Using Symmetry-Adapted Perturbation Theory (SAPT) in Psi4

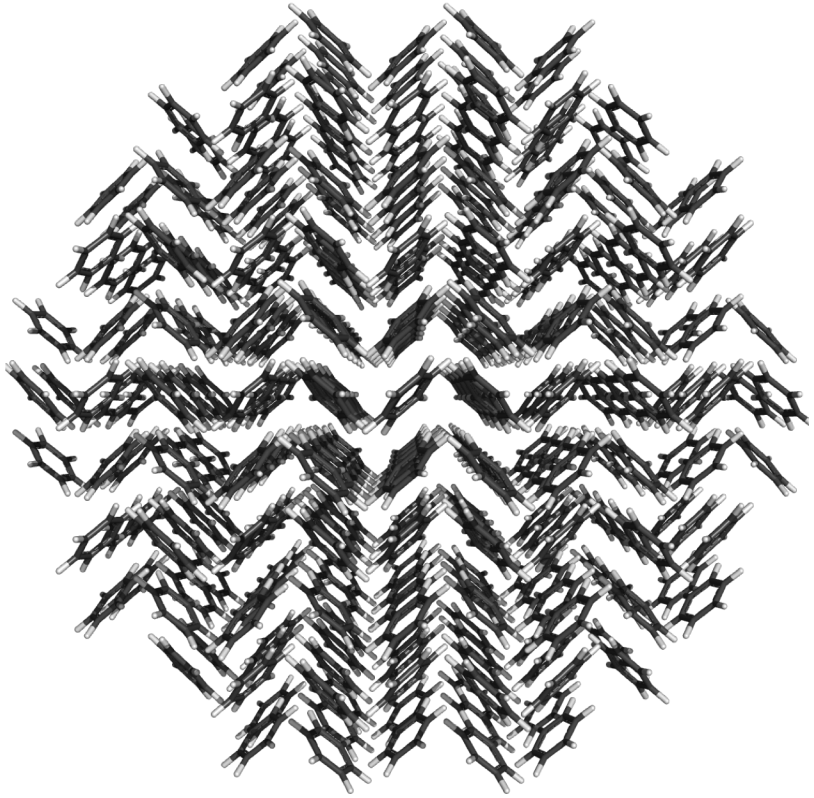
Zach Glick

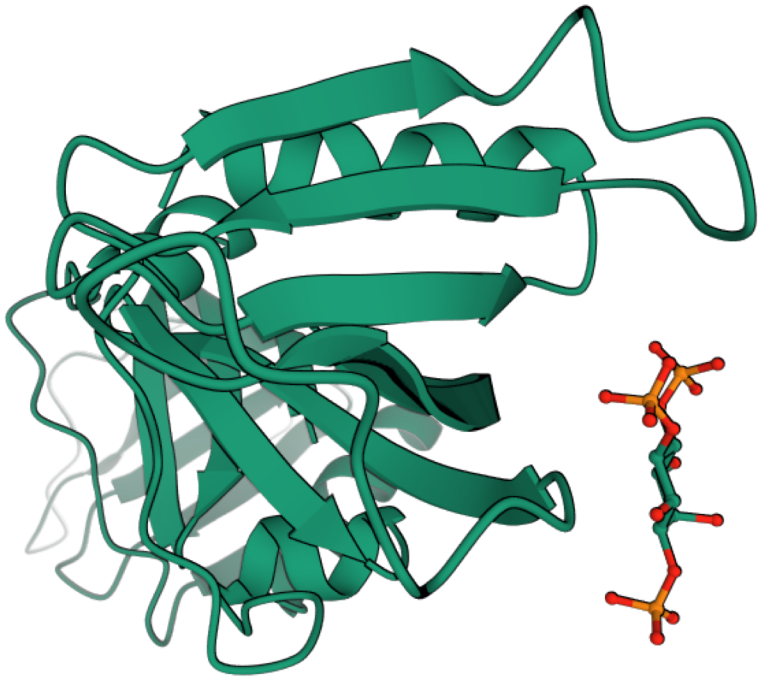
Georgia Tech

PsiCon 2020

What Is SAPT?

A method in electronic structure theory for calculating **non-covalent interactions**

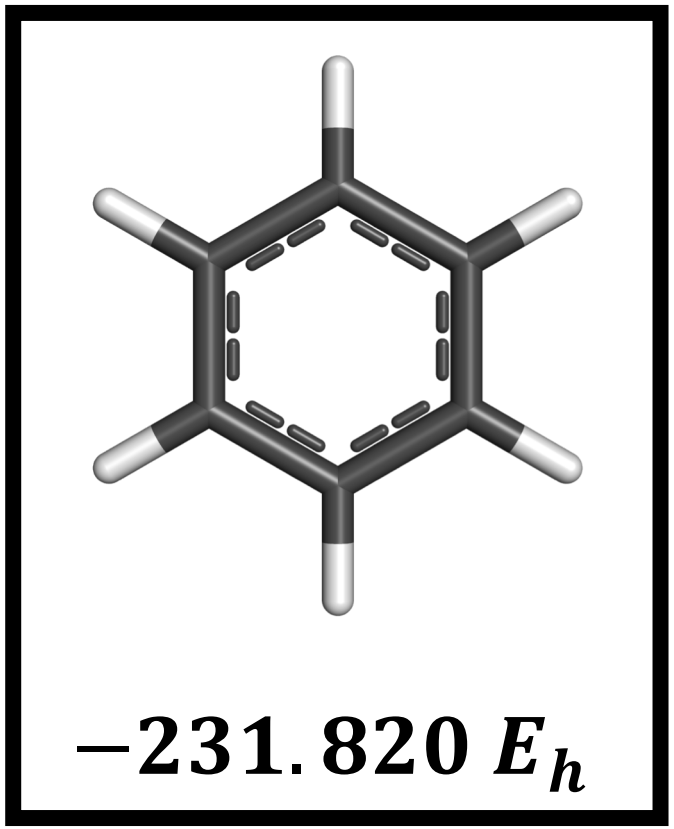




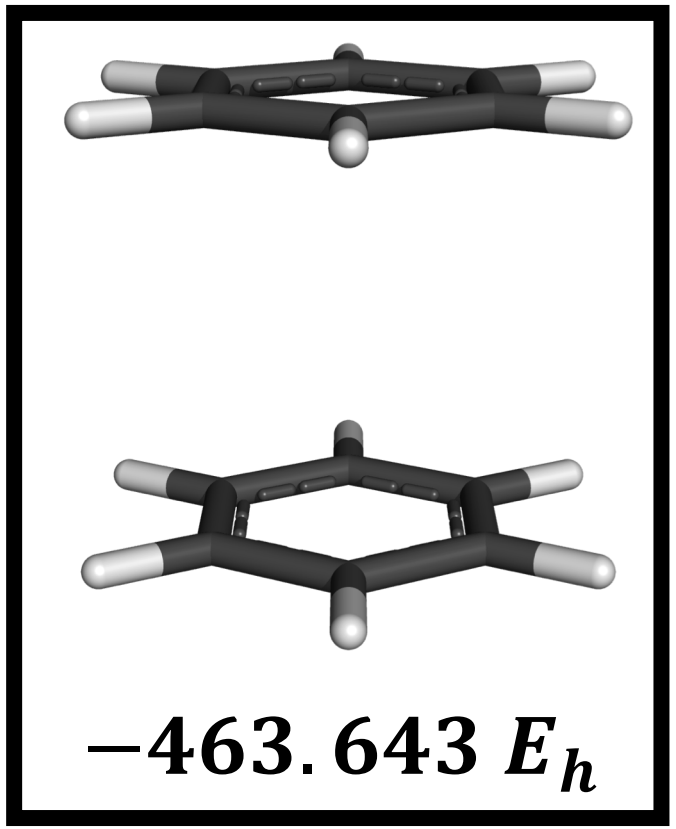
10.2210/pdb1BTN/pdb

What Is SAPT?

SAPT in Psi4 calculates two-body (dimer) interaction energies:



$-231.820\ E_h$



$-463.643\ E_h$

"Supermolecular" Definition:

$$\Delta E_{int} = E_{AB} - E_A - E_B$$

$$\Delta E_{int} \approx -2.71\ mE_h$$

$$-1.70\ {}^{kcal}/_{mol}$$

Sinnokrot, M. O., Sherrill, C. D. (2004). *J. Phys. Chem. A*

How Does SAPT Work?

$$\hat{H} = \hat{F}_A + \hat{F}_B + \hat{W}_A + \hat{W}_B + \hat{V}_{AB}$$

Total Hamiltonian — $\hat{H}$

Monomer Fock Operators — $\hat{F}_A + \hat{F}_B$

Intramonomer Correlation — $\hat{W}_A + \hat{W}_B$

Intermonomer Interaction — $\hat{V}_{AB}$

$$E_{SAPT} = E_{elst} + E_{exch} + E_{ind} + E_{disp}$$

$$E_{SAPT} = \sum_{m>0} \sum_{n \geq 0} E_{SAPT}^{(mn)}$$

E_{SAPT} : Total dimer IE
E_{elst} : Electrostatics
E_{exch} : Exchange / Steric Repulsion
E_{ind} : Induction / Polarization
E_{disp} : London Dispersion

Patkowski, K. (2020). *WIREs Comput Mol Sci.*

Levels of SAPT

$$E_{SAPT} = \sum_{m>0} \sum_{n \geq 0} E_{SAPT}^{(mn)} = E_{elst} + E_{exch} + E_{ind} + E_{disp}$$

E_{SAPT} : Total dimer IE
E_{elst} : Electrostatics
E_{exch} : Exchange / Steric Repulsion
E_{ind} : Induction / Polarization
E_{disp} : London Dispersion

$$E_{SAPT0} = E_{elst}^{(10)} + E_{exch}^{(10)} + E_{ind,resp}^{(20)} + E_{exch-ind,resp}^{(20)} + \delta E_{HF}^{(2)} + E_{disp}^{(20)} + E_{exch-disp}^{(20)}$$

$$E_{SAPT2} \mathrel{+}= E_{elst,resp}^{(12)} + E_{exch}^{(11)} + E_{exch}^{(12)} + {}^{t}E_{ind}^{(22)} + {}^{t}E_{exch-ind}^{(22)}$$

$$E_{SAPT2+} \mathrel{+}= E_{disp}^{(21)} + E_{disp}^{(22)}$$

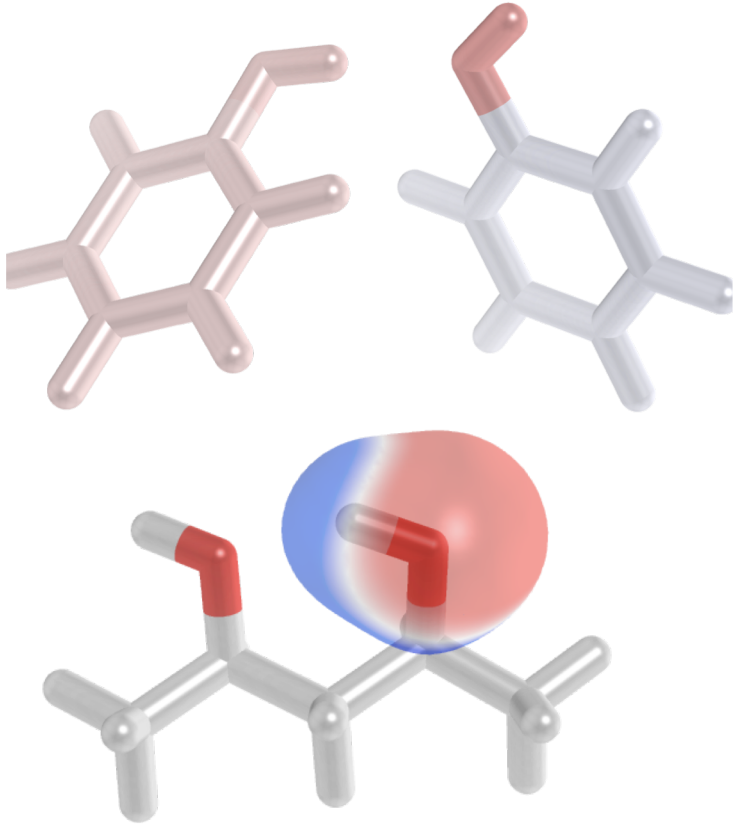
$$E_{SAPT2+(3)} \mathrel{+}= E_{elst,resp}^{(13)} + E_{disp}^{(30)}$$

$$E_{SAPT2+3} \mathrel{+}= E_{exch-disp}^{(30)} + E_{ind-disp}^{(30)} + E_{exch-ind-disp}^{(30)}$$

Parker, T. M., Burns, L. A., Parrish, R. M., Ryno, A. G., & Sherrill, C. D. (2014). *J. Chem Phys.*

Other SAPT in Psi4

- FSAPT0: Functional group SAPT
- ISAPT0: Intramolecular SAPT
- USAPT0: SAPT for open shell systems
- SAPT(DFT): Hartree-Fock -> Kohn-Sham



Useful SAPT Resources

- SAPT: http://www.psicode.org/psi4manual/master/sapt.html
- F/I SAPT: http://www.psicode.org/psi4manual/master/fisapt.html
- Sample Inputs: https://github.com/psi4/psi4/tree/master/samples
- This tutorial: https://github.com/zachglick/PsiCon2020-SAPT