The relation between the RPA, the GW selfenergy and analytic first derivatives

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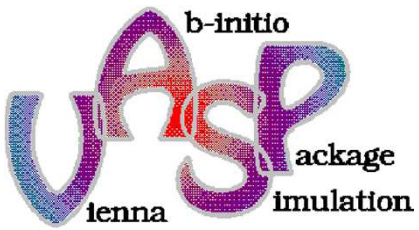
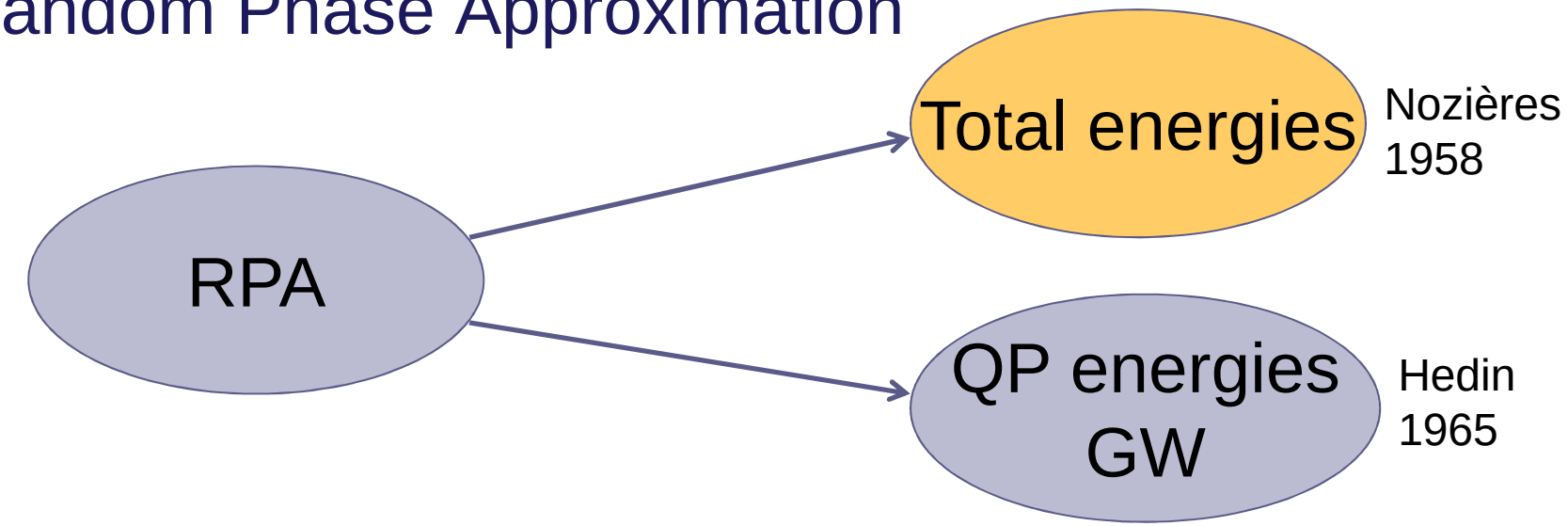


Overview

- RPA and GW a first look
  - Diagrammatic representation of both theories
  - Achieving good scaling with system size
- Relation between RPA and GW / forces in the RPA
- Few (very few) examples

Overview: Theory

- Random Phase Approximation



RPA → screened exchange

Outline of typical computational procedures

RPA is a perturbation theory usually performed on top of density functional theory
(and that is the only way it should be done)

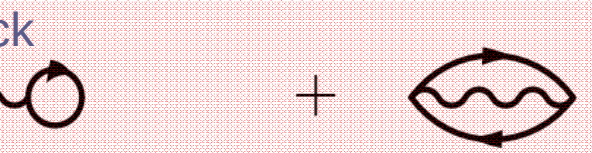
- Calculate the DFT ground-state
- Calculate all orbitals including unoccupied orbitals
- Calculate RPA total energy and/or GW QP-energies
- In the latest version of vasp (vasp.6)
  this can be comfortably done in a single steps
  - ALGO = GWr or
  - ALGO = ACFDTr ; LRPAFORCES = .TRUE.

RPA Derivation

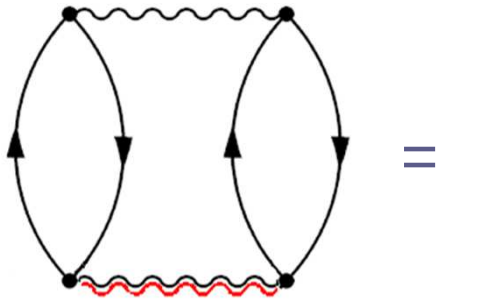
- Most elegant derivation using 2nd quantization
  - Gell-Mann Low theorem: adiabatic switching $\hat{H}_0 \rightarrow \hat{H}$
  - Time-order to normal-order using Wick's theorem
  - Linked cluster theorem
  - Graphical representation: Goldstone diagrams
- Møller–Plesset PT is a special case starting from HF
- Adiabatic connection fluctuation dissipation theorem and Görling-Levy perturbation theory
  - More involved algebra, different pathway
- Coupled cluster theory using an exponential ansatz for the wavefunction

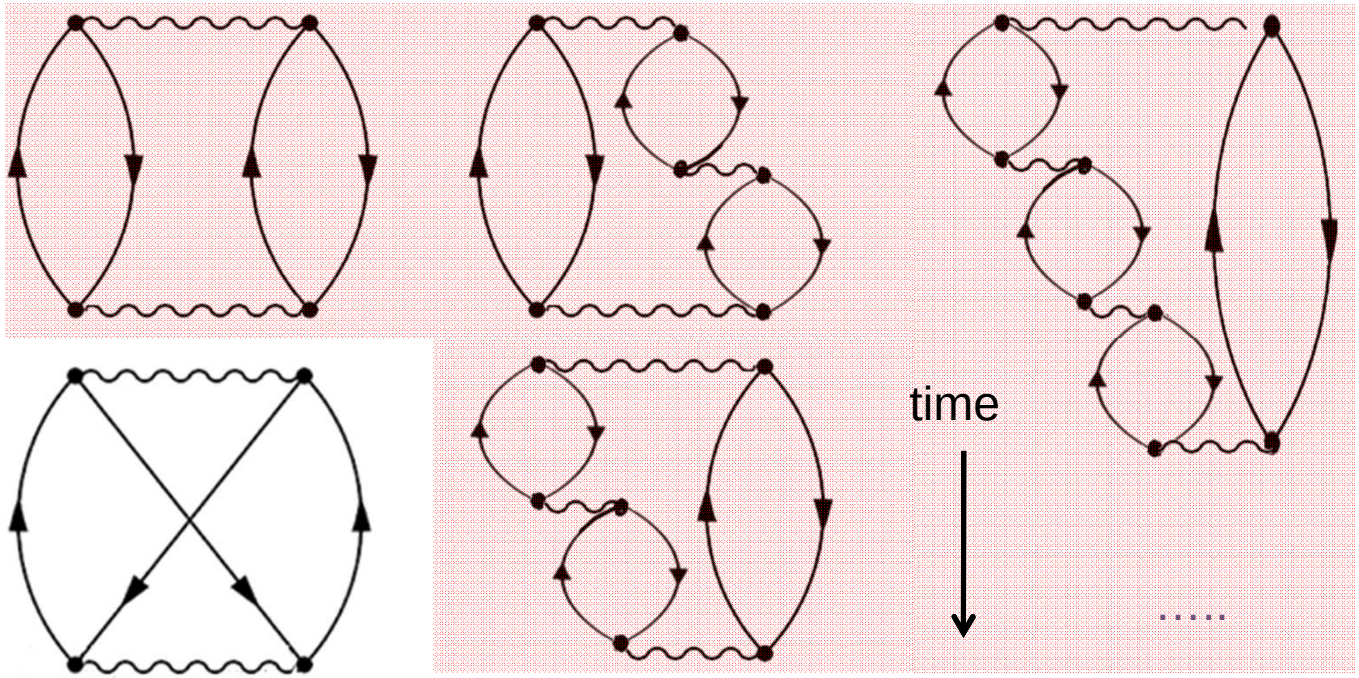
dRPA: all bubble diagrams

Hartree + Fock exchange energy



1st order





2.nd order

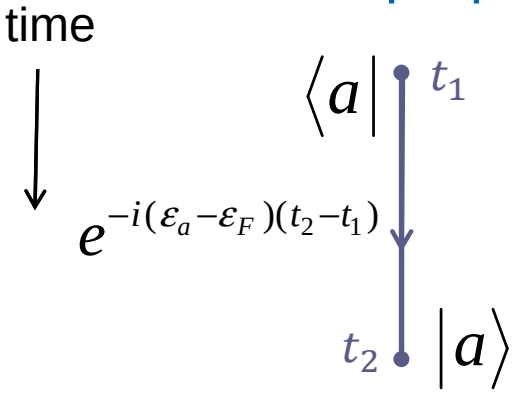
3.rd order

4.order

$$\ln(1-v\chi)+v\chi = -\frac{\mathrm{Tr}[\chi v \chi v]}{2} \quad -\frac{\mathrm{Tr}[\chi v \chi v \chi v]}{3} \quad -\frac{\mathrm{Tr}[\chi v \chi v \chi v \chi v]}{4}$$

Diagrams and single particle Green's function

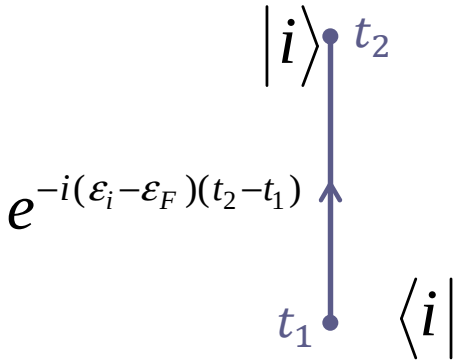
- Single particle Green's function: $G(\omega) = (\omega - T - V^{\mathrm{H}} - V^{xc})^{-1}$
- Straight line = Green's function describing the propagation of an electron or hole from position and time $(\mathbf{r}_1, t_1)$ to $(\mathbf{r}_2, t_2)$
- Particle propagator $\mathrm{G}(1,2) = \mathrm{G}(\mathbf{r}_1, \mathbf{r}_2, t_2 - t_1)$ $t_2 > t_1$



$$G_0(1,2) = \sum_{a \in \mathrm{virt}} \phi_a^*(\mathbf{r}_1)\phi_a(\mathbf{r}_2)e^{-i(\varepsilon_a - \varepsilon_F)(t_2 - t_1)}$$

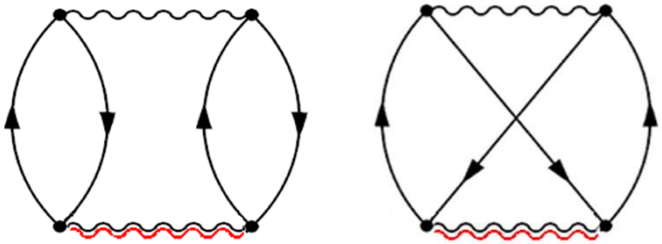
propagation by unperturbed H

- Hole propagator $\mathrm{G}(1,2)$ $t_2 < t_1$

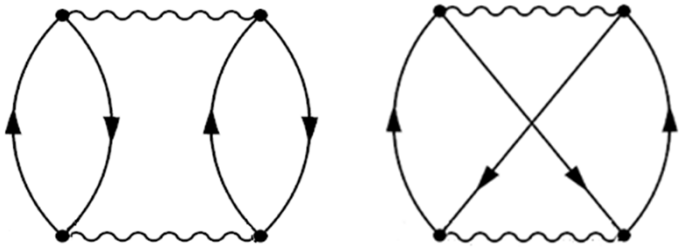


$$G_0(1,2) = -\sum_{i \in \mathrm{occ.}} \phi_i^*(\mathbf{r}_1)\phi_i(\mathbf{r}_2)e^{-i(\varepsilon_i - \varepsilon_F)(t_1 - t_2)}$$

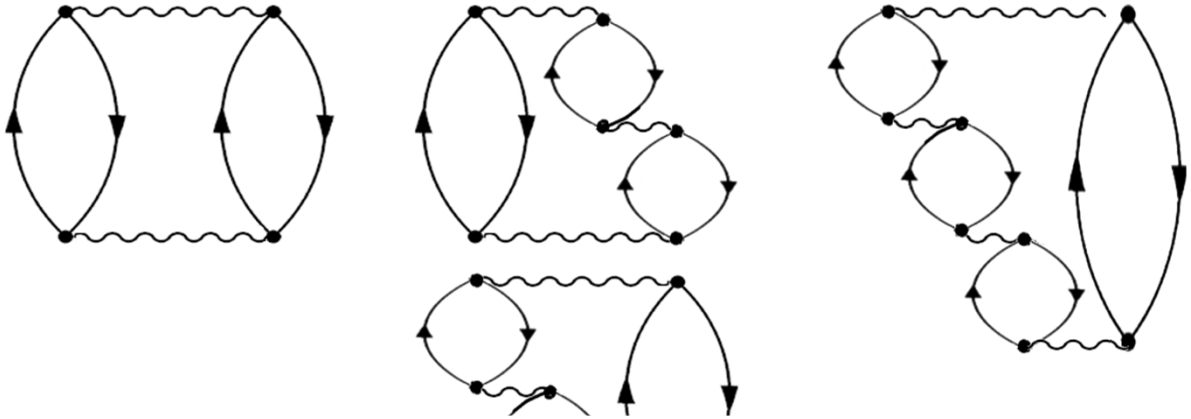
There are two limits to consider



- Large gap systems: exchange is hardly screened

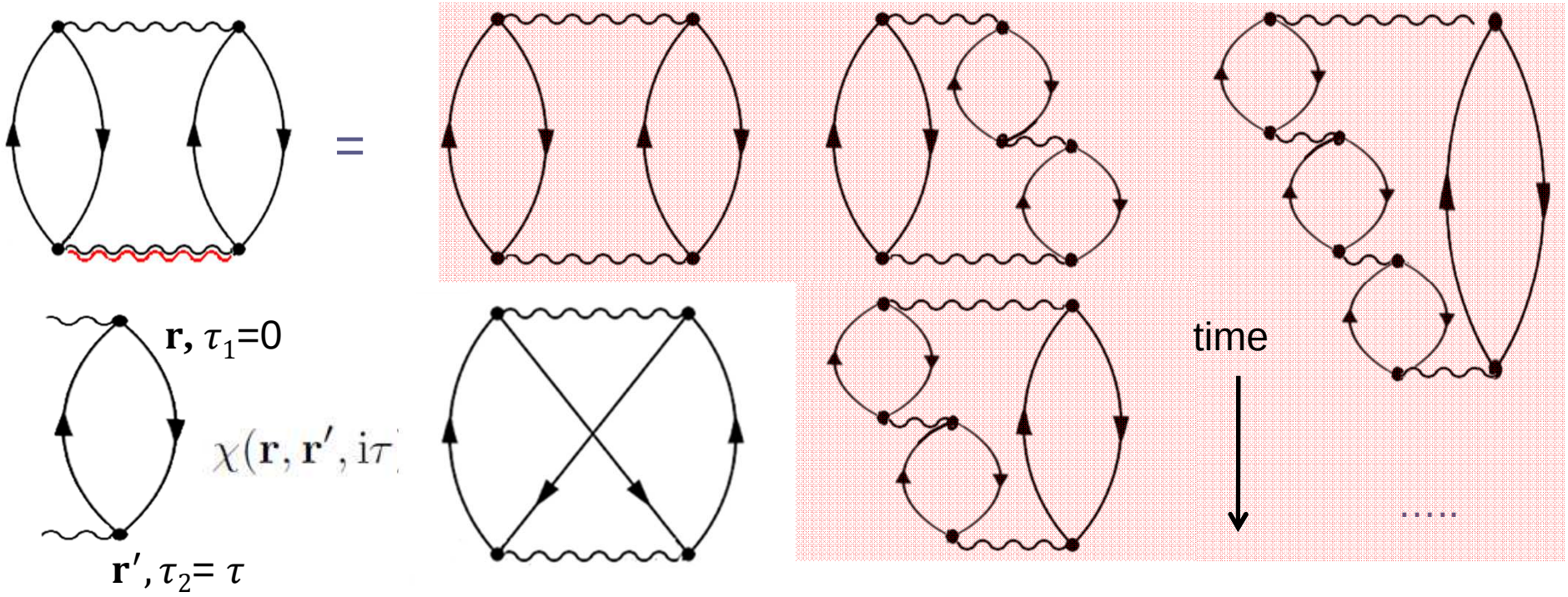


- Small gap: exchange tiny, and bubbles need to be summed to infinite order



dRPA: all bubble diagrams

Hartree + Fock exchange energy



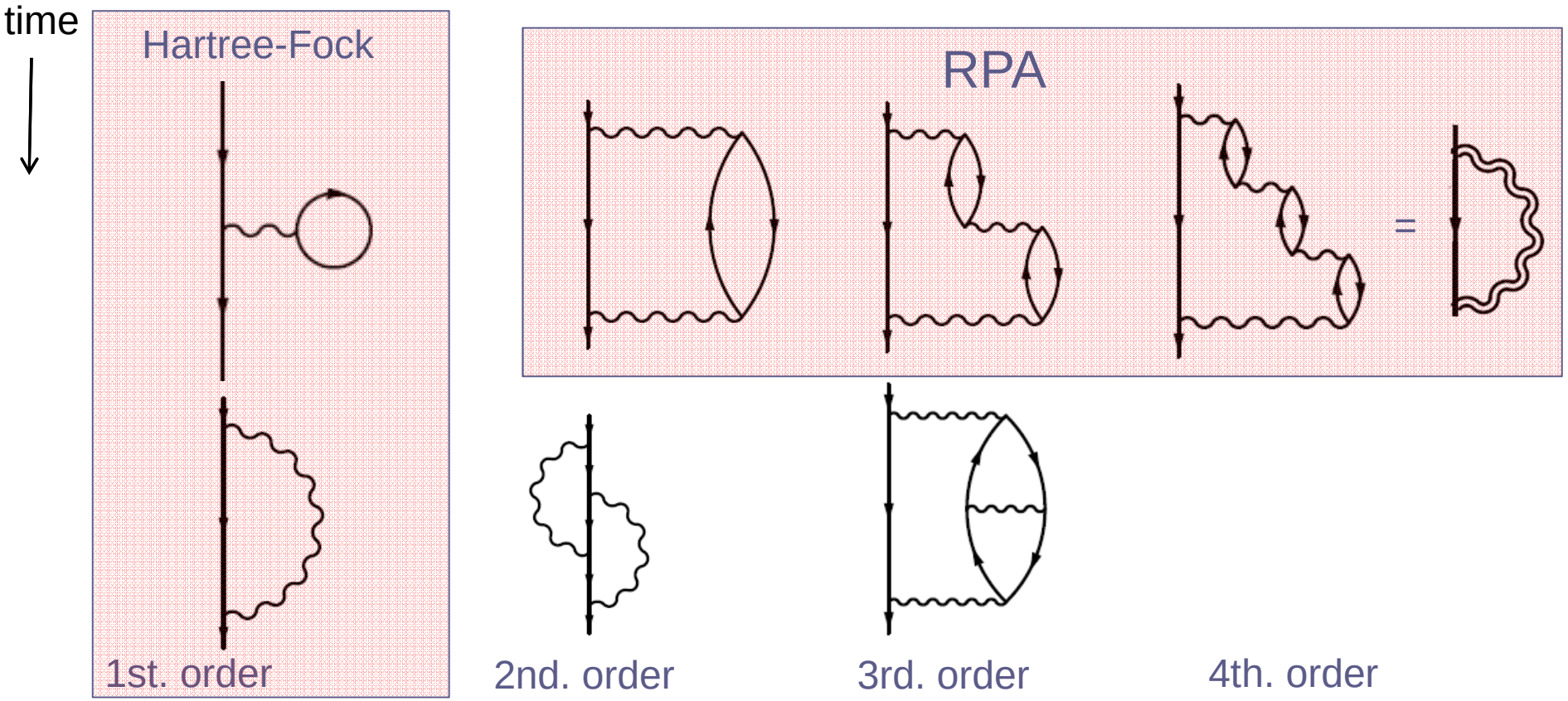
2.nd order 3.rd order 4.order

$$\ln(1-v\chi)+v\chi = -\frac{\mathrm{Tr}[\chi v \chi v]}{2} \quad -\frac{\mathrm{Tr}[\chi v \chi v \chi v]}{3} \quad -\frac{\mathrm{Tr}[\chi v \chi v \chi v \chi v]}{4}$$

Perturbation theory: Σ is a "function" of G

- All "Feynman" diagrams with one in-going and one out-going line yield the self-energy (properly amputed)
- $G(1,2) = \langle \Psi_0 | T\psi(1)\psi^+(2) | \Psi_0 \rangle$ and apply Wick theorem

  $\psi^+(2)$ creates particle at $\mathbf{r}_2, t_2$; $\psi(1)$ annihilate particle at $\mathbf{r}_1, t_1$



Low scaling dRPA and GW

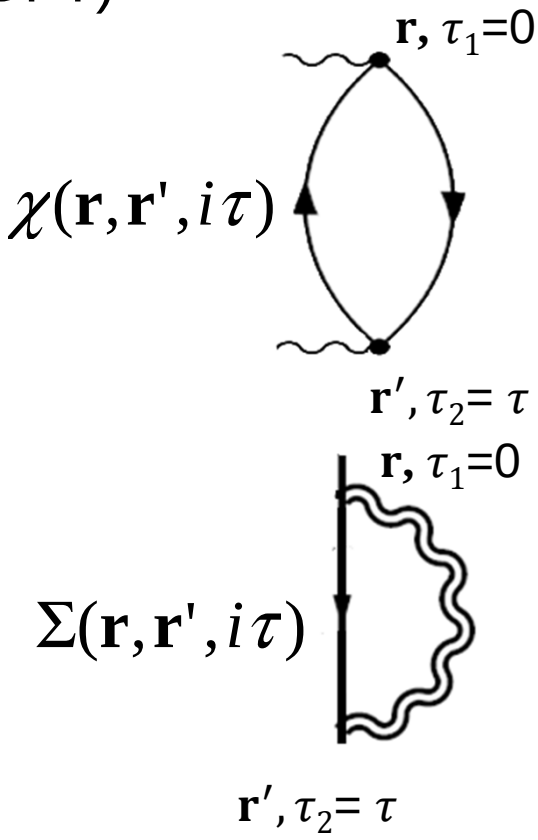
256 Si atoms: 50 million particle-hole channels (scaling N^5-N^6)

Low complexity RPA & GW code using plane waves

Desired: Cubic system size scaling N^3 (as DFT)

How do we achieve this:

$$\chi(\mathbf{r},\mathbf{r}',i\tau) = -G(\mathbf{r},\mathbf{r}',i\tau)G(\mathbf{r}',\mathbf{r},-i\tau)$$
$$\Sigma(\mathbf{r},\mathbf{r}',i\tau) = \quad G(\mathbf{r},\mathbf{r}',i\tau)W(\mathbf{r}',\mathbf{r},\pm i\tau)$$



Point wise multiplications in real space scales only quadratic with # of grid points

Hedin L. (1965), Phys. Rev. 139, A796.
Rojas, Godby, and Needs (1995), PRL 74, 1827.
Kaltak, Klimeš, Kresse (2014), PRB 90, 054115.

Dyson equations

However, many calculation steps are more conveniently done in frequency and reciprocal space:

$$W(i\omega) = v + v \quad \chi(i\omega) W(i\omega)$$

$$G(i\omega) = G_0 + G_0(i\omega)\Sigma(i\omega)G(i\omega)$$

$$E^{\mathrm{RPA}} = \ln(1 - v\chi(i\omega)) + v\chi(i\omega)$$

We need an

- Optimal time grid and optimal frequency grid
- Fourier transformations to go forth and back time ↔ frequency

Kaltak M., Klimeš J., Kresse G. , JCTC 10, 2498 (2014)

Optimum time grid from second order MP2

J. Almlöf (1991), *Chem. Phys. Lett.* 181, 319–320 and many more

- Optimal time grids are known from Laplace transformed MP2

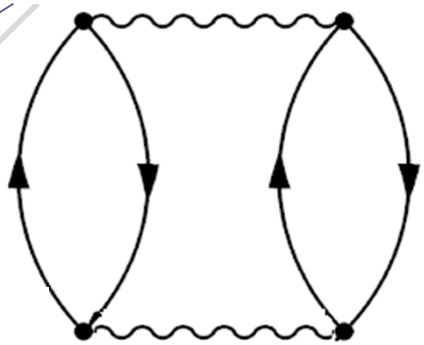
$$E^{(2)} = \frac{1}{2} \sum_{ijab} \frac{|\langle ij|ab\rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

Laplace transform

$$\frac{1}{x} = \int_0^\infty \mathrm{d}\tau \; \mathrm{e}^{-x\tau}$$

discretization

$$E^{(2)} = \frac{1}{2} \sum_{ijab} |\langle ij|ab\rangle|^2 \sum_{k=1}^{N_\tau} e^{\tau_k(\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b)}$$



- Minimize error function (L_2-norm, or maximum norm)

$$\hat{\eta}(x) = \frac{1}{x} - \sum_{k=1}^{N_\omega} w_k \mathrm{e}^{-x\tau_k}$$

Optimal frequency grid

Kaltak M., Klimeš J., Kresse G. , JCTC 10, 2498 (2014)

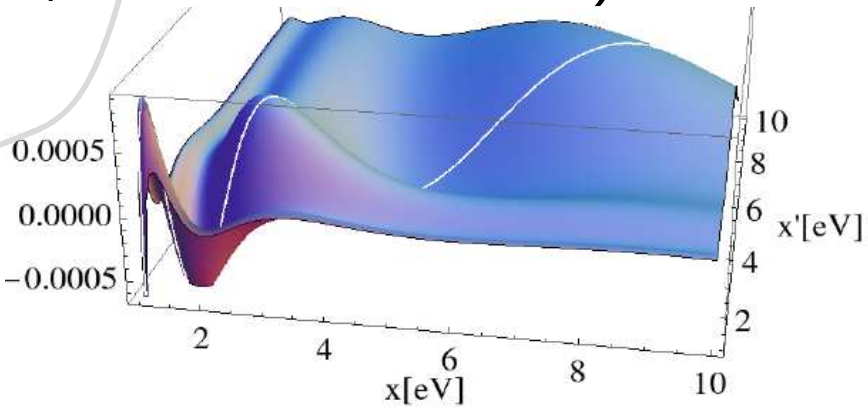
- Optimal frequency grids determined in analogous manner

$$E^{(2)} = \frac{1}{2}\sum_{ijab}\frac{|\langle ij|ab\rangle|^2}{\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b} \longrightarrow \frac{1}{2}\int d\omega \mathrm{Tr}[v\chi(\omega)v\chi(\omega)]$$

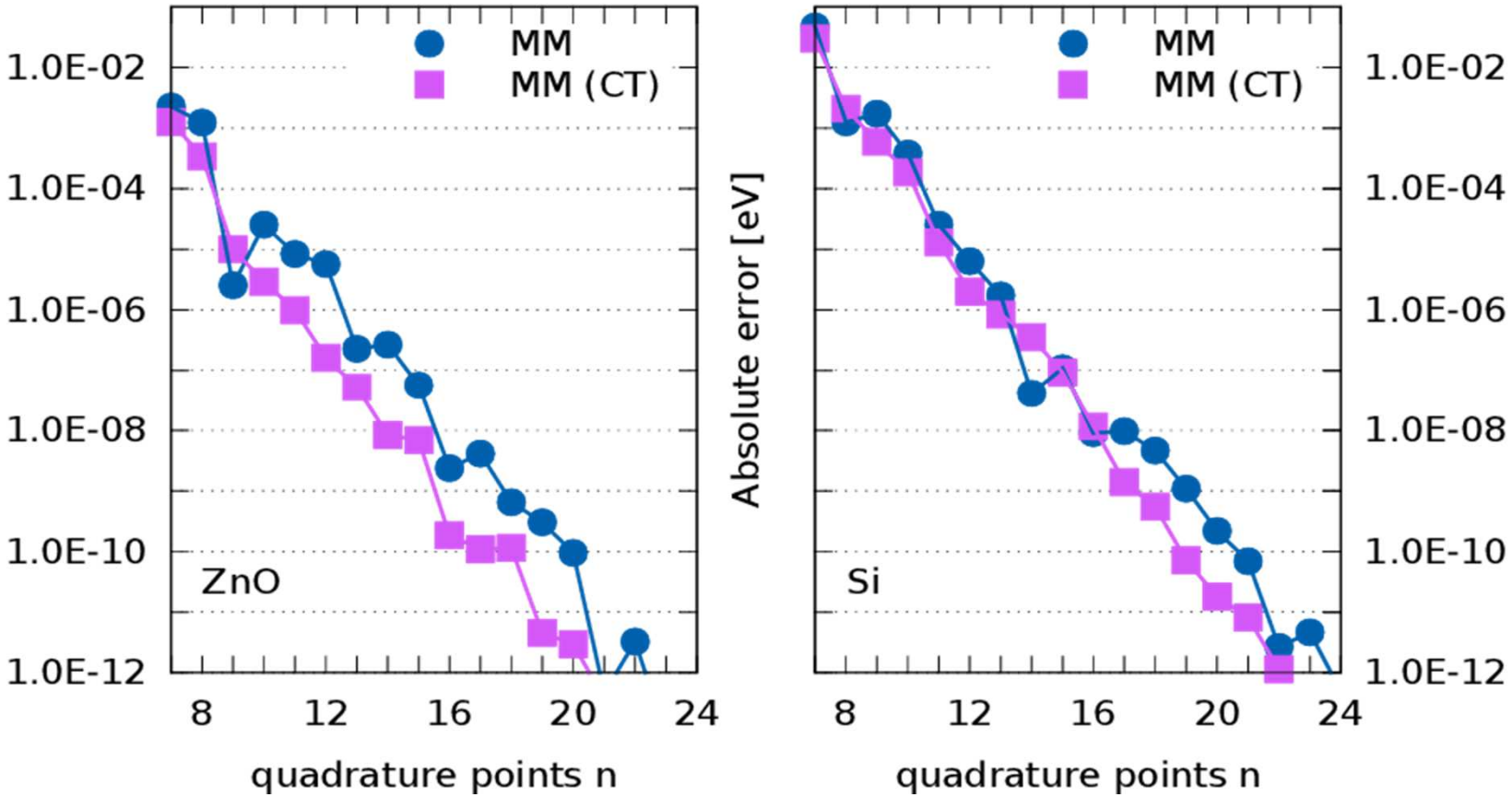
$$E^{(2)} = \frac{1}{2}\sum_{ijab}|..|^2\sum_{k=1}^{N_\omega}\gamma_k\frac{2(\epsilon_a-\epsilon_i)}{(\epsilon_a-\epsilon_i)^2+\omega_k^2}\frac{2(\epsilon_b-\epsilon_j)}{(\epsilon_b-\epsilon_j)^2+\omega_k^2}$$

- Minimize error function (L_2 norm, or maximum norm)

$$\eta(x) = \frac{1}{x} - \sum_{k=1}^{N_\omega}\gamma_k\frac{4x^2}{(x^2+\omega_k^2)^2}$$



How good are the grids: solid ZnO and Si



- N^4 RPA calculations entirely in frequency
- N^2 calculation of polarizability in time, then transformation to frequency
  200 atoms on 200 cores in about 1 hours

Kaltak, Klimeš, Kresse, JCTC 10, 2498 (2014), Kaltak, Klimeš, Kresse, PRB 90, 054115 (2014).

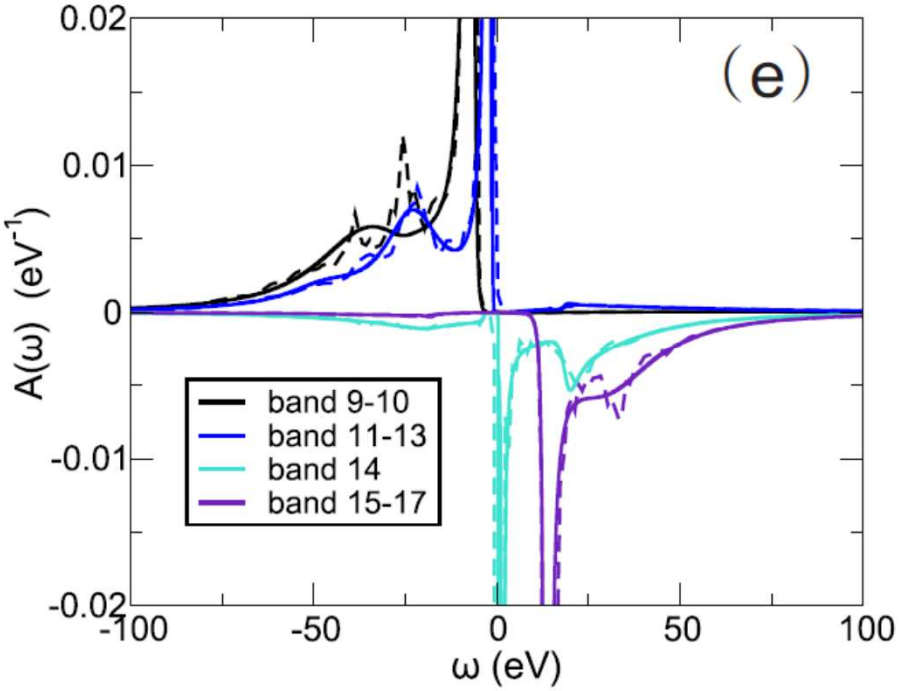
GW QP energies

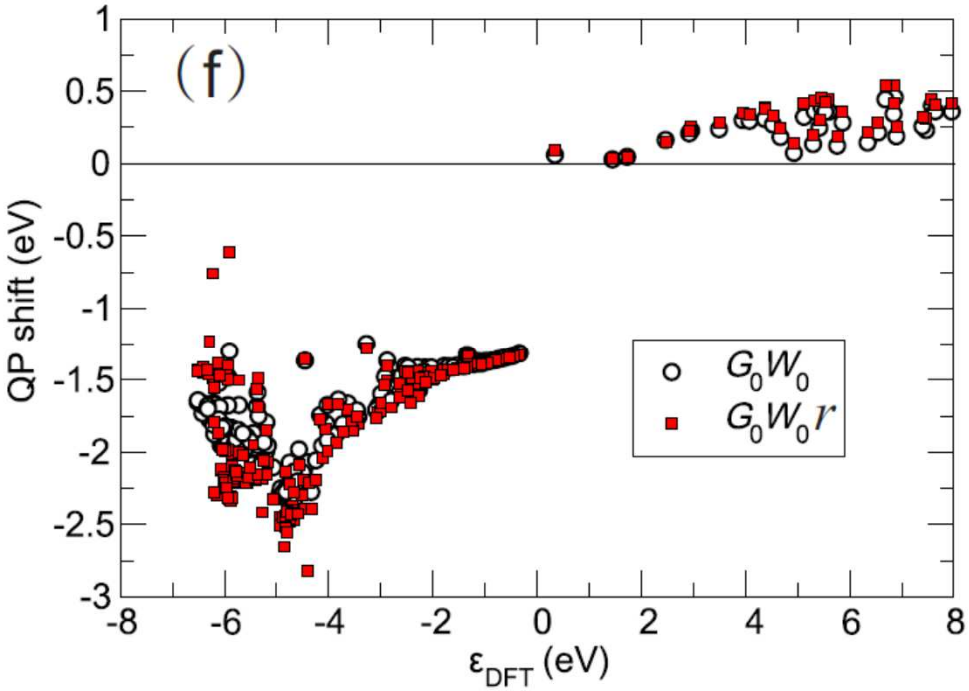
- Code works in imaginary time and frequency

$$\Sigma(\mathbf{r},\mathbf{r}',i\tau) = G(\mathbf{r},\mathbf{r}',i\tau)W(\mathbf{r},\mathbf{r}',i\tau) \rightarrow \mathrm{FFT} \rightarrow \Sigma(\mathbf{r},\mathbf{r}',\omega)$$

- Requires analytic continuation to real frequencies

  P. Liu, J. Klimes, M. Kaltak, Kresse, PRB 94, 165109 (2016).





Overview

- RPA and GW a first look
  - Diagrammatic representation of both theories
  - Achieving good scaling with system size
- Relation between RPA and GW / forces in the RPA
- Few (very few) examples

Derivative of Hartree-Fock energy

- Hartree and exact exchange energy

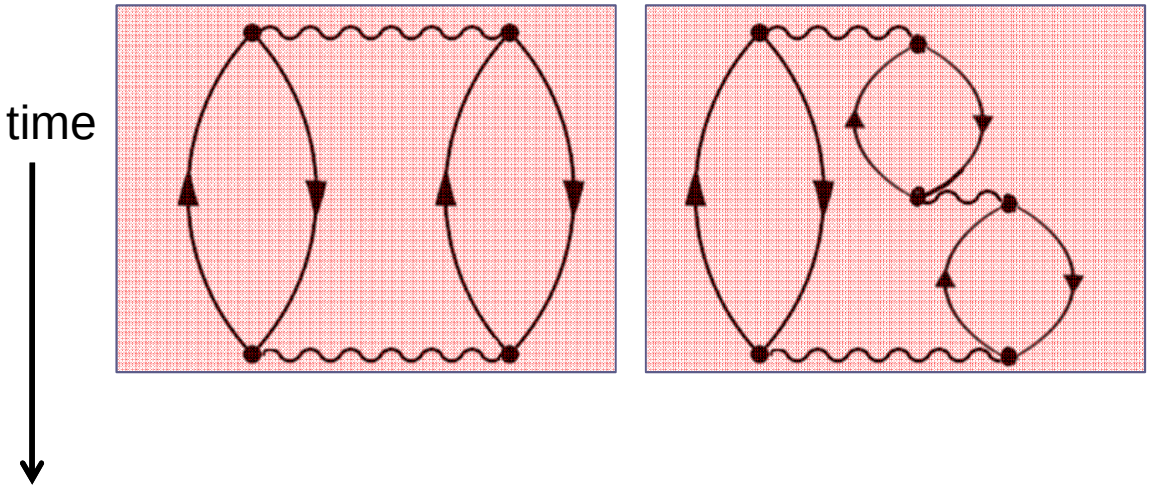
Hartree exchange

- Derivative with respect to G 

Hartree exchange

Text book knowledge

RPA and GW: $E^{RPA} = \ln(1 - v\chi_0) + v\chi_0$



$\chi(\mathbf{r}, \mathbf{r}', i\tau)$

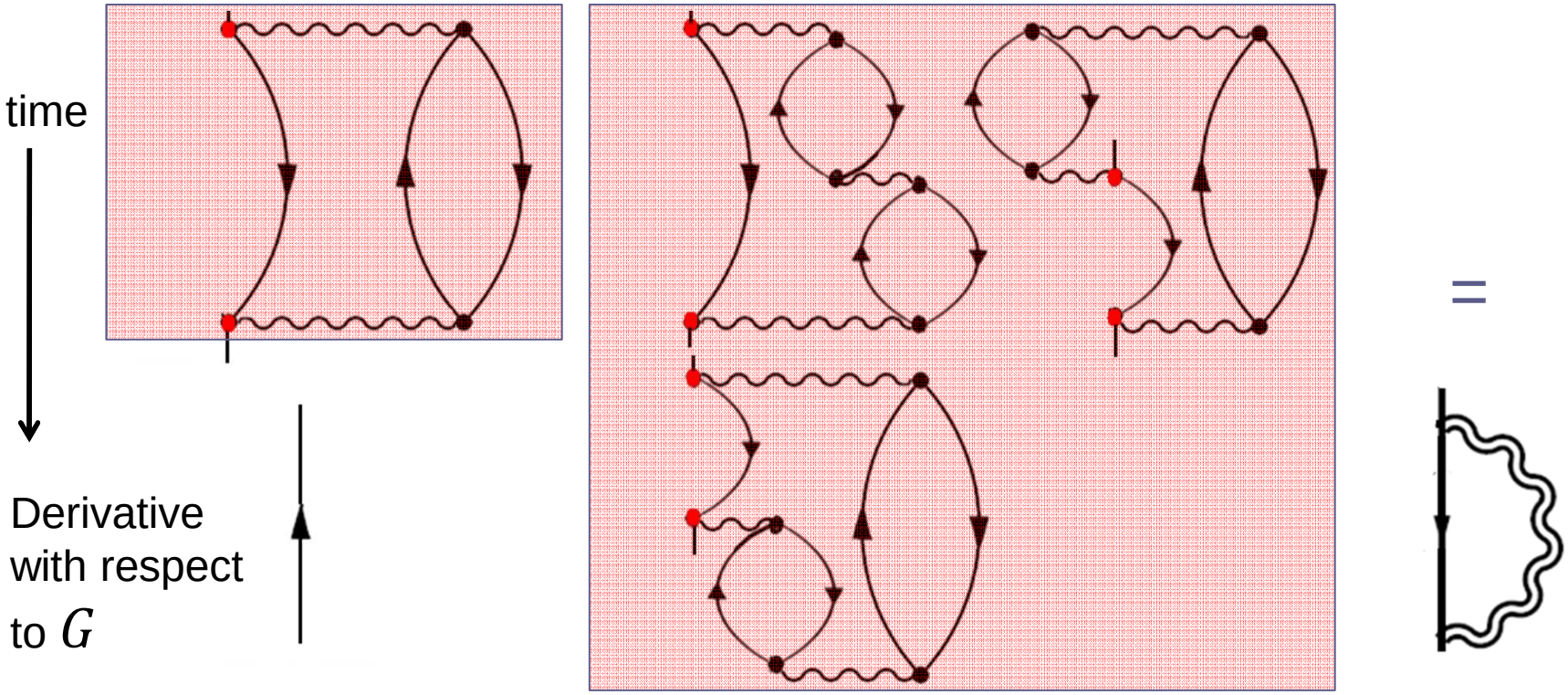
.....

2.nd order $-\frac{\mathrm{Tr}[\chi v \chi v]}{2}$

3.rd order $-\frac{\mathrm{Tr}[\chi v \chi v \chi v]}{3}$

RPA and GW: $E^{RPA} = \ln(1 - v\chi_0) + v\chi_0$

Dahlen, Leeuwen, & von Barth, Phys. Rev. A 73, 012511 (2006).



2.nd order

$G(\tau)[v\chi v](-\tau)$

3.rd order

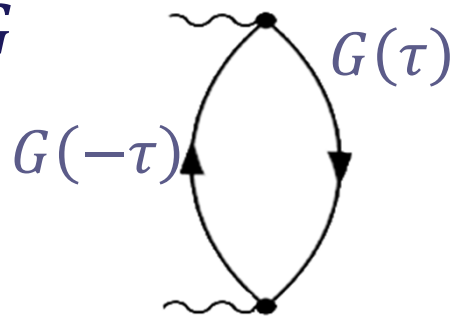
$G(\tau)[v\chi v\chi v](-\tau)$

all orders

$G(\tau)W(\tau)$

Relation between RPA and GW

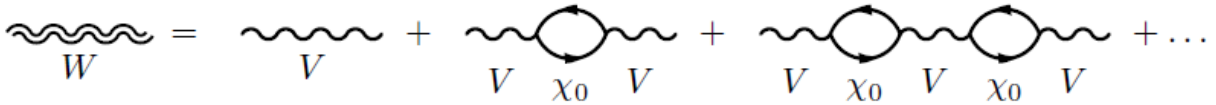
GW is the derivative of the RPA with respect to G



- Polarizability $\chi(\tau) = -G(\tau)G(-\tau)$
- Derivative $\dfrac{d\chi(\tau)}{dG(-\tau)} = -G(\tau)$
- Exchange and correlation energy:

$$E^{\mathrm{RPA}} = -Tr[v\chi(\omega) + \frac{1}{2}(v\chi(\omega))^2 + \frac{1}{3}(v\chi(\omega))^3 + \cdots]$$

- Derivative $\dfrac{d_E{}^{\mathrm{RPA}}}{d\chi(\omega)} = -v - v\chi(\omega)v - v\chi(\omega)v\chi(\omega)v \ldots = -W(\omega)$



- Putting pieces together

$$\frac{dE^{\mathrm{RPA}}}{dG(-\tau)} = W(\tau)G(\tau) = \Sigma^{GW}(\tau)$$

Relation between RPA and GW

- Comparison DFT and many-body perturbation theory

$$\frac{dE^{\mathrm{DFA-xc}}}{dG(0^-)[=\gamma]} = V^{\mathrm{xc}} \qquad \frac{dE^{\mathrm{RPA}}}{dG(-\tau)} = \Sigma^{GW}(\tau)$$

- Relations are „similar“
- Self-consistency using Σ^{GW} as a generalized KS-potential is a „possible“ prescription

$$G(\omega) = (\omega - T - V^{\mathrm{H}} - \Sigma^{GW}(\omega))^{-1}$$

- Just be aware that $\chi(\tau) = -G(\tau)G(-\tau)$ is not the proper irreducible polarizability (violates sum rules, not conserving)
- The calculated fluctuation contributions are in-accurate
- Can be “fixed” by including additional terms in irreducible P

$$\frac{d^2E^{\mathrm{RPA}}}{dG^2} = \frac{d\Sigma^{GW}}{dG}$$

vertex in GW/BSE theory

RPA-forces from RPA density matrix

Ramberger, Schäfer, & Kresse (2017). PRL, **118**, 106403.

- Forces can generally be written as

$$dE = \langle \Psi | d\mathbf{H} | \Psi \rangle + \langle d\Psi | \mathbf{H} | \Psi \rangle + \langle \Psi | \mathbf{H} | d\Psi \rangle$$

- Hellman-Feynman "theorem": if Ψ is an eigenstate of $\mathbf{H}$, the second and third term are zero

- In Green's function theory the equation above becomes

$$\langle d\Psi | \mathbf{H} | \Psi \rangle + \langle \Psi | \mathbf{H} | d\Psi \rangle \rightarrow \mathrm{Tr}\,[dG^{\mathrm{KS}}(T + V + \Sigma(i\omega))]$$

$$dG^{\mathrm{KS}}(i\omega) = G^{\mathrm{KS}}(i\omega)(dV^{\mathrm{KS}} + i\omega dS)G^{\mathrm{KS}}(i\omega) \quad \text{(Dyson-equation)}$$

$$\int d\omega \mathrm{Tr}[(T + V + \Sigma(i\omega)) \quad G^{\mathrm{KS}}(i\omega) dV^{\mathrm{KS}} G^{\mathrm{KS}}(i\omega)] =$$

$$\mathrm{Tr}[G^{\mathrm{KS}}(i\omega)(T + V + \Sigma(i\omega))G^{\mathrm{KS}}(i\omega) \quad dV^{\mathrm{KS}}]$$

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Forces: phonons in graphite and diamond

Ramberger, et al. PRL, **118**, 106403.

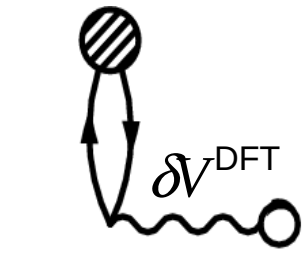
Cubic scaling

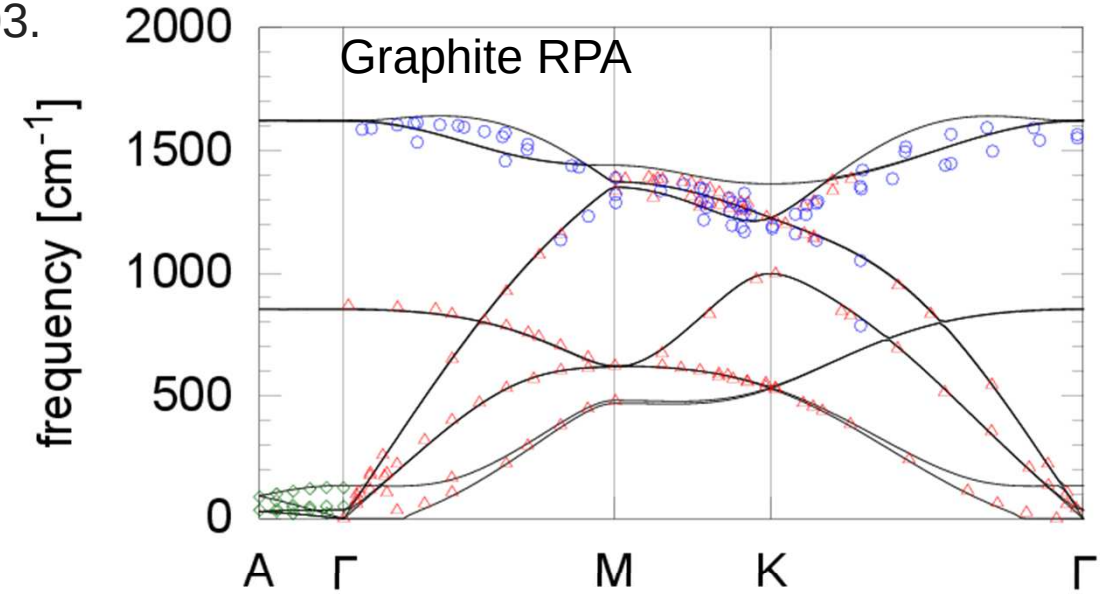
$$\rho^{(1)} = \int d\omega\, G(T+V+\Sigma)G$$

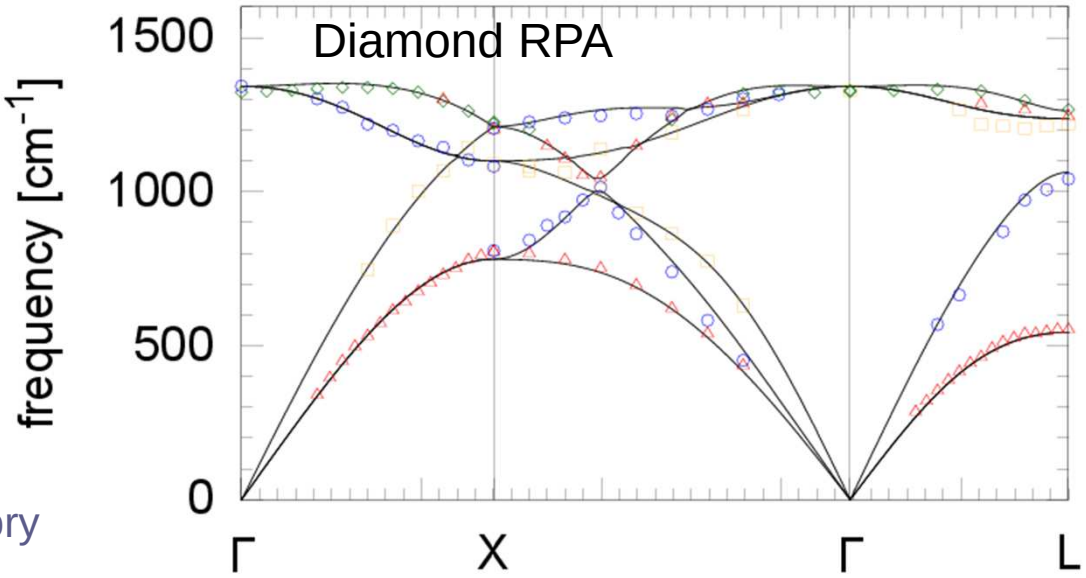
$$\gamma^{(1)} = \int d\omega\, \omega G(T+V+\Sigma)G$$

$$Tr\left[\rho^{(1)}\delta V^{DFT} + \gamma^{(1)}\delta S\right]$$

$$(T+V+\Sigma)$$

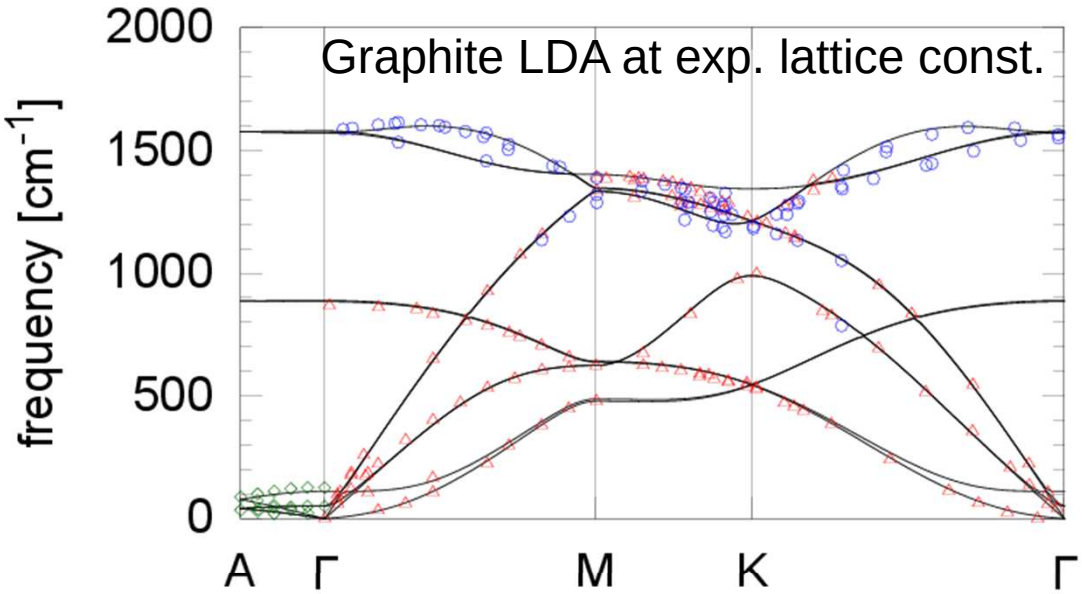


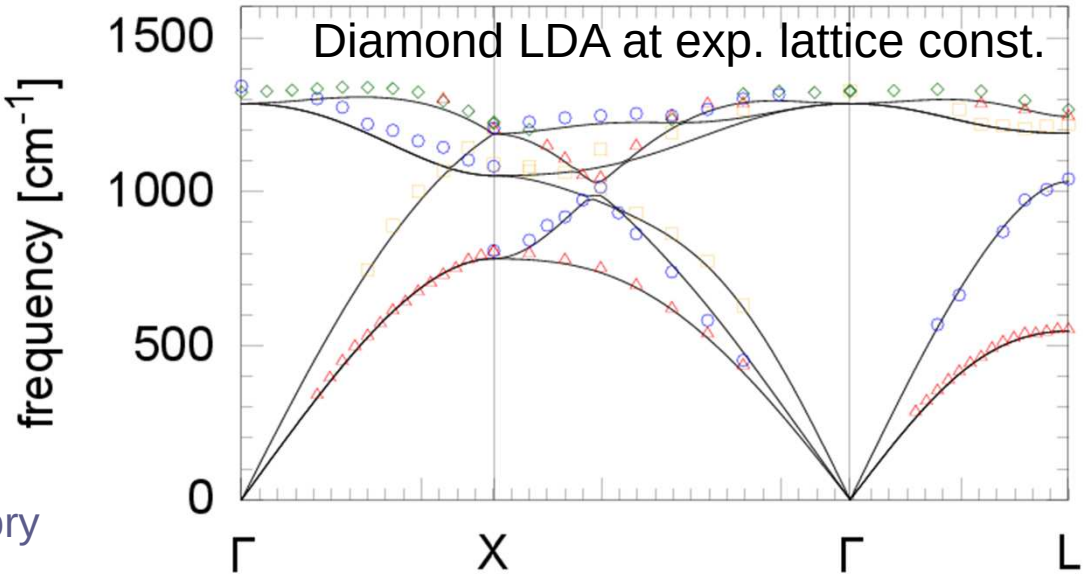


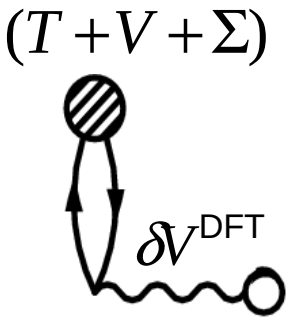


Turbomol: Burow et al., J. Chem. Theory Comput., **2014**, 10 (1), pp 180–194

Forces: phonons in graphite and diamond





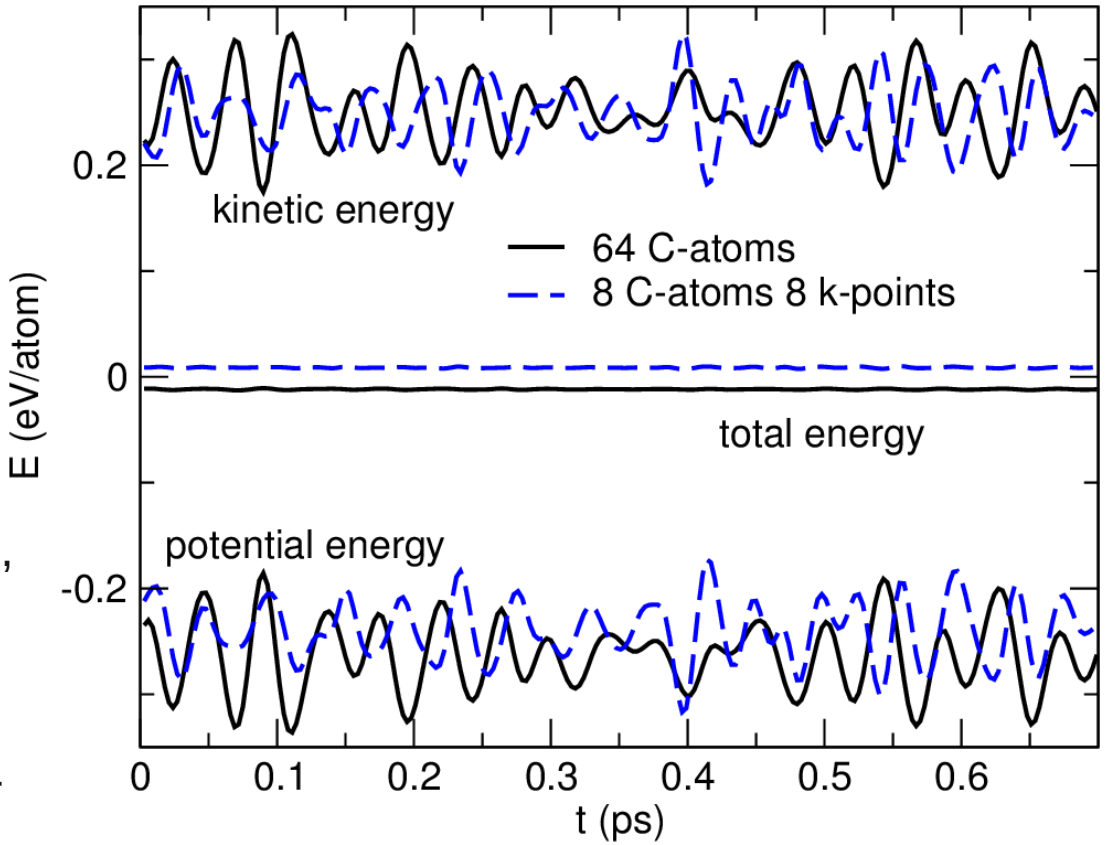


Turbomol: Burow et al., J. Chem. Theory Comput., **2014**, 10 (1), pp 180–194

Molecular Dynamics: diamond

Ramberger, Schäfer, & Kresse (2017). PRL, **118**, 106403.

- Fully integrated in VASP
- Energy stability as good as for DFT (almost ☺)
- Of course much, much slower than DFT
  - Three orders of magnitude, since forces are about a factor 10 slower than RPA energies
  - For forces factor 10 slower than HSE
  - Self-energy more involved than RPA correlation energy



Conclusion

- Relation between RPA and GW: Forces in the RPA
- Currently the RPA is the only (tracktable) alternative to DFT
- Few things to keep in mind:
  - Functional derivative of RPA energy is the GW self-energy
  - This allows to calculate forces straightforwardly
  - Self-consistent GW uses a non-physical polarizability (which is not the functional derivative of the RPA)

Underestimates fluctuation contributions severely which is sometimes hidden by the neglect of exchange diagrams

Acknowledgement

FWF for financial support SFB ViCoM

The group for their great work

You for listening