Noncovalent Interactions and Symmetry-Adapted Perturbation Theory

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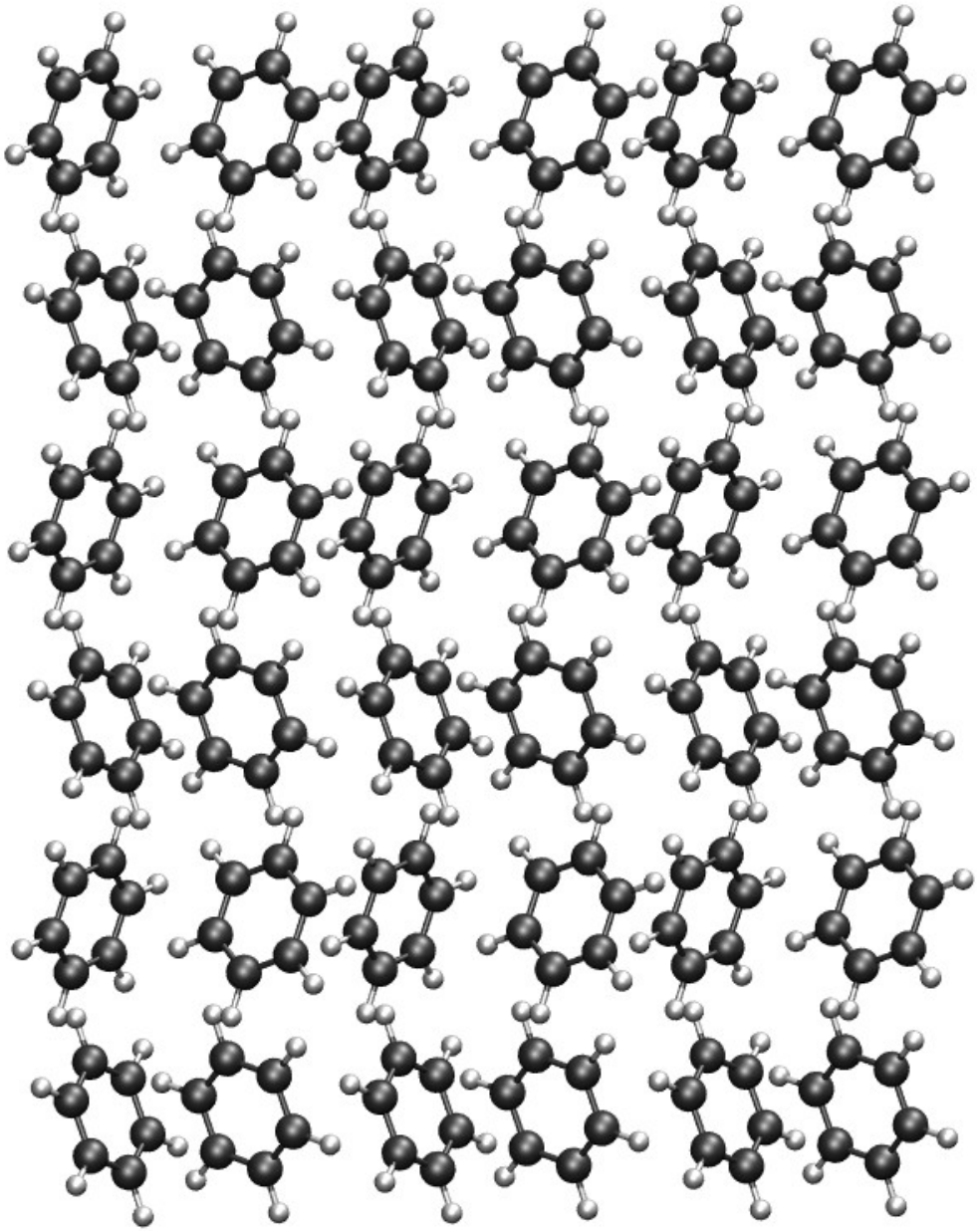
Outline

- Introduction
- Nonbonded Interactions
  - Energy Components
  - Computational Considerations
- Symmetry-Adapted Perturbation Theory
  - General Theory
  - Electrostatics
- Implementation of SAPT
  - Density Fitting and Cholesky Decompositions
  - Factorization of Higher-order Corrections

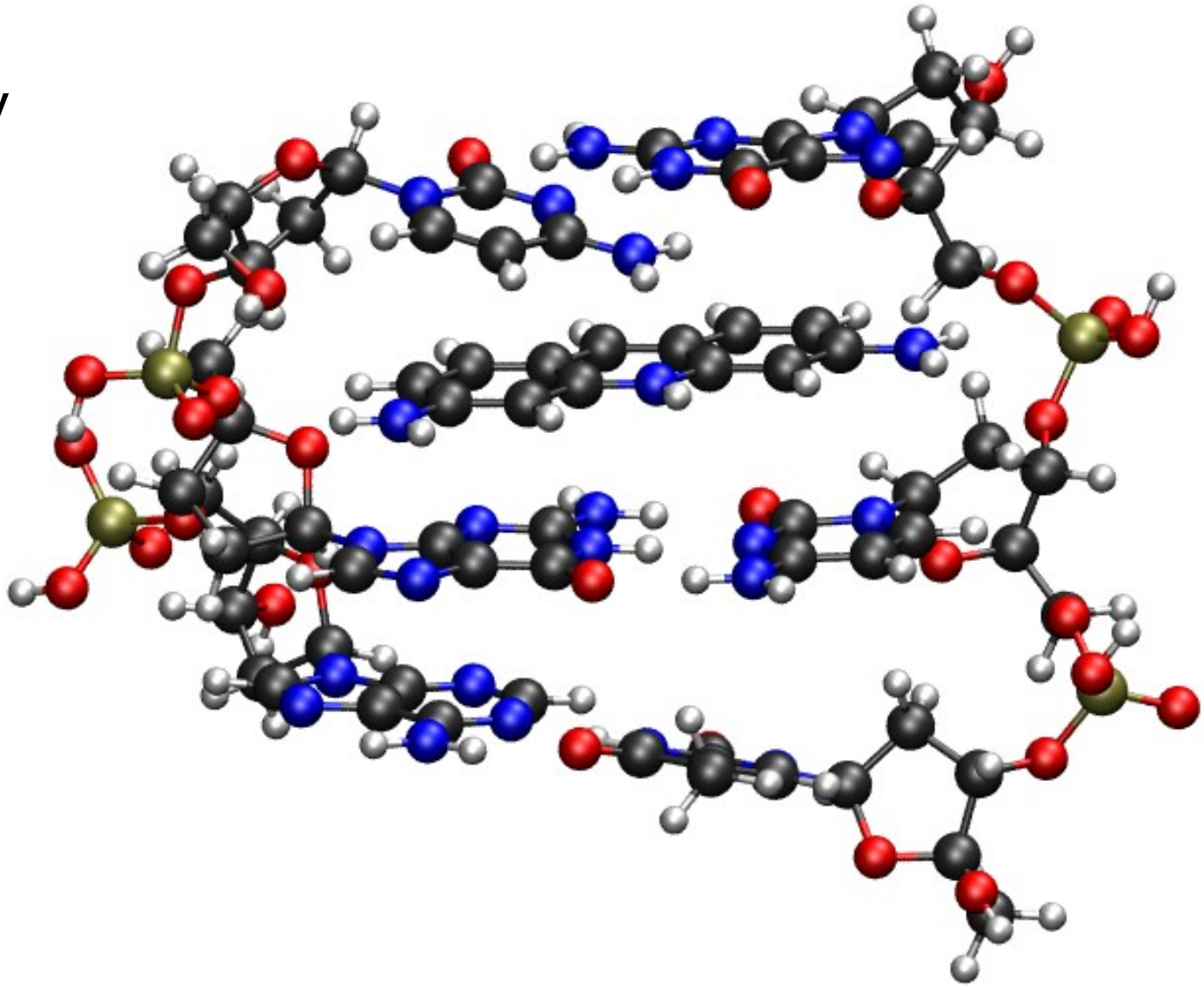
Noncovalent Interactions in Chemistry

- Organic Crystals
  - Lattice Energy
  - Structure



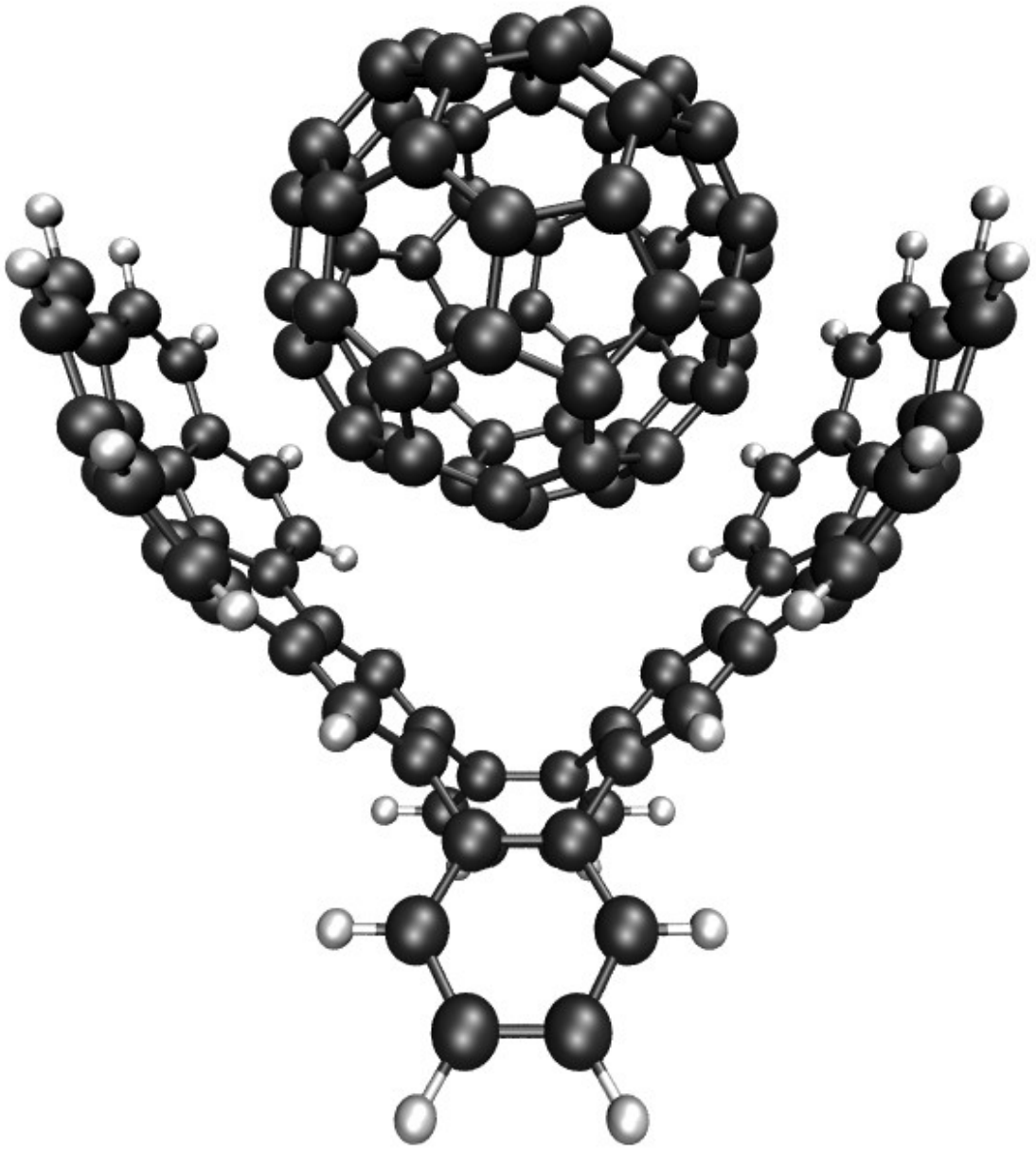
Noncovalent Interactions in Chemistry

- Organic Crystals
  - Lattice Energy
  - Structure
- Nucleic Acids
  - H-bonding
  - Stacking
  - Intercalation



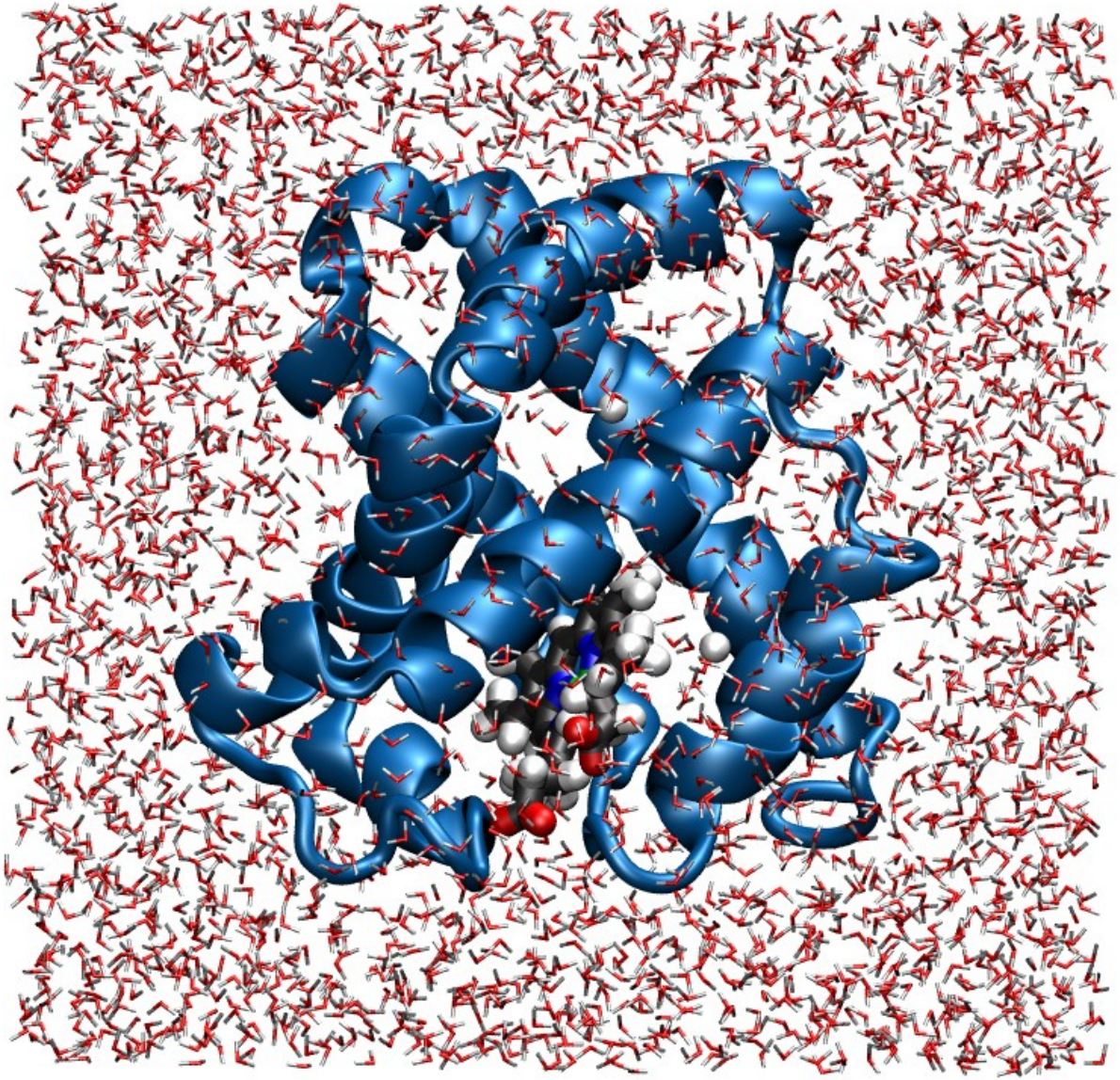
Noncovalent Interactions in Chemistry

- Organic Crystals
  - Lattice Energy
  - Structure
- Nucleic Acids
  - H-bonding
  - Stacking
  - Intercalation
- Nanotechnology



Noncovalent Interactions in Chemistry

- Organic Crystals
  - Lattice Energy
  - Structure
- Nucleic Acids
  - H-bonding
  - Stacking
  - Intercalation
- Nanotechnology
- Proteins
  - Structure
  - Solvation
  - Ligand Binding



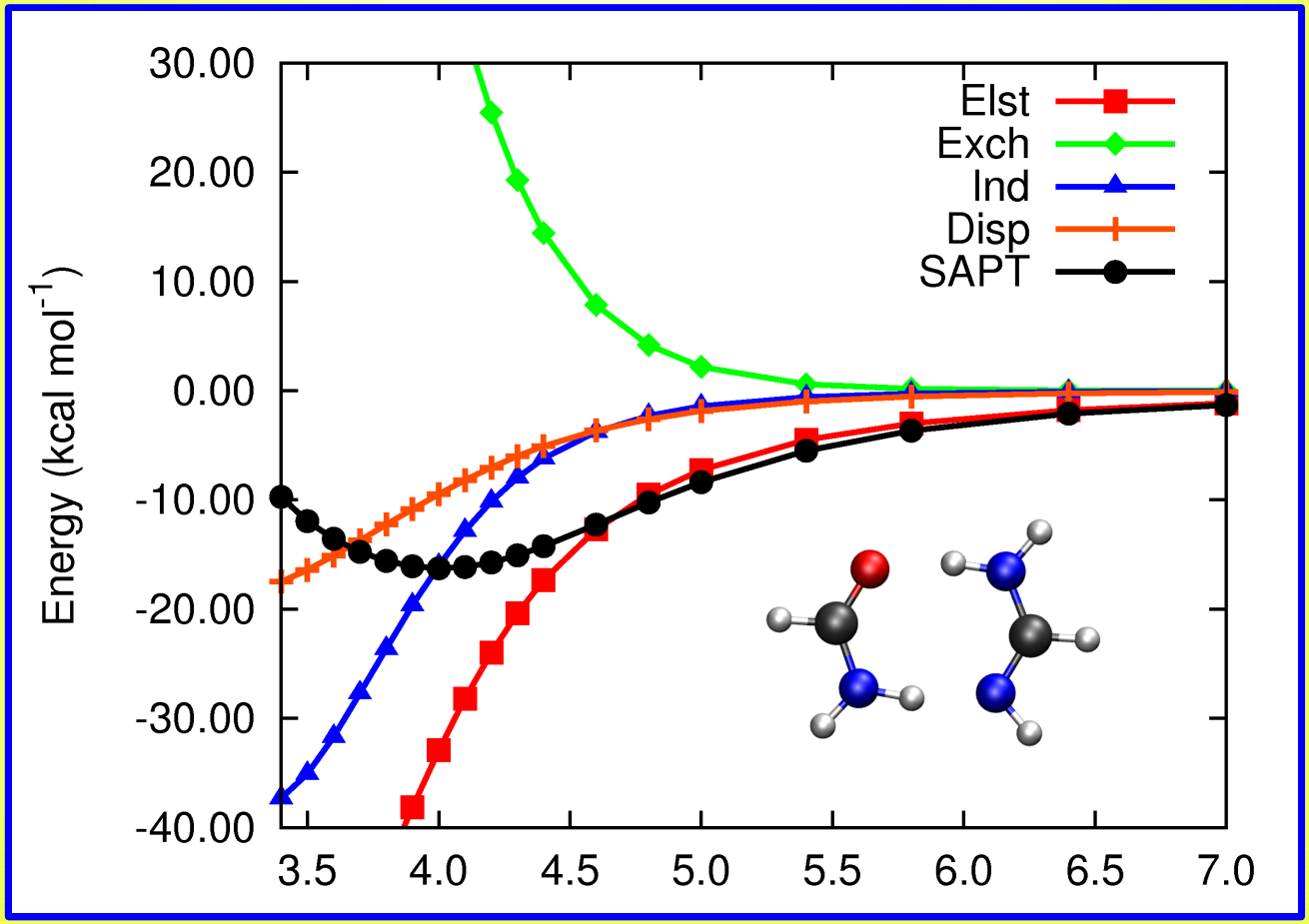
Energy Components

- Electrostatics
  - Classical Coulombic interactions
- Induction
  - Multipole – induced multipole
  - Charge Transfer
- London Dispersion
- Exchange-Repulsion
  - Purely quantum mechanical effect

Electrostatics

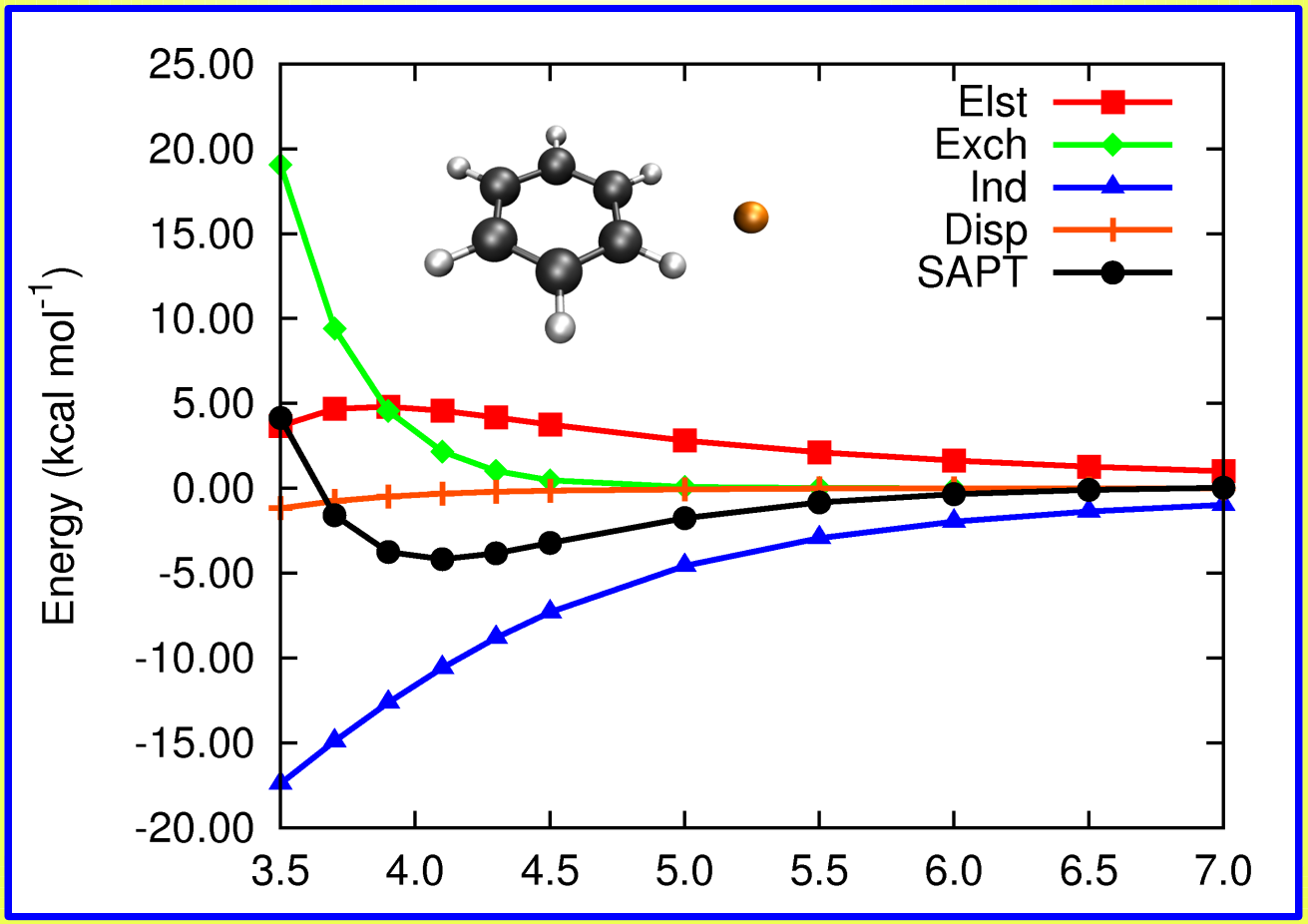
- Coulombic Interaction
  - Multipole expansion

$$E_{elst} = \frac{q_a \, q_b}{\epsilon \, r_{ab}}$$



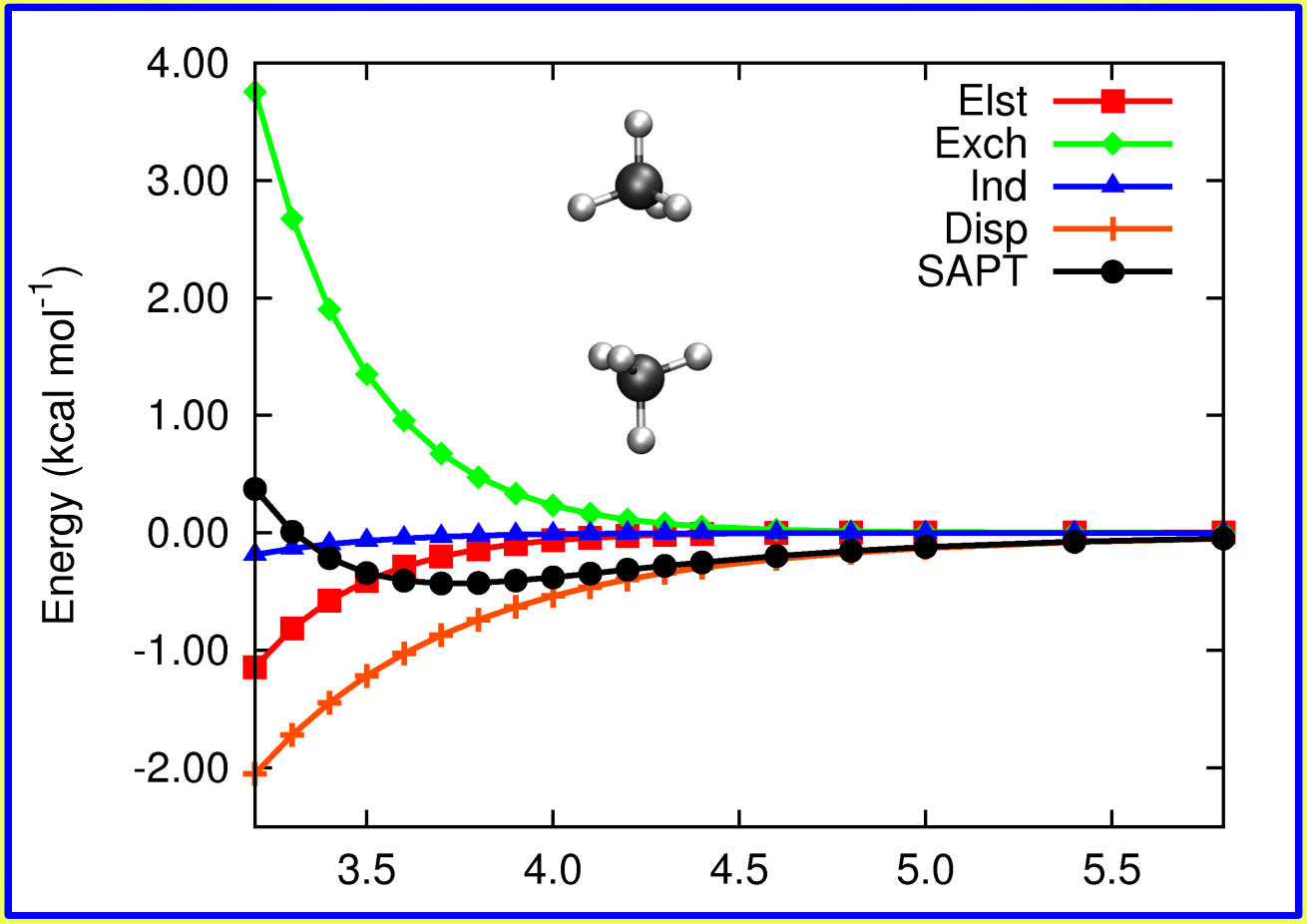
Induction

- Response Term
  - Dipole -> Induced Dipole



Dispersion

- London Dispersion Forces
  - Instantaneous charge fluctuations



Exchange-Repulsion

- Quantum Mechanical Effect
  - Pauli Repulsion
  - Not related to any physical observables
- Interchanging of electronic coordinates
- Contributions from:
  - Orbital Overlap
  - Exchange Integrals

Computing Electrostatics and Induction

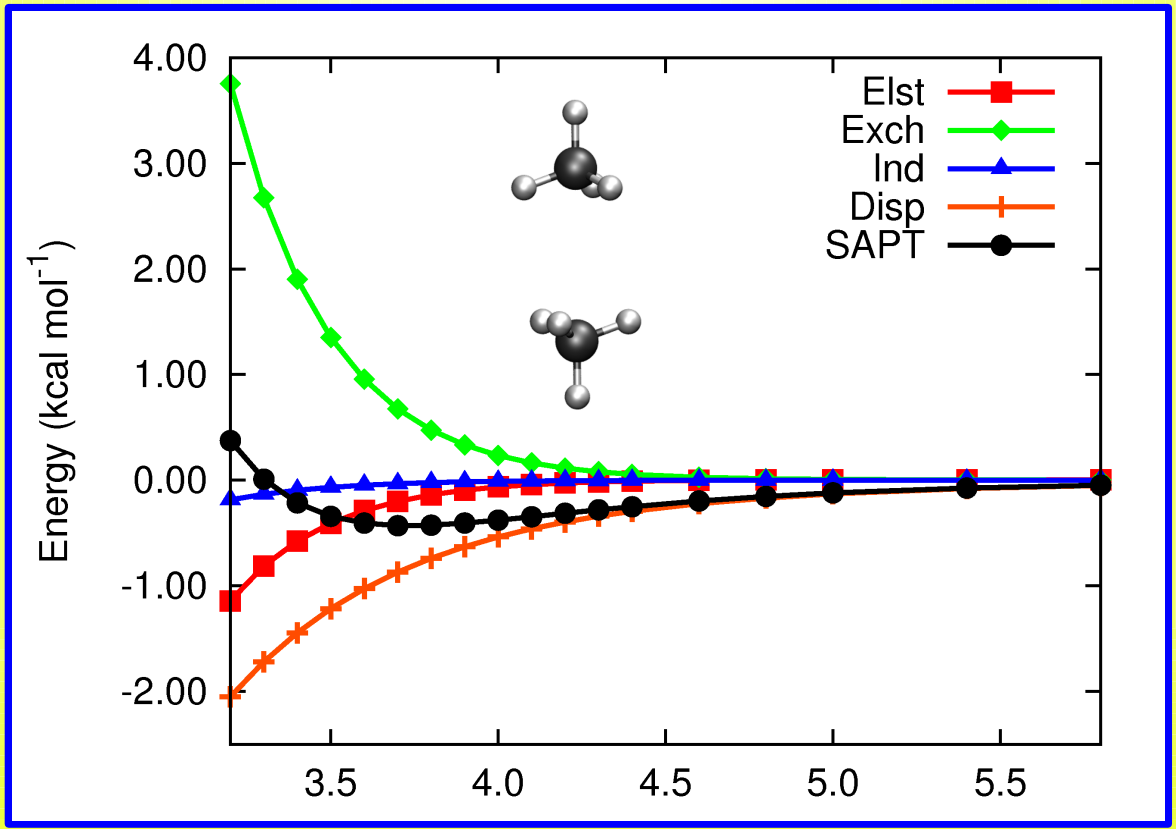
- Accuracy
  - Mean field theory
  - Quality of the density
- Charge Interpenetration

$$E_{elst} = \frac{q_a \, q_b}{\epsilon \, r_{ab}}$$

Computing Electrostatics and Induction

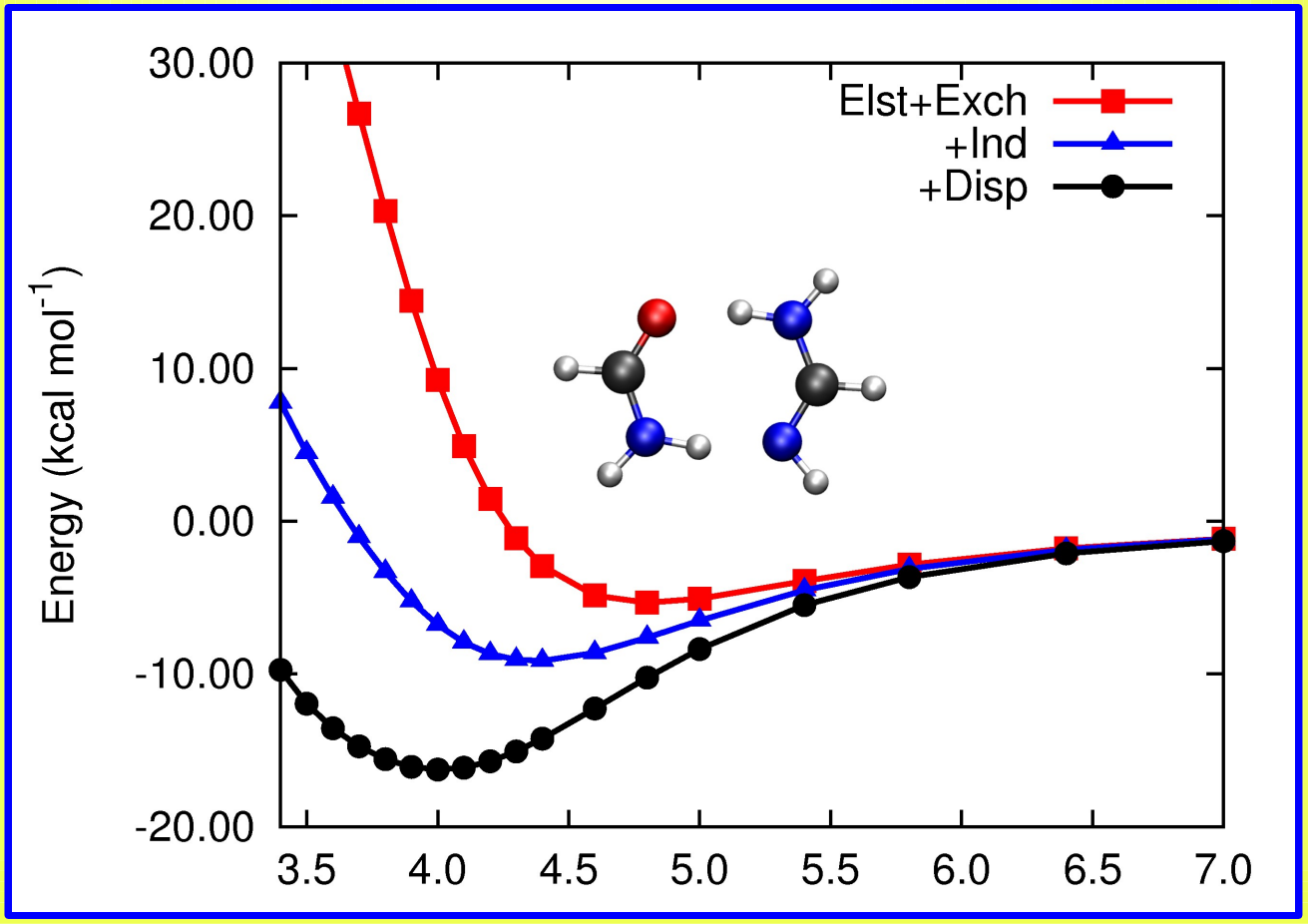
- Accuracy
  - Mean field theory
  - Quality of the density
- Charge Interpenetration

$$E_{elst} \not\equiv \frac{q_a\, q_b}{\epsilon\, r_{ab}}$$



Computing Dispersion

- Electron Correlation
- HF and DFT Fail!



Symmetry-Adapted Perturbation Theory

- Directly computes interaction energies
  - Perturbational
  - Supermolecular
- Computes each component separately
- Free from BSSE
- Size extensive
- Size consistent

$$\Psi_0 = \Psi_0^A \, \Psi_0^B$$

General SAPT

Electronic Schrödinger Equation

$$H_0 = -\frac{1}{2}\sum_i \nabla^2 - \sum_{a,i}\frac{Z_a}{r_{ai}} + \sum_{a>b}\frac{Z_a Z_b}{r_{ab}} + \sum_{i>j}\frac{1}{r_{ij}}$$

Define zeroth-order Hamiltonian for each monomer

$$H_0^A = -\frac{1}{2}\sum_{i_1} \nabla^2 - \sum_{a_1,i_1}\frac{Z_{a_1}}{r_{a_1 i_1}} + \sum_{a_1>a_2}\frac{Z_{a_1} Z_{a_2}}{r_{a_1 a_2}} + \sum_{i_1>i_2}\frac{1}{r_{i_1 i_2}} \quad a,i \in A$$

$$H_0^B = -\frac{1}{2}\sum_{j_1} \nabla^2 - \sum_{b_1,j_1}\frac{Z_{b_1}}{r_{b_1 j_1}} + \sum_{b_1>b_2}\frac{Z_{b_1} Z_{b_2}}{r_{b_1 b_2}} + \sum_{j_1>j_2}\frac{1}{r_{j_1 j_2}} \quad b,j \in B$$

Interaction Potential

Define Intermolecular Operator

$$V = H_0^{AB} - H_0^A - H_0^B$$

Explict form of *V*:

$$V = \sum_{i,j} \frac{1}{r_{ij}} - \sum_{b,i} \frac{Z_b}{r_{bi}} - \sum_{a,j} \frac{Z_a}{r_{aj}} + \sum_{a,b} \frac{Z_a Z_b}{r_{ab}}$$

Full Dimer Hamiltonian

$$H = H_0^A + W^A + H_0^B + W^B + V$$

Electrostatic Interactions

Use intermolecular operator

$$\nu(ij) = r_{ij}^{-1} + \frac{\nu_B(i)}{N_B} + \frac{\nu_A(j)}{N_A} + \frac{V_{AB}}{N_A N_B}$$

Integrate over the density of A and B

$$E_{elst} = \int \rho_A(i)\, \nu(ij)\, \rho_B(j)\, d\tau_i\, d\tau_j$$

Why do the number of electrons appear?

Alternative Formulation

Use second quantized form of *V*

$$V = (\kappa\lambda|\mu\nu)\, a^{\kappa}_{\lambda}\, b^{\mu}_{\nu} + (\nu_A)^{\nu}_{\mu}\, b^{\mu}_{\nu} + (\nu_B)^{\lambda}_{\kappa}\, a^{\kappa}_{\lambda} + V_{AB}$$

$$c^{\mu}_{\nu} = c^{\dagger}_{\mu} c_{\nu}$$

Evaluate the expectation value of *V*

$$E_{elst} = \langle\, \Psi^A_0\, \Psi^B_0 \,|\, V \,|\, \Psi^A_0\, \Psi^B_0 \,\rangle$$

$$E_{elst} = \langle\, \Psi^A_0\, \Psi^B_0 \,|\, (\kappa\lambda|\mu\nu)\, a^{\kappa}_{\lambda}\, b^{\mu}_{\nu} + (\nu_A)^{\nu}_{\mu}\, b^{\mu}_{\nu} + (\nu_B)^{\lambda}_{\kappa}\, a^{\kappa}_{\lambda} + V_{AB} \,|\, \Psi^A_0\, \Psi^B_0 \,\rangle$$

Electrostatics Cont.

$$E_{elst} = \langle\, \Psi_0^A\, \Psi_0^B \,|\, (\kappa\lambda|\mu\nu)\, a_\lambda^\kappa\, b_\nu^\mu \,|\, \Psi_0^A\, \Psi_0^B \,\rangle +$$

$$\langle\, \Psi_0^A\, \Psi_0^B \,|\, (\nu_A)_\mu^\nu\, b_\nu^\mu \,|\, \Psi_0^A\, \Psi_0^B \,\rangle +$$

$$\langle\, \Psi_0^A\, \Psi_0^B \,|\, (\nu_B)_\kappa^\lambda\, a_\lambda^\kappa \,|\, \Psi_0^A\, \Psi_0^B \,\rangle +$$

$$\langle\, \Psi_0^A\, \Psi_0^B \,|\, V_{AB} \,|\, \Psi_0^A\, \Psi_0^B \,\rangle$$

$$E_{elst} = (\kappa\lambda|\mu\nu)\, \langle\, \Psi_0^A\, \Psi_0^B \,|\, a_\lambda^\kappa\, b_\nu^\mu \,|\, \Psi_0^A\, \Psi_0^B \,\rangle +$$

$$(\nu_A)_\mu^\nu\, \langle\, \Psi_0^A\, \Psi_0^B \,|\, b_\nu^\mu \,|\, \Psi_0^A\, \Psi_0^B \,\rangle +$$

$$(\nu_B)_\kappa^\lambda\, \langle\, \Psi_0^A\, \Psi_0^B \,|\, a_\lambda^\kappa \,|\, \Psi_0^A\, \Psi_0^B \,\rangle +$$

$$V_{AB}\, \langle\, \Psi_0^A\, \Psi_0^B \,|\, \Psi_0^A\, \Psi_0^B \,\rangle$$

Electrostatics Cont.

$$E_{elst} = (\kappa\lambda|\mu\nu) \langle \Psi_0^A | a_\lambda^\kappa | \Psi_0^A \rangle \langle \Psi_0^B | b_\nu^\mu | \Psi_0^B \rangle$$

$$(\nu_A)_\mu^\nu \langle \Psi_0^B | b_\nu^\mu | \Psi_0^B \rangle +$$

$$(\nu_B)_\kappa^\lambda \langle \Psi_0^A | a_\lambda^\kappa | \Psi_0^A \rangle +$$

$$V_{AB} \langle \Psi_0^A \Psi_0^B | \Psi_0^A \Psi_0^B \rangle$$

$$E_{elst} = (\kappa\lambda|\mu\nu) \langle a_\lambda^\kappa \rangle \langle b_\nu^\mu \rangle +$$

$$(\nu_A)_\mu^\nu \langle b_\nu^\mu \rangle +$$

$$(\nu_B)_\kappa^\lambda \langle a_\lambda^\kappa \rangle +$$

$$V_{AB}$$

Electrostatic Interaction in SAPT

In terms of spin orbitals:

$$E_{elst} = (\alpha\alpha|\beta\beta) + (\nu_A)^{\beta}_{\beta} + (\nu_B)^{\alpha}_{\alpha} + V_{AB}$$

After spin integration:

$$E_{elst} = 4\,(aa|bb) + 2\,(\nu_A)^{b}_{b} + 2\,(\nu_B)^{a}_{a} + V_{AB}$$

SAPT0

$$E_{electrostatic} = E_{elst}^{(10)}$$

$$E_{exchange} = E_{exch}^{(10)}$$

$$E_{induction} = E_{ind,resp}^{(20)} + E_{exch-ind,resp}^{(20)} + \delta E_{ind,resp}^{(HF)}$$

$$E_{dispersion} = E_{disp}^{(20)} + E_{exch-disp}^{(20)}$$

SAPT2

$$E_{electrostatic} = E^{(10)}_{elst} + E^{(12)}_{elst,resp} + E^{(13)}_{elst,resp}$$

$$E_{exchange} = E^{(10)}_{exch} + E^{(11)}_{exch} + E^{(12)}_{exch}$$

$$E_{induction} = E^{(20)}_{ind,resp} + E^{(20)}_{exch-ind,resp} + {}^{t}E^{(22)}_{ind} + {}^{t}E^{(22)}_{exch-ind} + \delta E^{(HF)}_{ind,resp}$$

$$E_{dispersion} = E^{(20)}_{disp} + E^{(30)}_{disp} + E^{(21)}_{disp} + E^{(22)}_{disp} + E^{(20)}_{exch-disp},$$

Approximate Two-Electron Integrals in SAPT

- SAPT0
  - Scales $O(o^3v^2)$
  - Requires o^2v^2 integrals
- Conventional Integral Transformation
  - Scales $O(oN_{AO}^4)$
- Density Fitting and Cholesky Decompositions

$$(\mu\nu|\rho\sigma) \approx \sum_Q B^Q_{\mu\nu} B^Q_{\rho\sigma}$$

Density Fitting Approximation

$$(\mu\nu|\rho\sigma) \approx \sum_{PQ} (\mu\nu|P)[J^{-1}]_{PQ}(Q|\rho\sigma)$$

$$[J]_{PQ} = \int P(\mathbf{r}_1)\frac{1}{r_{12}}Q(\mathbf{r}_2)d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

$$B^Q_{\mu\nu} = \sum_P (\mu\nu|P)[J^{-\frac{1}{2}}]_{PQ}$$

$$(\mu\nu|\rho\sigma) \approx \sum_Q B^Q_{\mu\nu} B^Q_{\rho\sigma}$$

Cholesky Decompositions

$$L_{\rho\sigma}^{\rho\sigma} = \sqrt{(\rho\sigma|\rho\sigma) - \sum_{n=0}^{\rho\sigma_{max}-1} L_{\rho\sigma}^{n} L_{\rho\sigma}^{n}},$$

$$L_{\mu\nu}^{\rho\sigma} = \frac{1}{L_{\rho\sigma}^{\rho\sigma}} \left((\mu\nu|\rho\sigma) - \sum_{n=0}^{\rho\sigma_{max}-1} L_{\mu\nu}^{n} L_{\rho\sigma}^{n} \right), \mu\nu \neq \rho\sigma$$

$$(\mu\nu|\rho\sigma) \approx \sum_{Q} L_{\mu\nu}^{Q} L_{\rho\sigma}^{Q}$$

- Work is shifted away from the transformation

$$L_{ij}^{Q} = \sum_{\mu\nu} C_{\mu i}^{M\dagger} L_{\mu\nu}^{Q} C_{\nu j}^{N}$$

SAPT0 Factorizations

$$q12 = t^{a_1 b_1}_{r_1 s_1} \, \nu^{r_1 s_1}_{a_2 b_2} \, S^{a_2}_{b_1} \, S^{b_2}_{a_1}$$

SAPT2 Factorizations

$$E_{exch}^{(111)} = -4Re\theta_{a_1a_2}^{r_1r_2}\theta_{b_1b_2}^{s_1s_2}\nu_{r_1s_1}^{a_1b_1}S_{s_2}^{a_2}S_{r_2}^{b_2} - 4Re\theta_{r_1r_2}^{a_1a_2}\theta_{b_1b_2}^{s_1s_2}\nu_{a_1s_1}^{r_1b_1}S_{a_2}^{b_2}S_{s_2}^{r_2},$$