Targeting Real chemical accuracy at the EXascale

Interfacing TREXIO with GammCor

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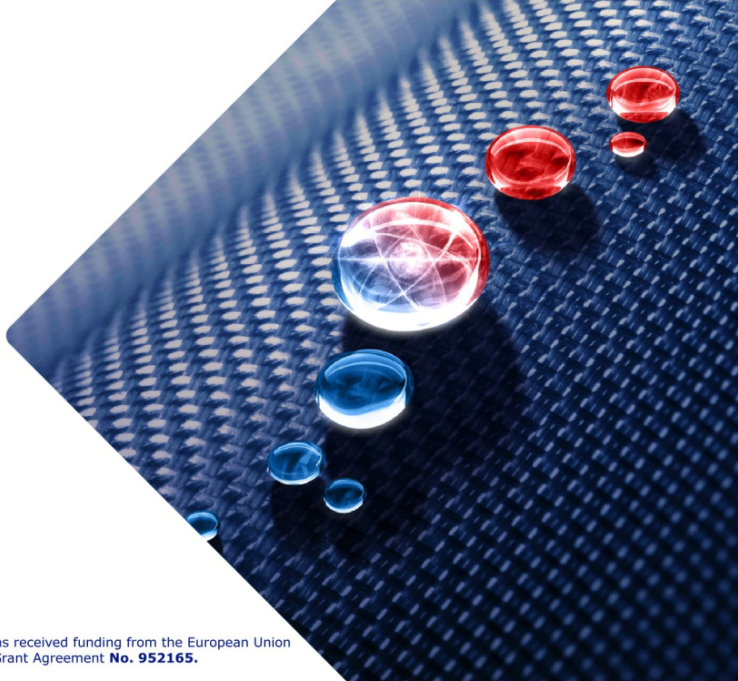

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Interaction energy for weakly interacting subsystems A and B

- Supermolecular energy

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

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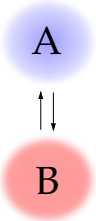
- Perturbation-theory way: expansion in orders of the interaction potential

$$E_{int} = E^{(1)} + E^{(2)} + \dots$$

  - E_{int} obtained directly, in a perturbative manner
  - based on monomer properties
  - partitioned into well-defined energy contributions
  - free of basis-set superposition error (BSSE)

$$\hat{H} = \underbrace{\hat{H}_A + \hat{H}_B}_{\hat{H}_0} + \hat{V}$$

$$\hat{V} = \sum_{i\in A}\sum_{k\in B}\frac{1}{r_{ik}} - \sum_{i\in A}\sum_{\beta\in B}\frac{Z_\beta}{|\mathbf{r}_i - \mathbf{R}_\beta|} - \sum_{k\in B}\sum_{\alpha\in A}\frac{Z_\alpha}{|\mathbf{r}_k - \mathbf{R}_\alpha|} + \sum_{\alpha\in A}\sum_{\beta\in B}\frac{Z_\alpha Z_\beta}{R_{\alpha\beta}}$$



- $\hat{V}$ treated as perturbation

$$\psi^n = \Phi^0 + R_0(E^n - V)\mathcal{F}\psi^{n-1}$$

$$E^n = \frac{\langle\Phi^0|\hat{V}\mathcal{G}\psi^{n-1}\rangle}{\langle\Phi^0|\mathcal{G}\psi^{n-1}\rangle}$$

- symmetry-forcing

$$\hat{H} = \underbrace{\hat{H}_A + \hat{H}_B}_{\hat{H}_0} + \hat{V}$$

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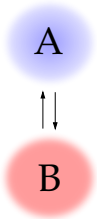


- $\hat{V}$ treated as perturbation

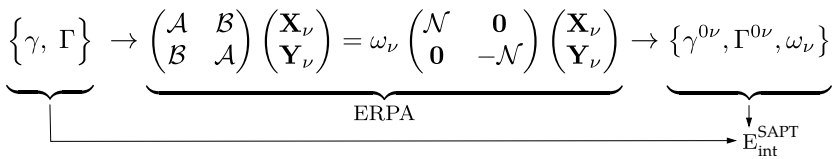
$$E^{(k)}_{\mathrm{SRS}} = E^{(k)}_{\mathrm{RS}} + E^{(k)}_{\mathrm{exch}}$$

- symmetrized Rayleigh-Schrodinger

$$E_{\mathrm{int}}^{\mathrm{SAPT}} = E_{\mathrm{elst}}^{(1)} + E_{\mathrm{exch}}^{(1)} + E_{\mathrm{ind}}^{(2)} + E_{\mathrm{exch-ind}}^{(2)} + E_{\mathrm{disp}}^{(2)} + E_{\mathrm{exch-disp}}^{(2)}$$

Advantages of SAPT

- all major polarization and exchange contributions to E_{int}
- correct asymptotic behavior through all orders
- Van der Waals minimum: accurate to within few percent
- many flavors: SAPT(DFT), SAPT(CCSD), SAPT0, SAPT2, ...



SAPT(MC) ≡ multiconfigurational SAPT

- requires only one- and two-particle reduced density matrices of the monomers
- based on response properties from extended random phase approximation (ERPA)
- general: may be applied with any MC wavefunction (CAS, GVB-PP, DMRG, CIPSI...)

$$\underbrace{\{\gamma,\ \Gamma\}}_{} \rightarrow \underbrace{\begin{pmatrix} \mathcal{A} & \mathcal{B} \\ \mathcal{B} & \mathcal{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}_\nu \\ \mathbf{Y}_\nu \end{pmatrix} = \omega_\nu \begin{pmatrix} \mathcal{N} & \mathbf{0} \\ \mathbf{0} & -\mathcal{N} \end{pmatrix} \begin{pmatrix} \mathbf{X}_\nu \\ \mathbf{Y}_\nu \end{pmatrix}}_{\text{ERPA}} \rightarrow \underbrace{\{\gamma^{0\nu}, \Gamma^{0\nu}, \omega_\nu\}}_{} \rightarrow E_{\text{int}}^{\text{SAPT}}$$

SAPT(MC) $\equiv$ multiconfigurational SAPT

- requires only one- and two-particle reduced density matrices of the monomers
- TREXIO is interfaced with GammCor for SAPT(CIPSI) calculations
- reduced density matrices for CIPSI obtained from Quantum Package

AO → NO transformation

$$\gamma = \sum_{\sigma} \langle \Psi | \hat{a}^{\dagger}_{q_\sigma} \hat{a}_{q_\sigma} | \Psi \rangle \longrightarrow \{n_p\}, C^{MO \to NO}$$

$$C^{\mathrm{AO}\to\mathrm{NO}} = C^{\mathrm{AO}\to\mathrm{MO}} C^{\mathrm{MO}\to\mathrm{NO}}$$

Table: TREXIO ingredients

group	variables	description
`rdm`	`1e`	1-RDM, γ
`mo`	`coefficients`	MO coefficients

First order: electrostatic energy

$$E^{(1)}_{\text{elst}} = 2\sum_{p\in A} n_p v^B_{pp} + 2\sum_{q\in B} n_q v^A_{qq} + 4\sum_{\substack{p\in A\\ q\in B}} n_p n_q v^{pq}_{pq} + V^{AB}$$

Table: TREXIO ingredients

group	variables	description
ao_1e	kinetic	$\langle p\|\hat{T}_e\|q\rangle$
	potential_n_e	$\langle p\|\hat{V}_{ne}\|q\rangle$
ao_2e	eri	$\langle pq\|rs\rangle$
nucleus	num, charge, coord	

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First order: exchange energy

$$E^{(1)}_{\mathrm{exch}} = 2\left(E^{(1)}_{\mathrm{elst}} - V_{AB}\right)\sum_{\substack{p\in A\\ q\in B}} n_p n_q \left(S^q_p\right)^2 + \ldots - 8\sum_{\substack{pqr\in A\\ sut\in B}} N^A_{pqru}\ N^B_{tusq}\ v^{rs}_{pt}$$

Table: TREXIO ingredients

group	variables	description
`ao_1e`	`overlap`	$\langle p\|q\rangle$
`rdm`	`2e`	2-RDM, Γ_{pqrs}

First order: exchange energy

$$E^{(1)}_{\mathrm{exch}} = 2\left(E^{(1)}_{\mathrm{elst}} - V_{AB}\right)\sum_{\substack{p\in A\\ q\in B}} n_p n_q \left(S^q_p\right)^2 + \ldots - 8\sum_{\substack{pqr\in A\\ sut\in B}} N^A_{pqru}\; N^B_{tusq}\; v^{rs}_{pt}$$

Table: TREXIO ingredients

group	variables	description
ao_1e	overlap	$\langle p\|q\rangle$
rdm	2e	2-RDM, Γ_{pqrs}

Second order: induction, dispersion energies

$$E_{\rm int}^{(2)} = E_{\rm ind}^{(2)} + E_{\rm disp}^{(2)} + E_{\rm exch-ind}^{(2)} + E_{\rm exch-disp}^{(2)}$$

$$\underbrace{\{\gamma,\,\Gamma\}}_{} \rightarrow \underbrace{\begin{pmatrix} \mathcal{A} & \mathcal{B} \\ \mathcal{B} & \mathcal{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}_\nu \\ \mathbf{Y}_\nu \end{pmatrix} = \omega_\nu \begin{pmatrix} \mathcal{N} & \mathbf{0} \\ \mathbf{0} & -\mathcal{N} \end{pmatrix} \begin{pmatrix} \mathbf{X}_\nu \\ \mathbf{Y}_\nu \end{pmatrix}}_{\text{ERPA}} \rightarrow \underbrace{\{\gamma^{0\nu}, \Gamma^{0\nu}, \omega_\nu\}}_{} \rightarrow E_{\rm int}^{(2)}$$

- all TREXIO ingredients already available (`ao`, `eri`, `rdm` groups)

$$\underbrace{\{\gamma,\,\Gamma\}}_{} \rightarrow \underbrace{\begin{pmatrix}\mathcal{A} & \mathcal{B}\\ \mathcal{B} & \mathcal{A}\end{pmatrix}\begin{pmatrix}\mathbf{X}_\nu\\ \mathbf{Y}_\nu\end{pmatrix} = \omega_\nu \begin{pmatrix}\mathcal{N} & \mathbf{0}\\ \mathbf{0} & -\mathcal{N}\end{pmatrix}\begin{pmatrix}\mathbf{X}_\nu\\ \mathbf{Y}_\nu\end{pmatrix}}_{\text{ERPA}} \rightarrow \underbrace{\{\gamma^{0\nu}, \Gamma^{0\nu}, \omega_\nu\}}_{} \rightarrow E_{\text{int}}^{\text{SAPT}}$$

Summary: TREXIO use in GammCor

- 1e and 2e integrals read in AO, transformed to NO
- 1-, 2-RDMs read in MO, transformed to NO
- TREXIO tests on CIPSI wave functions from Quantum Package