QuasiParticle Self-consistent $GW$ Approximation
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- Review of $GW$ approximation
- A new kind self-consistent (scGW) GWA
- Apply to broad classes of materials
  - sp compounds, d (f) metals, NiO, MnO, GaMnAs, ...
- Total energy through Luttinger Ward functional

Cast of Characters
F. Aryasetiawan (AIST) “grandfather” original $GW$ code from which existing method was developed.
S. Faleev (Sandia): made scGW work!
T. Miyake (TITech) Total energies w/ LW functional
Failures in the Local Density Approximation
(Standard ab initio Approximation in solids)

- bandgaps too small
- fails for correlated materials

- Systematic overbinding
- Significant errors in mechanical properties
GW Approximation: Analog to Hartree-Fock

Start from some non-interacting hamiltonian $H_0$.

1. $H_0 = -\frac{\nabla^2}{2} + V_{\text{eff}}(\mathbf{r}, \mathbf{r}') \Rightarrow G_0 = \frac{1}{\omega - H_0}$  \hspace{1cm} \text{Example: } H_0 = H^{\text{LDA}}$

2. $D = -i G_0 \times G_0$  \hspace{1cm} \text{Linear response polarization function}

3. $\varepsilon = 1 - \nu D$  \hspace{1cm} \text{Compute $\varepsilon$ within the time-dependent Hartree approximation (aka RPA)}

4. $W(r, r', \omega) = \int d\mathbf{r}'' \varepsilon^{-1}(r, r'', \omega) V(r'', r')$

Dynamically screened exchange

Recover HF theory by $\varepsilon \to 1$:  \hspace{1cm} W(r, r') \to v(r, r') = \frac{1}{|r - r'|}$
**GW and $G^{\text{LDA}}$ $W^{\text{LDA}}$ Approximation**

5. \( \Sigma(r, r', \omega) = \frac{i}{2\pi} \int d\omega' \, G(r, r', \omega + \omega') \, e^{i\delta\omega'} \, W(r'', r', \omega') \)

Self-energy \( \Sigma = iG_0W \)

6. \( H(r, r', \omega) = -\frac{\nabla^2}{2} + V^H(r) + V^{\text{ext}}(r) + \Sigma(r, r', \omega) \Rightarrow G = \frac{1}{\omega - H} = G[G_0] \)

**Key points:**
- Construct $G$ from $G_0$.
- QP levels are at poles $G$.
- $\Sigma$ is $\omega$-dependent and non-hermitian
- $H$ is nonlocal

If the non-interacting hamiltonian $H_0$ is $H_0 = H^{\text{LDA}}$ and $\Sigma = \Sigma^{\text{LDA}} = G^{\text{LDA}} \, W^{\text{LDA}}$. 
$G^{\text{LDA}} W^{\text{LDA}}$ Approximation

- Often $G^{\text{LDA}} W^{\text{LDA}}$ is referred to as the “GW” approximation.
  - Note that $\Sigma$ depends on the LDA
  - Additional common approximations:
    - Pseudopotential or shape approximations.
      - Exceptions: Ku, Equiluz; Arnaud; Kotani
    - LDA treatment for the core ($\Sigma \neq \Sigma^{\text{all}}$)
      - Exceptions: Aryasetiawan; Kotani
    - Plasmon-pole approximation
Implementations of $GW$ differ in the following:

- Treatment of core - usually use LDA core
- Use of plasmon-pole approximation: assume $\varepsilon(\omega)$ from $\varepsilon(0)$
- Approximations to potential (e.g. PP; ASA; semilocal $\Sigma$)
- Choice of basis for one-electron (usu. LDA) wave functions
- Choice of basis for screened Coulomb interaction $W$
- No Self-consistency

Present work is most accurate implementation to date:

- No plasmon-pole approximation
- Full-potential treatment (features in common w/ LAPW, PAW)
- LDA basis: smoothed Hankels + local orbitals (beyond linear)
- $W$ expanded in IPW + product basis inside MT spheres
- Core treated on footing similar to valence (HF at lowest level)
- New kind of self-consistency
Advantage: consistent treatment of RPA: Norm conservation

drawback: GW is a perturbation theory based on ansatz of existence of quasiparticles.

- $D$ and $W$ have physical interpretation as “response” and “screened exchange;” also $e^-, h^+$, have physical meaning.
- $\text{scGW}$ moves away from this picture ... no well-defined $e^-, h^+, D$ or $W$
Observed failings in self-consistent $GW$

- Bandwidth of homogeneous electron gas *widens* relative to noninteracting case—when it should *narrow* (Holm and von Barth, PRB 57, 2108 (1998))

- Si bandgap $\sim 1.9$ eV according to PP calculation: Schone and Eguiluz, PRL 81, 1662 (1998)
  (LAPW by Ku and Eguiluz, PRL 89, 126401 (2002), contradict this finding)

**Conventional wisdom**: Something wrong with $scGW$.

But $G^{LDA}W^{LDA}$ accurate to 0.1 eV.

Ergo, better to stick with $G^{LDA}W^{LDA}$. 
Results of $G^{\text{LDA}} W^{\text{LDA}}$ Approximation

Bandgaps in $sp$ systems

Minority bands of Fe

$\leftarrow$ Cation semicore $d$ states

Energy bands of NiO $\rightarrow$

Many other examples …
QuasiParticle Self-Consistent GW

Key principles:
- Self-consistency is essential (show later)
- Stay within QP picture:
  - $\Rightarrow$ Everything ($\Sigma$, true $G$, physical observables) should be functional of a *noninteracting* $G_0$.
  - $\Rightarrow$ Poles of $G_0$ should correspond to QP levels
- Why should $QP_{scGW}$ be better than $scGW$?

\[
G = \frac{1}{\omega - H_0 - \Sigma(\omega)} \approx \frac{1}{\omega - H_0 - \Sigma(\omega_0) - \left(\frac{\partial \Sigma}{\partial \omega}\right)_{\omega_0} (\omega - \omega_0)}
\]

- Pole of $G$ (QP weight) is reduced by $Z = 1 - \frac{\partial \Sigma}{\partial \omega}$ (shifted to high plasmon energies)
- Bare polarization $D = G \times G$ reduced by $Z_{occ} \times Z_{unocc}$
  - $D$ is too small $\Rightarrow \epsilon$ too small $\Rightarrow W = V/\epsilon$ too large
QuasiParticle Self-Consistent GW II

Guiding principle

- Find a prescription for a noninteracting $G_0$ where poles of $G_0 = \text{poles of } G$ (QP levels)

No unique choice for $G_0$!

Solution to exact many-body S-eqn does not depend on choice, but the closer $G_0$ is to $G$, the more rapidly the perturbation series converges.

How can we construct the optimum $G_0$?

- Given $G_0$ we can construct $G_0 \xrightarrow{GW \text{ or } \ldots} G$

- What is the best way to make $G \xrightarrow{?} G_0$?
Use Landau’s QP picture to deduce form of $H_0, G_0$

True $G(r, r', \omega)$ should written as

$$G(r, r', \omega) = \sum_i \frac{Z_i \psi_i(r) \psi^*_i(r')}{\omega - (E_i + i\Gamma_i)} + \text{residual part}$$

Landau’s QP picture says there should be a one-to-one correspondence between QP excitations and the true $G$.

The optimum $H_0, G_0$ defined by $\{E_i^0, \psi_i^0\}$ should reproduce the true $\{E_i, \psi_i\}$ as well as possible
QuasiParticle Self-Consistent GW IV

Need a prescription to generate an \textit{energy-independent} and \textit{hermitian} potential $V_{xc}(r,r')$ that is "as close as possible" to $\Sigma(r, r', E_i)$

Solution: minimize norm

\[
\sum_{ij} \left| \Sigma_{ij}(E_i) - V_{ij}^{xc} \right|^2
\]

Where

\[
\Sigma_{ij}(E_i) = \langle \psi_i | \Sigma(E_i) | \psi_j \rangle \quad V_{ij}^{xc} = \langle \psi_i | V^{xc} | \psi_j \rangle
\]

Can show that (with some modest approximations)

\[
V_{ij}^{xc} = \langle \psi_i | \frac{\text{Re} \Sigma(E_i) + \text{Re} \Sigma(E_j)}{2} | \psi_j \rangle
\]

Replaces LDA $V_{xc}$ in making $\{E_i, \psi_i\} : E_i(V_{xc}) = E_i(\Sigma)$
Recall Results of $G^{LDA} W^{LDA}$ Approximation ...

Bandgaps in $sp$ systems

 Minority bands of Fe

←Cation semicore $d$ states

Energy bands of NiO →

Many other examples ...
Results of scGW theory I: *sp* bonded systems

LDA: broken blue
QPscGW: green
$G^{\text{LDA}}W^{\text{LDA}}$: Dotted red
O: Experiment

- $m^*$ (scGW) = 0.073
- $m^*$ (LDA) = 0.022
- $m^*$ (expt) = 0.067

Gap too large by ~0.3 eV
Band dispersions ~0.1 eV

Ga $d$ level well described
Na bandwidth reduced by 15%
Results of scGW theory II: \textit{sp} bonded systems

Errors are small, highly systematic (not corrected for phonon contribution to gap!)

- \textbf{Γ–Γ transitions} overestimated by \(0.2 \pm 0.1\) eV
- \textbf{Other transitions} overestimated by \(0.1 \pm 0.1\) eV

\textbf{Sole exception: MgO}

Gaps for Si and Ge within \(~0.1\) eV of scGW using LAPW, Ku and Equiluz, \textit{PRL} 89, 126401 (2002)
Origin of errors in QPscGW levels (Semiconductors)

1. Exact many-body theory has vertex correction $\Gamma$:
   \[ \Sigma = GW \Gamma = G \varepsilon^{-1} V \Gamma \]

2. And we compute $\varepsilon$ only within the RPA (bubble diagrams)... time-dependent Hartree approximation: response is purely electrostatic -- no correlations included in the screening

$\Rightarrow \varepsilon$ should be underestimated

This is what happens:
comparing $\varepsilon_\infty$ to experiment ...

Proposal:
$\varepsilon_\infty$ too small $\Rightarrow W$ too large $\Rightarrow E_g$ too large.
QPscGW theory applied to simple $d$ bonded systems

Valence $d$ bandwidths $W_d$, relative position of $s$ and $d$ band bottoms, exchange splittings $E_x$, and magnetic moments in $3d$ compounds.

<table>
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<tr>
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<th>$W_d$ (eV)</th>
<th>$\varepsilon_{sd}$ (eV)</th>
<th>$E_x$ (eV)</th>
<th>$\mu_B$ (µB)</th>
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<td>LDA</td>
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<td>—</td>
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<tr>
<td>Cr</td>
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<td>1.38(?)</td>
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<td>3.5</td>
<td>3.4</td>
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QPscGW theory in TM oxides

Broadening of valence band

$\frac{1}{2} - 1\text{eV}$ error in fundamental gap

NiO: AFM insulator
Faleev, MvS, Kotani, PRL 2004

TiO$_2$: insulator with $\delta$-like CB
Magnetic systems

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<th>Expt</th>
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<td>NiO</td>
<td>AFM(i)</td>
<td>1.28</td>
<td>1.72</td>
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\[ \text{Gd:7\,f}+3\,\text{spd} \]
\[ \text{Er: 11\,f}+3\,\text{spd} \]

(ErAs, min spin).

Orbital-dependent exchange splits \( f \); only \( sp \) at Fermi s.
QPscGW theory in closed f-shell systems

**CeO$_2$**: insulator with $f$-like CB

Need for full self-consistency

**Gd**: FM metal

Breakdown of RPA:

$f$ levels split by ~16 eV.
Experiment: ~12 eV
**Systematics of errors in QPscGW QP levels**

- **Simple sp systems** very well described
  - Fundamental gap $E_g$ systematically overestimated by $\sim 0.2$ eV.
  - Small errors in $m^*$ for large $E_g$; scale with gap errors for small $E_g$
  - Small errors in all known band dispersions
  - Bandwidths widen when they should (e.g. diamond, oxides), narrow when they should (e.g. Na) and stay unchanged when they should

- **Simple transition metals** also very well described.
  - $\varepsilon_{sd, \ d}$ bandwidth, exchange splitting systematically better than LDA
  - Magnetic moment slightly overestimated

- **TM oxides** show slightly larger errors.
  - Error in $E_g$ is $\sim \frac{1}{2} - 1$ eV
  - Valence band well described in GW; poor in LDA

- **f-shell** materials somewhat less well described
  - $\text{CeO}_2$ demonstrates importance of full self-consistency
  - $\text{Gd, GdN, GdAs, GdP}$ seriously overestimate $f-f$ splitting

- Different errors for spin, charge degrees of freedom
Total Energies: Luttinger-Ward Functional

T. Miyake (TITech)
F. Aryasetiawan (AIST)
T. Kotani (Osaka):

Compare Luttinger-Ward, density-functionals:

\[
E = E^{LW}[G]; \quad \frac{\delta E^{LW}[G]}{\delta G} = 0; \quad G(r, r', i\omega) = \sum_n \frac{\psi_{n\sigma}(r)\psi_{n\sigma}^*(r')}{i\omega - \varepsilon_n}
\]

\[
E = E^{DF}[n]; \quad \frac{\delta E^{DF}[n]}{\delta n} = 0; \quad n(r) = \sum_{n\sigma} \psi_{n\sigma}(r)\psi_{n\sigma}^*(r)
\]

Both exact, both satisfy variational principle.
Both must be approximated to be tractable.
Luttinger-Ward Functional

\[ E^{LW}[G] = E_0 + \text{Tr} \left[ G_0^{-1} G - 1 \right] - \text{Tr} \left[ \ln G - \ln G_0 \right] + \Phi[G] \]

\( E_0, G_0 \) = Energy and Green's function for \( V_{ee} = 0 \)

\( \Phi \) = "Exchange-correlation energy"

\[ \cong \Phi^{RPA} = \Phi_x + \frac{1}{4} \text{Tr} \left[ \ln (1 - P_\nu)(1 - \nu P) + \nu P + P_\nu \right] \]

Key difference with DFT: \( G \) has much more variational freedom: orbitals, orbital-dependent (screened) exchange. Functional much less pathological

So far, use \( G = G^{\text{LDA}} \). (Aryasetiawan et al, PRL 88, 166401). Then

\[ E^{LW,RPA}[G^{\text{LDA}}] = E^{\text{LDA}} - E^{\text{LDA}}_{xc} + \Phi_x[G^{\text{LDA}}] + \Phi^{RPA}_c[G^{\text{LDA}}] \]
Volume dependence of total energy for Na, LW functional (Takheshi Miyake), using

\[ E^{LW,RPA}[G^{LDA}] = E^{LDA} - E^{LDA}_{xc} + \Phi_x[G^{LDA}] + \Phi^RPA_c[G^{LDA}] \]

Accuracy of functional not yet known (calculation of \( \Phi \) difficult to do)
Conclusions

- **Propose a new QPscGW theory**
  - Perturbations from a QP picture, as distinct from the conventional scGW theory
  - A formal justification provided
  - Apparently improves on true scGW in practice

- **QPscGW theory provides an accurate description of QP levels for most of periodic table.**
  - Checks for:
    - Simple \(sp\) systems
    - Elemental \(d\) systems
    - Complex \(d\) systems, including a variety of TM oxides
    - Closed \(f\)-shell systems
  - Dramatic improvements over LDA for many systems

- **Errors are:**
  - Consistently small, except for exchange splitting of Gd \(f\) states
  - Consistent with higher order diagrams left out of the theory

- **Starting point** for simplifications (larger scale) and many-body perturbation theory (approach to exact theory)

- **Total energy** from Luttinger-Ward functional (in progress)
Perturbation theory best when 
\[ \{E_i, \psi_i\} = \{E_i^0, \psi_i^0\} \] as closely as possible.
**LMTO Basis for All-Electron $GW$ method**

Eigenstates expanded as generalized Linear Muffin-Tin Orbitals (both efficient and accurate).

Standard LMTO basis: envelopes → $r^{-l}$ as $r \to 0$

Solves S-eqn for flat $V = V_{MTZ}$.

\[
H_s(\varepsilon, r) = \frac{1}{r} e^{-\sqrt{-\varepsilon} r}
\]

Smoothed Hankels: envelopes → $r^l$ as $r \to 0$.

\[
(\Delta + \varepsilon) H_L(r_s, \mathbf{r}) = -4\pi G_L(r_s, \mathbf{r}) = -4\pi Y_L(\nabla) g_0(r_s, \mathbf{r})
\]

\[
H_L(\varepsilon, r_s, \mathbf{q}) = \frac{-4\pi}{\varepsilon - \mathbf{q}^2} e^{4(\varepsilon - \mathbf{q}^2)/r_s^2} Y_L(-i\mathbf{q}) e^{-i\mathbf{q} \cdot \mathbf{R}}
\]

Solves Schrodinger eqn for this potential

\[
V(\mathbf{r}) = V_{MTZ} - 4\pi G_L(r_s, \mathbf{r}) / H_L(r_s, \mathbf{r})
\]
Two independent basis sets are required.

1. Orbital basis $\chi$ for wave functions. Then

$$ G(rt, r't') = \int \frac{d\omega}{2\pi} \sum_k e^{-i\omega(t-t')} \sum_{ij} G_{ij}(k, \omega) \chi_i^k(r) \chi_j^k(r') $$

Eigenstates $\psi_i^{kn}$ are expanded in basis functions $\chi_i$

$$ G_{ij}(k, \omega) = \sum_n \frac{\psi_i^{kn} \psi_j^{*kn}}{\omega - \epsilon_n^k + i\delta} $$

$\psi_i^{kn}$ and $\epsilon_n^k$ are found from solutions of the Schrodinger equation

$$ \sum_j \left( -\frac{\nabla^2}{2m} + \nu_{ext} + V_{Hij}^k + \Sigma_{ij}(k, \omega) \right) \psi_j^{kn} = \epsilon_n^k \psi_i^{kn} $$
**Muffin-Tin-Orbitals theory:**

Eigenfunctions $\psi^{kn}$ expanded in MTO’s $\chi_s$

$$\psi^{kn}(\mathbf{r}) = \sum_s u_{s}^{kn} \chi_s(\mathbf{r})$$

- local functions $\phi_{RLi}$ inside augmentation spheres, $i=1..2$ or $1..3$

- Plane waves in the interstitial

$$P_{G}^{k}(\mathbf{r}) = \begin{cases} 0 & \text{if } \mathbf{r} \in \text{any MT sphere} \\ \exp\left[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}\right] & \text{otherwise} \end{cases}$$

Then

$$\psi^{kn}(\mathbf{r}) = \sum_{RLi} \alpha_{RLi}^{kn} \phi_{RLi}^{k}(\mathbf{r}) + \sum_{G} \beta_{G}^{kn} P_{G}^{kn}(\mathbf{r})$$
Linear method has two $\phi_{RLi}$ per $RL$. Local orbitals have 3. With local orbitals, LDA energy bands accurate over a wide range.

Example: GaAs
Blue: this method
(Methfessel and van S.)
Red: old FP-LMTO method
(Methfessel and van S.)
Green: QMTO-ASA
(Andersen) — bands from 2nd gen. ASA $V(r)$. 
2. For GW, need $\psi\psi$ products to compute M.E. of coulomb

\[ \langle \psi\psi | v | \psi\psi \rangle = \langle \psi\psi | M \rangle \langle M | v | M \rangle \langle M | \psi\psi \rangle \]

$M =$ intermediate basis for expansion of products $\psi\psi$.
$= \text{product basis } B=\{\phi \times \phi\} \text{ inside MT spheres (Aryasetiawan)}$
$= \text{Plane waves } P \times P \rightarrow P \text{ in the interstitial (conventional methods)}$

**Therefore:**
A complete basis $M$ for products $\psi\psi$ is:

\[ M \equiv \{P^k_G (r), B^k_I (r)\} \]

Now

\[
\psi^{kn} (r) = \sum_{ai} \alpha_{ai}^{kn} \phi_{ai} (r) + \sum_{G} \beta_{G}^{kn} P_{G}^{kn} (r)
\]

\[
\psi^{k_1n_1} (r)\psi^{k_2n_2} (r) = \sum_{ai} B_{RI}^{k_1+k_2} (r) \times \langle \phi \phi \rangle \times \alpha \times \alpha
\]

\[ + \sum_{G} P_{G}^{k_1+k_2} (r) \times \langle PP \rangle \times \beta \times \beta \]
For a given potential and basis, make these quantities:

Eigenfunctions $\psi_{kn}$ and eigenvalues $\varepsilon_{kn}$

Coulomb matrix $v_{IJ}(k) = \langle M^k_I | v | M^k_J \rangle, I = \{RLi, G\}$

Eigenfunction products $\langle \psi_{qj} | \psi_{q-ki} | M^k_I \rangle, I = \{RLi, G\}$

Now we can carry out GW cycle. Make: $\Sigma_X, D, W, \Sigma_C$:

Exchange part $\Sigma_X$ of self-energy

$$\langle qj | \Sigma_X | qj \rangle = \sum_k \sum_i^{BZ \text{occ}} \langle \psi_{qj} | \psi_{q-ki} | \tilde{M}_I^k \rangle v_{IJ}(k) \langle \tilde{M}_J^k \psi_{q-ki} | \psi_{qj} \rangle$$

Where the $M$ must be orthogonalized

$$v(r, r') = \sum_{k,I,J}^{BZ} \langle \tilde{M}_I^k \rangle v_{IJ}(k) \langle \tilde{M}_J^k \rangle | \tilde{M}_I^k \rangle = \sum_J | M_J^k \rangle \langle M_J^k | M_I^k \rangle^{-1}$$
Polarization function $D$

\[
\frac{\sum_{\text{occ}} \sum_{\text{unocc}}^{\text{BZ}}}{k} \sum_{j} \sum_{i} \langle M_j^k \Psi_{q_j} | \Psi_{q-k_i} \rangle \langle \Psi_{q_j} | \Psi_{q-k_i} M_j^k \rangle \times \left( \frac{1}{\omega - \epsilon_{k_j} + \epsilon_{q-k_i} + i\delta} - \frac{1}{\omega + \epsilon_{k_j} - \epsilon_{q-k_i} - i\delta} \right)
\]

Important technical point:
Fast integration contour for $D$: (Faleev)
- Tetrahedron method $\Rightarrow$ Im$D$ on real axis.
- Hilbert transform to get Re$D$.

Screened Coulomb interaction: $W_{IJ}(q, \omega) = \left(1 - \nu D\right)^{-1} \nu$
Correlation part $\Sigma_C$ of self-energy

$$
\langle q_n | \Sigma_C | q_n \rangle = \sum_{k} \sum_{n'}^{	ext{All}} \langle \psi_{q_n} | \psi_{q-kn} \hat{M}^k_I \rangle \langle \hat{M}^k_J \psi_{q-kn'} | \psi_{q_n} \rangle
$$

$$
\times \int_{-\infty}^{\infty} \frac{i d\omega'}{2\pi} W_{IJ}(k, \omega') \frac{1}{\omega' - \omega - \varepsilon_{q-ki} \pm i\delta}
$$

(Use $-i\delta$ for occupied, $+i\delta$ for unoccupied states)

Standard integration contour for $\Sigma$:
GW starting from LDA (non self-consistent)

\[
\psi_{kn}^{\text{LDA}}(\mathbf{r}) \quad \text{and} \quad \varepsilon_{kn}^{\text{LDA}} \quad \rightarrow \quad \Sigma_{x}^{nn}, \quad D, \quad W, \quad \Sigma_{c}^{nn}(\omega)
\]

Need diagonal part \(\Sigma^{nn}\) of \(\Sigma\) at QP energies \(E_{kn}\).

\[
E_{kn} = \varepsilon_{kn} + 
\langle \Psi_{kn} | \Sigma(\mathbf{r}, \mathbf{r}', E_{kn}) | \Psi_{kn} \rangle - \langle \Psi_{kn} | V_{xc}^{\text{LDA}}(\mathbf{r}) | \Psi_{kn} \rangle
\]

Actually make \(\Sigma\) at LDA \(\varepsilon_{kn}\). Correct by using \(Z\) factor.

\[
E_{kn} = \varepsilon_{kn} + Z_{kn} \times 
\left[ \langle \Psi_{kn} | \Sigma(\mathbf{r}, \mathbf{r}', \varepsilon_{kn}) | \Psi_{kn} \rangle - \langle \Psi_{kn} | V_{xc}^{\text{LDA}}(\mathbf{r}) | \Psi_{kn} \rangle \right]
\]

\[
Z_{kn} = \left[ 1 - \langle \Psi_{kn} | \frac{\partial}{\partial \omega} \Sigma(\mathbf{r}, \mathbf{r}', \varepsilon_{kn}) | \Psi_{kn} \rangle \right]^{-1}
\]