

TYC modelling course

Module on electronic excitations, Green's functions

Lecturer: Johannes Lischner (Imperial College London)
j.lischner@imperial.ac.uk

This week:

- a hand-wavy introduction
- the concept of a Green's function

Next week:

- Feynman diagrams
- GW in practice

Photo emission spectroscopy

energy conservation:

$$h\nu + E_{N0} = E_{\text{kin}} + E_{N-1\lambda}$$

$\uparrow$
N electrons

ground state

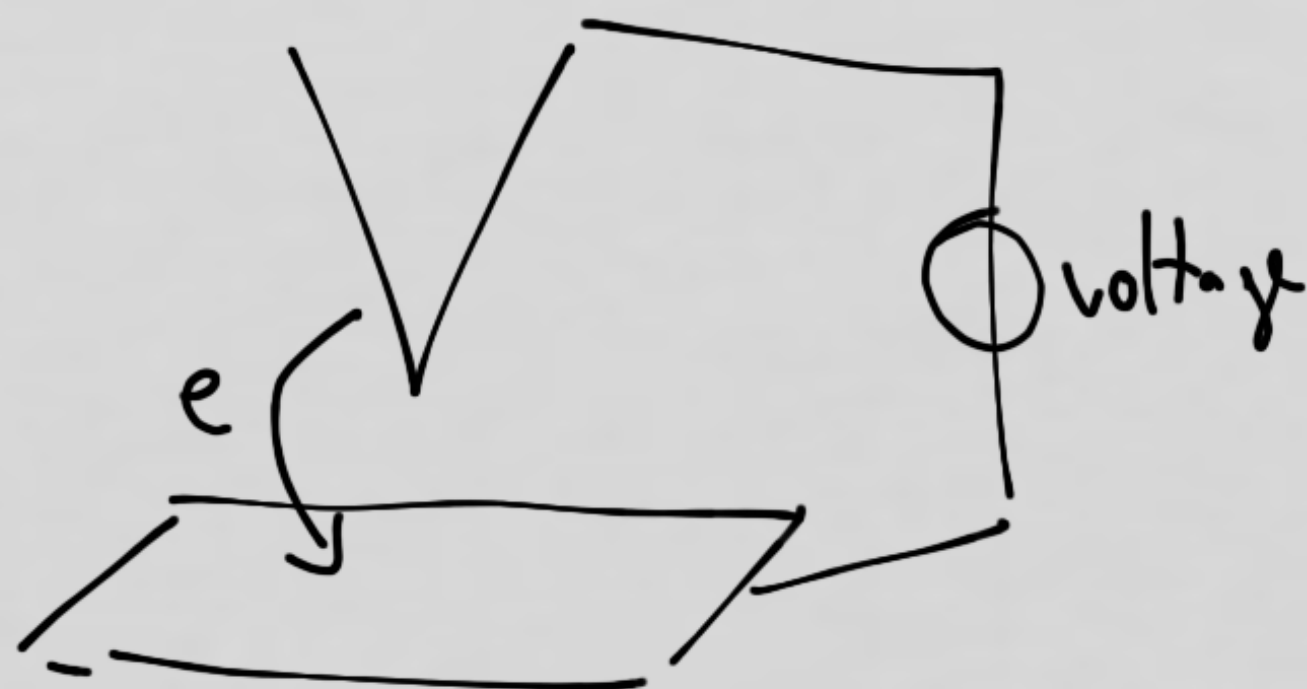
$\uparrow$
excited

$$h\nu - E_{\text{kin}} = - (E_{N0} - E_{N-1\lambda}) = - \epsilon_f$$

Other exp. techniques:



inverse photoemission



scanning tunneling
spectroscopy

Modelling photoemission

often: calculate electronic structure with DFT &
compare qp energies to Kohn-Shan energies

$$\left(-\frac{\nabla^2}{2} + v_{\text{ion}}(r) + v_H(r) + v_{\text{xc}}(r) \right) \psi_{\text{KS}}(r)$$

- But: only total ground state energy and
are meaningful in DFT
 $\Rightarrow$ KS energies are not!

exception: $\epsilon_{\text{HOMO}}^{\text{KS}} = -IP$ (Janak's theorem)

(in approximate DFT: $\epsilon_{\text{HOMO}}^{\text{KS}} \neq -IP$)

- band gaps are severely underestimated

Constructing a theory for gp energies

For molecules, Hartree-Fock often gives good agreement w/

Price: non-local Fock operator

$$v_F(r, r') = - \sum_n^{\text{occ}} \frac{\psi_n(r) \psi_n(r')}{|r - r'|} =$$

$$\left[-\frac{\nabla^2}{2} + v_{\text{ion}}(r) + v_H(r) \right] \psi_{\text{HF}}(r) + \underbrace{\int dr' v_F(r, r') \psi_{\text{HF}}(r')}_{\hat{v}_F |\psi_{\text{HF}}}$$

Assume: $\psi_{\text{HF}} \approx \psi_{\text{KS}}$

$$\epsilon_{\text{HF}} = \epsilon_{\text{KS}} + \langle \psi_{\text{HF}} | \hat{v}_F | \psi_{\text{HF}} \rangle$$

GW: replace $v_F(r, r')$ by a non-local, energy-dependent potential called a self-energy $\Sigma_{GW}(r, r', E)$
 $= \Sigma_{SX} + \Sigma_{CH}$

- screened exchange potential

$$\Sigma_{SX}(r, r', E) = - \sum_n^{\text{occ}} \psi_n(r) \psi_n^*(r') W(r, r', E = \epsilon)$$

- Coulomb hole term
simplified:

$$\Sigma_{CH}(r, r', E) = \frac{1}{2} \delta(r - r') \left[\underbrace{W(r, r', E = \epsilon)}_{\int dr'' v(r, r'') \rho(r'')} - v(r, r') \right]$$

$\Rightarrow$ describes potential at position of electron caused by induced charge density

$$\epsilon_{GW} = \epsilon_{KS} + \langle \psi_{KS} | \Sigma_{GW}(\epsilon_{GW}) - v_{xc} | \psi_{KS} \rangle$$

$\Rightarrow$ GW gives accurate qp energies & bands

Introduction to Green's functions

field operator $\hat{\psi}(r, t)$ and $\hat{\psi}^\dagger(r, t)$ describe
electrons at position r and time t .

Heisenberg picture: $\hat{\psi}(r, t) = e^{i\hat{H}t} \hat{\psi}(r)$

$$= \sum_n$$

$$\begin{aligned} \langle r' | \hat{\psi}^\dagger(r) | \text{VAC} \rangle &= \sum_n \psi_n^*(r) \underbrace{\langle r' | \hat{c}_n^\dagger | \text{VAC} \rangle}_{\psi_n(r')} \\ &= \delta(r - r') \end{aligned}$$

Green's function (aka propagator) describes propagation of electrons or holes through material

for holes:

$$\langle N, \sigma | \hat{\psi}^\dagger(r', t') \hat{\psi}(r, t) | N, 0 \rangle$$

t must be earlier than t'

for electrons:

$$\langle N, \sigma | \hat{\psi}(r, t) \hat{\psi}^\dagger(r', t') | N, 0 \rangle$$

t' must be earlier than t

Green's function:

$$G(r, r', t, t') = -i \langle N, 0 | \left\{ \begin{aligned} &\theta(t-t') \hat{\psi}(r, t) \hat{\psi}^\dagger(r', t') \\ &- \theta(t'-t) \hat{\psi}^\dagger(r', t') \hat{\psi}(r, t) \end{aligned} \right\} | N, 0 \rangle$$

$$\equiv -i \langle N, 0 | \hat{T} \{ \hat{\psi}(r, t) \hat{\psi}^\dagger(r', t') \} | N, 0 \rangle$$

time-ordering operator

Connection to exp - Lehmann representation

focus on hole part

$$\Theta(t'-t) \langle N_0 | \hat{\psi}^\dagger(r',t') \hat{\psi}(r,t) | N_0 \rangle$$

$\xrightarrow{E_{N_0}}$ $i\hbar t \hat{\psi}^\dagger(r') e^{-i\hat{H}t}$ $\xrightarrow{E_{N_0}}$ $i\hbar t \hat{\psi}(r) e^{-i\hat{H}t}$

$$= \Theta(t'-t) e^{iE_{N_0}(t'-t)} \sum_{\lambda} \langle N_0 | \hat{\psi}^\dagger(r') e^{-i\hat{H}(t'-t)} | N-1, \lambda \rangle \langle N-1, \lambda | \hat{\psi}(r) | N_0 \rangle$$

$\mathbb{I} = \sum_{\lambda} | N-1, \lambda \rangle \langle N-1, \lambda |$
 $e^{-iE_{N-1, \lambda}(t'-t)}$

$$G(r, r', \omega) = \sum_{N-1, \lambda} \frac{\langle N_0 | \hat{\psi}^\dagger(r') | N-1, \lambda \rangle \langle N-1, \lambda | \hat{\psi}(r) | N_0 \rangle}{\omega - [E_{N_0} - E_{N-1, \lambda}] - i\eta}$$

$+ \sum \frac{\langle N_0 | \hat{\psi}(r) | N+1, \lambda \rangle \langle N+1, \lambda | \hat{\psi}^\dagger(r') | N_0 \rangle}{\omega - [E_{N+1, \lambda} - E_{N_0}] + i\eta}$

Neglect el-el interactions

$|N0\rangle$ is single Slater determinant

and so are $|N \pm 1 \lambda\rangle$.

either one more/less electron in a single-particle state $\psi_n(r)$ w/ energy ϵ_n .

$$\Rightarrow E_{N0} - E_{N-1\lambda} = E_{N+1\lambda} - E_{N0} = \epsilon_n$$

$$\langle N-1\lambda | \hat{\psi}(r) | N0 \rangle = \sum_n \psi_n(r) \langle N-1\lambda | \hat{c}_n | N0 \rangle$$

$$= \psi_n(r)$$

$$G_0(r, r'; \omega) = \sum_n^{\text{occ}} \frac{\psi_n(r) \psi_n^*(r')}{\omega - \epsilon_n + i\eta} + \sum_n^{\text{empty}} \frac{\psi_n(r) \psi_n^*(r')}{\omega - \epsilon_n - i\eta}$$

$\delta_{nn'}$

Lecture 2

Introduction to GW

Last time: $\epsilon_{GW} = \epsilon_{KS} + \langle \psi_{KS} | \underbrace{\sum_{GW} (\epsilon_{GW}) - V_{xc}}_{\text{}} | \psi_{KS} \rangle$

$$\sum_{SX} = - \sum_n^{\text{occ}} \psi_n(r) \psi_n^*(r') W$$

$$\sum_{CH} = \frac{1}{2} \delta(r-r') [W(r,r', E)]$$

Green's function:

$$G(r, r', t, t') = -i \langle N0 | \hat{T} \underbrace{\psi(r, t) \psi^\dagger(r', t')}_{\text{field operator } e^{iHt}} | N0 \rangle$$

Lehmann representation:

$$G(r, r', \omega) = \sum_{N-1, \lambda} \frac{\psi_{N-1, \lambda}(r) \psi_{N-1, \lambda}^*(r')}{\omega - [\underbrace{E_{N0} - E_{N-1, \lambda}}_{\text{quasiparticle energies are } p}] - i\eta} + \sum_{N+1, \nu} \frac{\psi_{N+1, \nu}(r) \psi_{N+1, \nu}^*(r')}{\omega - E_{N+1, \nu} + i\eta}$$

Without e-e interactions:

$$G_0(r, r', \omega) = \sum_n^{\text{occ}} \frac{\psi_n(r) \psi_n^*(r')}{\omega - \epsilon_n + i\eta} + \sum_n^{\text{empty}} \frac{\psi_n(r) \psi_n^*(r')}{\omega - \epsilon_n - i\eta}$$

$$\Rightarrow G_{0nn'}(\omega) = \frac{1}{\omega - \epsilon_n \pm i\eta} \delta_{nn'}$$

Today: calculating G using perturbation

$$\hat{H} = \underbrace{\hat{H}_0}_{\text{kinetic energy}} + \hat{H}_{\text{int}}$$

interaction w/ nuclei

$$e^{i\hat{H}t} = e^{i(\hat{H}_0 + \hat{H}_{\text{int}})t} \approx e^{i\hat{H}_0 t} (1 + i$$

$\Rightarrow$ generates lots of terms

$\Rightarrow$ represent this term by Feynman

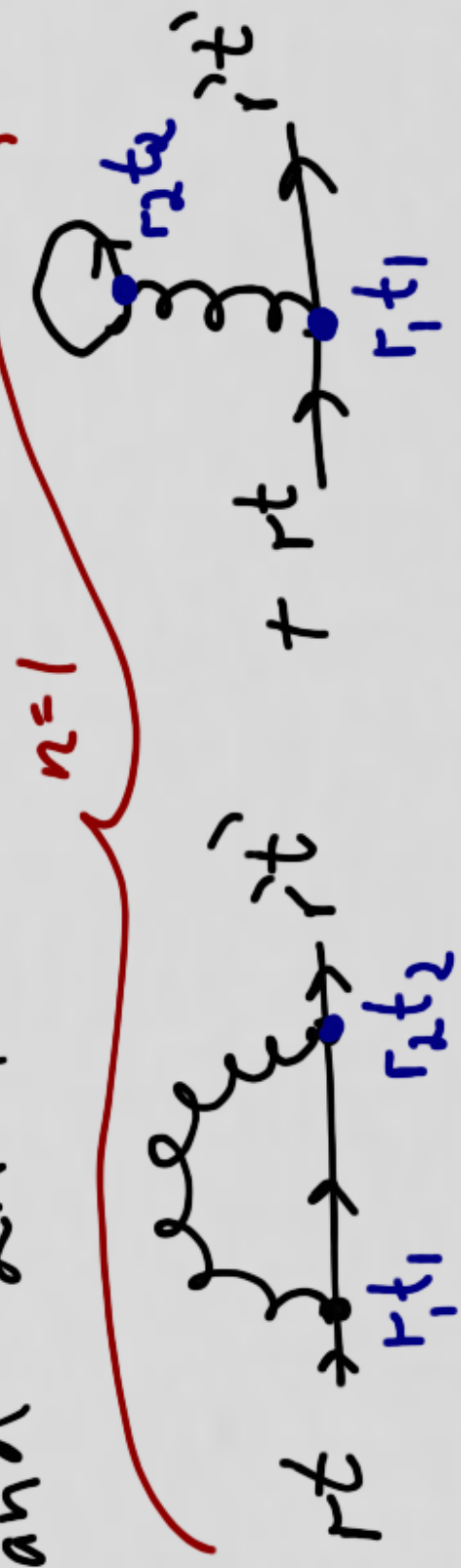
$$G_1(r, r', t, t') : r t \Rightarrow r' t'$$

$$G_0(r, r', t, t') : r t \rightarrow r' t'$$

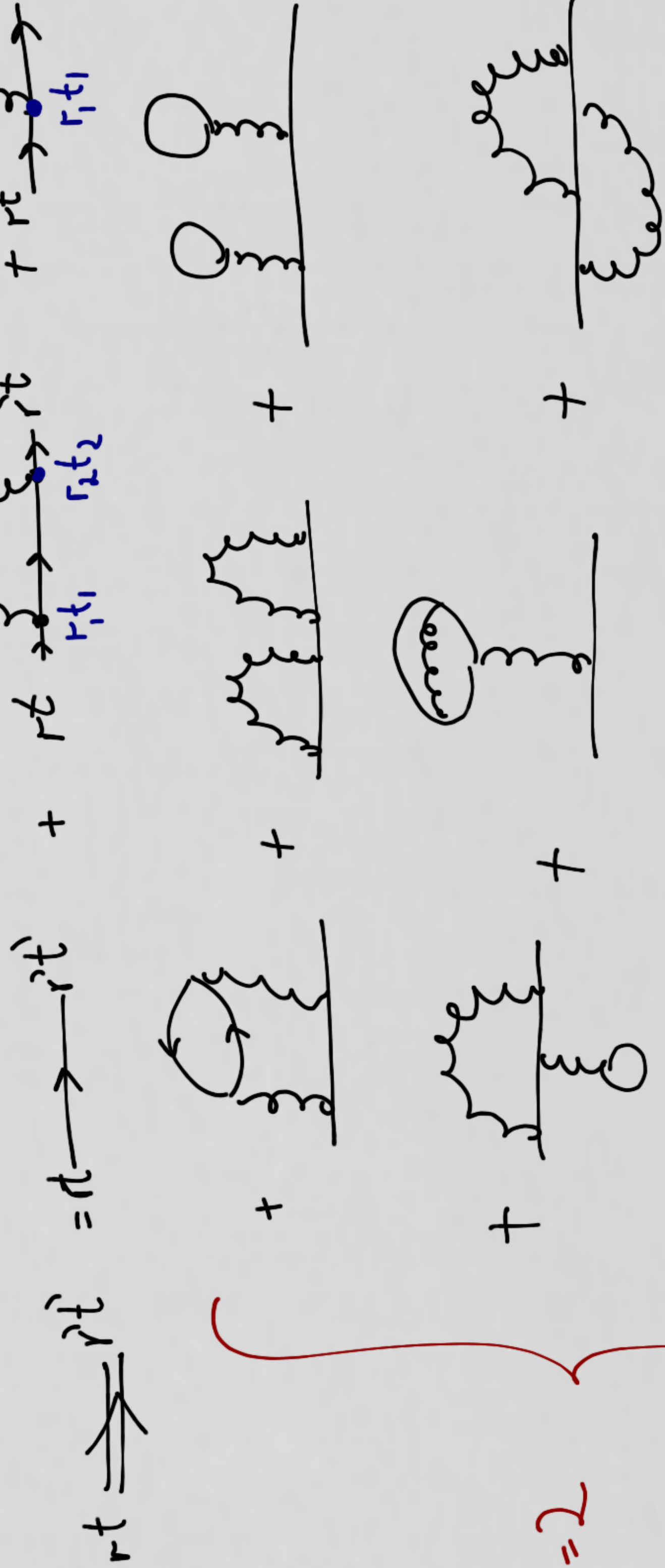
$$v(r, r', t, t') = v(r, r') \delta(t - t') : r t \text{ wavy } r' t'$$

Step 1: draw all topologically distinct connected diagrams with

n interaction lines and $2n+1$ Go-line



$n=0$

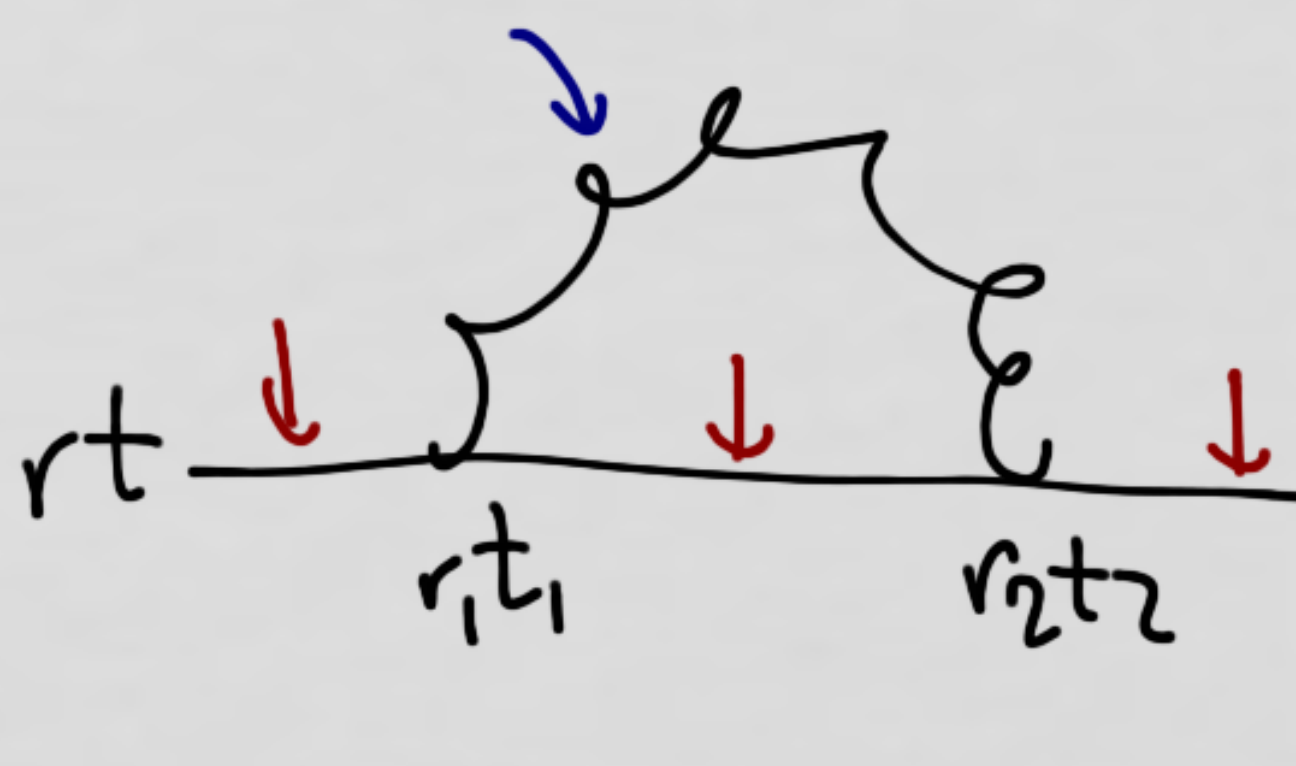


Step 2: label each point where interaction lines meet by

Step 3: write down product of interactions &

Step 4: multiply by $i^n (-1)^F$ with F being
of closed

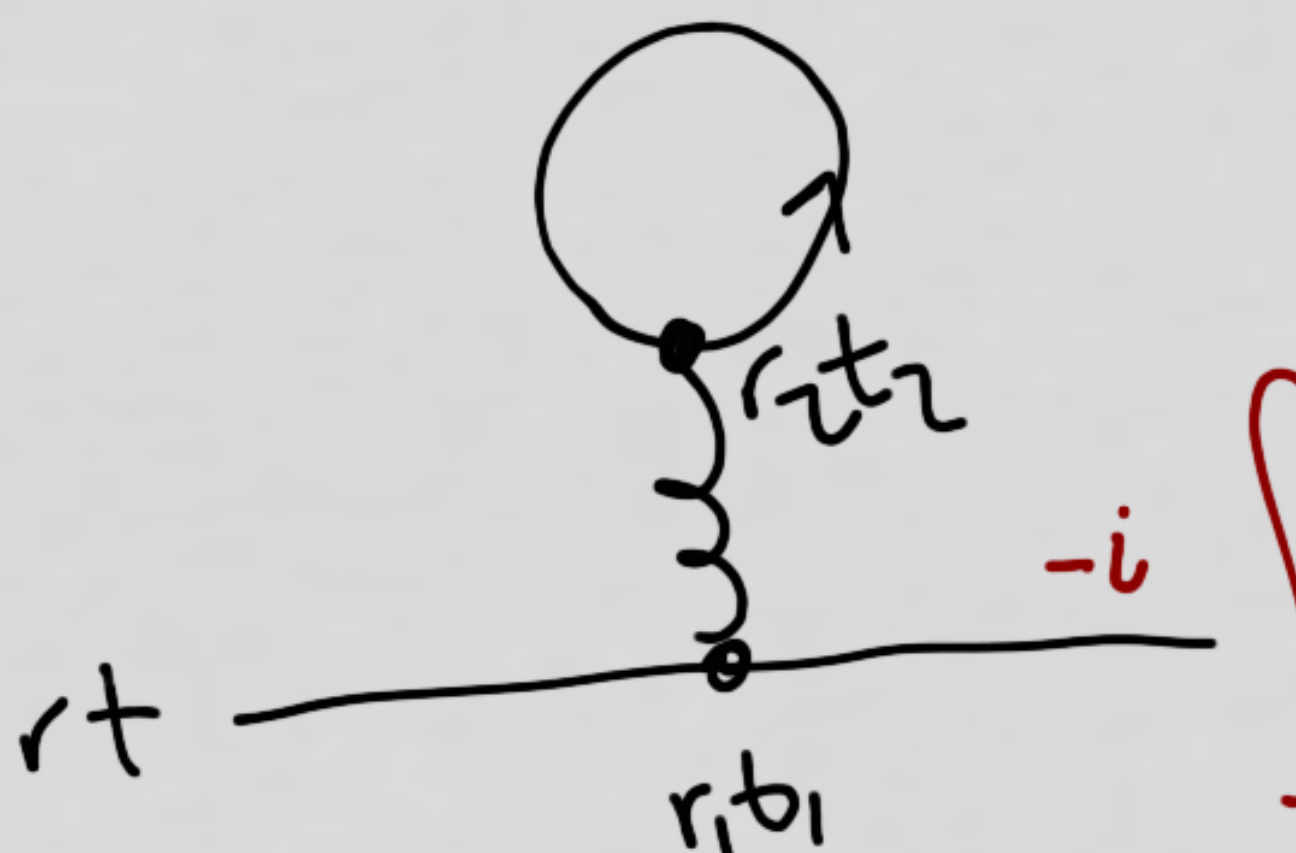
$n=1$



A Feynman diagram on a horizontal line representing time. The line has three points marked: rt on the left, r_1t_1 in the middle, and r_2t_2 on the right. Red arrows point down to each of these points. A wavy line connects r_1t_1 and r_2t_2 . A blue arrow points to the wavy line. To the right of the diagram is the expression:

$$i \int dr_1 dt_1 \int dr_2 dt_2 v(r_2 t_2, r_1 t_1) G_0(r_1 t_1, r_2 t_2) G_0(r_2 t_2, r_1 t_1)$$

$$\sum_n v(r_2, r_1) \frac{\psi_n(r) \psi_n^*(r)}{\omega - \epsilon_n}$$



A Feynman diagram on a horizontal line representing time. The line has two points marked: rt on the left and r_1t_1 on the right. A wavy line connects rt and r_1t_1 . A loop is attached to the wavy line at r_1t_1 . To the right of the diagram is the expression:

$$-i \int dr_1 dt_1 \int dr_2 dt_2 G_0(r_1 t_1, r_2 t_2) G_0(r_2 t_2, r_1 t_1) v(r_1 t_1, r_2 t_2)$$

Below this, a green arrow points to the following expression:

$$\int dr_2 \sum_n v(r_1, r_2) \frac{\psi_n(r_2) \psi_n^*(r_2)}{\omega - \epsilon_n \pm i\eta}$$

Structure of diagrammatic series

$$\Rightarrow = \rightarrow + \rightarrow \text{[cross-hatched circle]} \rightarrow$$

$$\text{[cross-hatched circle]} = \text{[diagram 1]} + \text{[diagram 2]} + \text{[diagram 3]}$$

contain only those diagrams from [cross-hatched circle] which cannot be separated into 2 pieces by cutting one Go line

$$\text{[cross-hatched circle]} = \text{[diagram 4]} + \text{[diagram 5]} + \dots$$

$$\text{[cross-hatched circle]} = \Sigma + \Sigma \rightarrow \Sigma + \Sigma \rightarrow \Sigma \rightarrow \Sigma$$

$$\Rightarrow = \rightarrow + \rightarrow \Sigma \rightarrow + \rightarrow \Sigma \rightarrow \Sigma \rightarrow$$

$$= \rightarrow + \rightarrow \Sigma \left[\rightarrow + \rightarrow \Sigma \rightarrow + \dots \right]$$

$$\Rightarrow = \rightarrow + \rightarrow \Sigma \rightarrow \Rightarrow \quad \text{Dyson equation}$$

Dyson equation:

$$G(r_1^1 t_1^1) = G_0(r_1^1 t_1^1) + \int d_1^1 t_1^1 d_2^1 t_2^1 G_0(r_1^1 t_1^1, r_2^1 t_2^1) \sum (r_1^1 t_1^1, r_2^1 t_2^1) G(r_2^1 t_2^1)$$

Use basis of single-particle orbitals and assume $\sum$ is diagonal:

$$G_{nn}(\omega) = G_{0nn}(\omega) + G_{0nn}(\omega) \sum_{nn}(\omega) G_{nn}(\omega) \left| G_{nn}^{-1} G_{0nn}^{-1} \right|$$

$$\Rightarrow G_{0nn}^{-1}(\omega) = G_{nn}^{-1}(\omega) + \sum_{nn}(\omega)$$

$$\Rightarrow G_{nn}^{-1}(\omega) = \underbrace{G_{0nn}^{-1}(\omega)}_{\omega - \epsilon_n} - \sum_{nn}(\omega)$$

$$G_{nn}^{-1}(\epsilon_{GW}) = 0,$$

$$\Rightarrow 0 = \epsilon_{GW} - \epsilon_n - \sum_{nn}(\epsilon_{GW})$$

$$\epsilon_{GW} = \epsilon_n + \langle \psi_n | \sum (\epsilon_{GW}) | \psi_n \rangle$$

Approximate self-energy

$$\Sigma = \text{[diagram: wavy line with a loop]} + \text{[diagram: wavy line with a bubble]} \quad \text{Hartree-Fock} \rightarrow \text{lacks screening}$$

$$\text{[diagram: wavy line with a bubble]} + \text{[diagram: wavy line with a bubble]} + \dots$$

$$\equiv \text{[diagram: wavy line with a bubble]} \quad \text{random phase approximation}$$

$$\begin{aligned} &= \text{[diagram: wavy line with a bubble]} + \text{[diagram: wavy line with a bubble]} + \dots \\ &= \text{[diagram: wavy line with a bubble]} \left[\text{[diagram: wavy line with a bubble]} + \text{[diagram: wavy line with a bubble]} + \dots \right] \\ &= \text{[diagram: wavy line with a bubble]} G(r, t) G(r, t) \end{aligned}$$

$$\overline{\overline{W}}(\omega) = \overline{\overline{v}} + \overline{\overline{v}} \overline{\overline{\chi_0}}(\omega) \overline{\overline{W}}(\omega)$$

$$= \left[\mathbb{1} - \overline{\overline{v}} \overline{\overline{\chi_0}}(\omega) \right]^{-1} \overline{\overline{v}}$$

non-interacting
density-density
response
function

$$\overline{\overline{\epsilon}}^{-1}(\omega)$$

$$\sum_{GW} = \text{[Diagram: A loop with a wavy line and a straight line, with vertices labeled } r, t \text{ and } r', t' \text{]} + i \overline{\overline{\chi}}(r, r'; t, t') \overline{\overline{W}}(r, r'; t, t')$$

$$\rightarrow i \int \frac{d\omega'}{2\pi} \overline{\overline{\chi}}(r, r'; \omega - \omega') \overline{\overline{W}}(r, r'; \omega)$$

$$\text{use } \overline{\overline{\chi}} \approx \chi_{KS} = \sum_n \frac{\psi_n(r) \psi_n^*(r')}{\omega - \epsilon_n \pm i\eta}$$

$$\sum_{occ} \psi(r) \psi_n^*(r') \overline{\overline{W}}(r, r'; \omega - \epsilon_n)$$

Additional approximations:

i) plasmon pole model

$$\text{Im } W(\bar{\omega}) \propto \delta(\bar{\omega} - \omega_{pl})$$

ii) static COHSEX : $\omega - \epsilon_n = 0$

$$- \underbrace{\int_0^\infty \frac{d\bar{\omega}}{\pi} \frac{\text{Im } W(r, r'; \bar{\omega})}{-\bar{\omega} + i\eta}}_{-\frac{1}{2} [\text{Re } W(r, r'; \omega=0) - v(r, r')]} \underbrace{\sum_n \psi_n(r) \psi_n^+(r')}_{\delta(r-r')}$$

GW in practice

Step 1: DFT calculation

$\Rightarrow$ need both occupied states and many unoccupied states.

Step 2: Screened interaction

$$\Rightarrow \text{calc } \chi_0(r, r'; \omega) = \sum_n^{\text{occ}} \sum_{n'}^{\text{unocc}} \frac{\psi_n^*(r) \psi_{n'}(r) \psi_{n'}^*(r') \psi_n(r')}{\epsilon_n - \epsilon_{n'} - \omega - i\eta}$$

$\nearrow$ sum over pairs of occupied & unoccupied states: slowly converges

$\Rightarrow \underline{\underline{\epsilon(\omega)}}$ & invert

$$\Rightarrow \underline{\underline{W(\omega) = \epsilon^{-1}(\omega) v}}$$

Step 3: construct self-energy (involves another sum over unoccupied states & frequency integral)