RPA step by step

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Philosophy of the talk

- less math
- physical
- historical ?

- more math
- physics gets hidden ?

add the aspect of equivalence to rCCD

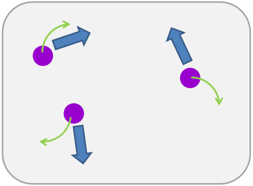
Dialects

- Different ways to derive *the* RPA equation
  - hand waving (historical)
  - physics (equation of motion)
  - chemistry (in context of ACFDT)
- The main idea :
  - RPA treats the excitations
  - via FDT, knowing all the exc. gives the correlation energy

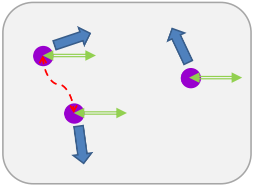
RPA : the origins

The way it was thought

- In a gaz of electron : organized oscillations
  - consequences of long-range Coulomb potential
  - explicit (LR collective behavior) AND (SR screened interaction)



$$\hat{H} = \hat{H}_{part} + \hat{H}_{inter} + \hat{H}_{field}$$



$$\hat{H} = \hat{H}_{part} + \hat{H}_{osc} + \hat{H}_{int\ part}$$

PhysRev. **82**, *625 (1951)*

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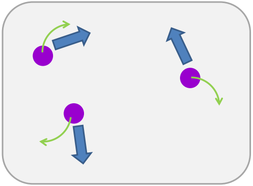

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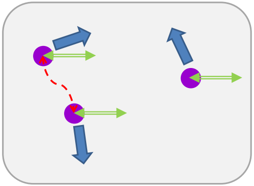


$\hat{H} = \hat{H}_{part} + \hat{H}_{osc} + \hat{H}_{int\ part}$

- Contribution from particules in phase with the oscillation
  - the rest, which have random phases , are zeroed out

PhysRev. **82**, *625 (1951)*

In the physics department...

EOM for $Q^\dagger |0\rangle = |q\rangle$: $\langle 0| \left[\delta Q, \left[H, Q^\dagger\right]\right] |0\rangle = \epsilon_{q0} \langle 0| \left[\delta Q, Q^\dagger\right] |0\rangle$

RPA : an approximation for Q

on a basis of operators $\{A_a, A_a^\dagger\}$ (creation and destruction of p-h pairs)

$$\boxed{Q = \sum_a \left[X_a A_a - Y_a A_a^\dagger\right]}$$

Fetter and Walecka, §59, 1971

In the physics department...

EOM for $Q^\dagger |0\rangle = |q\rangle$: $\langle 0| \left[\delta Q, \left[H, Q^\dagger\right]\right] |0\rangle = \epsilon_{q0} \langle 0| \left[\delta Q, Q^\dagger\right] |0\rangle$

RPA : an approximation for Q

on a basis of operators $\{A_a, A_a^\dagger\}$ (creation and destruction of p-h pairs)

$$\boxed{Q = \sum_a \left[X_a A_a - Y_a A_a^\dagger\right]}$$

$$\delta Q = \sum_a \left[\delta X_a A_a - \delta Y_a A_a^\dagger\right]$$

$$\delta X \square = \delta Y \triangle$$

$\delta X \square = 0$ and $\delta Y \triangle = 0$

$\square = 0$ and $\triangle = 0$

$$\left[A_a, \left[H, A_b^\dagger\right]\right] X_b - \left[A_a, \left[H, A_{-b}\right]\right] Y_b = \epsilon_{q0} X_b \left[A_a, A_b^\dagger\right]$$

$$-\left[A_{-a}^\dagger, \left[H, A_b^\dagger\right]\right] X_b + \left[A_{-a}^\dagger, \left[H, A_{-b}\right]\right] Y_b = \epsilon_{q0} Y_b \left[A_{-a}^\dagger, A_b\right]$$

Block Matrix Form

$$\boxed{\begin{pmatrix} A_{ab} & -B_{ab} \\ -B^*_{-a-b} & A^*_{-a-b} \end{pmatrix} \begin{pmatrix} X_b \\ Y_b \end{pmatrix} = \epsilon_{q0} \begin{pmatrix} N_{ab} & 0 \\ 0 & -N_{-a-b} \end{pmatrix} \begin{pmatrix} X_b \\ Y_b \end{pmatrix}}$$

Fetter and Walecka, §59, 1971

Range Separated Hybrid context

Constatation

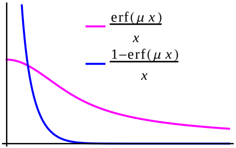
- DFT : good at short range
- Wavefunction methods : suitable at long range

The idea Mix the two :

$$\boxed{E \equiv E[v_{int}] = E[\rho] = \min_{\phi}\left\{\langle\phi|\ \hat{T} + \hat{V}_{ne} + \hat{W}_{Hx}^{lr} + \hat{W}_{c}^{lr}\ |\phi\rangle + E_{Hxc}^{sr}[n_\phi]\right\}}$$

where ϕ_0 via a Euler-Lagrange equation

with : $\hat{H}_0 = \hat{T} + \hat{V}_{ne} + \hat{V}_{Hx}^{lr} + \hat{V}_{Hxc}^{sr}$



A whole spectrum of possibilities

- srPBE+lrMP2
- srTPSS+lrCCSD
- and srDFT+lrRPA
- ...

PRA. **72**, *012510 (2005)*

Correlation energy

Remember : $E_{RSH} = \min_{\phi} \left\{ \langle\phi| \hat{T} + \hat{V}_{ne} + \hat{W}^{lr}_{Hx} + \hat{W}^{lr}_{c} |\phi\rangle + E^{sr}_{Hxc}[n_{\phi}] \right\}$

Adiabatic Connection

$$E_{\lambda} = \min_{\psi} \left\{ \langle\psi| \hat{T} + \hat{V}_{ne} + \hat{W}^{lr}_{Hx} + \lambda \hat{W}^{lr}_{c} |\psi\rangle + E^{sr}_{Hxc}[n_{\psi}] \right\}$$

PRA. **82**, *032502 (2010)*

Correlation energy

Remember : $E_{RSH} = \min_{\phi} \left\{ \langle \phi | \hat{T} + \hat{V}_{ne} + \hat{W}^{lr}_{Hx} + \hat{W}^{lr}_{c} | \phi \rangle + E^{sr}_{Hxc}[n_{\phi}] \right\}$

Adiabatic Connection

$$E_{\lambda} = \min_{\psi} \left\{ \langle \psi | \hat{T} + \hat{V}_{ne} + \hat{W}^{lr}_{Hx} + \lambda \hat{W}^{lr}_{c} | \psi \rangle + E^{sr}_{Hxc}[n_{\psi}] \right\}$$

- Integrate the derivate (Hellmann-Feynman)

$\int_0^1 \frac{\partial E_\lambda}{\partial \lambda} = E_{\lambda=1} - E_{\lambda=0} = \int_0^1 \langle \psi_\lambda | \hat{W}^{lr}_{c} | \psi_\lambda \rangle$

- Closer look on E_{RSH}

$E_{\lambda=1} = E_{RSH} + E^{lr}_{c}$

$E_{\lambda=0} = \min_{\psi} \left\{ \langle \psi | \hat{T} + \hat{V}_{ne} + \hat{W}^{lr}_{Hx} | \psi \rangle + E^{sr}_{Hxc}[n_{\psi}] \right\}$

$$\boxed{E^{lr}_{c} = \int_0^1 d\lambda \left[\langle \psi_\lambda | \hat{W}^{lr}_{c} | \psi_\lambda \rangle - \langle \phi_0 | \hat{W}^{lr}_{c} | \phi_0 \rangle \right]}$$

PRA. **82**, *032502 (2010)*

Correlation energy

Remember : $E_c^{lr} = \int_0^1 d\lambda \left[\langle\psi_\lambda| \hat{W}_c^{lr} |\psi_\lambda\rangle - \langle\phi_0| \hat{W}_c^{lr} |\phi_0\rangle\right]$

or, in space-spin coordinates :

- $E_c^{lr} = \frac{1}{2}\int d\lambda \int_{1,2,1',2'} w^{lr}_{(1,2;1',2')} \times \left[n^{lr}_{\lambda,2,(1,2;1',2')} - n^{lr}_{\lambda=0,2,(1,2;1',2')}\right]$
- $E_c^{lr} = \frac{1}{2}\int d\lambda \, Tr\left\{\mathbb{V}\mathbb{P}_{c,\lambda}\right\} = \frac{1}{2}\int d\lambda \sum_{pq,rs} \langle rq|sp\rangle \left(\mathbb{P}_{c,\lambda}\right)_{pq,rs}$

PRA. **82***, 032502 (2010)*

Correlation energy

$$\textbf{Remember :}\ E_c^{lr} = \int_0^1 d\lambda \left[\langle\psi_\lambda|\,\hat{W}_c^{lr}\,|\psi_\lambda\rangle - \langle\phi_0|\,\hat{W}_c^{lr}\,|\phi_0\rangle\right]$$

or, in space-spin coordinates :

- $E_c^{lr} = \frac{1}{2}\int d\lambda \int_{1,2,1',2'} w^{lr}_{(1,2;1',2')}\, x \left[n^{lr}_{\lambda,2,(1,2;1',2')} - n^{lr}_{\lambda=0,2,(1,2;1',2')}\right]$
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Fluctuation Dissipation Theorem

- Manipulate n_2

$$\left.\begin{array}{l} G_1(\tau)\propto n_1 \\ G_2(\tau)\propto n_2\,,\delta_{\llcorner\lrcorner}n_1 \\ \Pi(\tau)=i[G_2(\tau)-G_1(\tau)G_1(\tau)] \\ n_2=i\Pi(\tau)+n_1n_1-\delta_{\llcorner\lrcorner}n_1 \end{array}\right\} \Downarrow$$

$$\boxed{P^{lr}_{c,\lambda} = -\int_{-\infty}^{\infty}\frac{d\omega}{2\pi i}\left[\Pi^{lr}_\lambda(\omega) - \Pi^{lr}_0(\omega)\right] + \Delta}$$

PRA. **82***, 032502 (2010)*

RPA

Up to now

- from DFT to an RSH method in an ACFDT framework

$$E_c^{lr} = \frac{-1}{2} \int d\lambda \int \frac{d\omega}{2\pi} \int_{\sqcup} w_c^{lr} x \left[\Pi_\lambda^{lr}(\omega) - \Pi_0^{lr}(\omega) \right] + \Delta$$

We haven't talked about RPA yet...

This is only the framework

The approximation (seen from here)

- A solution of the Dyson equation within RPA : $G_{1,\lambda}^{lr} = G_{1,0}^{lr}$

Basically : $G_{1,\lambda}$ is constant over the adiabatic connection

$$\boxed{E_c^{lr} = \frac{-1}{2} \int d\lambda \int \frac{d\omega}{2\pi} \int_{\sqcup} w_c^{lr} x \left[\Pi_\lambda^{lr}(\omega) - \Pi_0^{lr}(\omega) \right]}$$

Matrix formulation for $\Pi_0(\omega)$ and $\Pi_\lambda(\omega)$

Lehmann Representation

$$\Pi^0(\omega) = \sum_{i,a} \left[\frac{\phi_i^*(1')\phi_a(1)\phi_a^*(2')\phi_i(2)}{\omega - \epsilon_{ai} + i\eta} + \frac{\phi_i^*(2')\phi_a(2)\phi_a^*(1')\phi_i(1)}{-\omega - \epsilon_{ai} - i\eta} \right]$$

$$\left[\Pi^0(\omega)\right]_{pq,rs} = \int_{1,2,1',2'} \phi_p(1')\phi_q^*(1)\Pi^0(\omega)\phi_r(2')\phi_s^*(2)$$

$$\Delta = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix}$$

$$\Lambda_0 = \begin{pmatrix} \boldsymbol{\epsilon} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\epsilon} \end{pmatrix}$$

$$\boxed{\Pi^0(\omega)^{-1} = \omega\Delta - \Lambda_0}$$

Matrix formulation for $\Pi_0(\omega)$ and $\Pi_\lambda(\omega)$

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$$\Lambda_0 = \begin{pmatrix} \epsilon & \mathbf{0} \\ \mathbf{0} & \epsilon \end{pmatrix}$$

$$\boxed{\Pi^0(\omega)^{-1} = \omega\Delta - \Lambda_0}$$

Bethe-Salpeter $\quad \Pi_\lambda(\omega)^{-1} = \Pi^0(\omega)^{-1} - f_{\lambda,Hxc}$

$$\boxed{\Pi_\lambda^{dRPA}(\omega)^{-1} = \Pi^0(\omega)^{-1} - \lambda\mathbb{V}}$$

$$\mathbb{V} = \begin{pmatrix} \mathbf{K} & \mathbf{K} \\ \mathbf{K} & \mathbf{K} \end{pmatrix}$$

$$K_{ia,jb} = \langle ab|ij\rangle$$

$$\boxed{\Pi_\lambda^{RPAx}(\omega)^{-1} = \Pi^0(\omega)^{-1} - \lambda\mathbb{W}}$$

$$\mathbb{W} = \begin{pmatrix} \mathbf{A}' & \mathbf{B} \\ \mathbf{B} & \mathbf{A}' \end{pmatrix}$$

$$A'_{ia,jb} = \langle ia||jb\rangle = \langle ib|aj\rangle - \langle ib|ja\rangle$$

$$B_{ia,jb} = \langle ab||ij\rangle = \langle ab|ij\rangle - \langle ab|ji\rangle$$

Matrix Formulation for $P_c = n_{2,\lambda} - n_{2,0}$

Remember : $P^{lr}_{c,\lambda} = -\int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} \left[\Pi^{lr}_{\lambda}(\omega) - \Pi^{lr}_{0}(\omega)\right]$

We only have Π_0^{-1} and Π_λ^{-1} for now ...

Spectral Representation

- Given the eigenvalues and eigenvectors :

  $(\Lambda_0 + \lambda\mathbb{F})\,\mathbb{C}_{\lambda,n} = \omega_{\lambda,n}\Delta\mathbb{C}_{\lambda,n}$, with $\mathbb{C}_{\lambda,n} = \begin{pmatrix} \mathbf{X}_{n,\lambda} \\ \mathbf{Y}_{n,\lambda} \end{pmatrix}$

- Construct Π_λ

  $$\boldsymbol{\Pi}_\lambda(\omega) = \sum_n \left\{ \frac{\mathbb{C}_{n,\lambda}\mathbb{C}^T_{n,\lambda}}{\omega - \omega_{n,\lambda} + i\eta} - \frac{\mathbb{C}_{-n,\lambda}\mathbb{C}^T_{-n,\lambda}}{\omega + \omega_{n,\lambda} - i\eta} \right\}$$

- Contour integration on the upper-half plane

  $\mathbb{P}^{RPA}_{c,\lambda} = \sum_n \left[\mathbb{C}_{-n,\lambda}\mathbb{C}^T_{-n,\lambda} - \mathbb{C}_{-n,0}\mathbb{C}^T_{-n,0}\right]$

JCTC. **7**, *3116 (2011)*

Flavors of RPA

Remember : $E_c^{lr} = \frac{1}{2}\int d\lambda Tr\left\{\mathbb{V}\mathbb{P}_{c,\lambda}\right\}$

Formally

$$E_c^{lr} = \frac{1}{2}\int d\lambda Tr\left\{\mathbb{V}\mathbb{P}_{c,\lambda}\right\} = \frac{1}{4}\int d\lambda Tr\left\{\mathbb{W}\mathbb{P}_{c,\lambda}\right\}$$

Within RPA

- $\mathbb{P}_{c,\lambda}^{RPA}$ is not fully anti-symmetric, so :

$$E_c^{\text{dRPA-I}} = \frac{1}{2}\int d\lambda Tr\left\{\mathbb{V}\mathbb{P}_{c,\lambda}^{\text{dRPA-I}}\right\}$$

- Historical one

$$E_c^{\text{dRPA-II}} = \frac{1}{2}\int d\lambda Tr\left\{\mathbb{W}\mathbb{P}_{c,\lambda}^{\text{dRPA-II}}\right\}$$

- similar to SOSEX

$$E_c^{\text{RPAx-I}} = \frac{1}{2}\int d\lambda Tr\left\{\mathbb{V}\mathbb{P}_{c,\lambda}^{\text{RPAx-I}}\right\}$$

- recently introduced

$$E_c^{\text{RPAx-II}} = \frac{1}{4}\int d\lambda Tr\left\{\mathbb{W}\mathbb{P}_{c,\lambda}^{\text{RPAx-II}}\right\}$$

- Almost as old as dRPA-I

Flavors of RPA

Remember : $(\Lambda_0 + \lambda\mathbb{F})\,\mathbb{C}_{\lambda,n} = \omega_{\lambda,n}\Delta\mathbb{C}_{\lambda,n}$

Plasmon Formulae (for dRPA-I and RPAx-II)

Given the orthonormality constraint $\mathbb{C}_{\lambda,m}^{T}\Delta\mathbb{C}_{\lambda,n} = \delta_{mn}$

$$\omega_{\lambda,n} = \mathbb{C}_{\lambda,n}^{T}\,(\Lambda_0 + \lambda\mathbb{F})\,\mathbb{C}_{\lambda,n}$$

$$\frac{d\omega_{\lambda,n}}{d\lambda} = \mathbb{C}_{\lambda,n}^{T}\mathbb{F}\mathbb{C}_{\lambda,n}$$

Flavors of RPA

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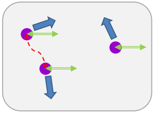
$$\frac{d\omega_{\lambda,n}}{d\lambda} = \mathbb{C}^T_{\lambda,n}\mathbb{F}\mathbb{C}_{\lambda,n}$$

Remember : $E_c^{lr} = \frac{1}{2}\int d\lambda\, Tr\left\{\mathbb{V}\sum_n\left[\mathbb{C}_{-n,\lambda}\mathbb{C}^T_{-n,\lambda} - \mathbb{C}_{-n,0}\mathbb{C}^T_{-n,0}\right]\right\}$

$$E_c^{\text{plasmon}} = \frac{1}{2}\int d\lambda \sum_n Tr\left\{\mathbb{C}_{-n,\lambda}\mathbb{F}\mathbb{C}^T_{-n,\lambda} - \mathbb{C}_{-n,0}\mathbb{F}\mathbb{C}^T_{-n,0}\right\}$$

$$\boxed{E_c^{\text{plasmon}} = \frac{1}{2}\sum_n\left\{\omega^{RPA}_{\lambda,n} - \omega^{TDA}_{\lambda,n}\right\}}$$



Equivalence to (d)rCCD

rCCD energy and amplitude

$$E_c^{rCCD} = \frac{1}{4}\sum \langle ij||ab\rangle$$

$$\begin{aligned} 0 = \langle ij||ab\rangle &+ t_{ik}^{ac}\epsilon_{ck}\delta_{bc}\delta_{jk} + \epsilon_{ck}\delta_{ac}\delta_{ik}t_{kj}^{cb} \\ &+ \langle ic||ak\rangle t_{kj}^{cb} + t_{ik}^{ac}\langle jc||bk\rangle \\ &+ t_{ik}^{ac}\langle kl||cd\rangle t_{lj}^{db} \end{aligned}$$

With the same notation

$$E_c^{rCCD} = \frac{1}{4}Tr(\mathbf{BT})$$

$$0 = \mathbf{B} + (\mathbf{A}' + \epsilon)\mathbf{T} + \mathbf{T}(\mathbf{A}' + \epsilon) + \mathbf{TBT}$$

Equivalent

- recently proven that this equation can be derived from RPA
- With the $\mathbf{T}$ found this way, $E_c^{drCCD} = E_c^{dRPA}$

Conclusion/Project

- A lot of different RPAs can be derived
  - ACFDT formulae
  - Plasmon derivation (analytic λ-integration)
  - Analytic ω-integration
  - in connexion with rCCD

- All have already been implemented (Paris/Nancy)

- The idea now (and here) :
  - Search more in the direction of RPA=rCCD
  - Derivation and Implementation of the forces