VARIATIONAL DIAGRAMMATIC MONTE CARLO METHOD TO SOLVE THE ELECTRONIC STRUCTURE PROBLEM

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First order perturbation theory in the screened Coulomb interactions [GW] obtains very good gaps in semiconductors [Hedin].

While $G_0W_0$ comes close to experimental gaps in semiconductors, we do not know the error-bar of the calculation.

In many metals and correlated solids DFT/GW fail, but we know only because of experiment.

The self-consistent GW tends to produce way too large gaps as compared to experiment (need the estimation of error-bar).

These methods are not BK conserving, and not functional derivable, and hence not stationary and robust with respect to small changes (discretization errors).

There is a need to go beyond GW in a systematic way (estimating error-bar).
Systematic improvements beyond DMFT

DMFT is very successful, but extensions are very expansive or uncontrolled

A. Georges and G.Kotliar (1992)

The controlled extension is the cluster-DMFT:
- Cellular DMFT (real space cluster) (Gabi Kotliar)
- DCA (momentum space cluster) (M. Jarrel, T. Mayer)

But complexity scales exponentially with cluster size.
Not clear how to treat long range Coulomb repulsion (beyond boson bath approximation).

Also diagrammatic expansions beyond DMFT (see RMP 90, 025003 (2018)):

- GW+DMFT
- DΓA
- Trilex
- Quadrilex
- Dual Fermions
- Dual Bosons

Complicated when extended beyond lowest order, i.e., require 6 leg vertex, 8 leg vertex (can not store such object).

Or uncontrolled (GW+DMFT, Trilex, Quadrilex)
Not clear how to treat long range Coulomb repulsion
• variational principle to determine best starting point for perturbative expansion (such as screening by Yukawa form)

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

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

Alternative type of combining diagrams using determinants:
  Riccardo Rossi, Rossi, PRL 119, 045701 (2017)
Variational Perturbation Theory

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

Anharmonic oscillator: \[ V(x) = \frac{1}{2} \omega^2 x^2 + gx^4 \]

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

Rearrange perturbation: \[ V(x) = \frac{1}{2} \Omega^2 x^2 + \xi (gx^4 + \frac{1}{2}(\omega^2 - \Omega^2)x^2) \]

\( \Omega \) variational parameter
\( \cdot \) counter-term

\( \xi = 1 \) set to unity at the end

Perform expansion: \[ E^{(1)}[\Omega], E^{(2)}[\Omega], \cdots \]

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:

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

\[ \xi = 1 \rightarrow \frac{\Omega}{4} + \frac{1}{4} \frac{\omega^2}{\Omega} + g \frac{3}{4\Omega^2} \]

Notice \( \omega = 0 \) is fine.

Perturbative correction

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

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

Exact result: \( E^{\text{exact}} = g^{1/3} 0.66798 \)

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

\[ L = \sum_{k\sigma} \psi_{k\sigma}^\dagger \left( \frac{\partial}{\partial \tau} - \mu - \frac{\hbar^2 \nabla^2}{2m} \right) \psi_{k\sigma} + \frac{1}{2V} \sum_{q \neq 0} \rho_q \frac{8\pi}{q^2} \rho_{-q} \frac{2}{|r - r'|} \rightarrow \frac{8\pi}{q^2} \]

\[ \frac{8\pi}{q^2} \]

\[ \frac{2}{|r - r'|} \rightarrow \frac{8\pi}{q^2} \]

Coulomb interaction long ranged
bad sign problem for diagMC

with Hubbard-Stratonovich can be transformed to

\[ L = \sum_{k\sigma} \psi_{k\sigma}^\dagger \left( \frac{\partial}{\partial \tau} - \mu - \frac{\hbar^2 \nabla^2}{2m} \right) \psi_{k\sigma} + \sum_{q \neq 0} \Phi_q^\dagger \frac{q^2}{8\pi} \Phi_q + \frac{i}{\sqrt{2V}} \sum_{q \neq 0} \rho_q \Phi_q^\dagger + \rho_{-q} \Phi_q \]

\[ \phi_q(r) \]

boson that mediates the interaction

\[ \psi_{k\sigma}(r) \]

electron operator
Uniform Electron gas, a testbed for method development

\[ L = L_0 + \Delta L(\xi) \]

\[ L_0 = \sum_{\mathbf{k}\sigma} \psi_{\mathbf{k}\sigma}^\dagger \left( \frac{\partial}{\partial \tau} - \mu - \frac{\hbar^2 \nabla^2}{2m} \right) \psi_{\mathbf{k}\sigma} \]

\[ \Delta L = \]

\[ \phi_q(\mathbf{r}) \]

boson that mediates the interaction

\[ \psi_{\mathbf{k}\sigma}(\mathbf{r}) \]

electron operator
VDMC for electron gas

\[ L = L_0 + \Delta L(\xi) \]

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

\[ \Delta L = - \sum_{\mathbf{k}\sigma} \psi_{\mathbf{k}\sigma}^\dagger v_{\mathbf{k}}(\xi) \psi_{\mathbf{k}\sigma} + \xi \sum_{\mathbf{q} \neq 0} \Phi_{\mathbf{q}}^\dagger \frac{\lambda_{\mathbf{q}}}{8\pi} \Phi_{\mathbf{q}} + \sqrt{\xi} \frac{i}{\sqrt{2V}} \sum_{\mathbf{q} \neq 0} \rho_{\mathbf{q}} \Phi_{\mathbf{q}}^\dagger + \rho_{-\mathbf{q}} \Phi_{\mathbf{q}} \]

\[ \phi_{\mathbf{q}}(\mathbf{r}) \]

boson that mediates the interaction

\[ \psi_{\mathbf{k}\sigma}(\mathbf{r}) \]

electron operator

original problem at \( \xi = 1 \).
**VDMC for electron gas**

\[ L = L_0 + \Delta L(\xi) \]

\[ L_0 = \sum_{k\sigma} \psi_{k\sigma}^\dagger \left( \frac{\partial}{\partial \tau} - \mu - \frac{\hbar^2 \nabla^2}{2m} + v_k(\xi = 1) \right) \psi_{k\sigma} + \sum_{q\neq 0} \Phi_q^\dagger q^2 + \frac{\lambda_q}{8\pi} \Phi_q \]

\[ \Delta L = -\sum_{k\sigma} \psi_{k\sigma}^\dagger v_k(\xi) \psi_{k\sigma} - \xi \sum_{q\neq 0} \Phi_q^\dagger \frac{\lambda_q}{8\pi} \Phi_q + \sqrt{\xi} \frac{i}{\sqrt{2V}} \sum_{q\neq 0} \rho_q \Phi_q^\dagger + \rho_{-q} \Phi_q \]

original problem at \( \xi = 1 \).

\[ G_k^0(i\omega) = \frac{1}{i\omega + \mu - \frac{k^2}{2m} - v_k} \]

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 \( \lambda \)

Counter-term makes sure that the exact answer is obtained for any \( v_k \) at large p.o.
What did we achieve?

\[
G_k^0(i\omega) = \frac{1}{i\omega + \mu - \frac{k^2}{2m} - v_k}
\]

Coulomb is static and short ranged with counter-term.

Electron propagator has “optimized potential” (DFT-KS or DMFT self-energy) +counter-term

Advantages:

- No need to deal with dynamic screening effects.
- No need to deal with long range Coulomb repulsion ("mother nature is usually local")
- Screening by \( \lambda \) regularizes the weight of Feynman diagrams at small \( q \), and considerably improves the DiagMC efficiency
- We can start with “the best” single particle propagator (DFT,DMFT,..)

Open questions:

- How to determine parameters \( \lambda \) and \( v_k \)
For UEG $v_k$ is chosen so that zero-th order is the screened Hartree-Fock, and we preserve Luttinger’s theorem in $G_0$ and $G$ at each order

$$v_k(\xi) = \xi \Sigma^x_k + \sum_{n=1}^{\infty} \xi^n \Delta \mu^{(n)}$$

where $\Delta \mu^{(n)}$ are numbers which take care of the shift of the chemical potential due to interaction.

In solids, a better choice is probably:

$$v_k(\xi = 1) = v_{LDA}^{KS} + \Delta \mu$$

$$v_k(\xi = 1) = \Sigma_{LDA+DMFT} + \Delta \mu$$

For DMFT, expansion in powers of interaction exist, which can be used to expand the counter-term:

$$v_k(\xi) = \sum_{n=1}^{\infty} \xi^n (\Sigma^{(n)}_{LDA+DMFT} + \Delta \mu^{(n)})$$

$$G_{LDA+DMFT}^{(n)}(k, \omega)$$

where

$$\Sigma_{LDA+DMFT} = \sum_{n=1}^{\infty} \Sigma^{(n)}_{LDA+DMFT}$$

$$\xi^n (\Sigma^{(n)}_{LDA+DMFT} + \Delta \mu^{(n)})$$
Screening length

**Average perturbation order:**

\[ \langle N \rangle = \text{Tr}(\lambda W_q) = \frac{\lambda}{q^2/(8\pi) - \bar{\Pi}_q} < \frac{\lambda}{-\bar{\Pi}_{q=0,\omega=0}} \]

**Possible choices for \( \lambda \):**

1) \( \lambda = -\bar{\Pi}_{q=0,\omega=0} \)

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

2) \( \frac{\lambda}{8\pi} = -\bar{\Pi}^N_{q=0,\omega=0} \)

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

3) \( \frac{d\bar{\Pi}_{q=0}}{d\lambda} = 0 \rightarrow \lambda \)

   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.
First order is the standard RPA:

\[ W_q = \left(v_q^{-1} - \Pi_q\right)^{-1} = \left(\frac{q^2 + \lambda}{8\pi} - \frac{\lambda}{8\pi} - \xi p^0_q - O(\xi^2) \ldots\right)^{-1} \]

Screened RPA

- \( \xi^2 \) (2n order correction)
- \( \xi^3 \) (3rd order correction)

\[ G_0^0(i\omega) = \frac{1}{i\omega + \mu - \frac{k^2}{2m} - v_k} \]

\[ v_k(\xi) = \xi(\Sigma_k - \Sigma_{k_F}) + \xi^2 s_2 + \xi^3 s_3 + \ldots \]
From sign problem to sign blessing

We want to calculate

\[ \int [dx]^N \sum_{\text{diag}} W_{\text{diag}} \leq \int [dx]^N \sum_{\text{diag}} |W_{\text{diag}}| \]

sign problem in MC!

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

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

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

Important observation: VDMC weight strongly depends on the internal variable arrangement:

in MC: \[ \int_{-1}^{1} \int_{-1}^{1} (w_1(k_1, k_2) + w_2(k_1, k_2)) dk_1 dk_2 \neq \int_{-1}^{1} \int_{-1}^{1} (w_1(k_1, k_2) + w_2(k_2, k_1)) dk_1 dk_2 \]
From sign problem to sign blessing

How to group diagrams to sign-blessed groups?

Symmetry preserved in each group:

Crossing symmetry, spin rotational symmetry,…

At the lowest order leads to “Hugenholtz diagrams”

\[
\begin{array}{c}
k_1 - q & k_1 + q & k_1 - q & k_1 + q & k_1 - q & k_1 + q \\
\end{array}
\]

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).

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

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

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

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

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)

Step 3:
Expand each vertex in Hugenholtz diagrams, to generate normal Feynman diagrams. Keep all momenta and time indices equal to those in $\log Z$ diagram.

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

Kun Chen & K. Haule, arXiv:1809.04651
Spin-susceptibility at $r_s=4$ \( \frac{1}{n} = \frac{4\pi r_s^3}{3} \)

Scan in $\lambda$ reveals the speed of convergence.

broad plateau in $\lambda$ at large order => converged value in the plateau.

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

see: Feynman & Kleinert, PRA 34, 5080 (1986)
Spin-susceptibility at $r_s=4$ \((1/n = \frac{4\pi r_s^3}{3})\)

spin susceptibility at $q=0$, $\omega=0$

\[\begin{align*}
\chi_s(q, \omega=0, \lambda) / N_F &\quad (\lambda/E_F) \\
N=1 &\quad N=2 \\
N=3 &\quad N=4 \\
N=5 &\quad N=6
\end{align*}\]

CFS

VCCFS

Convergence to exactly the same value, but oscillate

VCCFS scheme, a different BK conserving scheme

\[P_{\text{VCCFS}} = \begin{pmatrix}
-\xi & & \\
& -\xi & \\
& & 0
\end{pmatrix}
\]

Bethe-Salpeter ladders added

Kun Chen & K. Haule, arXiv:1809.04651
Spin-susceptibility 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.

<table>
<thead>
<tr>
<th>$r_s$</th>
<th>$\chi_s/N_F$</th>
<th>literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.152(2)</td>
<td>1.15-1.16</td>
</tr>
<tr>
<td>2</td>
<td>1.296(6)</td>
<td>1.27-1.31</td>
</tr>
<tr>
<td>3</td>
<td>1.438(9)</td>
<td>1.39-1.46</td>
</tr>
<tr>
<td>4</td>
<td>1.576(9)</td>
<td>1.51-1.62</td>
</tr>
</tbody>
</table>

Spin susceptibility for different momenta.
RPA 57% underestimates.
Spin-susceptibility

Spin susceptibility with and without vertex are almost indistinguishable at order $N=6$. Converged result for all momenta (at zero frequency)

dashed : vertex corrected
full line: without vertex corrections

RPA=1, is very wrong
quite featureless, no mignons or collective excitations.
However for deriving better LSDA approximations.

Kun Chen & K. Haule, arXiv:1809.04651
dielectric constant-direct comparison to DMC

Momentum dependence challenging for DMC because they treat finite system.

Can beat DMC at moderate $r_s$.

VDMC can give momentum (and frequency) response.

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

Kun Chen & K. Haule, arXiv:1809.04651
New result superior to DMC.

VDMC can give full momentum and frequency response.

DMC only $\omega=0$ or $t=0$.

DMC treats finite system, hence no small q-points


Kun Chen & K. Haule, arXiv:1809.04651
Charge response $\rho_s = 3$
Charge response $r_s = 4$

Extrapolation needed, convergence becomes hard

Some charge instability, remains unresolved after 90 years.

DMC: B.J. Alder; PRB 50, 14838 (1994)
Ongoing work: extending convergence to larger $r_s$

Calculate self-consistently vertex function from Dyson-Schwinger equation

But do not want to store entire information of

but only the “relevant” part

$$R = R(q, \theta_1, \theta_2, \phi)$$

$$\cos(\theta_1) = e_{k_0} \cdot e_{k_1}$$

$$\cos(\theta_2) = e_{k_0} \cdot \frac{q}{|q|}$$

$$\tan(\phi) = \frac{q \cdot e_{k_1} - (q \cdot e_{k_0})(e_{k_0} \cdot e_{k_1})}{(q, e_{k_0}, e_{k_1})}$$
(one loop):

$$R = \left( \frac{1}{\beta} \right) + \ldots$$

$$a \left( \{ V_1, V_2, \ldots, V_n \} \right) = \text{Det} G_0 (1, 1) G_0 (1, 2) \ldots G_0 (1, 2n) \ldots G_0 (2n, 1) G_0 (2n, 2) \ldots G_0 (2n, 2n)$$

$$a \left( \{ V_1, V_2, \ldots, V_n \} \right) = \text{Det} G_0 (1, 1) G_0 (1, 2) \ldots G_0 (1, 2n) \ldots G_0 (2n, 1) G_0 (2n, 2) \ldots G_0 (2n, 2n)$$

$$\Sigma_k =$$

The first order SwDy comparable to 4th order in VDMC.
Conclusion

• Variational Diag. MC very promising direction to extend DFT (or DFT+DMFT) towards controlled solution of solid state problem.

• Long range Coulomb repulsion makes even Hartree-Fock in solids very expensive (similar to GW). By leveraging the emergent locality of correlations, we can avoid the expensive description in terms of bare long-range interaction.

• Sign-problem can be turned into sign-blessing by grouping Feynman diagrams, using crossing symmetry and BK generating functional. Need to choose integration variables (momentum and times) optimally.

• Renormalization of four-point vertex function is a promising direction to explore.