Generalized Hartree Fock for Excited States

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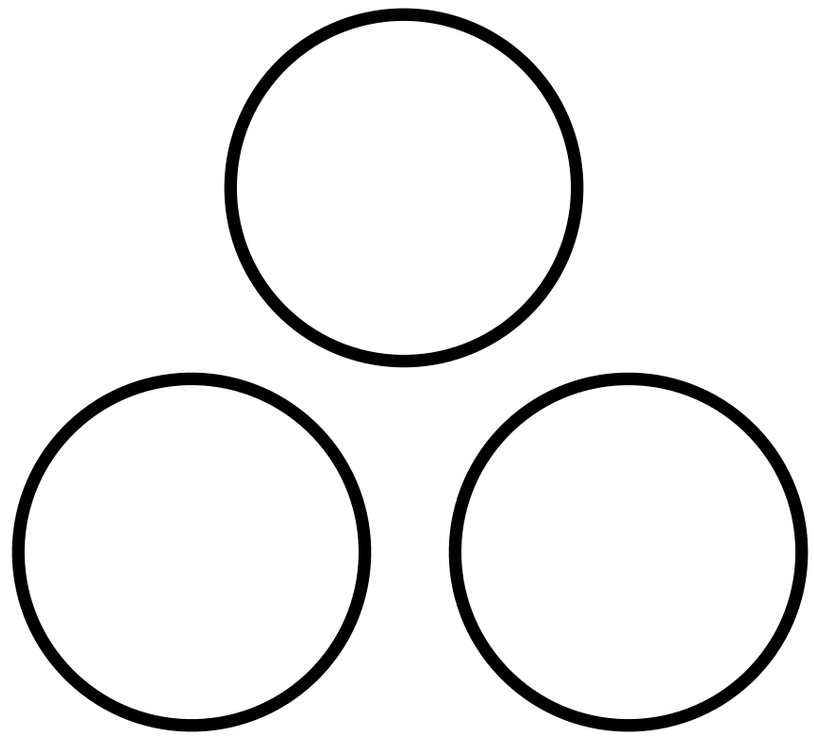
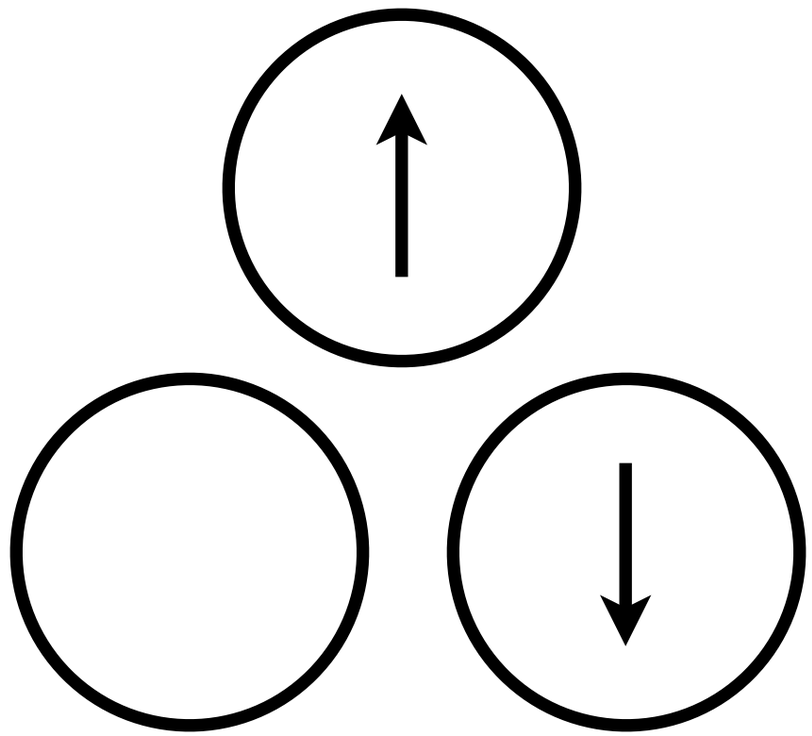
Ernest Davidson, Xiaosong Li*

Spin frustration leads to non-collinear magnetism



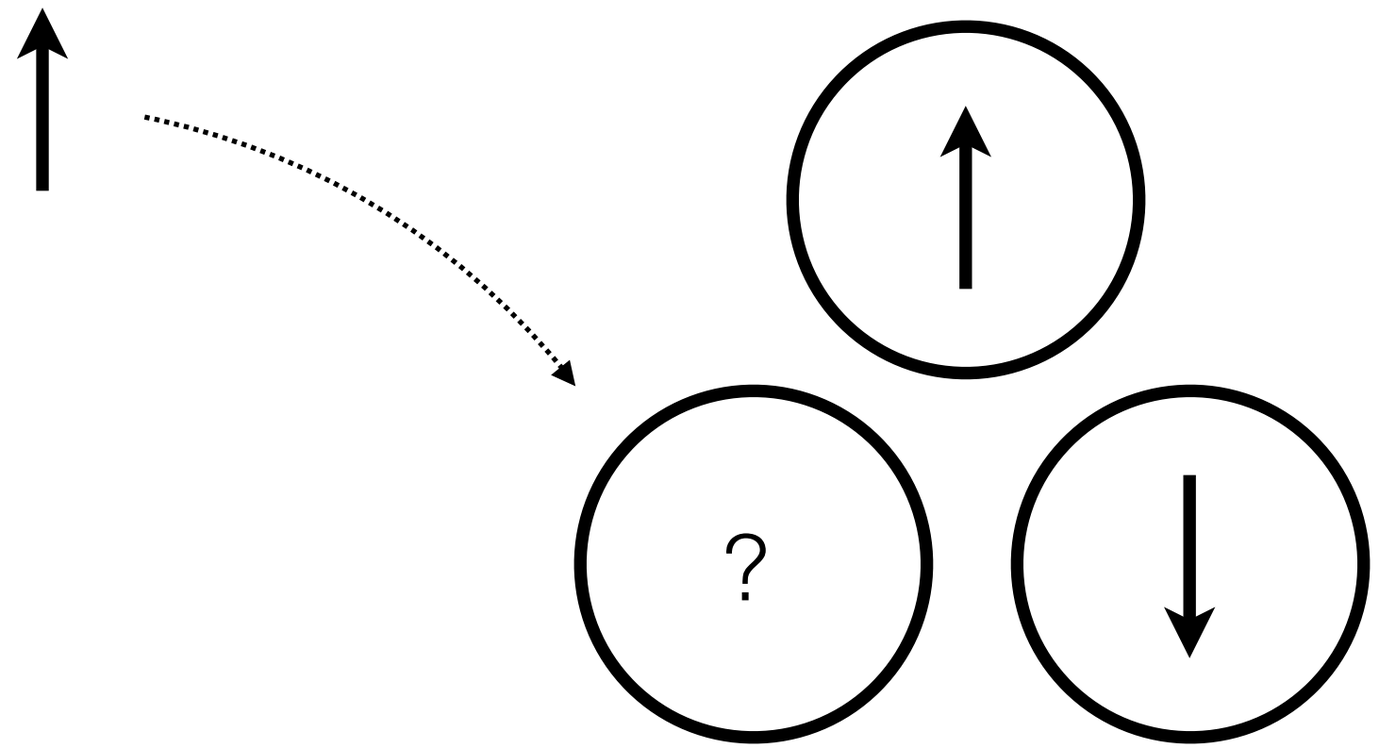
Take a three site lattice

Spin frustration leads to non-collinear magnetism



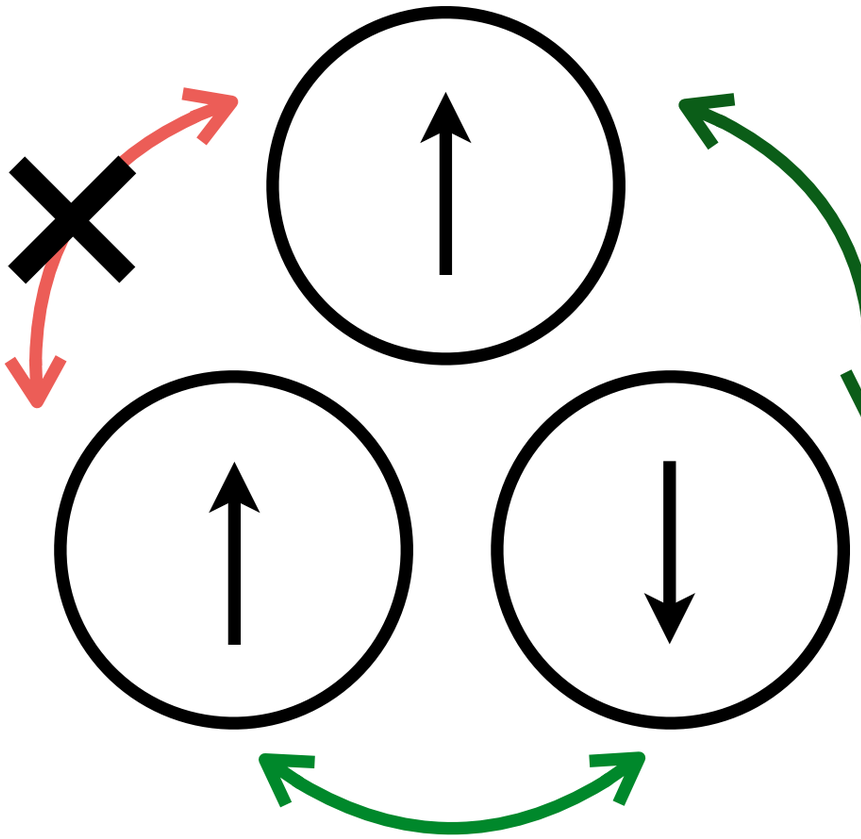
Add two electrons.
(Assume anti-ferromagnetism favored).

Spin frustration leads to non-collinear magnetism

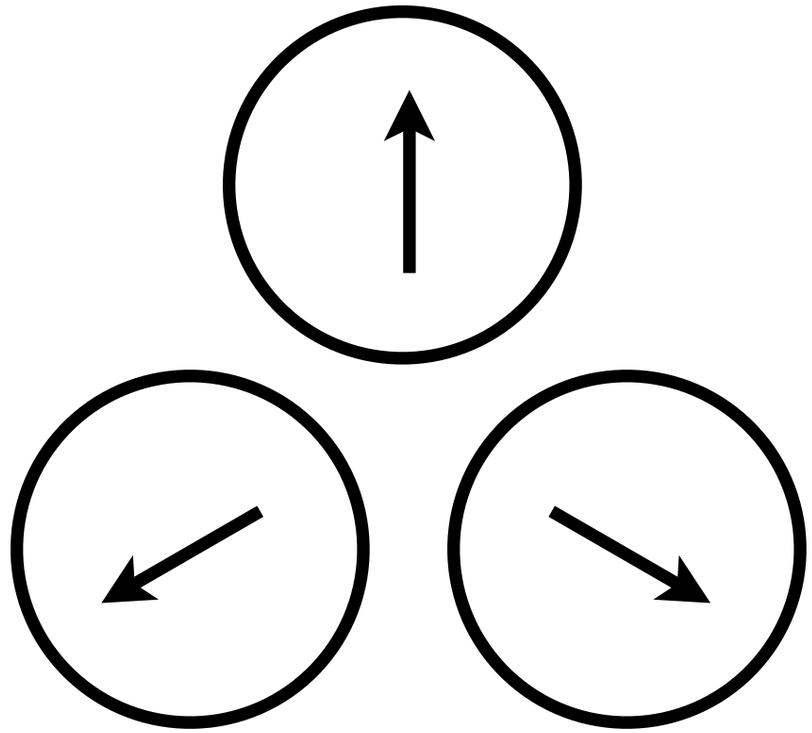


Now, add the third electron.
No spin orientation simultaneously favors
all anti-ferromagnetic exchange interactions

Spin frustration leads to non-collinear magnetism



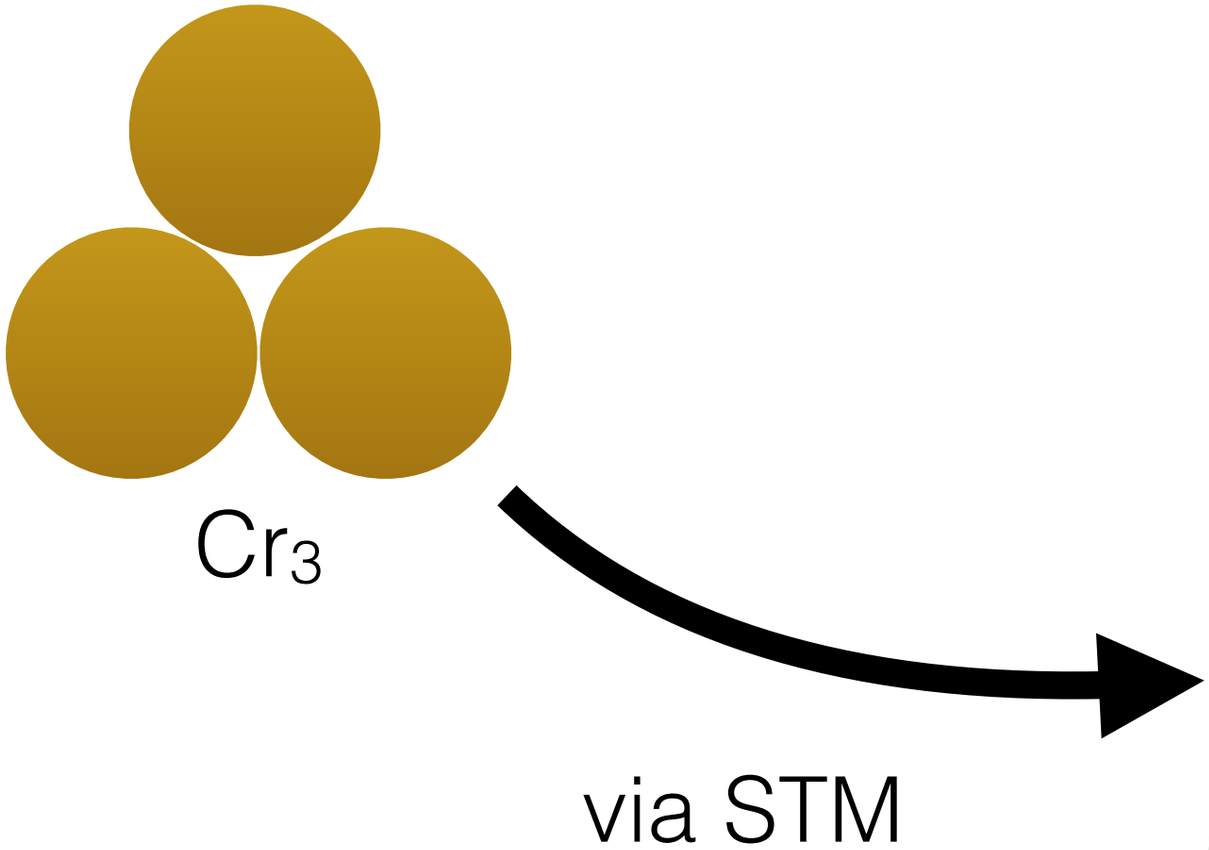
Collinear

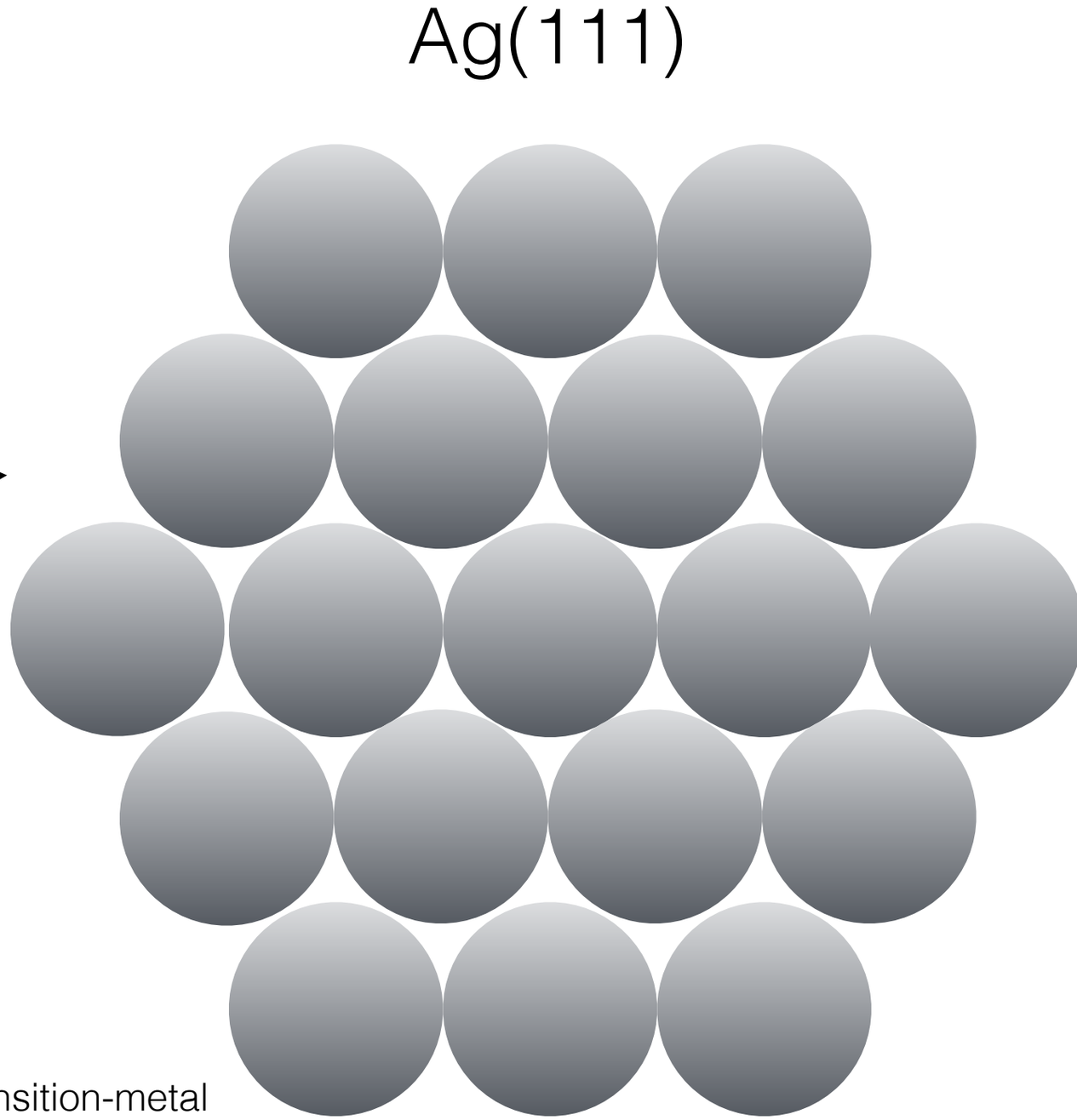


Non-collinear

Most electronic structure methods
cannot capture non-collinearity!

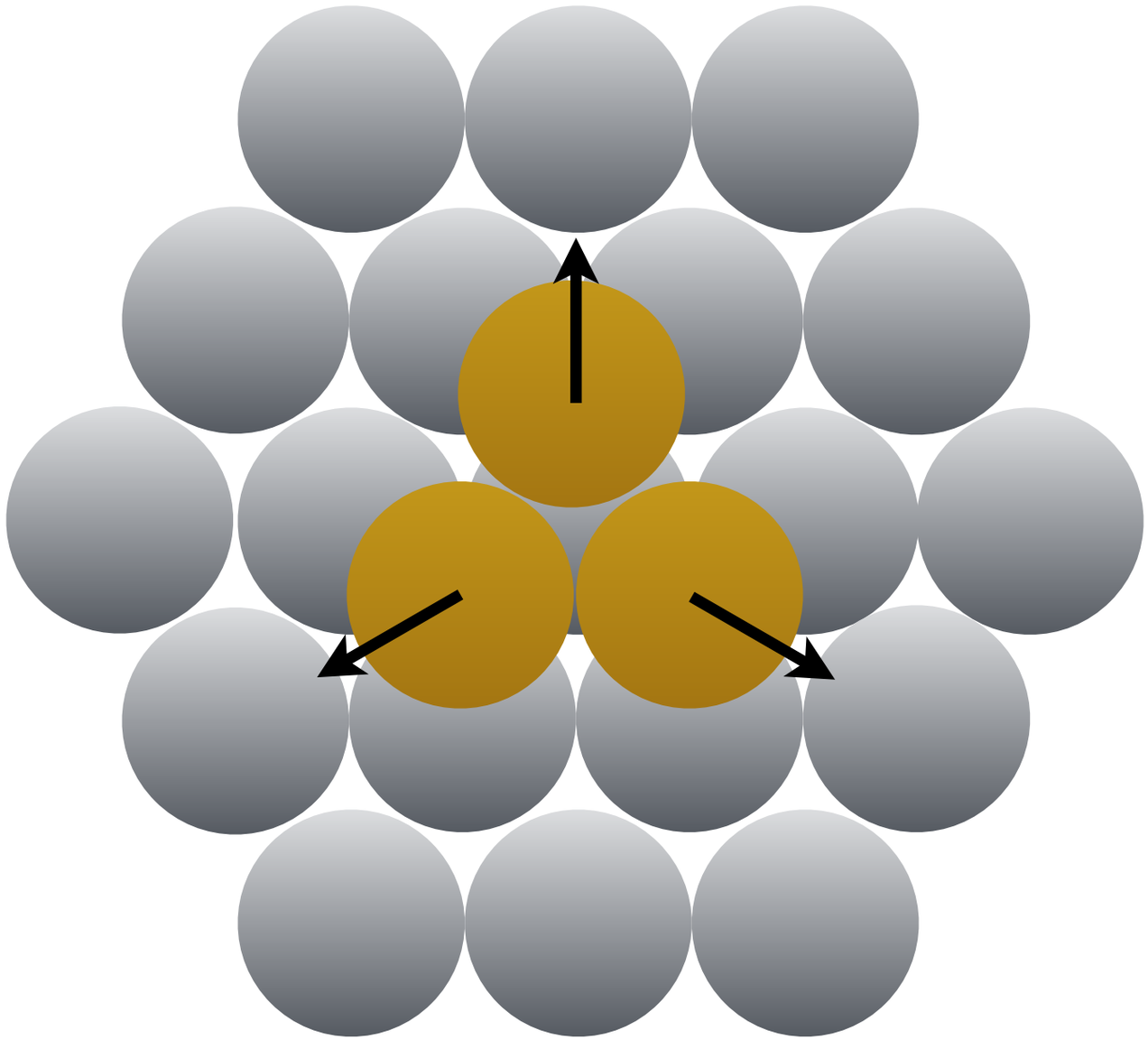
Generating non-collinear magnetism by spin frustration with transition metals





S Lounis. “Non-collinear magnetism induced by frustration in transition-metal nanostructures deposited on surfaces”. JPCM 26 (2014) 273201.

Generating non-collinear magnetism by spin frustration with transition metals



Lock metal trimer into D_{3h}

We would like to describe such systems with single reference methods.

Furthermore, we want to study how the systems can be manipulated with electromagnetic fields.

Generalized Hartree Fock (GHF)

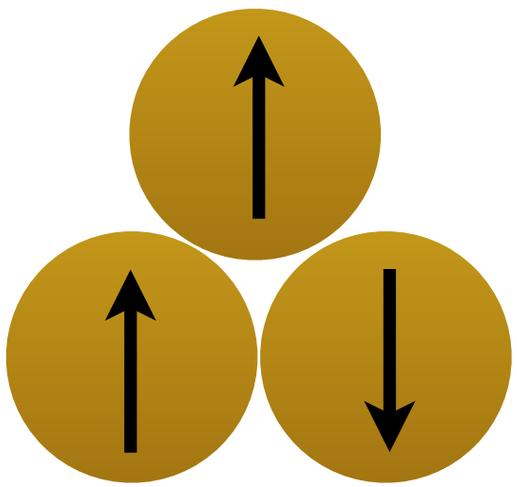
$$\phi_{GHF} = \phi_\alpha + \phi_\beta$$

$$\begin{pmatrix} \mathbf{F}^{\alpha\alpha} & \mathbf{F}^{\alpha\beta} \\ \mathbf{F}^{\beta\alpha} & \mathbf{F}^{\beta\beta} \end{pmatrix} \begin{pmatrix} \mathbf{C}^{\alpha} \\ \mathbf{C}^{\beta} \end{pmatrix} = \epsilon \begin{pmatrix} \mathbf{S} & \mathbf{0} \\ \mathbf{0} & \mathbf{S} \end{pmatrix} \begin{pmatrix} \mathbf{C}^{\alpha} \\ \mathbf{C}^{\beta} \end{pmatrix}$$

$$\mathbf{F}^{\sigma\tau} = \mathbf{h}^{\sigma\tau} + \delta_{\sigma\tau} \left[\mathbf{J}^{\alpha\alpha} + \mathbf{J}^{\beta\beta} \right] - \mathbf{K}^{\sigma\tau}$$

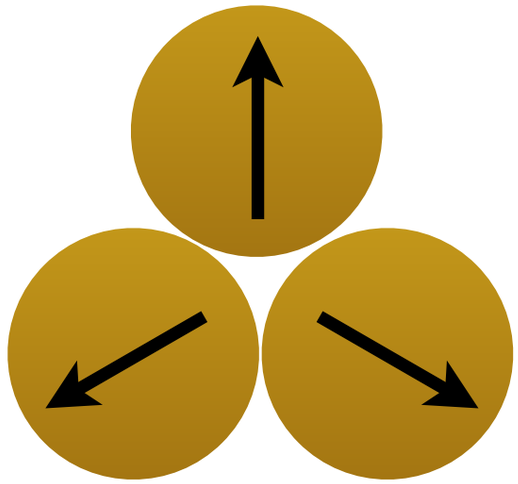
GHF is equivalent to a two-component spinor.
For spin frustrated systems, it gives a distinctly lower energy.

$$\phi_{GHF} = \phi_\alpha + \phi_\beta$$



Cr_3 / UHF / LANL2DZ

D_{3h} / 2.89A



Cr_3 / GHF / LANL2DZ

$\Delta E = 7.5$ kcal mol^{-1}

GHF **outperforms UHF** for energetics.

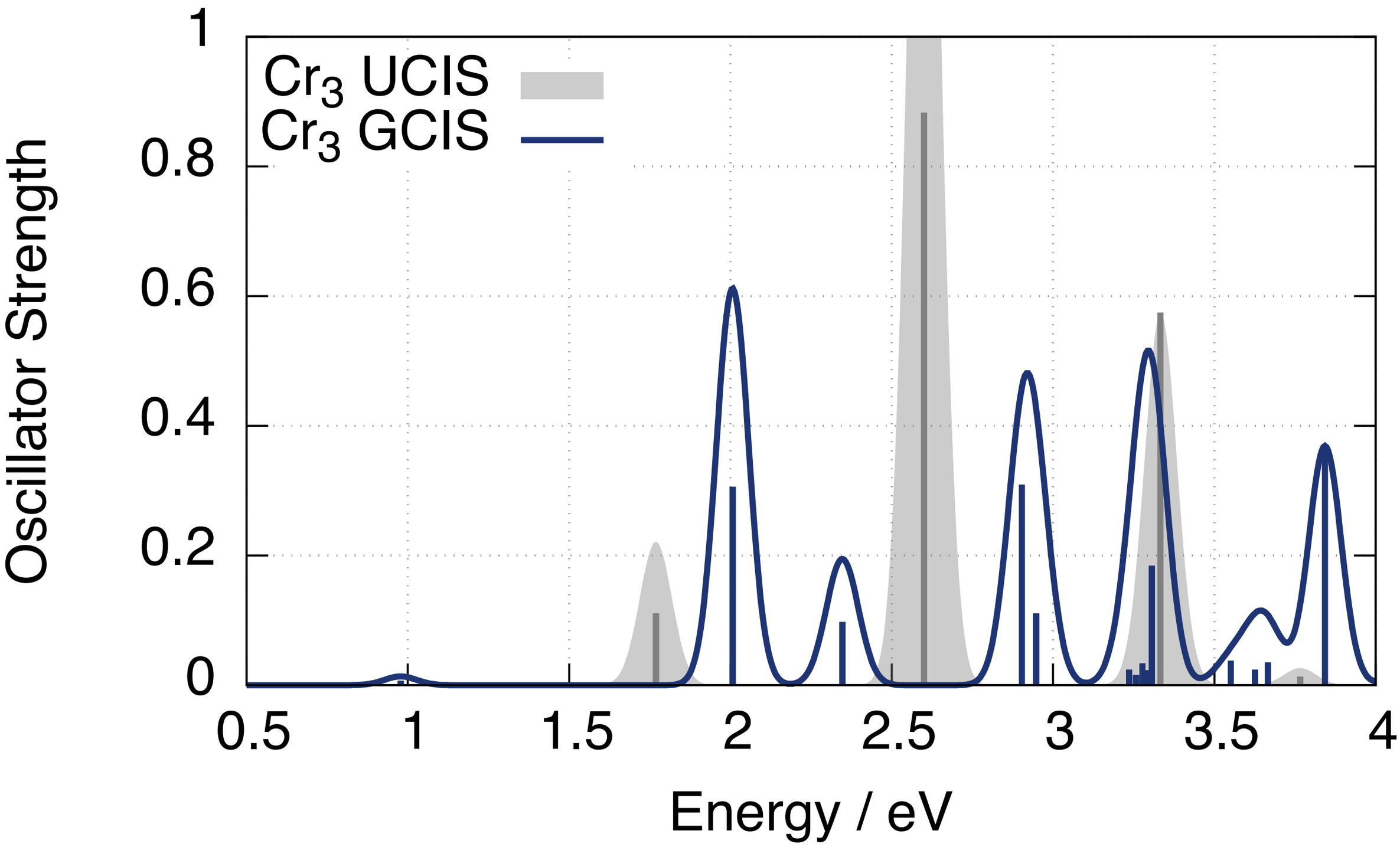
It is not, however, an eigenfunction of total spin or axial spin projection.

It is **uncertain if GHF is useful** for **excited state** and **property** calculations.

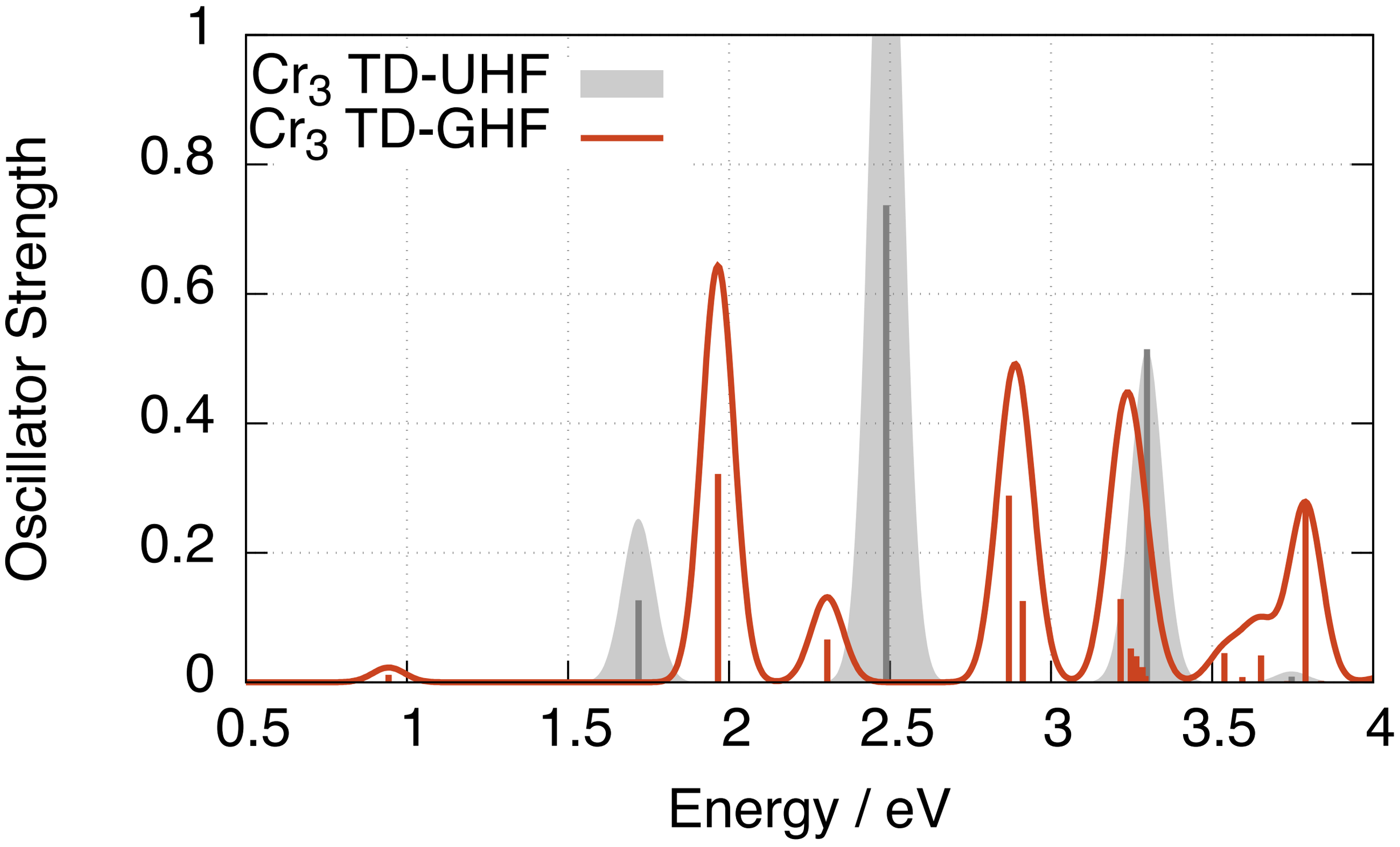
Briefly explored in 2000, properties not studied, restricted to real GHF.

Yamaki, *et al.* “MP2, Tamm-Dancoff, and RPA Based on the Generalized HF Solution”. IJQC 80 (2000) 701

Inserting the GHF orbitals into the CIS equations gives wildly different excitation energies and transition moments.



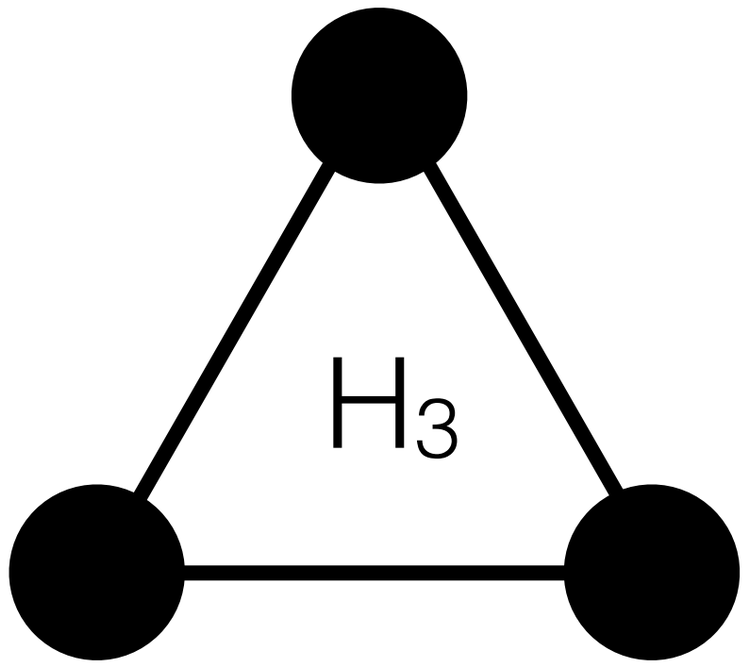
LR-TD-GHF gives the same story.



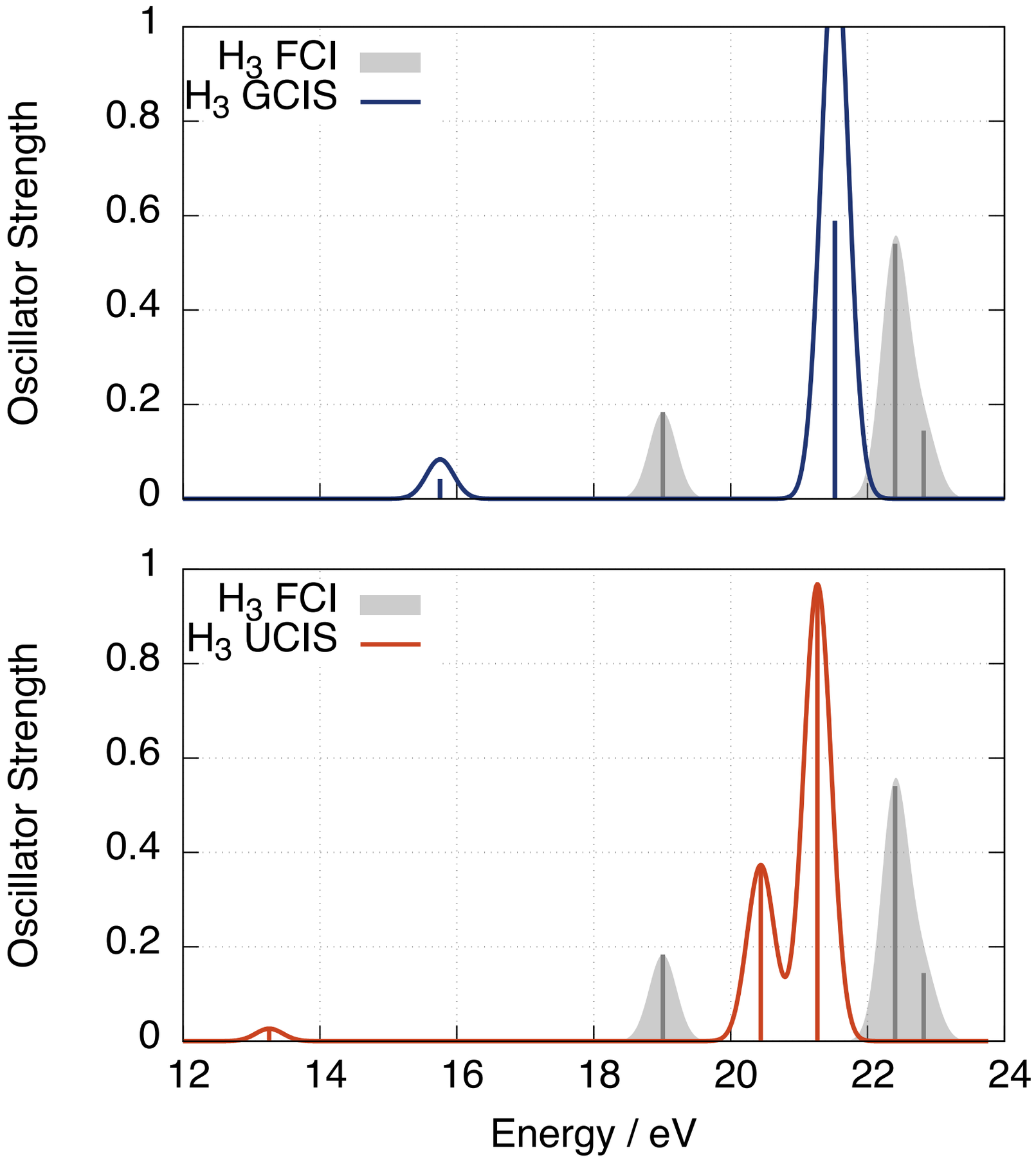
To determine which is more useful for excited states, ideally we'd perform multi-reference calculations.

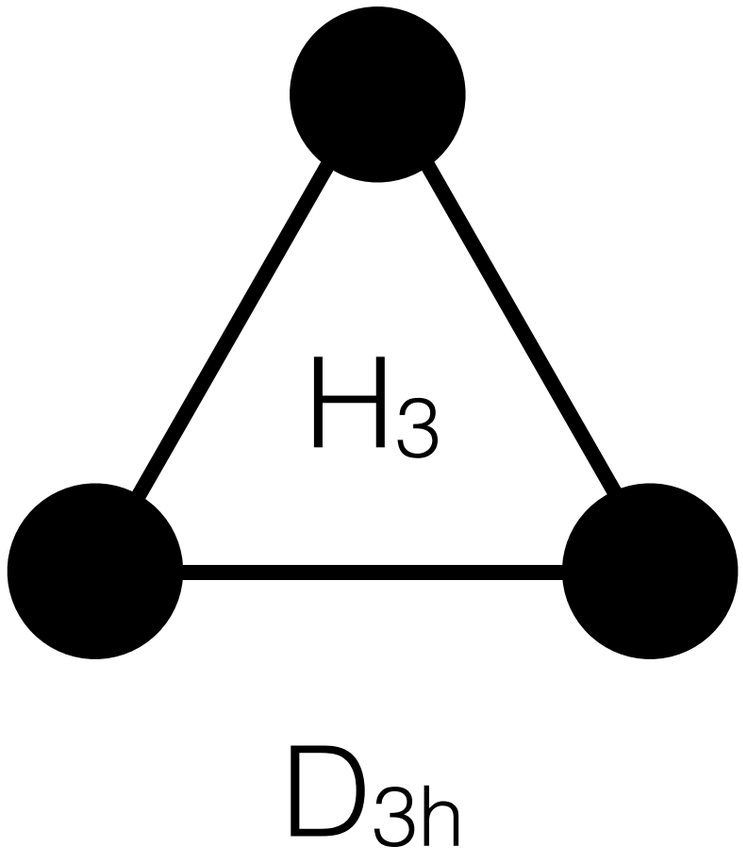
This is not currently feasible for Cr_3.

Toy model: H_3, minimal basis (STO-3G), 1 Angstrom.



The simplest model of non-collinear magnetism.

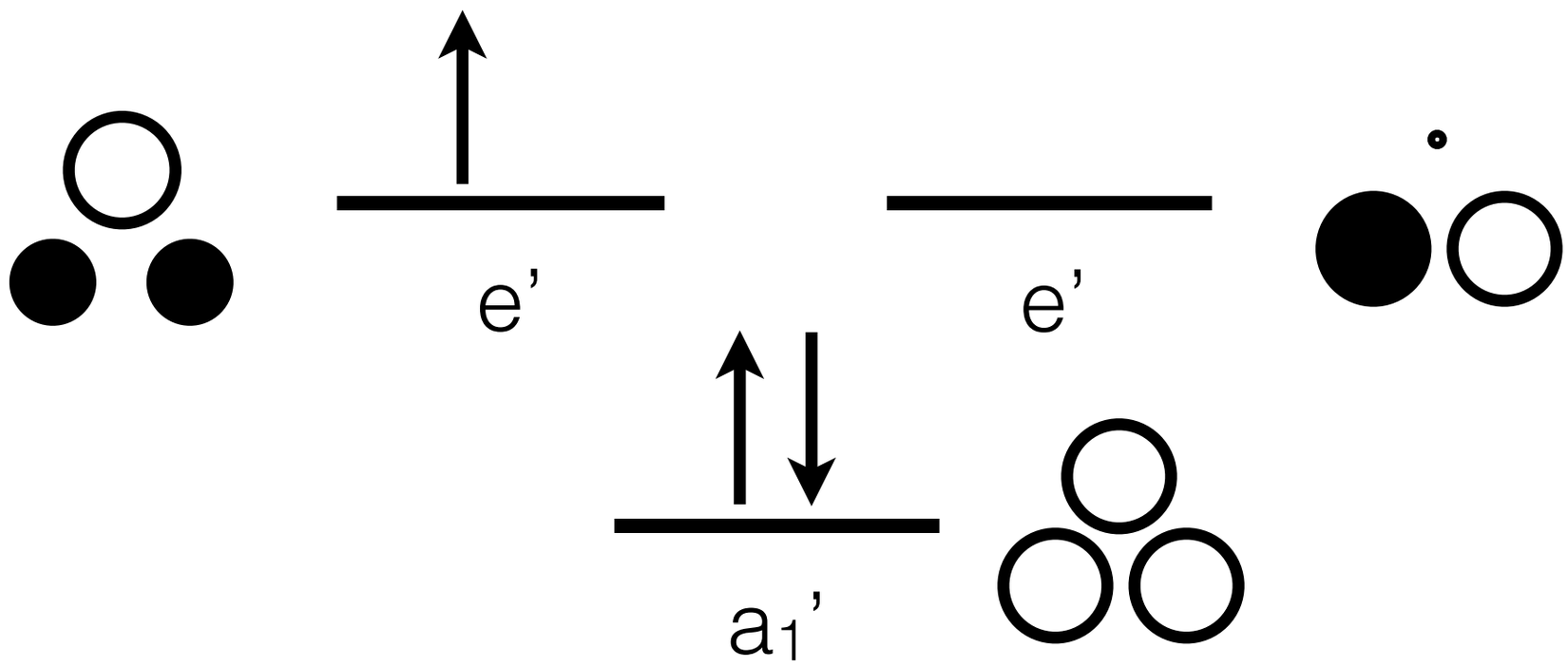

H3 FCI
H3 GCIS
H3 UCIS
Oscillator Strength
Energy / eV
0
0.2
0.4
0.6
0.8
1
12
14
16
18
20
22
24



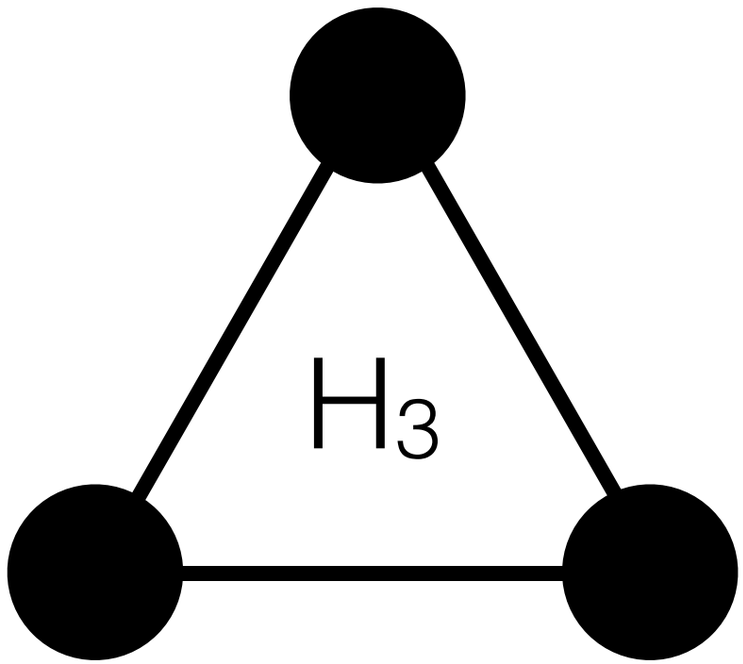
D_{3h}

Degenerate ground state

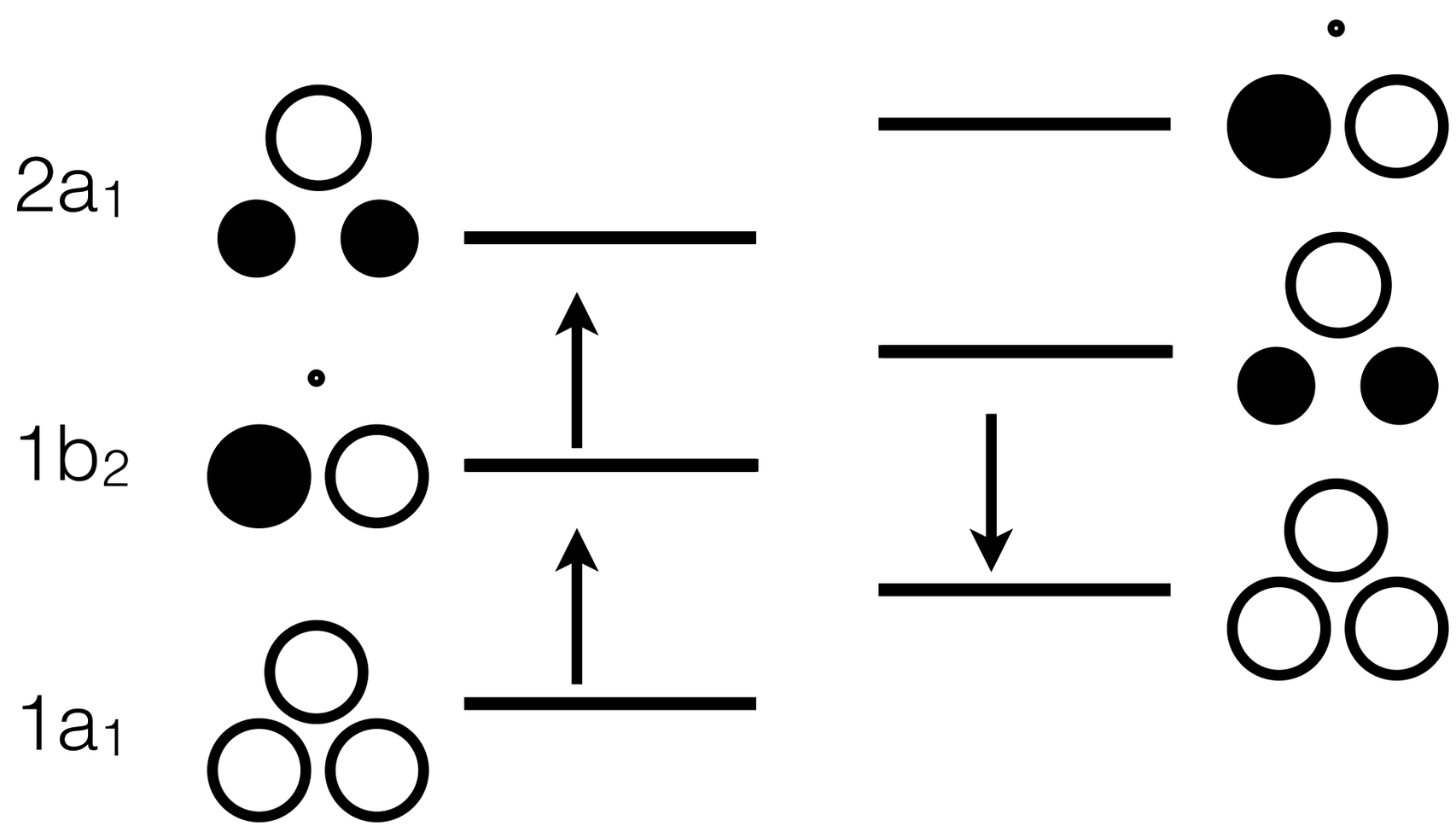
Full Configuration Interaction (FCI) captures this

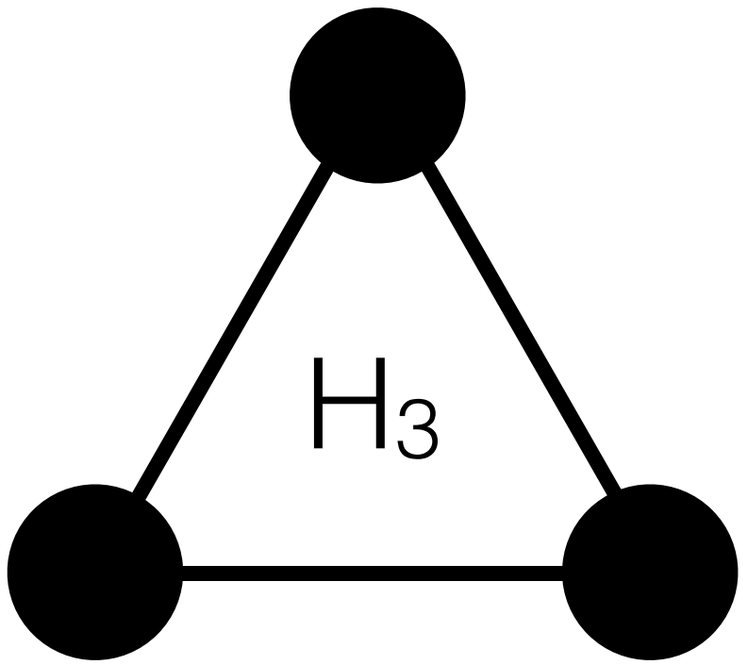


(+ other configuration)



UHF breaks the degeneracy,
spatial symmetry (C_{2v})





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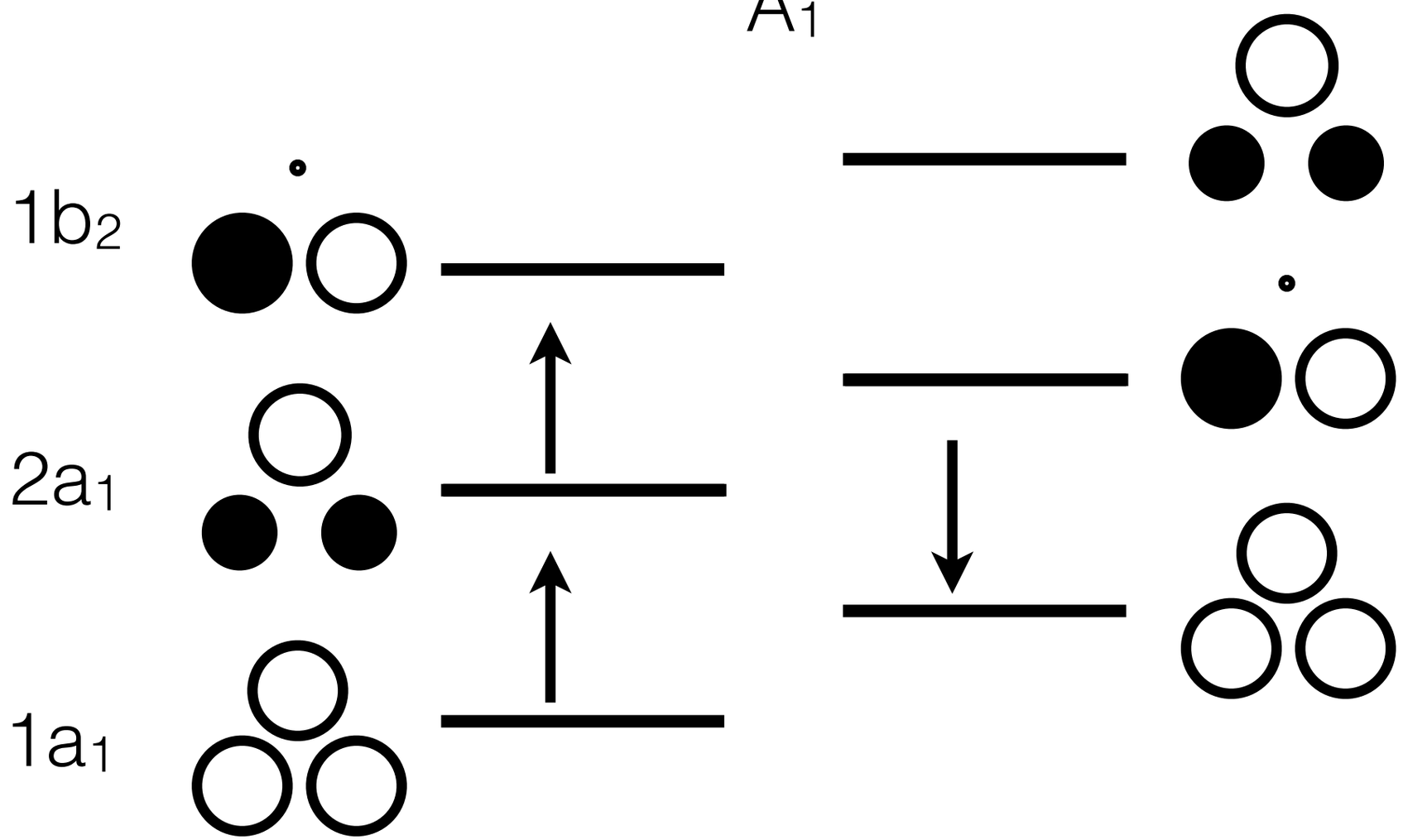
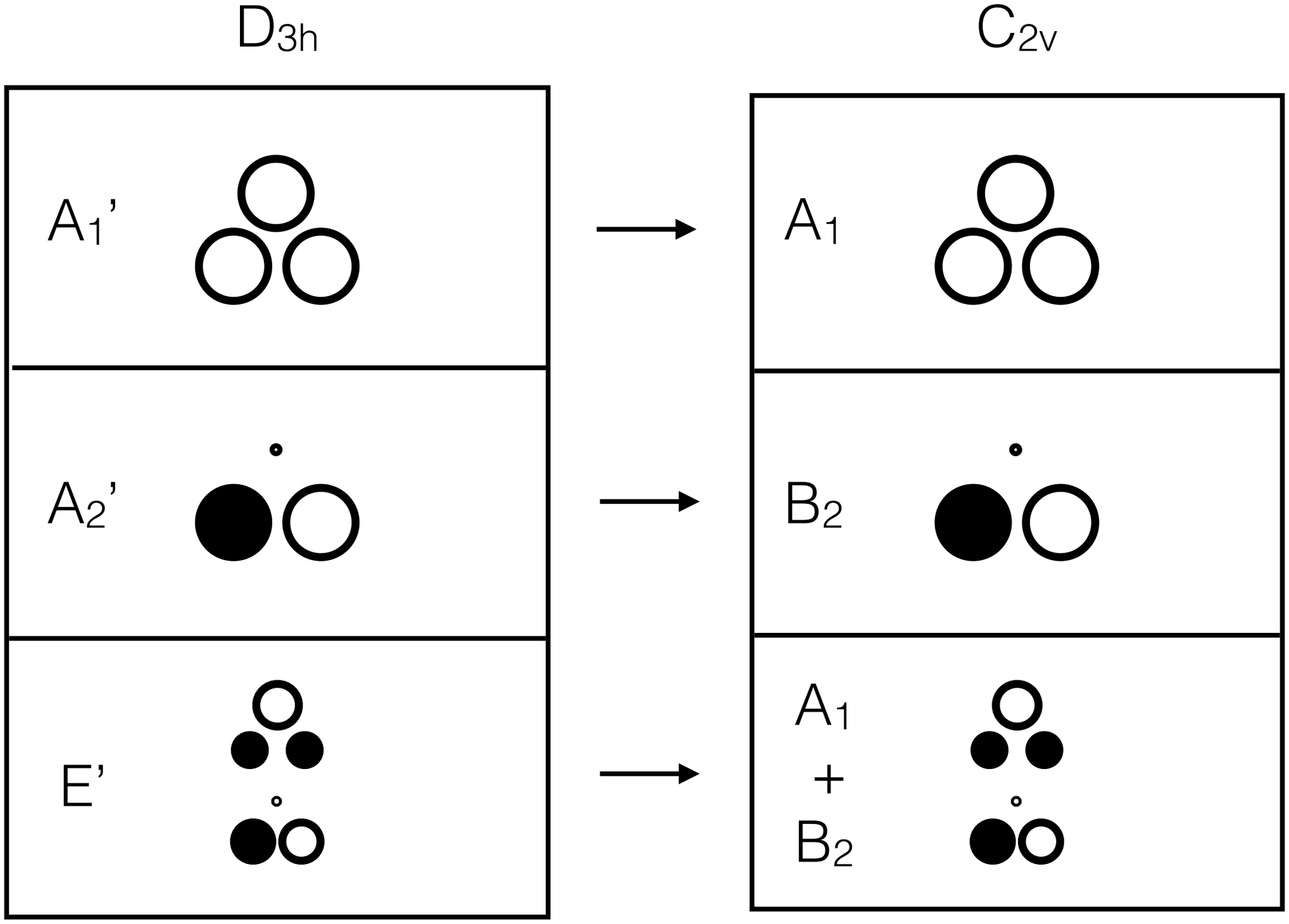


Of course, C_{2v} is a subgroup of D_{3h},
so we can relate the solutions



GHF orbital diagram
(approximate)

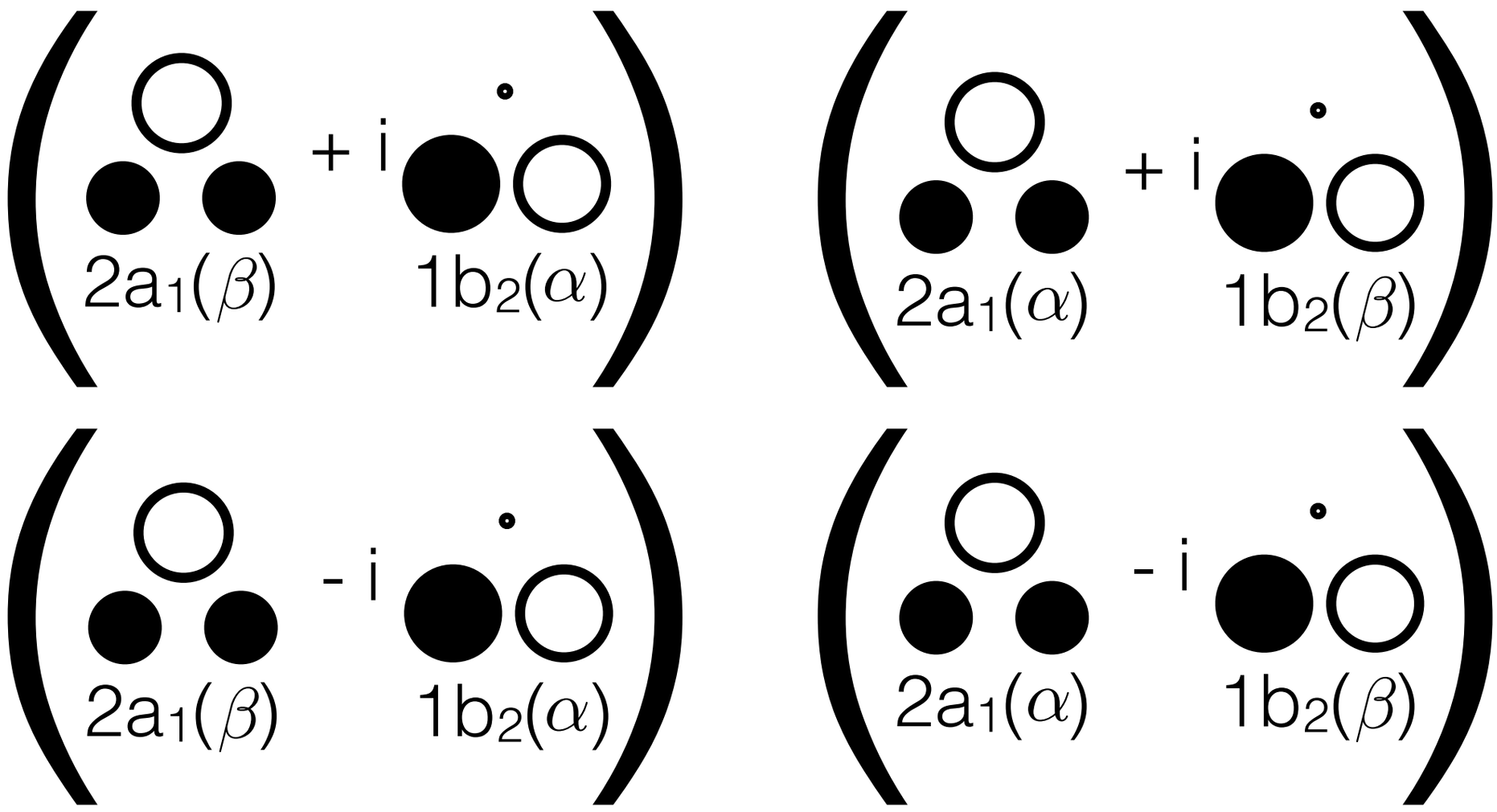
$2a_1(\beta)$ + i $1b_2(\alpha)$

$2a_1(\beta)$ - i $1b_2(\alpha)$, $2a_1(\alpha)$ - i $1b_2(\beta)$

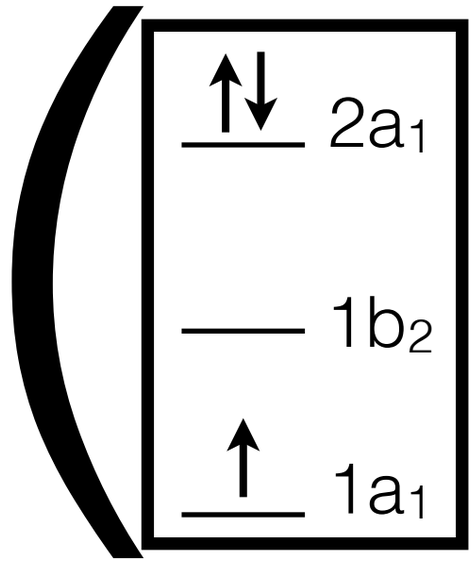
$2a_1(\alpha)$ + i $1b_2(\beta)$

$1a_1(\alpha)$, $1a_1(\beta)$

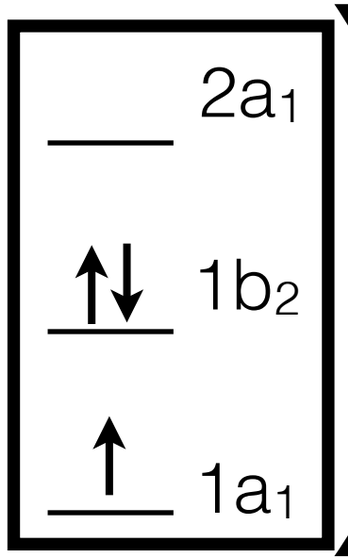
Four ‘almost’ e’ orbitals. Should be degenerate, but aren’t.



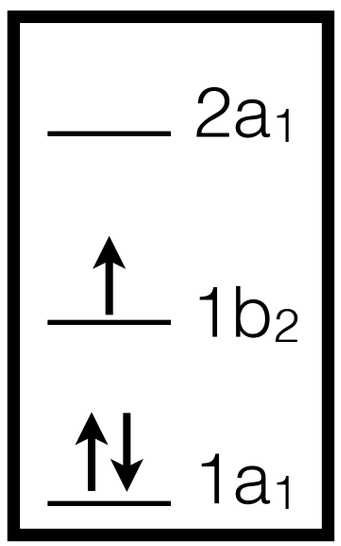
Why UCIS fails: example from FCI $1A_1$' state.

FCI $1A_1$' = N (

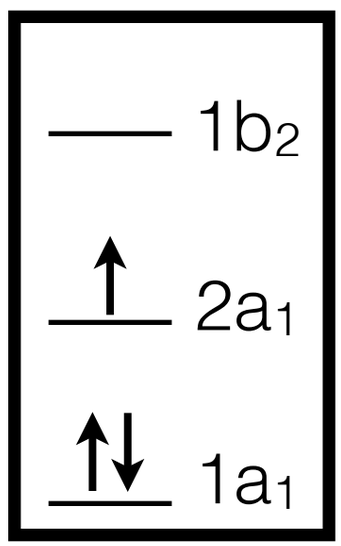
Single Ex from UHF A_1
Double Ex from UHF B_2

- 

Single Ex from UHF B_2
Double Ex from UHF A_1)

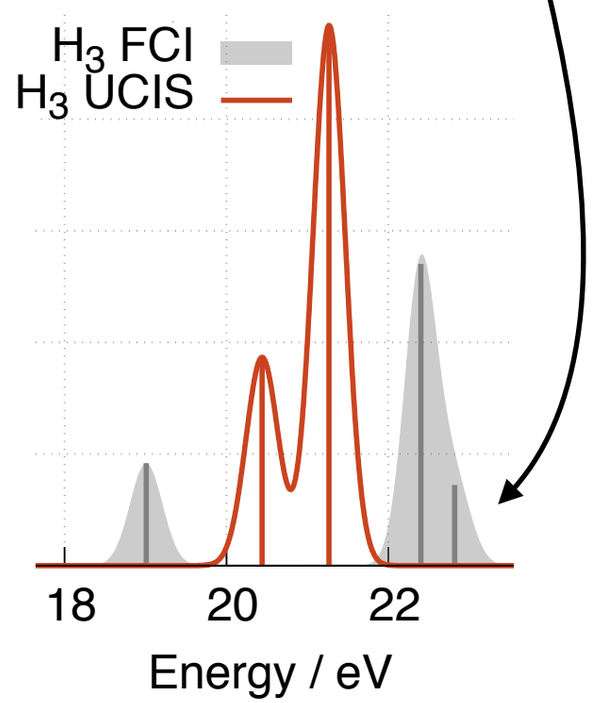


UHF B_2

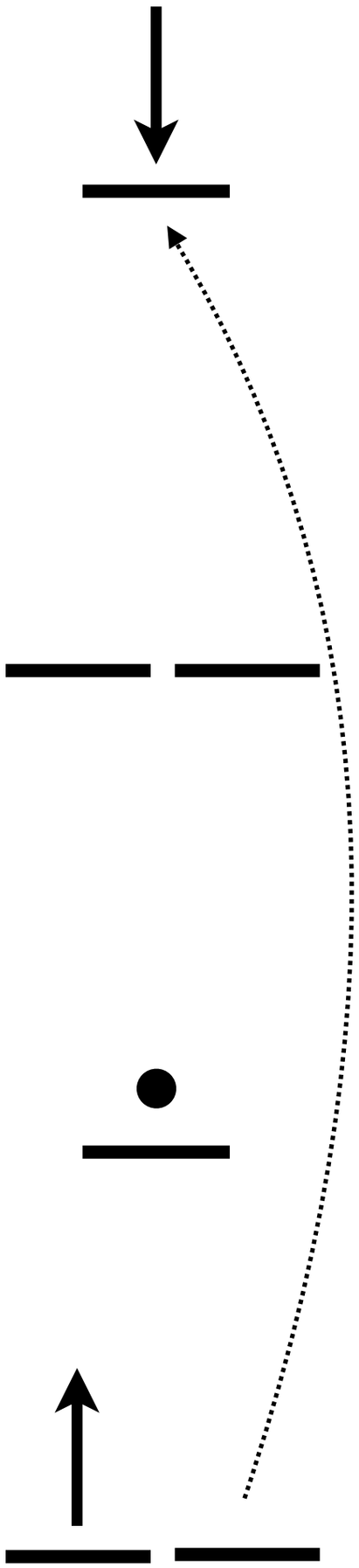


UHF A_1

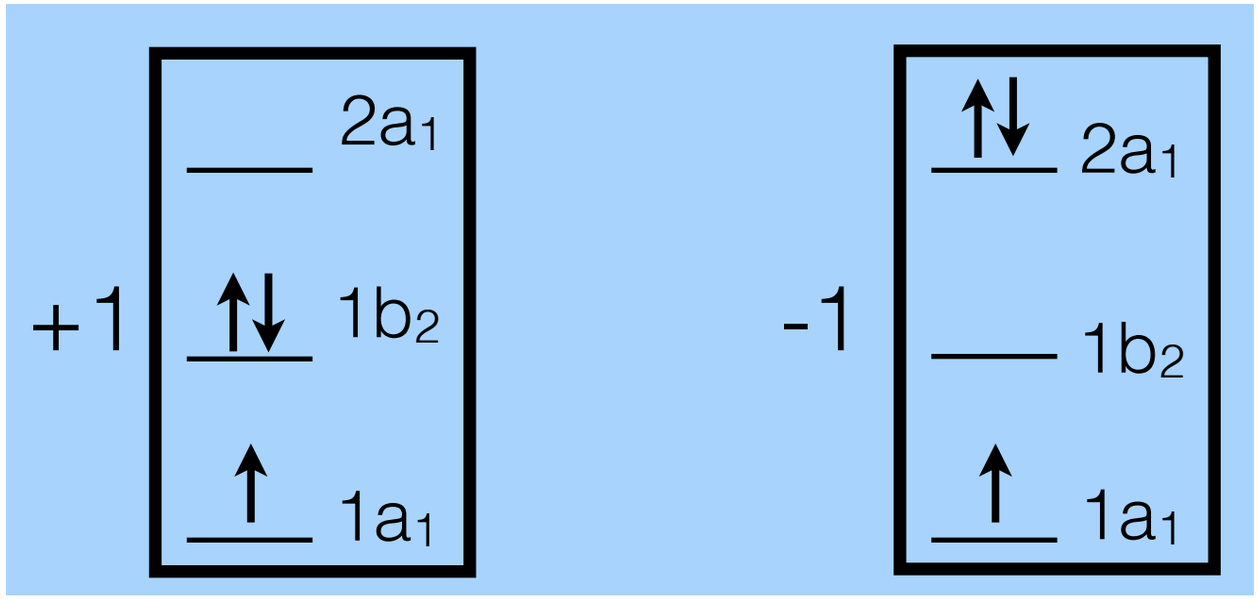
FCI state cannot be formed from single reference!



Consider a singly excited determinant out of GHF reference

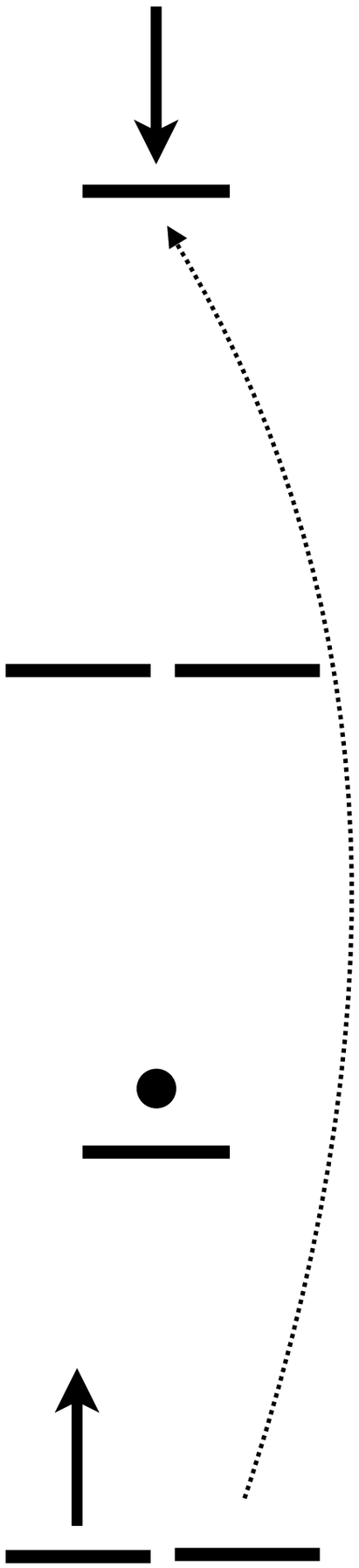


$$|\phi_6\phi_2\phi_3\rangle = -\frac{1}{2}|1a_1(\alpha)(2a_1(\beta) + ib_2(\alpha))(2a_1(\alpha) + ib_2(\beta))\rangle$$

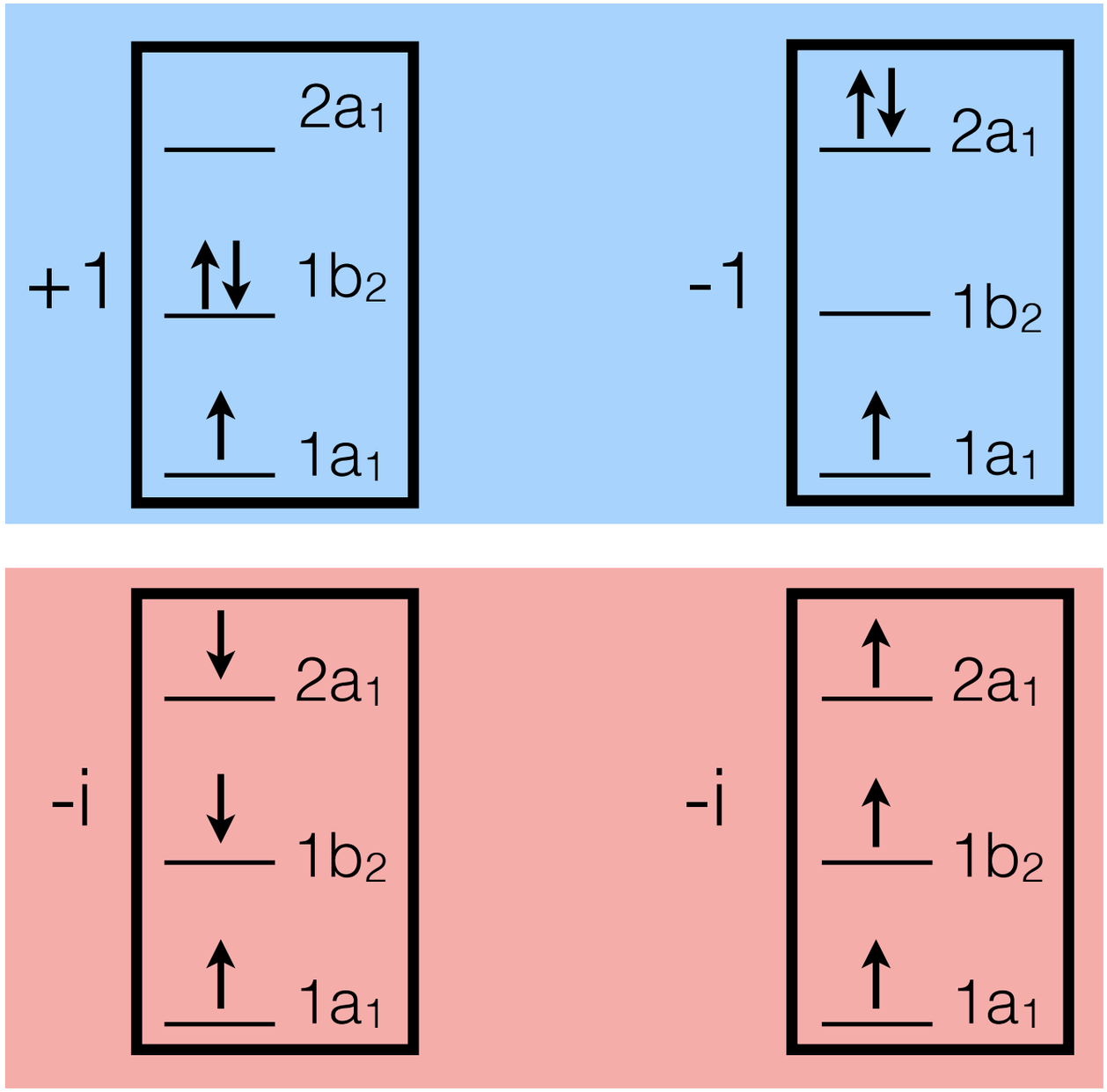


(M_s = 1/2)
Two configs
for FCI A_1

Consider a singly excited determinant out of GHF reference



$$|\phi_6\phi_2\phi_3\rangle = -\frac{1}{2}|1a_1(\alpha)(2a_1(\beta) + ib_2(\alpha))(2a_1(\alpha) + ib_2(\beta))\rangle$$



(M_s = 1/2)
Two configs
for FCI A_1

(M_s = 3/2, -1/2)

UHF won’t let you mix the things you need.

GHF gives you more flexibility,
but you better hope for some fortuitous cancellation.

Projecting out the higher spin determinants
is probably the best next step.

Jiménez-Hoyos, Carlos A., *et al*. "Projected Hartree–Fock theory." JCP 136 (2012) 164109.

Thank you

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UNIVERSITY of WASHINGTON

A far simpler case: BH molecule

BH, FCI/4-31G, 1.21Å		
ω (eV)	Osc. Str.	$\langle S^2 \rangle$
-25.1406986706	—	0.00
0.9600	0.0000	6.00
0.9600	0.0000	6.00
3.1671	0.0260	0.00
3.1671	0.0260	0.00

BH, UCIS/4-31G, 1.21Å		
ω (eV)	Osc. Str.	$\langle S^2 \rangle$
-25.0843428674	—	0.49
1.2910	0.0000	1.72
2.7892	0.0087	1.03
3.1739	0.0261	0.04
3.2511	0.0426	0.31

GHF no restriction on M_S, so 6 appx. $^3\Pi$ states

GHF maintains degeneracy of $^1\Pi$, compared to UCIS

BH, GCIS/4-31G, 1.21Å		
ω (eV)	Osc. Str.	$\langle S^2 \rangle$
-25.0849051758	—	0.55
0.4491	0.0000	—
0.7958	0.0000	—
0.7958	0.0000	—
1.3683	0.0000	—
1.3683	0.0000	—
2.7650	0.0090	—
3.2393	0.0330	—
3.2393	0.0330	—

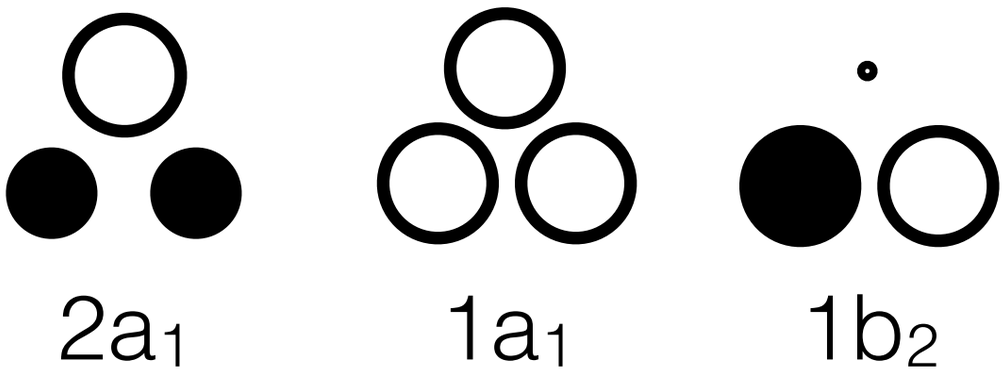
AVERAGE FCI STO-3G, C_{2v}		
Sym	ω (eV) / Osc. Str.	$\langle S^2 \rangle$
$A_1 + B_2$	-1.36438908 au	0.750
B_2	10.6389 / 0.0000	3.750
$A_1 + B_2$	19.0087 / 0.1835	0.750
B_2	22.4005 / 0.5407	0.750
A_1	22.8193 / 0.1446	0.750
$A_1 + B_2$	37.5085 / 0.0187	?

AVERAGE 'Full' UCIS STO-3G, C_{2v}		
Sym	ω (eV) / Osc. Str.	$\langle S^2 \rangle$
$A_1 + B_2$	-1.33320792 au	0.794
—	-0.2936 / 0.0000	—
—	0.3740 / 0.0000	—
$A_1 + B_2$	1.4073 / 0.005	0.850
—	9.7596 / 0.0000	—
B_2	13.2603 / 0.0265	2.530
—	16.4140 / 0.0000	—
—	20.1775 / 0.0000	—
A_1	20.4396 / 0.3730	0.750
B_2	21.2675 / 0.9677	0.917

GCIS STO-3G		
Sym	ω (eV) / Osc. Str.	$\langle S^2 \rangle$
?	-1.34044035 au	0.841
?	0.4667 / 0.0010	?
?	0.4667 / 0.0010	?
?	1.5260 / 0.0000	?
?	15.0002 / 0.0000	?
?	15.0459 / 0.0000	?
?	15.7552 / 0.0418	?
?	15.7552 / 0.0418	?
?	21.5224 / 0.5891	?
?	21.5224 / 0.5891	?

'Full' UCIS STO-3G, C_{2v}, B_2		
Sym	ω (eV) / Osc. Str.	$\langle S^2 \rangle$
B_2	-1.33598845 au	0.838
—	-0.3977 / 0.0000	—
—	0.7480 / 0.0000	—
A_1	2.2707 / 0.0077	0.750
—	9.8660 / 0.0000	—
B_2	13.4817 / 0.0240	2.531
—	16.7002 / 0.0000	—
—	20.2434 / 0.0000	—
A_1	20.7676 / 0.3832	0.750
B_2	21.4012 / 0.8952	0.793

'Full' UCIS STO-3G, C_{2v}, A_1		
Sym	ω (eV) / Osc. Str.	$\langle S^2 \rangle$
A_1	-1.32816998 au	0.750
—	-0.1895 / 0.0000	—
—	0.0000 / 0.0000	—
B_2	0.5438 / 0.0023	0.949
—	9.6532 / 0.0000	—
B_2	13.0389 / 0.0289	2.528
—	16.1277 / 0.0000	—
—	20.1116 / 0.0000	—
A_1	20.1116 / 0.3627	0.750
B_2	21.1337 / 1.0401	0.773


$2a_1$
$1a_1$
$1b_2$