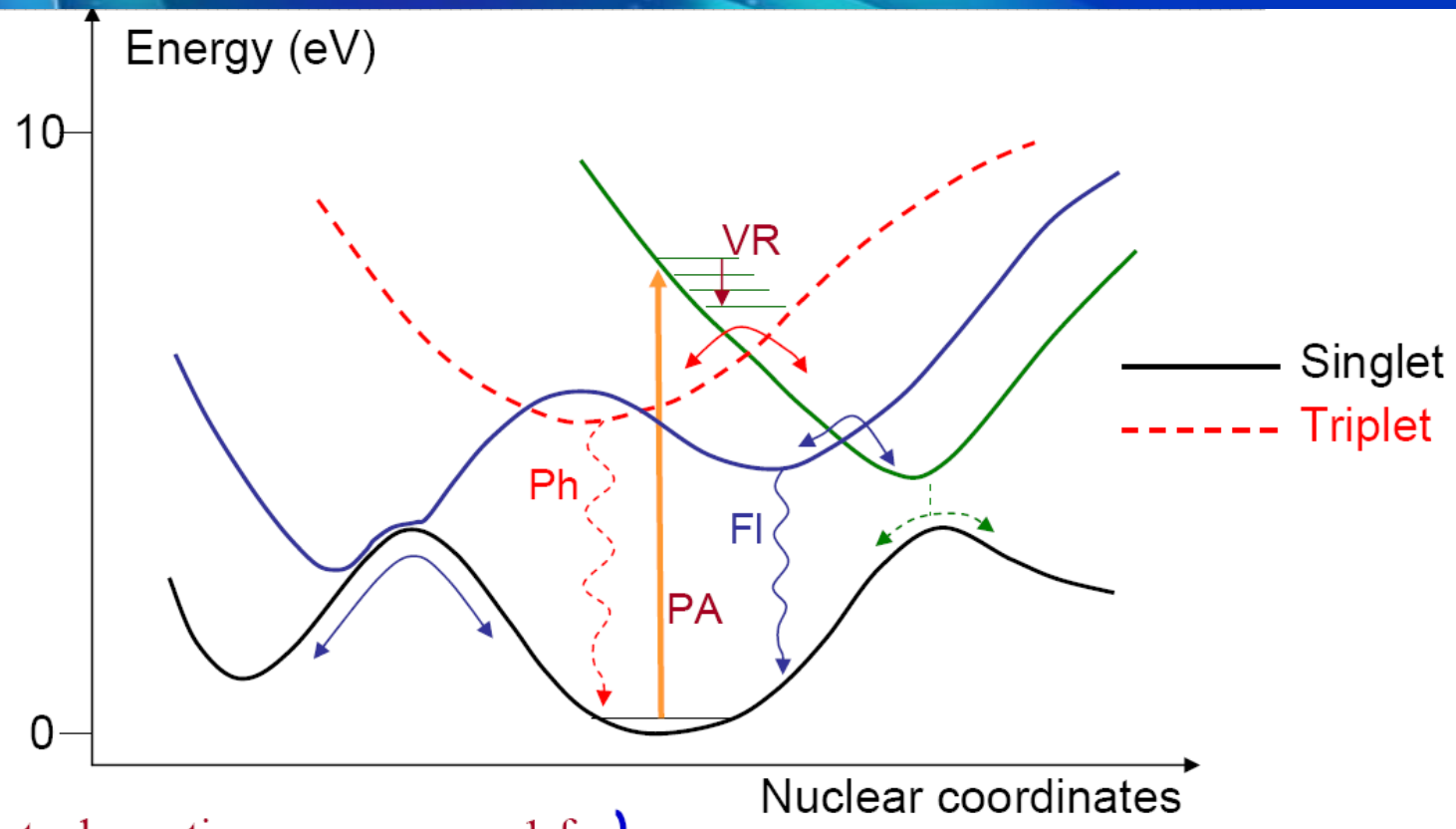
Modeling laser-induced spin crossover transition using time-dependent density functional theory

Alex-Adrian Farcas, Attila Bende

1. Types of state intersections
2. Calculation of the intersections
3. Methods
4. Python program
5. Singlet vs Triplet
6. Ni–tetrakis(pentafluorophenyl)porphyrin - phenylazopyridine (NiTPP-PAPy)
7. Bibliography



PA – photoabsorption	1 fs	*ab initio dynamics*
conical intersection	10-10^2 fs	
avoided crossing	10^2-10^4 fs	
VR – vibrational relaxation	10^2-10^5 fs	
intersystem crossing	10^5-10^7 fs	
Fl – fluorescence	10^6-10^8 fs	
Ph – phosforescence	10^{12}-10^{17} fs	

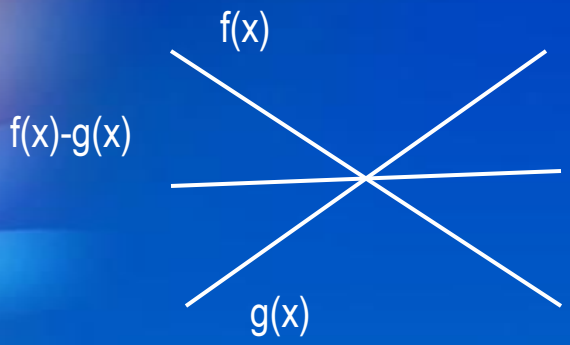
In the simplest case one can calculate excited state energies as energy differences of single-reference calculations.

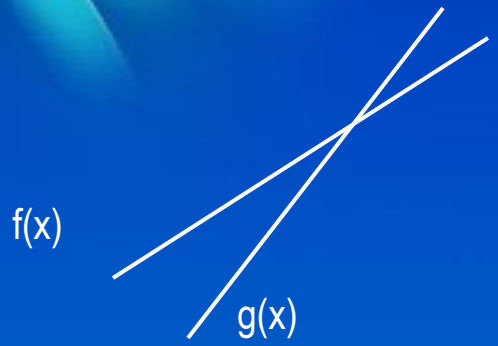
$$\Delta E(ex) = E(\text{excited state}) - E(\text{ground state}).$$

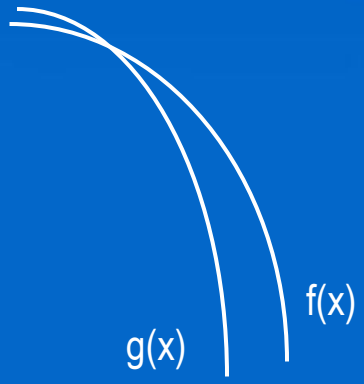
This can be done:

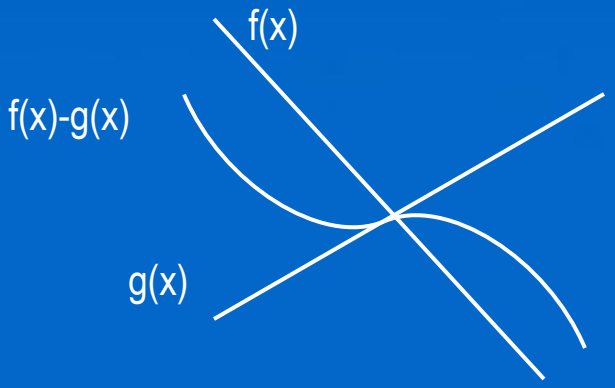
- For states of different symmetry (A', A", etc.)
- For states of different multiplicity (singlet, triplet)
- Possibly for states that occupy orbitals of different symmetry

Possible cases

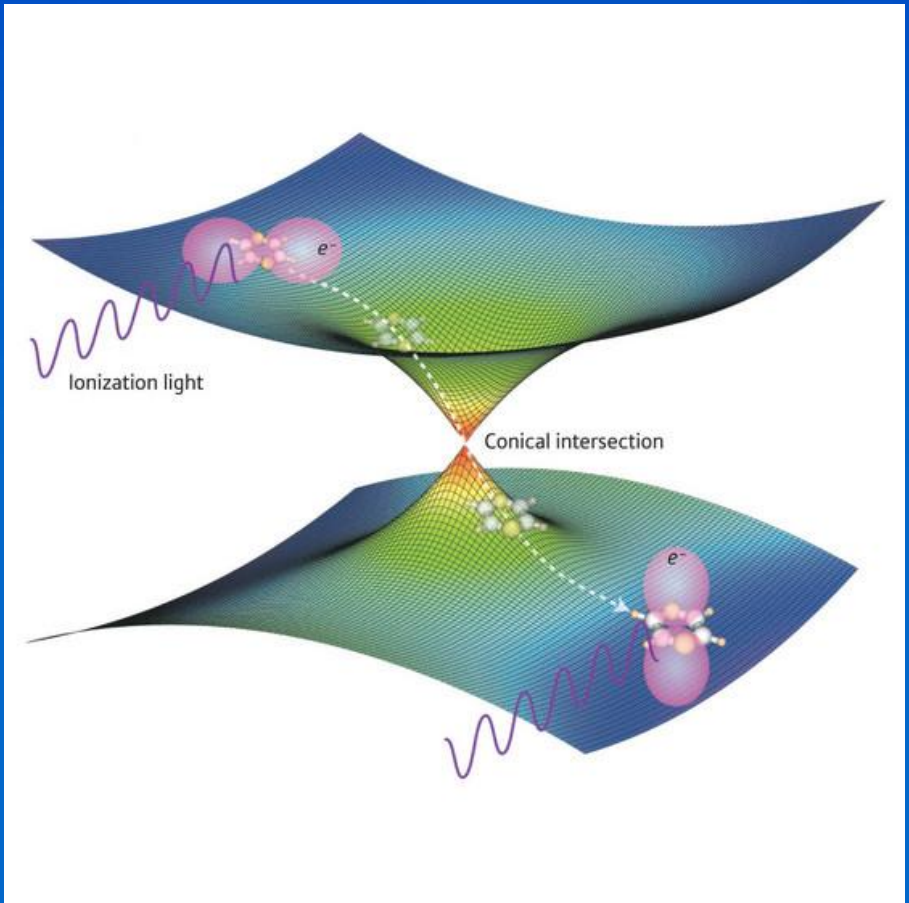








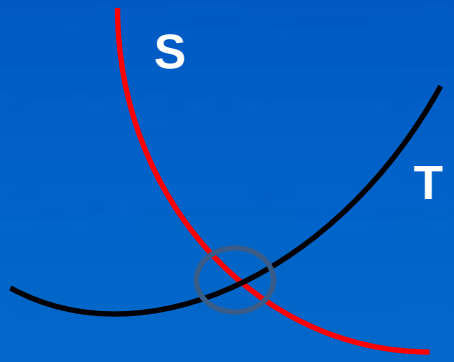
Different states intersection



riken.jp

Penalty function method

$$f(\mathrm{R}) = \frac{E_S + E_T}{2} + c_a c_b^2 \ln\left[1 + \left(\frac{E_T - E_S}{c_b}\right)^2\right]$$



Gradient:

$$\frac{\partial E}{\partial i} = (0.5 + s)\frac{\partial E_T}{\partial i} + (0.5 - s)\frac{\partial E_S}{\partial i}$$

i = x,y,z

where **s** is the scale functions $s \to 0$ if $E_T - E_S \to 0$

Gradient projection method

Minimization gradients:

$$f_1 = 2(E_I - E_J)\frac{g_{IJ}}{|g_{IJ}|}$$

$$f_2 = P\frac{\partial E_J}{\partial q}$$

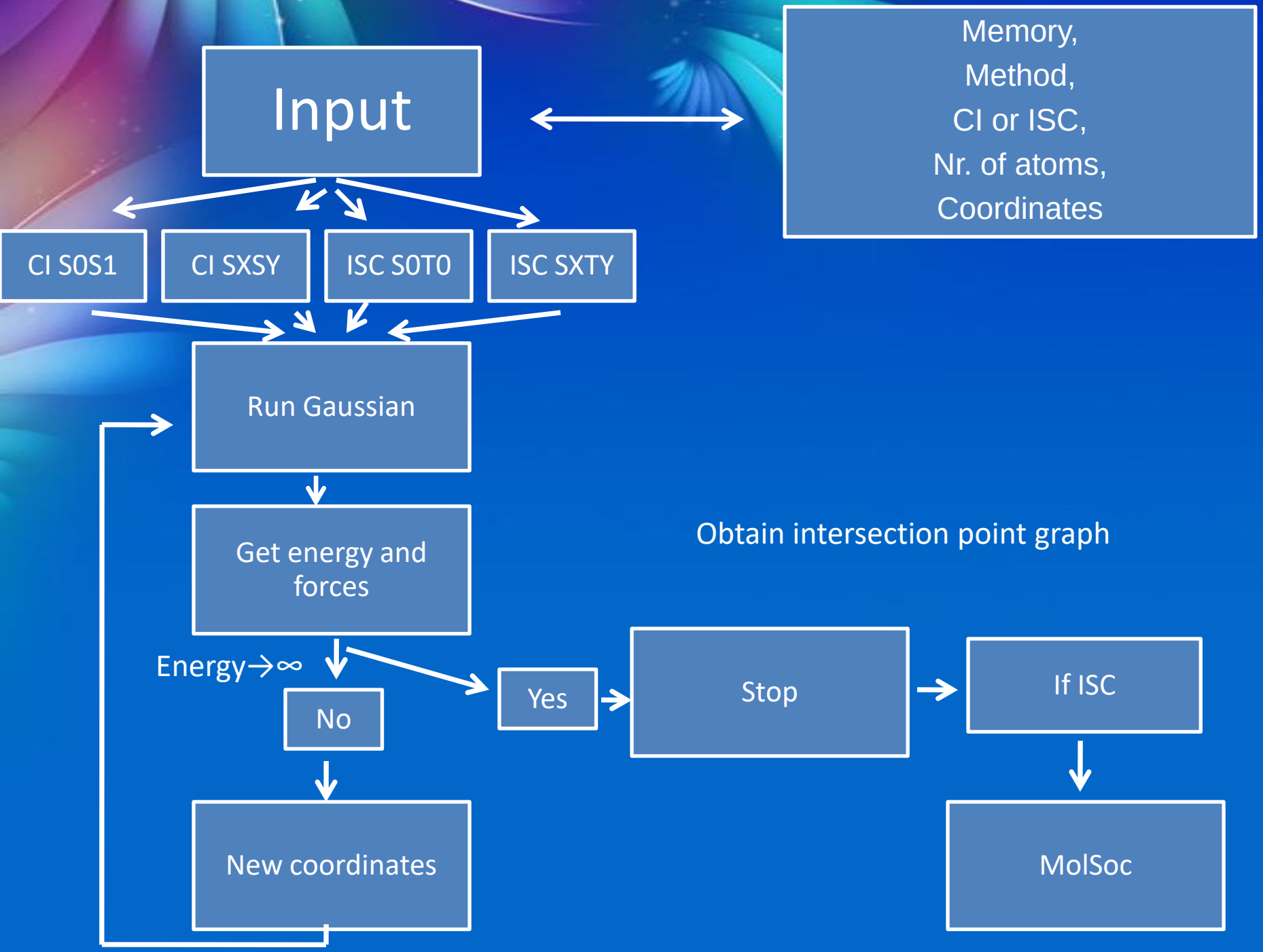
$$P = I - \tilde{g}_{IJ}\,\tilde{g}^{+}_{IJ} - \tilde{h}_{IJ}\,\tilde{h}^{+}_{IJ}$$

Projection matrix

$$g = c_3[c_4 f_1 + (1 - c_4) f_2]$$

Gradient

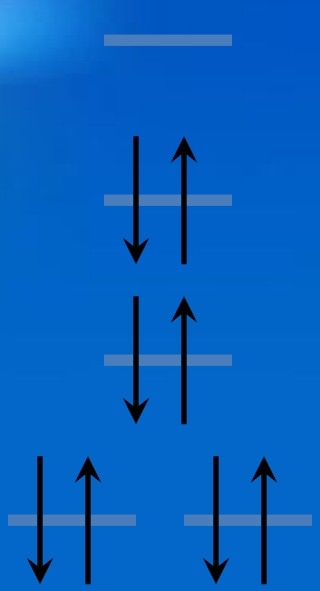
$$c_3 > 0 \qquad 0 < c_4 \le 1$$


Input
Memory,
Method,
CI or ISC,
Nr. of atoms,
Coordinates
CI S0S1
CI SXSY
ISC S0T0
ISC SXTY
Run Gaussian
Get energy and forces
Obtain intersection point graph
Energy→∞
No
Yes
Stop
If ISC
New coordinates
MolSoc

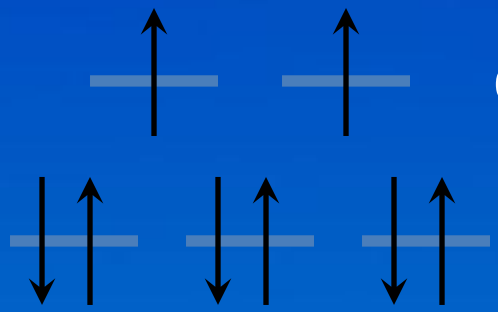
Singlet vs triplet spin states

Ni(II) → $3d^8$

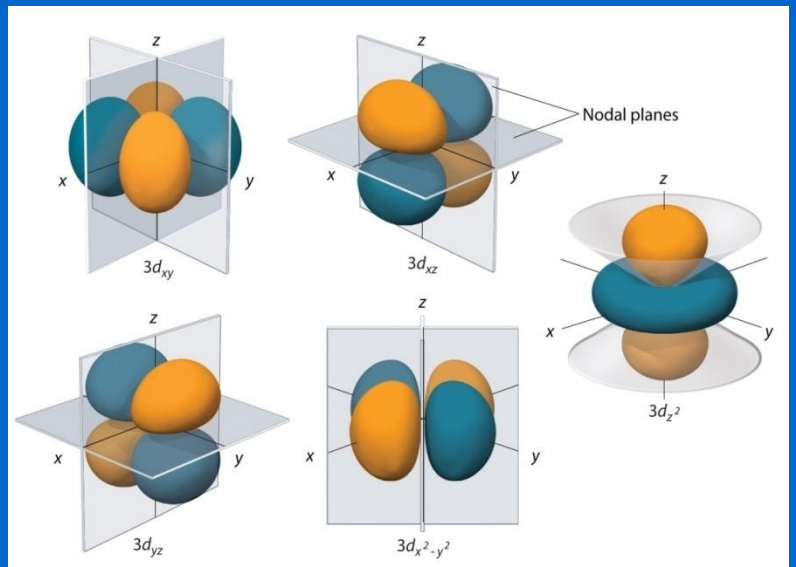
The Ni (II) electronic spin state in square-planar configuration:



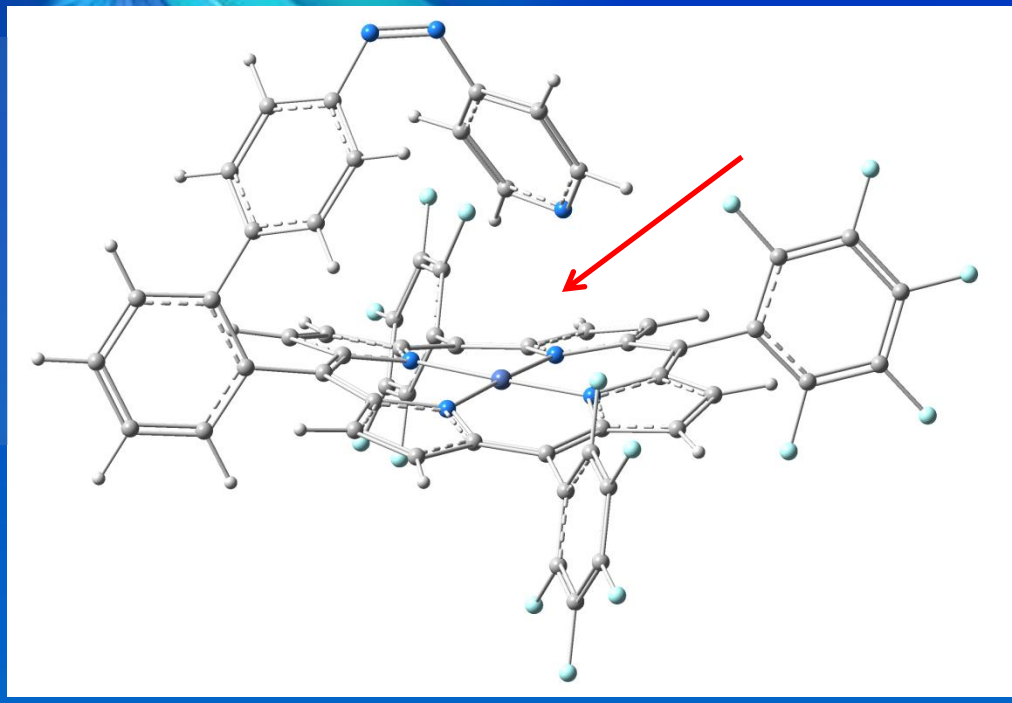
The Ni(II) spin state in octahedral configuration:



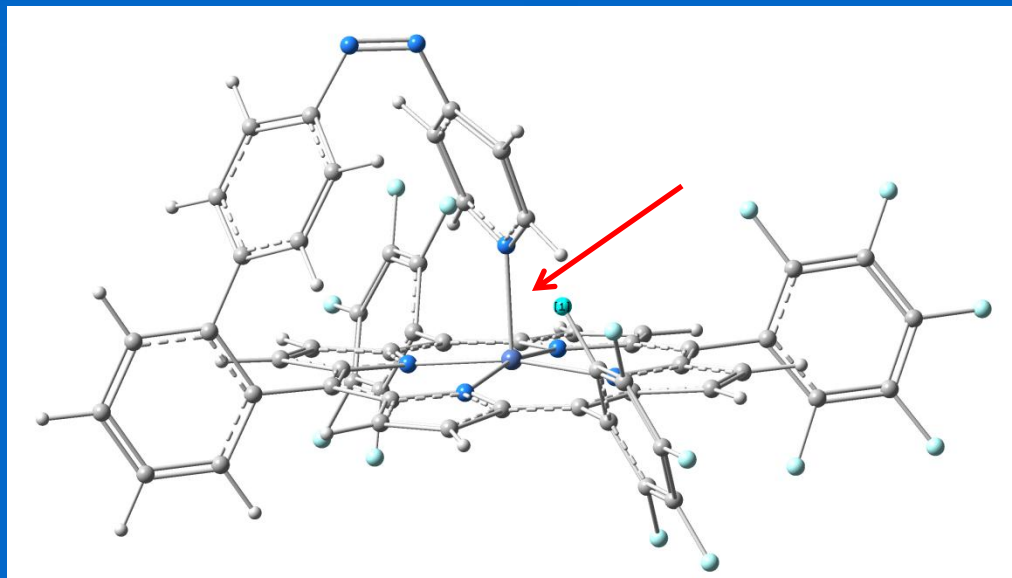
3d orbitals of Ni(II)



Ni–tetrakis(pentafluorophenyl) porphyrin - phenylazopyridine (NiTPP-PAPy)

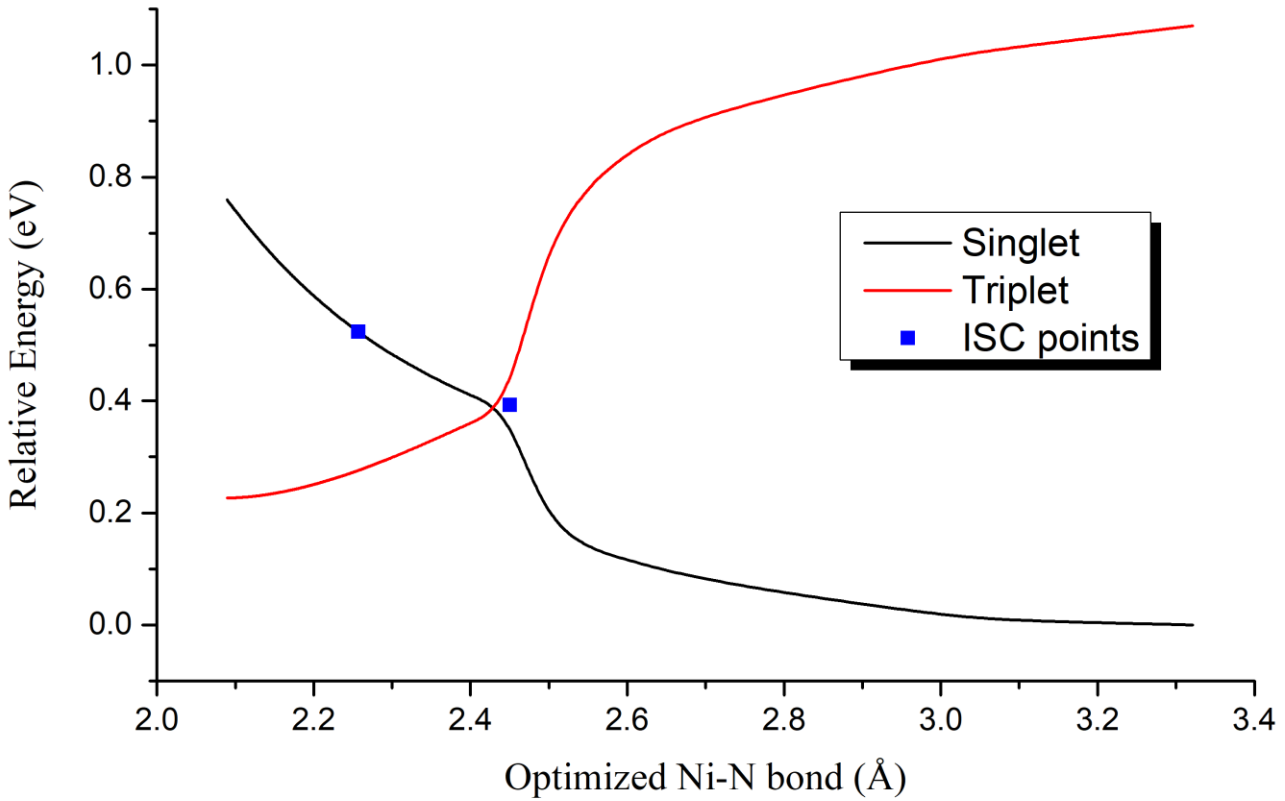


Singlet spin state



Triplet spin state

Ni–tetrakis(pentafluorophenyl)porphyrin - phenylazopyridine (NiTPP-PAPy)



Bibliography

•Thomas W. Keal · Axel Koslowski · Walter Thiel, Comparison of algorithms for conical intersection optimisation using semiempirical methods
•riken.jp
•Bernardi F,Olivucci M,Robb MA (1996) Chem Soc Rev25:321– 328
•DomckeW,YarkonyDR,KöppelH(eds)(2004)Conicalintersections: electronic structure, dynamics and spectroscopy. Advanced series in physical chemistry, vol 15. World Scientific, Singapore
•Schoenlein RW, Peteanu LA, Mathies RA, Shank CV (1991) Science 254:412–415
•Koga N, Morokuma K (1985) Chem Phys Lett 119:371–374
•Farazdel A, Dupuis M (1991) J Comput Chem 12:276–282
•RagazosIN,RobbMA,BernardiF,OlivucciM (1992) ChemPhys Lett 197:217–223
•Manaa MR, Yarkony DR (1993) J Chem Phys 99:5251–5256
•Anglada JM, Bofill JM (1997) J Comput Chem 18:992–1003
•KoslowskiA,BeckME,ThielW (2003) JComputChem24:714– 726
•Yarkony DR (2004) J Phys Chem A 108:3200–3205

Thank you for your attention!!!