Renormalization, singular kernels and tensor product approximation in quantum chemistry

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Overview

Tensor product approximations

Tensor product approximations in quantum chemistry are sensible to singularities at coalescence points of particles.
Rigorous results for electronic wavefunctions

- Partial wave analysis (Goddard, Hill, Kutzelnigg, Morgan)
- Hyperbolic cross approximation (Yserentant)
- Best N-term approximation with hyperbolic wavelets (HJF, Hachbusch, Schneider)

Similar results for more general and promising formats are still missing. However, it seems reasonable to assume that these formats are also plagued by some extend with this problem.

- Canonical and Tucker format
- Tensor trains (matrix product states)
- Hierarchical format

Renormalization

Originally invented as a subtraction scheme to get rid of ultraviolet divergencies in perturbative quantum field theory (Dyson, Salam, Weinberg, Bogoliubov, Parasiuk, Hepp).

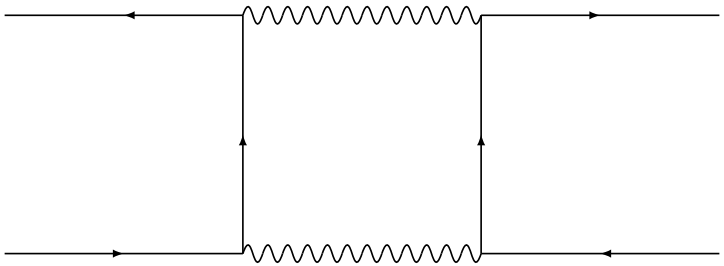
The renormalization theory is in this framework a constructive form of the Hahn-Banach theorem. K. Hepp

- Highly successful despite a certain lack of elegance (Dirac).
- Modern approach based on renormalization group theory (Stückelberg, Wilson).
- Applications in condensed matter physics, e.g. Kondo problem, Landau's Fermi liquid theory.

In the following, we focus on the subtraction scheme and what can be learned for the improvement of tensor product approximations.

Tensor product approximations in a broader sense

Feynman diagrams have some similarities with tensor product approximations



They can be considered as graphs which have to satisfy certain rules concerning their connectivity (Feynman rules).

- Mostly used in the framework of perturbation theory.
- Countless applications in high energy, statistical and condensed matter physics.
- Various network topologies possible, e.g., rings, ladders, parquet, etc.
- Hopf algebras provide a convenient algebraic framework (Connes, Kreimer).

Tensor product approximations in a broader sense

Let us consider e.g. a Feynman diagram $F(p_1, \ldots, p_m)$ depending on $p_1, \ldots, p_m$ external momenta. The diagram can be represented as a high dimensional integral with an integrand of the form

$$\prod_{i=1}^{m+n} f_i(p_i), \text{ with } i = m+1, m+n \text{ internal momenta}$$

where external and internal momenta satisfy certain linear relations (momentum conservation) with integration over remaining independent internal momenta. Propagators are of the form

$$f_i(p) = \frac{P_i(p)}{p^2 + \mu} \quad p \in \mathbb{R}^4 \text{ (Wick rotation)}$$

corresponding to singular kernel functions in configuration space, e.g.,

$$-(\partial_{i,1}^2 + \partial_{i,2}^2 + \partial_{i,3}^2 + \partial_{i,4}^2 - \mu)\tilde{f}(x_i, x_j) = \delta^4(x_i - x_j)$$

In quantum field theory, such calculations are hampered by **ultraviolet** and infrared divergencies.

Basic idea of renormalization

Simple example: let us consider the divergent integral ($\epsilon > 0$)

$$F(p_1) = \int_\epsilon^\infty \frac{p_2}{p_1 + p_2}\, dp_2 = p_2 - p_1 \ln(p_1 + p_2)\Big|_0^\infty$$

physicist's approach: consider the derivatives

$$F'(p_1) = -\int_\epsilon^\infty \frac{p_2}{(p_1 + p_2)^2}\, dp_2 \text{ (divergent integral)}$$

$$F''(p_1) = \int_\epsilon^\infty \frac{2p_2}{(p_1 + p_2)^3}\, dp_2 = \frac{p_1}{(p_1 + p_2)^2} - \frac{2}{p_1 + p_2}\Big|_\epsilon^\infty = \frac{1}{p_1} + O(\epsilon)$$

and go back by integration

$$F'(p_1) = \ln(p_1) + a, \text{ (divergent constant } a)$$

$$F(p_1) = p_1 \ln(p_1) - p_1 + ap_1 + b, \text{ (divergent constants } a, b)$$

Divergent terms, like $ap_1 + b$ are combined into effective coupling constants, masses, etc., e.g., $m = m_0 + a + \cdots$ (mass observed in experiment).

Basic idea of renormalization

Sketch of a renormalization scheme

- Taylor expansion of the integrand with respect to external momenta

$$\frac{p_2}{p_1+p_2} = 1 - \frac{p_1}{p_2} + \frac{2p_2}{(\lambda p_1 + p_2)^3} p_1^3, \ \lambda \in [0,1]$$

- Subtracting $T_2(p_1) = 1 - \frac{p_1}{p_2}$ from integrand, i.e.,

$$\int_\epsilon^\infty \left(\frac{p_2}{p_1+p_2} - \left(1 - \frac{p_1}{p_2}\right)\right) dp_2 = \int_\epsilon^\infty \frac{p_1^2}{p_2(p_1+p_2)}\, dp_2$$

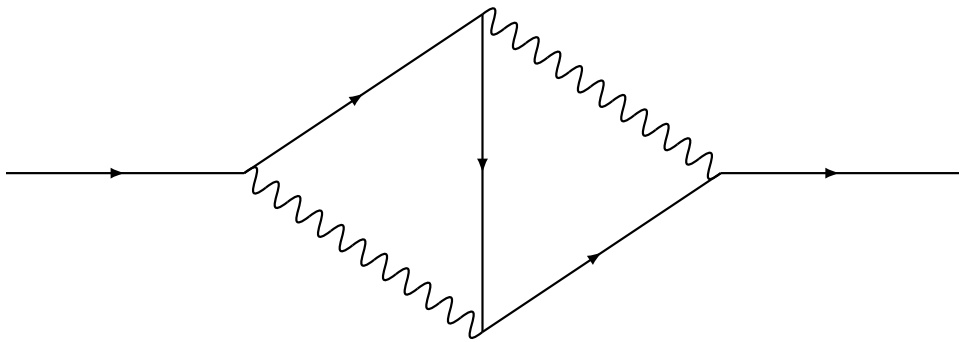
  yields a convergent integral.

- Combining divergent parts, like $T_2(p_1) = 1 - \frac{p_1}{p_2}$, to effective coupling constants, masses, etc.

Weinberg's theorem

In quantum field theory Weinberg's theorem answers important questions concerning convergence and asymptotic behaviour of Feynman diagrams

S. Weinberg, Phys. Rev. **118** (1960), 838-849



- Overall convergence of the Integral.
  - Simple power counting of propagators and vertices works only if all internal momenta go simultaneously to infinity.
  - Integration over subspaces must be taken into account as well.
- Asymptotic behaviour of Feynman diagrams with respect to external momenta.

Renormalization from a quantum chemistry point of view

- No ultraviolet divergencies, instead conical singularities (cusps) at coalescence points of particles.
  - Singularities express themselves by reduced (mixed) Sobolev and Besov regularity.
  - Put limits on convergence rates of tensor product approximations, e.g. MCSCF wavefunctions.
  - Reduced quantities, like density matrices, response or Green's functions are singular along their diagonals.
- Nonrelativistic propagators, e.g. (noninteracting) Green's functions (Feynman), amplitudes (Goldstone) and Coulomb interactions.
  - In contrast to propagators in quantum field theory, these are inhomogeneous and anisotropic quantities.
  - Conjecture: Pseudo-differential calculus provides an appropriate framework.

Renormalization from the quantum chemistry point of view

- Instead of Taylor polynomials in phase space, one can subtract asymptotic singular contributions in configuration space.
  - Singular analysis, i.e., asymptotic parametrices and Green operators, provides an appropriate framework.

    (HJF, G. Flad-Harutyunyan, B.-W. Schulze)
  - Adaptation of Weinberg's theorem required (overlapping singularities).
- How to deal with singular subtraction terms?
  - Cannot be simply combined into effective parameters of the model.
  - In any case, singularities are represented by low dimensional submanifolds, therefore a local treatment, e.g., in the framework of a local defect correction, seems possible.
  - Alternatively, it might be possible to treat singular contributions by a different and simpler model, using some universality features of the singular behaviour.

Many-particle models

Many-particle systems can be described by various quantities

- Wavefunctions $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_n)$: HF, MCSCF, CI, etc.
- Amplitudes for subsystems $\tau_{ij}(\mathbf{x}_1, \mathbf{x}_2)$ $i, j = 1, \ldots, n$: CC, CEPA, etc.
- Green's functions $G_1(\mathbf{x}_1, t_1, \mathbf{x}_2, t_2)$: GW, Bethe-Salpeter, etc.
- Densities $\rho_1(\mathbf{x})$, $\rho_2(\mathbf{x}_1, \mathbf{x}_2)$: DFT, etc.
- Density matrices $\gamma_1(\mathbf{x}_1, \mathbf{x}_2)$: Density matrix functionals, etc.
- Response functions $\chi(\mathbf{x}_1, t_1, \mathbf{x}_2, t_2)$: RPA, TDDFT, etc.

These quantities encode subtle asymptotic information in the limit $|\mathbf{x}_1 - \mathbf{x}_2| \to 0$ because of singular Coulomb interactions between particles.

Remark: asymptotic behaviour often smeared up by conventional discretization schemes.

Illustrative example

Two-electron harmonium atom with Hamiltonian operator

$$H = -\frac{1}{2}\Big(\Delta_1 + \Delta_2\Big) + \omega^2|\mathbf{x}_1|^2 + \omega^2|\mathbf{x}_2|^2 + \frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|}$$

Reduced one-particle density matrix of the ground state $\Psi_0(\mathbf{x}_1, \mathbf{x}_2)$

$$\gamma_1(\mathbf{x}_1, \mathbf{x}_2) = \int \Psi_0(\mathbf{x}_1, \mathbf{x}_3)\Psi_0(\mathbf{x}_2, \mathbf{x}_3)\, dx_3,$$

Leading order term of the singular asymptotic expansion, i.e., modulo $C^\infty(\mathbb{R}^3 \times \mathbb{R}^3)$ for $|\mathbf{x}_1 - \mathbf{x}_2| \to 0$ is of the form

$$\gamma_1(\mathbf{x}_1, \mathbf{x}_2) \sim |\mathbf{x}_1 - \mathbf{x}_2|^5 \sum_{l=0,2,4} \sum_{m=-l}^{l} g_{0,lm}(\mathbf{x}_1)\, Y_{lm}(\theta_{12}, \phi_{12}) + \mathcal{O}(|\mathbf{x}_1 - \mathbf{x}_2|^6)$$

- Much weaker than Kato's cusp condition for $\Psi_0(\mathbf{x}_1, \mathbf{x}_2) \sim c|\mathbf{x}_1 - \mathbf{x}_2|$.
- Determines decay rate of occupation numbers for natural orbitals.

RPA Coupled Cluster Model

CC model within the *random phase approximation*

$$\mathfrak{Q}\,(\mathcal{H}_0-\epsilon_{ij})\,\tau_{ij}(\underline{\mathbf{x}}_1,\underline{\mathbf{x}}_2)=-\mathfrak{Q}\,V^{(2)}_{[i,j]}(\underline{\mathbf{x}}_1,\underline{\mathbf{x}}_2)$$

$$-\mathfrak{Q}\,V^{(2)}(\mathbf{x}_1,\mathbf{x}_2)\tau_{ij}(\underline{\mathbf{x}}_1,\underline{\mathbf{x}}_2)-\tfrac{1}{4}\mathfrak{Q}\sum_{k,l}\tau_{kl}(\underline{\mathbf{x}}_1,\underline{\mathbf{x}}_2)\langle V^{(2)}_{[k,l]},\Psi^{(1)}_{ij}\rangle$$

$$+P(12/ij)\mathfrak{Q}\sum_{k}\tau_{i,k}(\underline{\mathbf{x}}_1,\underline{\mathbf{x}}_2)\,V^{(1)}_{kj}(\mathbf{x}_2)$$

$$-P(12/ij)\mathfrak{Q}\sum_{k}\int\tau_{i,k}(\underline{\mathbf{x}}_1,\underline{\mathbf{x}}_3)\,V^{(2)}_{kj}(\underline{\mathbf{x}}_3,\underline{\mathbf{x}}_2)\,d\underline{\mathbf{x}}_3$$

$$-\tfrac{1}{2}P(12/ij)\mathfrak{Q}\sum_{k,l}\iint\tau_{i,k}(\underline{\mathbf{x}}_1,\underline{\mathbf{x}}_3)\,V^{(2)}_{[k,l]}(\underline{\mathbf{x}}_3,\underline{\mathbf{x}}_4)\tau_{l,j}(\underline{\mathbf{x}}_4,\underline{\mathbf{x}}_2)\,d\underline{\mathbf{x}}_3\,d\underline{\mathbf{x}}_4$$

RPA Coupled Cluster Model

- Shifted non-interacting mean field Hamiltonian: $\mathcal{H}_0 - \epsilon_{ij}$
- Pair-amplitudes

$$\tau_{ij} \ : \ \left(\mathbb{R}^3 \otimes s\right) \otimes \left(\mathbb{R}^3 \otimes s\right) \ \to \ \mathbb{R}, \quad (\underline{\mathbf{x}}_1, \underline{\mathbf{x}}_2) \ \to \ \tau_{ij}(\underline{\mathbf{x}}_1, \underline{\mathbf{x}}_2),$$

  indices i, j, k, l refer to the occupied orbitals $1, 2, \ldots N$.
- Permutation operator: $P(12/ij) := 1 + (21)(ji) - (12)(ji) - (21)(ij)$
- Projection operator $\mathfrak{Q} := (1 - \mathfrak{q}_1)(1 - \mathfrak{q}_2)$ with $\mathfrak{q} := \sum_{i=1}^{N} |\phi_i\rangle\langle\phi_i|$ enforces Pauli's principle between pair-amplitudes

$$\mathfrak{Q}\tau_{ij}(\underline{\mathbf{x}}_1, \underline{\mathbf{x}}_2) = \tau_{ij}(\underline{\mathbf{x}}_1, \underline{\mathbf{x}}_2).$$

  and mean field part

$$\Psi^{(1)}_{ij}(\underline{\mathbf{x}}_1, \underline{\mathbf{x}}_2) := \phi_i(\underline{\mathbf{x}}_1)\phi_j(\underline{\mathbf{x}}_2) - \phi_j(\underline{\mathbf{x}}_1)\phi_i(\underline{\mathbf{x}}_2)$$

Goldstone diagrams and Ψ-DOs

In the following τ_{RPA} denotes an arbitrary Goldstone diagram.

$$\tau_{\mathrm{RPA}}(\mathbf{x}_1, \mathbf{x}_2) \equiv \tau_{\mathrm{RPA}}(\mathbf{x}, \mathbf{z}) \text{ with } \mathbf{x} := \mathbf{x}_1, \ \mathbf{z} := \mathbf{x}_1 - \mathbf{x}_2$$

Goldstone diagrams and classical Ψ-DOs

Symbol of a Goldstone diagram τ_{RPA} given by

$$\sigma_{\mathrm{RPA}}(\mathbf{x}, \boldsymbol{\eta}) := \int e^{-i\mathbf{z}\boldsymbol{\eta}} \tau_{\mathrm{RPA}}(\mathbf{x}, \mathbf{z}) \, d\mathbf{z}.$$

The symbol belongs to the standard Hörmander class $S^p(\mathbb{R}^3 \times \mathbb{R}^3)$ if it belongs to $C^\infty(\mathbb{R}^3 \times \mathbb{R}^3)$ and satisfies the estimate

$$\left| \partial_{\mathbf{x}}^{\alpha} \partial_{\boldsymbol{\eta}}^{\beta} \sigma_{\mathrm{RPA}}(\mathbf{x}, \boldsymbol{\eta}) \right| \lesssim \left(1 + |\boldsymbol{\eta}|\right)^{p - |\beta|} \quad \text{for all } \mathbf{x}, \boldsymbol{\eta} \in \mathbb{R}^3.$$

Goldstone diagrams and classical Ψ-DOs

Furthermore, it belongs to the class $S^p_{cl}(\mathbb{R}^3 \times \mathbb{R}^3)$, $p \in \mathbb{Z}$, of classical symbols if a decomposition

$$\sigma_{\mathrm{RPA}}(\mathbf{x}, \boldsymbol{\eta}) = \sum_{j=0}^{N-1} \sigma_{p-j}(\mathbf{x}, \boldsymbol{\eta}) + \sigma_{p-N}(\mathbf{x}, \boldsymbol{\eta}) \tag{5.1}$$

into symbols $\sigma_{p-j} \in S^{p-j}(\mathbb{R}^3 \times \mathbb{R}^3)$ and remainder $\sigma_{p-N} \in S^{p-N}(\mathbb{R}^3 \times \mathbb{R}^3)$ for any $N \in \mathbb{N}$ exits, such that for $\lambda \geq 1$ and η greater some constant, we have $\sigma_{p-j}(\mathbf{x}, \lambda\boldsymbol{\eta}) = \lambda^{p-j}\sigma_{p-j}(\mathbf{x}, \boldsymbol{\eta})$. The asymptotic expansion of a classical Goldstone symbol in Fourier space is related to a corresponding asymptotic expansion of its kernel function.

Theorem (Asymptotic behaviour of Goldstone diagrams)

Goldstone diagrams of RPA-CC pair-amplitudes can be considered as kernel functions of classical pseudo-differential operators **without logarithmic terms** *in their asymptotic expansions. Given a Goldstone diagram* τ_{RPA}*, whose corresponding symbol belongs to the symbol class* S^p_{cl}*,* $p \leq -4$*. Its asymptotic expansion, expressed in spherical coordinates* (z, θ, ϕ)*, is given by*

$$\tau_{\mathrm{RPA}}(\mathbf{x}, \mathbf{z}) \sim \sum_{0 \geq j} \tau_{p-j}(\mathbf{x}, z, \theta, \phi) \quad \textit{modulo } C^\infty(\mathbb{R}^3 \times \mathbb{R}^3),$$

$$\tau_{p-j}(\mathbf{x}, z, \theta, \phi) = z^{j-p-3} \sum_{\substack{l=0 \\ (j-p-l \text{ even})}}^{j-p-3} \sum_{m=-l}^{l} g_{j,lm}(\mathbf{x})\, Y_{lm}(\theta, \phi),$$

where functions $g_{j,lm}$ *belong to* $C^\infty(\mathbb{R}^3)$*.*

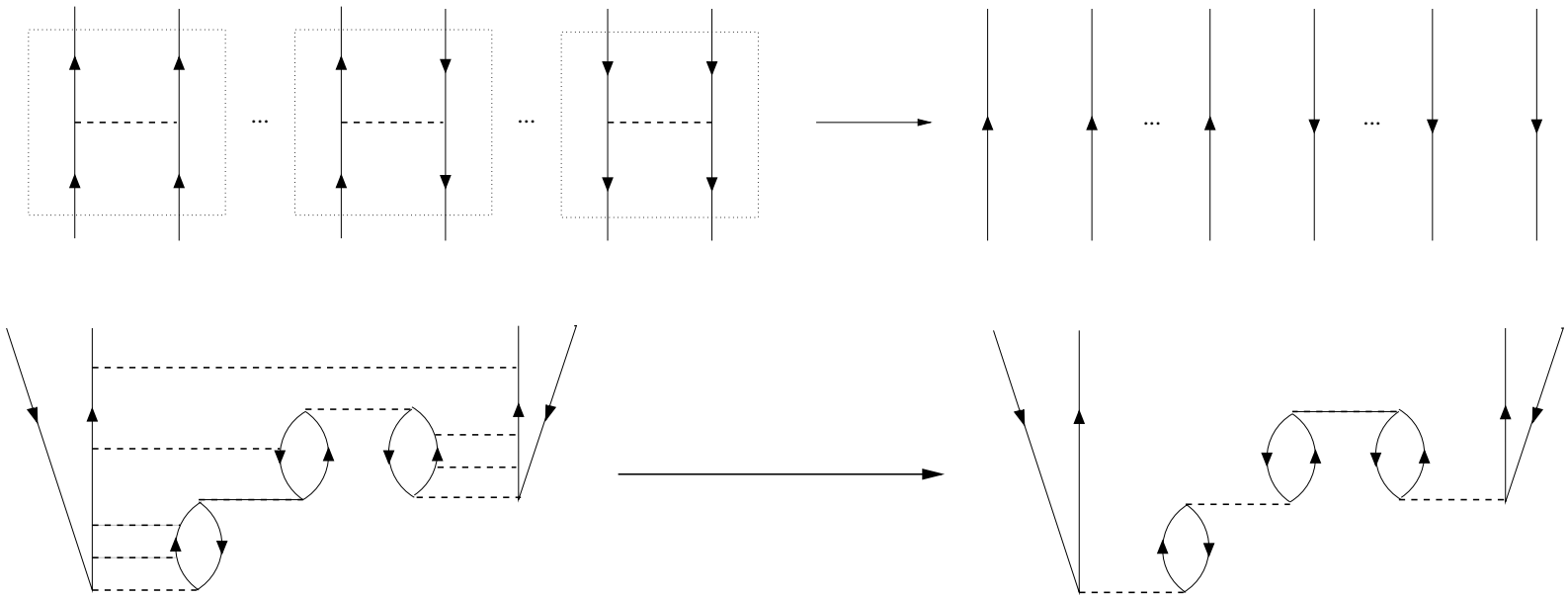
Theorem (Classification of Goldstone diagrams)

The symbol class of a diagram τ_{RPA} can be determined in the following manner

i) *Remove all ladder insertions in the diagram.*

ii) *Count the number of remaining interaction lines n.*

Then the corresponding symbol of the diagram τ_{RPA} belongs to the symbol class S_{cl}^{-4n}.



Corollary

The symbols of Goldstone diagrams representing the progression P_n of the n'th iteration step of standard RPA models can be classified according to the descending filtration of symbol classes

$$S_{\mathrm{cl}}^{-4(n+1)} \supset S_{\mathrm{cl}}^{-4(n+2)} \supset S_{\mathrm{cl}}^{-4(n+3)} \supset \cdots \supset S_{\mathrm{cl}}^{-4(2^{n+1}-1)}.$$

Corollary (Besov regularity)

Let τ_{RPA} represent a RPA diagram with corresponding symbol in S^p_{cl}, $p \leq -4$. Then τ_{RPA} belongs to $\tilde{\mathcal{B}}^{\alpha}_{q}(\Omega \times \Omega)$ for $q > -\frac{3}{1+p}$ and $\alpha = \frac{3}{q} - \frac{3}{2}$.

cf. HJF, W. Hackbusch and R. Schneider, ESAIM: M2AN **41** (2007) 261-279.

Local defect correction at edge and corner singularities

Elliptic PDE $Au = f$ with edge (corner) singularity on the right hand side.
Joint. work with W. Hackbusch (MPI Leipzig)

- Global basis Λ: Solve $A_\Lambda u_\Lambda = f_\Lambda$
- Local parametrix in a neighbourhood of the singularity

$$Au = f \quad \rightarrow \quad u = Pf - Gu$$

Asymptotic behaviour of solution

$$u \sim \tilde{u} + \mathcal{O}(r_{12}^n) \quad \text{with } \tilde{u} = Pf - Gu_\Lambda$$

- Local basis λ: Solve $A_\lambda \Delta\tilde{u}_\lambda = f_\lambda - (A\tilde{u})_\lambda$ with appropriate boundary conditions.
- Local defect $\tilde{u} + \Delta\tilde{u}_\lambda$ corrects matrix elements of global basis $\tilde{A}_\Lambda, \tilde{f}_\Lambda$
- Solve global problem again: $\tilde{A}_\Lambda \tilde{u}_\Lambda = \tilde{f}_\Lambda$.

Conclusions and Outlook

- Renormalization seems to be a possible route towards a universal subtraction scheme for singularities in electronic structure calculations.
  - Requires an analog to Weinberg's theorem.
  - Determination of singular subtractions using a generally applicable approach.
  - Derivation of a universal subtraction scheme in the spirit of Hepp's proof of renormalizability of QED.
  - Efficient treatment of singular subtractions.
- An extension of this scheme to hierarchical tensor product approximations seems possible.