Need for full calculations of electronic structure

SEMIEMPIRICAL QUANTUM CHEMISTRY APPROACH

❖Method based on the CIPSI package (Configuration Interaction by Perturbation of a multiconfiguration wave function Selected Iteratively, Laboratoire de Physique Quantique, Toulouse, France). (B. Huron et al., J. Chem. Phys. **58**, 5745, (1973), coll. F. Spiegelman)

❖ Atom/Ion treated as an effective one-electron system: Use of **ECPs (Effective core potentials or pseudopotentials)** with ℓ–dependent **CPPs (core-polarization potentials)** with parameters fitted on atomic energy spectra of the one-electron system

❖[ECP+CPP+1e$^-$]+[ECP'+CPP'+1e$^-$]: exact energy at R=∞

❖**Full Configuration Interaction (FCI)** to determine the structure of the dimer, considered as an effective two/three-electron polarizable system

❖ Automated calculations and data treatment for ALL Pairs, ALL symmetries, ALL interatomic distances, ALL transitions

❖ Convergence and accuracy checked against size of basis sets, and through detailed comparison with other methods

Typical sizes of FCI matrices:
From ~1000x1000 (A-Sr$^+$)
up to 10^5x10^5 (A-Sr)

Sr energy levels (cm^{-1})

	Exp	(a)		(b)		Exp	(a)		(b)	
	E_b^{exp}	E_b	δ_b	E_b	δ_b	E_e^{exp}	E_e	δ_e	E_e	δ_e
$5s^2\,^1S$	-0.61464148	-0.615471	-182	-0.615484	-184	0	0	0	0	0
$5s5p\,^3P^o$	-0.54765155	-0.548880	-269	-0.548899	-273	14702.6	14613	-87	14613	-88
$5s4d\,^3D^e$	-0.53147099	-0.529868	351	-0.529907	343	18253.7	18779	533	18781	528
$5s4d\,^1D^e$	-0.52283208	-0.520684	471	-0.520733	460	20149.7	20793	653	20795	645
$5s5p\,^1P^o$	-0.51577530	-0.517756	-434	-0.517792	-442	21698.5	21447	-252	21440	-257