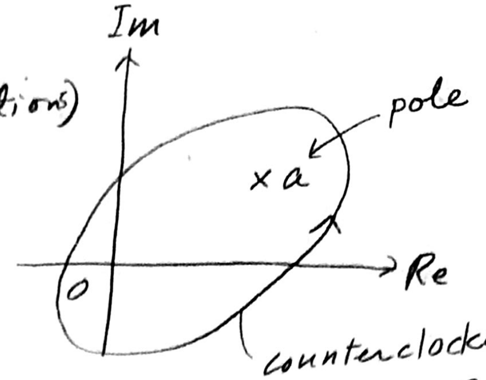
① Cauchy's integral formula
(not essential – just to perform some real integrations)

$$\oint_C \frac{f(z)}{\underbrace{z-a}_{\text{pole}}}\,dz = (2\pi i)\underbrace{f(a)}_{\text{Residue at } z=a}$$



see math text for proof, but the simplest case can be proven as follows: setting $z = a + \varepsilon e^{it}$

$$\oint_C \frac{1}{z-a}\,dz = \int_0^{2\pi} \frac{1}{(a+\varepsilon e^{it})-a}\underbrace{\frac{dz}{dt}}_{i\varepsilon e^{it}}\,dt = \int_0^{2\pi} i\,dt = 2\pi i$$

Contour is the circle of radius ε centered at a

② Green's function

Differential eq: $\mathcal{L}\, f(x) = g(x)$

↑ operator ↑ specific solution for RHS $g(x)$

Green's fxn : $\mathcal{L}\, G(x,x') = \delta(x'-x)$

then

$$f(x) = \int G(x,x')\, g(x')\, dx'$$

$$\because \mathcal{L}\underbrace{\int G(x,x')\,g(x')\,dx'}_{f(x)} = \int \underbrace{\mathcal{L}\, G(x,x')}_{\delta(x'-x)}\, g(x')\,dx' = g(x)$$

Schrödinger eq. : $\underbrace{(E-\hat{H})}_{\mathcal{L}}\,\varphi(x) = 0$

$$(E-\hat{H})\, G(x,x') = \delta(x'-x)$$

$\Rightarrow G = (E-\hat{H})^{-1}$

namesake only

③ Propagator or many-body Green's function

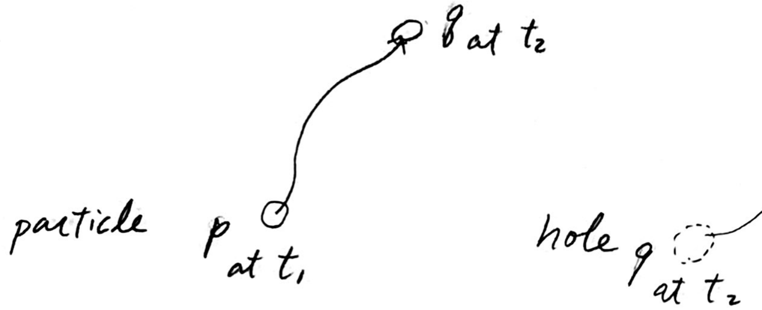
chronological op.

$$G_{pq}(t_2 - t_1) \equiv -i \langle \Psi | T\{ \hat{a}_q(t_2)\, \hat{a}_p^{+}(t_1) \} | \Psi \rangle$$

$|\Psi\rangle$: exact wfn of N-electron GS

$$\hat{a}_p(t) = e^{i\hat{H}t}\, \hat{a}_p\, e^{-i\hat{H}t}$$

$$T\{ \hat{a}_q(t_2)\hat{a}_p^{+}(t_1) \} = \begin{cases} \hat{a}_q(t_2)\, \hat{a}_p^{+}(t_1) & t_2 > t_1 \\ -\hat{a}_p^{+}(t_1)\hat{a}_q(t_2) & t_1 > t_2 \end{cases}$$



Feynman diagram's "line"

$G_{pq}(t_2 - t_1)$ is the amplitude of propagation: particle (hole) at the spacetime position (p, t_1) (q, t_2) propagating to particle (hole) at (q, t_2). (p, t_1)

④ Retarded and advanced Green's functions

$t_2 > t_1$

E exact energy of N-electron GS

$$G_{pq}(t_2-t_1) = -i\langle\Psi| e^{i\hat{H}t_2}\hat{a}_q e^{-i\hat{H}t_2} e^{i\hat{H}t_1}\hat{a}_p^{+} e^{-i\hat{H}t_1}|\Psi\rangle$$

retarded

$$= -i\langle\Psi| e^{iEt_2}\hat{a}_q e^{-i\hat{H}(t_2-t_1)}\hat{a}_p^{+} e^{-iEt_1}|\Psi\rangle$$

$$= -i\langle\Psi|\hat{a}_q e^{-i(\hat{H}-E)(t_2-t_1)}\hat{a}_p^{+}|\Psi\rangle$$

$t_1 > t_2$

$$G_{pq}(t_2-t_1) = i\langle\Psi|\hat{a}_p^{+} e^{i(\hat{H}-E)(t_2-t_1)}\hat{a}_q|\Psi\rangle$$

advanced

$$G_{pq}(t) = -i\theta(t)\langle\Psi|\hat{a}_q e^{-i(\hat{H}-E)t}\hat{a}_p^{+}|\Psi\rangle \quad \text{retarded}$$
$$+ i\theta(-t)\langle\Psi|\hat{a}_p^{+} e^{i(\hat{H}-E)t}\hat{a}_q|\Psi\rangle \quad \text{advanced}$$

Heaviside step function $\theta(t) = \begin{cases} 1 & t>0 \\ 0 & t<0 \end{cases}$

⑤ Fourier transform to pass to freq. domain

$$G_{pq}(\omega) = \int_{-\infty}^{\infty} G_{pq}(t) e^{i\omega t} dt$$

$$G_{pq}(t) = \int_{-\infty}^{\infty} G_{pq}(\omega) e^{-i\omega t} \frac{d\omega}{2\pi}$$

$t>0$ (retarded) part:

an infinitesimal positive

$$G_{pq}^{(r)}(\omega) = -i\langle\Psi|\hat{a}_q\left(\int_{-\infty}^{\infty}\theta(t)\,e^{-i(\hat{H}-E)t}\cdot e^{i(\omega+i\delta)t}\,dt\right)\hat{a}_p^{\dagger}|\Psi\rangle$$

$$= -i\langle\Psi|\hat{a}_q\left(\int_{0}^{\infty}e^{-i(\hat{H}-E-\omega-i\delta)t}\,dt\right)\hat{a}_p^{\dagger}|\Psi\rangle$$

0 at $t=\infty$

$$= -\langle\Psi|\hat{a}_q\left[\frac{e^{-i(\hat{H}-E-\omega-i\delta)t}}{\omega-\hat{H}+E+i\delta}\right]_0^{\infty}\hat{a}_p^{\dagger}|\Psi\rangle$$

$$= \langle\Psi|\hat{a}_q(\omega-\hat{H}+E+i\delta)^{-1}\hat{a}_p^{\dagger}|\Psi\rangle$$

cf. $G=(E-\hat{H})^{-1}$ analogy; namesake if not the same

$t<0$ (advanced) part:

$$G_{pq}^{(a)}(\omega) = i\langle\Psi|\hat{a}_p^{\dagger}\left(\int_{-\infty}^{\infty}\theta(-t)\,e^{i(\hat{H}-E)t}\,e^{i(\omega-i\delta)t}\,dt\right)\hat{a}_q|\Psi\rangle$$

$$= i\langle\Psi|\hat{a}_p^{\dagger}\left(\int_{-\infty}^{0}e^{i(\hat{H}-E+\omega-i\delta)t}\,dt\right)\hat{a}_q|\Psi\rangle$$

0 at $t=-\infty$

$$= \langle\Psi|\hat{a}_p^{\dagger}\left[\frac{e^{i(\hat{H}-E+\omega-i\delta)t}}{\hat{H}-E+\omega-i\delta}\right]_{-\infty}^{0}\hat{a}_q|\Psi\rangle$$

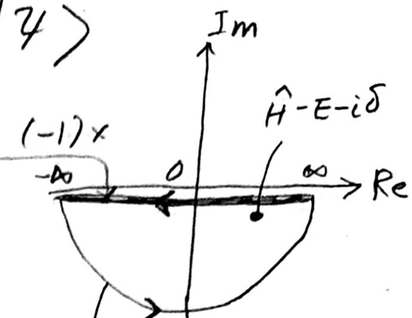
$$= \langle\Psi|\hat{a}_p^{\dagger}(\omega-E+\hat{H}-i\delta)^{-1}\hat{a}_q|\Psi\rangle$$

$\downarrow$

cf. $G=(E-\hat{H})^{-1}$

Inverse Fourier transform

$$G^{(r)}_{pq}(t) = \langle \Psi | \hat{a}_q \left(\int_{-\infty}^{\infty} \frac{e^{-i\omega t}}{\omega - \hat{H} + E + i\delta} \frac{d\omega}{2\pi} \right) \hat{a}^\dagger_p | \Psi \rangle$$



$$\int_{arc} \frac{e^{-i\omega t}}{\omega \cdots} \frac{d\omega}{2\pi} = 0 \text{ if } t>0 \quad \because \omega \sim -i\infty$$

$$= \begin{cases} \langle \Psi | \hat{a}_q \underbrace{(-i)\, e^{-i(\hat{H}-E-i\delta)t}}_{=(-1)\times\left(\oint_c \,-\, \int_{arc}\right)} \hat{a}^\dagger_p | \Psi \rangle & t>0 \\ \langle \Psi | \hat{a}_q \overbrace{\quad 0 \quad} \hat{a}^\dagger_p | \Psi \rangle & t<0 \end{cases}$$

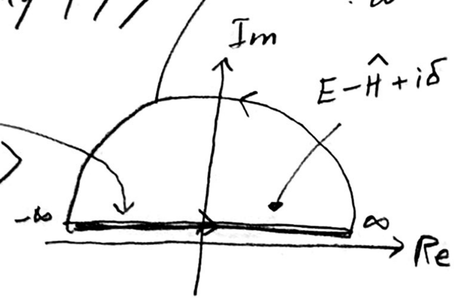
$\oint_c \to (2\pi i)\,\text{Res}$, $\quad \int_{arc} \to 0$

$\int_{arc} = 0$ if $t<0$ $\because \omega \sim +i\infty$

$$= -i\,\theta(t) \langle \Psi | \hat{a}_q\, e^{-i(\hat{H}-E-i\delta)t}\, \hat{a}^\dagger_p | \Psi \rangle$$

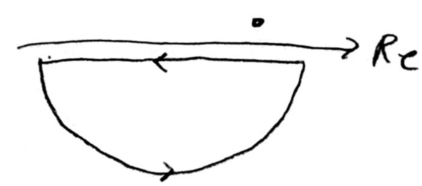
$$G^{(a)}_{pq}(t) = \langle \Psi | \hat{a}^\dagger_p \left(\int_{-\infty}^{\infty} \frac{e^{-i\omega t}}{\omega - E + \hat{H} - i\delta} \frac{d\omega}{2\pi} \right) \hat{a}_q | \Psi \rangle$$

$$\int_{arc} \frac{e^{-i\omega t}}{\omega \cdots} \frac{d\omega}{2\pi} = 0 \text{ if } t<0 \quad \because \omega \sim i\infty$$



$$= \begin{cases} \langle \Psi | \hat{a}^\dagger_p \underbrace{i\, e^{-i(E-\hat{H}+i\delta)t}}_{=\left(\oint_c \,-\, \int_{arc}\right)} \hat{a}_q | \Psi \rangle & t<0 \\ \langle \Psi | \hat{a}^\dagger_p \overbrace{\quad 0 \quad} \hat{a}_q | \Psi \rangle & t>0 \end{cases}$$

$\oint_c \to (2\pi i)\,\text{Res}$, $\quad \int_{arc} \to 0$



$\int_{arc} = 0$ if $t>0$ $\because \omega \sim -i\infty$

$$= i\,\theta(-t) \langle \Psi | a^\dagger_p\, e^{i(\hat{H}-E-i\delta)t}\, \hat{a}_q | \Psi \rangle$$

⑥ Exact and HF Green's function

exact energy of N-electron GS. exact (FCI) wfn N-electron GS

Exact $$G_{pq}(\omega) \equiv \langle \Psi | \hat{a}_q (\omega - \hat{H} + E)^{-1} \hat{a}_p^\dagger | \Psi \rangle + \langle \Psi | \hat{a}_p^\dagger (\omega - E + \hat{H})^{-1} \hat{a}_q | \Psi \rangle$$

HF $$G_{pq}^{(0)}(\omega) \equiv \langle \Phi^{(0)} | \hat{a}_q (\omega - \hat{H}^{(0)} + E^{(0)})^{-1} \hat{a}_p^\dagger | \Phi^{(0)} \rangle + \langle \Phi^{(0)} | \hat{a}_p^\dagger (\omega - E^{(0)} + \hat{H}^{(0)})^{-1} \hat{a}_q | \Phi^{(0)} \rangle$$

~~MPO~~ energy for N-electron GS

Fock operator

HF N-electron GS Slater det.

$$\hat{H}^{(0)} = \sum_{p,q} F_{pq} \hat{p}^\dagger \hat{q}$$

$$E^{(0)} = \sum_i^{occ.} \varepsilon_i \qquad = \sum_r \varepsilon_r \hat{r}^\dagger \hat{r}$$

$$= E^{(0)} + \sum_r \varepsilon_r \{\hat{r}^\dagger \hat{r}\}$$ (see Lecture on normal ordering)

if we set $\hat{a}_p^\dagger = \hat{p}^\dagger$, $\hat{a}_q = \hat{q}$, $G_{pq}(\omega)$ is <u>one-particle GF</u>

(they can be operator products; see below)

$$G_{pq}^{(0)}(\omega) = \langle 0 | \{\hat{q}\} (\omega - \sum_r \varepsilon_r \{\hat{r}^\dagger \hat{r}\})^{-1} \{\hat{p}^\dagger\} | 0 \rangle + \langle 0 | \{\hat{p}^\dagger\} (\omega + \sum_r \varepsilon_r \{\hat{r}^\dagger \hat{r}\})^{-1} \{\hat{q}\} | 0 \rangle$$

$$= \frac{\delta_{pq}}{\omega - \varepsilon_p} + \sum^{occ.}$$

⑦ Purpose of one-particle GF

adds an electron

$$G_{pq}(\omega) = \langle \Psi | \hat{q} \, (\omega - \hat{H} + E)^{-1} \hat{p}^\dagger | \Psi \rangle$$

$$+ \langle \Psi | \hat{p}^\dagger (\omega - E + \hat{H})^{-1} \hat{q} \, | \Psi \rangle$$

deletes an electron

$$= \sum_n \frac{\langle \Psi^N | \hat{q} \, | \Psi_n^{N+1} \rangle \langle \Psi_n^{N+1} | \hat{p}^\dagger | \Psi^N \rangle}{\omega - (E_n^{N+1} - E_0^N)}$$

EA sector

electron attachment energy

$$+ \sum_n \frac{\langle \Psi^N | \hat{p}^\dagger | \Psi_n^{N-1} \rangle \langle \Psi_n^{N-1} | \hat{q} | \Psi^N \rangle}{\omega - (E^N - E_n^{N-1})}$$

IP sector

ionization energy

G, in general, directly probes electron dynamics or propagation. One-particle GF, specifically, diverges whenever ω = IP or EA, quantities that are directly measured. If $\hat{a}_p^\dagger = \hat{a}^\dagger \hat{i}$, G defines two-particle GF, producing ω = excitation energies.

While exact G gives exact IP/EA, we seek systematic (such as perturbation) approximations to G.

Furthermore, the working equation for ω (that makes G divergent), i.e., the Dyson equation has the HF/KS-like one-particle form.

⑧ Dyson equation

Freeman Dyson
1923 – 2020

Feynman-Dyson perturbation series of Green's function

Stability of matter

QED – equivalence of Feynman's and Schwinger's formalisms

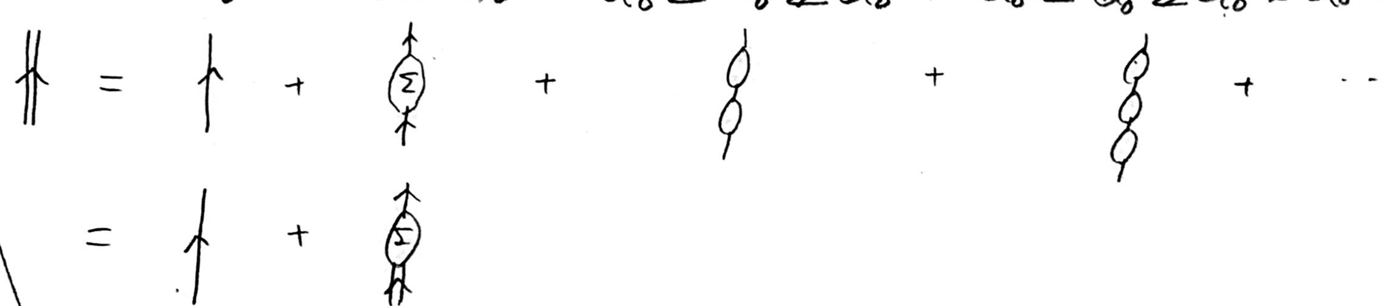
No Ph.D., "subversive"

$G_{pq}(\omega) \rightarrow N \times N$ matrix
↳ # spinorbitals

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

Dyson eq. : merely the definition of $N \times N$ $\Sigma_{pq}(\omega)$ — the Dyson self-energy (which will then has a nice property; see below)

$$G = G_0 + G_0\Sigma G_0 + G_0\Sigma G_0\Sigma G_0 + G_0\Sigma G_0\Sigma G_0\Sigma G_0 + \cdots$$



multiply G_0^{-1} from left, G^{-1} from right,

$$G_0^{-1} = G^{-1} + \Sigma \quad \text{(inverse Dyson eq.)}$$

we seek ω which makes G diverge and thus makes G^{-1} vanish

$$|G_0^{-1} - \Sigma| = 0$$

$$G_{pq}^{(0)} = \frac{\delta_{pq}}{\omega - \epsilon_p} \text{ in canonical HF reference}$$

$$|\omega\mathbb{1} - \epsilon - \Sigma| = 0$$

$$(\epsilon + \Sigma)U = U\omega$$

self-energy matrix

diagonal IP/EA matrix

diagonal Fock

Dyson orbital coeff.

Dyson eq.

$$\sum_q \left(F_{pq} + \underbrace{\Sigma_{pq}(\omega_p)}\right) U_{qr} = \omega_p U_{pr}$$

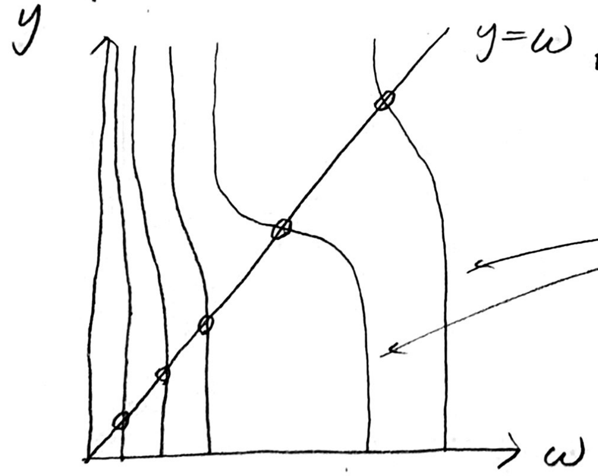
correlation correction to one-electron (i.e., Fock) op.

$\epsilon_p \delta_{pq}$ for canonical HF ref. (similar to KS eq in DFT)

cf. Sham-Schlüter mapping

if Σ_{pq} is exact, ω_p is exact IP/EA (from FCI).

Even though, the above equation is $N \times N$ eigenvalue eq. with only N eigenvalues, because of the ω-depen. of Σ_{pq}, it has exponentially many roots for both Koopmans' and non-Koopmans' IP/EAs



As a case in point, for $N=1$, we still have many roots at the intersections of LHS and RHS

Common (non systematic) approximations:

i) Diagonal approx. $\epsilon_p + \Sigma_{pp}(\omega_p) = \omega_p$ (root search)

ii) Freq.-independent approx. $\sum_q \left(\epsilon_p \delta_{pq} + \Sigma_{pq}(\epsilon_p)\right) U_{qr} = \omega_p U_{pr}$ (diagonalization)

iii) Diagonal, freq.-indep. $\epsilon_p + \Sigma_{pp}(\epsilon_p) = \omega_p$ (one-shot evaluation)

⑨ Feynman–Dyson perturbation approximation of Σ

$$\Sigma_{pq}(\omega) = \Sigma_{pq}^{(1)}(\omega) + \Sigma_{pq}^{(2)}(\omega) + \Sigma_{pq}^{(3)}(\omega) + \cdots$$

$\Sigma_{pq}^{(0)}$ doesnot exist; the zeroth-order IP/EA are ϵ_p (or their negatives)

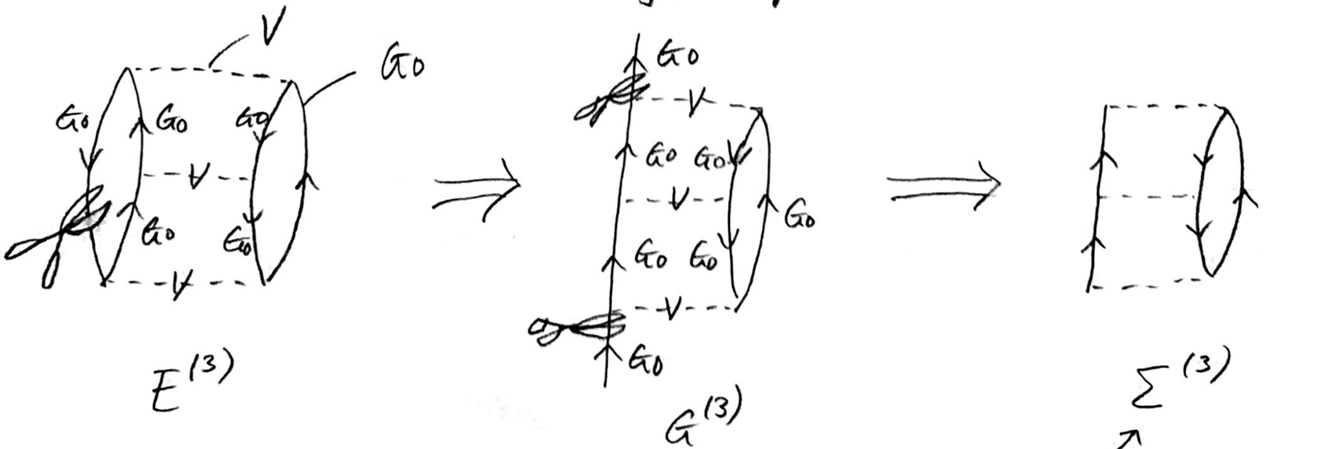
$\Sigma_{pq}^{(1)}$ is zero; the first-order IP/EA are also ϵ_p (as per Koopmans' theorem)

$\Sigma_{pq}^{(n)}$ $(n \geq 2)$ are defined diagrammatically.

For algebraic definitions and justification of the diagrammatic rules, see J. Chem. Phys. 147 044108 (2017).

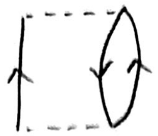
A Green's function diagram is a line (with internal structure)

ⓐ The nth-order GF diagrams are obtained by cutting open a nth-order MBPT energy diagram:

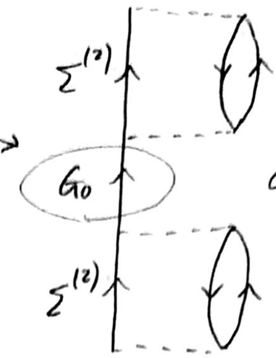


$$G = G_0 + G_0 \Sigma G_0 + G_0 \Sigma G_0 \Sigma G_0 + \cdots$$

(b) Delete all reducible diagrams



$\Sigma^{(2)}$ irreducible

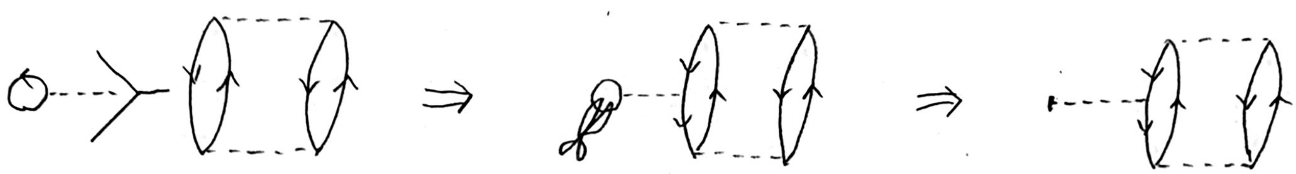


articulation line

$\Sigma^{(4)}$? no
reducible → X

$$G = G_0 + G_0 \Sigma G_0 + G_0 \Sigma G_0 \Sigma G_0 + \cdots$$

(c) Bubble-vertex insertion



zero-valued $E^{(3)}$ (in HF)

(d) Algebraic interpretation

(1) Label incoming external by p, outgoing external by q

(2) Label downgoing internal by i, j, k
upgoing internal by a, b, c

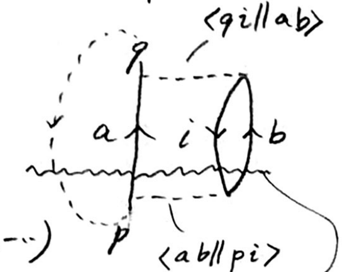
(3) Associate vertex with $\langle lo, ro \| li, ri \rangle$

(4) Associate each resolvent with $1/(\epsilon_i + \epsilon_j + \cdots - \epsilon_a - \epsilon_b - \cdots)$
where ficticious loop line's orbital energy is ω

(5) Sum over internals

(6) Multiply $(-1)^{h+l}$ (ficticious loop does NOT count)

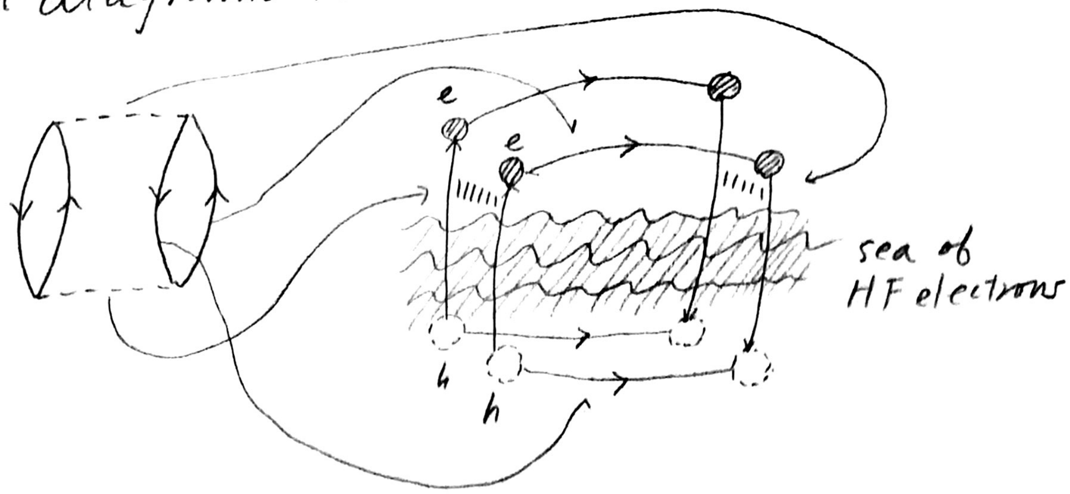
(7) Multiply $1/n!$ for n equivalent lines



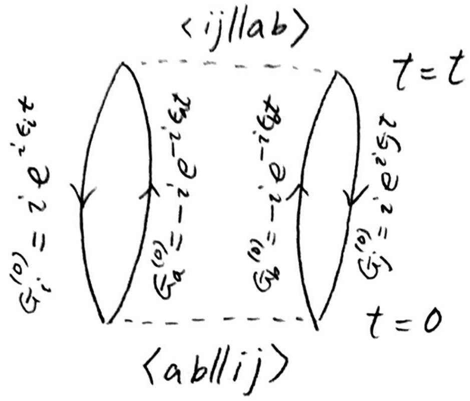
$$\frac{1}{\omega + \epsilon_i - \epsilon_a - \epsilon_b}$$

$$\left(\frac{1}{2}\right)(-1)^{1+1} \sum_{i,a,b} \frac{\langle qi \| ab \rangle \langle ab \| pi \rangle}{\omega + \epsilon_i - \epsilon_a - \epsilon_b}$$

(10) Feynman diagrams redux



i) Time-domain interpretation



equiv

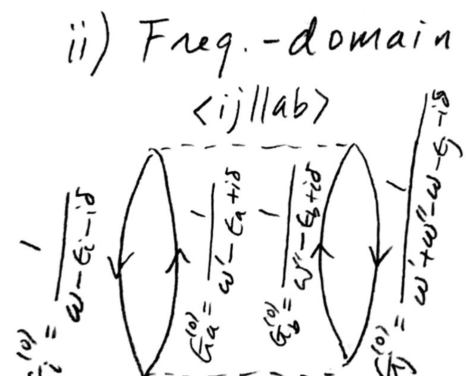
loop

$$E^{(2)} = \sum_{ijab} \left(\frac{1}{2}\right)^{2} (-1)^{2} (-i) \int_0^\infty dt\ \langle ij||ab\rangle\langle ab||ij\rangle\, e^{i(\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b+i\delta)t}$$

$$= \frac{(-i)}{4} \sum_{ijab} \langle ij||ab\rangle\langle ab||ij\rangle \left[\frac{e^{i(\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b+i\delta)t}}{i(\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b)}\right]_0^\infty$$

$$= \frac{1}{4} \sum_{ijab} \frac{\langle ij||ab\rangle\langle ab||ij\rangle}{\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b}$$

ii) Freq.-domain interpretation



(−i)

$$E^{(2)} = \sum_{ijab} \left(\frac{1}{2}\right)^{2} (-1)^{2} \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega''}{2\pi}\ \langle ij||ab\rangle\langle ab||ij\rangle$$

$$\times \frac{1}{\omega-\epsilon_i-i\delta}\ \frac{1}{\omega'-\epsilon_a+i\delta}\ \frac{1}{\omega''-\epsilon_b+i\delta}\ \frac{1}{\omega'+\omega''-\omega-\epsilon_j-i\delta}$$

↳ ω': no pole

$$= \frac{(-i)}{4} \sum_{ijab} \langle ij||ab\rangle\langle ab||ij\rangle \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega''}{2\pi}$$

$$\times \frac{1}{\omega-\epsilon_i-i\delta}\ \frac{1}{\omega''-\epsilon_b+i\delta}\ \frac{-i}{\epsilon_a+\omega''-\omega-\epsilon_j-i\delta}$$

↳ ω'': no pole

$$= \frac{(-i)}{4} \sum_{ijab} \langle ij||ab\rangle\langle ab||ij\rangle \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}$$

$$\times \frac{1}{\omega-\epsilon_i-i\delta}\ \frac{-1}{\epsilon_a+\epsilon_b-\omega-\epsilon_j-i\delta}$$

ω: no pole

$$= \frac{(-i)}{4} \sum_{ijab} \frac{(-i)\langle ij||ab\rangle\langle ab||ij\rangle}{\epsilon_a+\epsilon_b-\epsilon_i-\epsilon_j} = \frac{1}{4}\sum_{ijab}\frac{\langle ij||ab\rangle\langle ab||ij\rangle}{\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b}$$

iii) Real-space interpretation [Willow, Hirata, J. Chem. Phys. 140, 024111 (2014).]

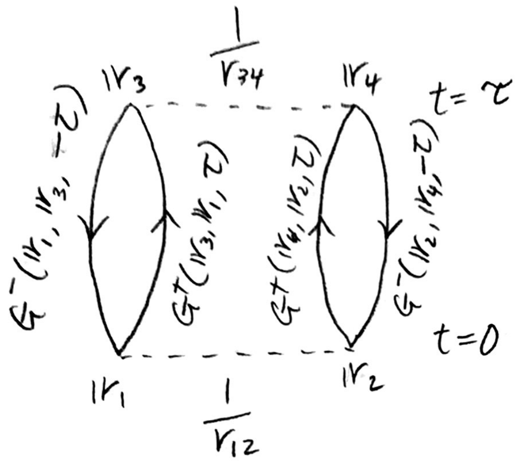
$$G^{+}(\mathbf{r}_d, \mathbf{r}_o, \tau) = \sum_a^{\text{vir.}} \varphi_a(\mathbf{r}_d)\, \varphi_a^*(\mathbf{r}_o)\, e^{-\epsilon_a \tau}$$

retarded — destination — origin

Spin-integrated

$$G^{-}(\mathbf{r}_d, \mathbf{r}_o, \tau) = \sum_i^{\text{occ.}} \varphi_i(\mathbf{r}_d)\, \varphi_i^*(\mathbf{r}_o)\, e^{-\epsilon_i \tau}$$

advanced



$$E^{(2)} = \int \cdots \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \int_0^\infty d\tau$$

$$\times (-2)\; G^-(\mathbf{r}_1, \mathbf{r}_3, -\tau)\, G^-(\mathbf{r}_2, \mathbf{r}_4, -\tau)$$

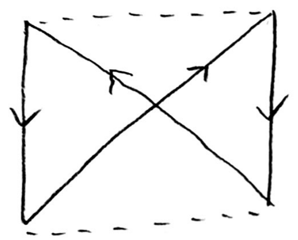
$$\times \; G^+(\mathbf{r}_3, \mathbf{r}_1, \tau)\, G^+(\mathbf{r}_4, \mathbf{r}_2, \tau)$$

$$\times \frac{1}{r_{12}} \frac{1}{r_{34}}$$

$$= -2 \sum_{ijab} \iint \varphi_i^*(\mathbf{r}_3)\, \varphi_j^*(\mathbf{r}_4) \frac{1}{r_{34}} \varphi_a(\mathbf{r}_3)\, \varphi_b(\mathbf{r}_4)\, d\mathbf{r}_3 d\mathbf{r}_4$$

$$\times \iint \varphi_a^*(\mathbf{r}_1)\, \varphi_b^*(\mathbf{r}_2) \frac{1}{r_{12}} \varphi_i(\mathbf{r}_1)\, \varphi_j(\mathbf{r}_2)\, d\mathbf{r}_1 d\mathbf{r}_2$$

$$\times \int_0^\infty e^{(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)\tau}\, d\tau$$



needs to be separately considered

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