

## 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  $\ell$ -dependent CPPs (core-polarization potentials) with parameters fitted on atomic energy spectra of the one-electron system

❖ [ECP+CPP+1e<sup>-</sup>]+[ECP'+CPP'+1e<sup>-</sup>]: 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

Sr energy levels (cm<sup>-1</sup>)

Typical sizes of FCI matrices:  
From ~1000x1000 (A-Sr<sup>+</sup>)  
up to 10<sup>5</sup>x10<sup>5</sup> (A-Sr)

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