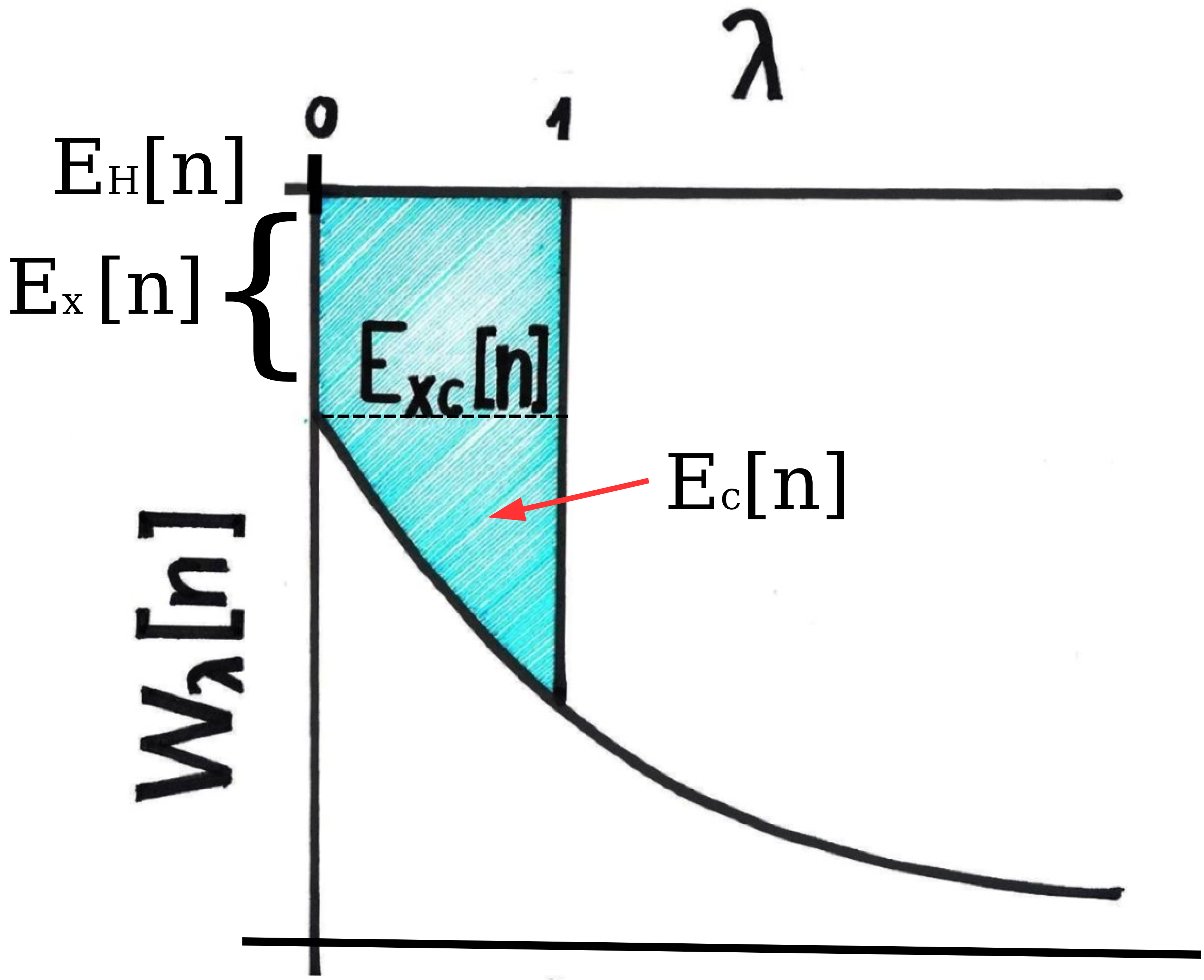
Advanced DFT

- General Variational Formulation
- Adiabatic Connection Formalism
- Exact Exchange
  - *Sharp-Horton, Talman-Shadwick,Sham-Shlueter, KLI*
- Fluctuation-Dissipation for Correlation (vdW aware)
  - *RPA, RPAx, ...*
- ISI Interaction Strength Interpolation
- SCE Strictly Correlated Electrons
  - *Kolmogorov optimal transport dual formulation*
- LIISA Locally Interpolated Interaction Strength Approx
- Homogeneous Electron Gas: HF, RPA, Wigner Crystal
- Lieb-Oxford Bound
- Virial Theorem and Scaling Relations
- Unambiguous Energy Densities



λ
0
1
$E_H[n]$
$E_x[n]$
$E_{xc}[n]$
$E_c[n]$
$W_\lambda[n]$

Adiabatic Connection Fluctuation-Dissipation Theorem

Formal expression for $E_{xc}[n]$ via coupling-constant integration

$$\hat{H}^{(\lambda)} = \hat{T}_e + \lambda \hat{W}_{ee} + \hat{V}_{ext}^{(\lambda)}$$

$$F_\lambda[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T}_e + \lambda \hat{W}_{ee} | \Psi \rangle$$

$$n(\mathbf{r}) = N \int |\Psi_\lambda(\mathbf{r}, \mathbf{r}_2, ..., \mathbf{r_N})|^2 d\mathbf{r}_2 ... d\mathbf{r}_N, \quad \forall \lambda$$

non-interacting electrons

$$\lambda = 0 \qquad F_0[n] = T_s[n], \qquad V_{ext}^{(0)} = V_{KS}$$

interacting electrons

$$\lambda = 1 \qquad F_1[n] = F[n], \qquad V_{ext}^{(1)} = V_{ext}$$

$$F[n] = T_s[n] + \int_0^1 d\lambda \frac{dF_\lambda}{d\lambda}$$

thanks to Hellmann-Feynman theorem ....

$$\frac{dF_\lambda}{d\lambda}[n] = \langle \Psi_\lambda^{[n]} | \hat{W}_{ee} | \Psi_\lambda^{[n]} \rangle$$

$$F[n] = T_s[n] + \int_0^1 d\lambda \langle \Psi_\lambda^{[n]} | \hat{W}_{ee} | \Psi_\lambda^{[n]} \rangle$$

$$\langle \Psi_0^{[n]} | \hat{W}_{ee} | \Psi_0^{[n]} \rangle = E_H[n] + E_x[n]$$

$$F[n] = T_s[n] + E_H[n] + E_x[n]$$
$$+ \int_0^1 d\lambda \left[\langle \Psi_\lambda^{[n]} | \hat{W}_{ee} | \Psi_\lambda^{[n]} \rangle - \langle \Psi_0^{[n]} | \hat{W}_{ee} | \Psi_0^{[n]} \rangle \right]$$

$$\hat{W}_{ee} = \frac{1}{2}\int d\mathbf{x}d\mathbf{y}\,\frac{e^2}{|\mathbf{x}-\mathbf{y}|}\,\phi^\dagger(\mathbf{x})\phi^\dagger(\mathbf{y})\phi(\mathbf{y})\phi(\mathbf{x})$$

$$\phi^\dagger(\mathbf{x})\phi^\dagger(\mathbf{y})\phi(\mathbf{y})\phi(\mathbf{x}) = \hat{n}(\mathbf{x})\hat{n}(\mathbf{y}) - \delta(\mathbf{x}-\mathbf{y})\;\hat{n}(\mathbf{x})$$

$$E_c[n] = \frac{1}{2}\int d\lambda \int d\mathbf{r}d\mathbf{r}'\,\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\,\left[\langle\Psi_\lambda^{[n]}|\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}')|\Psi_\lambda^{[n]}\rangle - \langle\Psi_0^{[n]}|\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}')|\Psi_0^{[n]}\rangle\right]$$

$$E_c[n] = \frac{1}{2}\int d\lambda \int d\mathbf{r}d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \left[\langle\Psi_\lambda^{[n]}|\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}')|\Psi_\lambda^{[n]}\rangle - \langle\Psi_0^{[n]}|\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}')|\Psi_0^{[n]}\rangle\right]$$

Inserting a resolution of the identity

$$\langle\Psi_0^\lambda|\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}')|\Psi_0^\lambda\rangle = \sum_n \langle\Psi_0^\lambda|\hat{n}(\mathbf{r})|\Psi_n^\lambda\rangle\langle\Psi_n^\lambda|\hat{n}(\mathbf{r}')|\Psi_0^\lambda\rangle$$

Notice that

$$\frac{2}{\pi}\int_0^\infty \frac{\gamma}{\gamma^2+u^2}\,du = 1, \;\; \forall\,\gamma > 0$$

and

$$\frac{2\gamma}{\gamma^2+u^2} = \frac{1}{\gamma+iu} + \frac{1}{\gamma-iu}$$

$$
\begin{aligned}
\langle \Psi_0^\lambda | \hat{n}(\mathbf{r}) \hat{n}(\mathbf{r}') | \Psi_0^\lambda \rangle \; &= \sum_n \langle \Psi_0^\lambda | \hat{n}(\mathbf{r}) | \Psi_n^\lambda \rangle \langle \Psi_n^\lambda | \hat{n}(\mathbf{r}') | \Psi_0^\lambda \rangle \\
&= \; \langle \Psi_0^\lambda | \hat{n}(\mathbf{r}) | \Psi_0^\lambda \rangle \langle \Psi_0^\lambda | \hat{n}(\mathbf{r}') | \Psi_0^\lambda \rangle \\
&+ \; \frac{\hbar}{\pi} \int_0^\infty du \sum_{n>0} \frac{\langle \Psi_0^\lambda | \hat{n}(\mathbf{r}) | \Psi_n^\lambda \rangle \langle \Psi_n^\lambda | \hat{n}(\mathbf{r}') | \Psi_0^\lambda \rangle}{E_n^\lambda - E_0^\lambda + i\hbar u} + c.c.
\end{aligned}
$$

Time dependent response function

$$i\partial_t \Psi_i(\mathbf{r},t) = H(\mathbf{r},t)\Psi_i(\mathbf{r},\mathbf{t}) \qquad \textit{real freq.} \quad \pm\omega$$

$$H(\mathbf{r},t) = H_0(\mathbf{r}) + (\delta V(\mathbf{r})e^{-i\omega t} + c.c.), \; [H_0(\mathbf{r}) - E_i]\Phi_i(\mathbf{r}) = 0,$$

$$\Psi_i(\mathbf{r},t) = \Phi_i(\mathbf{r})e^{-iE_i t} + \delta\Phi_i^{(+)}(\mathbf{r})e^{-i(E_i+\omega)t} + \delta\Phi_i^{(-)}(\mathbf{r})e^{-i(E_i-\omega)t}$$

$$[E_i + \omega - H_0]\delta\Phi_i^{(+)} = \delta V\Phi_i, \quad [E_i - \omega - H_0]\delta\Phi_i^{(-)} = \delta V^*\Phi_i,$$

$$\delta n(\mathbf{r},t) = \delta n^{(+)}(\mathbf{r})\; e^{-i\omega t} + \delta n^{(-)}(\mathbf{r})\; e^{+i\omega t}$$

$$\delta n^{(+)}(\mathbf{r}) = \langle \Phi_0|\hat{n}(\mathbf{r})|\delta\Phi_0^{(+)}\rangle + \langle \delta\Phi_0^{(-)}|\hat{n}(\mathbf{r})|\Phi_0\rangle, \quad \delta n^{(-)} = [\delta n^{(+)}]^*$$

$$\delta n^{(+)}(\mathbf{r}) = \sum_{n>0} \langle \Phi_0|\hat{n}(\mathbf{r})|\Phi_n\rangle \left(\frac{1}{E_0 - E_n + \omega} + \frac{1}{E_0 - E_n - \omega} \right) \langle \Phi_n|\delta V|\Phi_0\rangle$$

Time dependent response function

$$i\partial_t \Psi_i(\mathbf{r},t) = H(\mathbf{r},t)\Psi_i(\mathbf{r},\mathbf{t})$$ *imaginary freq.*

$$H(\mathbf{r},t) = H_0(\mathbf{r}) + \delta V(\mathbf{r})e^{ut}, \qquad [H_0(\mathbf{r}) - E_i]\Phi_i(\mathbf{r}) = 0,$$

$$\Psi_i(\mathbf{r},t) = \Phi_i(\mathbf{r})e^{-iE_it} + \delta\Phi(\mathbf{r})e^{-i(E_i+iu)t}$$

$$[E_i + iu - H_0]\delta\Phi_i = \delta V\Phi_i,$$

$$\delta n(\mathbf{r},t) = \delta n(\mathbf{r})\; e^{ut}$$

$$\delta n(\mathbf{r}) = \langle\Phi_0|\hat{n}(\mathbf{r})|\delta\Phi_0\rangle + \langle\delta\Phi_0|\hat{n}(\mathbf{r})|\Phi_0\rangle,$$

$$\delta n(\mathbf{r}) = \sum_{n>0}\langle\Phi_0|\hat{n}(\mathbf{r})|\Phi_n\rangle\left(\frac{1}{E_0 - E_n + iu} + \frac{1}{E_0 - E_n - iu}\right)\langle\Phi_n|\delta V|\Phi_0\rangle$$

$$\langle\Psi_0^\lambda|\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}')|\Psi_0^\lambda\rangle \;= \sum_n \langle\Psi_0^\lambda|\hat{n}(\mathbf{r})|\Psi_n^\lambda\rangle\langle\Psi_n^\lambda|\hat{n}(\mathbf{r}')|\Psi_0^\lambda\rangle$$

$$= \;\langle\Psi_0^\lambda|\hat{n}(\mathbf{r})|\Psi_0^\lambda\rangle\langle\Psi_0^\lambda|\hat{n}(\mathbf{r}')|\Psi_0^\lambda\rangle$$

$$+ \;\frac{\hbar}{\pi}\int_0^\infty du \sum_{n>0} \frac{\langle\Psi_0^\lambda|\hat{n}(\mathbf{r})|\Psi_n^\lambda\rangle\langle\Psi_n^\lambda|\hat{n}(\mathbf{r}')|\Psi_0^\lambda\rangle}{E_n^\lambda - E_0^\lambda + i\hbar u} + c.c.$$

$$= n(\mathbf{r})n(\mathbf{r}') - \;\frac{\hbar}{\pi}\int_0^\infty du \;\; \chi_\lambda(\mathbf{r},\mathbf{r}',iu)$$

$$E_c[n] = -\frac{\hbar}{2\pi}\int_0^1 d\lambda \int_0^\infty du \int d\mathbf{r}d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\left[\chi_\lambda(\mathbf{r},\mathbf{r}',iu) - \chi_0(\mathbf{r},\mathbf{r}',iu)\right]$$

in a more compact way

$$E_c[n] = -\frac{\hbar}{2\pi}\int_0^1 d\lambda \int_0^\infty du \; \mathrm{Tr}\; \{v_c\left[\chi_\lambda(iu) - \chi_0(iu)\right]\}$$

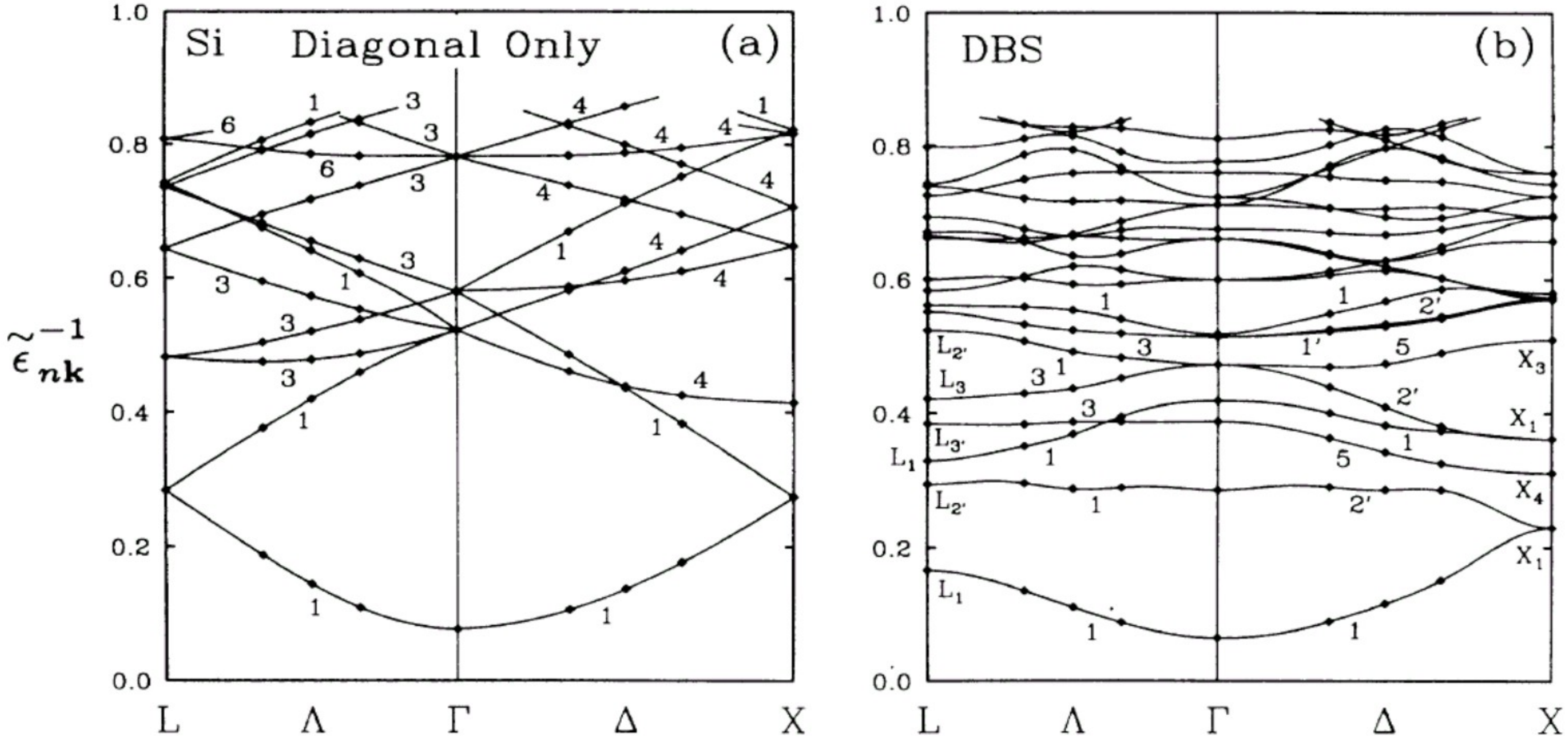
considering the eigen-problem for the dielectric matrix

$$v_c\chi_\lambda\, \omega_\alpha^\lambda \;=\; a_\alpha^\lambda\, \omega_\alpha^\lambda$$

$$E_c[n] = -\frac{\hbar}{2\pi}\int_0^1 d\lambda \int_0^\infty du \; \sum_\nu \{a_\alpha^\lambda - a_\alpha^0\}$$

- Moreover: Most eigenvalues a_α are close to zero

$$\epsilon_{RPA} = 1 - v_c \chi_0$$



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R. Car, E. Tosatti, S. Baroni, and S. Leelaprute, PRB 24, 985 (1981)
Mark S. Hybertsen and Steven G. Louie, PRB 35, 5585 (1987)
H. Wilson, F. Gygi, and G. Galli, PRB 78, 113303 (2008)

$$E_c[n] = -\frac{\hbar}{2\pi}\int_0^1 d\lambda \int_0^\infty du \int d\mathbf{r}d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\left[\chi_\lambda(\mathbf{r},\mathbf{r}',iu) - \chi_0(\mathbf{r},\mathbf{r}',iu)\right]$$

in a more compact way

$$E_c[n] = -\frac{\hbar}{2\pi}\int_0^1 d\lambda \int_0^\infty du \; \mathrm{Tr}\;\left\{v_c\left[\chi_\lambda(iu) - \chi_0(iu)\right]\right\}$$

where χ_λ is given by the Dyson-like equation

$$\chi_\lambda(iu) = \chi_0(iu) + \chi_0(iu)(\lambda v_c + f_{xc}^{(\lambda)}(iu))\chi_\lambda(iu)$$

$$\chi_0(\mathbf{r},\mathbf{r}',iu) = 2\Re \sum_{n>0} \frac{\langle\Phi_0|\hat{n}(\mathbf{r})|\Phi_n\rangle\langle\Phi_n|\hat{n}(\mathbf{r}')|\Phi_0\rangle}{E_0 - E_n + i\hbar u}$$

$$\chi_0(\mathbf{r},\mathbf{r}',iu) = 2\Re\sum_{n>0}\frac{\langle\Phi_0|\hat{n}(\mathbf{r})|\Phi_n\rangle\langle\Phi_n|\hat{n}(\mathbf{r}')|\Phi_0\rangle}{E_0 - E_n + i\hbar u}$$

Where the GS is

$$|\Phi_0\rangle = \mathcal{A}[\phi_{v_1},\phi_{v_2},...,\phi_{v_i},...,\phi_{v_N}], \quad E_0 = \sum_v \varepsilon_v$$

Single particle excitations are given by $\quad n = (v_i \to c_i)$

$$|\Phi_n\rangle = \mathcal{A}[\phi_{v_1},\phi_{v_2},...,\phi_{c_i},...,\phi_{v_N}], \quad E_n = E_0 + \varepsilon_{c_i} - \varepsilon_{v_i}$$

Double and higher excitations are defined similarly

$$n = (v_i \to c_i;\ v_j \to c_j, ...)$$

But $\hat{n}(\mathbf{r})$ couples the GS to single particle exitations only

$$\langle\Phi_n|\hat{n}(\mathbf{r})|\Phi_0\rangle = \phi^*_{c_i}(\mathbf{r})\phi_{v_i}(\mathbf{r}), \quad E_0 - E_n = \varepsilon_{v_i} - \varepsilon_{c_i}$$

$$\chi_0(\mathbf{r},\mathbf{r}',iu) = 2\Re \sum_{n>0} \frac{\langle\Phi_0|\hat{n}(\mathbf{r})|\Phi_n\rangle\langle\Phi_n|\hat{n}(\mathbf{r}')|\Phi_0\rangle}{E_0 - E_n + i\hbar u}$$

$$\chi_0(\mathbf{r},\mathbf{r}',iu) = 2\Re \sum_{c,v} \frac{\phi_v^*(\mathbf{r})\phi_c(\mathbf{r})\phi_c^*(\mathbf{r}')\phi_v(\mathbf{r}')}{\varepsilon_v - \varepsilon_c + i\hbar u}$$

from DFPT : for any $\delta V_{KS}(\mathbf{r};iu)$

$$\delta n(\mathbf{r},iu) = 2\Re \sum_v \phi_v(\mathbf{r})\ \delta\phi_v(\mathbf{r})$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS} - (\varepsilon_v + i\hbar u)\right]|\delta\phi_v\rangle = -P_c\delta V_{KS}|\phi_v\rangle$$

$$E_c[n] = -\frac{\hbar}{2\pi}\int_0^1 d\lambda \int_0^\infty du \int d\mathbf{r}d\mathbf{r}'\,\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\,[\chi_\lambda(\mathbf{r},\mathbf{r}',iu) - \chi_0(\mathbf{r},\mathbf{r}',iu)]$$

in a more compact way

$$E_c[n] = -\frac{\hbar}{2\pi}\int_0^1 d\lambda \int_0^\infty du\ \mathrm{Tr}\ \{v_c\,[\chi_\lambda(iu) - \chi_0(iu)]\}$$

where χ_λ is given by the Dyson-like equation

$$\chi_\lambda(iu) = \chi_0(iu) + \chi_0(iu)(\lambda v_c + f_{xc}^{(\lambda)}(iu))\chi_\lambda(iu)$$

Random Phase Approximation $\quad f_{xc}^{(\lambda)} = 0$

Random Phase Approximation: $f_{xc}^{\lambda} = 0$

$$\chi_{\lambda}^{RPA} = \chi_0 + \chi_0[\lambda v_c]\chi_{\lambda}^{RPA}$$

- We can define a generalized eigenvalue problem

$$\chi_0(iu)\,|\omega_\alpha(iu)\rangle = a_\alpha(iu) v_c^{-1}\,|\omega_\alpha(iu)\rangle$$

$$\chi_{\lambda}^{RPA} = \chi_0 + \lambda \chi_0 v_c \chi_{\lambda}^{RPA} \Rightarrow \quad \chi_{\lambda}^{RPA}|\omega_\alpha\rangle = \frac{a_\alpha}{1-\lambda a_\alpha} v_c^{-1}|\omega_\alpha\rangle$$

$\Rightarrow$ λ-integration is done analytically

$$\boxed{E_c = \frac{1}{2\pi}\int_0^{\infty} du \sum_{\alpha}\{a_\alpha(iu) + \ln(1 - a_\alpha(iu))\}}$$

PHYSICAL REVIEW B **79**, 205114 (2009)

Efficient calculation of exact exchange and RPA correlation energies in the adiabatic-connection fluctuation-dissipation theory

Huy-Viet Nguyen[1,2] and Stefano de Gironcoli[1,3]

PHYSICAL REVIEW B **90**, 045138 (2014)

Ab initio self-consistent total-energy calculations within the EXX/RPA formalism

Ngoc Linh Nguyen,[1,*] Nicola Colonna,[2] and Stefano de Gironcoli[2,3]

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Correlation energy within exact-exchange adiabatic connection fluctuation-dissipation theory: Systematic development and simple approximations

Nicola Colonna,[1] Maria Hellgren,[1] and Stefano de Gironcoli[1,2]

PHYSICAL REVIEW B **93**, 195108 (2016)

Molecular bonding with the RPAx: From weak dispersion forces to strong correlation

Nicola Colonna,[1,2] Maria Hellgren,[1,3,4] and Stefano de Gironcoli[1,5]

PHYSICAL REVIEW B **98**, 045117 (2018)

Beyond the random phase approximation with a local exchange vertex

Maria Hellgren,[1] Nicola Colonna,[2] and Stefano de Gironcoli[3,4]

THE END