# VARIATIONAL DIAGRAMMATIC MONTE CARLO AND THE UNIFORM ELECTRON GAS

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**DFT + Embedded DMFT Functional***

**Developed by Kristjan Haule at Rutgers University, ©Copyright 2007-2017.**

DOWNLOAD DFT+eDMFT

- Exact double-counting between LDA&DMFT
- Forces on atoms
- Structural relaxations within DMFT functional
- Phonons within DMFT
- LAPW precise basis set for all electrons

GW & LAPW in Python: https://github.com/ru-ccmt/PyGW3

Variational diagMC: https://github.com/haulek/VDMC

Support:
Simons Collaboration on the Many Electron Problem
Blavatnik Awards Young Scientists

Jouvence, June 13, 2022

# Why bother with uniform electron gas?

- Solution of UEG serves as a proof of principle that tests the capability of a method to address realistic materials with long range Coulomb repulsion (beyond simplified models).

- Such solution offers new insights into the ab-intion methods (DFTs and GWs), and more understanding of screening in solids.

Variational Diagrammatic Monte Carlo (VDMC) [1,2] allows

- very precise determination of certain physical observables in electron gas: effective mass, landau-liquid parameters, spin & charge susceptibilities.
- It also provides XC-kernel needed in TDDFT community [3].
- It settles the debate on bandwidth in electron gas, as relevant for Na metal.
- It is useful in other fields, i.e., warm dense matter field uses the same model at higher temperature, where VDMC performs even better.
- VDMC should be developed into electronic structure method for high-throughput calculation (like achieved in DFT community, as well as recently by DFT+eDMFT method [4]).

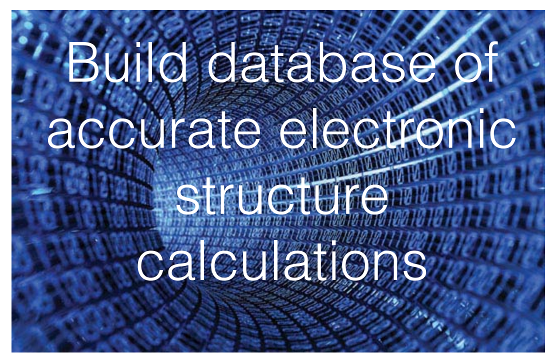
VDMC:

*[1] Kun Chen, K. Haule,* Nature Communications **10,** 3725 (2019)

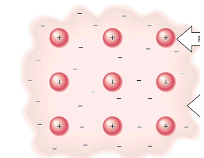
*[2] K. Haule, K. Chen,* Scientific Reports **12**, 2294 (2022)

*[3] J. P. F. LeBlanc,* K. Chen, N.V. Prokof'ev, K.H., Igor S. Tupitsyn, in preparation

*[4]Kamal Choudhary et.al., npj Computational Materials 6, 1 (2020).*



# History : Uniform electron gas



Is at the heart of the DFT success for materials property prediction.

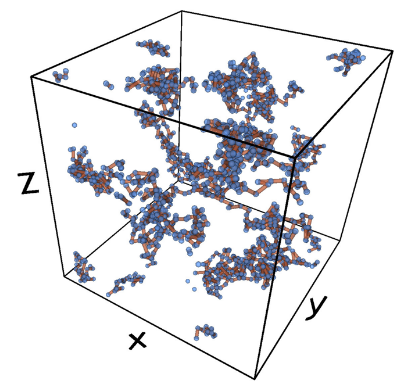
$$E_{xc}[n] \qquad V_{xc} = \frac{\delta E_{xc}[n]}{\delta n} \qquad f_{xc}[n](\mathbf{r},\mathbf{r}',\omega) = \frac{\delta V_{xc}[n](\mathbf{r},\omega)}{\delta n(\mathbf{r}'\omega)}$$

Remains essentially unknown to this day
Needed in TDDFT

| | |
|---|---|
| 1928 | Dirac's relativistic theory of the electron<br>Bloch's theory of electrons in solids<br>Pauli-Sommerfeld free electron theory of metals |
| 1934 | Wigner's proposal of the Wigner crystal |
| 1956 | Landau's theory of Fermi liquids |
| 1957 | BCS theory of superconductivity |
| 1964 | Hohenberg-Kohn-Sham DFT |
| 1980 | Ceperley-Alder QMC prediction of $E_{xc}$ |
| | many properties of UEG remain unknown |

Very little is known: spin susceptibility, Landau parameters, …

high temperature at warm dense matter (plasma) conditions




Diffusion MC simulation of UEG (trajectories in imaginary time)

J. Chem. Phys. **151**, 014108 (2019)

# The Uniform Electron Gas Problem

$$H=\sum_s\int d^3\mathbf{r}\,\psi_s^\dagger(\mathbf{r})[-\frac{\nabla^2}{2m}+V_{e-n}(\mathbf{r})]\psi_s(\mathbf{r})+\frac{1}{2}\sum_{ss'}\int d^3\mathbf{r}d^3\mathbf{r}'\psi_s^\dagger(\mathbf{r})\psi_{s'}^\dagger(\mathbf{r}')V_c(\mathbf{r}-\mathbf{r}')\psi_{s'}(\mathbf{r}')\psi_s(\mathbf{r})+H_{n-n}$$

$V_{e-n}$ electron-nuclei interaction

$H_{n-n}$ nuclei-nuclei interaction

$$V_C(\mathbf{r}-\mathbf{r}')=\frac{1}{4\pi\varepsilon_0|\mathbf{r}-\mathbf{r}'|}$$

neglecting spin-orbit coupling

Born-Oppenheimer : $H_{n-n}$ and $V_{e-n}$ just a classical potentials

---

Uniform electron gas: $V_{e-n}(\mathbf{r})=-\int d^3\mathbf{r}'V_C(\mathbf{r}-\mathbf{r}')n_0$ where $n_0$ is constant neutralizing density

e-n and n-n terms diverge, but they cancel out exactly, so that the final Hamiltonian is simplified to

$$H=\sum_{\mathbf{k},s}\frac{k^2}{2m}\psi_{\mathbf{k},s}^\dagger\psi_{\mathbf{k},s}+\frac{1}{2V}\sum_{\mathbf{q}\neq 0,\mathbf{k}\mathbf{k}',ss'}\psi_{\mathbf{k}+\mathbf{q},s}^\dagger\psi_{\mathbf{k}'-\mathbf{q},s'}^\dagger V_c(\mathbf{q})\psi_{\mathbf{k}'s'}\psi_{\mathbf{k},s}$$

notice the absence of q=0 term, which is diverging and cancels out.

# Significance of Uniform electron gas for DFT

$$E = \langle \Phi_0 | H | \Phi_0 \rangle = \langle \Phi_0 | T + H_{e-e} + V_{e-n} | \Phi_0 \rangle = \langle \Phi_0 | T + H_{e-e} | \Phi_0 \rangle + \int d^3\mathbf{r}\, V_{e-n}(\mathbf{r})\, n(\mathbf{r})$$

Hohenberg-Kohn theorem: Ground state electron density $n(\mathbf{r})$ is *V*-representable.

The knowledge of $n(\mathbf{r})$ alone gives knowledge of the external potential and hence the Hamiltonian H. If the Hamiltonian is uniquely determined from density, then the ground state is also a functional of the density only. (*The ground state might be degenerate, but the universality of the functional can still be proven.)*

Hohenberg-Kohn theorem: $\langle \Phi_0 | T + H_{e-e} | \Phi_0 \rangle$ is universal functional of the density $n(\mathbf{r})$,i.e.,

$$F[\{n\}] \equiv \langle \Phi_0^{n(\mathbf{r})} | T + H_{e-e} | \Phi_0^{n(\mathbf{r})} \rangle$$

$$F[\{n\}] = \langle \Phi_0^{n(\mathbf{r})} | \sum_s \int d^3\mathbf{r}\, \psi_s^\dagger(\mathbf{r})[-\frac{\nabla^2}{2m}]\psi_s(\mathbf{r}) + \frac{1}{2}\sum_{ss'} \int d^3\mathbf{r} d^3\mathbf{r}' \psi_s^\dagger(\mathbf{r})\psi_{s'}^\dagger(\mathbf{r}')V_c(\mathbf{r}-\mathbf{r}')\psi_{s'}(\mathbf{r}')\psi_s(\mathbf{r}) | \Phi_0^{n(\mathbf{r})} \rangle$$

Universal functional can be computed from the simplest possible interacting model, i.e., the uniform electron gas model???

# Significance of Uniform electron gas for DFT

It is unlikely that we will ever be able to compute functional F[{n}] exactly even for the uniform electron gas.

The functional is non-local even in UEG: $F[\{n\}] \equiv \langle \Phi_0^{n(\mathbf{r})} | T + H_{e-e} | \Phi_0^{n(\mathbf{r})} \rangle$

We want to find a part of the functional for which a local-type approximation is good.

$$E = \int d^3\mathbf{r} V_{e-n}(\mathbf{r}) n(\mathbf{r}) + E_H[\{n\}] + T_0[\{n\}] + E_{xc}[\{n\}]$$

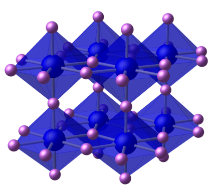
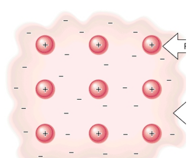
$$E_H[\{n\}] = \frac{1}{2} \int d^3\mathbf{r} d^3\mathbf{r}' n(\mathbf{r}) V_C(\mathbf{r}-\mathbf{r}') n(\mathbf{r}')$$

$T_0[\{n\}]$ is not the exact kinetic energy, but just the kinetic energy of the corresponding non-interacting system.

We do not even know how to express the total kinetic energy or the exchange energy as a functional of density.
They can be expressed exactly with the density matrix.

$E_{xc}[\{n\}]$ turns out to be a piece that is amenable to local approximation.

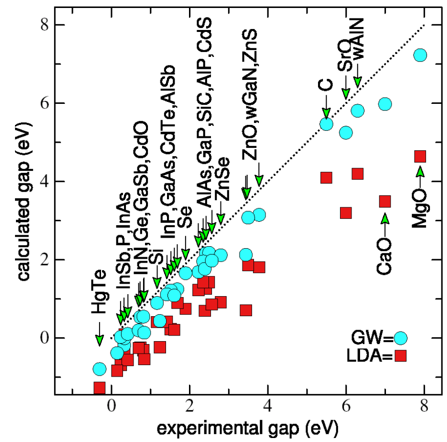
$$E_{xc} \approx \int d^3\mathbf{r}\, n(\mathbf{r}) \varepsilon_{xc}^{UEG}[n(\mathbf{r})]$$

LDA:  map solid point by point to UEG  to compute XC energy and XC potential

# Time dependent DFT=TDDFT

DFT is pretty good for ground state properties (exact DFT is exact)
But DFT has well known “gap problem” when trying to interpret KS spectra as physical excitations

Gaps in semiconductors:

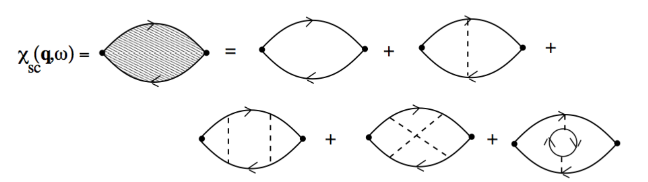



from Richard Martin et.al., Interacting electrons

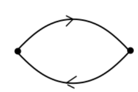
The same idea was extended by Gross&Kohn in 1985 to compute the excited state properties (PRL 55, 2850):

$$\chi^{-1}(\mathbf{r},\mathbf{r}';\omega) = \chi_{KS}^{-1}(\mathbf{r},\mathbf{r}';\omega) - V_C(\mathbf{r}-\mathbf{r}') - f_{xc}(\mathbf{r},\mathbf{r}',\omega)$$

density time response: $\chi(\mathbf{r},\mathbf{r}',\tau) = -\langle\psi^\dagger(\mathbf{r},\tau)\psi(\mathbf{r},\tau)\psi^\dagger(\mathbf{r}',\tau')\psi(\mathbf{r}',\tau')\rangle$




Kohn-Sham non-interacting response (RPA bubble):



# Time dependent DFT=TDDFT

**Hohenberg-Kohn for GS DFT:** One can not find two different $V_{e-n}$ potentials that give rise to the same electron density $n(\mathbf{r})$ in the ground state.

$$H(t) = T + H_{e-e} + V_{e-n}(t)$$ add time-dependence to external potential

**Runge–Gross theorem (PRL 52, 997, (1984)):**

One can not find two different $V_{e-n}(t)$ $V'_{e-n}(t)$ potentials that give rise to the same electron density $n(\mathbf{r}, t)$, if $n(\mathbf{r}, t)$ is time evolved by H(t) from the ground state.

Caveat: $V_{e-n}(t)$ has to be expandable in Taylor series (analytic in time) and $V_{e-n}(t)$ *and* $V'_{e-n}(t)$ differ for more than $c(t)$

**Gross&Kohn (PRL 55, 2850, (1985)):**

using time-dependent Schroedinger Eq. the response of the interacting electrons is

$$\chi^{-1}(\mathbf{r}, \mathbf{r}'; \omega) = \chi_{KS}^{-1}(\mathbf{r}, \mathbf{r}'; \omega) - V_C(\mathbf{r} - \mathbf{r}') - f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$$

where $$f_{xc}[\{n\}](\mathbf{r}, \mathbf{r}'; \omega) = \frac{\delta V_{xc}[\{n\}](\mathbf{r}, \omega)}{\delta n(\mathbf{r}', \omega)}$$ but what is $f_{xc}[\{n\}]$ ?

# Time dependent DFT=TDDFT

Original idea was to take the unknown $f_{xc}[\{n\}]$ from the uniform electron gas.

But we do not know $f_{xc}[\{n\}]$ in UEG.

If we assume $f_{xc}[\{n\}]$ is local to a point in 3D space and local in time (constant in frequency) than:

$$f_{xc}[\{n\}](\mathbf{r},\mathbf{r}';\omega=0) = \frac{\delta V_{xc}[\{n\}](\mathbf{r},\omega=0)}{\delta n(\mathbf{r}',\omega=0)} = \left.\frac{\delta^2 E_{xc}[\{n\}]}{\delta n^2}\right|_{n=n_0} \delta(\mathbf{r}-\mathbf{r}')$$

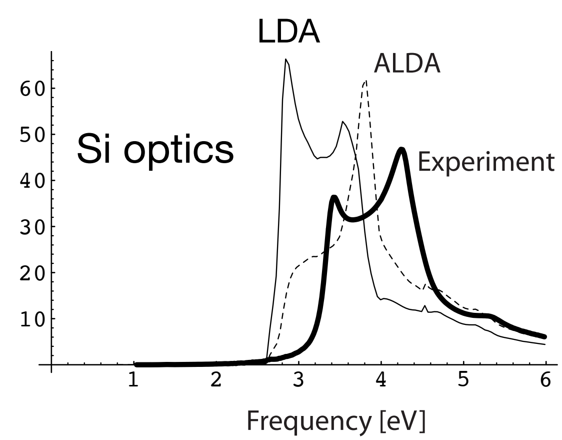
Adiabatic LDA

Considerably improves (compared to LDA) the excitation energies of molecules

*$^1S \rightarrow {}^1P$ excitation energies in two-valence-electron atoms.*

| Atom | $\omega_{exp}$ | $\omega_{ALDA}$ | $\omega^{(0)}_{LDA}$ |
|---|---|---|---|
| He | 1.56 Ry | 1.552 | – |
| Be | 0.388 | 0.399 | 0.257 |
| Mg | 0.319 | 0.351 | 0.249 |
| Ca | 0.216 | 0.263 | 0.176 |
| Zn | 0.426 | 0.477 | 0.352 |
| Sr | 0.198 | 0.241 | 0.163 |
| Cd | 0.398 | 0.427 | 0.303 |

Not much better gaps or optical excitations in semiconductors.



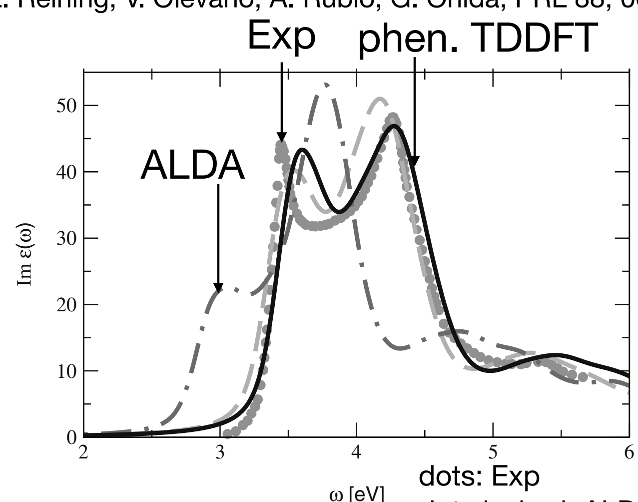
# Time dependent DFT=TDDFT

Optics is q->0 charge response, which is in TDDFT: $$\chi(\mathbf{q},\omega) = \frac{\chi_{KS}(\mathbf{q},\omega)}{1-\chi_{KS}(\mathbf{q},\omega)[\frac{4\pi e^2}{q^2} + f_{xc}(\mathbf{q},\omega)]}$$

If we want a substantial change of optics in semiconductors, than we require the form: $$\lim_{q\to 0} f_{xc}(\mathbf{q},\omega) = \frac{\alpha(\omega)}{\mathbf{q}^2}$$

*Should be singular in semiconductors at zero frequency, but not in metals, like UEG.*

L. Reining, V. Olevano, A. Rubio, G. Onida, PRL 88, 066404 (2002)




dots: Exp
dot-dashed: ALDA
dashed: GW+Bethe-Salpeter
continuous: phenomenological TDDFT

Phenomenological ansatz works really well:

$$f_{xc}(\mathbf{r},\mathbf{r}') = -\frac{0.2}{4\pi|\mathbf{r}-\mathbf{r}'|}$$

But each semiconductor needs different number

Conclusion: $f_{xc}$ is highly non-local

# Time dependent DFT=TDDFT

**Nazarov&Vignale&Chang (PRL 102, 113001, (2009)):**

Instead of TDDFT for density-density response function, we might use current-current response functions.

Time Dependent Current Density Functional Theory (TDCDFT):

$$\hat{\chi}^{-1}(\mathbf{q},\mathbf{q}',\omega) = \hat{\chi}_{KS}^{-1}(\mathbf{q},\mathbf{q}',\omega) - \hat{f}_{xc}(\mathbf{q},\mathbf{q}',\omega) - \frac{4\pi ec}{\omega^2}\delta_{\mathbf{q},\mathbf{q}'}\frac{\vec{e}_{\mathbf{q}}\otimes\vec{e}_{\mathbf{q}}}{\mathbf{q}^2}$$

where $\hat{\chi}$ is current-current response function.

$\hat{f}_{xc} \rightarrow f_{xc}^L \& f_{xc}^T$ has two components: longitunidal and transverse

Local approximation on longitudinal & transverse $f_{xc}$ seems a much better approximation as it leads to desired form for the charge $f_{xc}$

$$\lim_{\mathbf{q}\to 0} f_{xc}(\mathbf{q},0) = \frac{\alpha(\omega)}{\mathbf{q}^2}$$

Namely:
$$\lim_{\mathbf{q}\to 0} f_{xc}(\mathbf{q},\omega) = \frac{1}{n_0^2 q^2}\sum_{\mathbf{G}\neq 0}(\mathbf{G}\cdot\mathbf{e}_{\mathbf{q}})^2[f_{xc}^L(\mathbf{G},\omega) - f_{xc}^L(\mathbf{G},\omega=0)]|n_0(\mathbf{G})|^2$$

$f^L_{xc}(\omega)$ is not known in uniform electron gas, hence this was not evaluated yet.
Only phenomenological kernels are used in practice.

# Bandwidth of alkali metals, correspond to $r_s$~4

**Bandwidth of Na metal is controversial for 35 years:**

-ARPES bandwidth show reduction for 18-25% [1,2] (newer 2021 data 10%)
-some GW calculation reproduce reduction [3], most do not.
-DMC shows increased bandwidth, not reduced [5] because of fixed node approximation.


[1] E. Jensen & E.W. Plummer, PRL 55, 1912–1915, (1985).

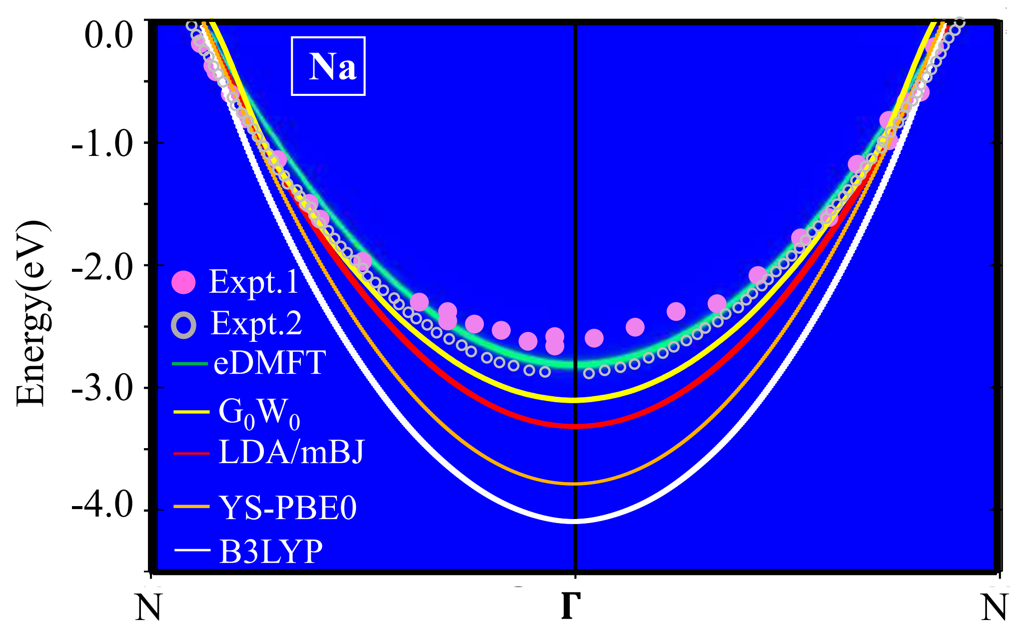
[2] I.-W. Lyo & E.W. Plummer, PRL 60, 1558–1561, (1988).

[3] J.E. Northrup, M.S. Hybertsen, & S.G. Louie, PRL 59, 819 (1987).

[4] X. Zhu, & A.W. Overhauser, RPB 33, 925(1986).

[5] R. Maezono, M.D. Towler, Y Lee, & R.J. Needs, PRB 68, 165103, (2003).

[6] J. McClain, J. Lischner, T. Watson, D.A. Matthews, E. Ronca, S.G. Louie, T.C. Berkelbach, G. K-L Chan, PRB 93, 235139 (2016)


Exp1: E. Jensen & E.W. Plummer, PRL 55, 1912–1915, (1985).

Exp2: D. V. Potorochin, B. Buechner et.al., arXiv:2112.00422

# Variational Diagrammatic Monte Carlo

***Diagrammatic MC: provided numerically exact solution by summing sufficiently high-order Feynman diagrams****

* N. Prokof'ev, B. Svistunov, PRL 81, 2514 (1998)
N. Prokof'ev. B. Svistunov, PRB 77, 020408 (2008)

Variational Diag-MC:

- *variational principle to determine best starting point* (such as screening by Yukawa form) *to achieve fast convergent series.*

- leverage *sign blessing*: exact summation of diagrams that largely cancel optimizing internal variables (such as the conserving Baym-Kadanoff group of Hugenholtz diagrams)

Kun Chen and K. Haule, Nature Communications **10**, 3725 (2019).

# Variational Perturbation Theory

Started with *Kleinert & Feynman*
Later improved by *Kleinert & Janke*

PHYSICAL REVIEW LETTERS

VOLUME 75 | 9 OCTOBER 1995 | NUMBER 15

**Convergent Strong-Coupling Expansions from Divergent Weak-Coupling Perturbation Theory**

W. Janke[1,2] and H. Kleinert[2]

[1]*Institut für Physik, Johannes Gutenberg-Universität Mainz, Staudinger Weg 7, 55099 Mainz, Germany*
[2]*Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany*

Anharmonic oscillator: $V(x) = \frac{1}{2}\omega^2 x^2 + g x^4$

Weak coupling series is diverging at small ω: $E_0 = \frac{\omega}{2} + g\frac{3}{4\omega^2} - g^2\frac{21}{8\omega^5} + g^3\frac{333}{16\omega^8} + \cdots$

Rearrange perturbation: $V(x) = \frac{1}{2}\Omega^2 x^2 + \xi\left(g x^4 + \boxed{\frac{1}{2}(\omega^2 - \Omega^2)x^2}\right)$

$\Omega$ variational parameter

counter-term

$\xi = 1$ set to unity at the end

Perform expansion in powers of $\xi$ : $E^{(1)}[\Omega], E^{(2)}[\Omega], \cdots$

Principle of minimum sensitivity: $\frac{dE^n[\Omega]}{d\Omega} = 0 \rightarrow \Omega^n_{optimal}$

Final expansion: $E^{(1)}[\Omega^1_{optimal}], E^{(2)}[\Omega^2_{optimal}], \cdots$

# Variational Perturbation Theory

Check first order:

$$H = H_0 + \xi(gx^4 + \frac{1}{2}(\omega^2 - \Omega^2)x^2)$$

Expansion:

$$E^{(1)} = \langle\psi_0|H|\psi_0\rangle = \frac{\Omega}{2} + \xi(g\frac{3}{4\Omega^2} + \frac{1}{2}\frac{\omega^2 - \Omega^2}{2\Omega}) \xrightarrow{\xi = 1} \frac{\Omega}{4} + \frac{1}{4}\frac{\omega^2}{\Omega} + g\frac{3}{4\Omega^2}$$

perturbative correction

Notice $\omega = 0$ is fine.

Principle of minimum sensitivity: $\frac{dE^{(1)}}{d\Omega} = \frac{1}{4} - \frac{\omega^2}{4\Omega^2} - g\frac{3}{2\Omega^3} = 0$

$$\Omega^3 - \omega^2\Omega - 6g = 0$$

At $\omega = 0$ $\Omega^{(1)}_{optimal} = (6g)^{1/3}$

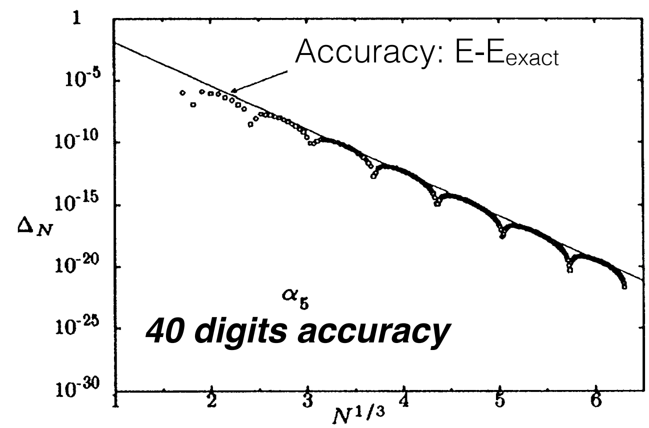
Final first order: $E^{(1)}[\Omega^{(1)}_{optimal}] = g^{1/3}\frac{3}{8}6^{1/3} \approx g^{1/3}\,0.68142$

Exact result: $E^{exact} = g^{1/3}0.66798$

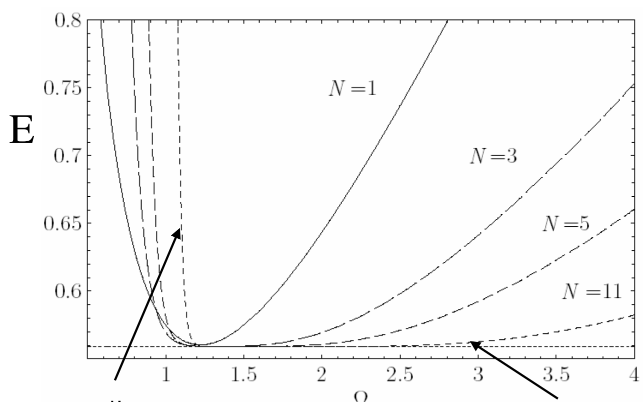
***Turned diverging series into fast converging series***

# Variational Perturbation Theory

Higher order terms are well behaved
and rapidly converging

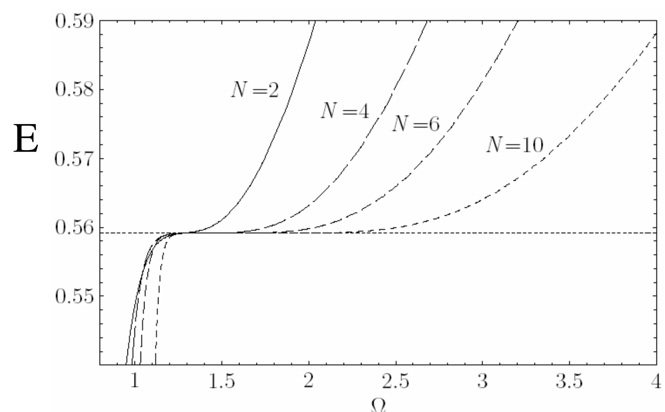



Even odd term optimization:




stronger divergence
at small w

larger plateau of
optimal value



# Variational Diagrammatic Monte Carlo

**Lagrangian + counter-terms:**

$$L = L_0 + \Delta L(\xi)$$

1) choose a good reference system (*$L_0$*), which allows for *emergent property.* We want to leverage the locality of correlations (*as known from success of LDA and DMFT*) to achieve fast convergence : screened short-range interaction in solids or DFT+DMFT solution the problem.

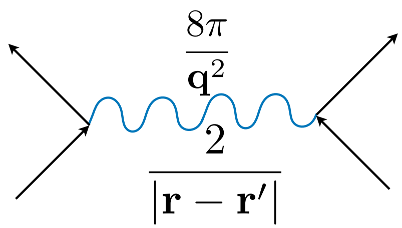
2) Optimize parameters in $\Delta L$ with principal of the minimal sensitivity, or renormalized condition. $\Delta L$ makes $L$ exact, hence $\Delta L$ is not just the interaction, but more complicated Lagrangian with counter-terms.

3) Use *Diagrammatic Monte Carlo* to evaluate Feynman expansion to high order until convergence (use *sign blessed groups* to avoid sign problem)

# Uniform Electron gas as testbed for method development

$$L = \sum_{\mathbf{k}\sigma} \psi^\dagger_{\mathbf{k}\sigma} \left( \frac{\partial}{\partial \tau} - \mu - \frac{\hbar^2 \nabla^2}{2m} \right) \psi_{\mathbf{k}\sigma} + \frac{1}{2V} \sum_{\mathbf{q}\neq 0} \rho_{\mathbf{q}} \frac{8\pi}{\mathbf{q}^2} \rho_{-\mathbf{q}}$$

$$\frac{2}{|\mathbf{r}-\mathbf{r}'|} \overset{\text{FT}}{\rightarrow} \frac{8\pi}{\mathbf{q}^2}$$




Coulomb interaction long ranged
bad sign problem for diagMC

with Hubbard-Stratonovich can be transformed to

$$L = \sum_{\mathbf{k}\sigma} \psi^\dagger_{\mathbf{k}\sigma} \left( \frac{\partial}{\partial \tau} - \mu - \frac{\hbar^2 \nabla^2}{2m} \right) \psi_{\mathbf{k}\sigma} + \sum_{\mathbf{q}\neq 0} \Phi^\dagger_{\mathbf{q}} \frac{q^2}{8\pi} \Phi_{\mathbf{q}} + \frac{i}{\sqrt{2V}} \sum_{\mathbf{q}\neq 0} \rho_{\mathbf{q}} \Phi^\dagger_{\mathbf{q}} + \rho_{-\mathbf{q}} \Phi_{\mathbf{q}}$$

$\phi_{\mathbf{q}}(\mathbf{r})$

boson that mediates the interaction

$\psi_{\mathbf{k}\sigma}(\mathbf{r})$

electron operator

# Uniform Electron gas, a testbed for method development

$$L = L_0 + \Delta L(\xi)$$

$$L_0 = \sum_{\mathbf{k}\sigma} \psi^\dagger_{\mathbf{k}\sigma} \left( \frac{\partial}{\partial \tau} - \mu - \frac{\hbar^2 \nabla^2}{2m} \right) \psi_{\mathbf{k}\sigma} + \sum_{\mathbf{q}\neq 0} \Phi^\dagger_{\mathbf{q}} \frac{q^2}{8\pi} \Phi_{\mathbf{q}}$$

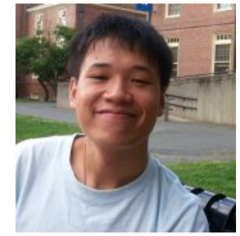
$$\Delta L = \frac{i}{\sqrt{2V}} \sum_{\mathbf{q}\neq 0} \rho_{\mathbf{q}} \Phi^\dagger_{\mathbf{q}} + \rho_{-\mathbf{q}} \Phi_{\mathbf{q}}$$

$\phi_{\mathbf{q}}(\mathbf{r})$ $\psi_{\mathbf{k}\sigma}(\mathbf{r})$

boson that mediates the interaction

electron operator

# VDMC for electron gas



Kun Chen

$$L = L_0 + \Delta L(\xi)$$

$$L_0 = \sum_{\mathbf{k}\sigma} \psi^\dagger_{\mathbf{k}\sigma} \left( \frac{\partial}{\partial \tau} - \mu - \frac{\hbar^2 \nabla^2}{2m} + v_{\mathbf{k}}(\xi = 1) \right) \psi_{\mathbf{k}\sigma} + \sum_{\mathbf{q}\neq 0} \Phi^\dagger_{\mathbf{q}} \frac{q^2 + \lambda_{\mathbf{q}}}{8\pi} \Phi_{\mathbf{q}}$$

$$\Delta L = -\sum_{\mathbf{k}\sigma} \psi^\dagger_{\mathbf{k}\sigma}\, v_{\mathbf{k}}(\xi)\, \psi_{\mathbf{k}\sigma} - \xi \sum_{\mathbf{q}\neq 0} \Phi^\dagger_{\mathbf{q}} \frac{\lambda_{\mathbf{q}}}{8\pi} \Phi_{\mathbf{q}} + \sqrt{\xi} \frac{i}{\sqrt{2V}} \sum_{\mathbf{q}\neq 0} \rho_{\mathbf{q}} \Phi^\dagger_{\mathbf{q}} + \rho_{-\mathbf{q}} \Phi_{\mathbf{q}}$$

original problem at $\xi = 1.$

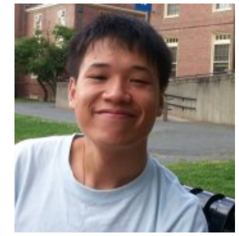
$\phi_{\mathbf{q}}(\mathbf{r})$

boson that mediates the interaction

$\psi_{\mathbf{k}\sigma}(\mathbf{r})$

electron operator

# VDMC for electron gas



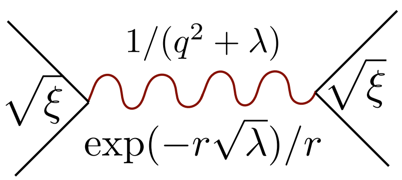
Kun Chen

$$L = L_0 + \Delta L(\xi)$$

$$L_0 = \sum_{\mathbf{k}\sigma} \psi^\dagger_{\mathbf{k}\sigma} \left( \frac{\partial}{\partial \tau} - \mu - \frac{\hbar^2 \nabla^2}{2m} + v_{\mathbf{k}}(\xi = 1) \right) \psi_{\mathbf{k}\sigma} + \sum_{\mathbf{q}\neq 0} \Phi^\dagger_{\mathbf{q}} \frac{q^2 + \lambda_{\mathbf{q}}}{8\pi} \Phi_{\mathbf{q}}$$

$$\Delta L = -\sum_{\mathbf{k}\sigma} \psi^\dagger_{\mathbf{k}\sigma}\, v_{\mathbf{k}}(\xi)\, \psi_{\mathbf{k}\sigma} - \xi \sum_{\mathbf{q}\neq 0} \Phi^\dagger_{\mathbf{q}} \frac{\lambda_{\mathbf{q}}}{8\pi} \Phi_{\mathbf{q}} + \sqrt{\xi} \frac{i}{\sqrt{2V}} \sum_{\mathbf{q}\neq 0} \rho_{\mathbf{q}} \Phi^\dagger_{\mathbf{q}} + \rho_{-\mathbf{q}} \Phi_{\mathbf{q}}$$

original problem at $\xi = 1$.

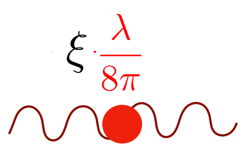



Coulomb interaction is static
and short ranged

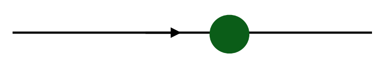
$$G^0_{\mathbf{k}}(i\omega) = \frac{1}{i\omega + \mu - \frac{k^2}{2m} - v_{\mathbf{k}}}$$

electron propagator is optimized

(DFT KS-potential or DMFT self-energy, etc)




Counter terms make sure that we get the
exact answer at large order for any λ



Counter-term makes sure that the exact
answer is obtained for any $v_k$ at large p.o.

Open question: How to determine parameters λ and $v_k$

# Screening length

**Possible choices for λ:**

*Average perturbation order:* $\langle N \rangle = \mathrm{Tr}(\lambda W_{\mathbf{q}}) = \dfrac{\lambda}{q^2/(8\pi) - \widetilde{\Pi}_{\mathbf{q}}} < \dfrac{\lambda}{-\widetilde{\Pi}_{\mathbf{q}=0,\omega=0}}$

1) $\lambda = -\widetilde{\Pi}_{\mathbf{q}=0,\omega=0}$

Makes sure that average p. order < 1
renormalized condition,
borrowed from renormalized perturbation theory

*Screened interaction:* $W_{\mathbf{q},\omega} = \dfrac{1}{\frac{q^2}{8\pi} - \Pi_{\mathbf{q},\omega}} \approx \dfrac{8\pi}{q^2 + \lambda}$

2) $\dfrac{\lambda}{8\pi} = -\widetilde{\Pi}^{N=1}_{\mathbf{q}=0,\omega=0}$

Exact cancelation of bubbles+c.t. at low energy
i.e., self-consistent determination of screening

3) $\dfrac{d\widetilde{\Pi}_{\mathbf{q}\omega=0}}{d\lambda} = 0 \to \lambda$

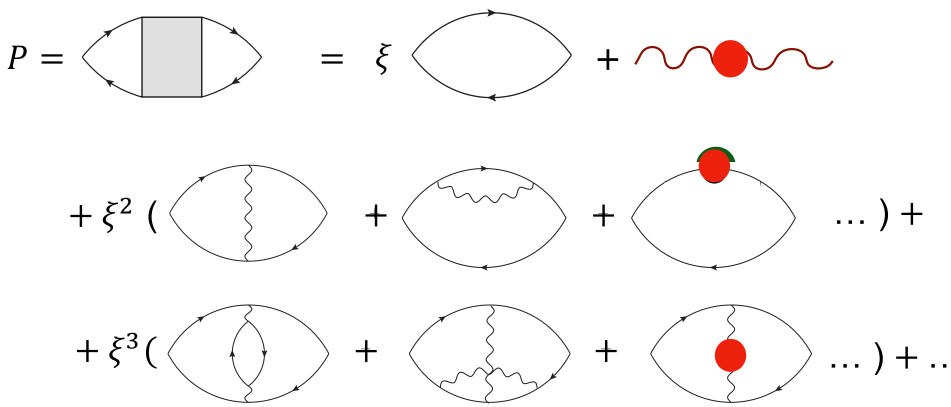
The principle of smallest sensitivity.
(borrowed from variational perturbation theory)

1) Poor convergence and rapid oscillations with orders (approx. 5-times too small)
2) To converge we need to go to order 25=8$\pi$ ! (approx. 5 times too large)
3) The best choice is due to variational perturbation theory, i.e., still quite small perturbation order, but quite monotonic convergence to exact answer.

# Example: expansion for polarization

First order is the standard RPA:

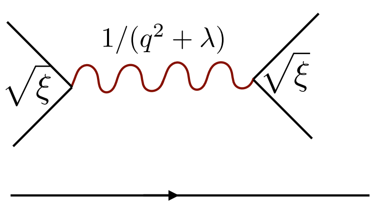
$$W_{\mathbf{q}} = (v_{\mathbf{q}}^{-1} - \Pi_{\mathbf{q}})^{-1} = \left( \frac{q^2+\lambda}{8\pi} - \xi \frac{\lambda}{8\pi} - \xi P^0_{\mathbf{q}} - O(\xi^2) \cdots \right)^{-1}$$



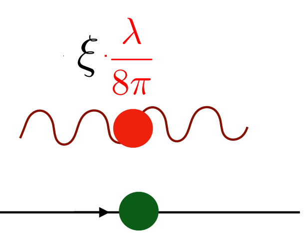

Screened RPA

2n order correction

3rd order correction




$$G^0_{\mathbf{k}}(i\omega) = \frac{1}{i\omega + \mu - \frac{k^2}{2m} - v_{\mathbf{k}}}$$




$$\boxed{v_{\mathbf{k}}(\xi) = \xi(\Sigma^x_{\mathbf{k}} - \Sigma^x_{k_F}) + \xi^2 s_2 + \xi^3 s_3 + \cdots}$$

# From sign problem to sign blessing

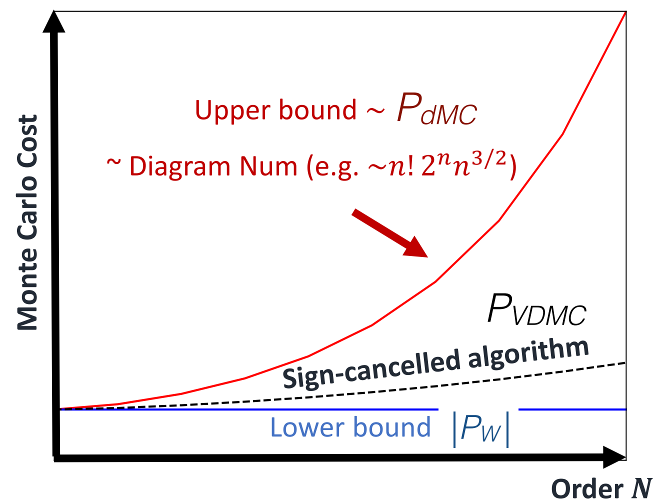
We want to calculate $\int [dx]^N \sum_{diag} W_{diag} \ll \int [dx]^N \sum_{diag} |W_{diag}|$

sign problem in diag-MC!

Physical weight: $|P_W| = \left| \int [dx]^N \sum_{diag} W_{diag} \right|$

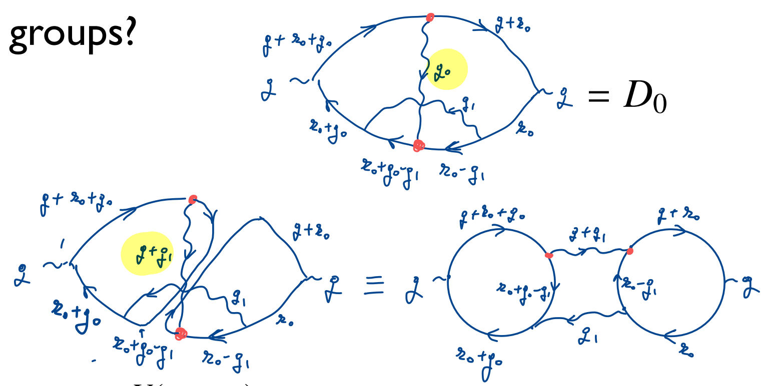
Weight in diagMC: $P_{dMC} = \int [dx]^N \sum_{diag} |W_{diag}|$

Weight in VDMC: $P_{VDMC} = \int [dx]^N |\sum_{diag} W_{diag}|$



# From sign problem to sign blessing

**How to group diagrams to sign-blessed groups?**



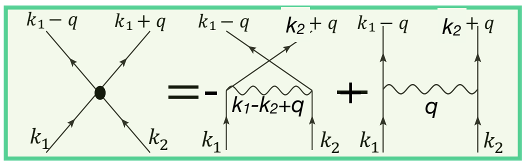

$$-D_0 \frac{V(\mathbf{q}+\mathbf{q}_1)}{V(\mathbf{q}_0)}$$

sum= $D_0\left(1-\dfrac{V(\mathbf{q}+\mathbf{q}_1)}{V(\mathbf{q}_0)}\right)$

### Symmetry preserved in each group:

Crossing symmetry, spin rotational symmetry,…

At the lowest order leads to “Hugenholtz diagrams”




### Ward identity (each MC step is conserving):

Baym-Kadanoff algorithm is used to construct groups of diagrams with consistent internal variables (preserve particle number, energy, momentum **in each MC step**).

$$S[\psi^\dagger,\psi;U] = S[\psi^\dagger,\psi] - \int d1d2\ \psi^\dagger(1)U(1,2)\psi(2)$$

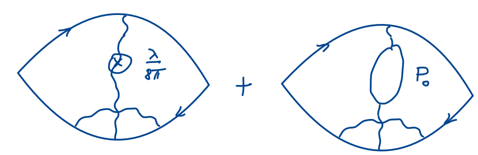
$$Z[U] = \int \mathscr{D}\psi^\dagger \mathscr{D}\psi e^{-S[\psi^\dagger,\psi;U]}$$

$$G(1,1') = \left.\frac{\delta \ln Z[U]}{\delta U(1',1)}\right|_{U\to 0}$$

$$\chi(1,2) = \left.\frac{\delta G(2,2^+;U)}{\delta U(1^+,1)}\right|_{U\to 0}$$

### Vertex renormalization:

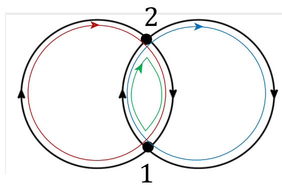
Make sure to combine diagram with the corresponding counter-term that cancels the high-energy contributions



# Example of 3rd order polarization diagrams

**Step 1:**

Start with Hugenholtz diagram for the free energy functional $\log Z$. Choose momentum loops (shortest path) and time indices.

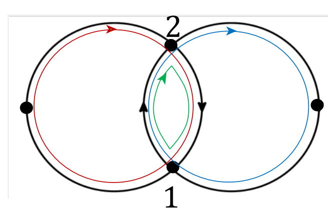



**Step 2:**

Attach two external vertices in all possible ways

$$\frac{\delta^2 \log Z}{\delta U^2}$$

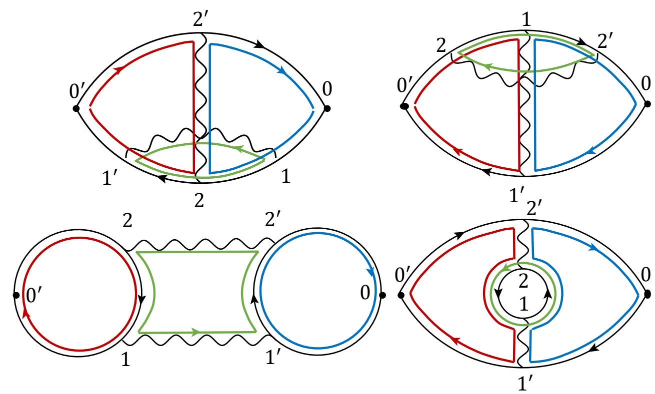
(creates a Baym-Kadanoff conserving group)



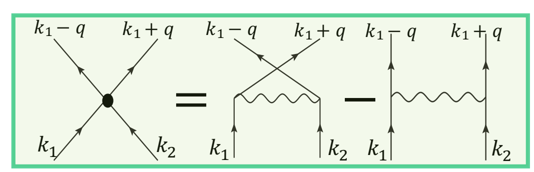

Kun Chen and K. Haule, Nature Communications **10**, 3725 (2019).

**Step 3:**

Expand each vertex in Hugenholtz diagrams, to generate normal Feynman diagrams. Keep all momenta and time indices equal to those in diagram. $\log Z$




Notice that $2^N$ diagrams are evaluated at once by Hugenholtz trick : GGG ($V_1$-$V_2$) ($V_1$-$V_2$)…

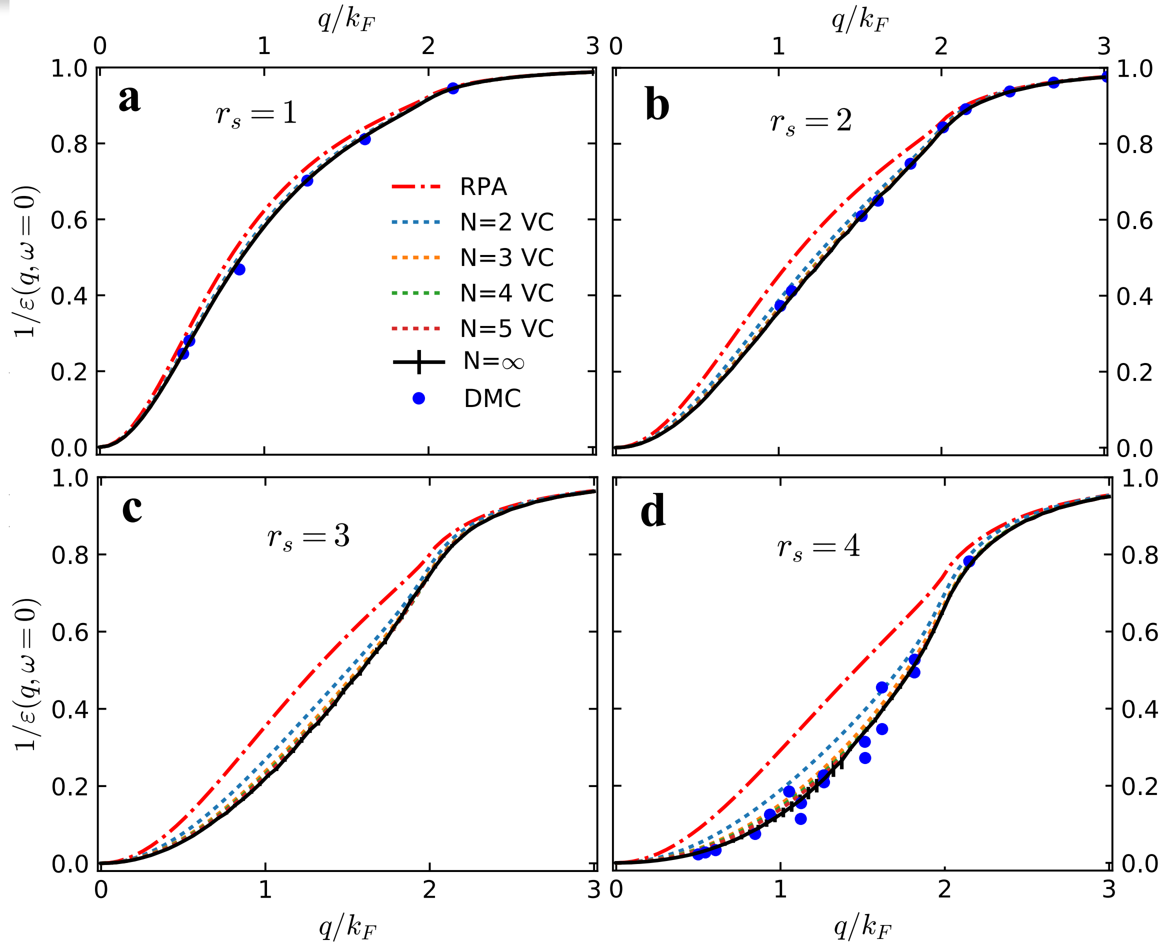


# dielectric constant-direct comparison to DMC

Momentum dependence challenging for DMC because they treat finite system.

New method beats DMC in precision.

DMC: B.J.Alder, PRB 50, 14838 (1994)

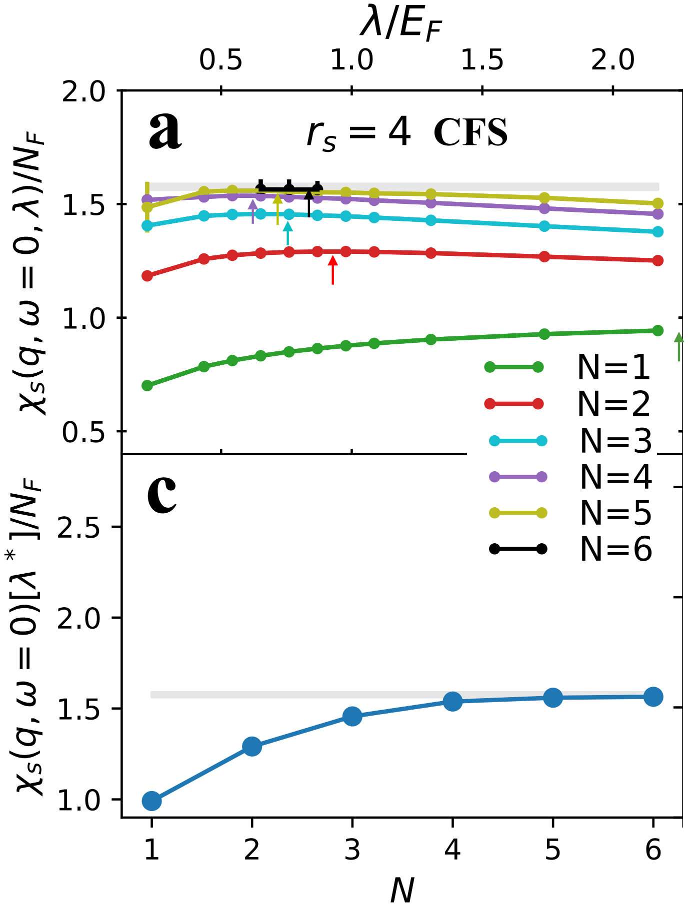



Kun Chen and K. Haule, Nature Communications **10**, 3725 (2019).

# Spin-susceptibility at $r_s$=4 ( $\frac{1}{n} = \frac{4\pi r_s^3}{3}$ )

see: Feynman & Kleinert, PRA 34, 5080 (1986)

spin susceptibility at q=0, ω=0




Kun Chen and K. Haule, Nature Communications **10**, 3725 (2019).

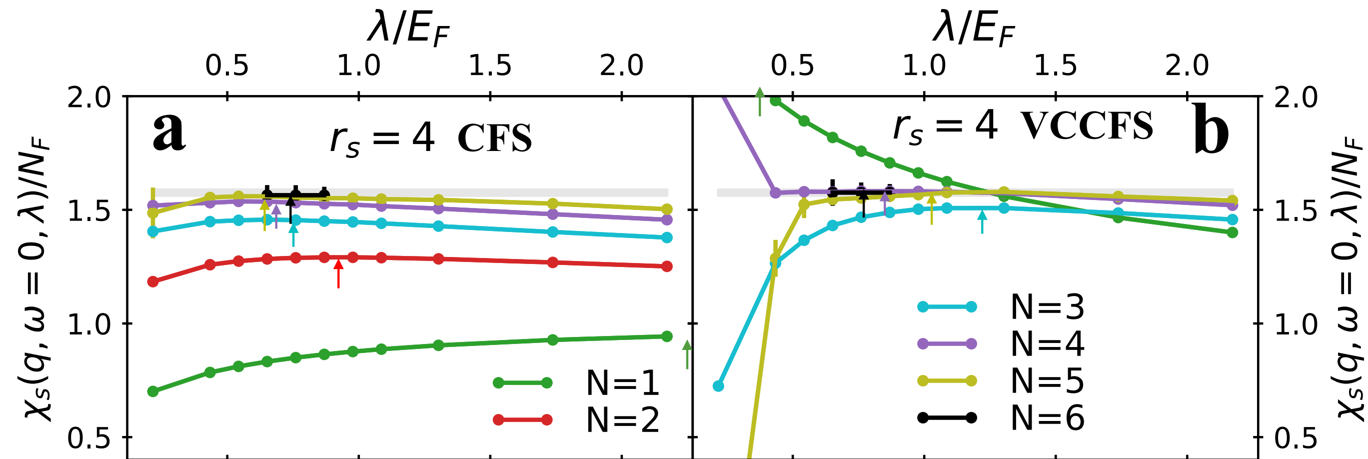
Scan in λ reveals the speed of convergence.

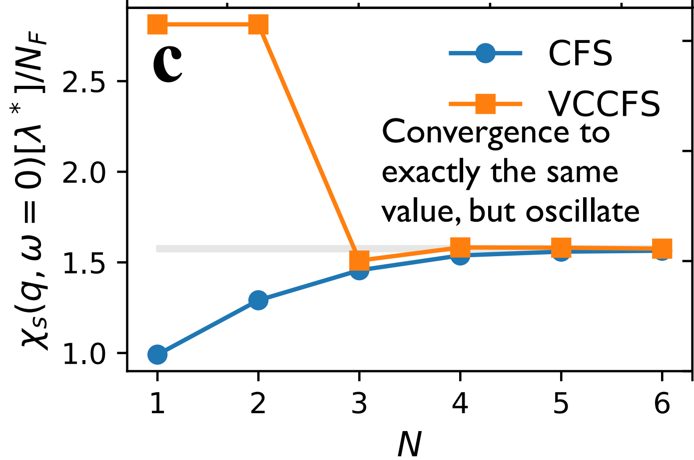
broad plateau in λ at large order => converged value in the plateau.

Values at the optimum (principle of minimal sensitivity) converge very fast

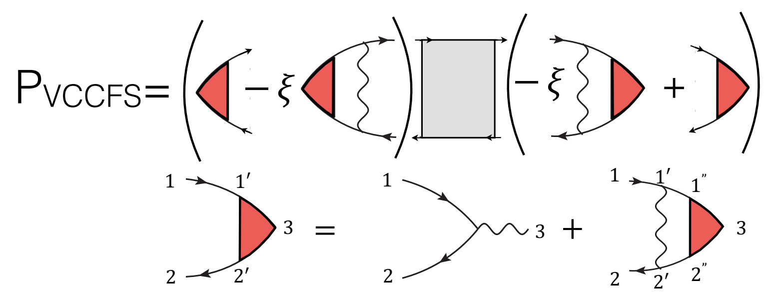
# Spin-susceptibility at $r_s$=4 ( $\frac{1}{n} = \frac{4\pi r_s^3}{3}$ )

spin susceptibility at q=0, ω=0




VCCFS scheme, a different BK conserving scheme




Bethe-Salpeter ladders added

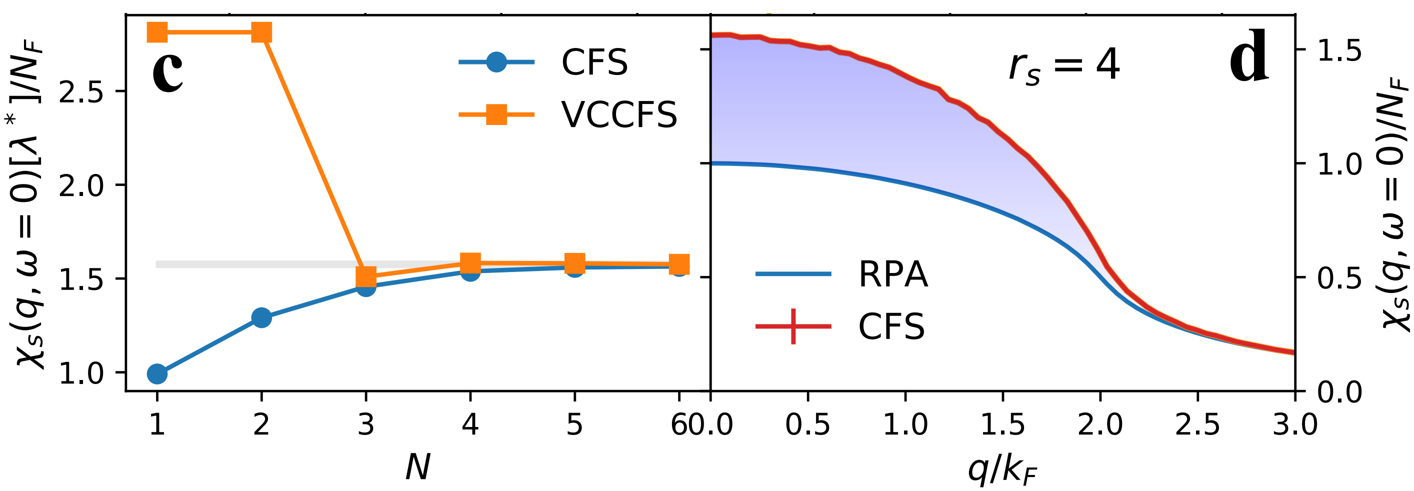
Kun Chen and K. Haule, Nature Communications **10**, 3725 (2019).

# Spin-susceptibility of electron gas at $r_s$=4 ( $\frac{1}{n} = \frac{4\pi r_s^3}{3}$ )

Calculated values at different densities.
VDMC get four significant digits at order N=6.
Consistent with literature, but significantly more precise.

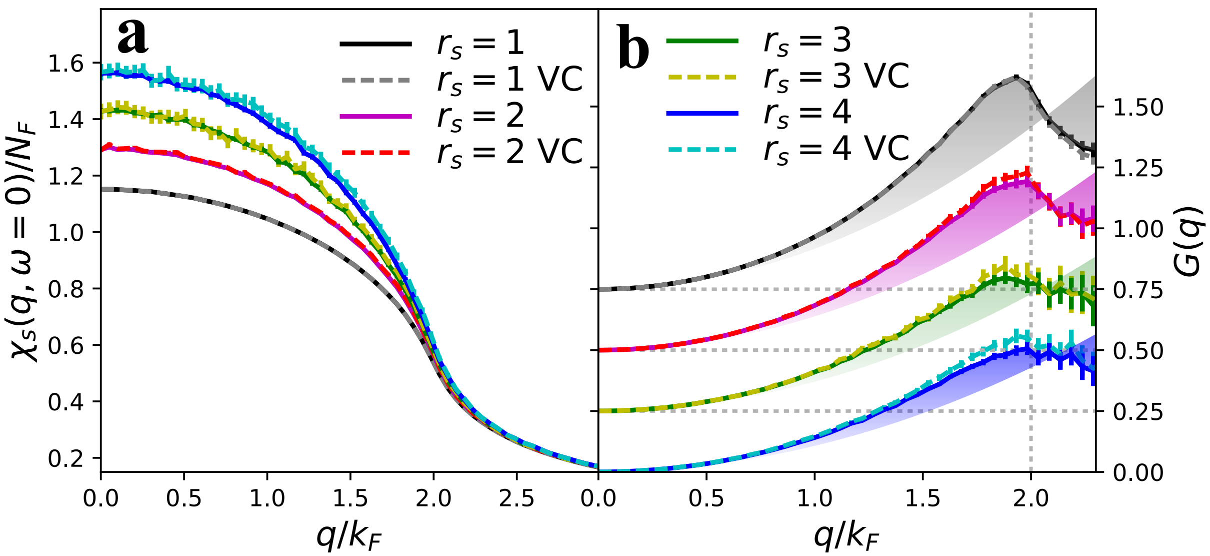
| $r_s$ | $\chi_s/N_F$ | literature |
|---|---|---|
| 1 | 1.152(2) | 1.15-1.16 |
| 2 | 1.296(6) | 1.27-1.31 |
| 3 | 1.438(9) | 1.39-1.46 |
| 4 | 1.576(9) | 1.51-1.62 |

spin susceptibility for different momenta.
RPA 57% underestimates.




Kun Chen and K. Haule, Nature Communications **10**, 3725 (2019).

# Spin-susceptibility & local field correction




Definition of local field correction: $\Pi_{\mathbf{q}} = ({\Pi^0_{\mathbf{q}}}^{-1} + V_{\mathbf{q}} G_{\mathbf{q}})^{-1}$

Spin/charge response with LDA is: $\Pi_{\mathbf{q}} = ({\Pi^0_{\mathbf{q}}}^{-1} + f_{xc})^{-1}$

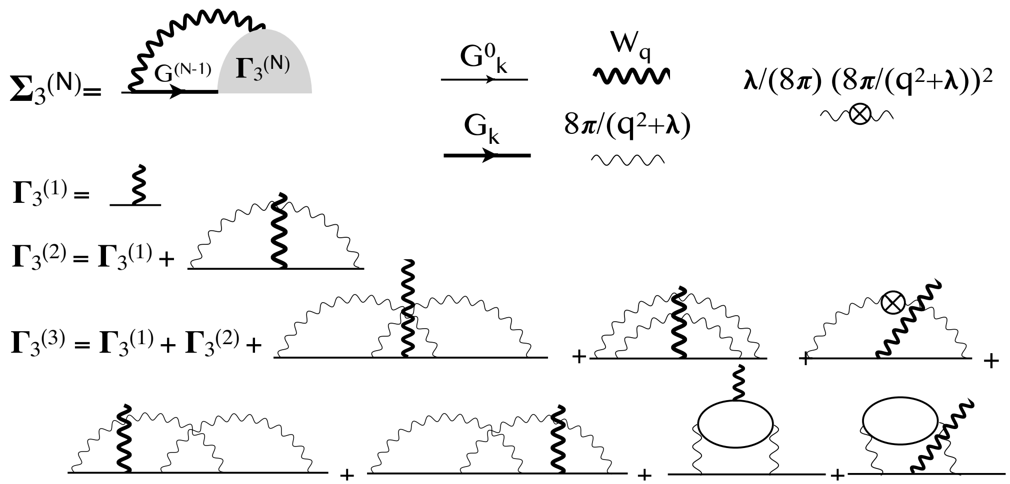
where $f_{xc} = \dfrac{\delta^2 E_{xc}}{\delta\rho^2}$

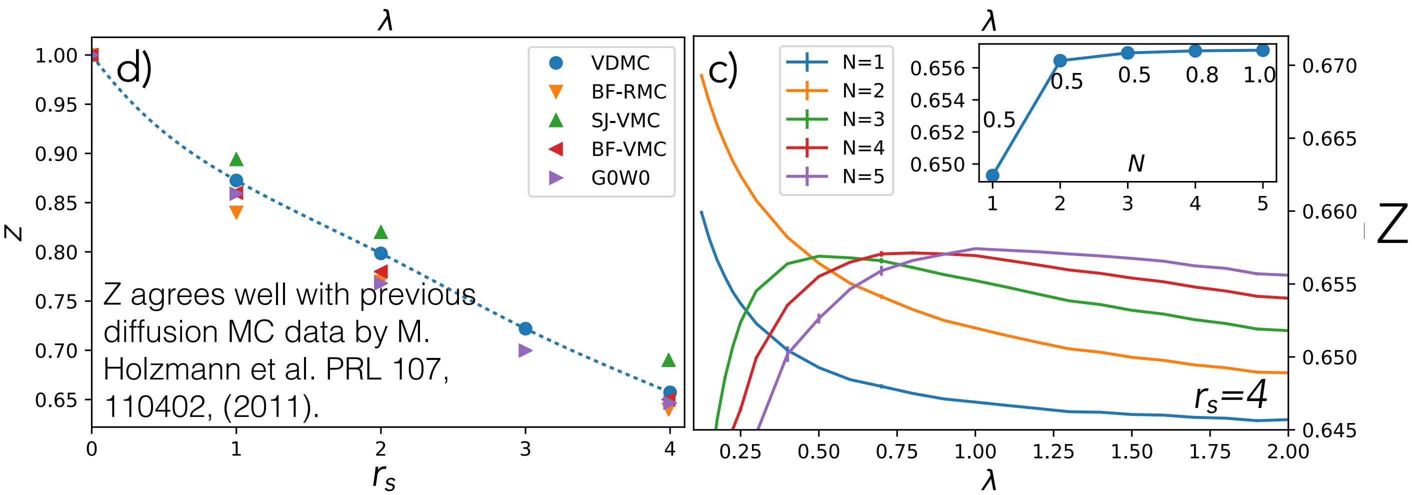
hence $G_{\mathbf{q}} = \dfrac{q^2}{8\pi} f_{xc}$

LDA excellent approximation up to k=k$_F$. RPA much worse.

# The single particle-quantities

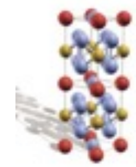
- For single-particle quantities we need to expand the three-particle vertex (Hedin-type Eq).
- We need to optimized $\lambda/E_F$ for W, and separately for Z, and find optimal $\lambda/E_F$ of the order of unity.
- Optimized $\lambda$ increases with increasing order, hence higher orders are even more local.



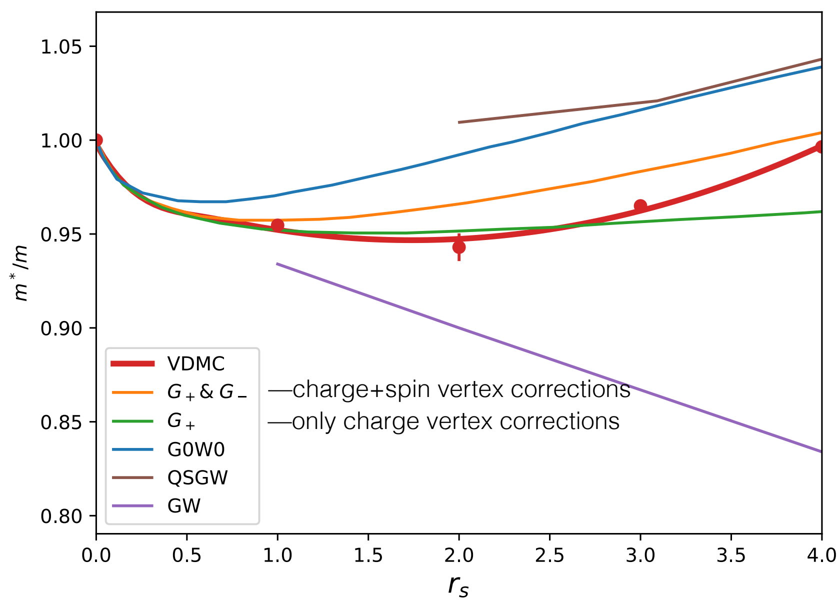




K. Haule and Kun Chen, Scientific Reports **12**, 2294 (2022)

# effective mass $\frac{m}{m^*} = Z\left(1 + \frac{m}{k_F}\frac{d\Sigma(k_F,\omega=0)}{dk}\right)$



- Over the last 50 years, the mass in electron gas was controversial, some theories predicting monotonic behavior with density, and other with a turning point.
- Important for understanding which method predicts better Bloch bands and bandwidths in moderately correlated systems.




Quasiparticle dispersion near the fermi level is defined by effective mass m*/m.

DFT assumes m*/m=1 (non-interacting Kohn-Sham ansatz)

Exact solution (VDMC) remarkably close to m*/m~1. Bounded by vertex corrected perturbation theory using *local field factors*.

G0W0 and QSGW overestimate mass
GW underestimates mass

*At the uniform density limit,* ***DFT ansatz is remarkably accurate,*** *better than GW.*

K. Haule and Kun Chen, Scientific Reports **12**, 2294 (2022)


[G0W0] L. Hedin, *Phys. Rev.* 139, A796–A823, (1965).
[G+&G-]Simion, G. E. & Giuliani, *PRB* 77, 035131,(2008).
[QSGW] A.Kutepov, G. Kotliar, arXiv:1702.04548
*[GW]* K.Van Houcke, et.al.,Phys. Rev. B **95**, 195131 (2017)

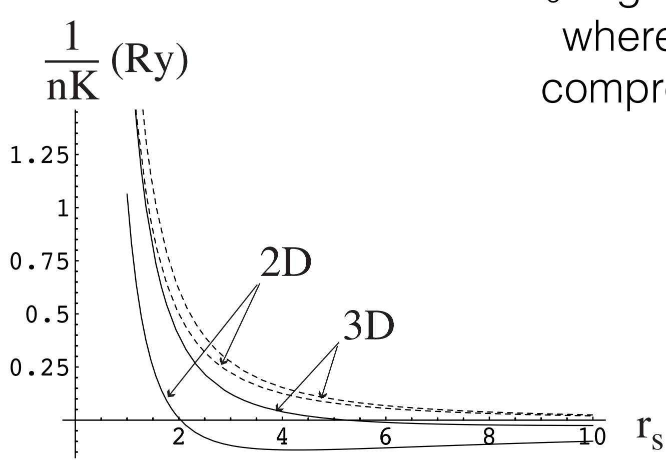
# Uniform electron gas: Landau parameters

Landau parameters for UEG.

have never been computed before by controlled method

| $r_s$ | $Z$ | $m^*/m$ | $F_0^a$ | $F_0^s$ |
|---|---|---|---|---|
| 1 | 0.8725(2) | 0.955(1) | -0.171(1) | -0.209(5) |
| 2 | 0.7984(2) | 0.943(3) | -0.271(2) | -0.39(1) |
| 3 | 0.7219(2) | 0.965(3) | -0.329(3) | -0.56(1) |
| 4 | 0.6571(2) | 0.996(3) | -0.368(4) | -0.83(2) |

$F^s_0$ is going critical at $r_s$=5.2, where polarization and compressibility diverges.

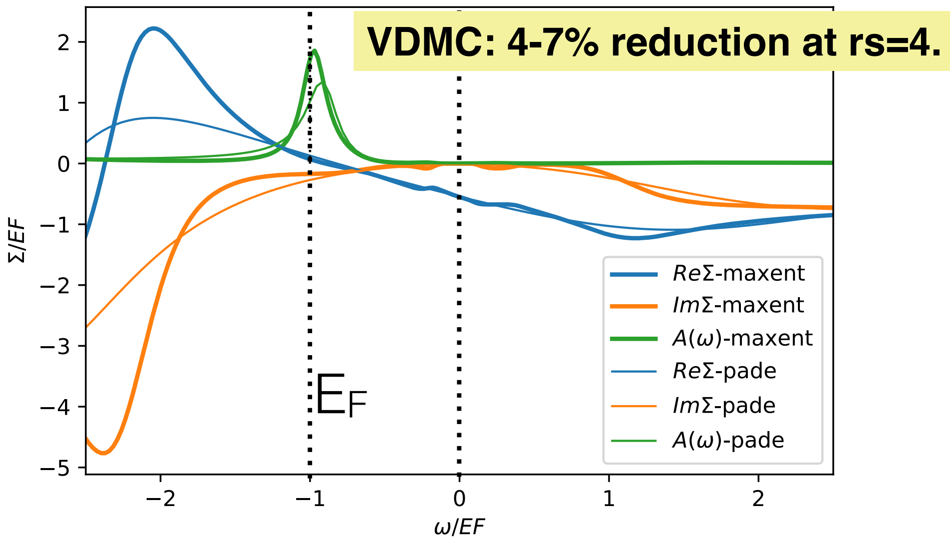



compressibility diverges at $r_s$=5.2, and expansion breaks down

Polarization also diverges at this point, signaling subtle instability

## Bandwidth of Na metal is controversial for 35 years:

-ARPES bandwidth show reduction for 18-25% [1,2]
-some GW calculation reproduce reduction [3], most do not.
-DMC shows increased bandwidth, not reduced [5].




K. Haule and Kun Chen, Scientific Reports **12**, 2294 (2022)


[1] E. Jensen & E.W. Plummer, PRL 55, 1912–1915, (1985).

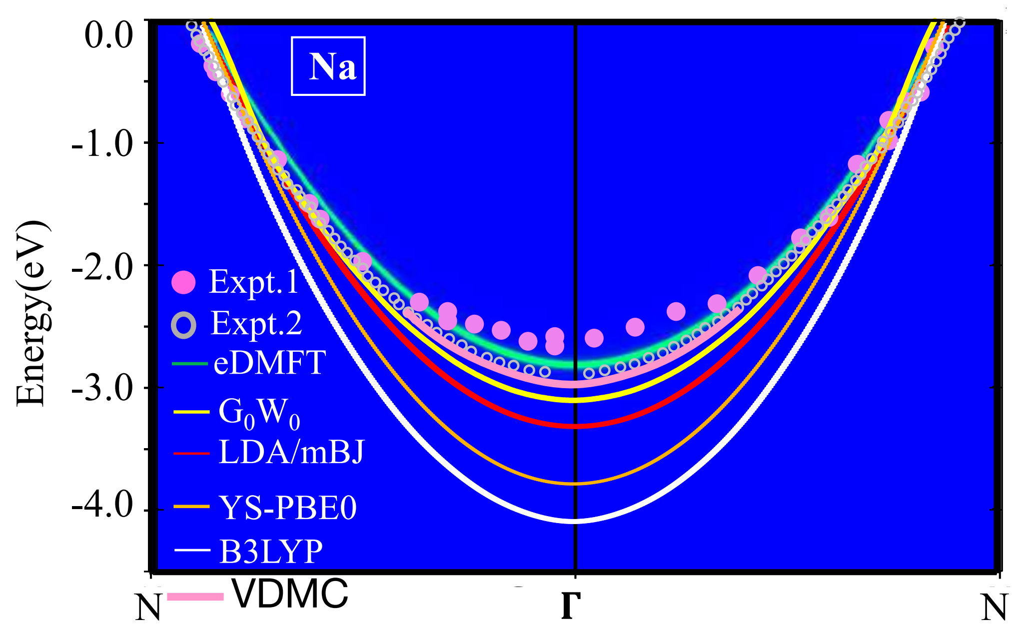
[2] I.-W. Lyo & E.W. Plummer, PRL 60, 1558–1561, (1988).

[3] J.E. Northrup, M.S. Hybertsen, & S.G. Louie, PRL 59, 819 (1987).

[4] X. Zhu, & A.W. Overhauser, RPB 33, 925(1986).

[5] R. Maezono, M.D. Towler, Y Lee, & R.J. Needs, PRB 68, 165103, (2003).

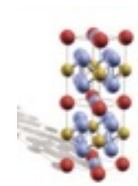
[6] J. McClain, J. Lischner, T. Watson, D.A. Matthews, E. Ronca, S.G. Louie, T.C. Berkelbach, G. K-L Chan, PRB 93, 235139 (2016)


Exp1: E. Jensen & E.W. Plummer, PRL 55, 1912–1915, (1985).

Exp2: D. V. Potorochin et.al., arXiv:2112.00422

# Real frequency quantities: exchange-correlation kernel

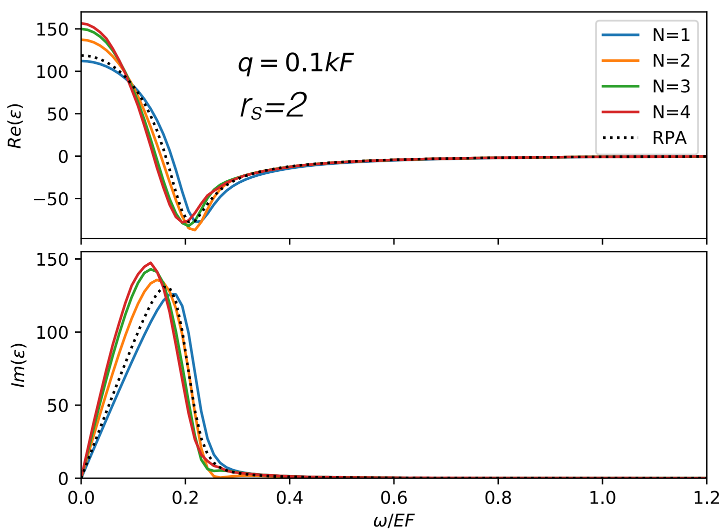


Recently we developed real-frequency diag-MC for uniform electron gas.

$$\chi(\mathbf{q},\omega) = P^0_{KS}(\mathbf{q},\omega) + P^0_{KS}(\mathbf{q},\omega)[V_q + f_{xc}(\mathbf{q},\omega)]\chi(\mathbf{q},\omega)$$

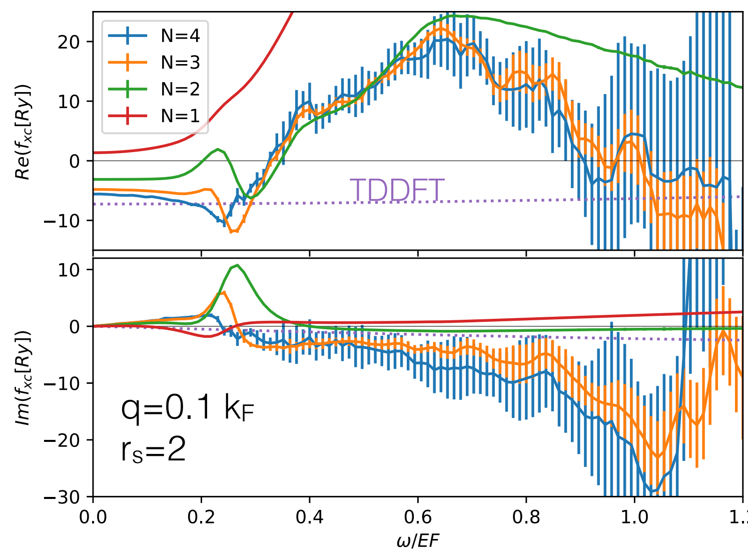
In UEG we compute: $$f_{xc}(q,\omega) = \frac{1}{P^0(q,\omega)} - \frac{V_q}{1-\varepsilon(q,\omega)}$$

dielectric function on real frequency axis




I. S. Tupitsyn, A. M. Tsvelik, R. M. Konik, and N. V. Prokof'ev, PRL **127**, 026403 (2021)

$f_{xc}(q,\omega)$ on real frequency axis

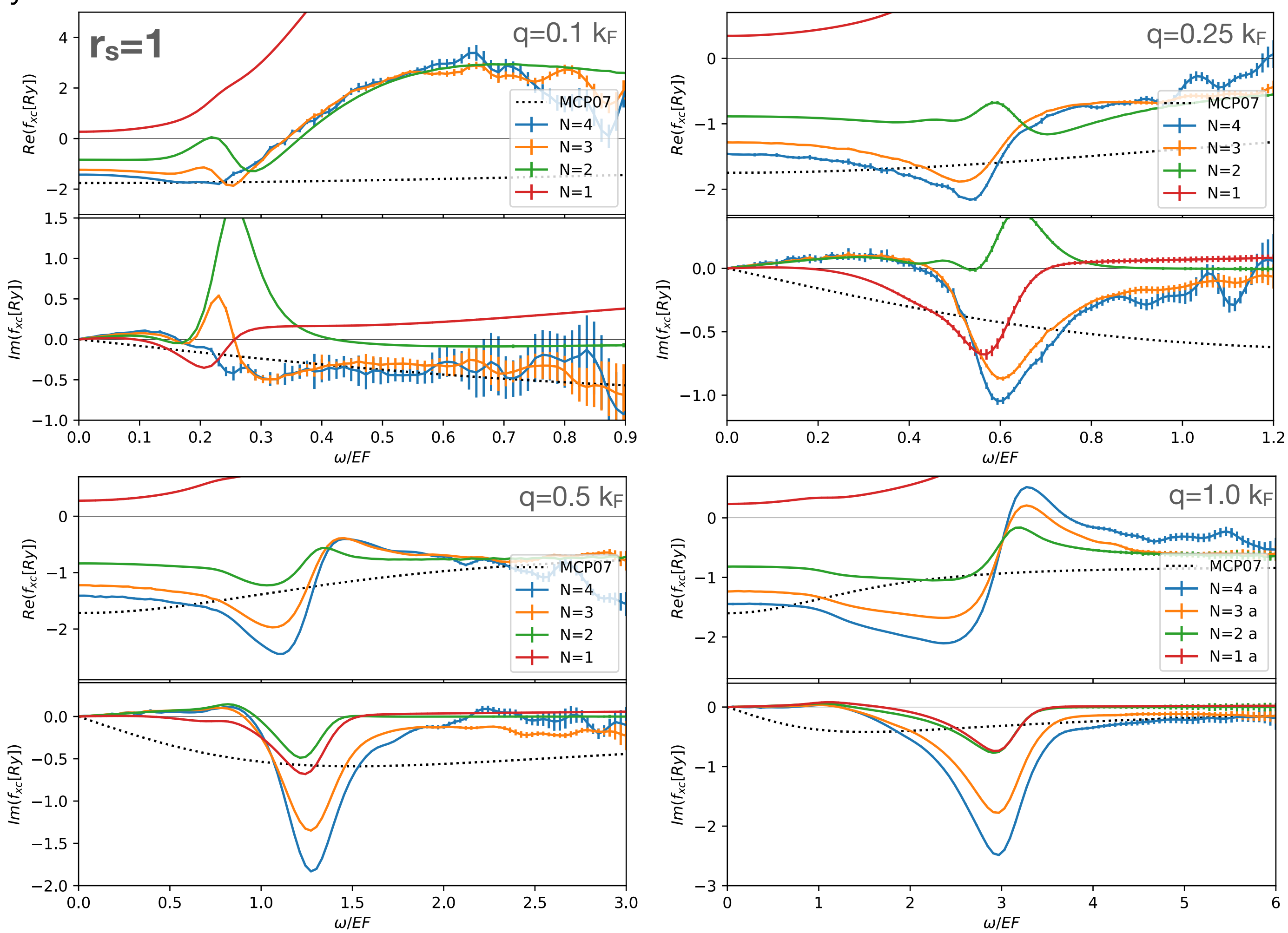



J. P. F. LeBlanc, K. Chen, N.V. Prokof'ev, K.H., Igor S. Tupitsyn, in preparation

Challenging to calculate, but a lot of non-trivial structure below EF.
Such change of sign was needed in Si to explain optical data (PRL 102, 11301 (2009)).

# Real frequency quantities: exchange-correlation kernel

$f_{xc}(q,\omega)$ on real frequency axis
several momenta

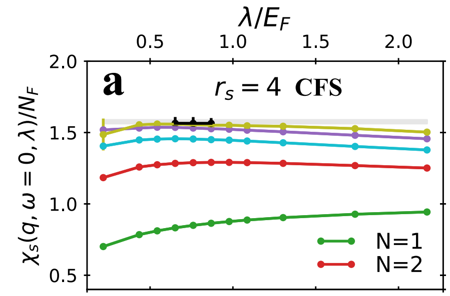


# Screening in UEG on the two particle level

We find the fastest convergence for spin/charge susceptibility when $\lambda/E_F \sim 1$

$$V(r) = \frac{e^2}{4\pi\varepsilon_0 r} e^{-r/\xi} \quad \text{where} \quad \xi = \frac{1}{\sqrt{\lambda}}$$

$$\xi = \frac{1}{\sqrt{\lambda}} \approx \frac{1}{\sqrt{E_F}} = \frac{3.69}{\sqrt{E_F[eV]}} r_B$$




Na metal is close to electron gas with $r_s \sim 4$ and $E_F \sim 3$eV

$$\xi_{Na} \approx 2r_B \approx 0.8 R_{MT} \approx 0.25a \quad \text{and} \quad U_{i\neq j}/U_{ii} \approx \exp(-4) \approx 0.018$$

Interaction is very well screened in metals and non-local interaction corrections are small.
Hund's coupling is very large, because Yukawa screening reduces $F_0$, but not much $F_2$,$F_4$.

Local point of view converging much faster than long-range point of view.


VDMC:

*[1] Kun Chen, K. Haule,* Nature Communications **10,** 3725 (2019)

*[2] K. Haule, K. Chen,* Scientific Reports **12**, 2294 (2022)