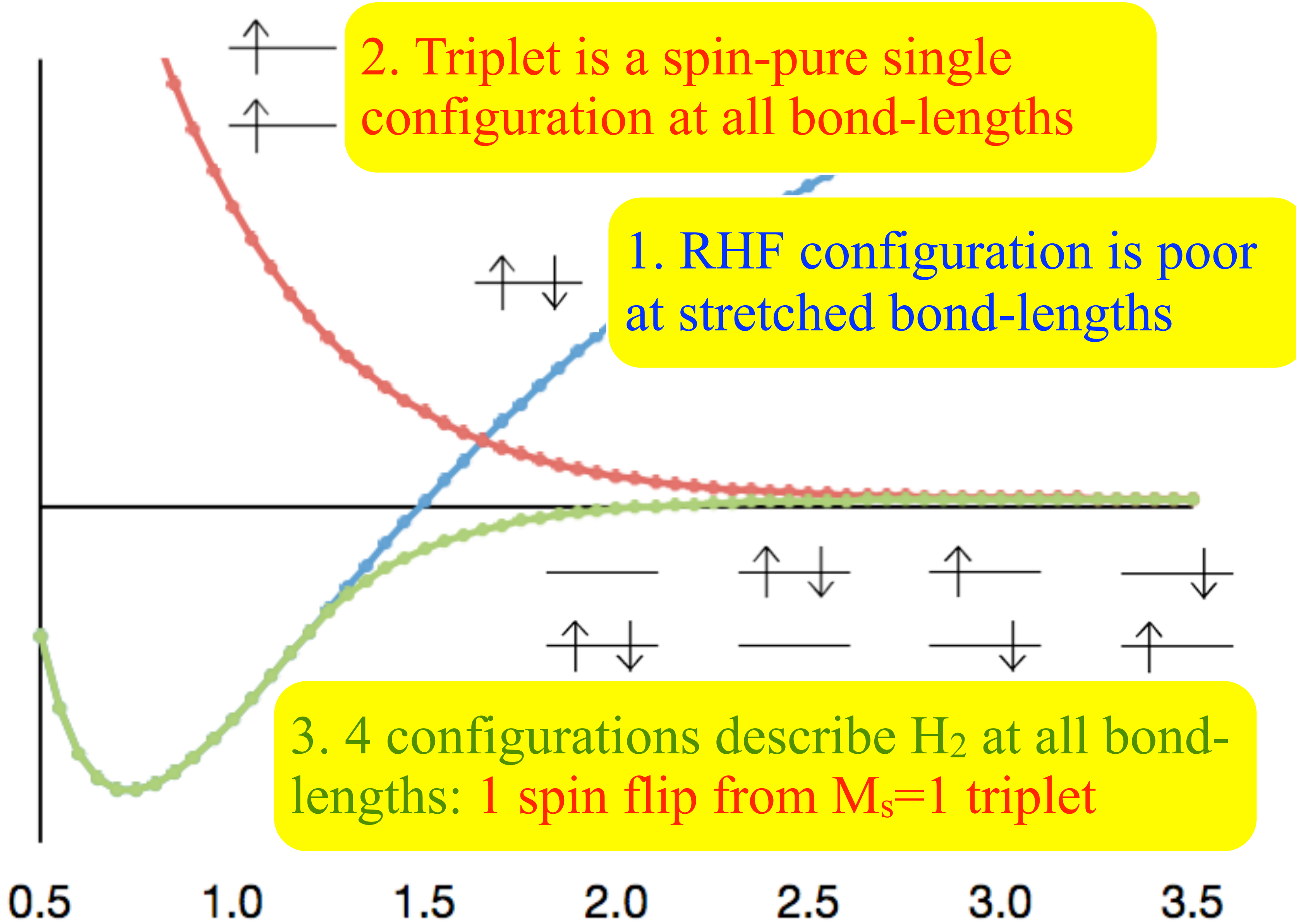
Spin-flipping (invented by Anna Krylov ~2000)
How it works for breaking a single bond



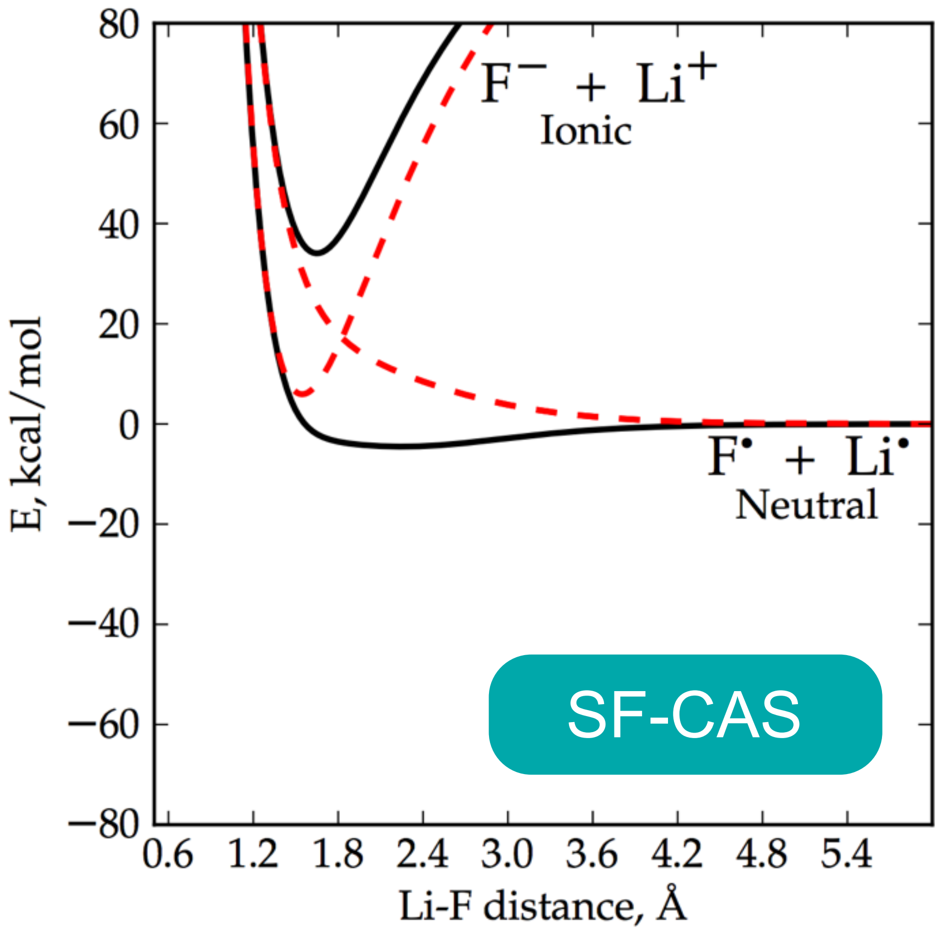
SF-NOCI: non-orthogonal configuration interaction (Nick Mayhall, Eric Sundstrom, Paul Horn)

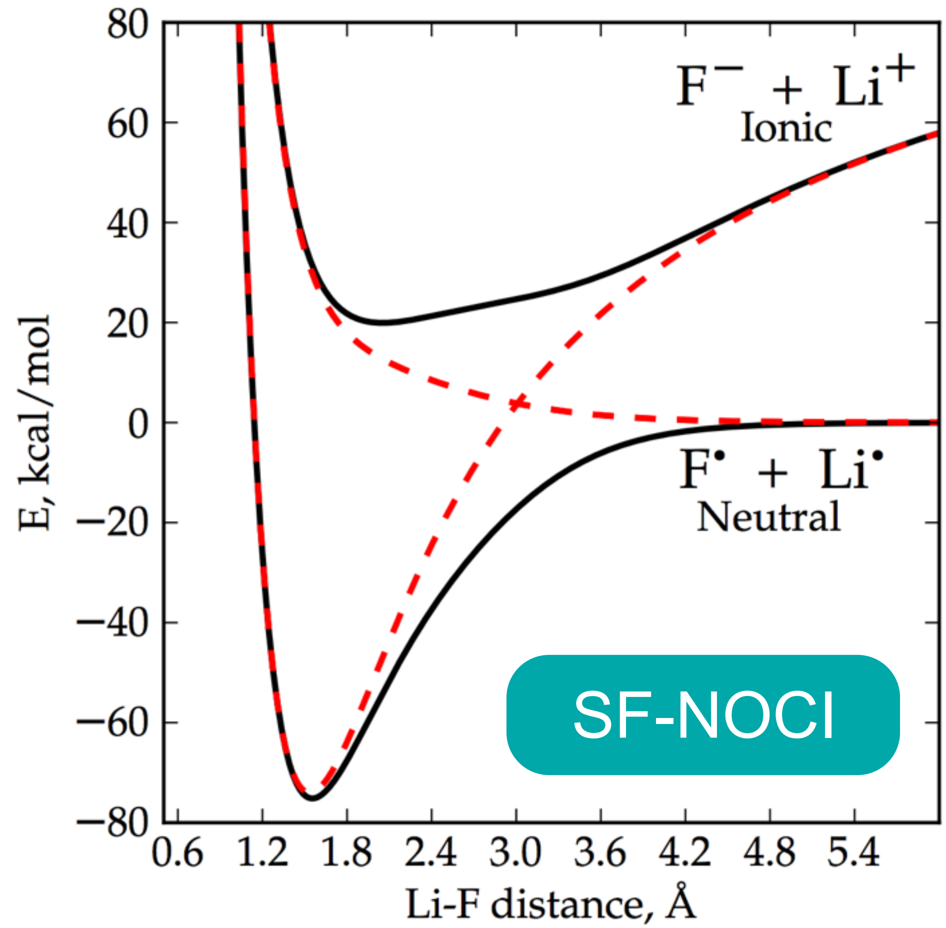
- Starting from SF-CAS
  - 1. Localize active-space orbitals & freeze them
    2. Relax each SF-CAS configuration individually
    3. Diagonalize H in this new "relaxed" determinant basis

- A very special form of non-orthogonal CI !!
  - No 2 configurations can coalesce
  - Each relaxation is well-conditioned (large gap)
  - Building the NOCI hamiltonian is highly efficient
  - Rate-determining relaxations are embarrassingly parallel

- N.Mayhall, P. Horn, E. Sundstrom, MHG, PCCP 16, 22694 (2014)
- For NOCI, see: E. Sundstrom, MHG, JCP 140, 114103 (2014).

Ionic / covalent competition in LiF (Nick Mayhall)

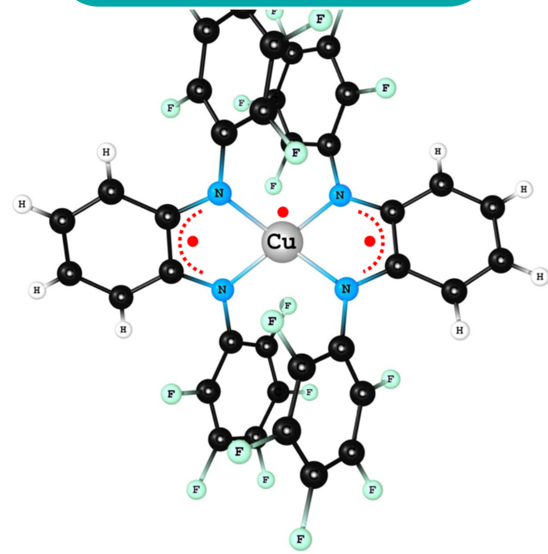




- SF-CAS uses triplet orbitals -- so ionic configuration is too high
- SF-NOCI strongly relaxes the ionic configuration. Not the covalent.
  - gives a qualitatively correct curve: ΔH_f(expt) = 82 kcal/mol

Low-lying states in $Cu^{II}(^{F}sbqdi)_2$ (eV) (Nick Mayhall)

$L^{\bullet}-M^{\bullet}-L^{\bullet}$



- 3 unpaired e's in 3 orbitals
  - Use quartet ROHF single reference
  - 2 low-lying doublets, 1 quartet
  - Higher ionic CT configurations....

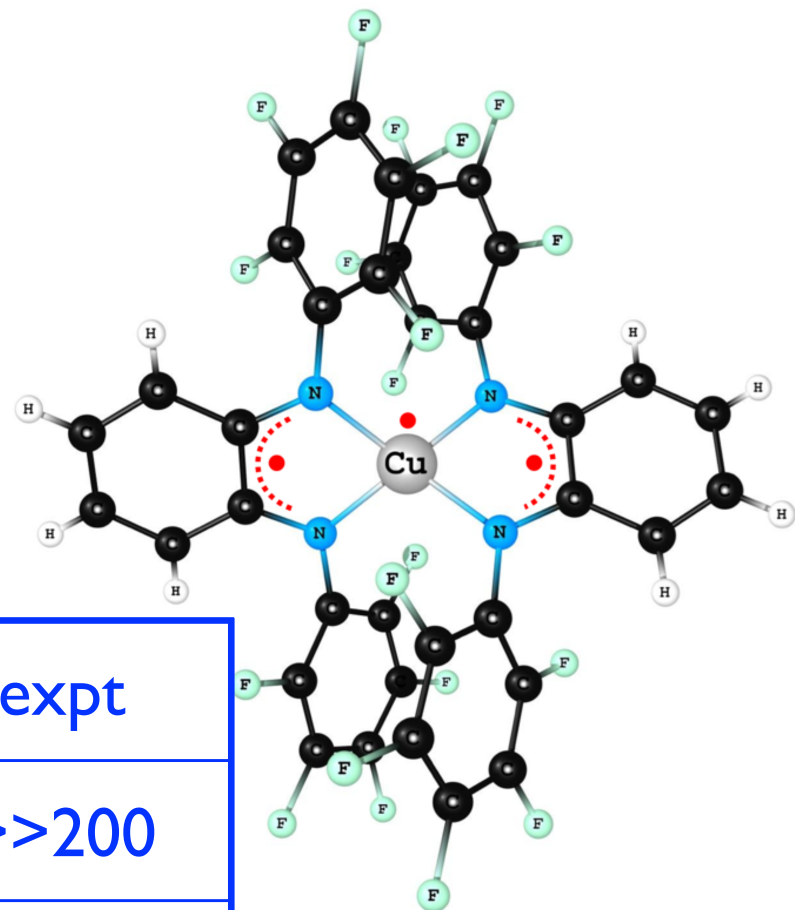
type	config	multiplicity	SF-CAS (eV)	SF-NOCI (eV)
local	αβα	doublet	0	0
local	ααβ+βαα	doublet	0.05	0.12
local	ααα	quartet	0.07	0.18
LLCT	+α−	doublet	4.6	2.6
LMCT	α−+	doublet	11.4	5
MLCT	α+−	doublet	13.8	7.8

Heisenberg couplings in $Cu^{II}(^{F}sbqdi)_2$ (Nick Mayhall)

$$\hat{H} = -2J\ \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B$$

- weakly interacting radical centers
- gives strong spin correlations

- SF-NOCI makes a big difference



	SF-CAS	SF-NOCI	expt
J(CuL) / cm^{-1}	-231	-548	>>200
J(LCu) / cm^{-1}	-165	-434	>>200
J(LL) / cm-1	-9	-36	small