RPA in the adiabatic-connection, plasmon-formula and ring-coupled-cluster formulations

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RPA = random-phase approximation

- a many-body method for:
  - excitation energies ($\omega_n = E_n - E_0$)
  - ground-state correlation energy (E_c) ← today
- used in:
  - quantum chemistry
  - condensed-matter physics } e^- ← today
  - nuclear physics p^+, n
- an old method (since the 1950s), revived interest since the 2000s in the context of DFT: RPA is seen as the simplest many-body method beyond second-order perturbation theory which can be used to improve over usual density functional approximations.
- Several formulations of RPA. Here, we will see:
  1) Adiabatic-connection (AC) formulation
  2) Plasmon-formula formulation
  3) Ring coupled-cluster doubles (CCD) formulation.

1) Adiabatic-connection formulation:

→ Adiabatic connection:

$$\left(\hat{T} + \lambda \hat{W} + \hat{V}^\lambda\right)|\Psi^\lambda\rangle = E_0^\lambda |\Psi^\lambda\rangle \qquad 0 \leq \lambda \leq 1$$

$\hat{W}$: ee interaction; $\hat{V}^\lambda$: one-e (local) potential; Ψ^λ: gs wave function

$\lambda = 0$: non-interacting KS system

$\lambda = 1$: interacting system

$\boxed{n^\lambda(r) = n(r), \forall \lambda}$

$$E^{\lambda=1} = E^{\lambda=0} + \int_0^1 d\lambda \frac{dE^\lambda}{d\lambda}$$

$$= \langle \Psi^{\lambda=0} | \hat{T} + \hat{V}^{\lambda=0} | \Psi^{\lambda=0}\rangle + \int_0^1 d\lambda \langle \Psi^\lambda | \hat{W} + \frac{d\hat{V}^\lambda}{d\lambda} | \Psi^\lambda\rangle$$

$$\hookrightarrow \int_0^1 d\lambda \langle \Psi^\lambda | \hat{W} | \Psi^\lambda\rangle + \langle \Psi^{\lambda=0} | \hat{V}^{\lambda=1} - \hat{V}^{\lambda=0} | \Psi^{\lambda=0}\rangle$$

one can use $\Psi^{\lambda=0}$ since density constant wrt λ

$$E_c = E^{\lambda=1} - \langle \Psi^{\lambda=0} | \hat{T} + \hat{W} + \hat{V}^{\lambda=1} | \Psi^{\lambda=0} \rangle$$

$$\boxed{E_c = \int_0^1 d\lambda \, \langle \Psi^\lambda | \hat{W} | \Psi^\lambda \rangle - \langle \Psi^{\lambda=0} | \hat{W} | \Psi^{\lambda=0} \rangle}$$ AC formula

→ In a real-valued spin orbital basis (eg. KS orbitals)

$$\hat{W} = \frac{1}{2} \sum_{pqrs} \langle ps | qr \rangle \, p^\dagger s^\dagger r q$$

$$\langle ps|qr\rangle = \langle rq | sp \rangle = W_{rs,pq}$$ matrix with double indices

$$E_c = \frac{1}{2} \int_0^1 d\lambda \sum_{pqrs} W_{rs,pq} P^\lambda_{c,pq,rs}$$ where $P^\lambda_{c,pq,rs} = \langle \Psi^\lambda | p^\dagger s^\dagger r q | \Psi^\lambda \rangle - \langle \Psi^{\lambda=0} | p^\dagger s^\dagger r q | \Psi^{\lambda=0} \rangle$

P^λ_c: correlation part of 2-e density matrix

$$\boxed{E_c = \frac{1}{2} \int_0^1 d\lambda \, \mathrm{tr}[W P_c^\lambda]}$$

→ Fluctuation-dissipation theorem:

$$\boxed{P_c^\lambda = -\int_{-\infty}^{+\infty} \frac{d\omega}{2\pi i} e^{-i\omega 0^+} [\chi^\lambda(\omega) - \chi^{\lambda=0}(\omega)]}$$

where $\chi^\lambda_{pq,rs}(\omega) = \sum_{n \neq gs} \frac{\langle \Psi^\lambda | p^\dagger q | \Psi_n^\lambda \rangle \langle \Psi_n^\lambda | s^\dagger r | \Psi^\lambda \rangle}{\omega - \underbrace{\omega_n^\lambda}_{E_n^\lambda - E^\lambda} + i0^+} - \frac{\langle \Psi^\lambda | s^\dagger r | \Psi_n^\lambda \rangle \langle \Psi_n^\lambda | p^\dagger q | \Psi^\lambda \rangle}{\omega + \omega_n^\lambda - i0^+}$

polarization propagator or linear-response function

The theorem can be proven by contour integrating over the lower-half ω plane and using residue theorem

→ Linear-response equation in RPA:

$$\boxed{\chi^\lambda(\omega)^{-1} = \chi^{\lambda=0}(\omega)^{-1} - \lambda W}$$ (dRPA or TDH)

Remark: if we antisymmetrized the integrals $W_{pq,rs} \longrightarrow W^{AT}_{pq,rs} = \langle rq | sp \rangle - \langle rq | pr \rangle$ we get RPAx or TDHF

$$\chi^\lambda(\omega)^{-1} = -\left[\begin{array}{c} \\ \mathrm{ov} \\ \mathrm{vo} \end{array} \begin{array}{c} \begin{array}{cc} \mathrm{ov} & \mathrm{vo} \end{array} \\ \begin{pmatrix} A^\lambda & B^\lambda \\ B^{\lambda} & A^\lambda \end{pmatrix} \end{array} - \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right]$$

$$\chi^{\lambda=0}_{ia,jb}(\omega) = \frac{\delta_{ij}\delta_{ab}}{\omega - (\varepsilon_a - \varepsilon_i) + i0^+} \quad \Big| \quad \chi^{\lambda=0}_{ai,bj} = \frac{-\delta_{ij}\delta_{ab}}{\omega + (\varepsilon_a - \varepsilon_i) - i0^+}$$

$$(\chi^{\lambda=0}(\omega))^{-1} = -\left[\begin{pmatrix} \Delta\varepsilon & 0 \\ 0 & \Delta\varepsilon \end{pmatrix} - \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right]$$

$$\begin{cases} A^\lambda_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + \lambda \overbrace{\langle ib|aj\rangle}^{W_{ia,jb}} \\ B^\lambda_{ia,jb} = \lambda \underbrace{\langle ij|ab\rangle}_{W_{ia,bj}} \end{cases}$$

$$\boxed{\begin{pmatrix} A^\lambda & B^\lambda \\ B^\lambda & A^\lambda \end{pmatrix}\begin{pmatrix} X_n^\lambda \\ Y_n^\lambda \end{pmatrix} = \omega_n^\lambda \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} X_n^\lambda \\ Y_n^\lambda \end{pmatrix}}$$

$(C_n^\lambda)^T \Delta C_n^\lambda = 1$

$(C_{-n}^\lambda)^T \Delta C_{-n}^\lambda = -1$

$$\Lambda^\lambda C_n^\lambda = \omega_n^\lambda \Delta C_n^\lambda$$

if ω_n^λ is eigenvalue with eigenvector $C_n^\lambda = \begin{pmatrix} X_n^\lambda \\ Y_n^\lambda \end{pmatrix}$
then $-\omega_n^\lambda$ is ―――――― $C_{-n}^\lambda = \begin{pmatrix} Y_n^\lambda \\ X_n^\lambda \end{pmatrix}$

spectral representation: $$\chi^\lambda(\omega) = \sum_{n>0} \frac{C_n^\lambda (C_n^\lambda)^T}{\omega - \omega_n^\lambda + i0^+} - \frac{C_{-n}^\lambda (C_{-n}^\lambda)^T}{\omega + \omega_n^\lambda - i0^+}$$

$$\Rightarrow P_c^\lambda = \sum_n C_n^\lambda (C_n^\lambda)^T - C_n^{\lambda=0}(C_n^{\lambda=0})^T$$

$$\Rightarrow \boxed{E_c = \frac{1}{2}\int_0^1 d\lambda \sum_n \mathrm{tr}\left[W C_n^\lambda (C_n^\lambda)^T - W C_n^{\lambda=0}(C_n^{\lambda=0})^T\right]}$$

2) <u>Plasmon-formula formulation:</u>

$$E_c = \frac{1}{2}\int_0^1 d\lambda \sum_n \cancel{\mathrm{tr}}\left[(C_n^\lambda)^T W C_n^\lambda - (C_n^{\lambda=0})^T W (C_n^{\lambda=0})\right]$$

$$(C_n^\lambda)^T \Lambda^\lambda C_n^\lambda = \omega_n^\lambda \quad \Rightarrow \quad \frac{d\omega_n^\lambda}{d\lambda} = (C_n^\lambda)^T \frac{d\Lambda^\lambda}{d\lambda} C_n^\lambda = (C_n^\lambda)^T W C_n^\lambda$$

$$\begin{pmatrix} \Delta\varepsilon & 0 \\ 0 & \Delta\varepsilon \end{pmatrix}\begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} = \omega^{\lambda=0}$$

$$\Rightarrow E_c = \frac{1}{2}\int_0^1 d\lambda \sum_n \left[\frac{d\omega_n^\lambda}{d\lambda} - (C_n^{\lambda=0})^T W (C_n^{\lambda=0})\right]$$

$$= \frac{1}{2}\sum_n \left[\omega_n^{\lambda=1} - \omega_n^{\lambda=0} - (C_n^{\lambda=0})^T W (C_n^{\lambda=0})\right]$$

$$= \frac{1}{2}\sum_n \left[\omega_n^{\lambda=1} - \omega_{n,TDA}^{\lambda=1}\right]$$

$$C_n^{\lambda=0} = \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \leftarrow n^{th}$$

$$A^\lambda X_n^\lambda = \omega_{n,TDA}^\lambda X_n^\lambda$$

3) ring coupled-cluster doubles formulation:

$$\begin{pmatrix} A & B \\ B & A \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix}\begin{pmatrix} \omega & 0 \\ 0 & \omega \end{pmatrix}$$

matrix of eignvectors with positive ω_n

diagonal matrix

$$\begin{cases} AX + BY = X\omega \\ BX + AY = -Y\omega \end{cases} \iff \begin{cases} A + BYX^{-1} = X\omega X^{-1} \\ B + AYX^{-1} = -Y\omega X^{-1} \end{cases}$$

$T = YX^{-1}$ amplitudes

$$\iff \begin{cases} A + BT = X\omega X^{-1} \\ B + AT = -YX^{-1}X\omega X^{-1} = -T\, X\omega X^{-1} \end{cases}$$

$$\iff B + AT = -T(A + BT)$$

$$\iff \boxed{B + AT + TA + TBT = 0}$$ Riccati equation

$$E_c = \frac{1}{2}\,\mathrm{tr}[\omega - A] = \frac{1}{2}\,\mathrm{tr}[X\omega X^{-1} - A]$$

$$= \frac{1}{2}\,\mathrm{tr}[(A + BT) - A] = \frac{1}{2}\,\mathrm{tr}[BT]$$

$$= \frac{1}{2}\,\mathrm{tr}[WT]$$

RPAx-SO2: exchange terms in A and B for calculating of T but not in W

Challenges:

* What is the best way of including exchange terms in RPA?
* How to deal with instabilities (open-shell systems, symmetry-breaking)?
* How to define a MR-RPA for strong correlation?

Appendices

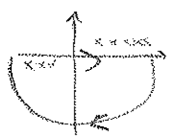
* <u>AC formula starting from HF</u>:

$$(\hat{T} + \lambda \hat{W} + \hat{V}^{\lambda})|\Psi^{\lambda}\rangle = E^{\lambda}|\Psi^{\lambda}\rangle \quad \text{with} \quad \hat{V}^{\lambda} = \hat{V}_{ne} + (1-\lambda)\hat{V}_{Hx}$$

$$\Rightarrow E_c = \int_0^1 d\lambda\, \langle\Psi^{\lambda}|\hat{W} - \hat{V}_{Hx}|\Psi^{\lambda}\rangle - \langle\Psi^{\lambda=0}|\hat{W} - \hat{V}_{Hx}|\Psi^{\lambda=0}\rangle$$

$$E_c = \frac{1}{2}\int_0^1 d\lambda\, tr[W P_c^{\lambda}] + \int_0^1 d\lambda\, tr[V_{Hx}\gamma_c^{\lambda}]$$

* <u>Proof and general form of FDT</u>:



$$-\oint \frac{d\omega}{2\pi i}\chi^{\lambda}_{pq,rs}(\omega) = \sum_n \langle\Psi^{\lambda}|p^{\dagger}q|\Psi_n^{\lambda}\rangle\langle\Psi_n^{\lambda}|s^{\dagger}r|\Psi^{\lambda}\rangle$$
$$= \langle\Psi^{\lambda}|p^{\dagger}q s^{\dagger}r|\Psi^{\lambda}\rangle - \langle\Psi^{\lambda}|p^{\dagger}q|\Psi^{\lambda}\rangle\langle\Psi^{\lambda}|s^{\dagger}r|\Psi^{\lambda}\rangle$$
$$= \langle\Psi^{\lambda}|p^{\dagger}s^{\dagger}rq|\Psi^{\lambda}\rangle + \delta_{qs}\langle\Psi^{\lambda}|p^{\dagger}r|\Psi^{\lambda}\rangle - \langle\Psi^{\lambda}|p^{\dagger}q|\Psi^{\lambda}\rangle\langle\Psi^{\lambda}|s^{\dagger}r|\Psi^{\lambda}\rangle$$

$$\Rightarrow -\oint \frac{d\omega}{2\pi i}\left[\chi^{\lambda}_{pq,rs}(\omega) - \chi^{\lambda=0}_{pq,rs}(\omega)\right] = P^{\lambda}_{c,pq,rs} + \Delta^{\lambda}_{pq,rs}$$

where $\Delta^{\lambda}_{pq,rs} = \langle\Psi^{\lambda}|p^{\dagger}q|\Psi^{\lambda}\rangle\langle\Psi^{\lambda}|s^{\dagger}r|\Psi^{\lambda}\rangle - \delta_{qr}\langle\Psi^{\lambda}|p^{\dagger}r|\Psi^{\lambda}\rangle - (\text{idem with } \lambda=0)$

The additional term vanishes only if the one-e density matrix is constant wrt λ.

* <u>Pseudo-hermiticity</u>:

$$\Lambda C = \omega \Delta C \qquad \Lambda^{\dagger} = \Lambda$$

$$\underbrace{\Delta^{-1}\Lambda}_{H} C = \omega C \qquad H = \begin{pmatrix} A & B \\ -B & -A \end{pmatrix}$$

H is pseudohermitian wrt Λ, i.e. $H^{\dagger} = \Lambda H \Lambda^{-1}$ (assuming Λ has an inverse)

<u>Proof</u>: $\Lambda H \Lambda^{-1} = \Lambda\Delta^{-1}\Lambda\Lambda^{-1} = \Lambda\Delta^{-1} = (\Delta^{-1}\Lambda)^{\dagger} = H^{\dagger}$

If Λ is positive definite, H has <u>real</u> eigenvalues

<u>Proof</u>: $H = \Lambda^{-1}H^{\dagger}\Lambda = \Lambda^{-1/2}\underbrace{\Lambda^{-1/2}H^{\dagger}\Lambda^{1/2}}_{M}\Lambda^{1/2}$

$M^{\dagger} = (\Lambda^{-1/2}H^{\dagger}\Lambda^{1/2})^{\dagger} = \Lambda^{1/2}H\Lambda^{-1/2} = \Lambda^{1/2}\Lambda^{-1}H^{\dagger}\Lambda\Lambda^{-1/2} = \Lambda^{-1/2}H^{\dagger}\Lambda^{1/2} = M$

H is similar to the Hermitian matrix M

* <u>Positive-definiteness</u>

in dRPA: $A^{\lambda}_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + \lambda(ia|jb)$

$B^{\lambda}_{ia,jb} = \lambda(ia|jb)$

B can be unitarily transform to the diagonal matrix $\lambda(i'a'|i'a')$ which is positive definite since the e-e interaction is positive definite. $\int f(x)\frac{1}{x-x'}f(x')dxdx' = \int (f(k))^2 \frac{4\pi}{k^2} dk > 0$

$$\begin{pmatrix} A & B \\ B & A \end{pmatrix} \xrightarrow[\text{transf}]{\text{unitary}} \begin{pmatrix} A+B & 0 \\ 0 & A-B \end{pmatrix}$$

$\left.\begin{matrix} A+B \\ A-B \end{matrix}\right\}$ are positive definite (if $\varepsilon_a - \varepsilon_i > 0$)

$\Rightarrow \begin{pmatrix} A & B \\ B & A \end{pmatrix}$ is positive definite

with exchange (RPAx), it is generally not positive definite.
TDHF

If stable minimum, the HF Hessian is positive but we can still have zero eigenvalues when breaking a continuous symmetry (such as $\hat{S}^2$) → two situations: proper and improper modes

proper → OK

improper → RPA hamiltonian not diagonalizable!

* <u>Spectral representation of the RPA matrix</u>

$$\Lambda C_n = \omega_n \Delta C_n$$

$$C_m^T \Lambda C_n = \omega_n C_m^T \Delta C_n \quad \text{and} \quad \left(C_n^T \Lambda C_m = \omega_m C_n^T \Delta C_m\right)^T$$

$$= C_m^T \Lambda C_n = \omega_m C_m^T \Delta C_n$$

$$\Rightarrow (\omega_n - \omega_m) C_m^T \Delta C_n = 0$$

so, $\boxed{\text{if } \omega_n \neq \omega_m : \quad C_m^T \Delta C_n = 0}$ orthogonality

normalisation: $\begin{cases} C_n^T \Delta C_n = X_n^T X_n - Y_n^T Y_n = 1 \\ C_{-n}^T \Delta C_{-n} = Y_n^T Y_n - X_n^T X_n = -1 \end{cases}$

$$\Lambda - \omega\Delta = \sum_n (\omega_n - \omega)\Delta C_n C_n^T \Delta + (\omega_n + \omega)\Delta C_{-n} C_{-n}^T \Delta$$

proof: * $(\Lambda - \omega\Delta)C_m = \sum_n (\omega_n - \omega)\Delta C_n \underbrace{C_n^T \Delta C_m}_{=\delta_{nm}} + (\omega_n + \omega)\Delta C_{-n} \underbrace{C_{-n}^T \Delta C_m}_{0}$

$$= (\omega_m - \omega)\Delta C_m$$

* $(\Lambda - \omega\Delta)C_{-m} = -(\omega_m + \omega)\Delta C_{-m}^T$

2

$$(\Lambda - \omega\Delta)^{-1} = \sum_n \left(\frac{C_n C_n^T}{\omega_n - \omega} + \frac{C_{-n} C_{-n}^T}{\omega_n + \omega} \right)$$

Proof:

$$(\Lambda - \omega\Delta)^{-1} (\Lambda - \omega\Delta) = \left(\sum_n \frac{C_n C_n^T}{\omega_n - \omega} + \frac{C_{-n} C_{-n}^T}{\omega_n + \omega} \right) \left(\sum_m (\omega_m - \omega) \Delta C_m C_m^T \Delta + (\omega_m + \omega) \Delta C_{-m} C_{-m}^T \Delta \right)$$

$$= \sum_n C_n C_n^T \Delta - C_{-n} C_{-n}^T \Delta = 1$$

$$(\Lambda - \omega\Delta)(\Lambda - \omega\Delta)^{-1} = \left(\sum_m (\omega_m - \omega) \Delta C_m C_m^T \Delta + (\omega_m + \omega) \Delta C_{-m} C_{-m}^T \Delta \right) \left(\sum_n \frac{C_n C_n^T}{\omega_n - \omega} + \frac{C_{-n} C_{-n}^T}{\omega_n + \omega} \right)$$

$$= \sum_n \Delta C_n C_n^T - \Delta C_{-n} C_{-n}^T = 1$$

$$1 = \sum_n C_n C_n^T \Delta - C_{-n} C_{-n}^T \Delta = \sum_n \Delta C_n C_n^T - \Delta C_{-n} C_{-n}^T$$

Proof:

$$1 C_m = \left(\sum_n C_n C_n^T \Delta - C_{-n} C_{-n}^T \Delta \right) C_m = C_m$$

$$1 C_{-m} = C_{-m}$$

$$\Rightarrow \quad 1 = \sum_n C_n C_n^T \Delta - C_{-n} C_{-n}^T \Delta \qquad \Delta^2 = 1$$

$$\Rightarrow \quad \Delta^2 = \sum_n \Delta C_n C_n^T \Delta^2 - \Delta C_{-n} C_{-n}^T \Delta^2$$

$$1 = \sum_n \Delta C_n C_n^T - \Delta C_{-n} C_{-n}^T$$