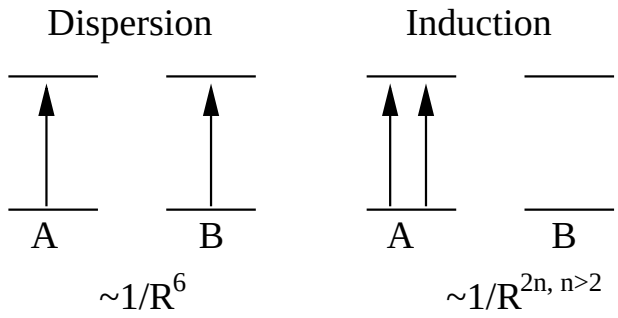
Intermolecular Interactions and VB

Peter Reinhardt

Laboratoire de Chimie Théorique, Université Pierre et Marie Curie,
75252 Paris CEDEX 05, France
email: Peter.Reinhardt@upmc.fr

Symmetry-adapted perturbation theory

- Single Slater determinant: HF, DFT
- 3 series: $E_{\text{int}} = \sum_{ijk} E_{\text{pol}}^{(ijk)} + E_{\text{exch}}^{(ijk)}$
- Extension to several references: MCSCF, VB, BOVB
- Electrostatics, 2nd order Induction and Dispersion



- Replace excitations by transition dipoles
- Example N_2O
- Virtual orbitals? UHF matrices for each determinant

Dispersion : $E_{\rm pol}^{(200)}$

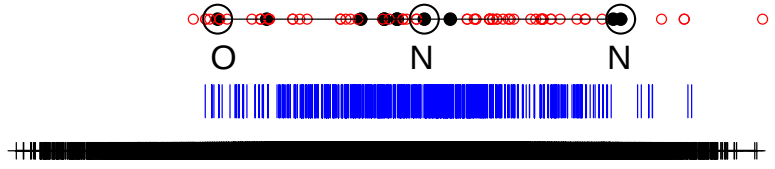
$$E_{\rm MP2} \;=\; \frac{1}{4}\sum_{iajb}\frac{\left((ia|jb)-(ib|ja)\right)^2}{\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b}$$

becomes in spin-orbitals

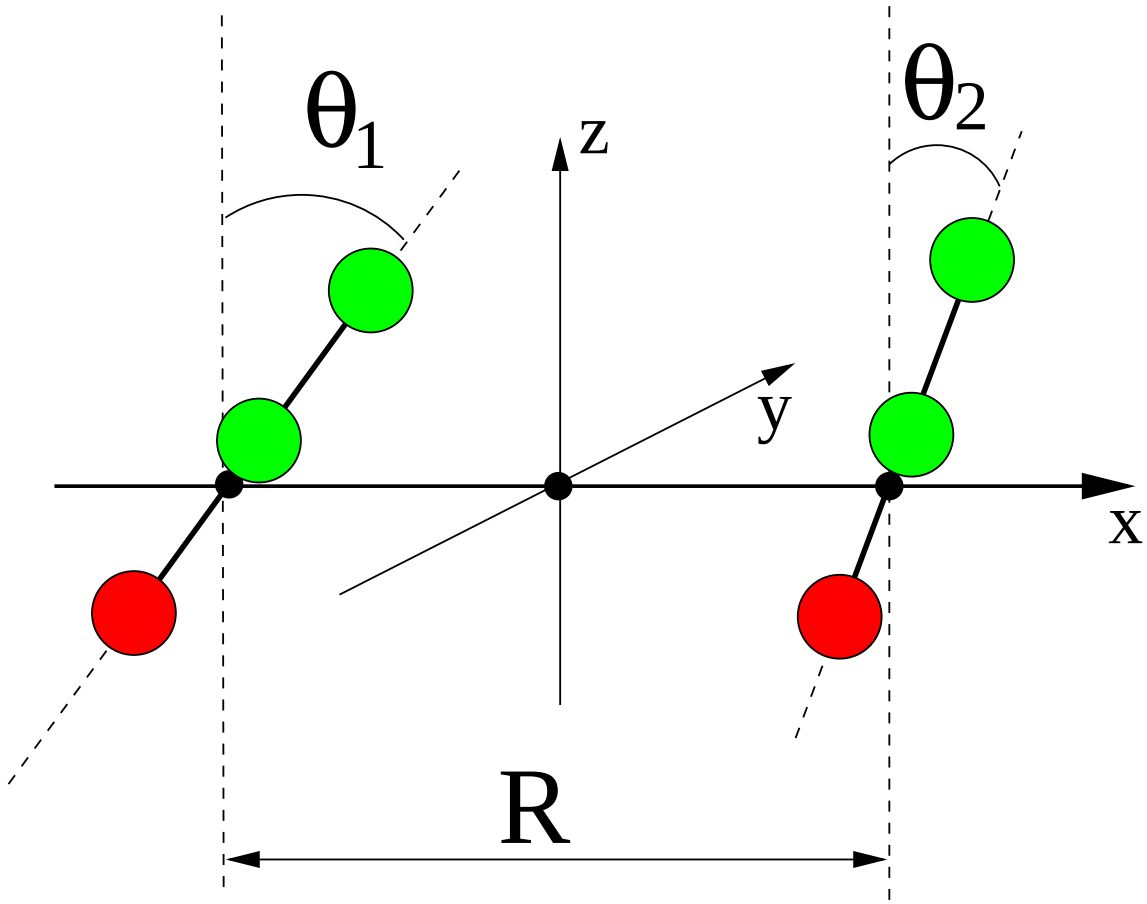
$$E_{\rm MP2}^{\rm disp} \;\approx\; \sum_{i,a\in A}\sum_{j,b\in B}\frac{(ia|jb)^2}{\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b}$$

Approximate

$$(ia|jb) \;\longrightarrow\; \frac{\vec{\mu}_{i\to a}\cdot\vec{\mu}_{j\to b}}{R_{AB}^3}-3\,\frac{(\vec{\mu}_{i\to a}\cdot\vec{\mathrm{R}}_{AB})(\vec{\mu}_{j\to b}\cdot\vec{\mathrm{R}}_{AB})}{R_{AB}^5}\sim\frac{1}{R_{AB}^3}$$

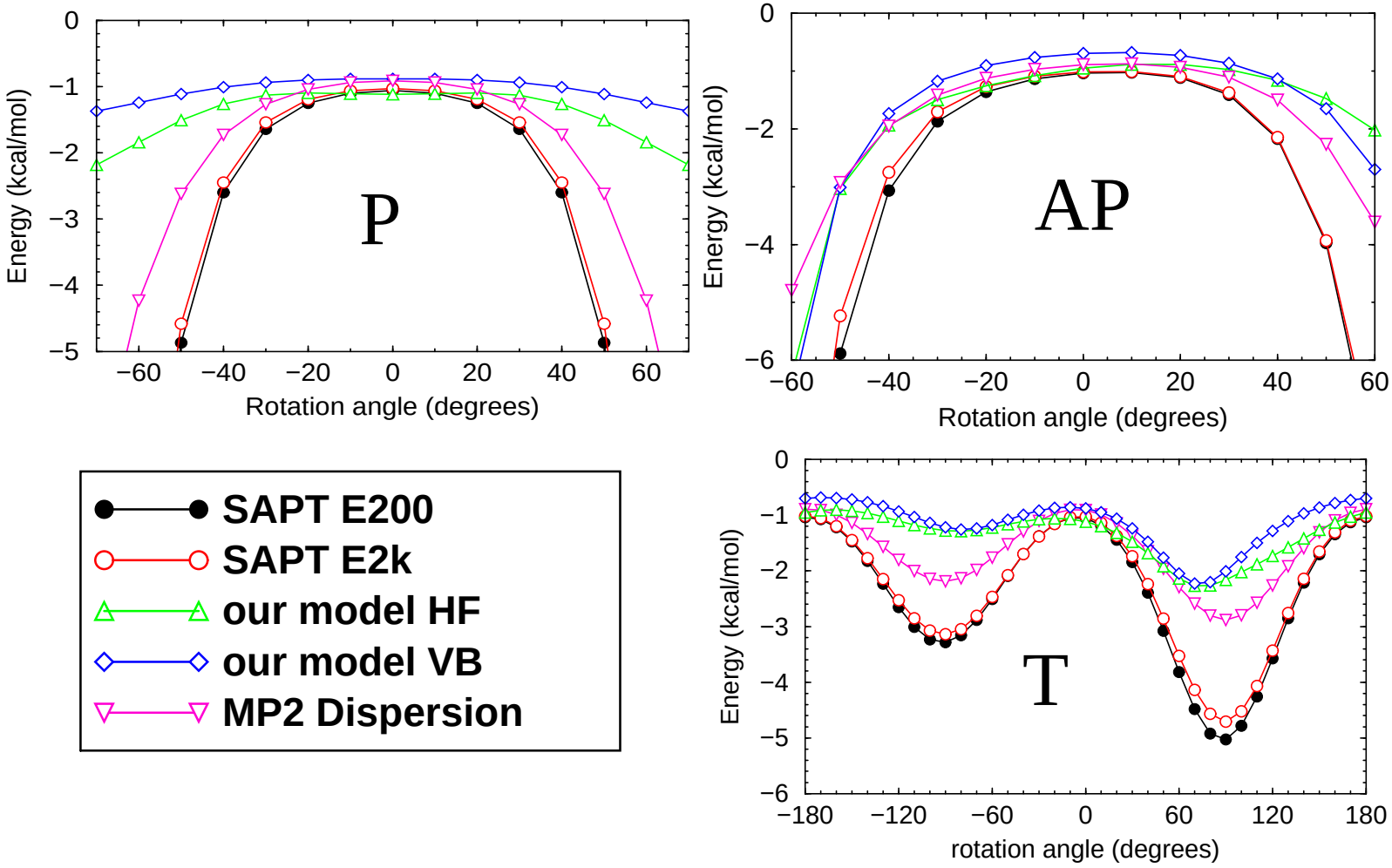


On to work



3 geometry variations: Parallel, Anti-Parallel, rotation of one only (T)

Dispersion : $E_{\rm pol}^{(200)}$



P. Reinhardt, Comp.Theor.Comput., (2017) in press