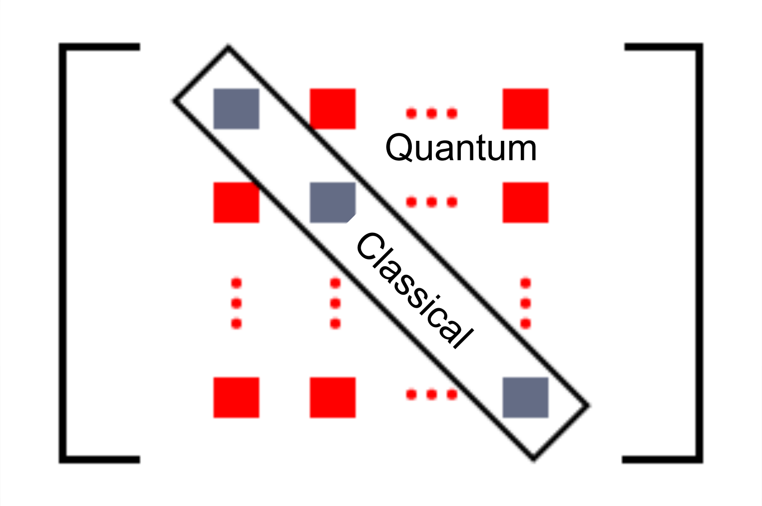


Many-body Green's function & DFTs

A pedagogical introduction
and
my own view of DFT

See, Guistino RevModPhys "Electron-phonon interactions from first principles"
Hansen and McDonald "Theory of simple liquids"

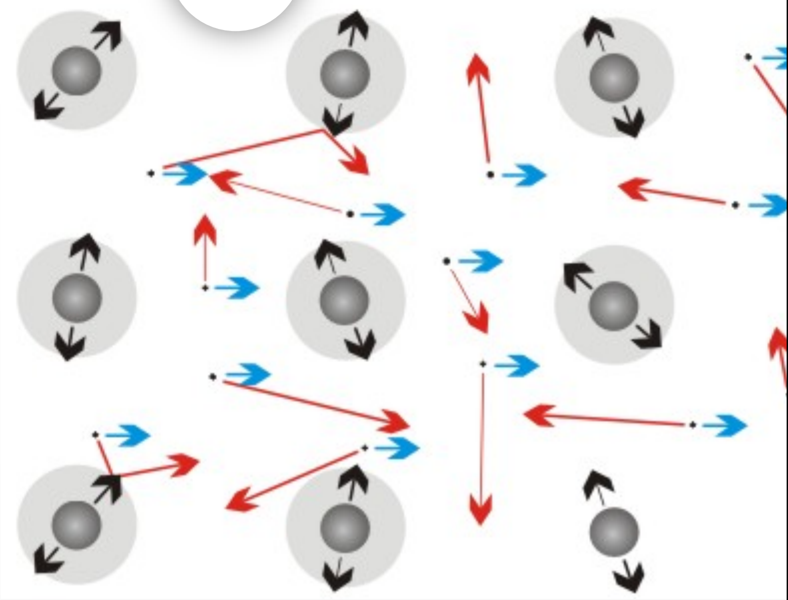
Contents

A) Electrons
B) Classical particles
C) Electron and phonon

Starting Hamiltonian

Electrons & Nuclei

Our target is the interacting electrons and/or nuclei



$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{U}_{ee} + \hat{U}_{nn} + \hat{U}_{en}$$

Focusing on electrons

Born-Oppenheimer

$$\hat{H} = \hat{T}_n + \hat{U}_{nn} + \int dx\, \hat{\psi}^\dagger(x) \left[-\frac{\hbar^2}{2m_e}\nabla^2 + \hat{V}_n(r) \right] \hat{\psi}(x)$$
$$+ \frac{1}{2}\int dx dx' v(r, r')\, \hat{\psi}^\dagger(x)\hat{\psi}^\dagger(x')\hat{\psi}(x')\hat{\psi}(x)$$

$$\hat{\psi}(x) = \sum_i \varphi_i^{\mathrm{KS}}(x)\hat{a}_i$$

Kohn-Sham orbitals
(with modification)

Green's functions

$$G(xt, x't') = -\frac{i}{\hbar}\langle 0|\hat{T}[\psi(xt)\psi^\dagger(x't')]|0\rangle$$

$$G_2(121'2') = -\left(\frac{i}{\hbar}\right)^2 \langle 0|\hat{T}[\psi(1)\psi(2)\psi^\dagger(2')\psi^\dagger(1')]|0\rangle$$

$$\psi(xt) = e^{i\hbar^{-1}(T+V_1+V_2)t}\psi(x)e^{-i\hbar^{-1}(T+V_1+V_2)t}$$

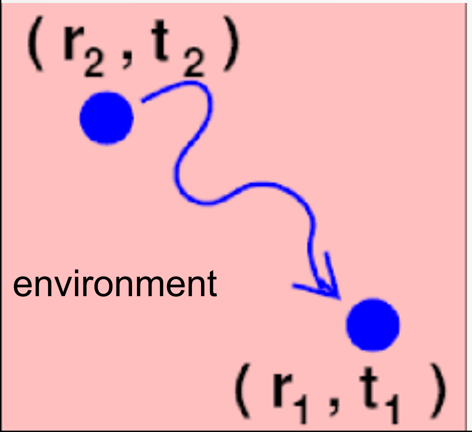
$$V_1 = \int n(x)\varphi(x)dx$$

External potential coupled to density

$$\langle n(x)\rangle = -i\hbar G(x,x)$$

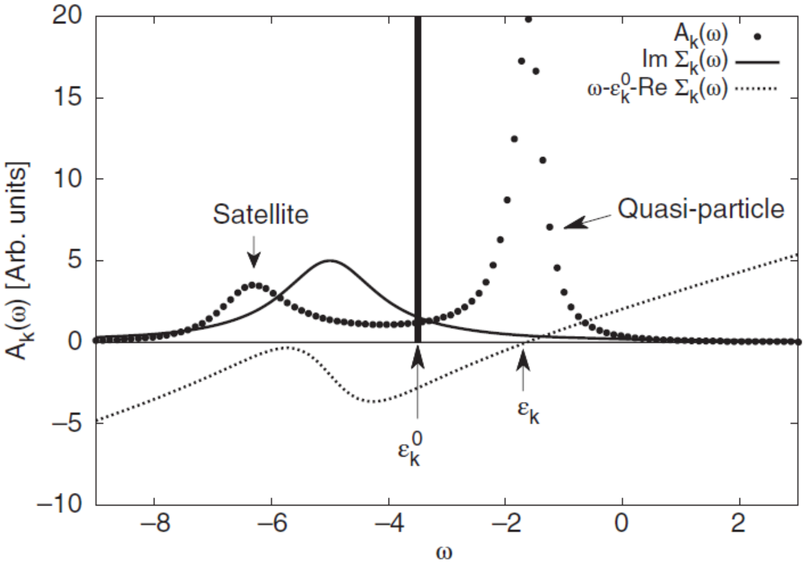
$$V_2 = \frac{\lambda}{2}\int v(x,x')n(x)n(x')dxx'$$

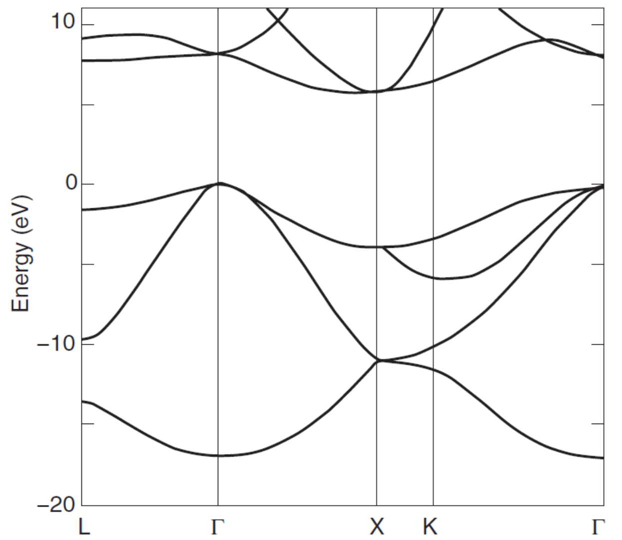
Coupling constant



Spectral function

$$2\pi A_k(\omega) = \left| \mathrm{Im} \int dxx' \, \varphi_k^*(x)\varphi_k(x')G(x,x',\omega) \right|$$





Lehman representation

$$G(x,x',\omega) = \sum \frac{g_k(x)g_k^*(x')}{\omega - (E_k^{N+1} - E_0^N) + i\eta} + \sum \frac{f_k(x)f_k^*(x')}{\omega + (E_k^{N-1} - E_0^N) - i\eta}$$

$$f_k(x) = \langle \Psi_k^{N-1} | \hat{\psi}(x) | \Psi_0^N \rangle$$

$$g_k(x) = \langle \Psi_0^N | \hat{\psi}(x) | \Psi_k^{N+1} \rangle$$

"orbital"

One-body Green's function

$$G(xt, x't') = -\frac{i}{\hbar}\langle 0|\hat{T}[\psi(xt)\psi^\dagger(x't')]|0\rangle$$

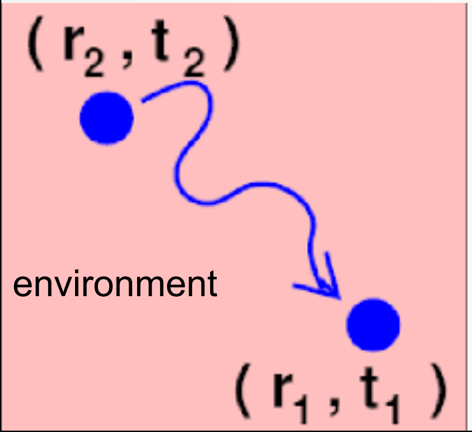
Move under a given external potential

$$\left[i\hbar\frac{\partial}{\partial t} + \frac{\hbar^2}{2m_e}\nabla^2 - \varphi(rt)\right]G(xt, x't') = \delta(xt, x't')$$

$$-\frac{i}{\hbar}\int dx''dt''\, v(r, r'')\langle 0|\hat{T}[n(x''t'')\psi(xt)\psi^\dagger(x't')]|0\rangle$$

Hierarchical equation!

$$\equiv L(1323^+) = -G_2 + G * G$$



$$[\hat{\psi}(\boldsymbol{x}_1), \hat{H}] = h(\boldsymbol{r}_1)\hat{\psi}(\boldsymbol{x}_1) + \int d\boldsymbol{x}_2\, \hat{\psi}^\dagger(\boldsymbol{x}_2)v(\boldsymbol{r}_1, \boldsymbol{r}_2)\hat{\psi}(\boldsymbol{x}_2)\psi(\boldsymbol{x}_1)$$

Functional derivative method

$$L(2313^{+}) = \frac{\delta}{\delta\varphi(3)} G(21)$$

- Kato, Kobayashi, Namiki
- Schwinger
- Hedin, Lundquvist

$$\mathrm{cf}\ \left.\frac{\delta n(1)}{\delta\varphi(2)}\right|_{\varphi\to 0} = \chi(12) = -\mathrm{i}L(121^{+}2^{+})$$

⬇

$$\int dx''dt''\left[i\hbar\frac{\partial}{\partial t} + \frac{\hbar^2}{2m_e}\nabla^2 - \varphi(rt) - i\hbar v(rt, r''t'')\frac{\delta}{\delta\varphi(r''t'')}\right]G(x''t'', x't') = \delta(xt, x't')$$

Further step: Introduction of self-energy

$$\int dx''dt''\left[i\hbar\frac{\partial}{\partial t}+\frac{\hbar^2}{2m_e}\nabla^2-\varphi(rt)-i\hbar v(rt,r''t'')\frac{\delta}{\delta\varphi(r''t'')}\right]G(x''t'',x't')=\delta(xt,x't')$$

⬇

$$\int dx''dt''\left[i\hbar\frac{\partial}{\partial t}+\frac{\hbar^2}{2m_e}\nabla^2-\varphi(xt)-\Sigma(xt,x''t'')\right]G(x''t'',x't')=\delta(xt,x't')$$

Self-energy

$$\frac{\delta}{\delta\varphi(r't')}G(xt,x''t'') \rightarrow \frac{\delta}{\delta\varphi(3)}G(12)$$

$$= -\int d45\, G(14)\frac{\delta G^{-1}(45)}{\delta\varphi(3)}G(52)$$

$$= -\int d456\, G(14)\frac{\delta G^{-1}(45)}{\delta V_{\text{tot}}(6)}\frac{\delta V_{\text{tot}}(6)}{\delta\varphi(3)}G(52)$$

$$\frac{\delta G^{-1}(45)}{\delta V_{\text{tot}}(6)} \rightarrow -\Gamma(456) \qquad \frac{\delta V_{\text{tot}}(6)}{\delta\varphi(3)} \rightarrow \epsilon^{-1}(63)$$

$$-\int d3\, v(13)\frac{\delta}{\delta\varphi(3)}G(12^+) = \int d456\, G(14)\Gamma(456)\left[\int d3\, v(13)\epsilon^{-1}(63)\right]G(52)$$

$$\int d3\, v(13)\epsilon^{-1}(63) \equiv W(16^+)$$

$$\equiv -i\hbar^{-1}\Sigma(15)$$

Equation of motion (summary)

$$\int d3 \left[i\hbar \frac{\partial}{\partial t_1} + \frac{\hbar^2}{2m_e} \nabla^2(1) - \varphi(1) - \Sigma(13) \right] G(32) = \delta(12)$$

$$\Sigma(12) = i\hbar \int d34\, G(13)\Gamma(324)\mathrm{W}(41^+)$$

$$\Gamma(123) = \delta(12)\delta(13) + \int d4567 \frac{\delta\Sigma(12)}{\delta G(45)} G(46)G(75)\Gamma(673)$$

$$\mathrm{W}(12) = \int d3\, \epsilon^{-1}(13) v(32)$$

Screened Coulomb and polarization

$$\frac{\delta\varphi(1)}{\delta V_{\mathrm{tot}}(2)} = \epsilon(12)$$

chain rule

$$\mathrm{W}(12) = \int d3\, \epsilon^{-1}(13) v(32)$$

$$= v(12) + \int d34\, v(13) \frac{\delta\langle\hat{n}(3)\rangle}{\delta V_{\mathrm{tot}}(4)} W(42)$$

Interaction with correlated density fluctuation

$$P(34)$$

Relation with density correlation

$$\mathrm{i}D(12) \equiv \langle\Psi_0|T[\tilde{n}_{\mathrm{H}}(1)\tilde{n}_{\mathrm{H}}(2)]|\Psi_0\rangle \qquad \tilde{n}_{\mathrm{H}} \equiv \hat{n} - \langle\hat{n}\rangle$$

$$\hbar P(12) = D(12)$$

Equation of motion (summary)

$$\int d3\left[i\hbar\frac{\partial}{\partial t_1}+\frac{\hbar^2}{2m_e}\nabla^2(1)-\varphi(1)-\Sigma(13)\right]G(32)=\delta(12)$$

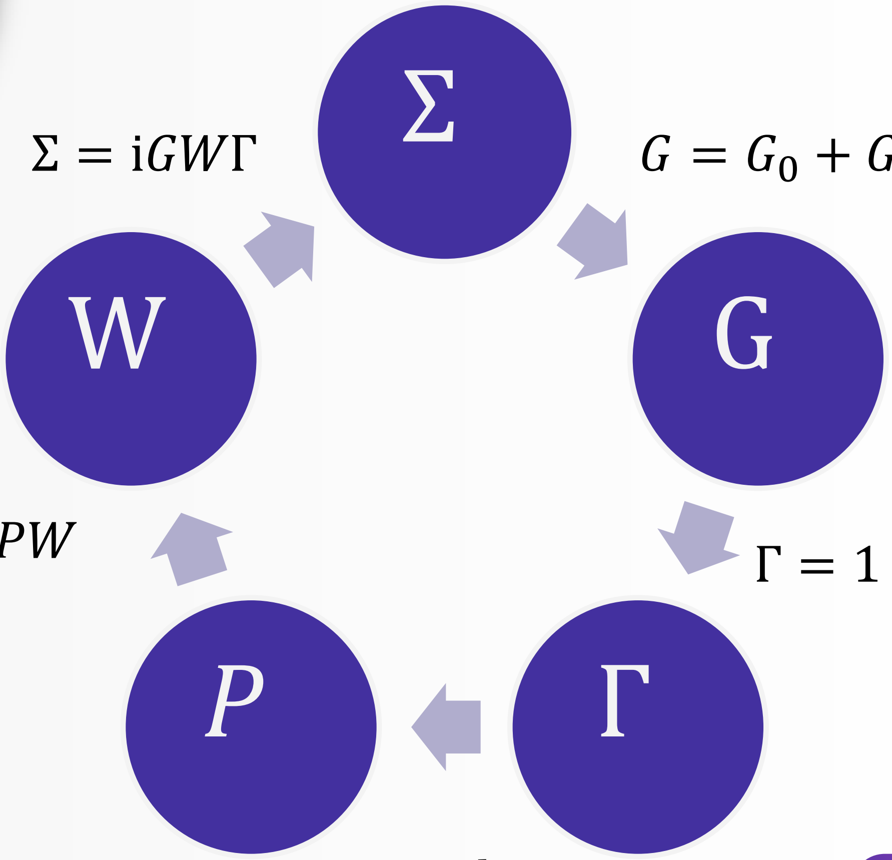
$$\Sigma(12)=i\hbar\int d34\,G(13)\Gamma(324)\mathrm{W}(41^+)$$

$$\Gamma(123)=\delta(12)\delta(13)+\int d4567\frac{\delta\Sigma(12)}{\delta G(45)}G(46)G(75)\Gamma(673)$$

$$\mathrm{W}(12)=v(12)+\int d34\,v(13)P(34)W(42)$$

$$P(12)=-\mathrm{i}\hbar\int d34\,G(13)G(41^+)\Gamma(342)$$

Hedin's equation



$$\Sigma = \mathrm{i}GW\Gamma$$

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

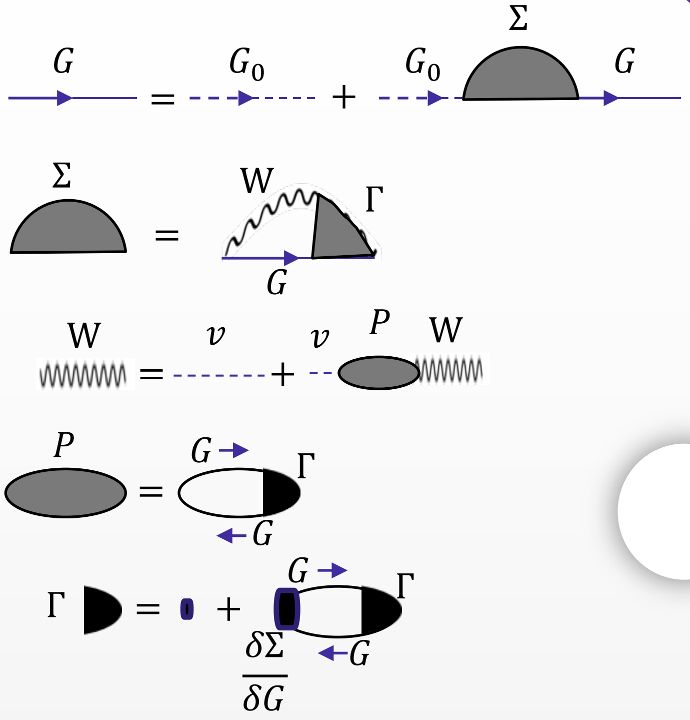
$$\Gamma = 1 + \frac{\delta\Sigma}{\delta G}GG\Gamma$$

$$P = -i\hbar GG\Gamma$$

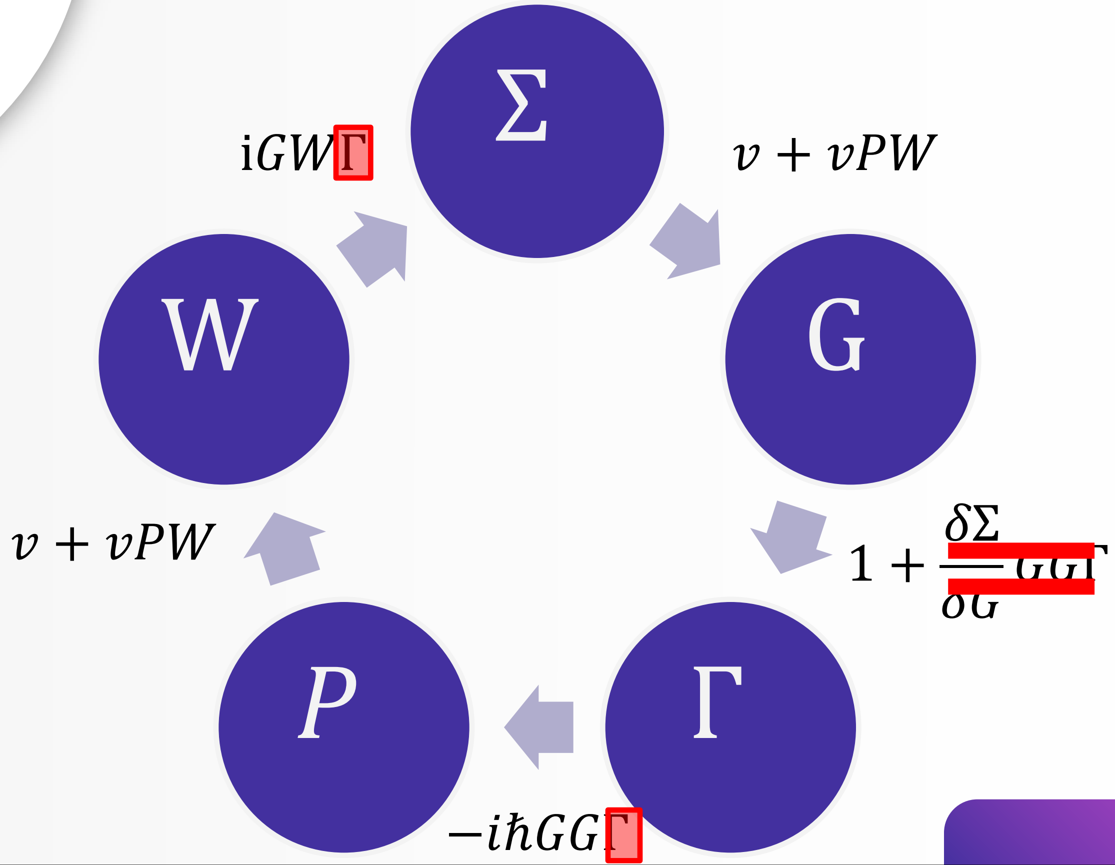
$$W = v + vPW$$

Hedin's equation

Feynman diagram



GW approximation



GW approximation

$$\Sigma_{\mathrm{xc}}(12) = i\hbar \int d34\, G(13)\Gamma(324)\mathrm{W}(41^{+})$$ Effective potential (triplet)

$$W^{\mathrm{eff}}(1^{+}23) = \int d4\, \Gamma(324)\mathrm{W}(41^{+})$$

GW approximation

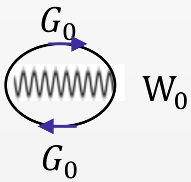
$$\Sigma_{xc}(12) = i\hbar \int d34\, G(13)\Gamma(324)\mathrm{W}(41^{+})$$ Effective potential (triplet)

$$W^{\mathrm{eff}}(1^{+}23) = \int d4\, \Gamma(324)\mathrm{W}(41^{+})$$

$$\Sigma_{xc}(12) = \mathrm{i}G(12)W(1^{+}2)$$

$$\int d3 \left[i\hbar \frac{\partial}{\partial t_1} - h(1) - \mathrm{i}G(13)W(1^{+}3) \right] G(32) = \delta(12)$$

$G(12) \rightarrow G_0(12)$ then W(12) can be recognized as effective interaction between Kohn-Sham states



GW approximation

$$\Sigma_{\mathrm{xc}}(12) = \mathrm{i}G(12)W(1^{+}2)$$

$$= \mathrm{i}G(12)\left(v(12) + \int d4\, v(14)\chi(43)v(32)\right)$$

screening due to classical response

If completely time-independent,

$$\Sigma_{\mathrm{xc}}(xx') = -n(rr')W(xx')$$

Similar in structure to hybrid DFT

Modeling functional

$$E[G] = \frac{1}{2}\int d1 \lim_{2\to 1}\left[\hbar\frac{\partial}{\partial t_1} + \mathrm{i}\frac{\hbar^2}{2m_e}\nabla^2(1) - \mathrm{i}V_{\mathrm{tot}}(1)\right]G(12)$$

Galitskii–Migdal (1958)

$$= E_{\mathrm{HF}}[G] + \frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\mathrm{Tr}[G(\mu + \mathrm{i}\omega)\Sigma_c(\mu + \mathrm{i}\omega)]$$

GW approximation

$$\Sigma_c(r, r', t - t') \to \mathrm{i}G(r, r', t - t')[W(r, r', t - t') - v(r, r')]$$

G_0W_0 approximation

Modeling functional

$$E[G] = \frac{1}{2}\int d1 \lim_{2\to 1}\left[\hbar\frac{\partial}{\partial t_1} + \mathrm{i}\frac{\hbar^2}{2m_e}\nabla^2(1) - \mathrm{i}V_{\mathrm{tot}}(1)\right]G(12)$$

Galitskii–Migdal (1958)

$$= E_{\mathrm{HF}}[G] + \frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\mathrm{Tr}[G(\mu+\mathrm{i}\omega)\Sigma_c(\mu+\mathrm{i}\omega)]$$

$$\to E_{\mathrm{HF}}[\varphi^{\mathrm{KS}}] + \frac{1}{2}\mathrm{Tr}[vG^{\mathrm{KS}}G^{\mathrm{KS}} + \log(1 - vG^{\mathrm{KS}}G^{\mathrm{KS}})]$$

RPA Bohm-Pines (1953)

Non-interacting system (HF) → lowest order w.r.t. Γ

Modeling functional

$\equiv \chi_0(12)$

$$\chi(12) = -\mathrm{i}G(12)G(21^+) - \mathrm{i}\int d345G(13)G(41^+)\left(\delta(34)v(35) + \frac{\delta\Sigma_{\mathrm{xc}}(34)}{\delta n(5)}\right)\chi(52)$$

$$W_0(12) = v(12) + \int d4v(14)\chi(43)v(32)$$

$\rightarrow \delta(34)f_{\mathrm{xc}}(35)$

$$E_c[\varphi^{\mathrm{KS}}] = \frac{1}{2}\mathrm{Tr}[vG^{\mathrm{KS}}G^{\mathrm{KS}} + \log(1 - vG^{\mathrm{KS}}G^{\mathrm{KS}})]$$

Welcome to the classical world!

$$\Xi[\phi] = \sum_{N=0}^{\infty} \int \frac{1}{N!} \exp[-\beta V_N] \left(\prod_{i=1}^{N} z \exp[-\beta \phi(r_i)] \right) \qquad z \equiv \frac{\exp[\beta\mu]}{\Lambda^3} : \text{activity}$$

$V_N(r_1, \cdots, r_N) = \frac{1}{2} \sum_{i \neq j} v(r_i, r_j)$ Lennard Johns potential $v(r) = Ar^{-12} - Br^{-6}$

Potential versus density: Ω versus $\mathcal{F}$

$$\Omega[\psi] = -k_B T \log(\Xi) \quad \Longleftrightarrow \quad \Omega\big[\psi[\rho]\big] = \mathcal{F}[\rho] + \int \psi[\rho](1)\rho(1)d1$$

ψ:Potential corresponding to the equilibrium density ρ

$\Lambda^3 z^*(r) = \exp\big[\beta\big(\mu - \phi(r)\big)\big]$: local activity

$\beta\big(\mu - \phi(r)\big) \equiv \beta\psi(r) \equiv \bar{\psi}(r)$: dimensionless potential

Intrinsic free energy $\mathcal{F} = \mathcal{F}^{\mathrm{id}} + \mathcal{F}^{\mathrm{ex}}$

$$\frac{\delta\beta\mathcal{F}^{\mathrm{id}}}{\delta\rho^{(1)}(r)} = \ln\big[\Lambda^3\rho^{(1)}(r)\big] : \text{ideal gas}$$

Quantity of central importance

N-particle density
$\rho^{(n)}(1,\dots,n) = \frac{z^*(1)\cdots z^*(n)}{\Xi}\frac{\delta^n\Xi}{\delta z^*(1)\cdots\delta z^*(n)}$
$g^{(n)}(1,\dots,n) = \frac{\rho^{(n)}(1,\dots,n)}{\rho^{(1)}(1)\cdots\rho^{(1)}(n)}$

Potential versus density: Ω versus $\mathcal{F}$

	Functional of ψ (external potential)	Functional of ρ (equilibrium density)
energy	Grand potential Ω	Intrinsic free energy $\mathcal{F} = \mathcal{F}^{\mathrm{id}} + \mathcal{F}^{\mathrm{ex}}$
equilibrium condition	$\frac{\delta\Omega}{\delta\psi(r)} = -\rho^{(1)}(r)$	$\frac{\delta\mathcal{F}}{\delta\rho^{(1)}(r)} = \psi(r)$
Correlation fn.	$\frac{\delta^n\beta\Omega}{\delta\bar{\psi}(1)\cdots\delta\bar{\psi}(n)} = -H^{(n)}(1,\cdots,n)$	$\frac{\delta^n\beta\mathcal{F}^{\mathrm{ex}}[\rho^{(1)}]}{\delta\rho^{(1)}(1)\cdots\delta\rho^{(1)}(n)} = -c^{(n)}(1,\cdots,n)$
1st order	$H^{(1)}(r) = \rho^{(1)}(r)$	$c^{(1)}(\mathrm{r}) = \ln[\Lambda^3\rho^{(1)}(r)] - \bar{\psi}(r)$
interrelation	$-\bar{\psi}(r) + \ln[\Lambda^3 H^{(1)}(r)] = c^{(1)}(r)$	
2nd order	$H^{(2)}(1,2) = \frac{\delta\rho^{(1)}(1)}{\delta\bar{\psi}(2)}$	$\frac{\delta\bar{\psi}(1)}{\delta\rho^{(1)}(2)} = \frac{\delta(1-2)}{\rho^{(1)}(1)} - c^{(2)}(1,2)$
OZ eq.	$h^{(2)}(1,2) = c^{(2)}(1,2) + \int c^{(2)}(1,3)\rho^{(1)}(3)h^{(2)}(3,2)d(3)$	

$$H^{(n)}(1,\cdots,n) \equiv \langle\left(\hat{\rho}(1) - \rho^{(1)}(1)\right)\cdots\left(\hat{\rho}(n) - \rho^{(1)}(n)\right)\rangle$$

$$H^{(2)}(1,2) = \rho^{(1)}(1)\rho^{(1)}(2)h^{(2)}(1,2) + \rho^{(1)}(1)\delta(1-2)$$

Hierarchical structure

Hierarchical equation for $H^{(n)}$		Hierarchical equation for $c^{(n)}$	
$\frac{\delta H^{(2)}(12)}{\delta\bar{\psi}(3)}$	$= -H^{(3)}(123)$	$\frac{\delta c^{(2)}(12)}{\delta\rho^{(1)}(3)}$	$= -c^{(3)}(123)$
$\frac{\delta H^{(3)}(123)}{\delta\bar{\psi}(4)}$	$= -H^{(4)}(1234)$	$\frac{\delta c^{(3)}(123)}{\delta\rho^{(1)}(4)}$	$= -c^{(4)}(1234)$

Kirkwood superposition approximation (valid for low density)

$$g^{(3)}(123) = g(12)g(23)g(31)\left[1 - h(12)h(23)h(31) - \rho \int d4\, h(14)h(24)h(34) + \cdots\right]$$

Rewrite this using $\rho^{(n)}(1, \cdots, n)$

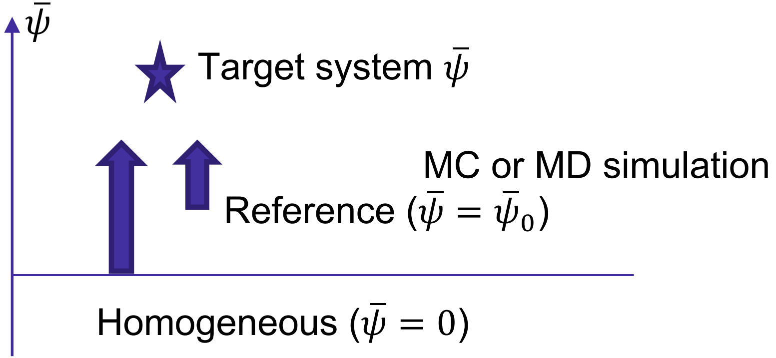
	Hierarchical equation for $\rho^{(n)}$
$\frac{\delta\rho^{(1)}(1)}{\delta\bar{\psi}(2)}$	$= \rho^{(2)}(12) - \rho^{(1)}(1)\rho^{(2)}(2) + \delta_{12}\rho^{(1)}(1)$
$\frac{\delta\rho^{(2)}(12)}{\delta\bar{\psi}(3)}$	$= (\delta_{13} + \delta_{23})\rho^{(2)}(12) - \rho^{(1)}(3)\rho^{(2)}(12) + \rho^{(3)}(123)$
$\frac{\delta\rho^{(3)}(123)}{\delta\bar{\psi}(4)}$	$= (\delta_{14} + \delta_{24} + \delta_{34})\rho^{(3)}(123) + \rho^{(1)}(4)\rho^{(3)}(123) + \rho^{(4)}(1234)$

After truncating the hierarchy, one can approach the target system either via

1. adiabatic application of external potential $\bar{\psi}$

or

2. Taylor expansion around $\bar{\psi}_0$



One can alternatively rewrite the hierarchy using the λ-derivative

$$\frac{\partial}{\partial \lambda}\rho^{(m)}(1,\dots,m) = \rho_{\lambda}^{(m)}(1,\dots,m)$$

Functional Renormalization Group (FRG) equation

	Hierarchical equation for $\rho^{(n)}$
$\frac{\delta\rho^{(1)}(1)}{\delta\bar{\psi}(2)}$	$= \rho^{(2)}(12) - \rho^{(1)}(1)\rho^{(2)}(2) + \delta_{12}\rho^{(1)}(1)$
$\frac{\delta\rho^{(2)}(12)}{\delta\bar{\psi}(3)}$	$= (\delta_{13} + \delta_{23})\rho^{(2)}(12) - \rho^{(1)}(3)\rho^{(2)}(12) + \rho^{(3)}(123)$
$\frac{\delta\rho^{(3)}(123)}{\delta\bar{\psi}(4)}$	$= (\delta_{14} + \delta_{24} + \delta_{34})\rho^{(3)}(123) + \rho^{(1)}(4)\rho^{(3)}(123) + \rho^{(4)}(1234)$

FRG Hierarchy $\rho^{(n)}$

Scaled interaction
$v(i,j) \to \lambda v(i,j)$

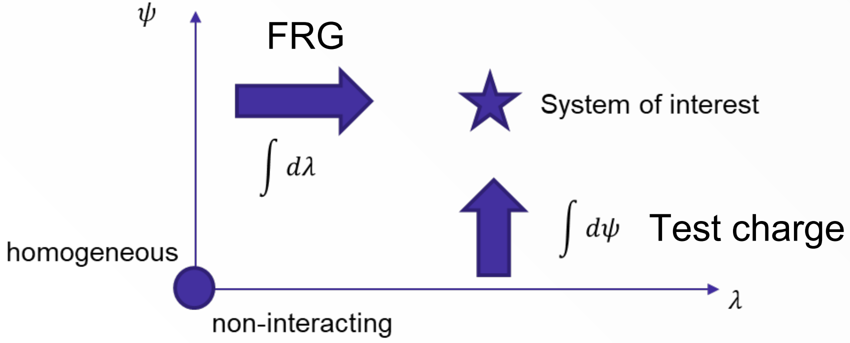
$$\left(\partial_\lambda + \sum_{i,j} \beta v(i,j)\right)\rho_\lambda^{(m)}(1,\dots,m)$$

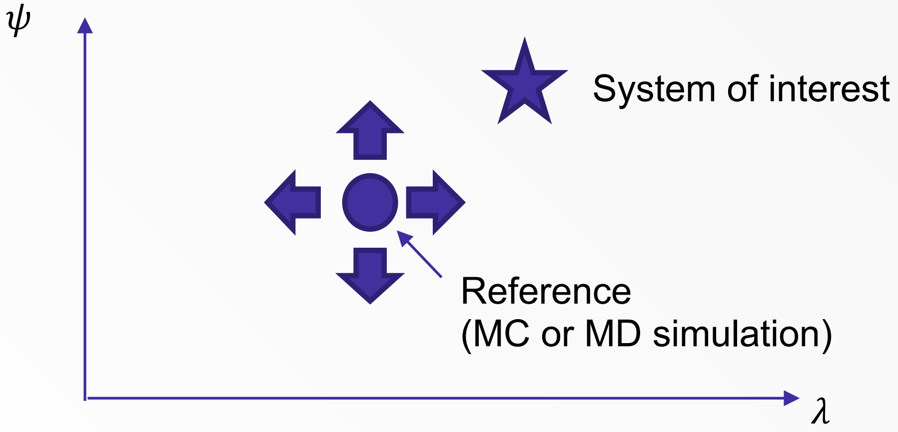
$$= -\frac{1}{2}\beta \int v(a,b)\left[\rho_\lambda^{(m+2)}(1,\dots,m,a,b)\right] d(ab) + \int \rho_\lambda^{(m+1)}(1,\dots,m,a)\left[\psi(a) - \sum_i \beta v(a,i)\right] d(a)$$

$$-\rho_\lambda^{(m)}(1,\dots,m)\left[\int \rho(a)\,\psi(a) d(a) - \sum_i \psi(i) - \frac{1}{2}\beta \int v(a,b)\rho_\lambda^{(2)}(a,b) d(ab)\right]$$

Yokota *et al.* (2021)

Construction of the functional





Percus test charge method for distinguishable particles

Fix a particle at the origin $r = 0$.

Homogeneous

Inhomogeneous

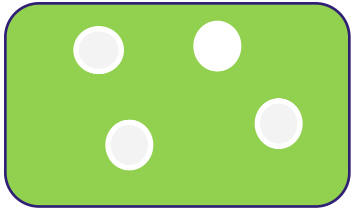
$$\rho^{(1)}(r) = \rho_0 \to \rho_0 + \delta\rho(r)$$

$$\delta\rho(r) = \rho_0 h^{(2)}[\rho_0](r, 0)$$

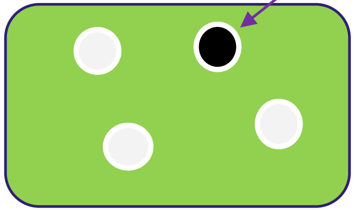
Modified by the pair correlation

Percus test charge method for distinguishable particles

Fix a particle at the origin $r = 0$.



Homogeneous



Inhomogeneous

$$\rho^{(1)}(r) = \rho_0 \rightarrow \rho_0 + \delta\rho(r)$$

$$\delta\rho(r) = \rho_0 h^{(2)}[\rho_0](r,0)$$

Modified by the pair correlation

$$\rho_0 = z \exp\left[\bar{\psi}_0 + c^{(1)}[\rho_0]\right]$$

⇩

$$\rho_0 + \rho_0 h^{(2)}[\rho_0](1,0) = \rho_0 \exp[-\beta v(1,0) + c^{(1)}[\rho_0 + \delta\rho](1) - c^{(1)}[\rho_0](1)]$$

$$= \rho_0 \exp\left[-\beta v(1,0) + \sum_{n=2}^{\infty} \frac{1}{n!} \int c^{(n)}[\rho_0](1, \cdots, n)\delta\rho(1) \cdots \delta\rho(n) d(2) \cdots d(n)\right]$$

The Kirkwood superposition approximation (KSA)

$$g_{123} = g_{12}g_{23}g_{31}$$

equivalent to the (three-particle) direct correlation $c^{(3)}$

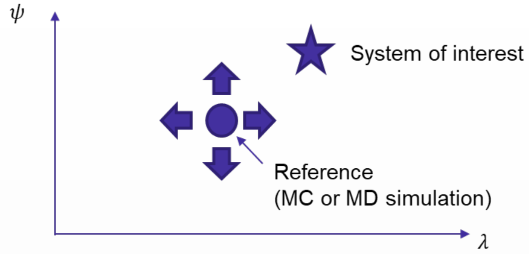
$$c^{(3)}(1,2,3) = f\left(\rho, c^{(2)}, h^{(2)}\right)\text{: a simple sum product}$$

$$\frac{\delta^3 \beta \mathcal{F}^{\text{ex}}[\rho^{(1)}]}{\delta\rho^{(1)}(1)\delta\rho^{(1)}(2)\delta\rho^{(1)}(3)} = -c^{(3)}(1,2,3)$$

In principle, one can get $c^{(n)}(1,\cdots n)$ by fixing $n-2$ particles.

$\mathcal{F}^{\text{ex}}\left[\rho_0^{(1)} + \delta\rho^{(1)}\right]$ (free energy functional) can be constructed

Machine learning of the functional



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Weighted density approximation

$$\bar{\rho}_i(r) = \int w_i(r - r')\rho^{(1)}(r')dr'$$

Density near the field point r

$$\mathcal{F}^{\mathrm{ex}}[\rho] = \int f[\{\bar{\rho}_i(r)\}]\,\rho^{(1)}(r)dr$$

Local functional

Fundamental measure theory

"Exact" form for $f's$ is known for hard spheres

Rosenfeld PRL (1989)

Back to quantum world!

In most cases, (electrons and phonons) $\neq$ (electrons and nuclei)

Harmonic approximation + α

Density correlations

$$D_{\mathrm{e}}(12) = -i\hbar^{-1}\langle \hat{T}\delta\hat{n}_{\mathrm{e}}(1)\delta\hat{n}_{\mathrm{e}}(2)\rangle$$

$$D_{\mathrm{n}}(12) = -i\hbar^{-1}\langle \hat{T}\delta\hat{n}_{\mathrm{n}}(1)\delta\hat{n}_{\mathrm{n}}(2)\rangle$$

Density correlations

$$D_{\mathrm{e}}(12) = -i\hbar^{-1}\langle \hat{T}\delta\hat{n}_{\mathrm{e}}(1)\delta\hat{n}_{\mathrm{e}}(2)\rangle$$

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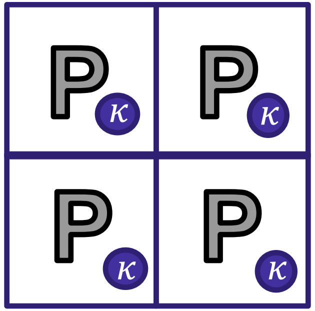
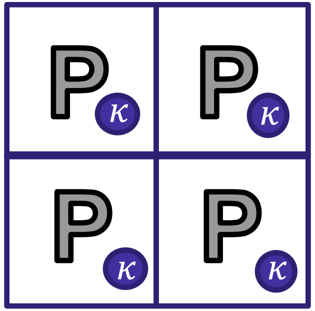


κ's nucleus at p-th cell

$$\hat{n}_{\mathrm{n}}(r) = \sum_{\kappa p} Z_{\kappa}\delta\left(r - \tau_{\kappa p}^{0} - \Delta\hat{\tau}_{\kappa p}\right)$$

Density correlations



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Displacement vector

κ's nucleus at p-th cell

$$\hat{n}_{\mathrm{n}}(r) = \sum_{\kappa p} Z_\kappa \delta(r - \tau^0_{\kappa p} - \Delta\hat{\tau}_{\kappa p})$$

$$\hat{n}_{\mathrm{n}}(r) \simeq n^0_{\mathrm{n}}(r) + \sum_{\kappa p} Z_\kappa \Delta\hat{\tau}_{\kappa p} \cdot \nabla\delta(r - \tau^0_{\kappa p}) - \frac{1}{2}\sum_{\kappa p} Z_\kappa \Delta\hat{\tau}_{\kappa p} \cdot \nabla\nabla\delta(r - \tau^0_{\kappa p}) \cdot \Delta\hat{\tau}_{\kappa p}$$

$$D_{\mathrm{n}}(12) = \sum_{\kappa\alpha p,\kappa'\alpha' p'} Z_\kappa \nabla_{1,\alpha}\delta(r_1 - \tau^0_{\kappa p}) D_{\kappa\alpha p,\kappa'\alpha' p'}(t_1 t_2) Z_{\kappa'} \nabla_{1,\alpha'}\delta\left(r_2 - \tau^0_{\kappa' p'}\right)$$

$$D_{\kappa\alpha p,\kappa'\alpha' p'}(t_1 t_2) = -\mathrm{i}\hbar^{-1}\left\langle \hat{T}\Delta\hat{\tau}_{\kappa\alpha p}(t)\Delta\hat{\tau}_{\kappa'\alpha' p'}(t')\right\rangle$$

Correlation of displacements

Screened interactions of electrons modified by phonon excitation

$$W(12) = v(12) + \int d34\, v(13)P(34)W(42)$$

$$W_{\mathrm{e}}(12) = \int d34 \epsilon^{-1}(13)v(32)$$

$$W_{\mathrm{ph}}(12) = \int d34 W_{\mathrm{e}}(13)D(34)W_{\mathrm{e}}(24)$$

$$\frac{\delta\langle\hat{n}_{\mathrm{n}}(1)\rangle}{\delta\varphi(2)} = -i\hbar^{-1}\langle\hat{T}\delta\hat{n}_{\mathrm{tot}}(1)\delta\hat{n}_{\mathrm{n}}(2)\rangle$$

Kato, Kobayashi, Namiki

$$W = W_{\mathrm{e}} + W_{\mathrm{ph}}$$

Hedin Lundqvist (‘69)

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Coulomb interaction

$$W_{\mathrm{ph}}(12) = \sum_{\substack{\kappa\alpha p \\ \kappa'\alpha' p'}} \int d34\, \epsilon_{\mathrm{e}}^{-1}(13)\nabla_{3,\alpha} v\left(r_3 - \tau_{\kappa p}^{0}\right) D_{\kappa\alpha p,\kappa'\alpha' p'}(t_1 t_2)\epsilon_{\mathrm{e}}^{-1}(24)\nabla_{4,\alpha} v\left(r_4 - \tau_{\kappa' p'}^{0}\right)$$

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Equation of motion (EOM) of D ← EOM of $\Delta\hat{\tau}$

Add external potential as $\sum_{\kappa p} F_{\kappa p} \cdot \Delta\hat{\tau}_{\kappa p}$

$$M_\kappa\, \partial^2 \Delta\hat{\tau}_{\kappa p}/\partial t^2 = -M_\kappa \hbar^{-2}\left[\left[\Delta\hat{\tau}_{\kappa p}, \hat{H}\right]\hat{H}\right]$$

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Harmonic approximation

$$\hat{n}^{(\kappa p)}(r) \equiv \hat{n}_{\text{all}}(r) - Z_{\kappa p}\delta\left(r - \tau_{\kappa p}\right)$$

$$= Z_\kappa \int dr dr' \left[-\frac{\delta\langle \hat{n}^{(\kappa p)}(rt)\rangle}{\delta F_{\kappa' \alpha' p'}(t')} v(r,r')\nabla'_\alpha \delta\left(r' - \tau^0_{\kappa p}\right) + \left\langle \hat{n}^{(\kappa p)}(rt)\right\rangle v(r,r')\nabla'_\alpha \nabla'_\gamma \delta\left(r' - \tau^0_{\kappa p}\right) D_{\kappa \alpha p,\kappa' \alpha' p'}(t')\right]$$

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$$= -\sum_{\kappa \alpha p, \kappa' \alpha' p'} \int dt'' \, \underline{\Pi_{\kappa \alpha p, \kappa' \alpha' p'}(tt'')} D_{\kappa \alpha p, \kappa' \alpha' p'}(t'' t')$$

self-energy

← When D is small and harmonic

Screened interactions of electrons modified by phonons

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← When D is small and harmonic

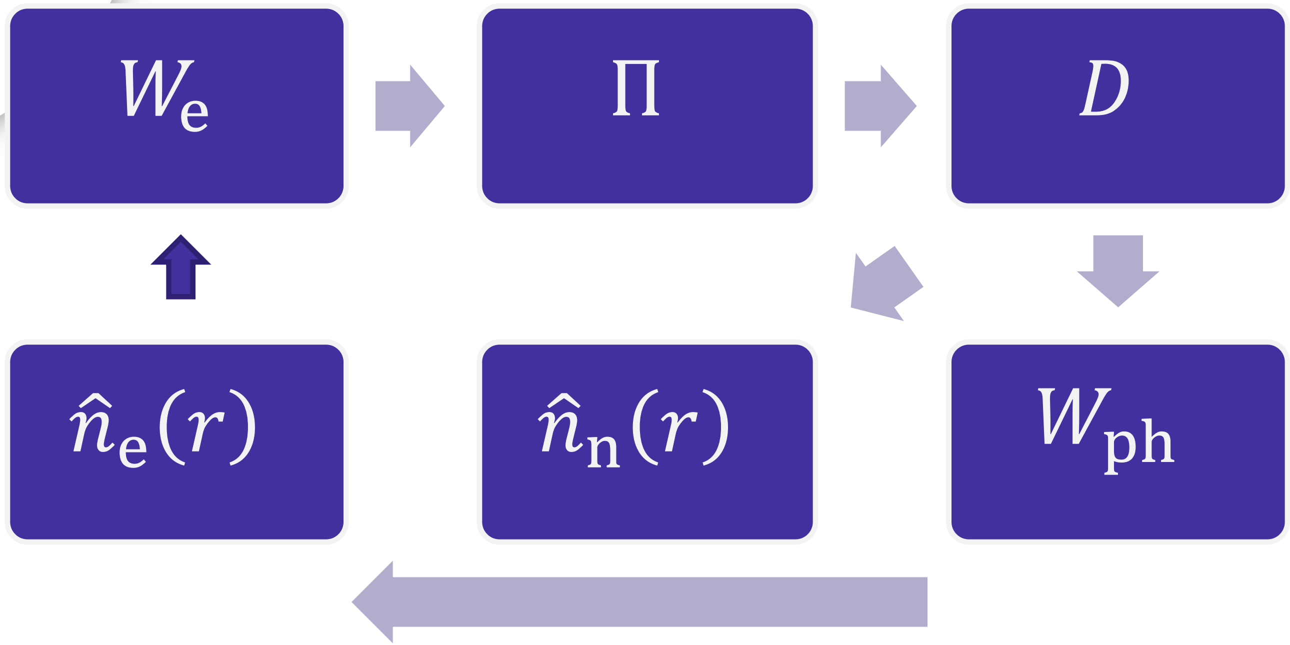
self-energy

$$\int dr dr' \left[\delta_{\kappa p,\kappa' p'}\delta(tt')\nabla_\alpha \langle\hat{n}(r)\rangle v(r,r') Z_{\kappa'} \nabla'_{\alpha'} \delta\left(r' - \tau^0_{\kappa' p'}\right) + Z_\kappa \nabla_\alpha \delta(r - \tau^0_{\kappa p}) W_e(rt, r't') Z_{\kappa'} \nabla'_{\alpha'} \delta\left(r' - \tau^0_{\kappa' p'}\right)\right]$$

$$= \Pi^{A}\delta(tt') + \Pi^{NA}(tt')$$

Adiabatic and non-adiabatic terms

Inclusion of phonon excitation



What is D? Relation to "phonon"

$$\Delta\tau_{\kappa\alpha p} = \sqrt{\frac{M_0}{N_p M_\kappa}} \sum_{q\nu} e^{iq\cdot R_p} e_{\kappa\alpha\nu}(q) \sqrt{\frac{\hbar}{2M_0\omega_{q\nu}}} \left(\hat{a}_{q\nu} + \hat{a}^\dagger_{q\nu}\right)$$

$$D_{\kappa\alpha p,\kappa'\alpha' p'}(tt') \to D_{q\nu,q'\nu'}(tt') = D^{\mathrm{A}}_{q\nu,q'\nu'}(tt') + D^{\mathrm{NA}}_{q\nu,q'\nu'}(tt')$$

$$D^{\mathrm{A}}_{q\nu,q'\nu'}(tt') = -i\left\langle \hat{T}\left[\hat{a}^\dagger_{q\nu}(t)\hat{a}_{q\nu}(t') + \hat{a}_{-q\nu}(t)\hat{a}^\dagger_{-q\nu}(t')\right]\right\rangle \delta_{\nu\nu'}$$

$$D(\omega) = D^{\mathrm{A}} + D^{\mathrm{A}}\Pi^{\mathrm{NA}}(\omega)D(\omega)$$ Formally (when homogeneous in time)

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$$D(\omega) = D^{\mathrm{A}} + D^{\mathrm{A}}\Pi^{\mathrm{NA}}(\omega)D(\omega)$$ Formally (when homogeneous in time)

$$\Pi^{\mathrm{NA}}_{q\nu,q'\nu'}(\omega) = \int dr dr' \left[\int dr''\, \epsilon_{\mathrm{e}}(r,r''\omega) g^{b}_{q\nu}(r'')\right] P_{\mathrm{e}}(r,r'\omega) \left[\int dr'''\, \epsilon^{-1}_{\mathrm{e}}(r',r'''\omega) g^{b*}_{q\nu}(r''')\right] - \int dr dr' q^{\mathrm{b}}_{\mathrm{q}\nu}(r) P_{\mathrm{e}}(r,r'0) q^{\mathrm{b}}_{\mathrm{q}\nu}(r')$$

$$q^{\mathrm{b}}_{\mathrm{q}\nu}(r) \equiv \Delta_{q\nu} V^{\mathrm{en}}(r)$$

$$V^{\mathrm{en}}(r) \equiv \sum_{\kappa p T} V_\kappa(r - \tau_{\kappa p} - T)$$ T: Lattice vector (periodic systems)

Summary

- It is not easy to simulate a matter based on the many-body theory.
- The theory, however, gives a hint for constructing a density functional.
- Different methods have been developed in different fields, and in this context, exchanging the idea will induce a breakthrough.