Low-lying Electronic States of Molecules AB_n ($A = Sc - Ni$, $B = Cu/Ag/Au$, $n = 1, 2$)

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Outline

The d-Block Elements

3	4	5	6	7	8	9	10	11	12
$_{21}$**Sc**	$_{22}$**Ti**	$_{23}$**V**	$_{24}$**Cr**	$_{25}$**Mn**	$_{26}$**Fe**	$_{27}$**Co**	$_{28}$**Ni**	$_{29}$**Cu**	$_{30}$Zn
$_{39}$Y	$_{40}$Zr	$_{41}$Nb	$_{42}$Mo	$_{43}$Tc	$_{44}$Ru	$_{45}$Rh	$_{46}$Pd	$_{47}$**Ag**	$_{48}$Cd
La-Lu	$_{72}$Hf	$_{73}$Ta	$_{74}$W	$_{75}$Re	$_{76}$Os	$_{77}$Ir	$_{78}$Pt	$_{79}$**Au**	$_{80}$Hg
Ac-Lr	$_{104}$Rf	$_{105}$Db	$_{106}$Sg	$_{107}$Bh	$_{108}$Hs	$_{109}$Mt	$_{110}$Ds	$_{111}$Rg	$_{112}$Cn

$\rightsquigarrow$ **8** $\cdot$ **3** $=$ **24** heteronuclear diatomic molecules **AB**

$$\mathbf{A}\ (^{2S+1}L_J) + \mathbf{B}\ (^2S_{1/2}) \longrightarrow \mathbf{AB}\ (^{2S,2S+2}\Lambda_\Omega)$$

$$(2S+1 \geq 2,\ 0 \leq L \leq 3,\ 0 \leq \Lambda \leq L)$$

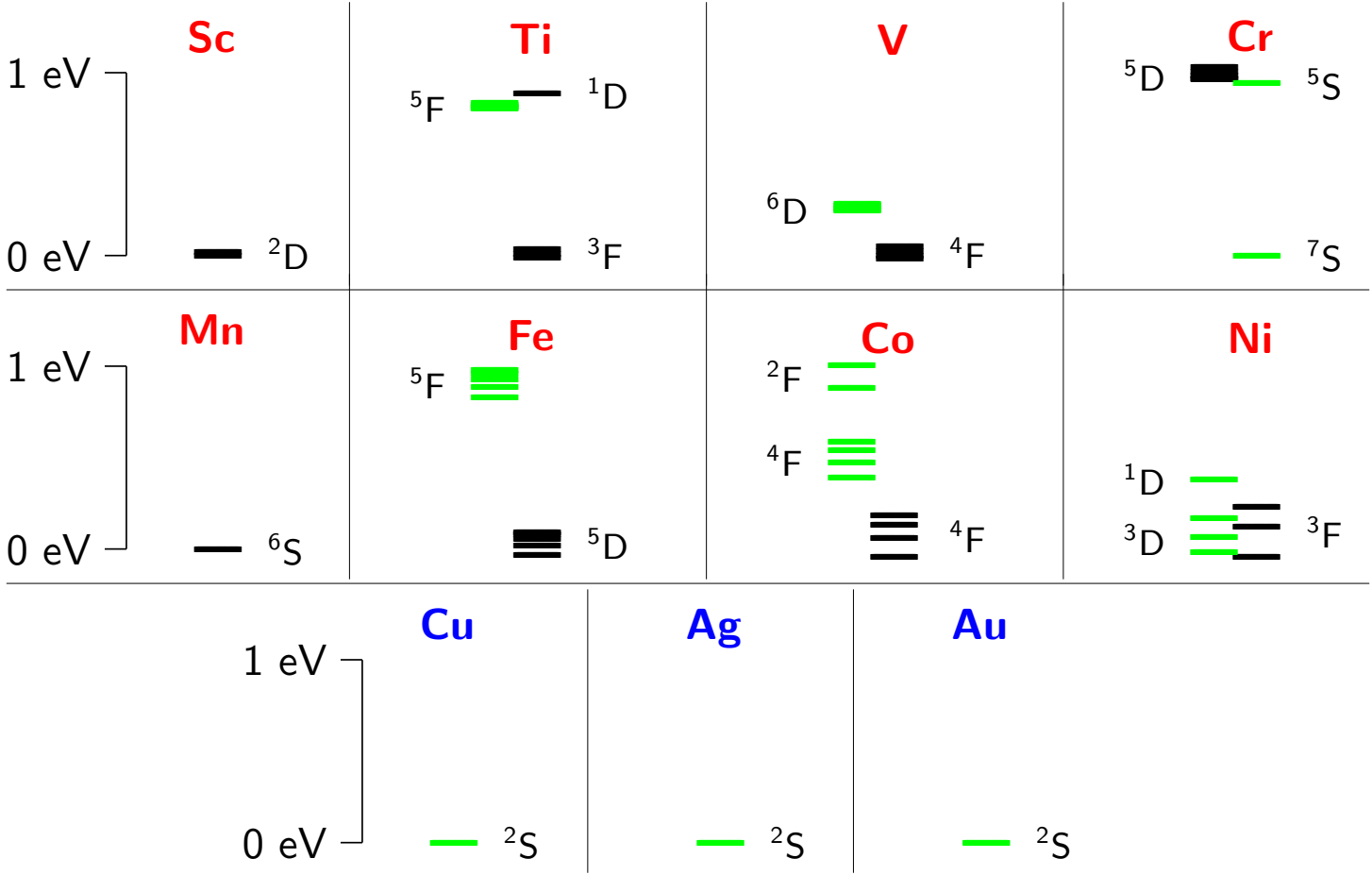
$\rightsquigarrow$ **8** $\cdot$ **3** $=$ **24** heteronuclear triatomic molecules $\mathbf{AB_2}$ (**A-B-B** and **B-A-B**)

Diatomic Molecules from d-Block Elements

- **24** heteronuclear diatomic molecules **AB** [1]
- Only about half of them are known from experiment (**CrCu**, **NiCu**, **CrAg**, **MnAg**, **NiAg**, [**Sc**–**Ni**]**Au**)
- Prototype models for
  – active centres in heterogeneous catalysis
  – chemical bonding in small metal atom clusters
- Challenges for theory:
  – electron correlation, relativity, QED (certainly in case of **Au** [2])
  – several (or many) low-lying electronic states

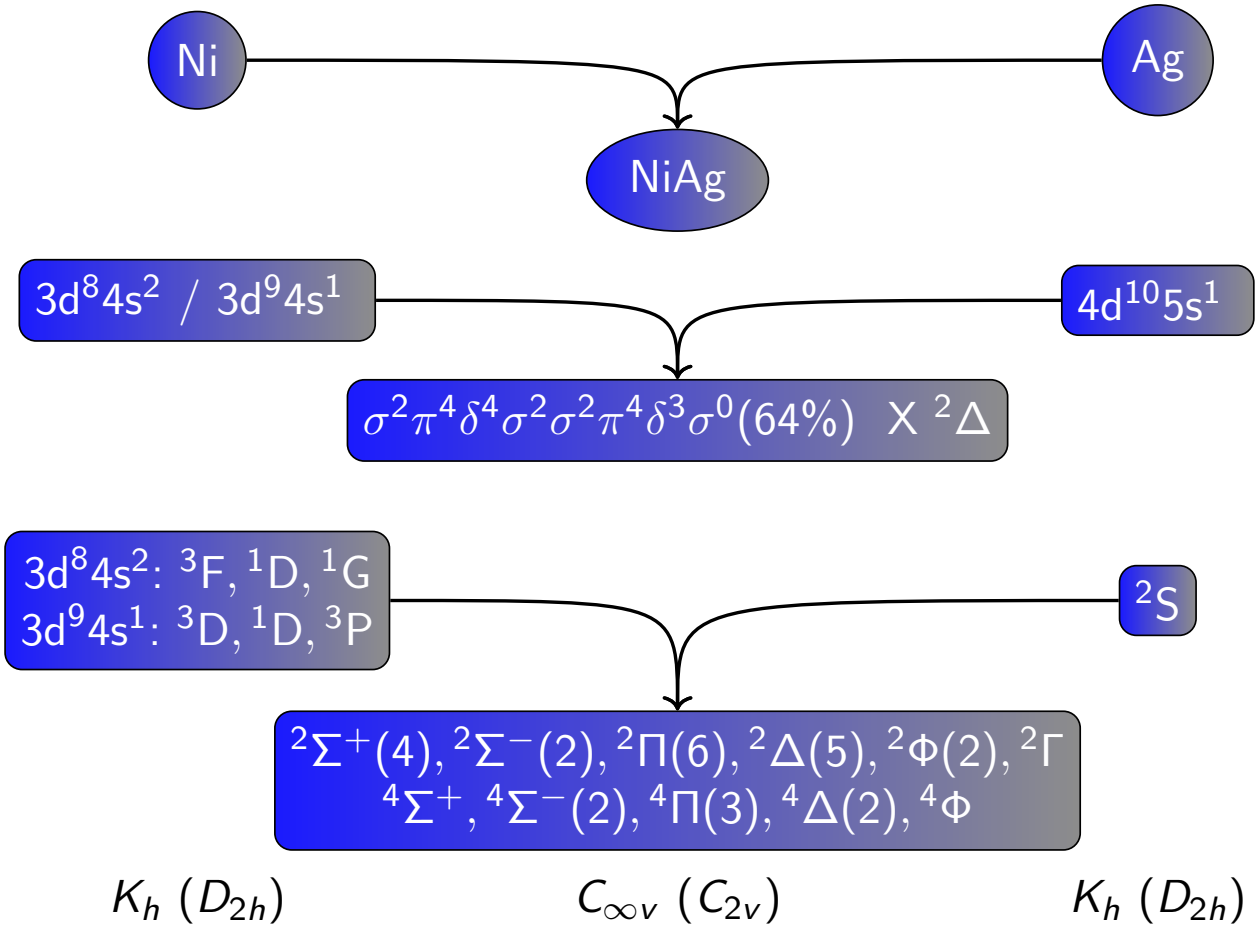
[1] D. Alizadeh Sanati, D. Andrae, submitted
[2] L. F. Pašteka *et al.*, *Phys. Rev. Lett.* **118** (2017) 023002

Lowest Atomic Terms ($T_e \leq 1$ eV)[1]



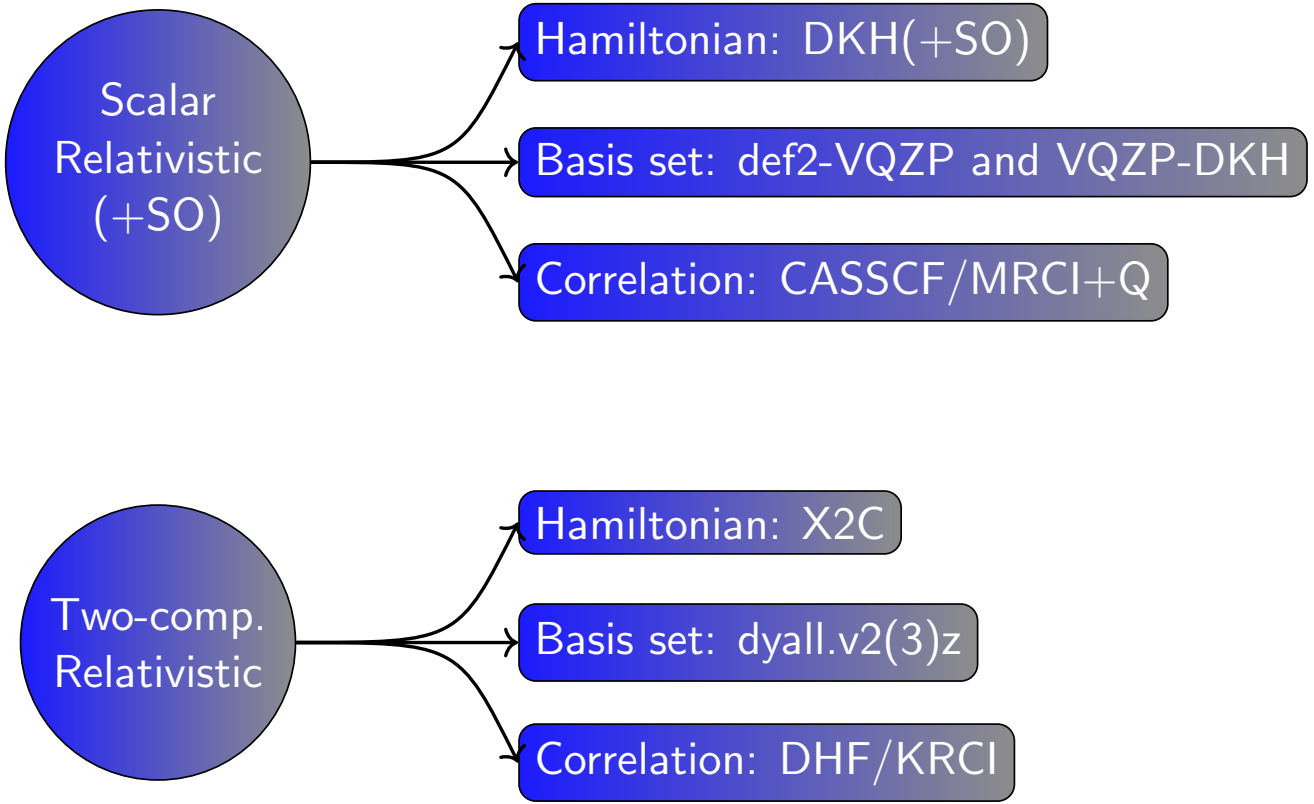
[1] Data source: NIST Atomic Spectra Database (**BLACK**: terms from $d^n s^2$; **GREEN**: terms from $d^{n+1} s^1$).

An Example: Configurations and Terms[1] for NiAg



[1] E. Wigner, E. E. Wittmer, *Z. Phys.* **51** (1928) 859

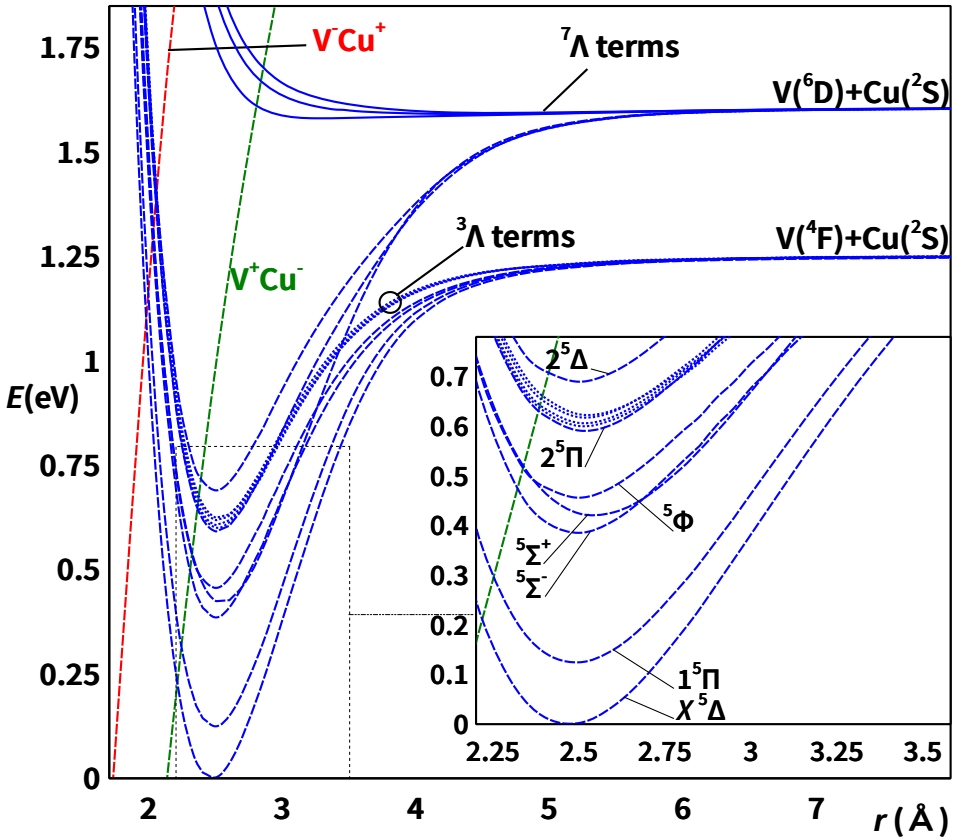
Methods[1]



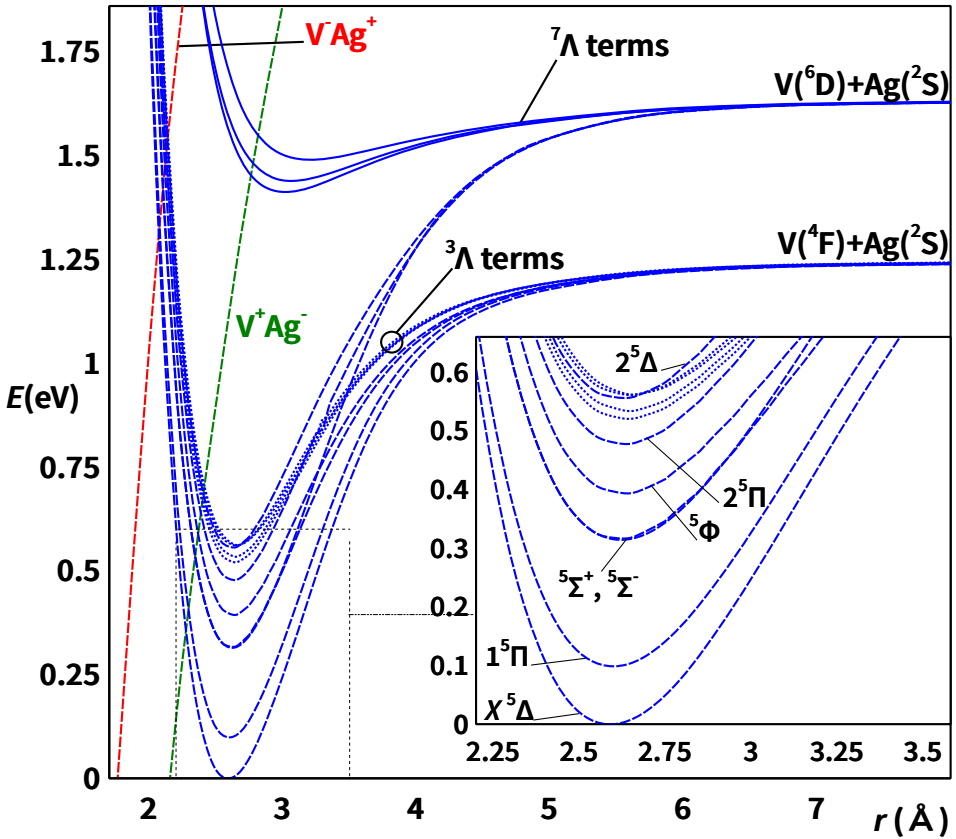
[1] Program packages used: MOLPRO, ORCA, DIRAC

Selected Results

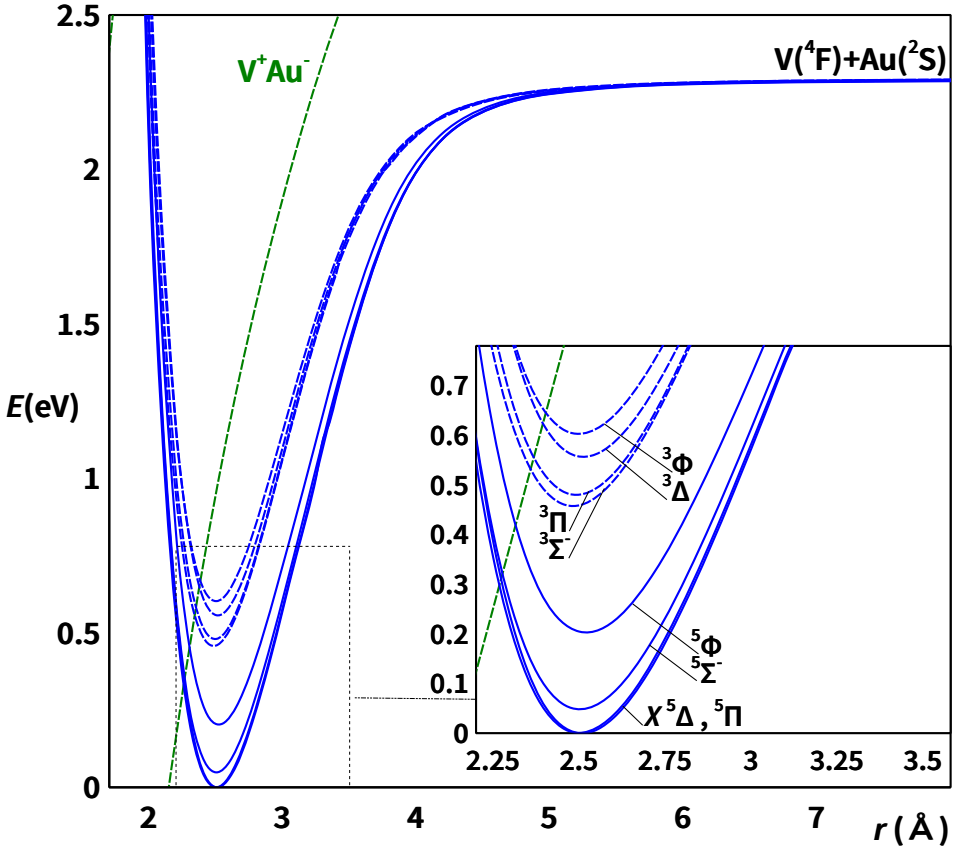
VCu / VAg / VAu (SR-MRCI+Q)



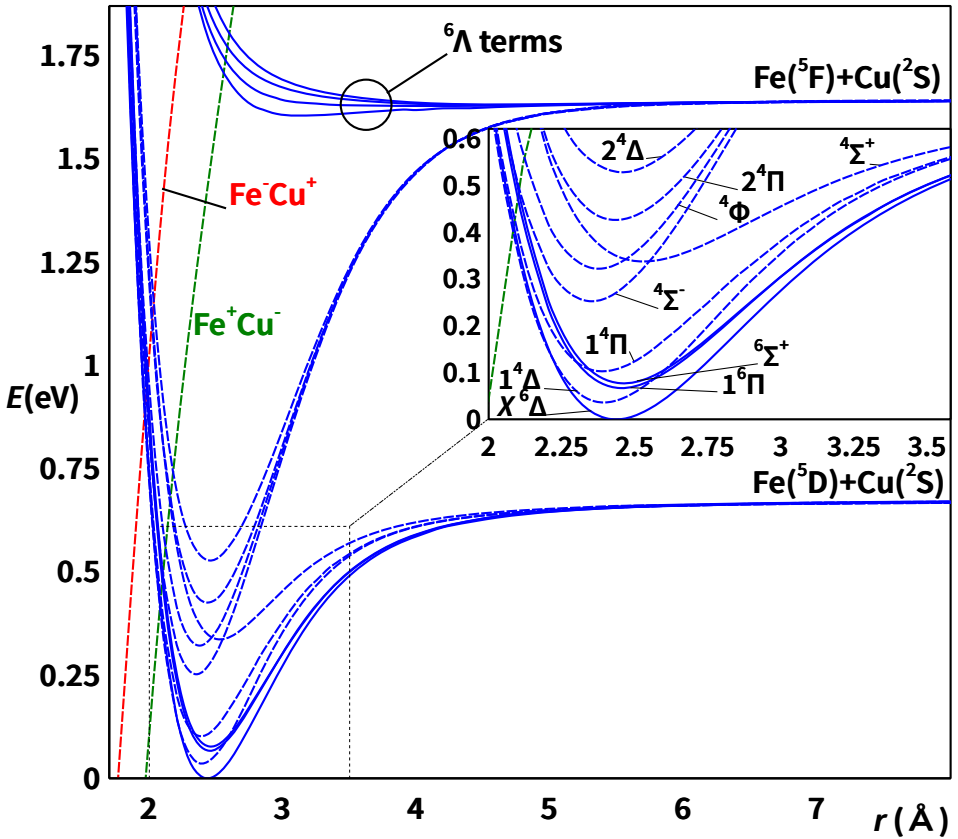
VCu / VAg / VAu (SR-MRCI+Q)



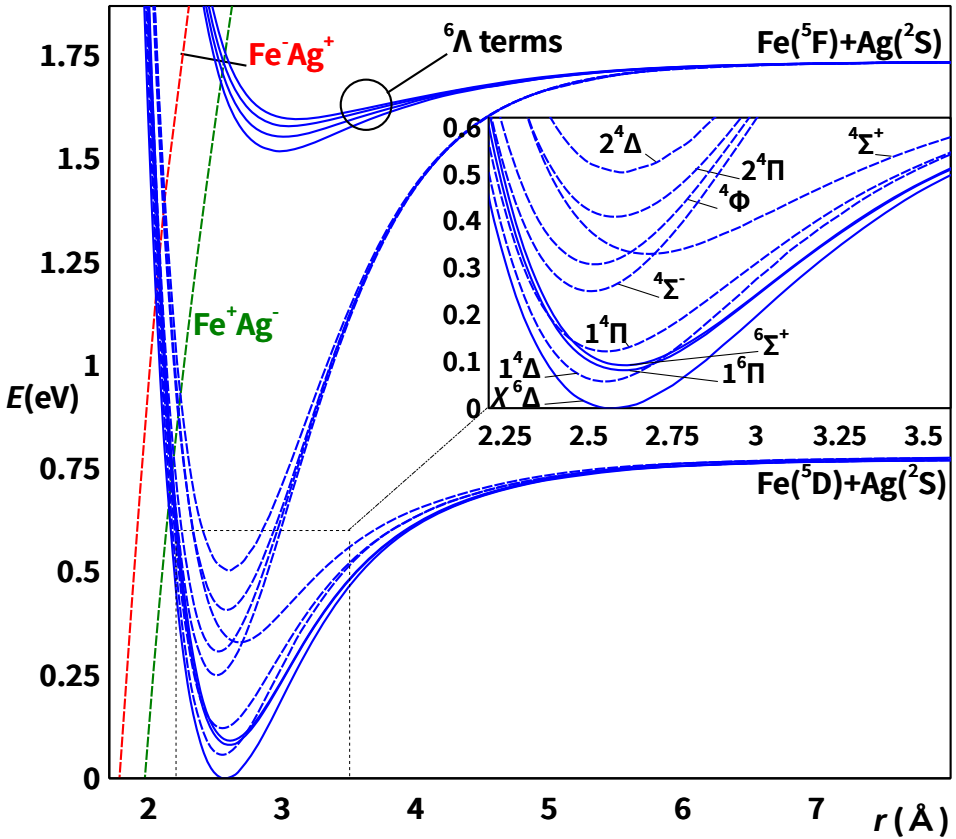
VCu / VAg / VAu (SR-MRCI+Q)



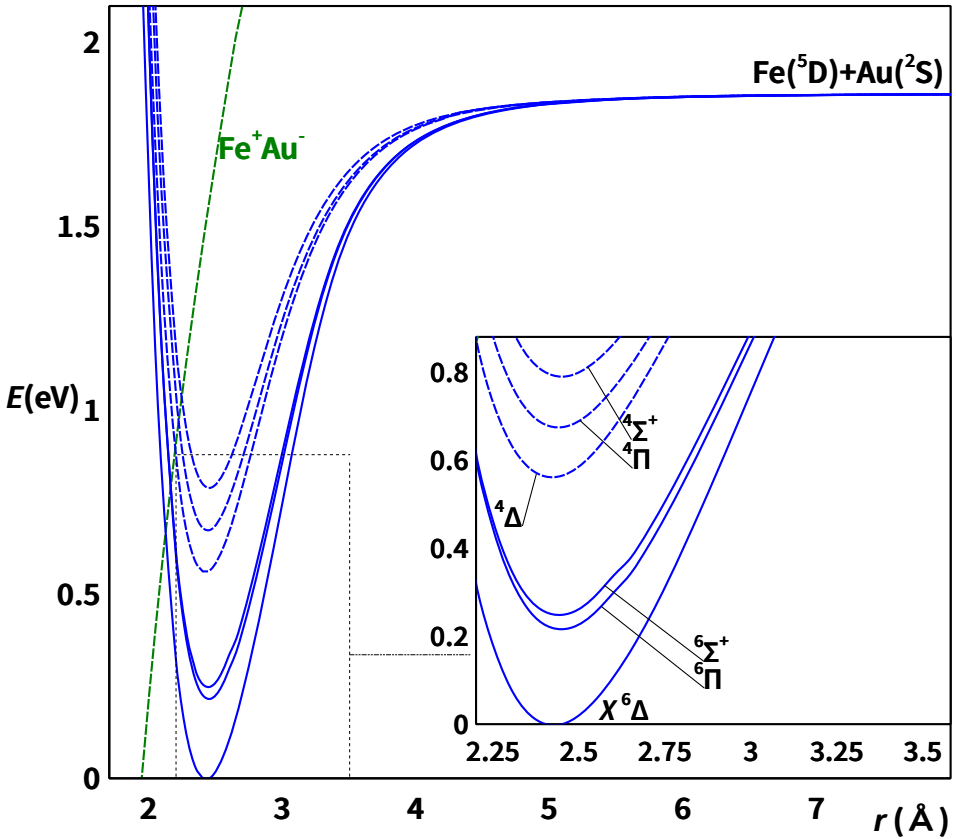
FeCu / FeAg / FeAu (SR-MRCI+Q)



FeCu / FeAg / FeAu (SR-MRCI+Q)

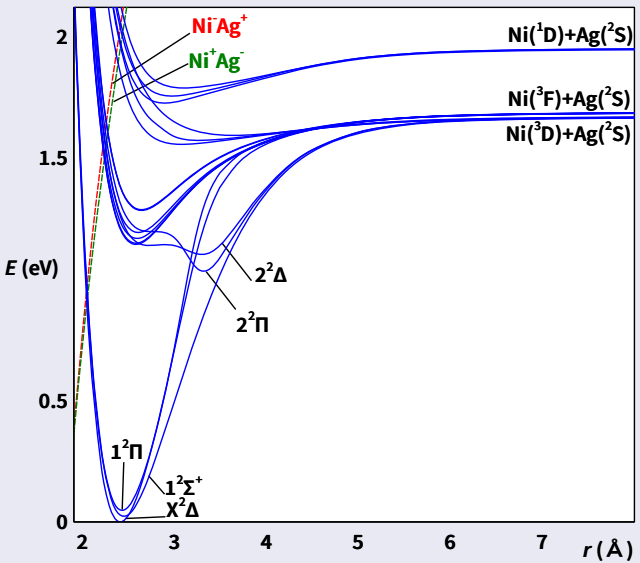


FeCu / FeAg / FeAu (SR-MRCI+Q)



NiAg: Role of Spin-Orbit Coupling

without SO coupling



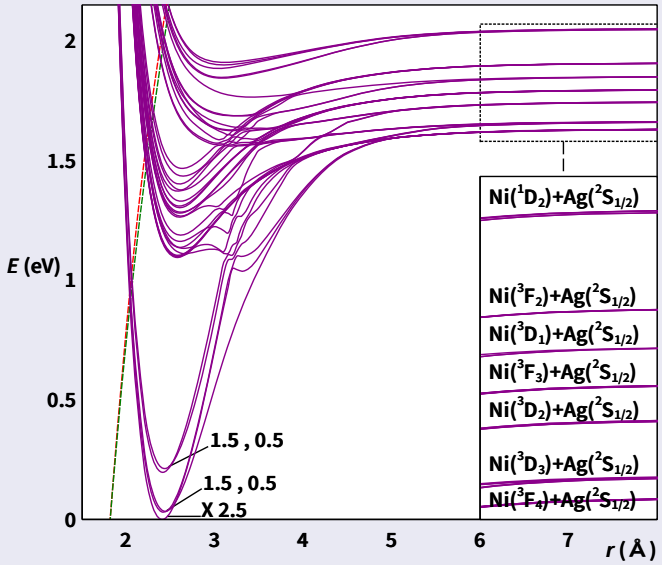
$X\ ^2\Delta$:

$r_e = 2.41$ Å

$\omega_e = 237.3\ \mathrm{cm}^{-1}$

$D_e = 1.68(^3\mathrm{F})$ eV

with SO coupling



$X\ ^2\Delta_{5/2}$:

$r_e = 2.40$ Å

$\omega_e = 234.1\ \mathrm{cm}^{-1}$

$D_e = 1.63(^3\mathrm{F}_4),\ 1.66(^3\mathrm{D}_3)$ eV

SO Coupling in Ground States

ACu	Ground State		
	$X^{2S+1}\Lambda^a$	$X^{2S+1}\Lambda_\Omega{}^b$	$X\Omega^c$
ScCu	$X^3\Delta$	$X^3\Delta_1$	$X1$
TiCu	$X^4\Phi$	$X^4\Phi_{3/2}$	$X3/2$
VCu	$X^5\Delta$	$X^5\Delta_0$	$X0$
FeCu	$X^6\Delta$	$X^6\Delta_{9/2}$	$X9/2$
CoCu	$X^3\Phi$	$X^3\Phi_4$	$X4$
NiCu	$X^2\Delta$	$X^2\Delta_{5/2}$	$X5/2$

[a] SR-MRCI / [b] SR-MRCI(+SO) / [c] X2C-KRCI

Ground States of AB

Element	Atom		Diatomic Molecules	
	A^0	**A**$^+$	**AB**	**AH**
Sc	$^2D_{3/2}$	$^3D_1$	$X^3\Delta_1$	$X^1\Sigma^+$
Ti	$^3F_2$	$^4F_{3/2}$	$X^4\Phi_{3/2}$	$X^4\Phi$
V	$^4F_{3/2}$	$^5D_0$	$X^5\Delta_0$	$X^5\Delta_{0^+}$
Cr	$^7S_3$	$^6S_{5/2}$	$X^6\Sigma^+_{5/2}$	$X^6\Sigma^+$
Mn	$^6S_{5/2}$	$^7S_3$	$X^7\Sigma^+_3$	$X^7\Sigma^+$
Fe	$^5D_4$	$^6D_{9/2}$	$X^6\Delta_{9/2}$	$X^4\Delta_{7/2}$
Co	$^4F_{9/2}$	$^3F_4$	$X^3\Phi_4$	$X^3\Phi_4$
Ni	$^3F_4$	$^2D_{5/2}$	$X^2\Delta_{5/2}$	$X^2\Delta_{5/2}$

Summary on AB

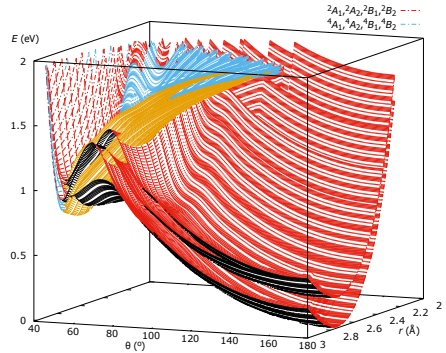
- Low-lying states of **24** heteronuclear diatomic molecules **AB** [1] (**A** = Sc–Ni, **B** = Cu/Ag/Au)
- $>$ **200** potential energy curves (ΛS coupling) (r_e, ω_e, $\omega_e x_e$, D_e, ...)
- Spin-orbit coupling: *a posteriori* (perturbative) / *a priori*
  - DKH + CASSCF + MRCI (+ SO): atoms, diatomic molecules **AB**
  - X2C + DHF + KRCI: atoms, diatomic molecules **ACu**

  SO coupling largely quenched in **AB** ground states
- D_e(**AAu**) $>$ D_e(**A**[**Cu**/**Ag**])
- "Mapping" between electronic ground states: $\mathbf{A}^+$ ($^{2S+1}L_J$) $\leftrightarrow$ **AB** ($^{2S+1}\Lambda_\Omega$, $\Lambda = L$, $\Omega = J$)

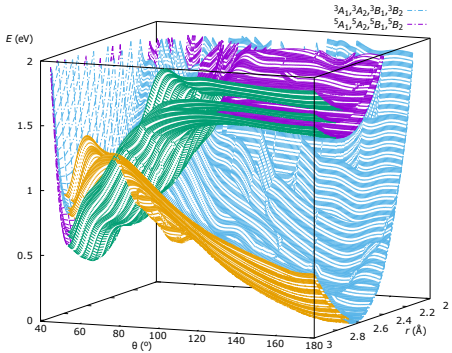
[1] D. Alizadeh Sanati, D. Andrae, submitted

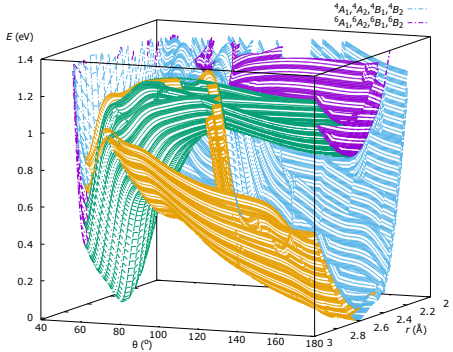
Ag(Sc/Ti/V/Cr)Ag

AgScAg

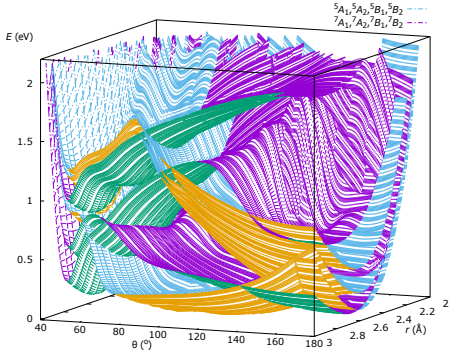


AgTiAg





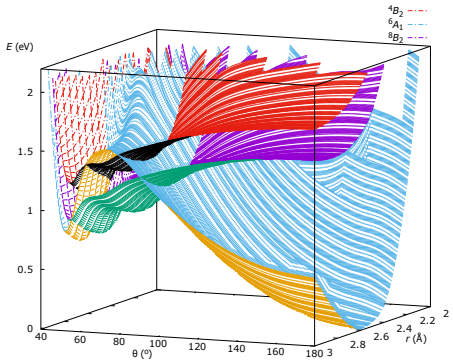
AgVAg



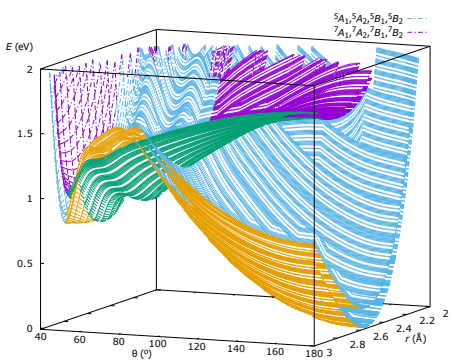
AgCrAg

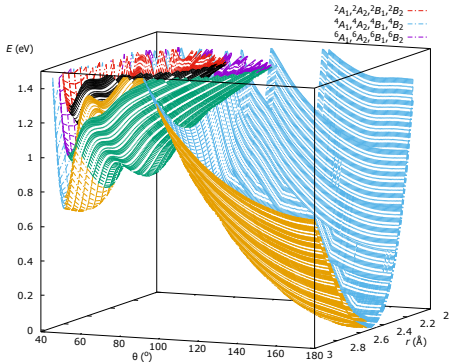
Ag(Mn/Fe/Co/Ni)Ag

AgMnAg

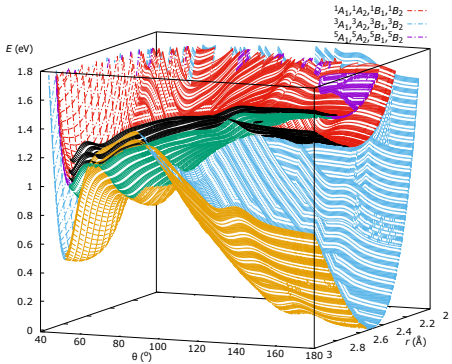


AgFeAg





AgCoAg



AgNiAg

Acknowledgments: DAAD, ZEDAT/HPC (FU Berlin)

Thank you very much for your attention!