From density functional to many-body Green's function and beyond

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Acknowledgement

1. DFT calculation

- Shusuke Kasamatsu, Takeo Kato (ISSP, the University of Tokyo)

2. Many-body Green's function

- Yoshifumi Noguchi, Daichi Hirose (ISSP)

3. Tensor decomposition

- Wataru Uemura (RIKEN), Airi Kawasaki (ISSP)

1. Practical aspect of DFT simulation

Universal Hohenberg-Kohn functional may exit but…

Density functional theory (DFT)

- KS-DFT needs a reference system, which is ideally close to the target system.
  - Kinetic energy functional from independent particle model as $T_s[\rho]$ and then take the residual as the Hartree and exchange-correlation.

reference target

Adiabatic connection

$$\int_0^1 V_\lambda \, d\lambda$$

Various versions of KS-DFT

- One could use Hartree-Fock (HF) as $T[\rho] + J[\rho] - K[\rho]$, and take the residual as the correlation.
  - Conventionally, HF exchange is introduced afterwards in the exact exchange scheme.

- Likewise, one could use a Hubbard-like model to augment correlation although in practice on-site Coulomb term, U, is added afterwards in DFT+U as

$$E^{\mathrm{xc}}_{\mathrm{GGA/LDA}}[\rho] + E_{\mathrm{U}}[\rho]$$

$$E_{\mathrm{U}}[\rho] = \frac{U}{2}\sum_{i\neq j} n_i n_j - U\frac{N(N-1)}{2}$$

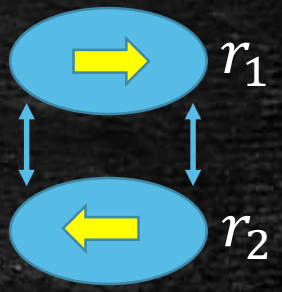
Correlation functional from adiabatic connection & fluctuation dissipation

- Nonlocal correlation functional is also added afterwards to describe the weakly interacting van der Waals system, thus

$$E^{\mathrm{xc}}_{\mathrm{GGA/LDA}}[\rho] + E^{\mathrm{c}}_{\mathrm{vdW}}[\rho] + E_{\mathrm{U}}[\rho]$$

DFT + vdW-DF + U

$$-\int_0^\infty \frac{d\omega}{2\pi}\int_0^1 d\lambda \mathrm{Tr}\left(\frac{\Delta\chi_\lambda(r_1, r_2; i\omega)}{|r_1 - r_2|}\right)$$

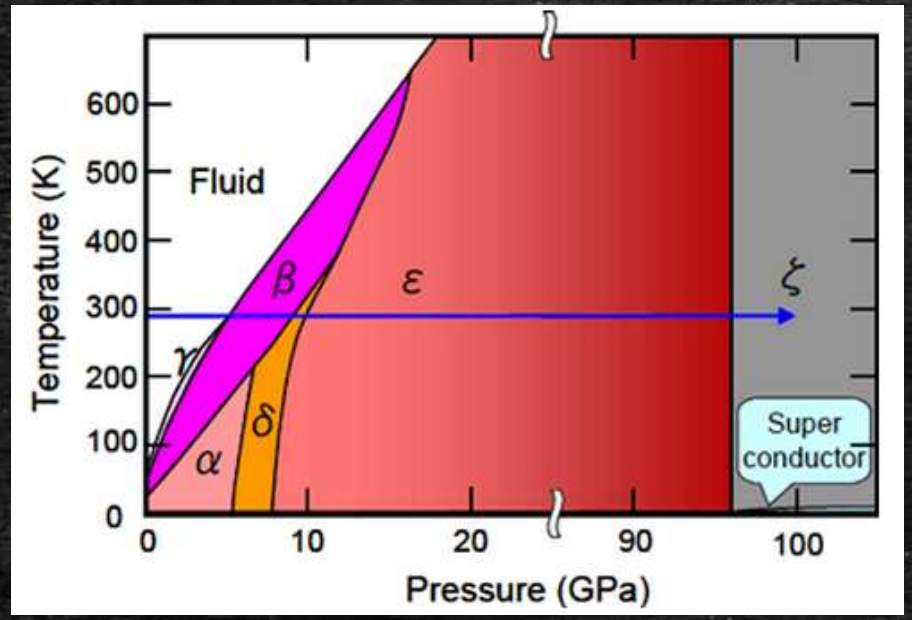


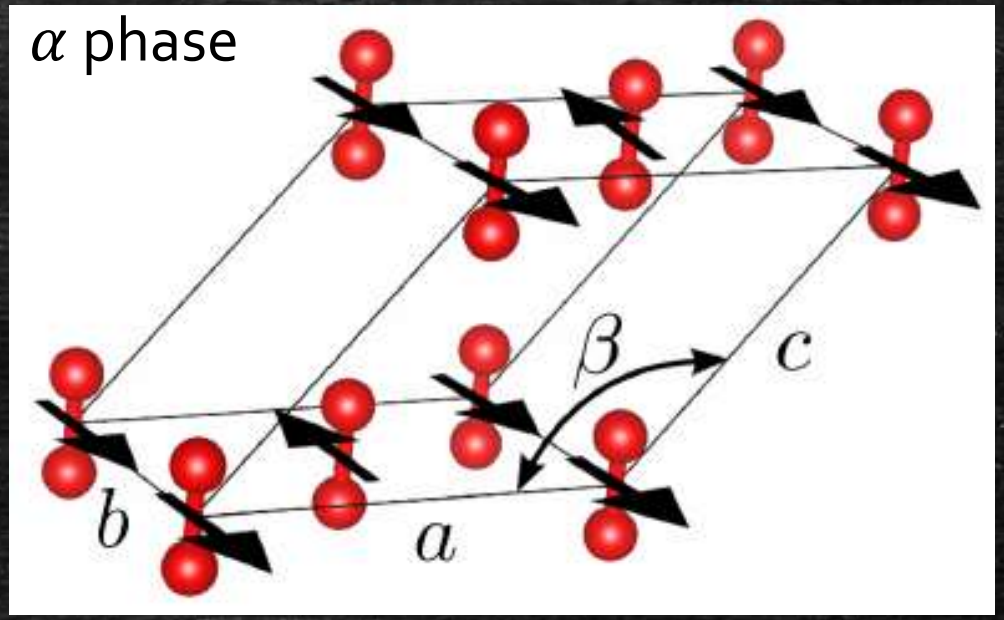
This "flexibility" is the key to practical material simulation

Example of successful application

Solid oxygen

Solid oxygen at low temperature and high pressure

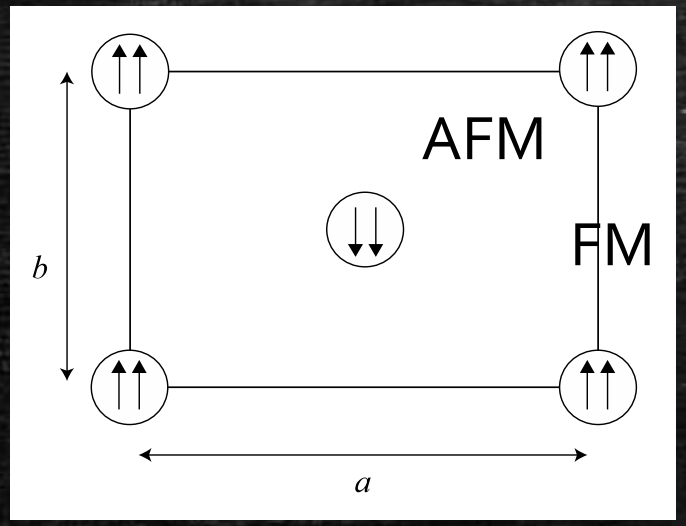




- Oxygen molecule has a spin triplet ground state
- They interact weakly via vdW and magnetic interactions

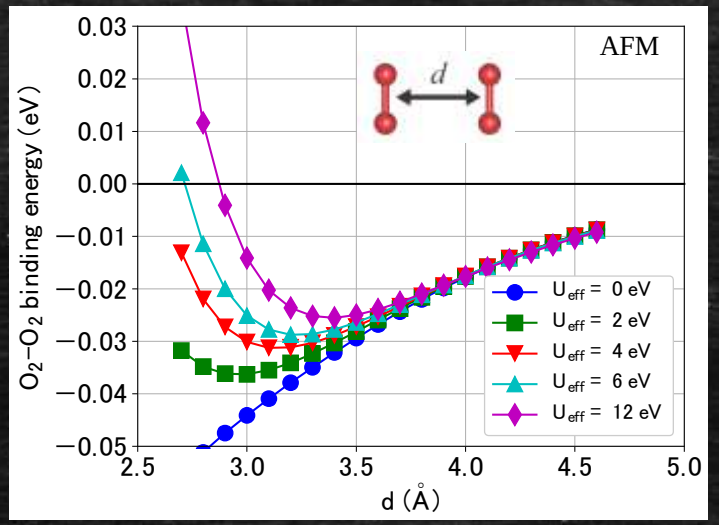
Inter-molecular interaction and U of oxygen 2p

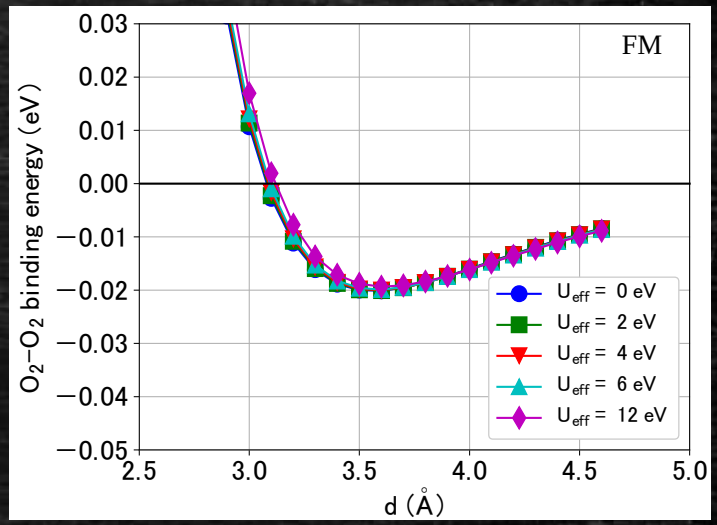
3.4Å



5.4Å

vdW-DF-optB86b (VASP)

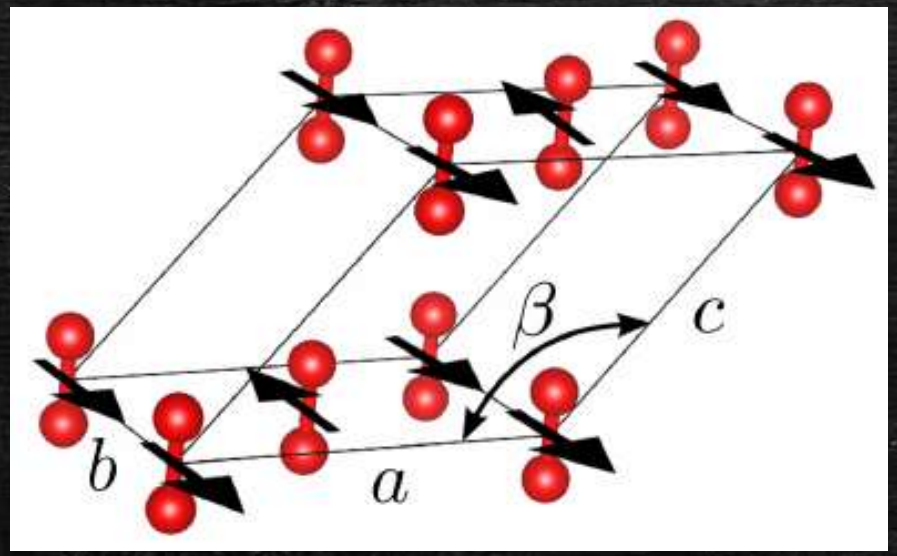




Two explanations:

- Exchange vs correlation
- Magnetic coupling $V_{\uparrow\downarrow} \simeq -\frac{t^2}{\Delta E}$

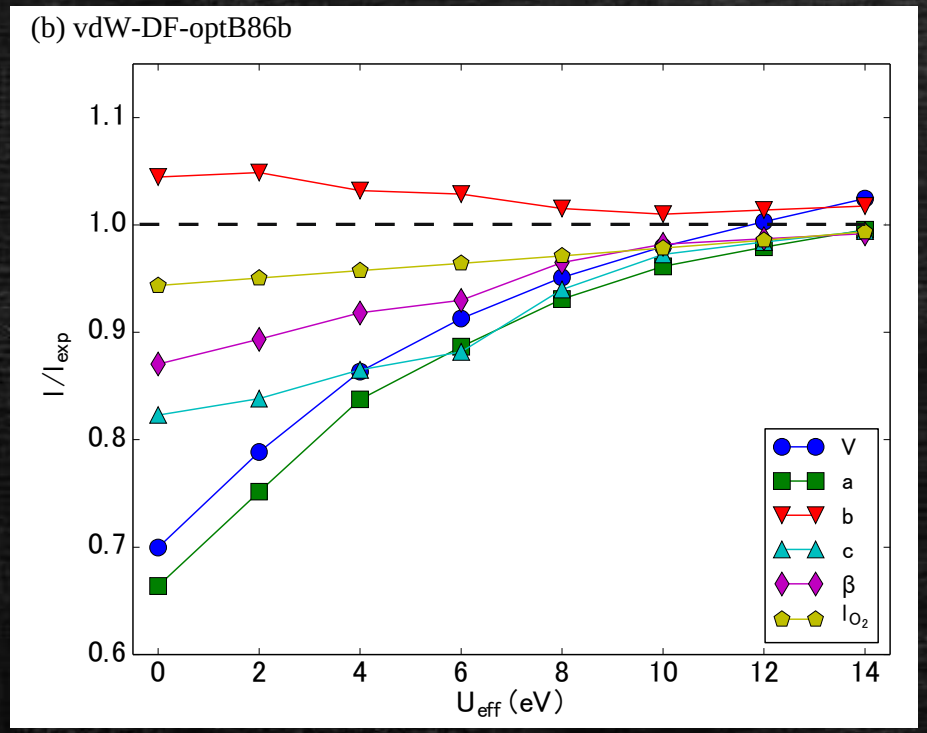
Volume and shape of the primitive cell of α phase



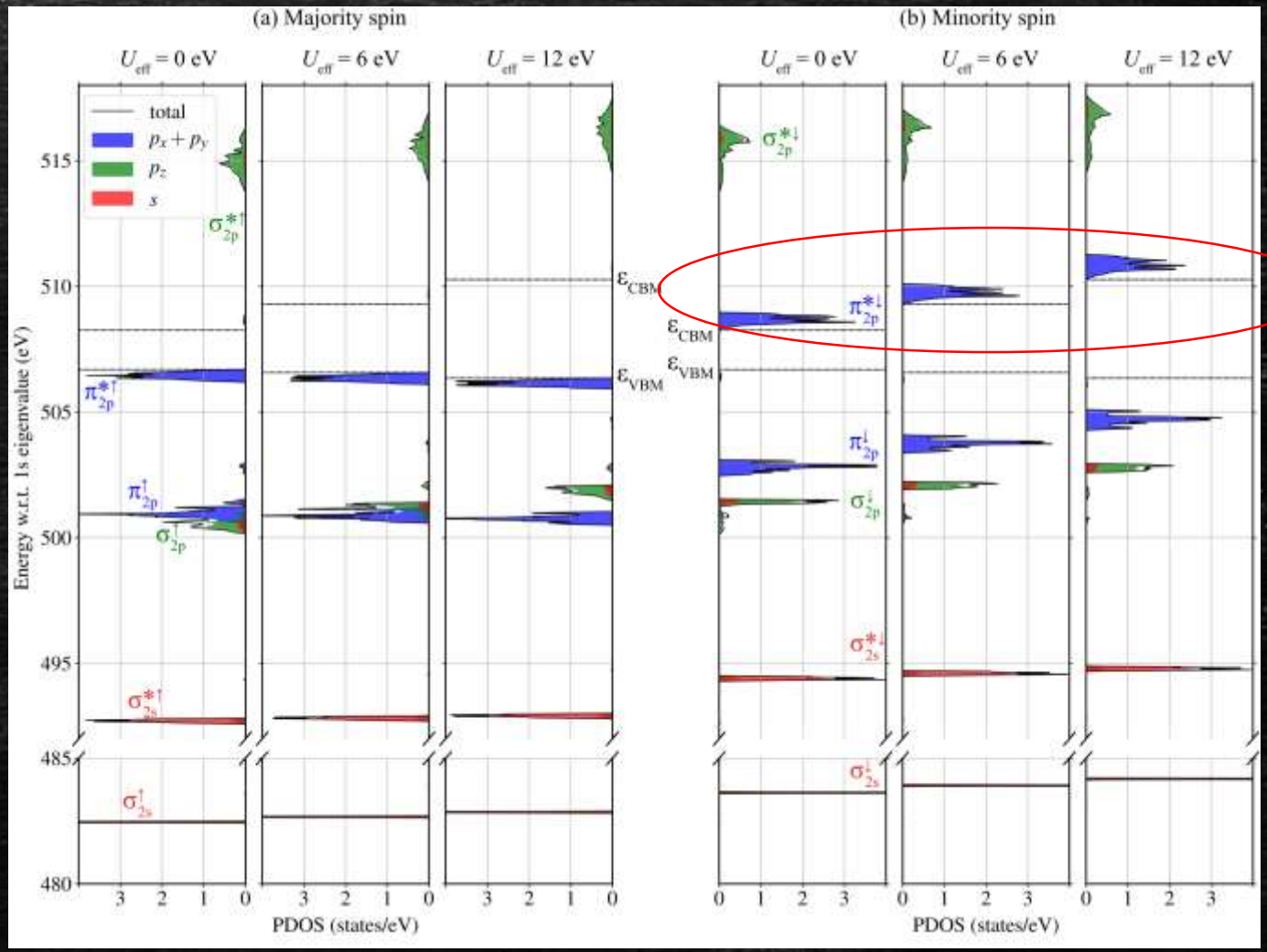
	$V(\text{Å}^3)$	$a(\text{Å})$	$b(\text{Å})$	$c(\text{Å})$	$\beta(^\circ)$	$B(\text{GPa})$
Expt.	69.5	5.4	3.4	5.1	133	~6
LSDA	42.0	3.9	3.0	4.2	119	
GGA(PBE)	75.4	4.2	4.2	4.9	119	1.2
vdW-revPBE	65.9	4.5	3.8	4.4	121	5.0
vdW-revPBE+U(5eV)	74.1	5.4	3.6	5.0	130	4.7
vdW-optB86b	48.6	3.6	3.6	4.2	115	
vdW-optB86b+U(12eV)	69.7	5.3	3.5	5.0	131	4.4
vdW-SGC	75.7	5.4	3.6	4.6	122	

S. Kasamatsu, T. Kato, OS; to appear in PRB

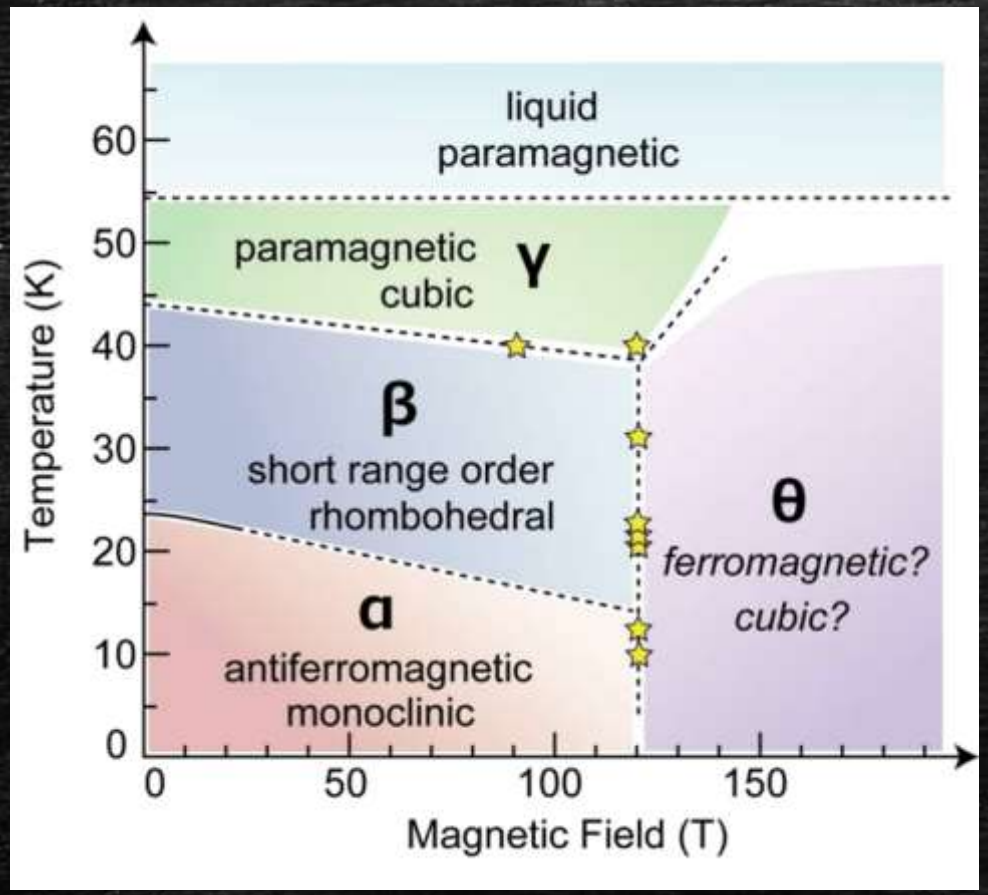
Explanation by band gap opening



$$V_{\uparrow\downarrow} \simeq -\frac{t^2}{\Delta E}$$



Prediction of new magnetic phase (θ)



Assuming a cubic structure

$$E(\theta) - E(\alpha) = -g\mu_B B_{\text{ext}}$$

$$B_{\text{ext}} \simeq 70\text{T} \leftrightarrow 120\ \text{T (expt.)}$$

T. Nomura et al. JLTP (2012)

GGA + vdW-DF + U

- This scheme happens to be appropriate for solid oxygen
- With DFT + α with *proper* physical model, there is a way to quantitatively predict a property of a material. So, it is important to advance
  - availability of various reference systems
  - availability of various exchange correlation functionals
- Challenging theme still exists in
  - Excited states
  - Strongly correlated electron systems

2. Methods for excited states

1. Time-dependent DFT
   - Generally problematic for charge-transfer and Rydberg excitations, which are crucially important for solar-cell and electroluminescence applications
2. Many-body Green's function
3. Configuration interaction (mixing) or exact diagonalization
   - Requires large memory and much CPU time

Green's function

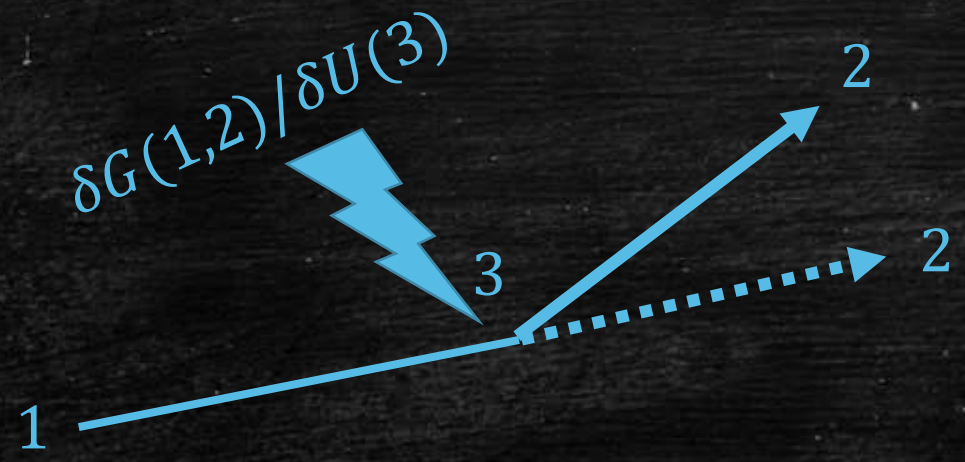
Coulombic

$$\left[i\partial_{t_1} + \frac{1}{2}\partial_{x_1}^2 - u(1)\right] G(1,2) + i\int d2V_C(1,2)\mathrm{G}(1,2;1',2') = \delta(1,1')$$

External perturbation

$$\mathrm{G}(1,3;2,3^+) = \mathrm{G}(1,2)\mathrm{G}(3,3^+) - \delta G(1,2)/\delta U(3)$$

Schwinger's trick (response to local potential)



Hartree potential & total potential

$$u^H(3) \equiv \int d3V_C(1,3)G(3,3^+)$$

$$U(3) \equiv u(3) + u^H(3)$$

Green's function

Coulombic

$$\left[i\partial_{t_1} + \frac{1}{2}\partial_{x_1}^2 - u(1)\right] G(1,2) + i\int d2 V_C(1,2)\mathrm{G}(1,2;1',2') = \delta(1,1')$$

External perturbation

$$\mathrm{G}(1,3;2,3^+) = \mathrm{G}(1,2)\mathrm{G}(3,3^+) - \delta G(1,2)/\delta U(3)$$

Schwinger's trick (response to local potential)

$$\left[i\partial_{t_1} + \frac{1}{2}\partial_{x_1}^2\right] G(1,2) - \int d2\Sigma(1,2)\mathrm{G}(2,1) = \delta(1,1')$$

$$\Sigma(1,2) = u^H(1)\delta(1,2) + i\int d43 V_C(1^+,4)\frac{\delta G(1,3)}{\delta U(4)} G^{-1}(3,2)$$

Self energy: $\Sigma^{\mathrm{H}}(1,2) + \Sigma^{\mathrm{xc}}(1,2)$

Let us now remove U and u

Let us remove U

Green's function

vertex $$\Gamma(1,2;3) \equiv -\frac{\delta G^{-1}(1,2)}{\delta U(3)} = \delta(1,2)\delta(1,3) + \frac{\delta \Sigma^{\mathrm{xc}}(1,2)}{\delta U(3)}$$

$$= \delta(1,2)\delta(1,3) + \int d4567 \frac{\delta \Sigma^{\mathrm{xc}}(1,2)}{\delta G(4,5)} G(4,6)G(7,5)\Gamma(6,7;3)$$

exchange-correlation

$$\Sigma^{\mathrm{xc}}(1,2) = i\int d34 V_C(1^+,3)\frac{\delta G(1,4)}{\delta u(3)} G^{-1}(4,2)$$

$$= -i\int d345 V_C(1^+,3)\underbrace{\frac{\delta V_C(4)}{\delta u(3)}}_{\equiv \epsilon^{-1}(4,3)} G(1,5)\Gamma(5,2;4)$$

$$\equiv W(1^+,4)$$

Let us remove U

Green's function

Dynamically screened Coulomb

$$W(1,2) \equiv \int d3 V_C(3,2) \frac{\delta V_C(1)}{\delta u(3)}$$

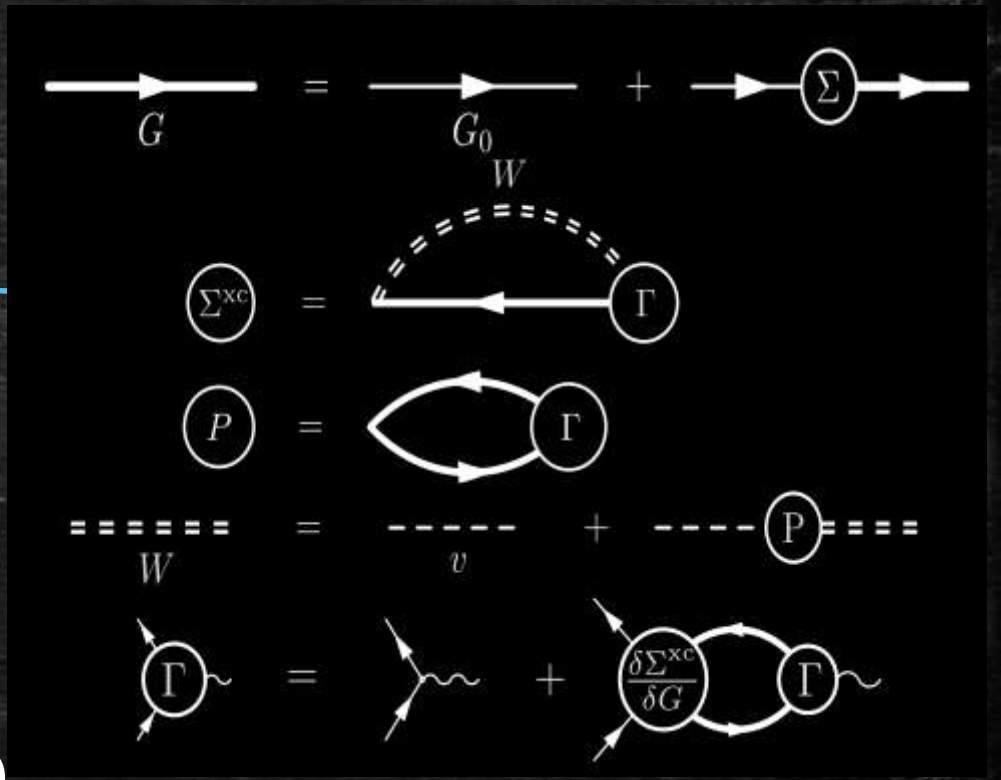
$$= V_C(1,2) + \int d345 V_C(1,4) \underbrace{\frac{\delta G(4,4^+)}{\delta U(5)}}_{\equiv P(4,5)} \underbrace{\frac{\delta U(5)}{\delta u(3)}}_{= W(5,2)} V_C(3,2)$$

Polarization

$$P(1,2) = i \int d34 G(1,3) \frac{\delta G^{-1}(3,4)}{\delta U(2)} G(4,1^+)$$

$$= -i \int d34 G(1,3) G(4,1^+) \Gamma(3,4;2)$$

Hedin's equation



$$G(1,2) = G^0(1,2) + \int d34 G^0(1,3)\Sigma(3,4)G(4,2)$$

$$\Sigma^{xc}(1,2) = i\int d34 W(1^+,3)G(1,4)\Gamma(4,2;3)$$

$$P(1,2) = -i\int d34\, G(1,3)G(4,1^+)\Gamma(3,4;2)$$

$$W(1,2) = V_C(1,2) + \int d34 V_C(1,3)P(3,4)W(4,2)$$

$$\Gamma(1,2;3) = \delta(1,2)\delta(1,3) + \int d4567 \frac{\delta\Sigma^{xc}(1,2)}{\delta G(4,5)} G(4,6)G(7,5)\Gamma(6,7;3)$$

Describes excess electron in a material

GW approximation

$$G(1,2) = G^0(1,2) + \int d34 G^0(1,3)\Sigma(3,4)G(4,2)$$

$$\Sigma^{xc}(1,2) = i\int d34 W(1^+,3)G(1,4)\Gamma(4,2;3)$$

$$\Sigma = GW$$

$$P(1,2) = -i\int d34\, G(1,3)G(4,1^+)\Gamma(3,4;2)$$

$$\mathrm{P} = GG$$

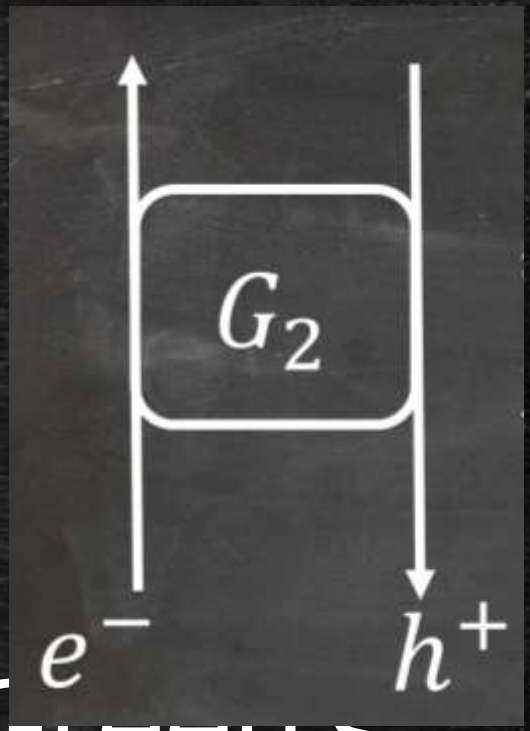
$$W(1,2) = V_C(1,2) + \int d34 V_C(1,3)P(3,4)W(4,2)$$

Random phase approx.

$$\Gamma(1,2;3) = \delta(1,2)\delta(1,3) + \int d4567 \frac{\delta\Sigma^{xc}(1,2)}{\delta G(4,5)} G(4,6)G(7,5)\Gamma(6,7;3)$$

$$\Gamma = 1$$

Self-consistent GW *vs* one-shot GW (=perturbation to Kohn-Sham)



So far discussing one-body Green's function

to describe one excess particle (electron or hole) in a material
But, photo-excitation requires two particles, electron AND hole

Bethe-Salpeter equation

Excess two particles (electron and hole)

Response to non-local external potential $u(1,2)$

$$\underbrace{\frac{\delta G(1,1')}{\delta u(2,2')}}_{\equiv L(1,1',2,2')} = G(1,2)G(2',1') + \int d33'44' G(1,3)G(3',1') \underbrace{\frac{\delta \Sigma(3,3')}{\delta \mathrm{G}(4,4')}}_{\equiv K(3,3',4,4')} \frac{\delta \mathrm{G}(4,4')}{\delta u(2,2')}$$

Bethe-Salpeter equation

Excess two particles (electron and hole)

Response to non-local external potential $u(1,2)$

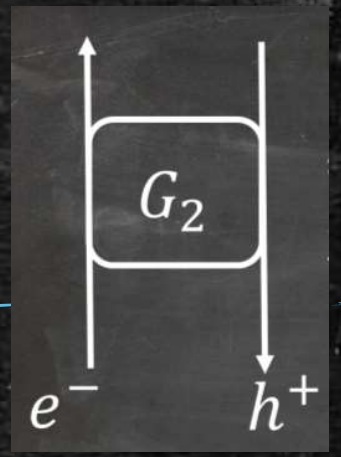
$$\underbrace{\frac{\delta G(1,1')}{\delta u(2,2')}}_{\equiv L(1,1',2,2')} = G(1,2)G(2',1') + \int d33'44' G(1,3)G(3',1') \underbrace{\frac{\delta \Sigma(3,3')}{\delta G(4,4')}}_{\equiv K(3,3',4,4')} \frac{\delta G(4,4')}{\delta u(2,2')}$$

e-h interaction kernel

Can be similarly formulated by applying GWA

$$\begin{cases} K^{x}(3,3',4,4') = \delta(3,3')\delta(4,4')V_C(3,4) & \text{Bare Coulomb exchange} \quad \text{repulsive} \\ K^{d}(3,3',4,4') = -\delta(3,4)\delta(3'4')W(3^+,3') & \text{Screened direct} \quad \text{attractive} \\ K'(3,3',4,4') = -G(3,3')\dfrac{\delta W(3,3^+)}{\delta G(4,4')} & \end{cases}$$

Bethe-Salpeter equation



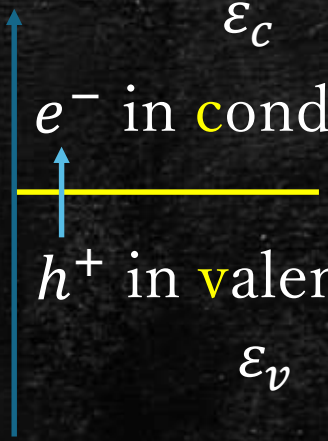
$$L(1,1';2,2',\omega) = i\sum_i \left[\frac{\chi_i(x_1,x_1')\chi_i^*(x_2',x_2)}{\omega-\Omega_i} - \frac{\chi_i(x_2,x_2')\chi_i^*(x_1',x_1)}{\omega+\Omega_i}\right]$$

$$\chi_i(x,x') \equiv -\langle \Psi_{\mathrm{gr}}|\psi^\dagger(x')\psi(x)|\Psi_i\rangle = \sum_v\sum_c A_{vc}^i\psi_c(x)\psi_v^*(x') + B_{vc}^i\psi_c(x)\psi_v^*(x')$$

Physical meaning of GW+BSE & link to TD-DFT

$$L(1,1';2,2',\omega) = i\sum_i \left[\frac{\chi_i(x_1,x_1')\chi_i^*(x_2',x_2)}{\omega-\Omega_i} - \frac{\chi_i(x_2,x_2')\chi_i^*(x_1',x_1)}{\omega+\Omega_i}\right]$$

$$\chi_i(x,x') \equiv -\langle\Psi_{\mathrm{gr}}|\psi^\dagger(x')\psi(x)|\Psi_i\rangle = \sum_v\sum_c A_{vc}^i\psi_c(x)\psi_v^*(x') + \underbrace{B_{vc}^i\psi_c(x)\psi_v^*(x')}_{=0 \text{ under TDA}}$$



$$(\varepsilon_c-\varepsilon_v)A_{cv}^i + \textstyle\sum_{v'c'}\langle vc|K|v'c'\rangle A_{v'c'}^i = \Omega_i A_{cv}^i$$

equivalent to

$$|\Psi_i\rangle = \sum_v\sum_c A_{vc}^i\hat{a}_v^\dagger\hat{a}_c^\dagger|0\rangle$$ Exciton wave function

Comparison with TD-DFT linear response

$$(E_c - E_v)A_{vc} + \sum_{v'c'} K^{AA}_{vc,v'c'}(\Omega)A_{v'c'} + \sum_{v'c'} K^{AB}_{vc,v'c'}(\Omega)B_{v'c'} = \Omega A_{vc}$$

$$(E_c - E_v)B_{vc} + \sum_{v'c'} K^{BA}_{vc,v'c'}(\Omega)A_{v'c'} + \sum_{v'c'} K^{BB}_{vc,v'c'}(\Omega)B_{v'c'} = -\Omega B_{vc}$$

$$K^{AA}_{vc,v'c'}(\Omega) = i\int d3456\psi_v(x_4)\psi^*_c(x_3)K(35,46,\Omega)\psi^*_{v'}(\mathrm{x}_5)\psi_{c'}(x_6)$$

$$K^{AB}_{vc,v'c'}(\Omega) = i\int d3456\psi_v(x_4)\psi^*_c(x_3)K(35,46,\Omega)\psi^*_{v'}(\mathrm{x}_6)\psi_{c'}(x_5)$$

$K_{vc,v'c'} \leftrightarrow V_C + K_{\mathrm{xc};vc,v'c'}(\Omega)$ Linear response TD-DFT derived by Casida

GW + Bethe-Salpeter equation (BSE) for excited states

- GW is Hedin's equation with "diagonal" vertex approximation
- It can be solved either self-consistently or starting from DFT-KS.
  - The latter is called one-shot GW or G_0W_0. ->Many-body perturbation theory.
- G_0W_0 +BSE works fine for delocalized states but does not for systems with localized states.

	in eV	G_0W_0+BSE, G_0W_0	Expt. (EOM-CCSD)
N_2	E_{ex}	7.9	9.31(9.47)
	E_{IP}	15.4	15.6(16.7)
CO	E_{ex}	7.7	8.51(8.62)
	E_{IP}	13.9	14.0(15.1)
H_2O	E_{ex}	6.4	7.40(7.66)
	E_{IP}	12.7	12.6(13.9)

G_0W_0 error enhanced in BSE

D. Hirose, Y. Noguchi, OS; PRB(2015)

GW and BSE for small molecules

	in eV	G_0W_0+BSE, G_0W_0	Expt. (EOM-CCSD)
N_2	E_{ex}	7.9	9.31(9.47)
	E_{IP}	15.4	15.6(16.7)
CO	E_{ex}	7.7	8.51(8.62)
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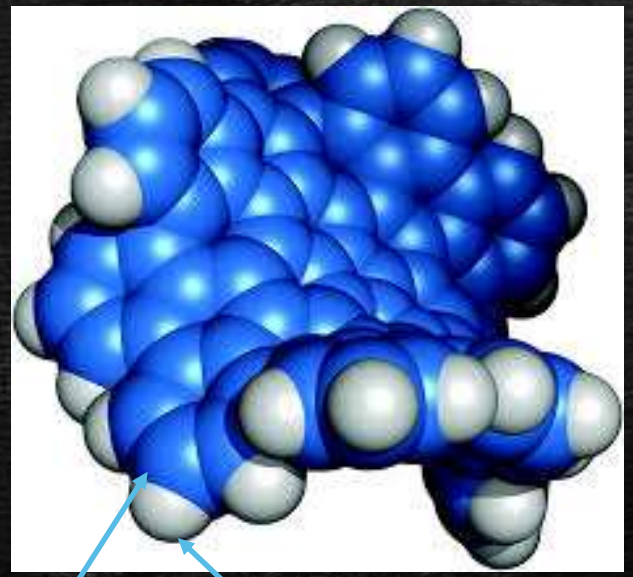
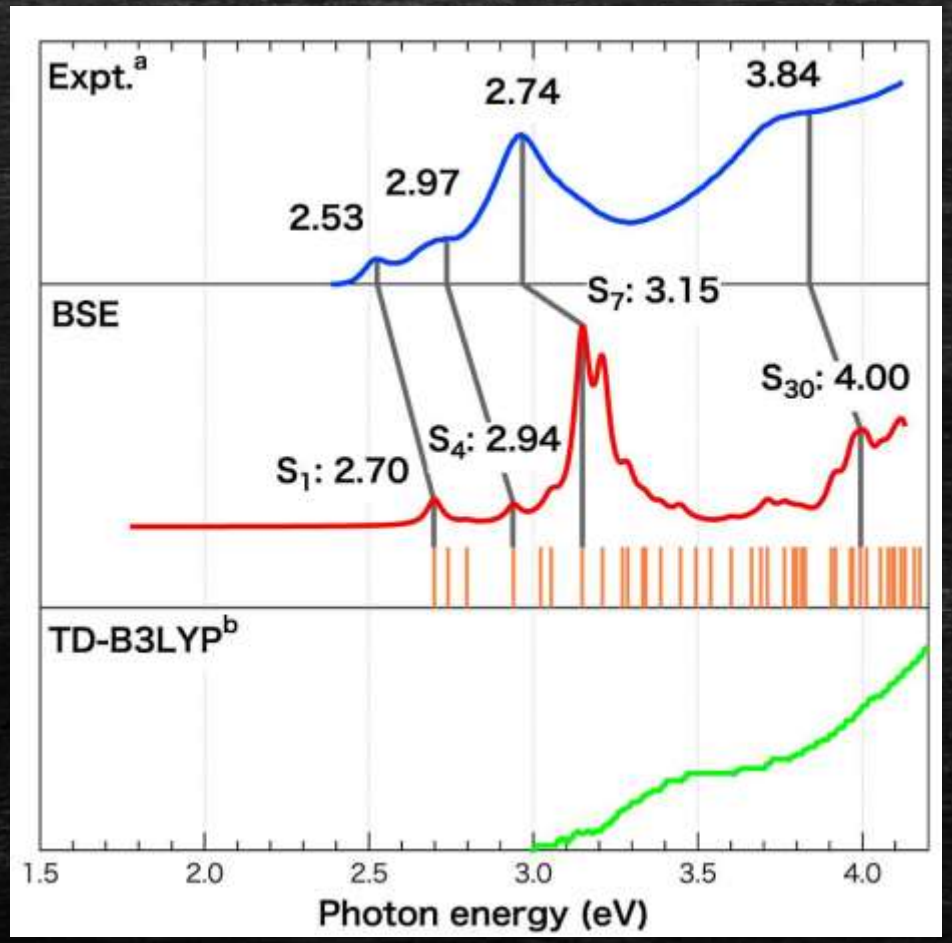
G_0W_0 error enhanced in BSE

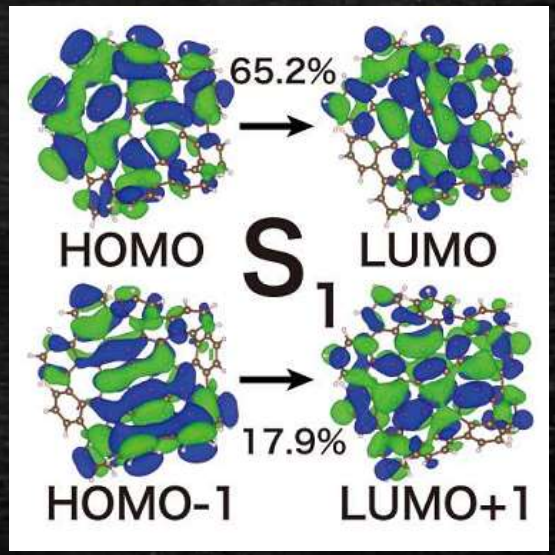
D. Hirose, Y. Noguchi, OS; PRB(2015)

Photo-absorption spectrum of warped nanographene



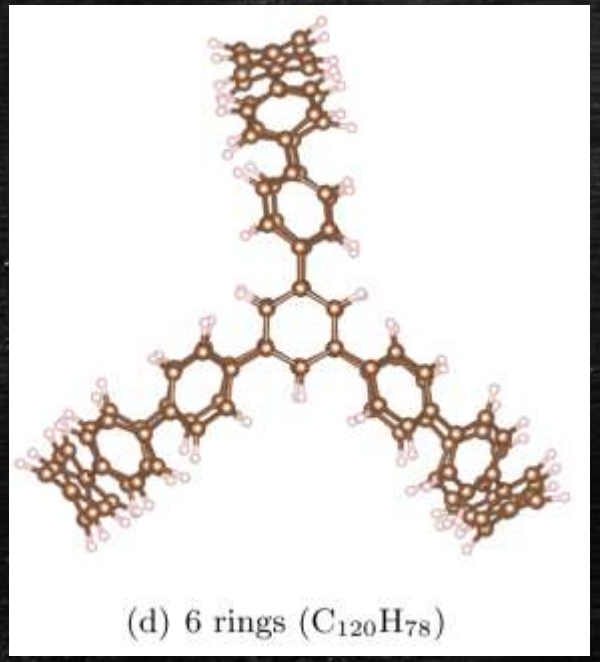


$$\frac{4\pi e^2}{\omega^2}\sum_i \left|\langle \Psi_{\mathrm{gr}}|z|\Psi_i\rangle\right|^2 \delta\left(\omega-\Omega_i\right)$$

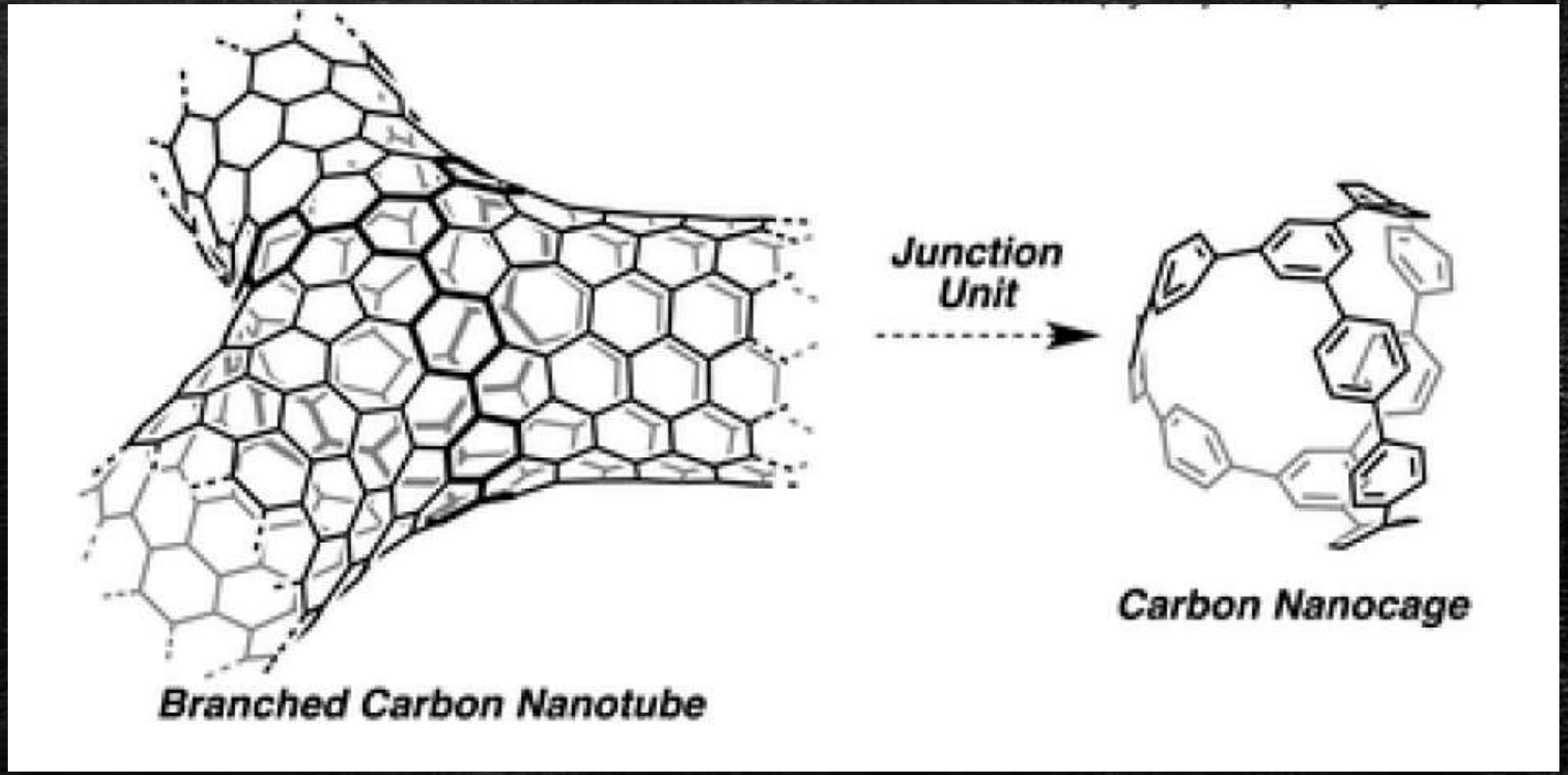


Y. Noguchi, OS; JCP(2015)

~200 atoms are the target of G_0W_0-BSE simulation

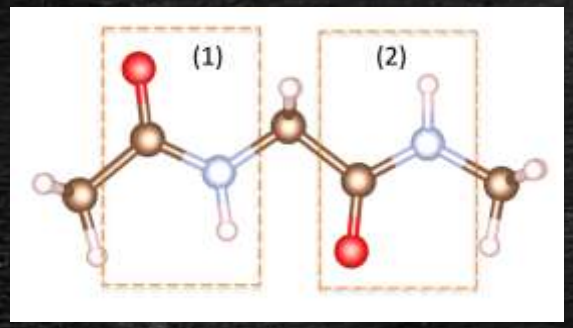


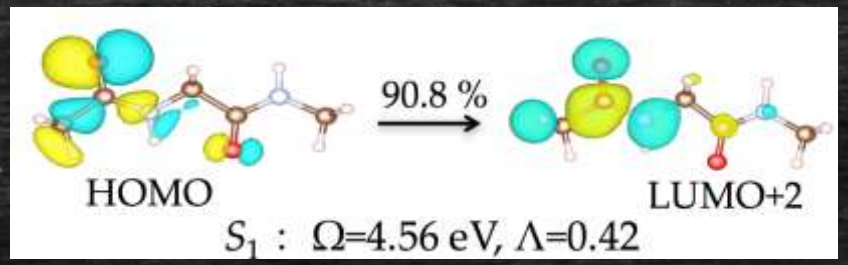
(d) 6 rings ($C_{120}H_{78}$)



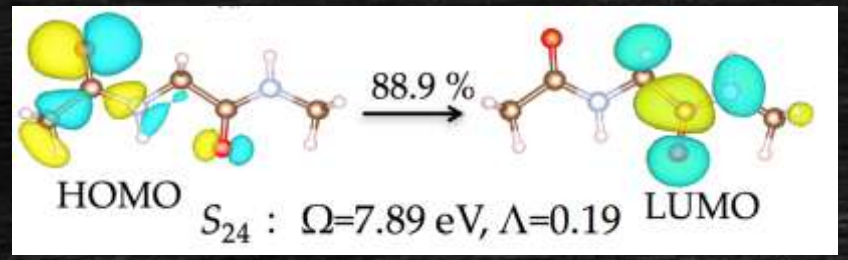
D. Hirose, Y. Noguchi, OS; JCP(2017)

Types of exciton of a model dipeptide

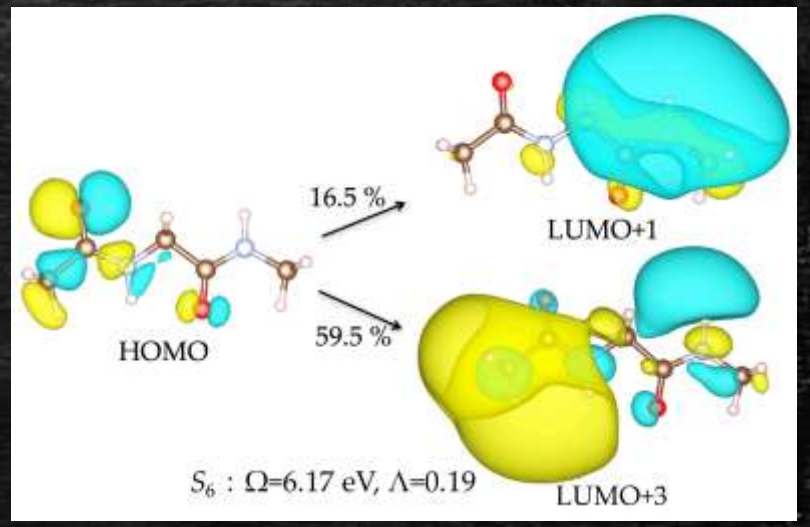




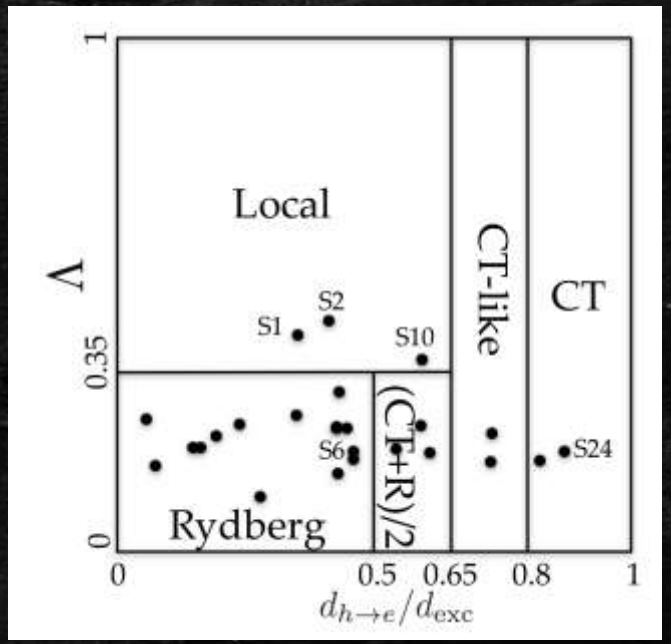
local



charge transfer (CT)



Rydberg



e-h overlap

e-h distance

$$\Psi(x,x') = \sum_v \sum_c A_{vc}^i \psi_c(x) \psi_v^*(x')$$

Excited states from N-particle Green's function

- Excess particles, e^- and h^+, are calculated by N particle Green's function method. Currently N=1 and 2, so that the two-electron excitation (N=4) is a future target.
- GW and one-shot approximations have so far been popular, but self-consistent GWΓ calculations are launched.
- Strongly correlated systems require handling of complicated vertex, Γ, which is too demanding.
- Resulting exchange-correlation self-energy will provide a hint to construct the TD-DFT exchange-correlation kernel.

3. Strongly correlated electrons

from wave function theory

Strongly correlated systems

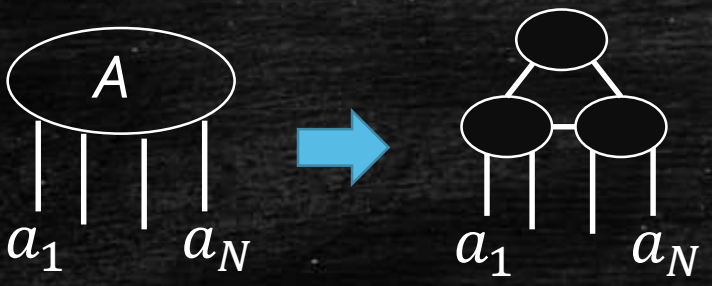
- It generally requires non-perturbative approach.
- Ideally, reference systems of strong correlation are preferable
  - embedding schemes like DFT + DMFT (dynamical mean field theory) assume local correlation
- Configuration interaction may be more advantageous than
  - quantum Monte Carlo --- statistical fluctuation
  - many-body Green's function --- infinite diagrams.

How to describe coefficient of configuration interaction

- CI using antisymmetric tensor of order N

$$|\Psi\rangle = \sum_{a} A_{a_1,\cdots,a_N}\ \hat{c}^{\dagger}_{a_1} \cdots \hat{c}^{\dagger}_{a_N}|0\rangle$$

$_M C_N$: curse of dimension



curse of nonlinearity

- CI-coef. using tensor product

$$\sum_{\{b\}} A^{b_1,\cdots,b_p}_{a_1,\cdots,a_n} \otimes A^{b_{p+1},\cdots,b_{p+q}}_{a_{n+1},\cdots,a_{n+m}} \otimes \cdots$$

Data compression using tensor decomposition

30dB

original PCP CP

jpeg2k Mjpeg2k jpeg

A. T. Mahfoodh, IEEE (2013)

CANDECOMP/PARAFAC (CP)

$$T_{abc} = \sum_{\lambda} A_a^{\lambda} B_b^{\lambda} C_c^{\lambda}$$

Let us consider

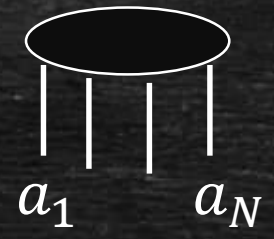
Data compression (encoding) of WF

leaving aside complexity of the decoding

(Symmetric) tensor decompositions

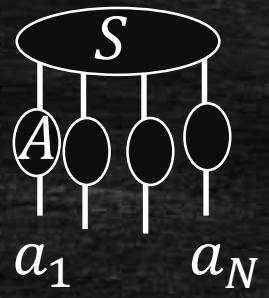
CANDECOMP/PARAFAC (CP)

$$T_{a_1 a_2 \cdots a_N} = \sum_{\lambda} A^{\lambda}_{a_1} A^{\lambda}_{a_2} \cdots A^{\lambda}_{a_N}$$



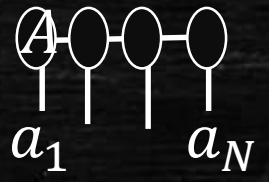
Tucker

$$T_{a_1 a_2 \cdots a_N} = \sum_{\lambda} S_{\lambda_1 \cdots \lambda_N} A^{\lambda_1}_{a_1} A^{\lambda_2}_{a_2} \cdots A^{\lambda_N}_{a_N}$$



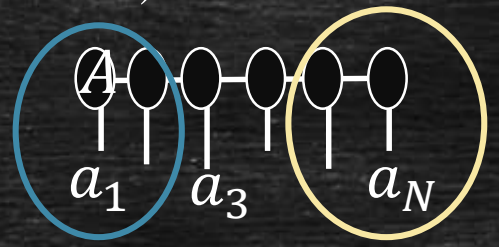
Tensor train (Matrix product)

$$T_{a_1 a_2 \cdots a_N} = \sum_{\lambda} A^{\lambda_1}_{a_1} A^{\lambda_1 \lambda_2}_{a_2} \cdots A^{\lambda_{N-1}}_{a_N}$$



WF encoding in density matrix renormalization group

Tensor train (Matrix product)



$$T_{a_1 a_2 \cdots a_N} = \sum_{\lambda} A^{\lambda_1}_{a_1} A^{\lambda_1 \lambda_2}_{a_2} A^{\lambda_2 \lambda_3}_{a_3} A^{\lambda_3 \lambda_4}_{a_4} A^{\lambda_4 \lambda_5}_{a_5} \cdots A^{\lambda_{N-1}}_{a_N}$$

$$\bar{A}^{\lambda_2}_{a_1 a_2} \qquad \bar{A}^{\lambda_4}_{a_5 \cdots a_N}$$

$$= \sum_{\mu \in \mathrm{All}} U^{\lambda_2}_{a_1 \mu} e^{\lambda_2}_{\mu} V^{\lambda_2}_{a_2 \mu} \simeq \sum_{\mu=1}^{D} U^{\lambda_2}_{a_1 \mu} e^{\lambda_2}_{\mu} V^{\lambda_2}_{a_2 \mu}$$

Iteratively reducing the degrees of freedom

Tensor decompositions in terms of pairs

1. Decomposition of Levi-Civita (permutation tensor)

$$\epsilon_{a_1,\cdots a_N} = \sum_{\sigma \in S_N} \mathrm{sgn}(\sigma)\, \epsilon_{\sigma(a_1),\sigma(a_2)} \cdots \epsilon_{\sigma(a_{N-1}),\sigma(a_N)} \equiv \mathrm{Pf}(\epsilon)_{a_1,\cdots a_N}$$

2. Tensorization of an antisymmetric matrix A using Pfaffian

$$\mathrm{Pf}(A)_{a_1,\cdots a_N} \Leftarrow \sum_{\sigma \in S_N} \mathrm{sgn}(\sigma)\, A_{\sigma(a_1),\sigma(a_2)} \cdots A_{\sigma(a_{N-1}),\sigma(a_N)} = \overbrace{A \otimes A \cdots \otimes A}^{\text{N/2 times}}$$

3. General antisymmetric tensor can be decomposed using matrices as

$$A_{a_1,\cdots a_N} = \sum_{i=1}^{\text{Rank}} \mathrm{Pf}(A^i)_{a_1,\cdots a_N} = \overbrace{A^1 \otimes \cdots \otimes A^1}^{\text{N/2 times}} + \overbrace{A^2 \otimes \cdots \otimes A^2}^{\text{N/2 times}} + \cdots$$

CP decomposition

Meaning of the tensor decompositions

1. Antisymmetrized geminal powers (AGP) in canonical representation

$$\sum_a \epsilon_{a_1,\cdots a_N}\, \hat{c}^\dagger_{a_1} \cdots \hat{c}^\dagger_{a_N} |0\rangle = \left(\epsilon_{ab} \hat{c}^\dagger_a \hat{c}^\dagger_b\right)^{N/2} |0\rangle$$

2. General AGP = BCS, HF-Bogoliubov, or GCM with fixed N

$$\sum_a \mathrm{Pf}(A)_{a_1,\cdots a_N}\, \hat{c}^\dagger_{a_1} \cdots \hat{c}^\dagger_{a_N} |0\rangle = \left(A_{ab} \hat{c}^\dagger_a \hat{c}^\dagger_b\right)^{N/2} |0\rangle \equiv \hat{A}^{N/2} |0\rangle$$

3. Linear combination of AGP (AGP-CI)

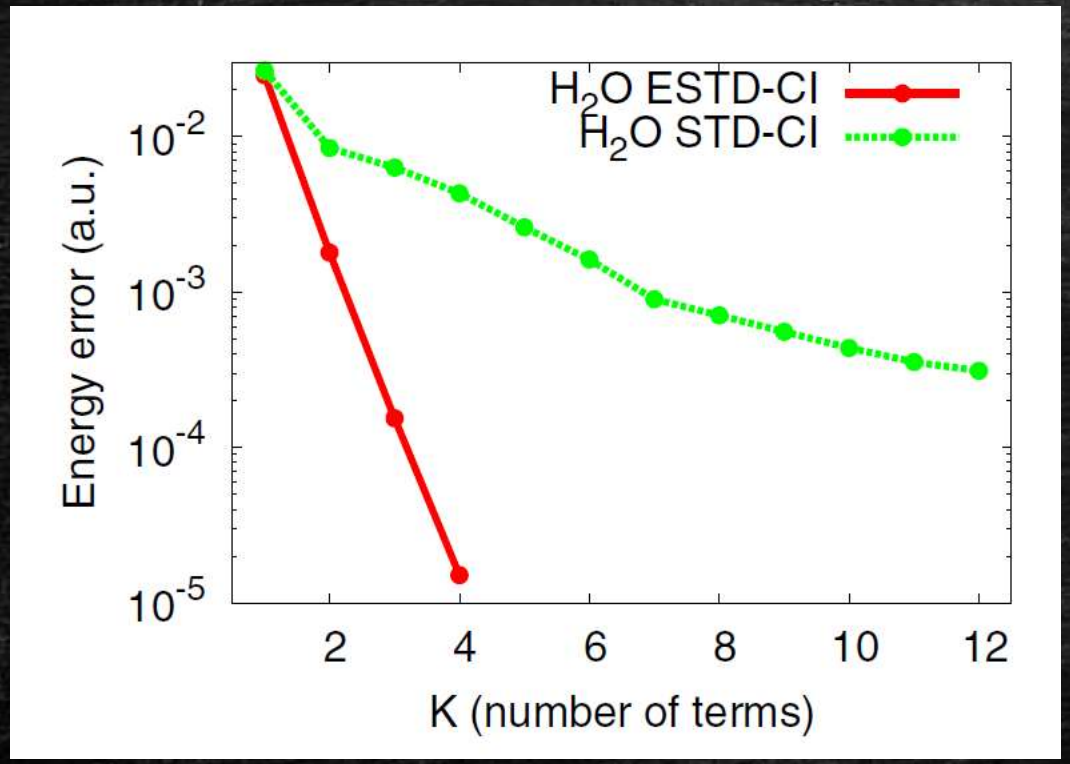
$$\sum_i \sum_a \mathrm{Pf}(A^i)_{a_1,\cdots a_N}\, \hat{c}^\dagger_{a_1} \cdots \hat{c}^\dagger_{a_N} |0\rangle = \sum_i \left(A^i_{ab} \hat{c}^\dagger_a \hat{c}^\dagger_b\right)^{N/2} |0\rangle \equiv \sum_i \left(\hat{A}^i\right)^{N/2} |0\rangle$$

cf. Theory of Fermion pairs

- Interacting boson model (nuclear physics)
- Valence shell electron pair repulson theory, GVB,,, (chemistry)

AGP-CI of a water molecule

Uemura, Kasamatsu & OS, PRA (2015)



$$\sum_{i=1}^{K}\left(\sum_{ab} A_{ab}^{i}\hat{c}_a^{\dagger}\hat{c}_b^{\dagger}\right)^{N/2}|0\rangle$$

STO-3G (Gaussian type atomic orbital basis

A's are fully optimized (non-perturbative)

4 terms are sufficient to converge the total-energy

Approximate tensor rank = 4

Property of AGP $|\Psi^{AGP}\rangle = \hat{A}^{N/2}|0\rangle \equiv |A\rangle$

- A mean field theory of the pair, which is exact for a two-body system
- Closely related to BCS, HFB & GCM (nuclear physics)

$$|\Psi^{BCS}\rangle = \exp(\hat{A})|0\rangle \qquad |\Psi^{AGP}\rangle = \exp(\hat{A}t)|0\rangle\Big|_{t^{N/2}}$$

- 1st order density matrix is related to the 2nd order one (Onishi formula)

$$\frac{\langle B|\hat{c}_n^\dagger \hat{c}_m|A\rangle}{\langle B|A\rangle} = \left[\left(1+AB^H\right)^{-1}AB^H\right]_{mn}$$

$$\frac{\langle B|\hat{c}_p^\dagger \hat{c}_q^\dagger \hat{c}_s \hat{c}_r|A\rangle}{\langle B|A\rangle} = \frac{\langle B|\hat{c}_p^\dagger \hat{c}_r|A\rangle}{\langle B|A\rangle}\frac{\langle B|\hat{c}_q^\dagger \hat{c}_s|A\rangle}{\langle B|A\rangle} - \frac{\langle B|\hat{c}_q^\dagger \hat{c}_r|A\rangle}{\langle B|A\rangle}\frac{\langle B|\hat{c}_p^\dagger \hat{c}_s|A\rangle}{\langle B|A\rangle} + \left[\left(1+AB^H\right)^{-1}A\right]_{rs}\left[B^H\left(1+AB^H\right)^{-1}\right]_{qp}$$

AGP + DFT = possible alternative to Kohn-Sham

- Kohn-Sham theory takes non-interacting electron system as the reference and relate the density (1st order DM) to the interaction energy not included in HF (2nd order DM).

$$E_{\mathrm{xc}}(\mathrm{HF}) \rightarrow E_{\mathrm{xc}}(\mathrm{AGP})$$

Similarly,

- Taking AGP-reference will be another direction to go although unsuccessful yet as far as I know.
- Will be more advantageous if an interacting AGP theory is available.

Theory of interacting AGP

- AGP-CI $|\Psi\rangle = \left[\hat{A}^{(1)}\hat{A}^{(1)}\cdots\hat{A}^{(1)} + \hat{A}^{(2)}\hat{A}^{(2)}\cdots\hat{A}^{(2)} + \cdots\right]|0\rangle$
- "Different geminal for different pair" as alternative symmetric decomposition

$$|\Psi\rangle = \hat{A}^{(1)}\hat{A}^{(2)}\cdots\hat{A}^{(N/2)}|0\rangle$$

Waring decomposition into non-interacting AGP's

$$= \left[\hat{B}^{(1)}\hat{B}^{(1)}\cdots\hat{B}^{(1)} + \hat{B}^{(2)}\hat{B}^{(2)}\cdots\hat{B}^{(2)} + \cdots\right]|0\rangle$$

$$\hat{B}^{(i)} \equiv c_{i1}\hat{A}^{(1)} + c_{i2}\hat{A}^{(2)} + \cdots + c_{iN/2}\hat{A}^{(N/2)}$$

Waring decomposition of homogeneous polynomial

$$p_M(x, y, \cdots, z) \equiv \sum_{n_1 \cdots n_N}^{n_1+\cdots+n_N=M} C_{n_1,\cdots n_N} x^{n_1} \cdots z^{n_N}$$

$$p_M(x, y, \cdots, z) = \sum_{\lambda}^{\text{rank}} a^{\lambda} \left(c_1^{\lambda} x + c_2^{\lambda} y + \cdots + c_N^{\lambda} z\right)^M$$

$$\text{rank} < \frac{{}_{M+N}C_M}{\text{N+1}} \equiv \text{generic rank}$$

ex.

$$xyz = \frac{(x+y+z)^3}{24} - \frac{(x+y-z)^3}{24} - \frac{(x-y+z)^3}{24} + \frac{(x-y-z)^3}{24}$$

Extension of “different geminal for different pair”

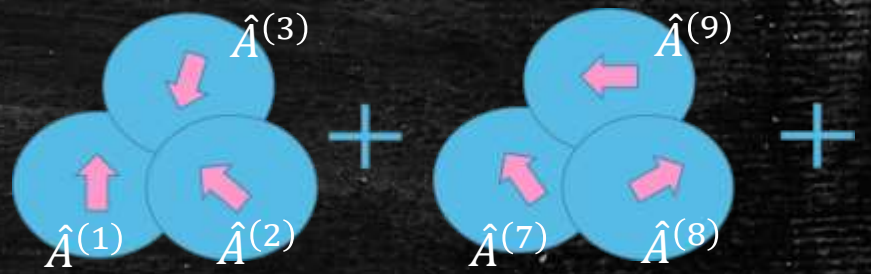
- An extension using surplus geminals and a homogeneous polynomial

$$|\Psi\rangle = \sum_{i_1<i_2\cdots<i_{N/2}<M} \hat{A}^{(i_1)}\hat{A}^{(i_2)}\dots\hat{A}^{(i_{N/2})}|0\rangle$$

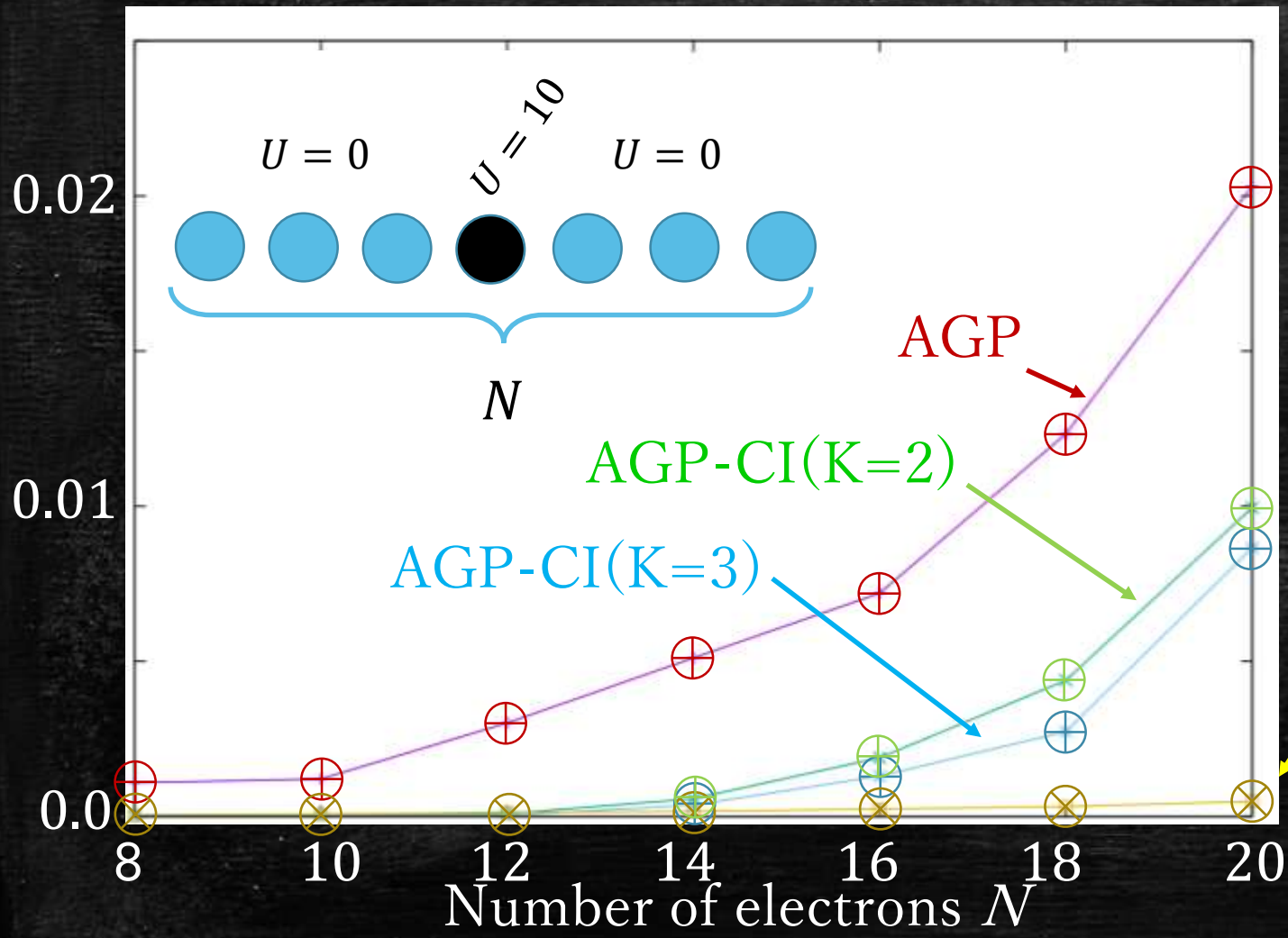
$$\equiv e_N\left(\hat{A}^{(1)},\cdots,\hat{A}^{(M)}\right)|0\rangle$$

Elementary symmetric polynomial of A’s

$$e_1(x,y,z) = x+y+z$$
$$e_2(x,y,z) = xy+yz+zx$$



1D Anderson single-impurity model (U=10)



AGP augmented by the 4-body correlation term at the impurity site i

$$|\Psi\rangle = (\hat{F}^2 + \hat{G})\hat{F}^{N-2}|0\rangle$$

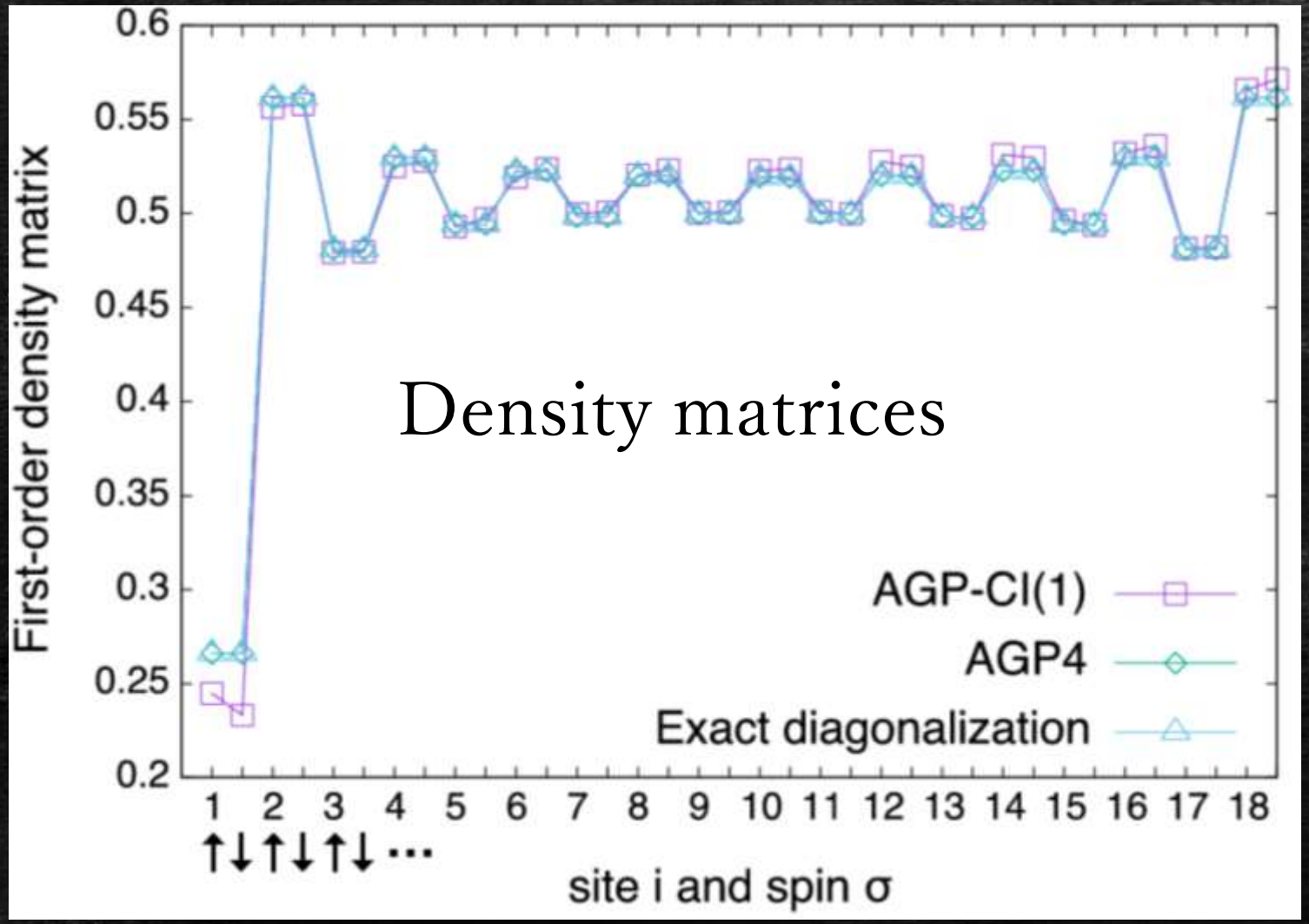
$$\hat{F} = \sum_{ab} F_{ab}\hat{c}_a^\dagger \hat{c}_b^\dagger$$

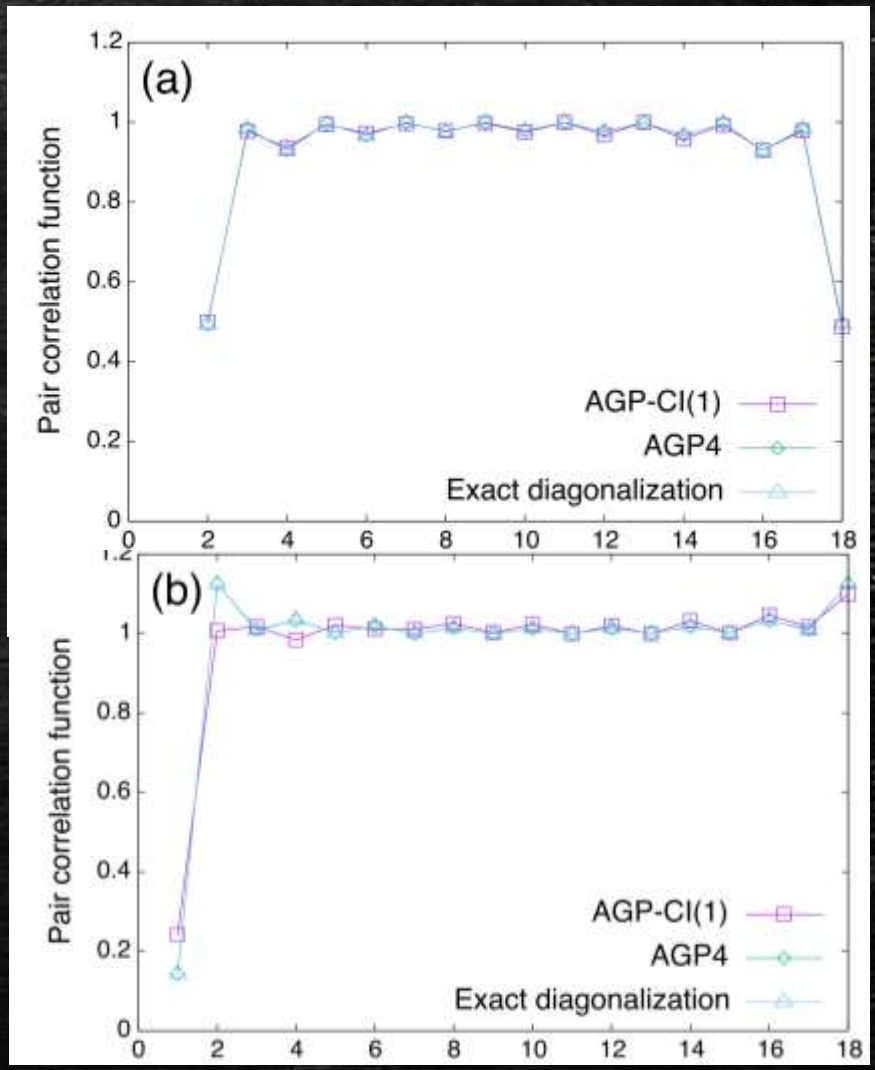
$$\hat{G} = \sum_{ab} G_{abi\uparrow i\downarrow}\hat{c}_a^\dagger \hat{c}_b^\dagger \hat{c}_{i\uparrow}^\dagger \hat{c}_{i\downarrow}^\dagger$$

A. Kawasaki & OS; JCP(2016)

A. Kawasaki & OS; JCP(2016)

1D Anderson single-impurity model (U=10)





Short summary

- AGP is a mean-field theory of particle pairs and is called as an extended Hartree-Fock
- With AGP's, one can compactly encode the wave function using the tensor decomposition techniques
- Data decoding, however, requires CPU time scaled exponentially
- Tensor decomposition is currently developed in mathematics and is applied to information technology like signal processing and face recognition

Conclusion

- Density functional theory provides economical and reliable computational methods, provided that the target system can be properly modeled.
- Preparing various reference systems and exchange-correlation functionals should be an important research topic.
- Many-body Green's function methods have advanced recently, further stimulating advance of TD-DFT.
- Tensor decomposition may provide a way to attack the strongly correlated electron systems within DFT.