NV Center in Diamond ISC

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Intersystem Crossing

Intersystem crossing rate due to SOC (λ) between triplet and singlet states

$$\Gamma = 4\pi\hbar\lambda^2 \, F(\Delta)$$

The overlap integral $F(\Delta, T)$ is computed as (using 1D effective phonon):

$$F(\Delta, T) = \sum_n p(i, n, T) \sum_m \left| \langle \chi_{in}(Q) | \chi'_{fm}(Q) \rangle \right|^2 \delta\left(m\hbar\omega_f - n\hbar\omega_i - \Delta E_{if}\right)$$

The SO Hamiltonian:

$$H_{SO} = \sum_i \lambda_\perp \left(L_{x,i} S_{x,i} + L_{y,i} S_{y,i}\right) + \lambda_z L_{z,i} S_{z,i}$$

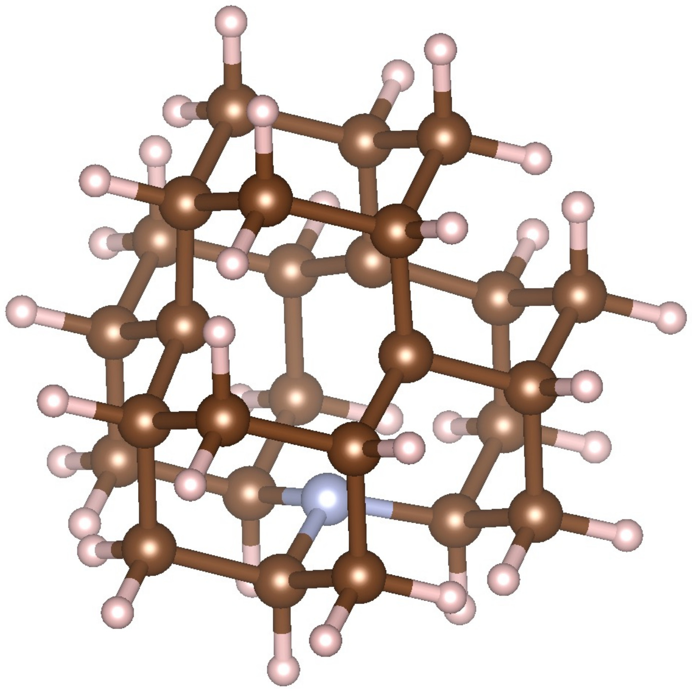
can be computed in ORCA and is responsible for spin-flip process

$\lambda_\perp$: $|1, \pm 1\rangle \rightarrow |0,0\rangle$ $\quad$ λ_z: $|1,0\rangle \rightarrow |0,0\rangle$ $\quad$ $(|S, m_s\rangle)$

SOC in ORCA

NV Center cluster is constructed by cutting a $\sim 3\text{Å}$ from a bulk NV center in Diamond calculation

The atoms are fixed, and dangling bonds are terminated with H



{'C': 27, 'H': 36, 'N': 1}

SOC in ORCA

Note calculation is done in the singlet state (S=0, Multiplicity = 1)

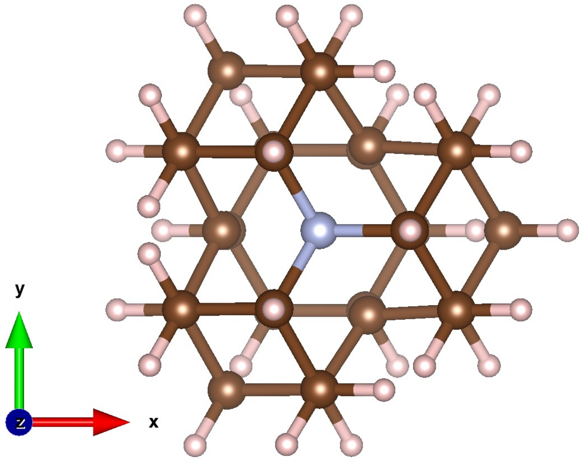
```
# functional/basis
! PBE def2-TZVP

# TDDFT block
%TDDFT  NROOTS  5
        DOSOC   TRUE
        PRINTLEVEL 3
END

# geometry
* xyzFile -1 1 nv_cluster.xyz

# parallelization
%PAL NPROCS 72 END
```

ORCA Input file

It is important to include "printlevel 3" so m_s projections can be directly read
Otherwise, they can be computed from x/y projections:

$$m_s(\pm 1) = \perp = \sqrt{\frac{|x|^2 + |y|^2}{2}}$$

The orientation of the cluster will change your result! In my example the principal axis of NV (111) is aligned to the z axis



SOC in ORCA

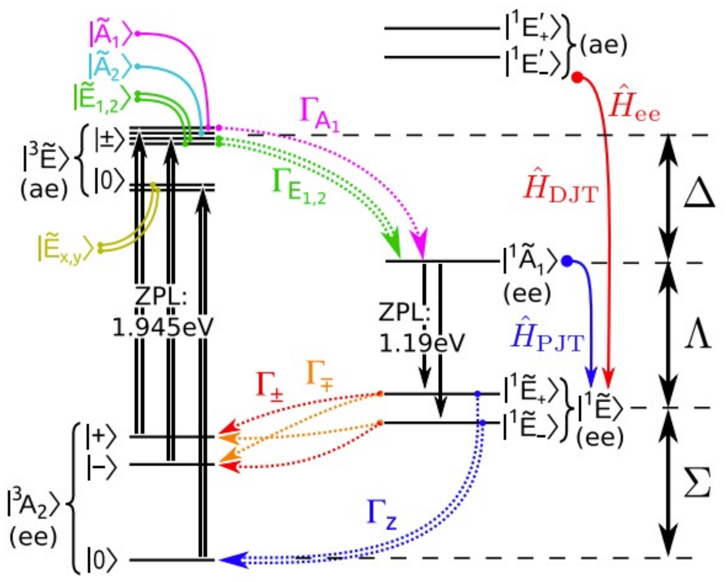
ORCA Output file

Search for “SOCME”, if “printlevel 3” was used you can look for the MS projection section

Roots are ordered 0,1,2… for Singlet and 1,2,3,… for Triplet.
In the case of studying the $|^3E\rangle \rightarrow |^1A_1\rangle$ transition of NV, this corresponds to T=2, S=1

```
---------------------------------------------------------------------
            CALCULATED SOCME BETWEEN TRIPLETS AND SINGLETS
---------------------------------------------------------------------
    Root                          <T|HSO|S>  (Re, Im) cm-1
  T       S          MS= 0                    -1                           +1
---------------------------------------------------------------------
  1       0    (0.00e+00 , 2.13e+00)   (-2.61e-03 , 3.42e-01)    (-2.61e-03 , -3.42e-01)
  1       1    (0.00e+00 , 2.68e-04)   (-1.06e-01 , 2.09e-04)    (-1.06e-01 , -2.09e-04)
  1       2    (0.00e+00 , -1.26e-03)   (-1.89e-01 , 6.82e-04)    (-1.89e-01 , -6.82e-04)
  1       3    (0.00e+00 , -8.10e-04)   (7.31e-01 , -1.50e-03)    (7.31e-01 , 1.50e-03)
  1       4    (0.00e+00 , 2.99e+00)   (-4.81e-03 , 4.91e-02)    (-4.81e-03 , -4.91e-02)
  1       5    (0.00e+00 , 1.91e-02)   (-3.55e-01 , 2.54e-04)    (-3.55e-01 , -2.54e-04)
  2       0    (0.00e+00 , -8.23e-04)   (-1.91e+00 , -4.75e-03)    (-1.91e+00 , 4.75e-03)
  2       1    (0.00e+00 , 1.35e-01)   (-3.33e-03 , 1.50e+00)    (-3.33e-03 , -1.50e+00)
  2       2    (0.00e+00 , -1.47e-02)   (-1.04e-04 , -1.72e-01)    (-1.04e-04 , 1.72e-01)
  2       3    (0.00e+00 , 1.21e-01)   (4.02e-04 , -3.44e-01)    (4.02e-04 , 3.44e-01)
  2       4    (0.00e+00 , -8.02e-04)   (-7.46e-02 , 7.08e-04)    (-7.46e-02 , -7.08e-04)
```

λ_z (MS= 0) $\lambda_\perp$ (-1, +1)



PRB **98**, 085207 (2018)

Calculating their norm, and converting to GHz we get:

$\lambda_\perp$ (GHz)	λ_z (GHz)
44.97	4.05

Exp $\lambda_z = 5$ GHz

Previous Theory *PRB* **96**, 081115(R) (2017)

$\lambda_\perp$ (GHz)	λ_z (GHz)
56.3	15.8

Intersystem Crossing

NV Center in Diamond result

$$\Gamma = 4\pi\hbar\lambda_\perp^2\, F(\Delta),\, F(\Delta, T) = \sum_n p(i,n,T) \sum_m \left|\langle \chi_{in}(Q) | \chi'_{fm}(Q) \rangle\right|^2 \delta\left(m\hbar\omega_f - n\hbar\omega_i - \Delta E_{if}\right)$$

Geometry used

Work	Initial	Final	S	$ZPL\ (eV)$	$\lambda_\perp\ (GHz)$	Γ (MHz)
Ours	*triplet es*	*singlet gs*	1.83	0.4	44.97	2.3
Gali*	*triplet es*	*singlet gs*	2.61	0.4	56.3	--

Exp: 8 and 16 MHz (there are two observed ISC when considering the vibronic nature of the triplet exicted state which we did not consider)

* From Gali PRB2017, HR approximation with excluded e phonons

** The singlet es ($|^1A_1\rangle$) cannot be simulated by DFT so the singlet gs geometry is used instead and an approximate ZPL energy of 0.4 eV is used, see Gali's paper for further discussion

*** For more accurate depiction of the ISC in Diamond the vibronic nature of $|^3E\rangle$ must be considered