New Analytical Approach to Improve Predictions of ab-initio Density Functional Theory

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SCIENTIA

Atomic Nuclei

- ~3000 nuclei in the known chart
- Complicated **quantum many-body problems**
  - A~100
  - Spin & Isospin
- Poorly understood at microscopic level

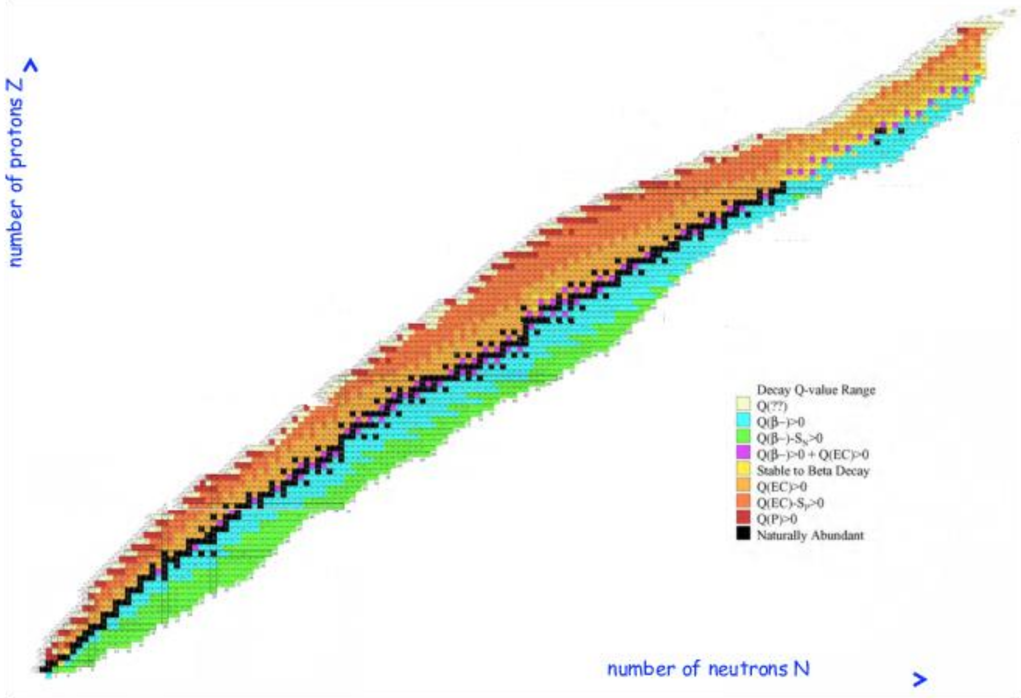
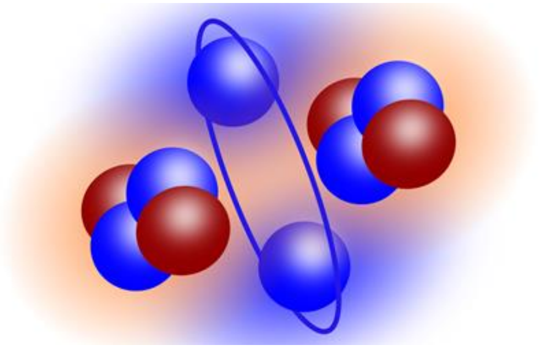
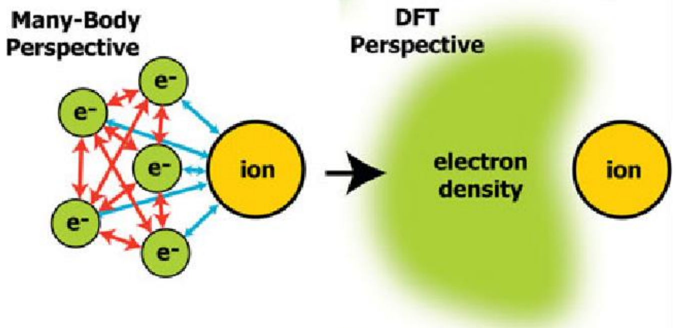


Chart of Nuclei (R. Diehl/Springer)



Recently discovered molecule-like Structure of atom ground state (P.Li/Chinese Academy of Sciences).

Quantum many-body problems



From usual QM to DFT (M.T. Lusk/Springer)

- Time-independent Schrodinger equation for *N* nucleons

Hamiltonian

$$\hat{H}\Psi(x_1, x_2, \ldots, x_N) = E\Psi(x_1, x_2, \ldots, x_N)$$

N-body wave function

where $x_i = (\vec{r}_i, \sigma_i, s_i)$ → very complicated to solve for *N*>3

position isospin spin

- Study **one-body density** instead → integrate out information of *N*-1 particles

$$\rho(\vec{r}) = \sum_{\sigma,s} \int |\Psi(x, x_2, \ldots, x_N)|^2 dx_2 \ldots dx_N$$

→ **Density Functional Theory** (DFT): reformulate the N-body quantum problem originally described by Ψ in terms of $\rho(\vec{r})$

Hohenberg-Kohn (HK) theorem

- Consider a Hamiltonian in the presence of an external field U

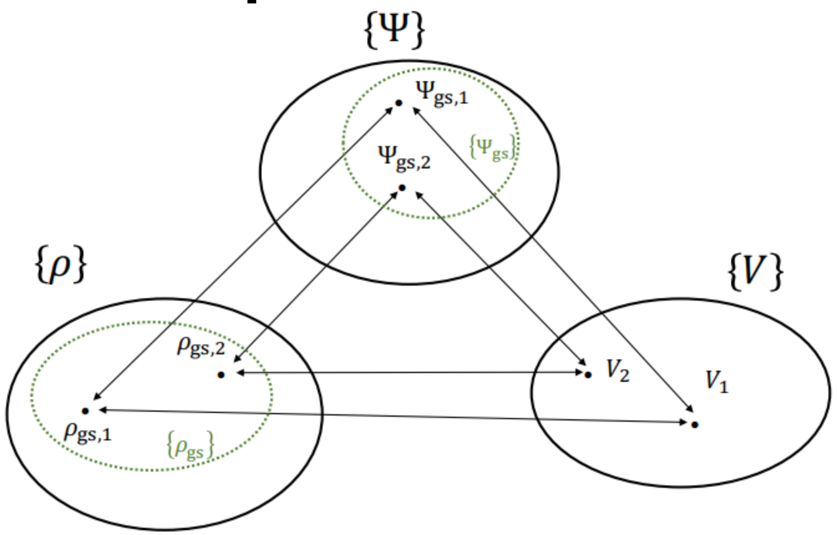
$$\hat{H} = \hat{T} + \hat{U}_{ee} + \hat{V} \qquad \hat{V} = \int dx \Psi^\dagger(x) u(\vec{r}) \Psi(x)$$

kinetic | Electron-electron interaction | External potential

- **HK 1st theorem: $u(\vec{r})$ and $\rho_{gs}(\vec{r})$ have a one-to-one correspondence**

- Hence, $u(\vec{r})$ and $\rho_{gs}(\vec{r})$ correspond to a unique Ψ_{gs}
  → Consider $\Psi_{gs}[\rho]$ a **functional** of ρ

  i.e. $\Psi_{gs}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \rightarrow \Psi_{gs}[\rho]$



HK 1st theorem (T. Yokota/PhD thesis)

Hohenberg-Kohn (HK) theorem

- Define **Energy Density Functional (EDF)**

$$E[\rho] = \langle \Psi_{\text{gs}}[\rho] | \, (\hat{T} + \hat{U} + \hat{V}) \, | \Psi_{\text{gs}}[\rho] \rangle$$

- **HK 2nd theorem:** $E[\rho] \geq E_{gs}$ **with equality taken for** $\boldsymbol{\rho = \rho_{gs}}$

- Hence, determine this EDF → ground state behaviour of the N-body system

- Can decompose $E[\rho]$ as $E[\rho] = F[\rho] + \int d\vec{r} V(\vec{r})\rho(\vec{r})$

  → $F[\rho]$ is called the **universal functional**, independent of external fields

Kohn-Sham (KS) scheme

- HK theorem → existence of EDF $\boldsymbol{E}[\boldsymbol{\rho}]$, but how to get it?

- **KS scheme**: decompose the universal functional

$$F[\rho] = T_0[\rho] + I[\rho]$$

Non-interacting kinetic energy

Interaction energy

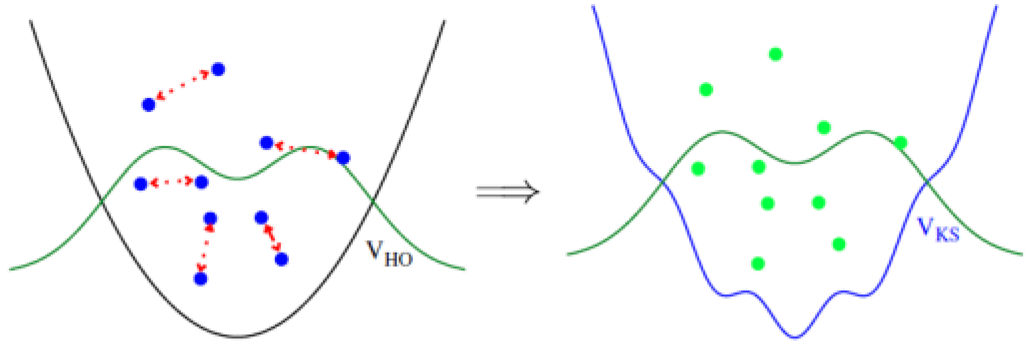
$$I[\rho] = \underbrace{\int d^3\vec{r} \int d^3\vec{r}\,' V(\vec{r},\vec{r}\,')\rho(\vec{r})\rho(\vec{r}\,')}_{\text{Hartree energy } E_H} + E_{xc}$$

Exchange-correlation energy

- Varying $F[\rho]$ w.r.t ρ

$$\left.\frac{\delta T_0}{\delta \rho}\right|_{\rho_{gs}} + \underbrace{\int d^3\vec{r}\,' V(\vec{r},\vec{r}\,')\rho_{gs}(\vec{r}\,') + \left.\frac{\delta E_{xc}}{\delta \rho}\right|_{\rho_{gs}}}_{\text{Effective potential } V_{KS}} + u(\vec{r}) = \mu$$

- Chemical potential μ is introduced as an Lagrange multiplier (particle # conservation)



Kohn-Sham (KS) scheme

$$\frac{\delta T_0}{\delta \rho} + \underbrace{\int d^3\vec{r}' U(\vec{r},\vec{r}')\rho(\vec{r}') + \frac{\delta E_{xc}}{\delta \rho} + u(\vec{r})}_{V_{KS}} = \mu$$

- Behaviours of **ground state energy** E_{gs} by considering the Schrodinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}[\rho_{gs}](\vec{r})\right)\phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r})$$

  for one-particle states $\phi_i(\vec{r})$.

- Solve this Schrodinger equation to get E_{gs} (numerically)

- But how to determine E_{xc}?

Determination of the $F[\rho]$

- Can write

$$F[\rho] = T_0[\rho] + E_H[\rho] + E_{xc}^{LDA}[\rho] + E_{xc}^{GGA}[\rho, |\nabla\rho|] + E_{xc}^{Meta-GGA}[\rho, |\nabla\rho|, |\nabla^2\rho|] + \dots$$

→ add terms for better and better approximations (Jacob's Ladder)

- **Local density approximation** (LDA): system ~ homogeneous

→ E_{xc} only depends on ρ

$$E_{xc}[\rho] \approx \int d^3\vec{r} E_{xc}^{LDA}(\rho(\vec{r}))\rho(\vec{r})$$

→ Not accurate enough, e.g. overbinding problem

- **Generalised Gradient Approximation** (GGA): E_{xc} also depends on $\nabla\rho$

$$E_{xc}[\rho] \approx \int d^3\vec{r} E_{xc}^{GGA}(\rho(\vec{r}), |\nabla\rho(\vec{r})|)\rho(\vec{r})$$

Functional Renormalisation group aided DFT

- New systematic approach in recent years using Functional Renormalisation group (FRG) → FRG aided DFT (**FRG-DFT**)

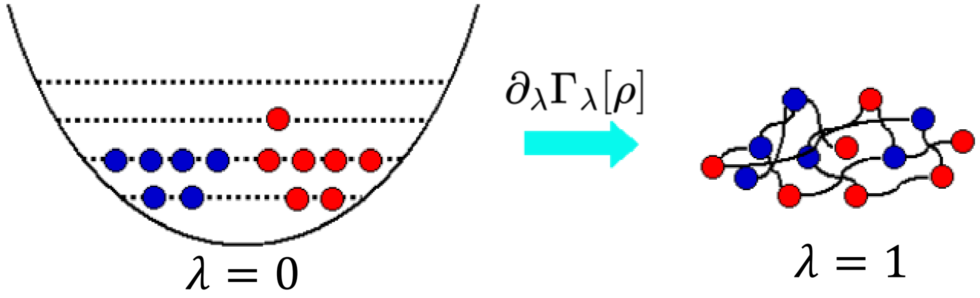
- EDF ←→ effective action $$E[\rho] = \lim_{\beta \to \infty} \frac{\Gamma[\rho]}{\beta}$$

$$\text{Action } S \xrightarrow{\text{Get rid of contributions that we are not interested in}} \text{Effective Action } \Gamma$$

- Why FRG-DFT?
  - Ab-initio non-perturbative method
  - RG-like flow equations are powerful calculation tools
  - Possible extension to improve the analysis of excited states using DFT

Functional Renormalisation group aided DFT

- General idea: know what happens **when interaction is off, then gradually turn the interaction**
- Quantitively $U \rightarrow U_\lambda$:
  - $\lambda = 0$: non-interacting, $U_{\lambda=0} = 0$;
  - $\lambda = 1$: fully interacting, $U_{\lambda=1} = 0$

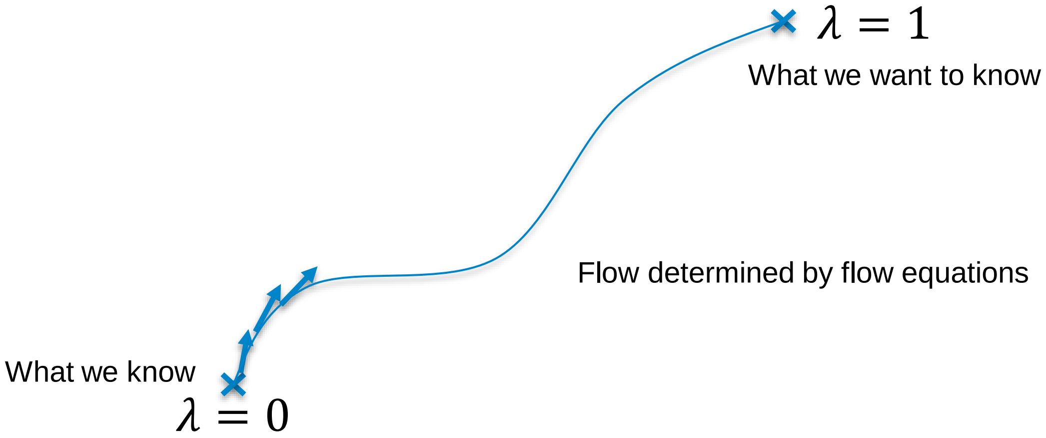


(Schwenk & Polonyi, arXiv:0403011 [nucl-th])

→ Determine the initial conditions at $\lambda = 0$, and evaluate the flow equations

$$\partial_\lambda \Gamma_\lambda[\rho] = \frac{1}{2} \int_{X,X'} \partial_\lambda U_{2b,\lambda}(X, X') + \Gamma_\lambda^{(2)-1}[\rho](X_{\epsilon'}, X') - \rho(X)\delta(\vec{\boldsymbol{r}} - \vec{\boldsymbol{r}}'))$$

$X = (\tau, \vec{r})$ with imaginary time $t = -i\tau$



Functional Renormalisation group aided DFT

- Current progress in FRG-DFT limited to E_{xc}^{LDA}, DE to solve

$$\partial_\lambda \Gamma_{\mathrm{xc},\lambda}[\rho] = \frac{1}{2}\int_{X,X'} \partial_\lambda U_{2b,\lambda}(X,X') \times \left(\Gamma^{(2)-1}_{\mathrm{xc},\lambda}[\rho](X_{\epsilon'},X') - \rho(X)\delta(\vec{\boldsymbol{r}}-\vec{\boldsymbol{r}}')\right)$$

→ Difficult to solve in practice

2-rd order derivative w.r.t ρ

- In LDA, expand Γ_λ around the ground state density field $\rho_{gs,\lambda}$ (**vertex expansion**)

$$\Gamma_\lambda[\rho] = \Gamma_\lambda[\rho_{gs,\lambda}] + \mu_\lambda \int_X (\rho(X) - \rho_{gs,\lambda}(X)) + \sum_{n=2}^{\infty} \frac{1}{n!}\int_{X_1,\ldots,X_n} \Gamma^{(n)}_\lambda[\rho_{gs,\lambda}](X_1,\ldots,X_n) \times \prod_i^n (\rho(X_i) - \rho_{gs,\lambda}(X_i))$$

→ can be used to derive the flow equations

n-th order derivative w.r.t ρ

- Our aim: extend FRG-DFT to compute E_{xc}^{GGA} using **derivative expansion** scheme

$$\Gamma_{\mathrm{xc},\lambda}[\rho] \approx \int d\tau \int d\boldsymbol{x} \left(g_\lambda^{(0,0)}(\rho(\tau,\boldsymbol{x})) + \frac{1}{2} g_\lambda^{(2,0)}(\rho(\tau,\boldsymbol{x}))(\partial_\tau \rho(\tau,\boldsymbol{x}))^2 + \frac{1}{2} g_\lambda^{(2,1)}(\rho(\tau,\boldsymbol{x}))(\nabla\rho(\tau,\boldsymbol{x}))^2 + O(\partial^4)\right)$$

Expansion coefficients to be determined

Flow equations

$$\Gamma_{\mathrm{xc},\lambda}[\rho] \approx \int d\tau \int d\boldsymbol{x} \left(g_\lambda^{(0,0)}(\rho(\tau,\boldsymbol{x})) + \frac{1}{2} g_\lambda^{(2,0)}(\rho(\tau,\boldsymbol{x}))(\partial_\tau \rho(\tau,\boldsymbol{x}))^2 + \frac{1}{2} g_\lambda^{(2,1)}(\rho(\tau,\boldsymbol{x}))(\nabla \rho(\tau,\boldsymbol{x}))^2 + O(\partial^4) \right)$$

- **Fourier Transform** $\dfrac{\delta^2 \Gamma_{\mathrm{xc},\lambda}}{\delta\rho(\tau_1,\boldsymbol{x}_1)\delta\rho(\tau_2,\boldsymbol{x}_2)}$ in the homogeneous case

$$\int d\tau \int d\boldsymbol{r} e^{i\omega\tau - i\boldsymbol{p}\cdot\boldsymbol{r}} \frac{\delta^2 \Gamma_{\mathrm{xc},\lambda}}{\delta\rho(\tau,\boldsymbol{r})\delta\rho(0,\boldsymbol{0})}[\rho_{\mathrm{hom}}] = g_\lambda^{(0,0)\prime\prime}(\rho_{\mathrm{hom}}) + g_\lambda^{(2,0)}(\rho_{\mathrm{hom}})\omega^2 + g_\lambda^{(2,1)}(\rho_{\mathrm{hom}})\boldsymbol{p}^2 + O((\omega,\boldsymbol{p})^4)$$

- Apply the **momentum conservation law**

$P = (\omega, \vec{p})$

$$\Gamma_\lambda^{(n)}[\rho_{\mathrm{hom}}](P_1,\ldots,P_n) = (2\pi)^3 \beta \delta^{(4)}(P_1 + \cdots + P_n) \tilde{\Gamma}_\lambda^{(n)}(P_1,\ldots,P_{n-1})$$

- Express $\Gamma_{xc}^{(n)}$ in terms of **Green's function** $\tilde{G}_\lambda^{(2)}(P) = \dfrac{1}{\tilde{\Gamma}_\lambda^{(2)}(P)}$

- $g_\lambda^{(0,0)}$ depends only on ρ → homogeneous part (LDA) of EDF $g_\lambda^{(0,0)}(\rho_{\mathrm{hom}}) = \dfrac{\Gamma_{\mathrm{xc},\lambda}[\rho_{\mathrm{hom}}]}{\beta \mathcal{V}}$

Flow equations

$$\Gamma_{\mathrm{xc},\lambda}[\rho] \approx \int d\tau \int d\boldsymbol{x} \left(g_\lambda^{(0,0)}(\rho(\tau,\boldsymbol{x})) + \frac{1}{2} g_\lambda^{(2,0)}(\rho(\tau,\boldsymbol{x}))(\partial_\tau \rho(\tau,\boldsymbol{x}))^2 + \frac{1}{2} g_\lambda^{(2,1)}(\rho(\tau,\boldsymbol{x}))(\nabla \rho(\tau,\boldsymbol{x}))^2 + O(\partial^4) \right)$$

- Homogeneous term:

$$\partial_\lambda g_\lambda^{(0,0)}(\rho_{\mathrm{hom}}) = \frac{1}{2} \int \frac{d\boldsymbol{p}}{(2\pi)^3} \tilde{U}(\boldsymbol{p}) \left(\frac{1}{\beta} \sum_\omega \tilde{G}_\lambda^{(2)}(P) - \rho_{\mathrm{hom}} \right), \quad g_0^{(0,0)}(\rho_{\mathrm{hom}}) = 0$$

- Inhomogeneous terms:

$$\partial_\lambda g_\lambda^{(2,0)}(\rho_{\mathrm{hom}}) = \frac{1}{2} \lim_{\omega\to 0} \lim_{p \to 0} \frac{\partial^2}{\partial \omega^2} I_\lambda(\omega, p) \qquad \partial_\lambda g_\lambda^{(2,1)}(\rho_{\mathrm{hom}}) = \frac{1}{2} \lim_{\omega\to 0} \lim_{p \to 0} \frac{\partial^2}{\partial p^2} I_\lambda(\omega, p)$$

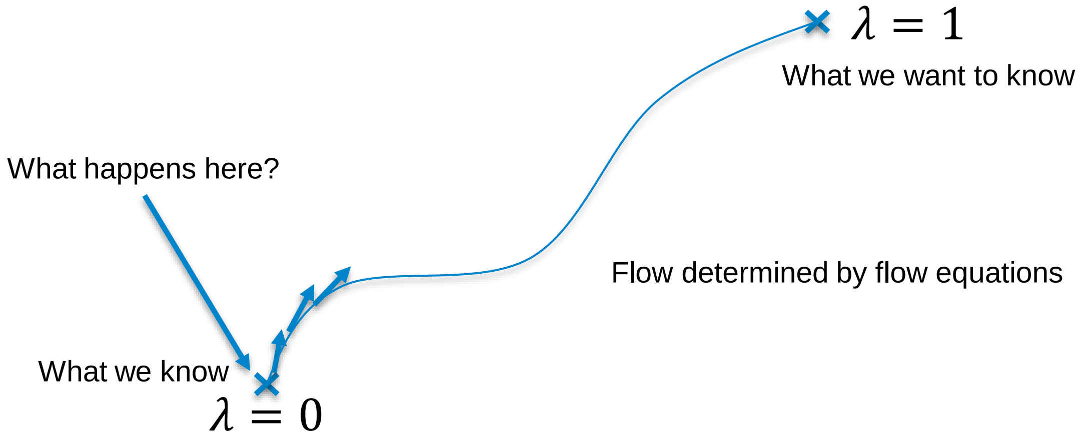
$$\begin{aligned} I_\lambda(P) = & \frac{1}{2} \int_{P_1} \tilde{U}(P_1) \Big(\tilde{G}_\lambda^{(2)}(P_1) \tilde{\Gamma}_\lambda^{(3)}(-P_1, P_1 - P) \tilde{G}_\lambda^{(2)}(P_1 - P) \tilde{\Gamma}_\lambda^{(3)}(-P_1 + P, P_1) \tilde{G}_\lambda^{(2)}(P_1) \\ & + \tilde{G}_\lambda^{(2)}(P_1) \tilde{\Gamma}_\lambda^{(3)}(-P_1, P_1 + P) \tilde{G}_\lambda^{(2)}(P_1 + P) \tilde{\Gamma}_\lambda^{(3)}(-P_1 - P, P_1) \tilde{G}_\lambda^{(2)}(P_1) \\ & - \tilde{G}_\lambda^{(2)}(P_1) \tilde{\Gamma}_\lambda^{(4)}(-P_1, P_1, P) \tilde{G}_\lambda^{(2)}(P_1) \Big) \end{aligned}$$

Initial Conditions

$$I_\lambda(P) = \frac{1}{2}\int_{P_1} \tilde{U}(P_1)\Big(\underline{\tilde{G}^{(2)}_\lambda}(P_1)\underline{\tilde{\Gamma}^{(3)}_\lambda}(-P_1, P_1 - P)\tilde{G}^{(2)}_\lambda(P_1 - P)\tilde{\Gamma}^{(3)}_\lambda(-P_1 + P, P_1)\tilde{G}^{(2)}_\lambda(P_1)$$
$$+ \tilde{G}^{(2)}_\lambda(P_1)\tilde{\Gamma}^{(3)}_\lambda(-P_1, P_1 + P)\tilde{G}^{(2)}_\lambda(P_1 + P)\tilde{\Gamma}^{(3)}_\lambda(-P_1 - P, P_1)\tilde{G}^{(2)}_\lambda(P_1)$$
$$- \tilde{G}^{(2)}_\lambda(P_1)\underline{\tilde{\Gamma}^{(4)}_\lambda}(-P_1, P_1, P)\tilde{G}^{(2)}_\lambda(P_1)\Big)$$

- $\tilde{\Gamma}^{(3,4)}_\lambda$ hence $\tilde{\Gamma}^{(3,4)}_{\lambda=0}$ determined by

$$\left.\frac{\delta(\tilde{G}^{(2)}_\lambda)^{-1}}{\delta\rho}\right|_{\lambda=0} \quad \text{and} \quad \left.\frac{\delta^2(\tilde{G}^{(2)}_\lambda)^{-1}}{\delta\rho^2}\right|_{\lambda=0}$$



- $\tilde{G}^{(n)}_{\lambda=0}$ determined by free Feynman Propagators $\tilde{G}^{(2)}_{F,0}$

$$\tilde{G}^{(n)}_0(P_1, ..., P_{n-1}) = -\frac{1}{2}\underbrace{\sum_{\sigma\in S_{n-1}}}_{\text{Permutation group}}\int_P \prod_{k=0}^{n-1}\tilde{G}^{(2)}_{F,0}\left(\sum_{i=1}^{k} P_{\sigma(i)} + P\right)$$

Evaluating the limits

$$\partial_\lambda g_\lambda^{(2,0)}(\rho_{\text{hom}})\frac{1}{2}\lim_{\omega\to 0}\lim_{p\to 0}\frac{\partial^2}{\partial\omega^2}I_\lambda(\omega,p) \qquad \partial_\lambda g_\lambda^{(2,1)}(\rho_{\text{hom}})\frac{1}{2}\lim_{\omega\to 0}\lim_{p\to 0}\frac{\partial^2}{\partial p^2}I_\lambda(\omega,p)$$

- By $\tilde{\Gamma}_\lambda^{(3,4)}$, I_λ becomes $I_\lambda(P) = -\dfrac{C_\lambda(P)}{\tilde{G}_\lambda^{(2)}(P)^2}$

  where $C_{\lambda=0}$ can be expressed as

θ = step function $\qquad \xi(\vec{p}) = \dfrac{\vec{p}^2}{2} - \mu_0$

$$C_{\lambda=0}(P) = 2N_s\int\frac{d^3\mathbf{p}'}{(2\pi)^3}\int\frac{d^3\mathbf{p}''}{(2\pi)^3}U(\mathbf{p}')\theta\left(-\xi\left(\mathbf{p}''\right)\right)\left(\theta\left(-\xi\left(\mathbf{p}+\mathbf{p}'+\mathbf{p}''\right)\right)-\theta\left(-\xi\left(\mathbf{p}'+\mathbf{p}''\right)\right)\right)$$

$$\times\left[\frac{\left(\xi\left(\mathbf{p}''+\mathbf{p}\right)-\xi\left(\mathbf{p}''\right)\right)^2-\omega^2}{\left(\omega^2+\left(\xi\left(\mathbf{p}''+\mathbf{p}\right)-\xi\left(\mathbf{p}''\right)\right)^2\right)^2}-\frac{\left(\xi\left(\mathbf{p}''+\mathbf{p}+\mathbf{p}'\right)-\xi\left(\mathbf{p}''+\mathbf{p}'\right)\right)\left(\xi\left(\mathbf{p}''+\mathbf{p}\right)-\xi\left(\mathbf{p}''\right)\right)-\omega^2}{\left(\omega^2+\left(\xi\left(\mathbf{p}''+\mathbf{p}+\mathbf{p}'\right)-\xi\left(\mathbf{p}''+\mathbf{p}'\right)\right)^2\right)\left(\omega^2+\left(\xi\left(\mathbf{p}''+\mathbf{p}\right)-\xi\left(\mathbf{p}''\right)\right)^2\right)}\right]$$

- Both $\lim_{\omega,\vec{p}\to 0} C_{\lambda=0}(P) = \infty$ and $\lim_{\omega,\vec{p}\to 0}\tilde{G}_{\lambda=0}^{(2)}(P)^2 = \infty$ → Still cannot evaluate the limits

Evaluating the limits

$$\partial_\lambda g_\lambda^{(2,0)}(\rho_{\mathrm{hom}})\frac{1}{2}\lim_{\omega\to 0}\lim_{p\to 0}\frac{\partial^2}{\partial\omega^2}I_\lambda(\omega,p) \qquad \partial_\lambda g_\lambda^{(2,1)}(\rho_{\mathrm{hom}})\frac{1}{2}\lim_{\omega\to 0}\lim_{p\to 0}\frac{\partial^2}{\partial p^2}I_\lambda(\omega,p)$$

- Evaluate $C_{\lambda=0}(P)$ and $\tilde{G}^{(2)}_{\lambda=0}(P)^2$ separately
  → more explicit expression for $I_{\lambda=0}(P)$

- The limits of $\frac{\partial^2}{\partial\vec{p}^2}I_{\lambda=0}(P)$ henceforth obtained can be evaluate
  → $\boldsymbol{g^{(2,1)}_{\lambda=0}(\rho_{hom})}$ **solved**

- Still unclear if $g^{(2,0)}_{\lambda=0}(\rho_{hom})$ can be solved in the same way…

Summary & Outlook

- DFT is the only known way to study quantum many-body problems with large N
- FRG is a powerful tool for the **ab-initio construction of DFT**
- We **extended FRG-DFT to GGA** based on the derivative expansion method
  → incorporate in FRG-DFT how EDF depends on the density field gradient
- A limit remained to be evaluated & physical interpretations?
- Needs to be numerically and mathematically validated

Thank you for listening!