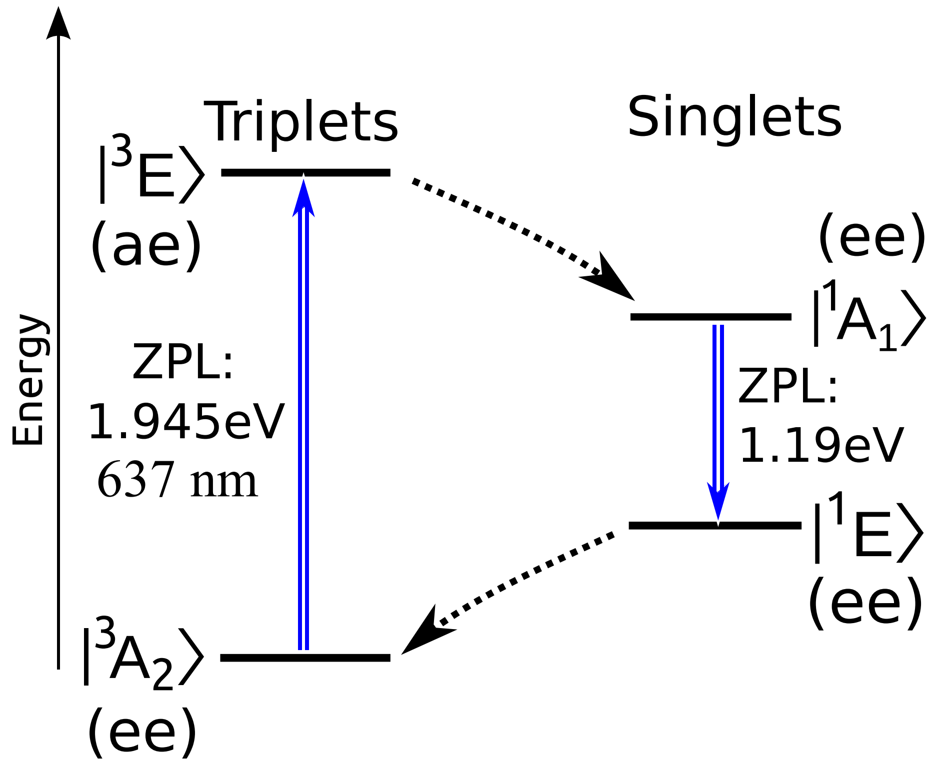
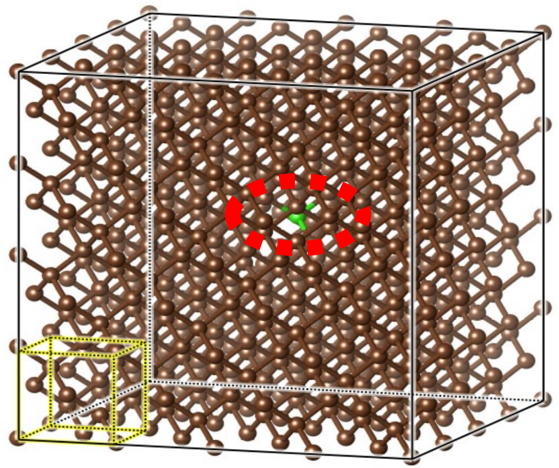
Electronic structure of NV





← *512-atom diamond supercell with* NV *inside*

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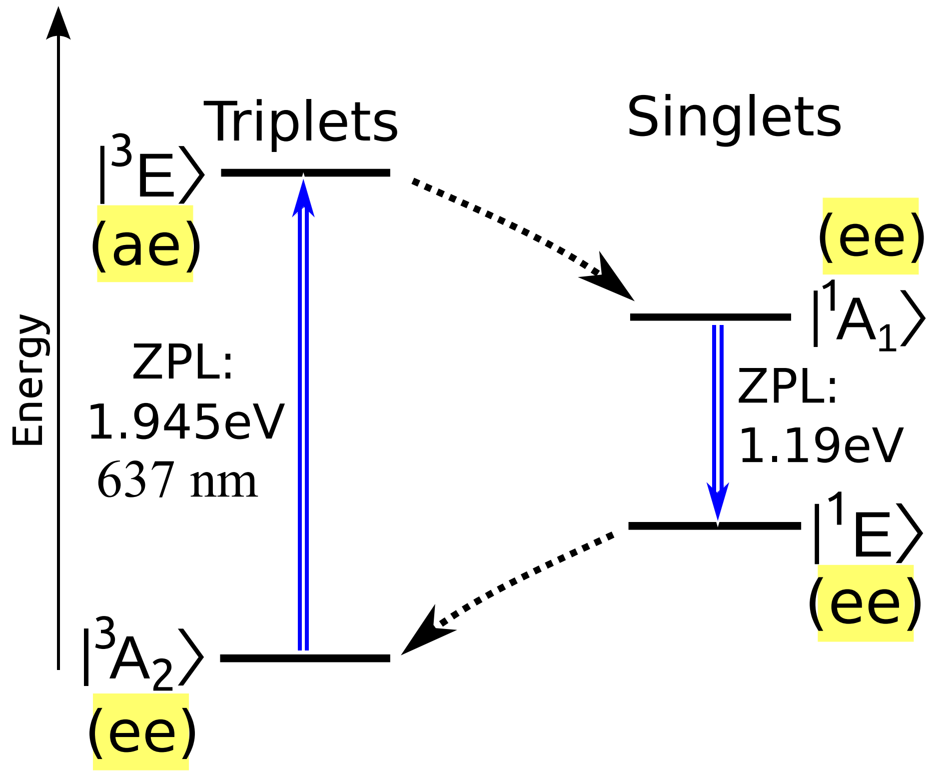
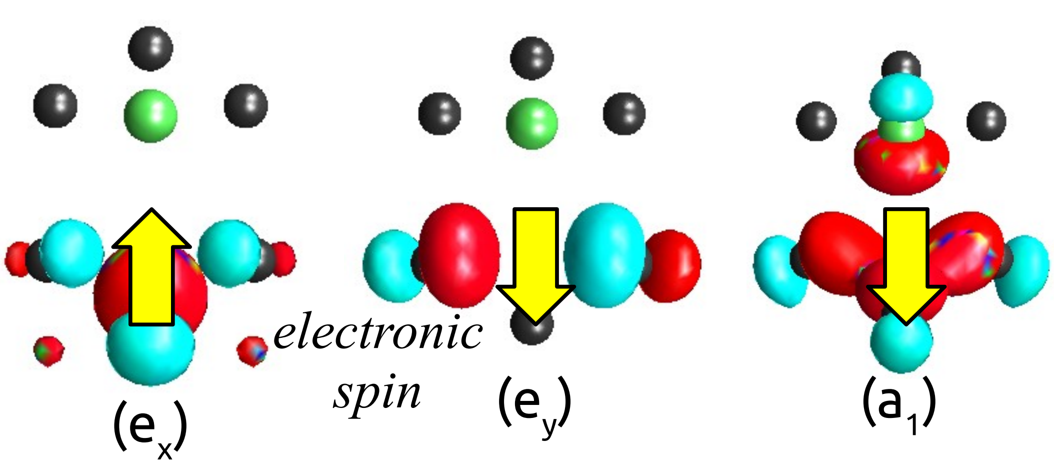




Electronic structure in short:

pick two orbitals above

for

two particle wavefunctions

also arrange their electronic spin

|³A₂⟩:

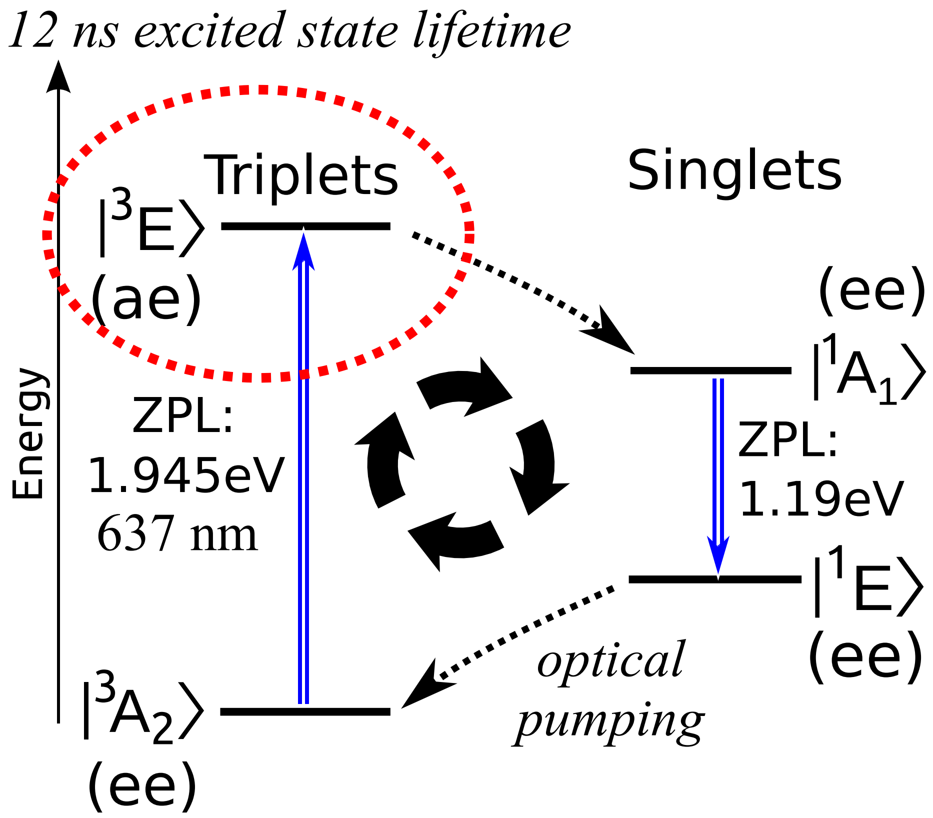
m_S - *electronic spin:* +1,0,-1

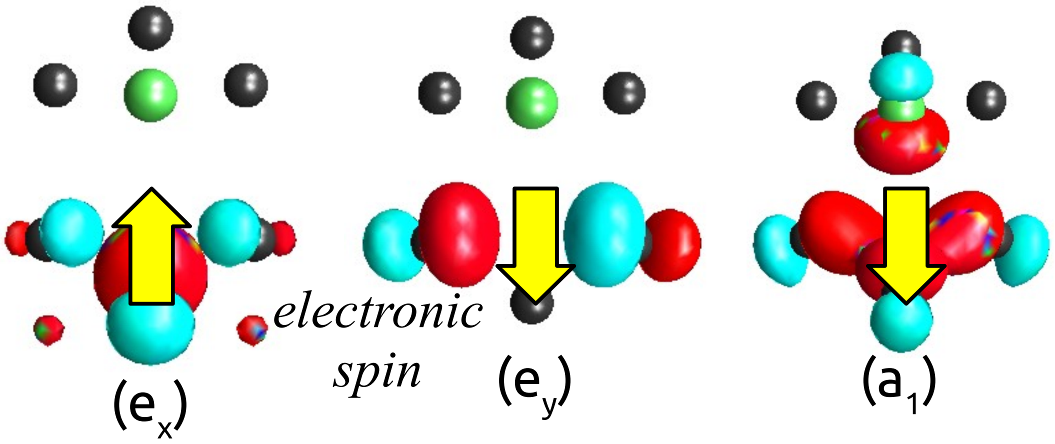
|³E⟩:

m_L - *orbital quantum number:* +1, -1 *or* e_x, e_y

m_S - *electronic spin:* +1,0,-1

Electronic structure of NV





Electronic structure in short:

pick two orbitals above
for
two particle wavefunctions
also arrange their electronic spin

$|^3E\rangle$:

orbital degeneracy: m_L - *orbital quantum number:* +1, -1 *or* e_x, e_y

m_S - *electronic spin:* +1,0,-1

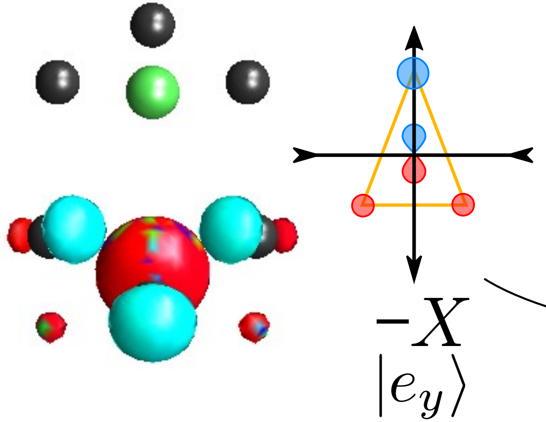
$|^3A_2\rangle$:

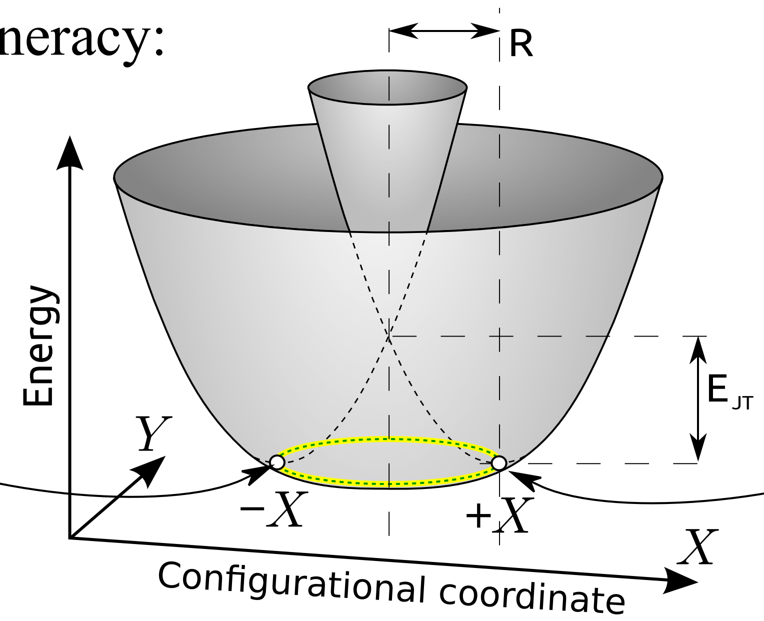
m_S - *electronic spin:* +1,0,-1

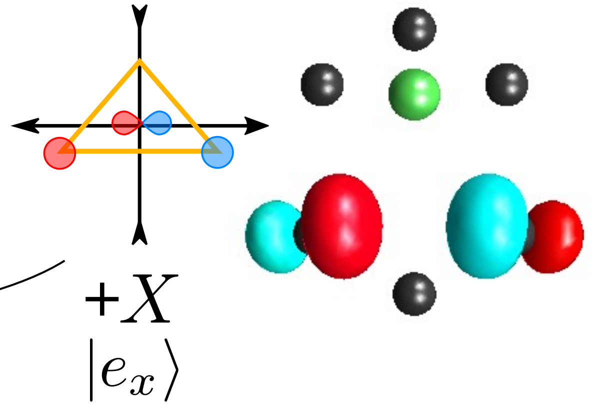
Jahn teller effect within $|{}^3E\rangle$

(ae$_x$) or (ae$_y$) orbital degeneracy:

two-particle system







orbitals induce strain on geometry

ladder operators
for vibration modes:

$$\hat{X}, \hat{Y} = \frac{1}{\sqrt{2}}\left(a^{\dagger}_{X,Y} + a_{X,Y}\right)$$

"E" 2x *degenerate* vibration mode
interacts with
"e" 2x *degenerate* orbital

$$\hat{H}_{DJT} = F\left[\begin{pmatrix}1 & \\ & -1\end{pmatrix}\hat{X} + \begin{pmatrix} & 1\\ 1 & \end{pmatrix}\hat{Y}\right]$$

Structure of ZFS tensor within |3E⟩

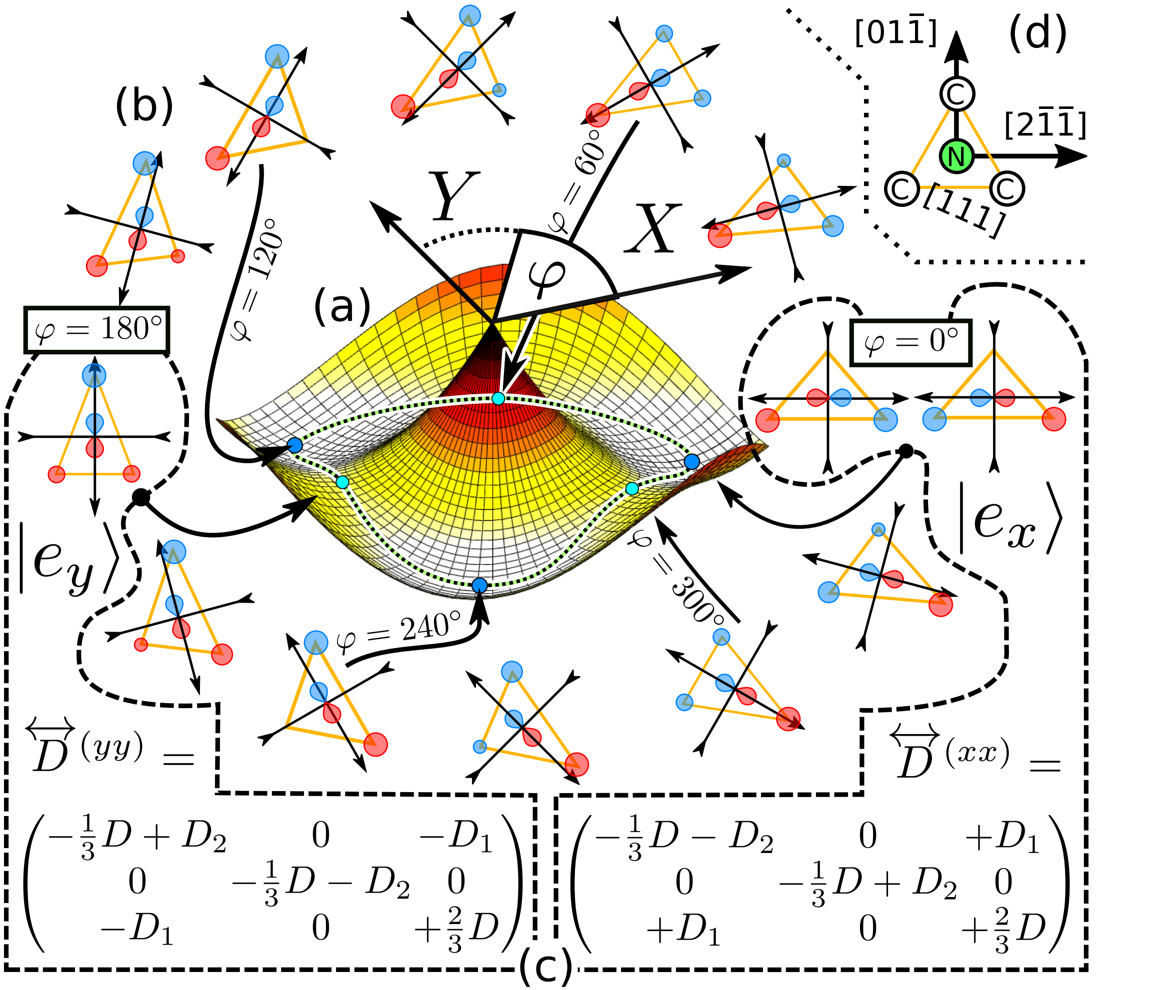
ZFS for the ground state:

$$\overleftrightarrow{D} = \begin{pmatrix} -\frac{1}{3}D & 0 & 0 \\ 0 & -\frac{1}{3}D & 0 \\ 0 & 0 & +\frac{2}{3}D \end{pmatrix}$$

$$\hat{H} = \overrightarrow{S}\,\overleftrightarrow{D}\,\overleftarrow{S}$$

☞JT distortion induces distorted $|e_x\rangle, |e_y\rangle$ orbitals

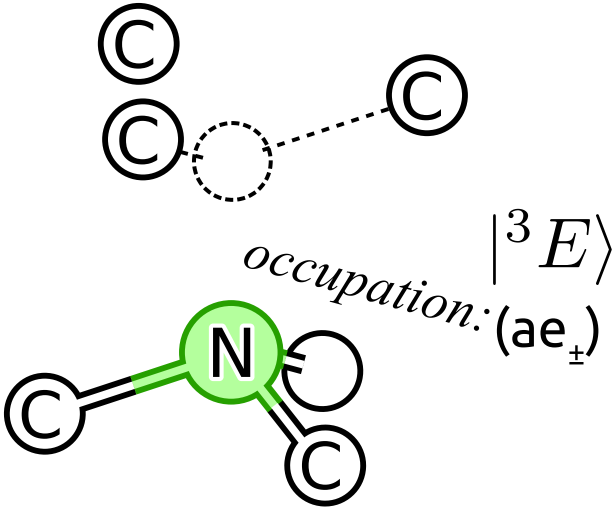
☞JT motion induces large changes in ZFS! $\overleftrightarrow{D}$
or in hyperfine: $\overleftrightarrow{A}$
or in quadrupole: $\overleftrightarrow{Q}$ tensors

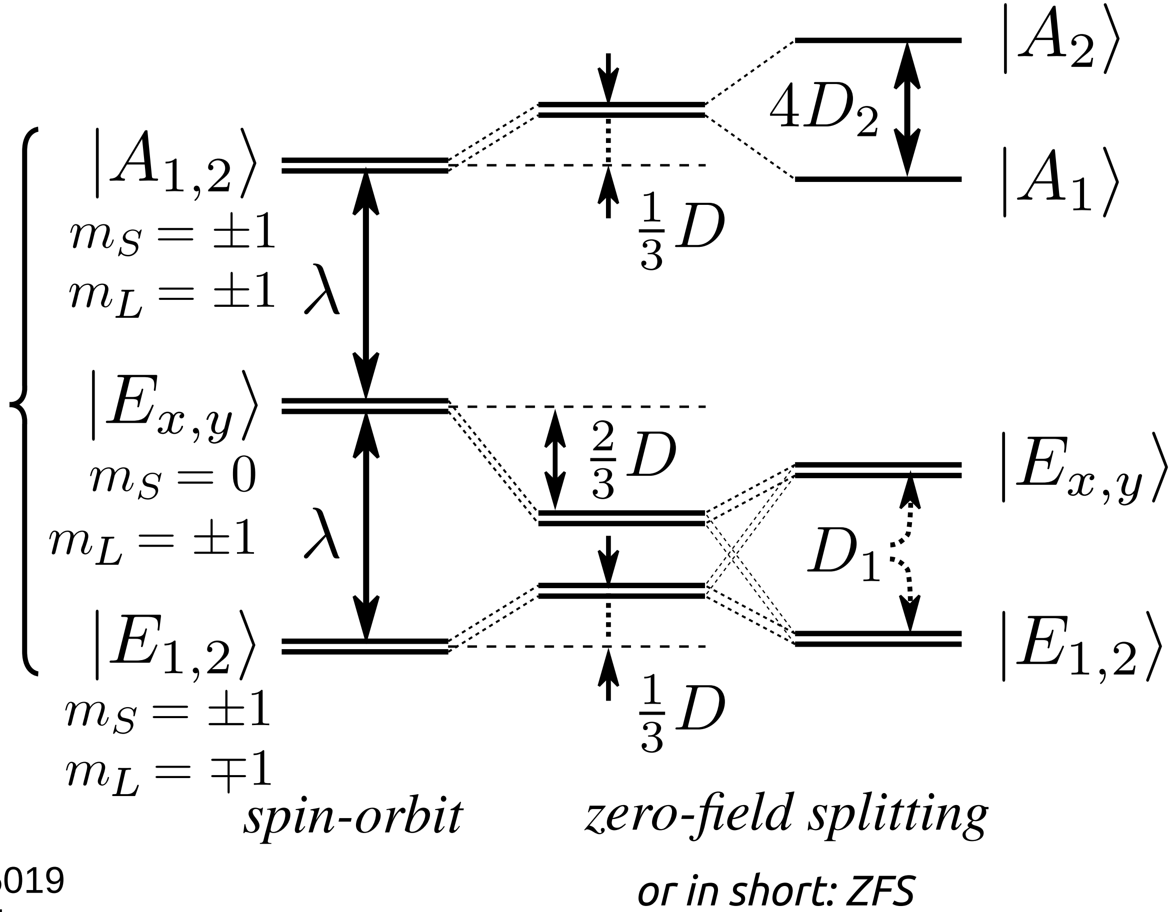


The $|{}^3E\rangle$ excited triplet *(fine structure)*

m_L - *orbital quantum number* $|e_\pm\rangle = (|e_x\rangle \pm |e_y\rangle)/\sqrt(2)$

m_S - *electronic spin*





group theoretical approach for NV's ZFS:

M W Doherty et al 2011 New J. Phys. 13 025019

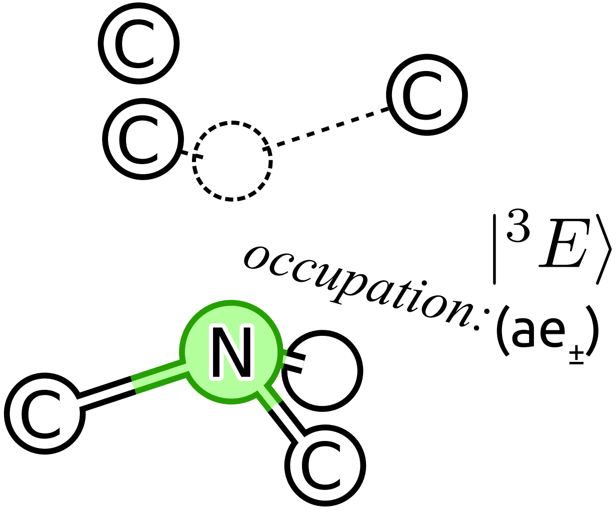
J R Maze et al 2011 New J. Phys. 13 025025

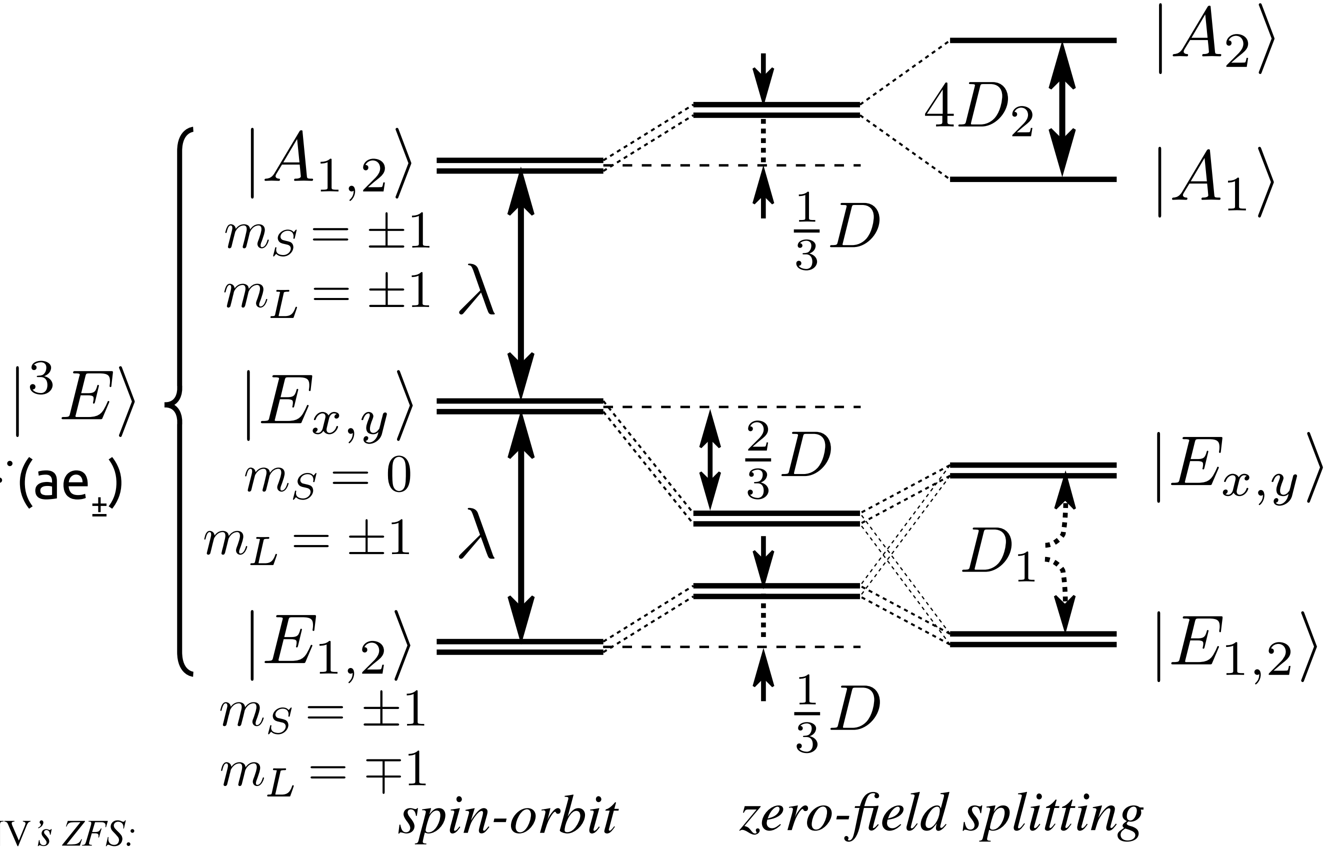
The $|{}^3E\rangle$ excited triplet *(fine structure)*

m_L - *orbital quantum number* $|e_\pm\rangle = (|e_x\rangle \pm |e_y\rangle)/\sqrt(2)$

m_S - *electronic spin*

m_I - ^{14}N *nuclear spin*





or in short: ZFS

group theoretical approach for NV's ZFS:

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Spin Hamiltonian for the $|^3A_2\rangle$ ground state

$$\hat{H} = D^{(g)}\left(\hat{S}_z^2 - \frac{1}{3}S(S+1)\right) + Q^{(g)}\left(\hat{I}_z^2 - \frac{1}{3}I(I+1)\right) + A_{\parallel}^{(g)}\hat{S}_z\hat{I}_z + \frac{1}{2}A_{\perp}^{(g)}\left(\hat{S}_+\hat{I}_- + \hat{S}_-\hat{I}_+\right)$$

spin-spin ZFS   nuclear quadrupole   hyperfine interaction

$$+\sum_{ij} A_{ij}^{\mathrm{C}_1}\hat{S}_i\hat{I}_j^{\mathrm{C}_1} + \ldots$$

^{13}C hyperfine
$A_C \sim$ MHz
not discussed now

$\hat{S}_z, \hat{S}_\pm, |m_S = \pm 1, 0\rangle$ electronic S=1 spin of NV(-)

$\hat{I}_z, \hat{I}_\pm, |m_I = \pm 1, 0\rangle$ nuclear I=1 spin of ^{14}N

Spin Hamiltonian for the |^{3}E⟩ excited level

spin-orbit

$$\hat{H}_0 = \lambda^{(e)}\hat{\sigma}_z\hat{S}_z +$$

$$D^{(e)}\left(\hat{S}_z^2 - \frac{1}{3}S(S+1)\right) + Q^{(e)}\left(\hat{I}_z^2 - \frac{1}{3}I(I+1)\right) + A_{\parallel}^{(e)}\hat{S}_z\hat{I}_z + \frac{1}{2}A_{\perp}^{(e)}\left(\hat{S}_+\hat{I}_- + \hat{S}_-\hat{I}_+\right)$$

spin-spin ZFS   nuclear quadrupole   hyperfine interaction

$$\hat{W} = D_1^{(e)}\left[(\hat{S}_z\hat{S}_+ + \hat{S}_+\hat{S}_z)\hat{\sigma}_- + (\hat{S}_z\hat{S}_- + \hat{S}_-\hat{S}_z)\hat{\sigma}_+\right] + D_2^{(e)}\left[\hat{S}_-^2\hat{\sigma}_- + \hat{S}_+^2\hat{\sigma}_+\right] +$$

$$Q_1^{(e)}\left[(\hat{I}_z\hat{I}_+ + \hat{I}_+\hat{I}_z)\hat{\sigma}_- + (\hat{I}_z\hat{I}_- + \hat{I}_-\hat{I}_z)\hat{\sigma}_+\right] + Q_2^{(e)}\left[\hat{I}_-^2\hat{\sigma}_- + \hat{I}_+^2\hat{\sigma}_+\right] +$$

$$A_1^{(e)}\left[(\hat{I}_z\hat{S}_+ + \hat{I}_+\hat{S}_z)\hat{\sigma}_- + (\hat{I}_z\hat{S}_- + \hat{I}_-\hat{S}_z)\hat{\sigma}_+\right] + A_2^{(e)}\left[(\hat{S}_-\hat{I}_-\hat{\sigma}_- + \hat{S}_+\hat{I}_+\hat{\sigma}_+\right]$$

orbital flip: $\hat{\sigma}_\pm|e_\pm\rangle = |e_\mp\rangle$ *nuclear+electronic spin-orbit*

Spin Hamiltonian for the $|^3E\rangle$ excited level

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spin-spin ZFS — nuclear quadrupole — hyperfine interaction

$\Delta m_I = \pm 1$ — ^{14}N ***nuclear spin flips*** — $\Delta m_I = \pm 2$

$$\hat{W} = D_1^{(e)}\left[(\hat{S}_z\hat{S}_+ + \hat{S}_+\hat{S}_z)\hat{\sigma}_- + (\hat{S}_z\hat{S}_- + \hat{S}_-\hat{S}_z)\hat{\sigma}_+\right] + D_2^{(e)}\left[\hat{S}_-^2\hat{\sigma}_- + \hat{S}_+^2\hat{\sigma}_+\right] +$$

$$Q_1^{(e)}\left[(\hat{I}_z\hat{I}_+ + \hat{I}_+\hat{I}_z)\hat{\sigma}_- + (\hat{I}_z\hat{I}_- + \hat{I}_-\hat{I}_z)\hat{\sigma}_+\right] + Q_2^{(e)}\left[\hat{I}_-^2\hat{\sigma}_- + \hat{I}_+^2\hat{\sigma}_+\right] +$$

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orbital flip: $\hat{\sigma}_\pm|e_\pm\rangle = |e_\mp\rangle$

nuclear+electronic spin-orbit

Quality of *ab initio* results

ab initio DFT can predict the spin Hamiltonian parameters ±20% precision

"DFT works!"

theoretical (experimental)

spin-orbit	$\lambda_1^{(e)} = 4.8$[a] $(5.3$[b]$)$ GHz	$D^{(g)} = 2.98$[p.w.] $(2.87$[e]$)$ GHz	
	$A_{\parallel}^{(g)} = -1.7$[c] $(-2.14$[d]$)$ MHz	$D^{(e)} = 1.67$[p.w.] $(1.42$[e]$)$ GHz	*spin-spin ZFS*
	$A_{\perp}^{(g)} = -1.7$[c] $(-2.70$[d]$)$ MHz	$D_1^{(e)} = -290$[p.w.] $(200/\sqrt{2}$[e]$)$ MHz	
hyperfine	$A_{\parallel}^{(e)} = -41$[p.w.] $(-40$[f]$)$ MHz	$D_2^{(e)} = +901$[p.w.] $(1550/2$[e]$)$ MHz	
	$A_{\perp}^{(e)} = -27$[p.w.] $(-23$[g]$)$ MHz	$Q^{(g)} = -5.37$[h] $(-4.95$[h]$)$ MHz	
	$A_1^{(e)} = -92$[p.w.] (n.a.) kHz	$Q^{(e)} = -3.91$[p.w.] (n.a.) MHz	*quadrupole interaction*
	$A_2^{(e)} = +49$[p.w.] (n.a.) kHz	$Q_1^{(e)} = +17.3$[p.w.] (n.a.) kHz	
radiative lifetime of $\|{}^3E\rangle$	$\tau_{\mathrm{rad.}}^{-1} =$ (12 ns) $(83$[i]$)$ MHz	$Q_2^{(e)} = +17.2$[p.w.] (n.a.) kHz	

(g) ground state triplet: $|{}^3A_2\rangle$

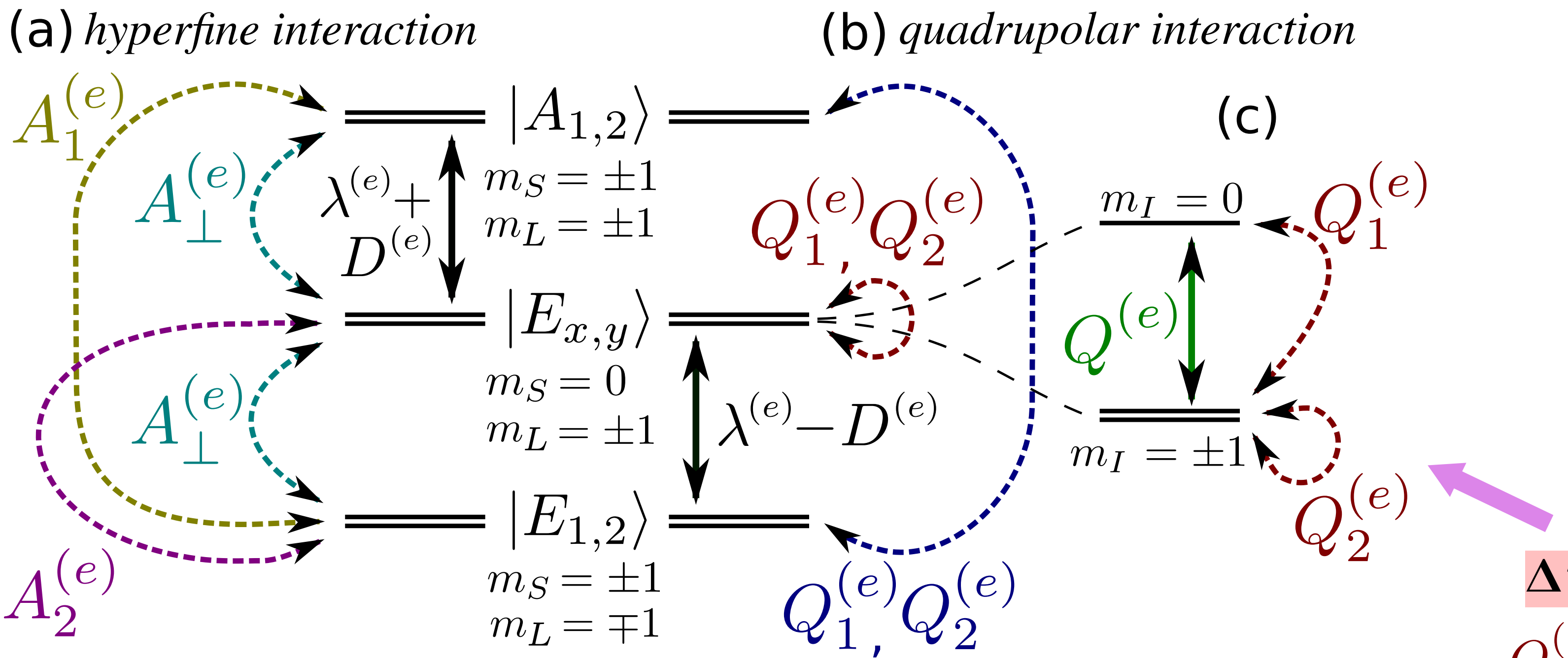
(e) excited level triplet: $|{}^3E\rangle$

"p" *and* "q" *Ham reduction factors within Jahn-Teller theory are required*

p.w.: present work

Processes that flip the ^{14}N nuclear spin

(e) – excited ^{3}E state



flips ^{14}N spin by

Δm_I =±1 flip

$A^e_\perp \hat{S}_+ \hat{I}_-$

$|A_\perp/D| \sim 0.01$

$Q_1^{(e)}(\hat{I}_z \hat{I}_+ \hat{\sigma}_- + \ldots)$

$|Q_1/Q| \sim 0.004$

Δm_I =±2 flip

$Q_2^{(e)}(\hat{I}_-^2 \hat{\sigma}_- + \ldots)$

ESLAC: *excited state level anticrossing*

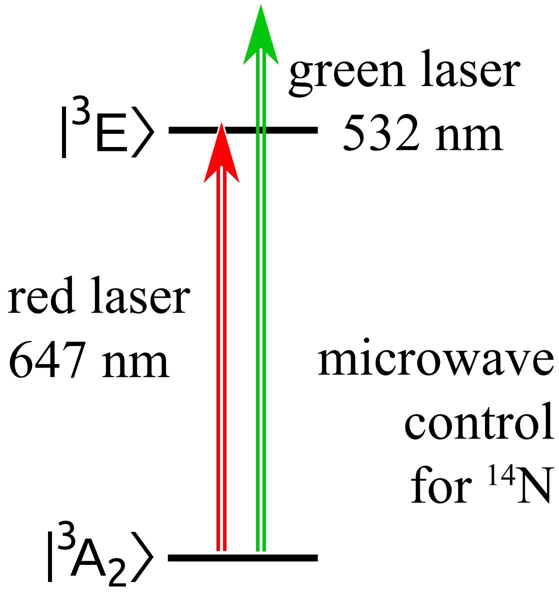
$A_2^{(e)}(\hat{S}_- \hat{I}_- \hat{\sigma}_- + \ldots)$

$A_1^{(e)}(\hat{I}_z \hat{S}_+ \hat{\sigma}_- + \ldots)$

$|A_{1,2}/D| \sim 10^{-6}$ *negligible...*

without applied magnetic field

^{14}N nuclear spin manipulation



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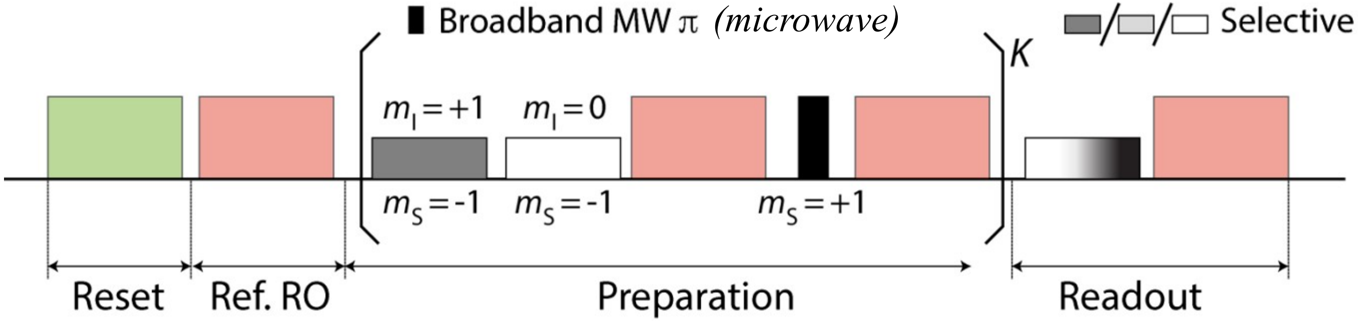
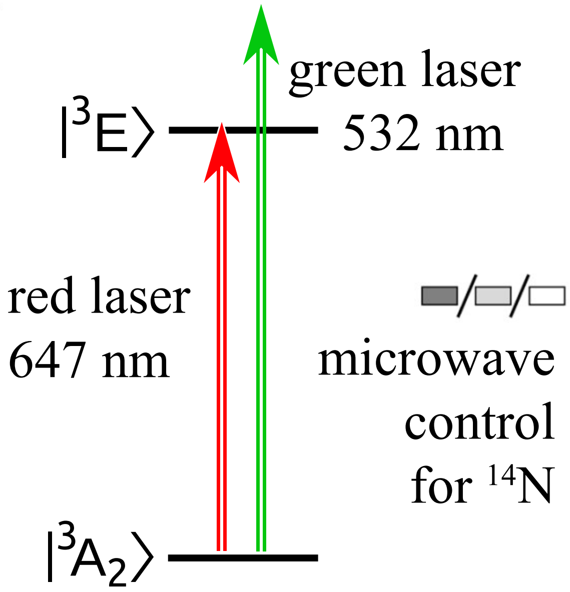
experimental

Nuclear splin flip probabilities

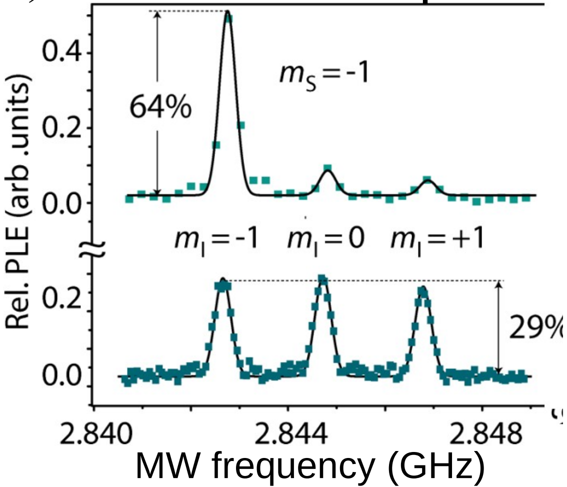




1) ***Reset:*** Initialize NV(-)'s spin to m_S = 0

2) ***Preparation:*** Initialize ^{14}N nuclear spin to m_I = +1 *or* -1 *or* 0

3) ***Readout:*** Optical readout of m_S and m_I both (~20 μs)



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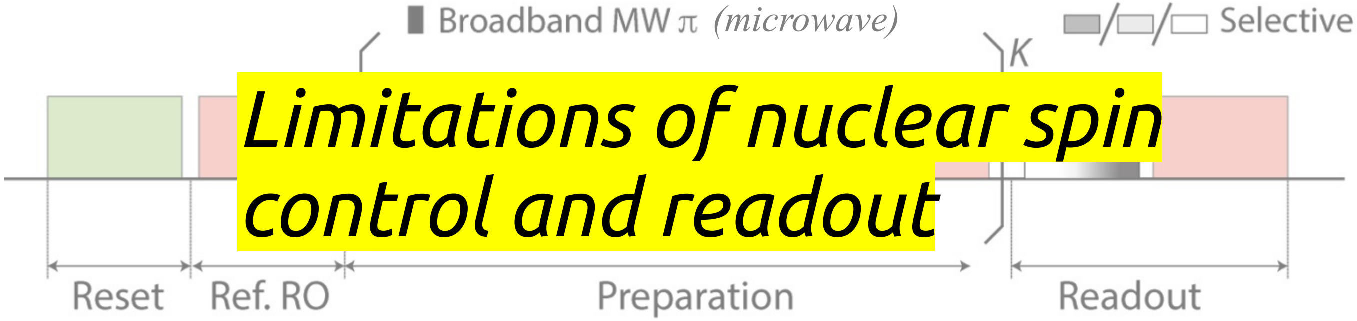
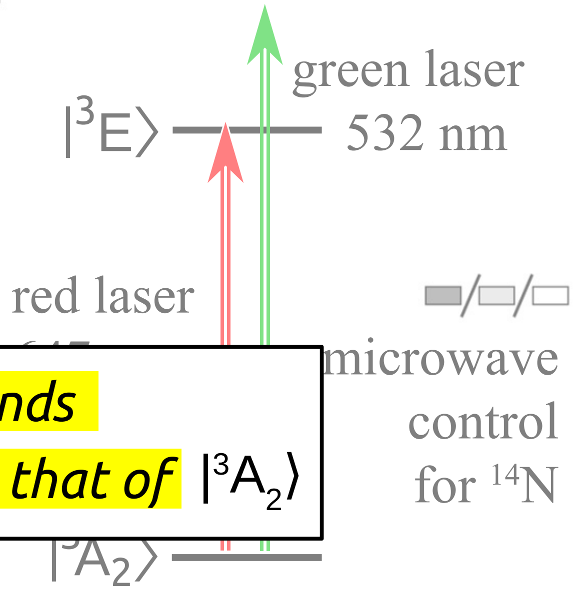


Limitations of nuclear spin control and readout

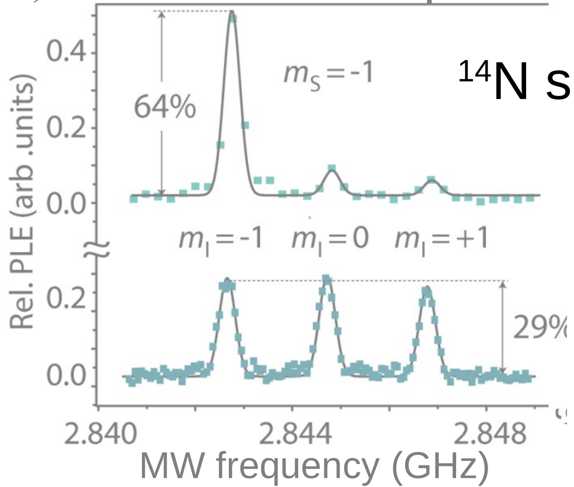
1) ***Reset:*** Initialize NV(-)'s spin to $m_S = 0$

2) ***Preparation:*** Initialize ^{14}N nuclear spin

2) ***Readout:*** Optical readout of m_S



this is not hours or seconds
compared to T1 time to that of |^{3}A$_2$⟩



^{14}N spin relaxes: ~20 µs total stay within |^{3}E⟩
or N~1000 opt. cycles (red laser)

see also:
npj Quantum Inf 3, 33 (2017)

transition	theory	expt.
$\|m_I = \pm 1\rangle \rightarrow \|m_I = \mp 1\rangle$	0.11	0.18(3)
$\|m_I = \pm 1\rangle \rightarrow \|m_I = 0\rangle$	0.08	0.16(3)
$\|m_I = 0\rangle \rightarrow \|m_I = \pm 1\rangle$	0.16	0.25(3)

Summary

☞ Complete ab-initio theory for $\overleftrightarrow{D}$, $\overleftrightarrow{Q}$, $\overleftrightarrow{A}$ tensors (spin-spin ZFS, quadrupole, hyperfine)
→ not only trivial D, Q, $A_\perp$ $A_\parallel$ terms
→ including the nontrivial, orbital driven D_1, D_2, Q_1, Q_2, A_1, A_2 parameters

☞ During optical cycles within $|^3E\rangle$:
→ "new" ^{14}N nuclear spin relaxation channels open

Δm_I =±1 by $A_\perp^e \hat{S}_+ \hat{I}_-$ (hyperfine)

Δm_I =±2 by $Q_2^{(e)}(\hat{I}_-^2 \hat{\sigma}_- + \ldots)$ (nuclear quadrupole) orbital-nuclear spin interaction

☞ Limitations for optical control and readout for nuclear spin
→ ^{14}N nuclear spin relaxes much faster in $|^3E\rangle$ than that in $|^3A_2\rangle$
→ longer than ~μs total stay within $|^3E\rangle$ *(readout & preparation)*
→ or more than N>~1000 opt. cycles

Summary

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→ including the nontrivial, orbital driven D_1, D_2, Q_1, Q_2, A_1, A_2 parameters

Outlook: *Apply on "G4V" defects*
SiV(-), GeV(-), SnV(-), PbV(-)

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→ "new" ^{14}N nuclear spin relaxation channels open

Δm_I =±1 by $A_\perp^e \hat{S}_+ \hat{I}_-$ (hyperfine)

Δm_I =±2 by $Q_2^{(e)}(\hat{I}_-^2 \hat{\sigma}_- + \ldots)$ (nuclear quadrupole)

orbital-nuclear spin interaction

☞ Limitations for optical control and readout for nuclear spin

→ ^{14}N nuclear spin relaxes much faster in $|^3E\rangle$ than that in $|^3A_2\rangle$

→ longer than ~μs total stay within $|^3E\rangle$ *(readout & preparation)*

→ or more than N>~1000 opt. cycles

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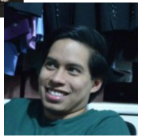
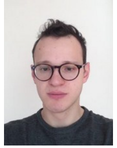

Thank you for your kind attention!

experimental:
Phys. Rev. Lett. 131, 236901 (2023)
Resonant versus nonresonant spin readout of a NV center in diamond under cryogenic conditions
R Monge, T Delord, G Thiering, Á Gali, CA Meriles

theoretical model:
doi.org/10.48550/arXiv.2402.19418

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nano group Budapest
wiki.kfki.hu/nano

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MOMENTUM OF INNOVATION

^{13}C hyperfine for G4V centers in diamond

Hyperfine *on* ^{13}C *sites will be entangled to* ***orbital*** *degrees of freedom too!*

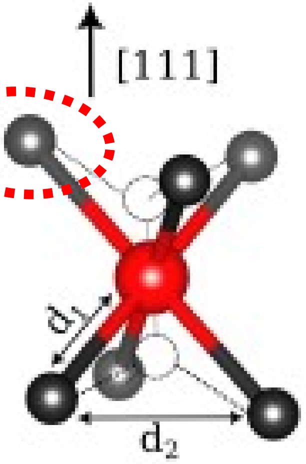
$$\hat{W} = \overleftarrow{S}\overleftrightarrow{A}_0\overrightarrow{I} + q(\overleftarrow{S}\overleftrightarrow{A}_x\overrightarrow{I}\hat{\sigma}_z + \overleftarrow{S}\overleftrightarrow{A}_y\overrightarrow{I}\hat{\sigma}_x)$$

three 3x3 hyperfine matrices:

$\overleftrightarrow{A}_0$: *"normal" hyperfine*

$\overleftrightarrow{A}_x, \overleftrightarrow{A}_y$: *"orbital" hyperfine for one* ^{13}*C site*

hyperfine for one ^{13}C site:



for Dynamic Jahn-Teller systems

should be visible below ~20 K

>50 K orbital averaging should occur

similarly to that of NV's ^{3}*E excited state*

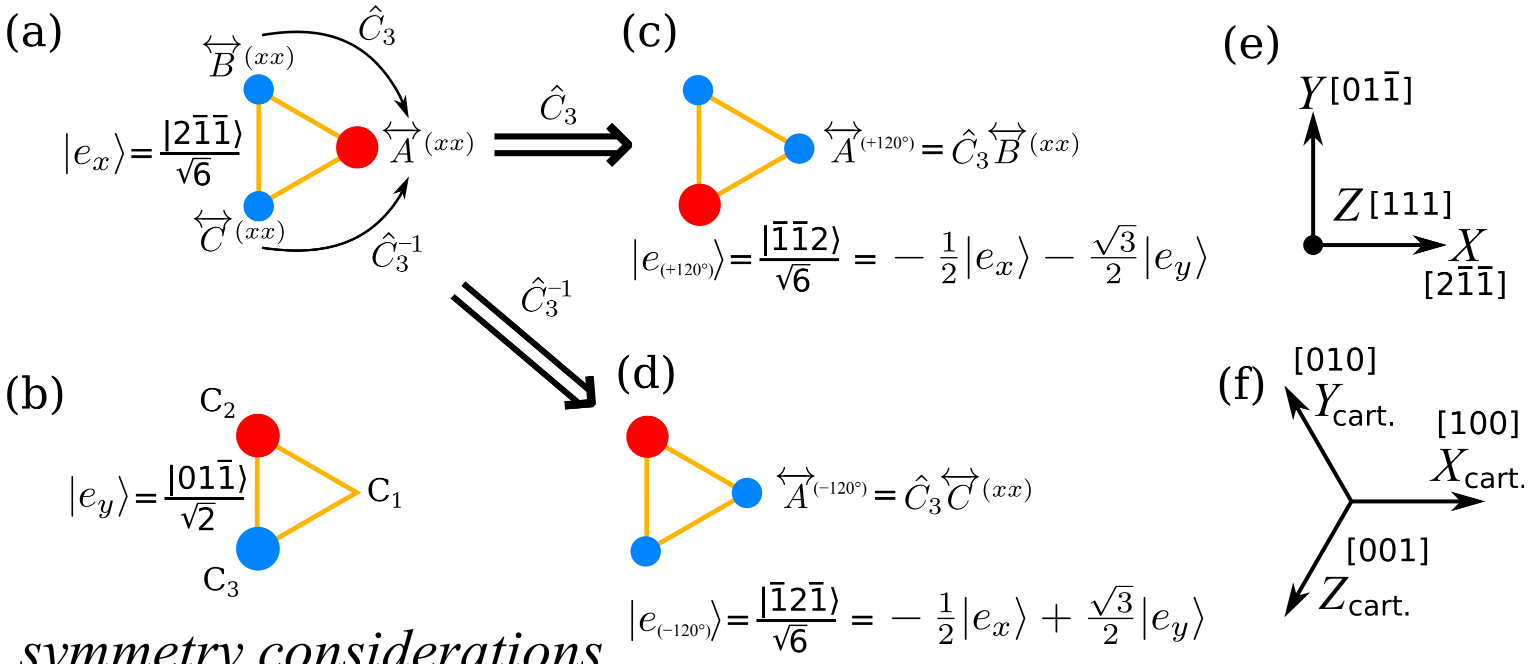
$\langle\hat{\sigma}_z\rangle = \langle\hat{\sigma}_x\rangle = 0$ *(thermal average)*

$$\hat{\sigma}_x = \begin{pmatrix} & 1 \\ 1 & \end{pmatrix} = |e_x\rangle\langle e_y| + |e_y\rangle\langle e_x|$$

$$\hat{\sigma}_z = \begin{pmatrix} 1 & \\ & -1 \end{pmatrix} = |e_x\rangle\langle e_x| - |e_y\rangle\langle e_y|$$

How to interpret ab-initio data

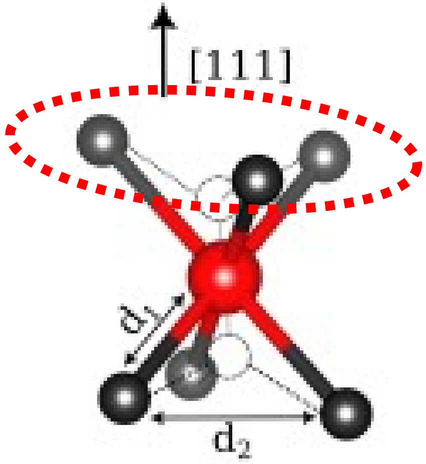
Three different $\overleftrightarrow{A}$, $\overleftrightarrow{B}$, $\overleftrightarrow{C}$ hyperfine tensors on 3 equivalent ^{13}C sites



symmetry considerations,
"orbital rotation"

electronic wavefunction phases

directly from ab-initio calculations



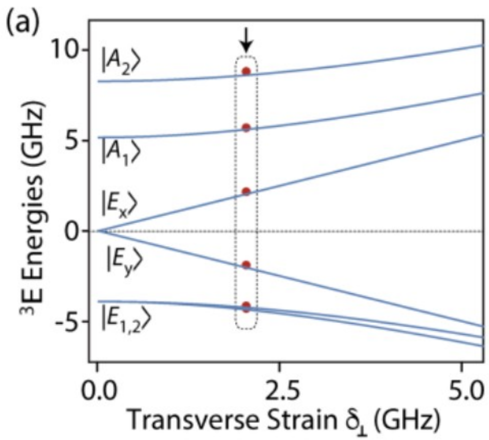
static Jahn-Teller distortion → e_x, e_y orbitals split the hyperfine tensors too!

Nuclear splin flip probabilities

Coherent time evolution for Q_2

$$p\left(|E_y\rangle \otimes |\mp\rangle \to |E_y\rangle \otimes |\pm\rangle\right) = \left(Q_2^{(e)} n \tau_{\mathrm{rad}}\right)^2 = 0.109,$$

$$p\left(|E_y\rangle \otimes |\mp\rangle \to |E_x\rangle \otimes |\pm\rangle\right) = 0,$$



3 Ghz
local strain
splitting

Fermi's golden rule for hyperfine transitions

$$p\left(|E_x\rangle \otimes |0\rangle \to |E_{1,2}\rangle \otimes |\pm 1\rangle\right) = 2 \times \left(\frac{A_\perp^{(e)}}{\lambda^{(e)} - D^{(e)}}\right)^2 \times n = 0.112,$$

$$p\left(|E_x\rangle \otimes |0\rangle \to |A_1\rangle \otimes |\pm 1\rangle\right) = 2 \times \frac{1}{2}\left(\frac{A_\perp^{(e)}}{\lambda^{(e)} + D^{(e)} - D_2^{(e)}}\right)^2 \times n = 0.017,$$

$$p\left(|E_x\rangle \otimes |0\rangle \to |A_2\rangle \otimes |\pm 1\rangle\right) = 2 \times \frac{1}{2}\left(\frac{A_\perp^{(e)}}{\lambda^{(e)} + D^{(e)} - D_2^{(e)}}\right)^2 \times n = 0.021,$$