Progress & challenges with Luttinger-Ward approaches for going beyond DFT

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Ismail-Beigi, *Phys. Rev. B* (2010)

Overview

1. Review DFT and some of its problems

2. Some DFT fixes

3. Luttinger-Ward functional

4. RPA-*GW* correlation : exact and approximate forms

5. Variational optimization of Luttinger-Ward : trouble!

6. Gradient optimization and Quasiparticle Self-consistent *GW*

DFT review

Energy functional $E[n]$ of electron density $n(r)$

$$E[n] = KE + E_{ion} + E_H + E_{xc}$$

Minimizing over $n(r)$ gives

- Ground-state energy E_0
- Ground-state density $n(r)$

Minimum condition $\frac{\delta E}{\delta n(r)} = 0$ equivalent to Kohn-Sham equations

$$\left[-\frac{\nabla^2}{2} + V_{ion}(r) + V_H(r) + V_{xc}(r)\right]\psi_j(r) = \epsilon_j\psi_j(r) \qquad V_{xc}(r) = \frac{\delta E_{xc}}{\delta n(r)}$$

- LDA/GGA for E_{xc} : good geometries and total energies
- Bad band gaps

DFT gap problems

Quantitative errors for weak to moderate correlation

Material	LDA	Expt.
Diamond	3.9	5.48
Si	0.5	1.17
LiCl	6.0	9.4

Qualitative failures for transition metal oxides

Material	LDA	Expt.
CuO	0.0	1.4
FeO	0.0	2.4
NiO	0.2	4.0-4.3

Some reasons for failures

DFT has *effective* electronic states with *local* potential

$$\left[\frac{-\hbar^2\nabla^2}{2m} + V_{ion}(r) + V_H(r) + V_{xc}(r)\right]\psi_j(r) = \epsilon_j\psi_j(r)$$

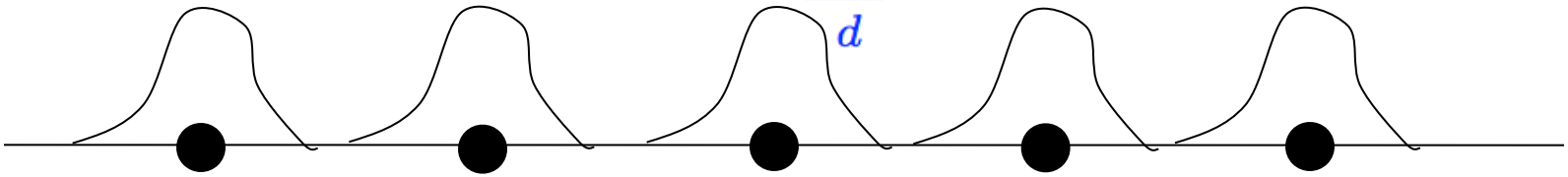
However, many-body theory says *real* quasiparticles obey Dyson equation

$$\left[\frac{-\hbar^2\nabla^2}{2m} + V_{ion}(r) + V_H(r)\right]\psi_j(r) + \int dr'\Sigma_{xc}(r,r',\epsilon_j)\psi_j(r') = \epsilon_j\psi_j(r)$$

Self-energy $\Sigma_{xc}(r,r',\omega)$ is correct potential: is *non-local* and *energy-dependent*

Static Hubbard-U form, OK for localized states (e.g. DFT+U)

$$\Sigma(r,r',\omega) \approx U\sum_d \psi_d(r)\psi_d(r')^*$$



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Some DFT fixes

LDA/GGA+U [1] : static Hubbard U physics on
chosen localized orbitals (e.g. transition metal *d*)

Dynamical mean-field theory [2] : in high degree of correlation
on a localized basis; solves model impurity system exactly

Have adjustable parameters:
- atomic-like orbitals chosen?
- values of Hubbard parameters U, J, etc. ?

Are *physically* motivated: choose physics that is missing and figure out a way to add it

[1] Anisimov, Aryasetiawan & Lichtenstein, *J. Phys. Cond. Mat* (1997)
[2] Kotliar, Savrasov, Haule, Oudovenko, Parcollet & Marianetti, *Rev. Mod. Phys.* (2006)

GW approach for bands

$$\left[\frac{-\hbar^2\nabla^2}{2m} + V_{ion}(r) + V_H(r)\right]\psi_j(r) + \int dr' \Sigma_{xc}(r, r', \epsilon_j)\psi_j(r') = \epsilon_j\psi_j(r)$$

Most common approx. : $\Sigma_{xc} \approx iGW$ $\quad W = \varepsilon^{-1} * \frac{1}{|r - r'|}$

Majority of calculations are perturbative:

- Start with DFT of some flavor, Σ_{xc}- V_{xc} is perturbation
- Works pretty well in practice
- Results may depend on starting point*

Newer schemes: (approximate) self-consistent band structures for *GW* Dyson equation (scCOHSEX and QSGW)*

Ideally: correct total energy *and* quasiparticle bands

* Faleev, van Schilfgaarde, Kotani, *PRL* (2004)
* Bruneval, Vast, Reining, Izquierdo, Sirotti, Barrett, *PRL* (2006)
* van Schilfgaarde, Kotani, Faleev, *PRL* (2006)

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Green's function reminders

One-particle Green's function

$$iG(r,r',t-t') = \langle T\hat{\psi}(r,t)\hat{\psi}(r',t')^{\dagger}\rangle e^{-\eta|t-t'|} \qquad \eta \to 0^{+}$$

$$n(r) = -iG(r,r,0^{-}) \qquad \rho(r,r') = -iG(r,r',0^{-})$$

Non-interacting G_0 given by $G_0(r,r',\omega) = \sum_n \frac{\psi_n(r)\psi_n(r')^*}{\omega - \epsilon_n \pm i\eta}$

$$H_0\psi_n = (T + V_{ion} + V_0)\psi_n = \epsilon_n\psi_n$$

$$G_0(\omega)^{-1} = \omega I - [T + V_{ion} + V_0]$$

True many-body G given by

$$G(\omega)^{-1} = \omega I - [T + V_{ion} + V_H + \Sigma_{xc}(\omega)]$$

Luttinger-Ward functional

Based on one-particle Green's function $G(r,r',\omega)$

Energy functional of $G(r,r',\omega)$

$$E[G,G_0] = KE + E_{ion} + E_H + \Phi_{xc}[G] + \int_{-\infty}^{\infty} \frac{d\omega e^{i\omega\eta}}{2\pi i} \mathrm{trace}\Big\{ I - G_0(\omega)^{-1}G(\omega) + \ln G_0(\omega)^{-1}G(\omega) \Big\}$$

where non-interacting G_0 is $G_0(\omega)^{-1} = \omega I - [T + V_{ion} + V_0]$

Extremizing over G gives

- Ground-state energy E_0
- True $G(r,r',\omega)$: real quasiparticle bands and gaps

$$G(\omega)^{-1} = \omega I - [T + V_{ion} + V_H + \Sigma_{xc}(\omega)] \qquad \Sigma_{xc} = \frac{\delta\Phi_{xc}[G]}{\delta G}$$

Independent particle Green's func.

What class of G to plug into $E[G, G_0]$?

Full $G(r, r', \omega)$: to hard to store/manipulate, unknown constraints

Simple idea: use or find "best" independent particle picture
i.e. restrict G to be of independent particle form

Can set $G = G_0$ with no further error

Total energy is simplified

$$E[G_0, G_0] = KE[\rho_0] + E_{ion}[n_0] + E_H[n_0] + \Phi_{xc}[G_0]$$

Standard form for RPA-*GW* correlation

$$\Phi_{xc} = \frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi i}\,tr\left\{\ln\bar{\varepsilon}(\omega)\right\} \qquad \Sigma_{xc} = \frac{\delta\Phi_{xc}}{\delta G} = iGW$$

✓ RPA includes exchange and dynamic screening

✓ Automatically includes van der Waals interaction

✓ GW generally improves energy alignments

✘ *Very* expensive to evaluate

- o Continuous infinite integral
- o Matrix logarithm
- o Hard to converge trace

✘ Physical content is not obvious

- o How to approximate?
- o How to improve systematically?

RPA energy: what it's made of

$$\Phi_{xc} = E_X[\rho_0] + \frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi i}\,tr\Big\{\ln\varepsilon(\omega)\Big\} - \frac{1}{2}\sum_{c,v}\langle cv|V|cv\rangle$$

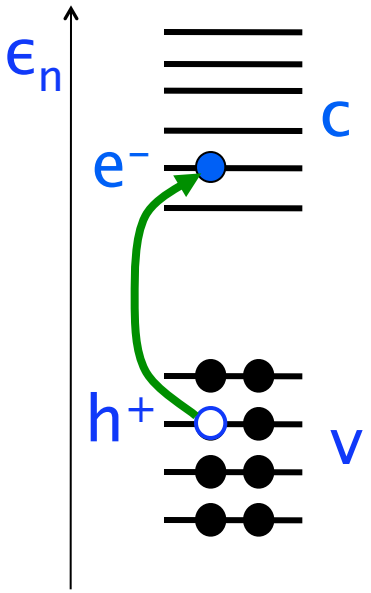
RPA dielectric matrix

$$\varepsilon(\omega) = I - VP(\omega)$$

Bare Coulomb matrix $V(r,r') = \dfrac{1}{|r-r'|}$

RPA polarizability matrix

$$P(\omega) = \sum_{c,v}\frac{2(\epsilon_c - \epsilon_v)|cv\rangle\langle cv|}{\omega^2 - (\epsilon_c - \epsilon_v)^2}$$



$$\langle r|cv\rangle = \psi_c(r)\psi_v(r')^*$$

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RPA energy: exact rewrite

$$\Phi_{xc} = E_X[\rho_0] + \frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi i}\,tr\Big\{\ln\varepsilon(\omega)\Big\} - \frac{1}{2}\sum_{c,v}\langle cv|V|cv\rangle$$

$$\Phi_{xc} = E_X[\rho_0] + \frac{1}{2}\sum_{p}\omega_p - \frac{1}{2}\sum_{c,v}(\epsilon_c - \epsilon_v) - \frac{1}{2}\sum_{c,v}\langle cv|V|cv\rangle$$

where ω_p where are eigenmodes of RPA/Casida equation

$$\omega_p^2 A_{cv,p} = (\epsilon_c - \epsilon_v)^2 A_{cv,p} + \sum_{c',v'} 2\sqrt{(\epsilon_c - \epsilon_v)(\epsilon_{c'} - \epsilon_{v'})}\langle cv|V|c'v'\rangle A_{c'v',p}$$

Same as F. Furche, *J. Chem. Phys.* (2008)

Plasmons and correlation energy...

Suppose we write the Hamiltonian for the electron gas in the following way:

$$H = \sum_i \frac{p_i^2}{2m} + \sum_{k>k_c} \frac{2\pi e^2}{k^2}\left(\rho_k^+ \rho_k - N\right) + \sum_{k<k_c} \frac{2\pi e^2}{k^2}\left(\rho_k^+ \rho_k - N\right)$$

⋮

What we have done is to redescribe the long-range part of the Coulomb interaction,

$$\sum_k (2\pi e^2/k^2)\, \rho_k^+ \rho_k$$

in terms of the plasmons. The plasma waves will carry out only zero-point oscillations; hence we have effectively frozen out the long-range part of the Coulomb interaction. We can easily calculate the reduction in system energy associated with this process. The energy of the system is

$$E_o^{(1)} = \langle 0 | \sum_i \frac{p_i^2}{2m} | 0 \rangle + \sum_{k<k_c} \frac{\hbar\omega_p}{2} - \frac{2\pi N e^2}{k^2} + \langle 0 | H_{sr} | 0 \rangle$$

$$\Phi_c = \sum_p \frac{\hbar\omega_p}{2} - \frac{1}{2}\sum_{c,v}[\epsilon_c - \epsilon_v + \langle cv|V|cv\rangle]$$

David Pines, *Elementary Excitations in Solids*, (1963), pp. 102-108

Exact rewrite benefits

Optical spectra with TDDFT or *GW*-Bethe Salpeter: same structure as RPA/Cassida

Energy expression simple and straight-forward to converge

$$\Phi_{xc} = E_X + \frac{1}{2}\sum_p \omega_p - \frac{1}{2}\sum_{c,v}\left(\epsilon_c - \epsilon_v + \langle cv|V|cv\rangle\right)$$

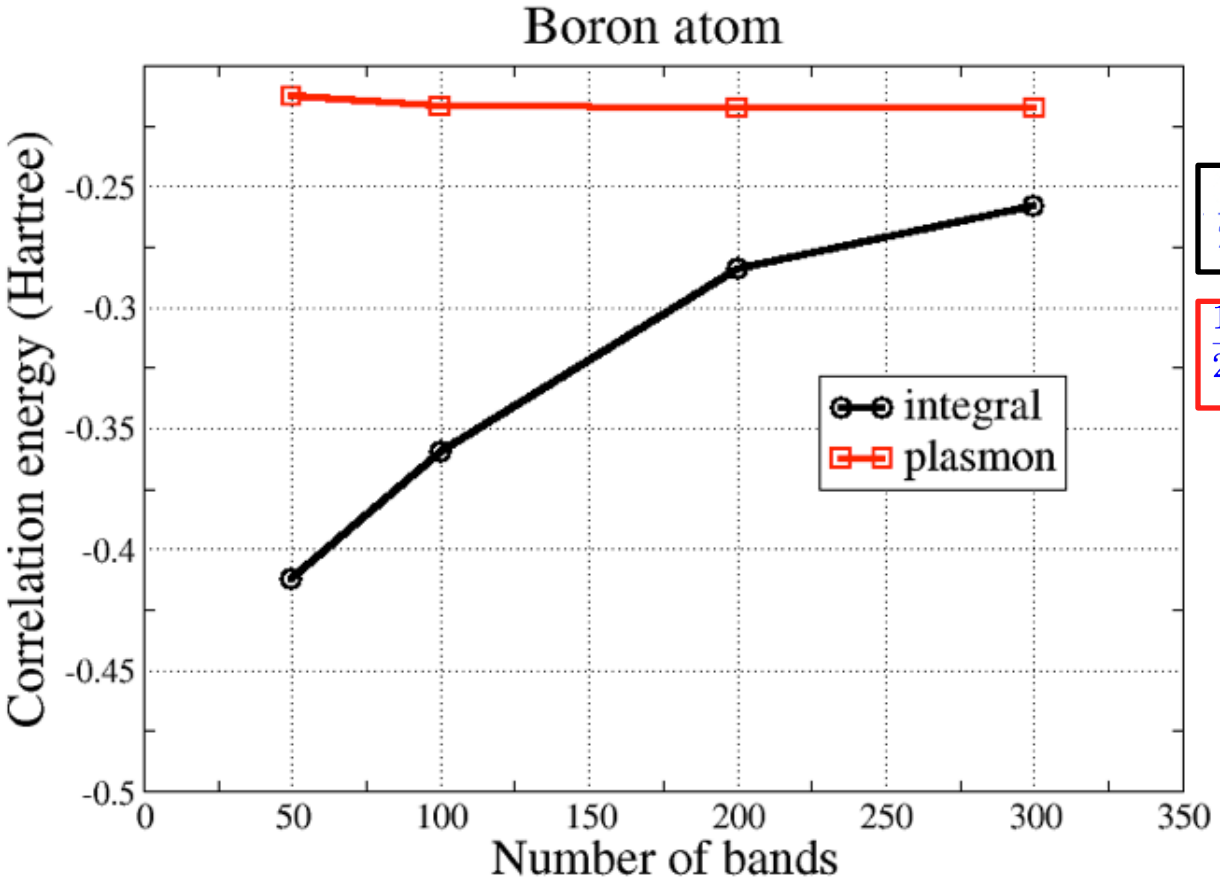
Good convergence rate (next slide)

Sum over all plasma modes is a trace: efficient matrix square root algorithms?

$$\sum_p \omega_p = \mathrm{trace}\{(\Omega^2)^{1/2}\}$$

$$\Omega^2_{cv,c'v'} = (\epsilon_c - \epsilon_v)^2\delta_{cv,c'v'} + 2\sqrt{(\epsilon_c - \epsilon_v)(\epsilon_{c'} - \epsilon_{v'})}\langle cv|V|c'v'\rangle$$

Convergence



$$\frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi i}\,tr\Big\{\ln\varepsilon(\omega)\Big\}-\frac{1}{2}\sum_{c,v}\langle cv|V|cv\rangle$$

$$\frac{1}{2}\sum_{p}\omega_p-\frac{1}{2}\sum_{c,v}(\epsilon_c-\epsilon_v)-\frac{1}{2}\sum_{c,v}\langle cv|V|cv\rangle$$

Rapid convergence versus number of single-particle states included in calculation

Where is *W* ?

$$\Phi_{xc} = E_X[\rho_0] + \frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi i}\,tr\Big\{\ln\varepsilon(\omega)\Big\} - \frac{1}{2}\sum_{c,v}\langle cv|V|cv\rangle$$

$$\Phi_{xc} = E_X + \frac{1}{2}\sum_{p}\omega_p - \frac{1}{2}\sum_{c,v}\Big(\epsilon_c - \epsilon_v + \langle cv|V|cv\rangle\Big)$$

- Neither in terms of screened interaction W
- W : have physical feeling & ideas about screening,

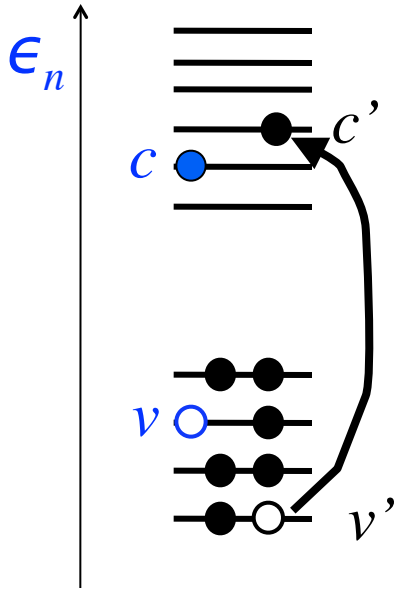
  how to approx. or improve -- e.g. plasmon-pole models
- Nice/useful to have expression in terms of W ?

Approximate rewrite

$$\Phi_{xc} \approx E_X + \frac{1}{2}\sum_{c,v}\sqrt{(\epsilon_c-\epsilon_v)^2 + 2(\epsilon_c-\epsilon_v)\langle cv|W_{cv}(\epsilon_c-\epsilon_v)|cv\rangle}$$

$$-\frac{1}{2}\sum_{c,v}\Big(\epsilon_c-\epsilon_v+\langle cv|V|cv\rangle\Big)$$

- Sums over transitions cv
- Correlation for cv : expectation of a screened Coulomb interaction W_{cv}
- "Self-interaction corrected" : W_{cv} from all *other* transitions ; cv doesn't screen itself!



$$W_{cv}(\omega) = \epsilon_{cv}(\omega)^{-1}V$$

$$\epsilon_{cv}(\omega) = I - VP_{cv}(\omega)$$

$$P_{cv}(\omega) = \sum_{c'v'\neq cv}\frac{2(\epsilon_{c'}-\epsilon_{v'})|c'v'\rangle\langle c'v'|}{\omega^2-(\epsilon_{c'}-\epsilon_{v'})^2}$$

Approximate rewrite (2)

$$\Phi_{xc} \approx E_X + \frac{1}{2}\sum_{c,v}\sqrt{(\epsilon_c-\epsilon_v)^2+2(\epsilon_c-\epsilon_v)\langle cv|W_{cv}(\epsilon_c-\epsilon_v)|cv\rangle}$$

$$-\frac{1}{2}\sum_{c,v}\Big(\epsilon_c-\epsilon_v+\langle cv|V|cv\rangle\Big)$$

- Simplest idea: static screening approximation means

$$\Phi_{xc} \approx E_X + \frac{1}{2}\sum_{c,v}\sqrt{(\epsilon_c-\epsilon_v)^2+2(\epsilon_c-\epsilon_v)\langle cv|W_{cv}(0)|cv\rangle}$$

$$-\frac{1}{2}\sum_{c,v}\Big(\epsilon_c-\epsilon_v+\langle cv|V|cv\rangle\Big)$$

- Expand square root in powers of W_{cv} and $W_{cv} \to W$

$$\Phi_{xc} \approx \frac{1}{2}\sum_{v}\langle v|W(0)-V|v\rangle - \frac{1}{2}\sum_{v,v'}\langle vv'|W(0)|vv'\rangle$$

This XC functional gives COHSEX self-energy

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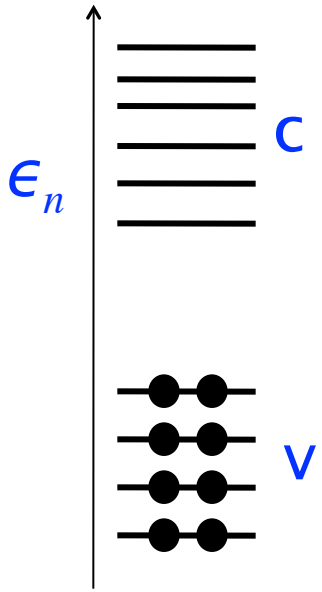
How to choose G_0?

$$G = G_0 = \sum_n \frac{|n\rangle\langle n|}{\omega - \epsilon_n} = (\omega I - H_0)^{-1}$$

"Best" single-particle picture and G_0 ... ?

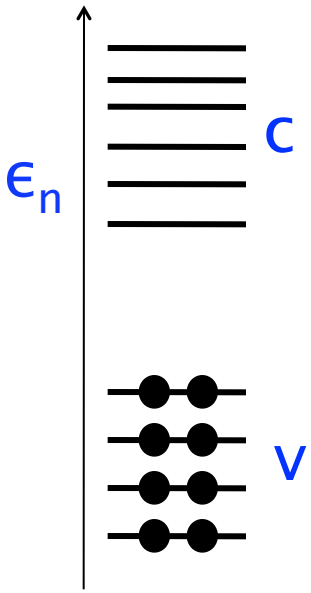


- DFT-based : LDA / GGA / DFT+U / ...
  - ✓come from optimizing an energy functional
  - ✘ wrong functional (not Luttinger-Ward)
- Self-consistent bands: scCOHSEX, QS*GW*, ...
  - ✓Solve Dyson equation (approximately)
  - ✘ Not obviously from variation of Luttinger-Ward

Why not optimize Luttinger-Ward $E[G_0,G_0]$ over G_0 ?

Extremization debacle

Extremize $E[G_0, G_0]$ over $G_0 = \sum_n \frac{|n\rangle\langle n|}{\omega - \epsilon_n}$



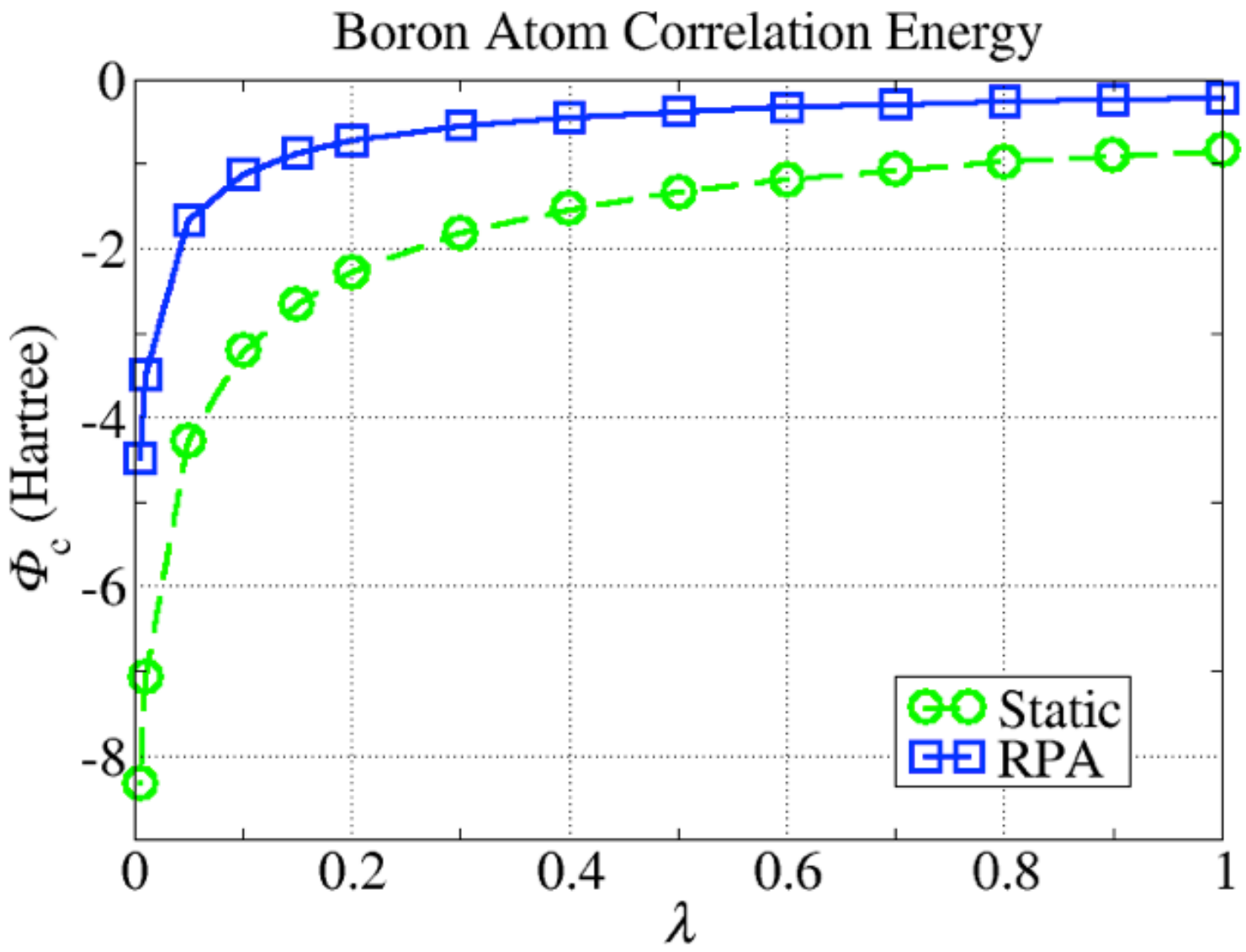
Example:

- start with DFT band structure $\{\epsilon_n\}$
- vary $\{\epsilon_n\}$ to optimize $E[G_0, G_0]$

Fails completely! Two problems

1. RPA $\Phi_{xc}[G_0]$ and $E[G_0, G_0]$: no lower bound (go to -∞)

2. $E[G_0, G_0]$: no extremum over varying $\{\epsilon_n, \psi_n\}$



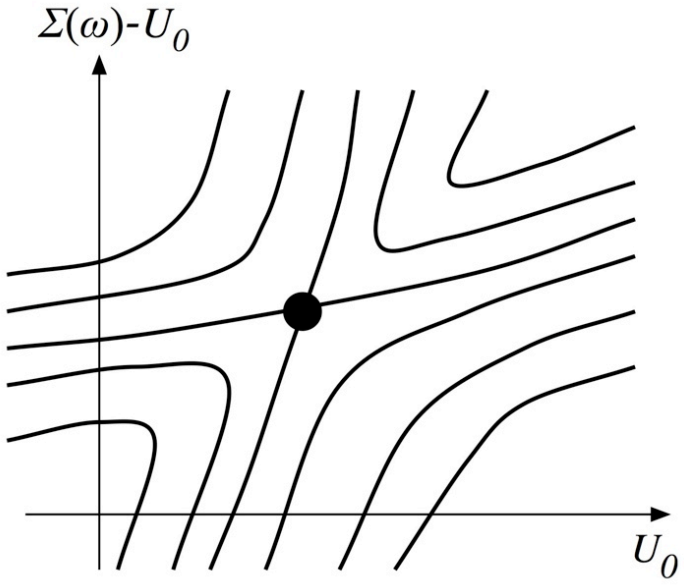
$$\epsilon_c - \epsilon_v \quad \rightarrow \quad \lambda(\epsilon_c - \epsilon_v)$$

Extremization: what to do?

$$G_0 = (\omega I - [T + V_{ion} + V_H + U_0])^{-1}$$

$$G = (\omega I - [T + V_{ion} + V_H + \Sigma_{xc}(\omega)])^{-1}$$

- Brute force: work with full $G(r,r',\omega)$
  i.e. dynamic $\Sigma_{xc}(r,r',\omega)$
  very expensive computationally



Level curves of $E[G,G_0]$

- Constrain G_0 , i.e. U_0
  - Local $U_0(r)$ → well behaved $E[G_0,G_0]$ ... but non-locality is important to getting properties right*
  - Nonlocal $U_0(r,r')$ --- hybrids, scCOHSEX, QSCGW, ...
    Which is better? Better in which sense?

* Dahlen & von Barth, *PRB* and *J. Chem. Phys.* (2004)
* Dahlen, van Leeuwen, von Barth, *PRA* (2006)
* Hellgren & von Barth, *PRB* (2007)

Hybrid-like scheme?

Choose optimal amount of non-locality, e.g. like hybrids?

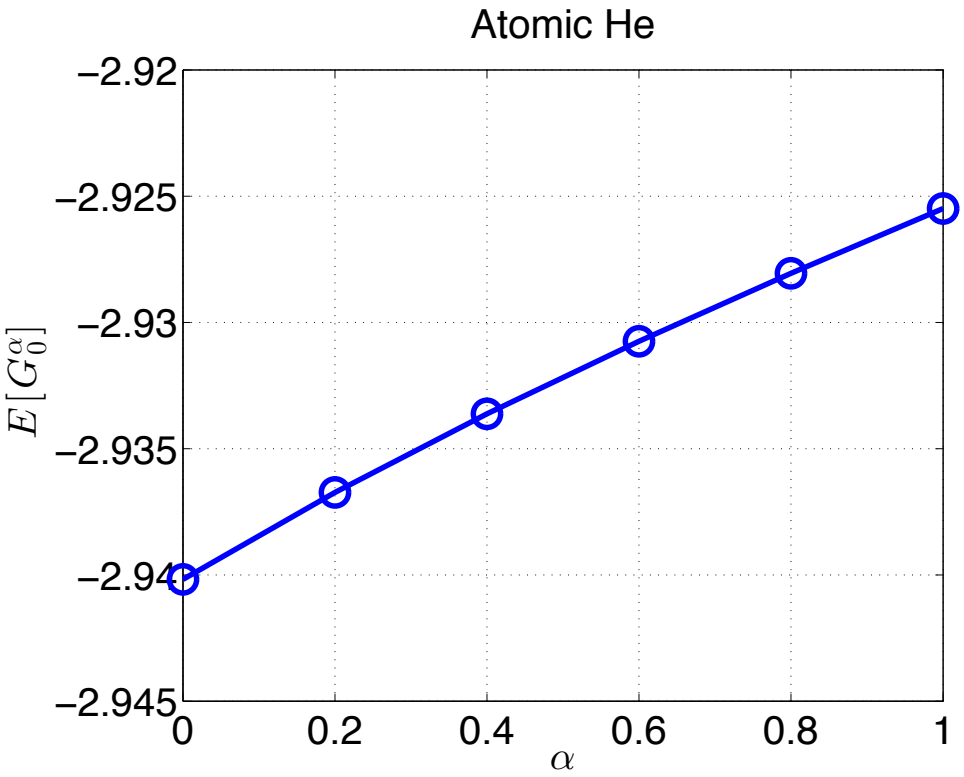
Mix amount α of Fock exchange

$$\left[\frac{-\hbar^2\nabla^2}{2m} + V_{ion}(r) + V_H(r) + (1-\alpha)V_{xc}(r)\right]\psi_j(r) + \alpha\int dr'\,\Sigma_x(r,r')\psi_j(r') = \epsilon_j\psi_j(r)$$

1. Given α : solve self-consistency → $\{\epsilon_n, \psi_n\}^\alpha$ → $G_0{}^\alpha$
2. Calculate $E[G_0{}^\alpha]$
3. Look for optimum versus α

Fails! No optimum...

Need to think harder...



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"Best" G_0 : smallest gradient?

Extremum (real answer)

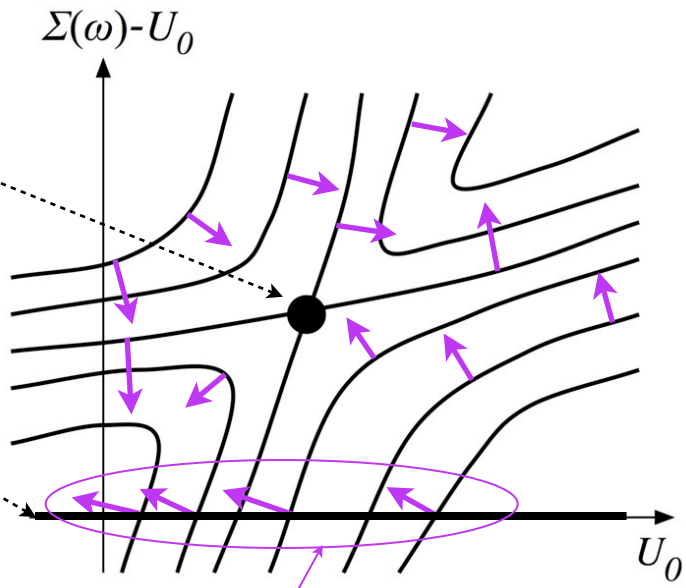
$$G = (\omega I - [T + V_{ion} + V_H + \Sigma_{xc}(\omega)])^{-1}$$

Non-interacting form

$$G_0 = (\omega I - [T + V_{ion} + V_H + U_0])^{-1}$$

Trial Green's function

$$G_t = (\omega I - [T + V_{ion} + V_H + \Sigma_t(\omega)])^{-1}$$



Level curves of $E[G_t, G_0]$

Gradient of E versus $\Sigma_t(\omega)$

$$\frac{\delta E}{\delta \Sigma_t(\omega)} = 2\pi i \cdot G_t(G_t^{-1} - G_0^{-1} + \Sigma_{xc} - U_0)G_t$$

Gradient on non-interacting axis $\Sigma_t(\omega)=U_0$

$$\left.\frac{\delta E}{\delta \Sigma_t(\omega)}\right|_{G_0} = 2\pi i \cdot G_0(\Sigma_{xc} - U_0)G_0$$

Minimizing gradient length

|Gradient|^2 is

$$|\nabla E|^2 = \int_{-\infty}^{\infty} d\omega \left| \frac{\delta E}{\delta \Sigma_t(\omega)} \right|^2 = 4\pi^2 \sum_{m,n} \int_{-\infty}^{\infty} d\omega \frac{|\langle m|\Sigma_{xc}(\omega) - U_0|n\rangle|^2}{|(\omega - \epsilon_m \pm i\eta)(\omega - \epsilon_n \pm i\eta)|^2}$$

Diagonal $n{=}m$ cases

$$\text{if} \quad \langle n|\Sigma_{xc}(\epsilon_n)|n\rangle \neq \langle n|U_0|n\rangle \quad \rightarrow \quad \sim \frac{|\langle n|\Sigma_{xc}(\epsilon_n) - U_0|n\rangle|^2}{\eta^3}$$

$$\text{if} \quad \langle n|\Sigma_{xc}(\epsilon_n)|n\rangle = \langle n|U_0|n\rangle \quad \rightarrow \quad \sim \frac{|\langle n|\Sigma'_{xc}(\epsilon_n)|n\rangle|^2}{\eta}$$

Minimizing gradient length (2)

|Gradient|^2 is

$$|\nabla E|^2 = \int_{-\infty}^{\infty} d\omega \left| \frac{\delta E}{\delta \Sigma_t(\omega)} \right|^2 = 4\pi^2 \sum_{m,n} \int_{-\infty}^{\infty} d\omega \frac{|\langle m|\Sigma_{xc}(\omega) - U_0|n\rangle|^2}{|(\omega - \epsilon_m \pm i\eta)(\omega - \epsilon_n \pm i\eta)|^2}$$

Off-diagonal $n \neq m$ cases

$$\sim \frac{|\langle m|\Sigma_{xc}(\epsilon_m) - U_0|n\rangle|^2 + |\langle m|\Sigma_{xc}(\epsilon_n) - U_0|n\rangle|^2}{\eta(\epsilon_m - \epsilon_n)^2}$$

Quadratic function of $\langle m|U_0|n\rangle$

Minimum happens when

$$\langle m|U_0|n\rangle = \frac{1}{2}\Big\{ \langle m|\Sigma_{xc}(\epsilon_m)|n\rangle + \langle m|\Sigma_{xc}(\epsilon_n)|n\rangle \Big\}$$

QS*GW* : shortest gradient

Energy functional gradient length minimum for
non-interacting exchange-correlation potential U_0

$$\langle m|U_0|n\rangle = \frac{1}{2}\Big\{\langle m|\Sigma_{xc}(\epsilon_m)|n\rangle + \langle m|\Sigma_{xc}(\epsilon_n)|n\rangle\Big\}$$

This is the Quasiparticle Self-consistent *GW* (QSGW) scheme*

Note : all entries not equally important!

Diagonal cases $\langle n|U_0|n\rangle = \langle n|\Sigma_{xc}(\epsilon_n)|n\rangle$
dominant over
off-diagonals

* Kotani, van Schilfgaarde & Faleev, *PRL* (2006) and *PRB* (2007)

Summary

- Exact rewrite of RPA correlation energy:
  straightforward
  good convergence

- Approximate formulae built on screened interaction
  allows construction of approximate self-energies
  based on screening function

- Finding “best” band structure via naive extremizing of
  Luttinger-Ward functional : ill defined

- Luttinger-Ward gradient optimization & QS*GW*