

Total energies from many body perturbation theory

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Funded by the Austrian FWF



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wien



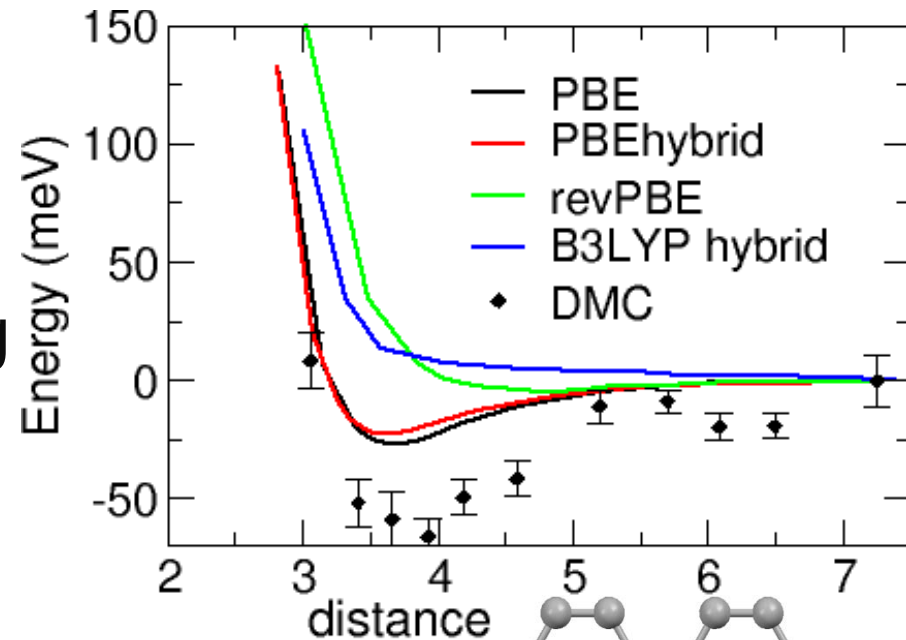
Motivation

● Band gap error

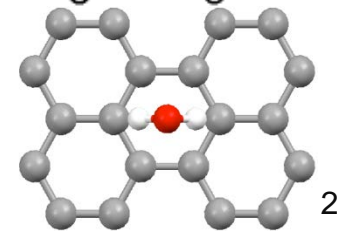
- Huge errors in band gaps
- Electronic properties: Prediction of defect properties is difficult (or impossible)

● Errors in total energies

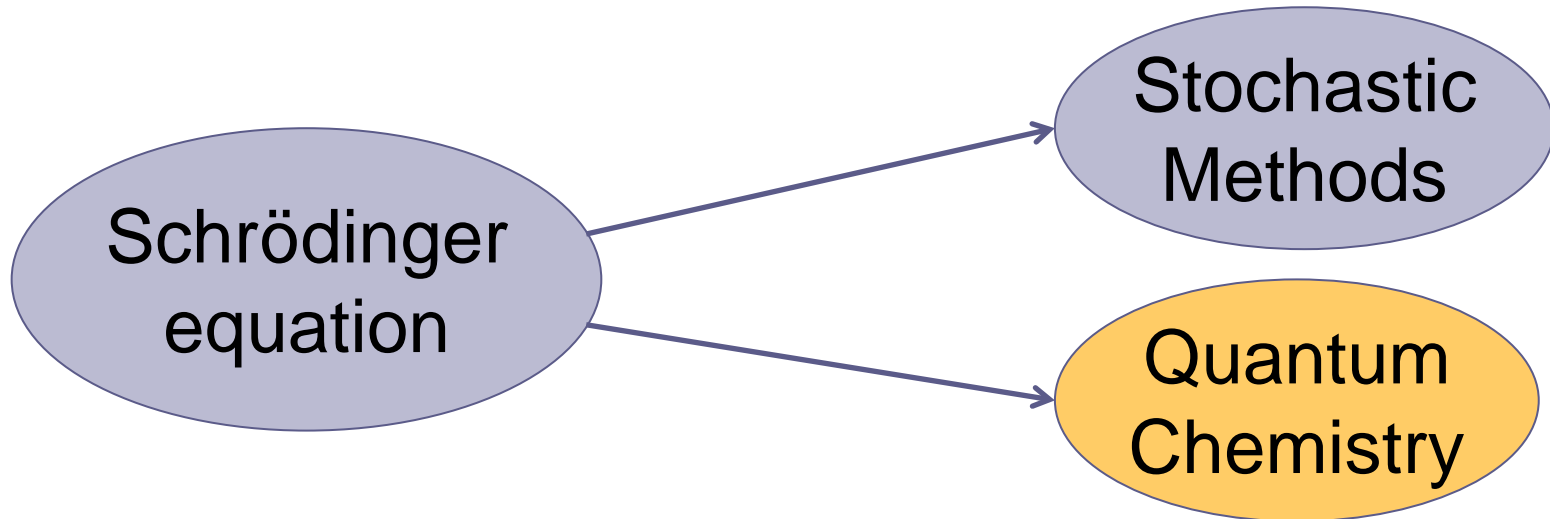
- Van der Waals bonding
- Covalent bonding
- Strong correlation



no $1/r^5$



- Accurate total energies for extended systems



- For solids no method yet available

- Chemical accuracy
- Lattice constants to within 0.1 %

CCSD

RPA+
SOSEX

RPA

Motivation: We do need more accurate methods

Available DFT methods for *solids and surfaces have issues*

- Band gaps much too small
- Van der Waals interactions
- DFT far from chemical accuracy even for simple metals and simple covalent systems
- Strongly correlated electrons

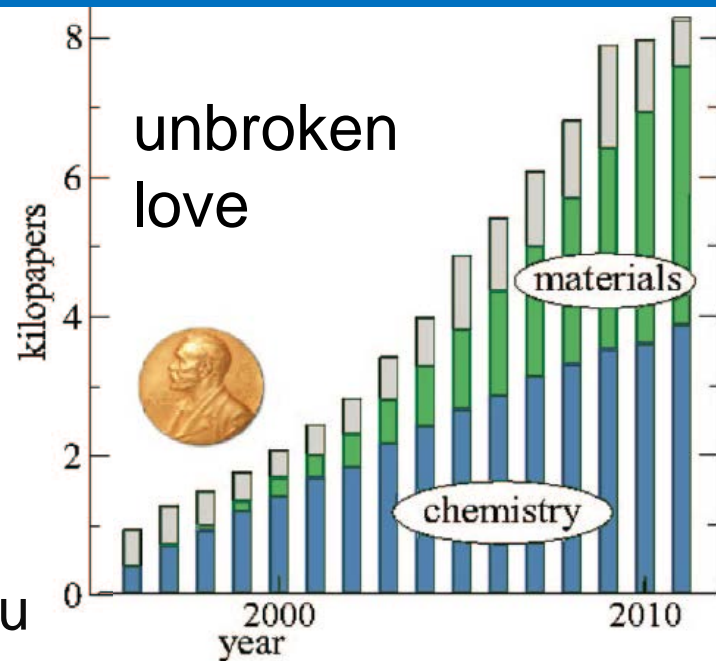
ΔH (kJ/mol)	PBE	EXP
$\text{Al} + \text{N}_2 \rightarrow \text{AlN}$	262	350
$\text{Mg} + \text{H}_2 \rightarrow \text{MgH}_2$	52	78
$\text{Si} + \text{C} \rightarrow \text{SiC}$	51	69
$\text{CO} \rightarrow \text{CO@Rh}$	183	144

We need something more accurate

- In solid state physics, we almost exclusively compare with experiment rarely with more accurate methods
- For small molecules validation exists: hierarchy of QC methods
CI \rightarrow coupled cluster \rightarrow Møller Plesset perturbation theory

Motivation: Why not only DFT

- DFT: Things users despise (Burke, JCP 136, 150901)
 - No simple rule for reliability
 - No systematic route to improve
 - Too many functionals to choose from
 - Can only be learned from a DFT guru
- No functional serving all needs is in sight, although the number of functionals is huge
- Our goal since about 2005:
 - Find something that works in most cases – black box
 - No strong correction in this talk

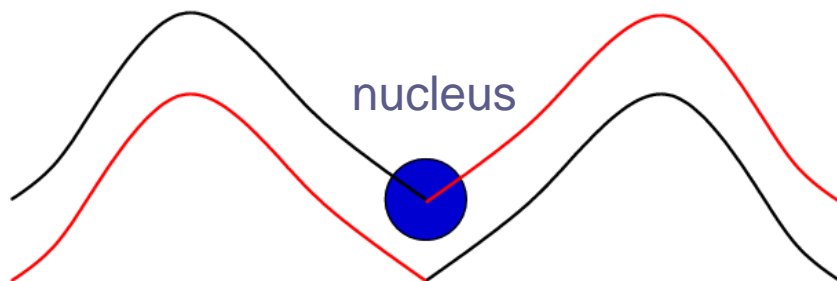


- Introduction
- Total energies from diagrammatic methods
 - Full CI methods
 - MP2, and coupled cluster methods
- Approximation methods
 - RPA
- Review of results
 - Prototypical systems
 - d-metals
 - Surface energy and adsorption energies
- Errors introduced by RPA

The problem of DFT: Correlation

electron 1

electron 2



nucleus

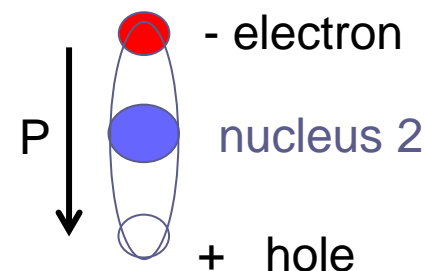
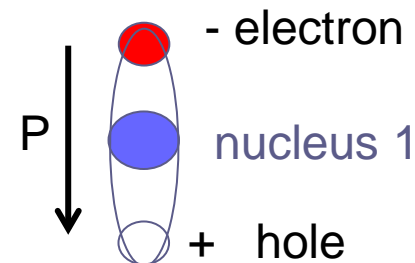
$$\Psi(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{r}_3, \dots)$$

Cusp for non-equal spin

Exchange for equal spin

$\mathbf{r}_1 - \mathbf{r}_2$

Van der Waals



- Electrons are correlated, when one electron is to the left the other one will try to avoid this region and move over to the right, and vice versa
- This is intrinsically non-local and although DFT should be able to handle this situation, it is very difficult to obtain this information from the density alone

Correlation energy in quantum chemistry

- Correlation energy is defined as the difference between the exact energy and the Hartree Fock energy
- Often obtained by order by order perturbation theory
- As before, summing an infinite subset of diagrams is desirable:
in many cases order by order perturbation theory diverges, whereas the infinite sum converges
 - Consider Taylor expansion of $\ln(1 - x)$:

$$\ln(1 - x) + x = -\frac{x^2}{2} - \frac{x^3}{3} - \frac{x^4}{4} - \dots$$

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Quantum Chemistry methods: CI expansion

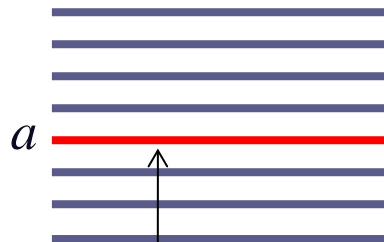
Ψ_0



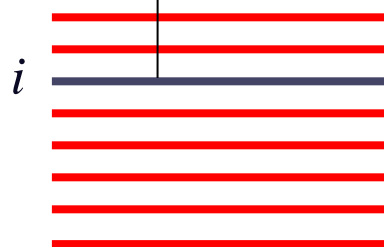
Ground state orbitals:
HF determinant
or KS determinant
 $\mathbf{h}\phi_n(\mathbf{r}) = \varepsilon_n\phi_n(\mathbf{r})$



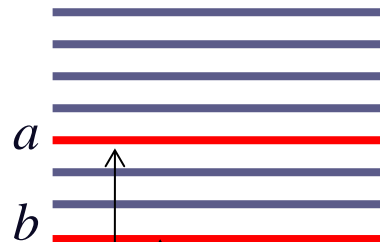
Ψ_i^a



Single
excitation



Ψ_{ij}^{ab}



Double
excitation



Converges slowly
with number of
excitations

Not size extensive,
if truncated

Scales combinatorial

32 orbitals/ 8 elect.

$$\binom{32}{8} \approx 10^{26}$$

coefficients

$$\Phi(r_1, r_2, r_3, \dots) = \Psi_0 + \sum_{i,a} T_i^a \Psi_i^a + \sum_{ij,ab} T_{ij}^{ab} \Psi_{ij}^{ab} + \dots$$

The crux of CI expansion (including RPA)

- Energies and QP energies converge like **1/total number of basis functions** irregardless of basis func.
- This is known since decades in QC; alleviated using f_{12} methods and RI, Jastrow factor

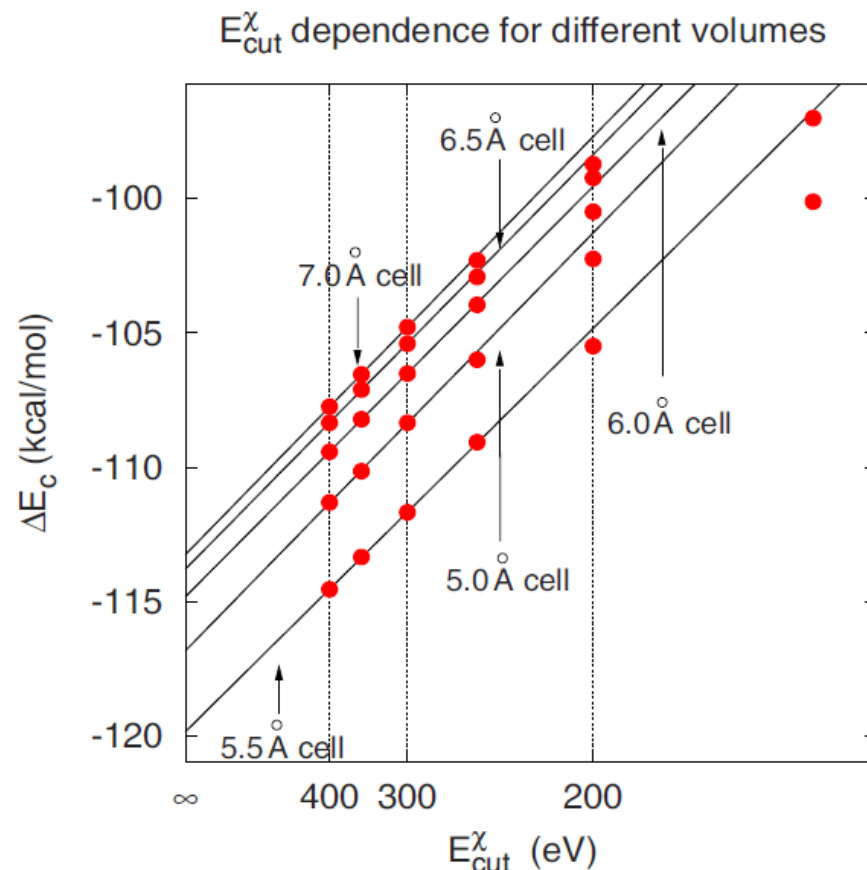
Kutzelnigg, Theor. Chim. Acta 68, 445 (1985).

Harl, Kresse, PRB 77, 045136 (2008).

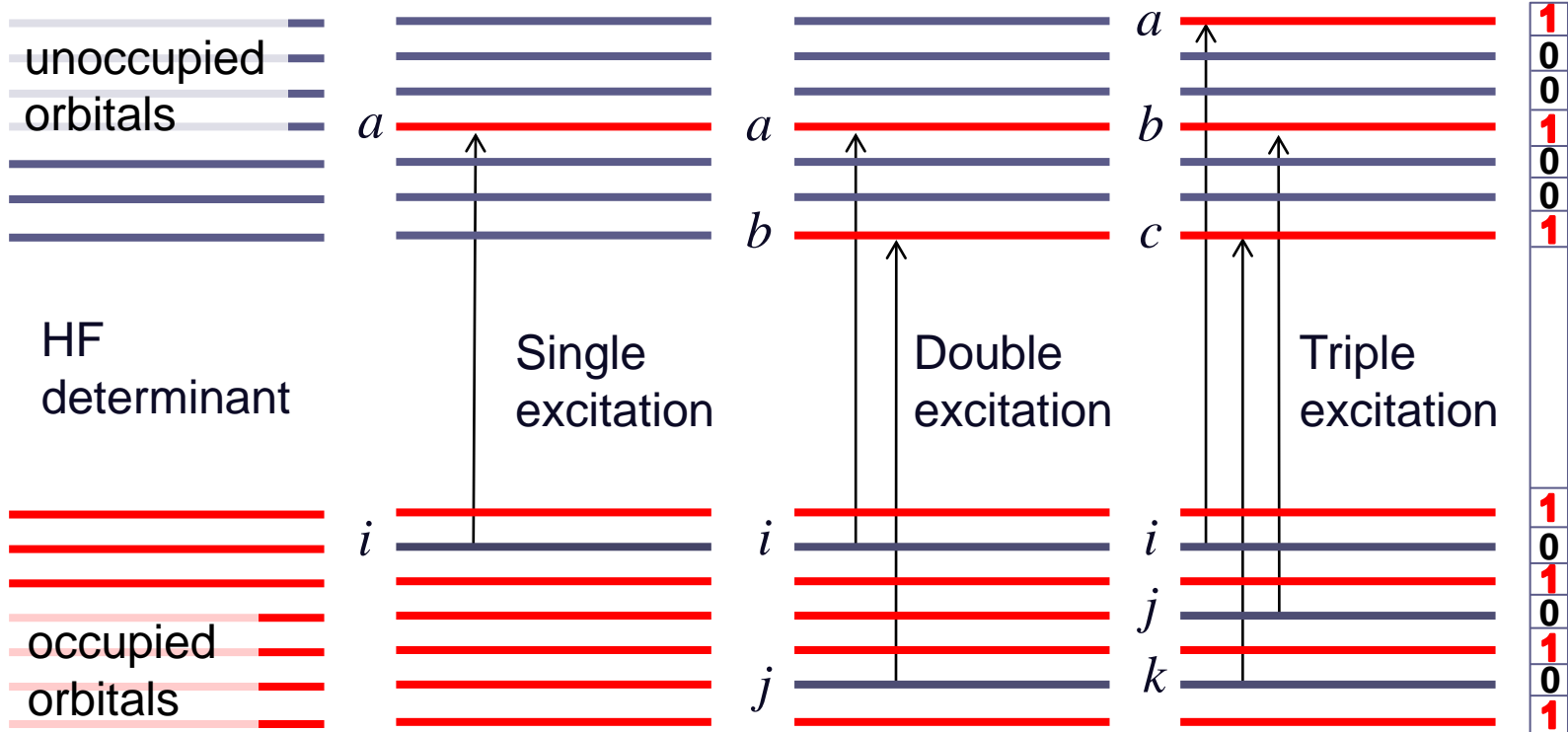
Shepherd, et al. PRB 86, 35111 (2012).

Klimes, Kaltak, Kresse, PRB 90, 075125 (2014).

$$-\frac{1}{2}|\rho(\mathbf{G} - \mathbf{G}')|^2 \frac{4\pi}{\mathbf{G}'^2} \frac{4\pi}{\mathbf{G}^2} \frac{2}{\mathbf{G}^2 + \mathbf{G}'^2}$$



Booth, Thom, A. Alavi, J. Chem. Phys. 131, 054106 (2009).



32 one-electron orbitals → 32 bits to encode **one** walker = determinant + counter to count number of walkers on that determinant
 on some determinants (e.g. HF) millions of walkers are located
 on other tiny probability to find any walker

Booth, Thom, A. Alavi, J. Chem. Phys. 131, 054106 (2009).

Master equation for spawning new walker on determinant I from a specific starting determinant J
(Schrödinger equation in imaginary time)

$$-\frac{d\Psi_I}{d\tau} = (\mathbf{H}_{II} - \varepsilon)\Psi_I + \sum_J \mathbf{H}_{IJ}\Psi_J$$

\mathbf{H}_{IJ} is the matrix element of the many electron Hamiltonian between determinant I and determinant J

- Hamiltonian contains only 1- and 2-electron operator (ν)
- The determinants can only differ by at most 2 occupied and 2 unoccupied indices
- $\varepsilon > E_{\text{ground-state}}$ number of walkers increases

Issues: why live is never simple

S10-I8 Alavi; Cleland, Booth, and A. Alavi, J. Chem. Phys. 132, 041103 (2010).

- There are **two** many electron wave functions that solve the Schrödinger $H\Psi = E\Psi$ equation

$$\pm \Psi; \quad \text{or in solids } e^{i\phi}\Psi$$

- Walkers with positive and negative sign on the same determinant will annihilate each other
- Will sign coherence for wave functions ever be realized, or could a “phase” separation occur ?

Yes, however, the number of necessary walkers grows weakly **exponentially (NP hard problem)**

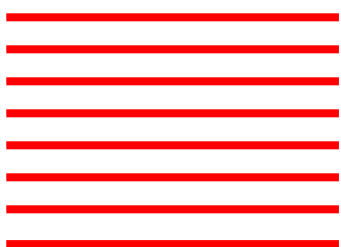
- Initiator method helps to reduce pre-factors

Perturbation theory: $\hat{H}^{DFT} \rightarrow \hat{H}^{many-body}$

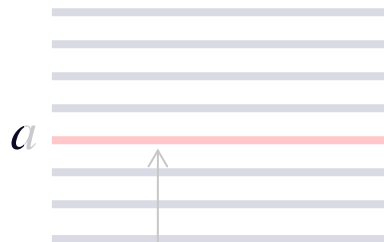
Ψ_0



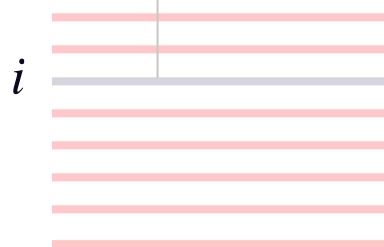
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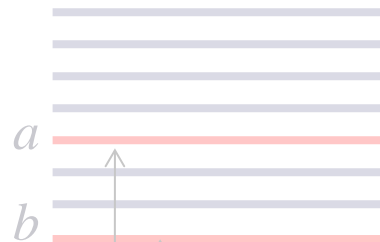
Ψ_i^a



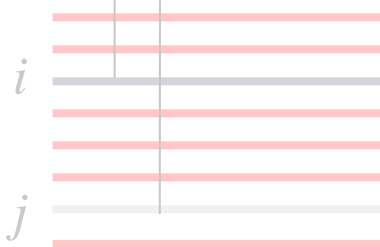
Single
excitation



Ψ_{ij}^{ab}



Double
excitation



$$\Phi(r_1, r_2, r_3, \dots) = \Psi_0 + \sum_{i,a} T_i^a \Psi_i^a + \sum_{ij,ab} T_{ij}^{ab} \Psi_{ij}^{ab} + \dots$$

Perturbation theory, 1st order

- Start from density functional theory
- 1st order perturbation theory is simple

Evaluate the total many electron energy using the previously determined occupied DFT or HF one-electron orbitals

- For DFT orbitals

$$\left\langle \Psi_0^{\text{DFT}} \left| \hat{H}^{\text{many-body}} \right| \Psi_0^{\text{DFT}} \right\rangle = E^{\text{HF}} (\{ \phi_i^{\text{DFT}} \mid i \in \text{occ} \}) = E^{\text{EXX}}$$

HF energy using the DFT orbitals

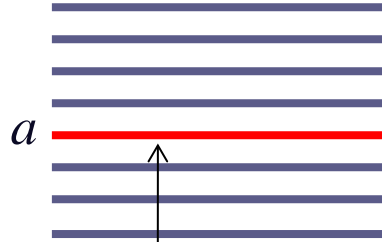
- Diagrams:

$n(\mathbf{r})$	$v(\mathbf{r}, \mathbf{r}')n(\mathbf{r}')$	$\gamma(\mathbf{r}, \mathbf{r}')$
		$v(\mathbf{r}, \mathbf{r}')$
		$\gamma(\mathbf{r}', \mathbf{r})$
Hartree		exchange

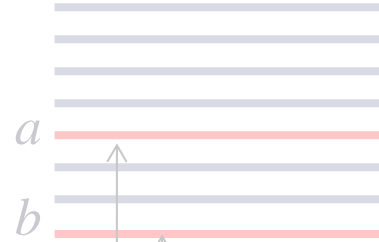
Perturbation theory: single excitations

 Ψ_0

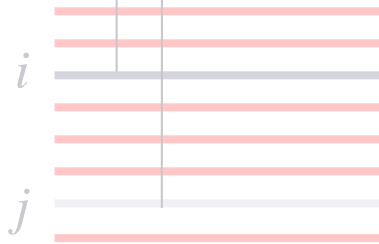

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 Ψ_i^a


Single
excitation


 Ψ_{ij}^{ab}


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$$\Phi(r_1, r_2, r_3, \dots) = \Psi_0 + \sum_{i,a} T_i^a \Psi_i^a + \sum_{ij,ab} T_{ij}^{ab} \Psi_{ij}^{ab} + \dots$$

2nd order: “Singles”

- Standard Rayleigh–Schrödinger 2nd order PT:

- Singles

$$E_c^{\text{SE}} = - \sum_{\substack{a \in \text{virt}, \\ i \in \text{occ}}} \frac{|\langle \Psi_i^a | \hat{H} - \hat{H}^{\text{mean-field}} | \Psi_0 \rangle|^2}{E_i^a - E_0}$$

- For DFT orbitals

$$- \sum_{\substack{a \in \text{virt}, \\ i \in \text{occ}}} \frac{|\langle i | \hat{V}^{\text{HF}} - \hat{V}^{\text{KS}} | a \rangle|^2}{\epsilon_a - \epsilon_i}$$

- Singles are zero for HF orbitals, since $\hat{V}^{\text{HF}} - \hat{V}^{\text{HF}} = 0$

A. Szabo and N. S. Ostlund, Modern Quantum Chemistry (McGraw-Hill, 1989)

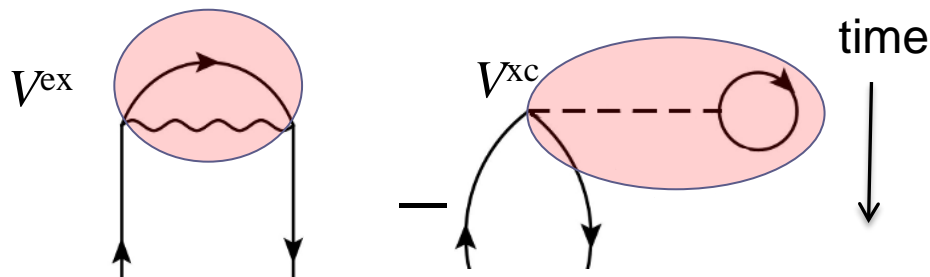
X. Ren, A. Tkatchenko, P. Rinke, and M. Scheer, PRL 106, 153003 (2011).

2nd order: “Singles”

S6-I4: X. Ren, A. Tkatchenko, P. Rinke, and M. Scheer, PRL 106, 153003 (2011).
 A. Szabo and N. S. Ostlund, Modern Quantum Chemistry (McGraw-Hill, 1989).

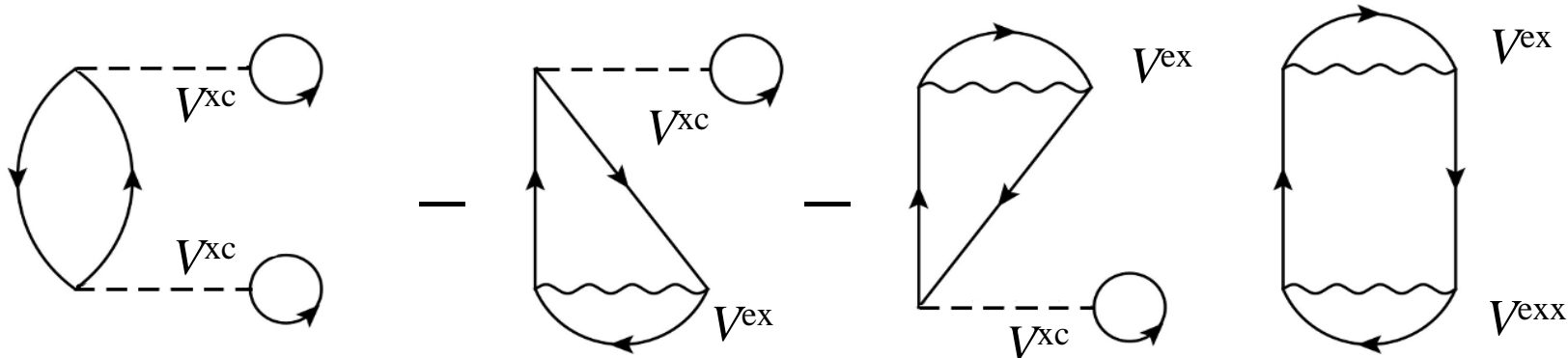
- Change of one electron orbitals as a result of change from DFT to HF Hamiltonian

$$\langle i | \hat{V}^{ex} - \hat{V}^{xc} | a \rangle / (\epsilon_a - \epsilon_i)$$



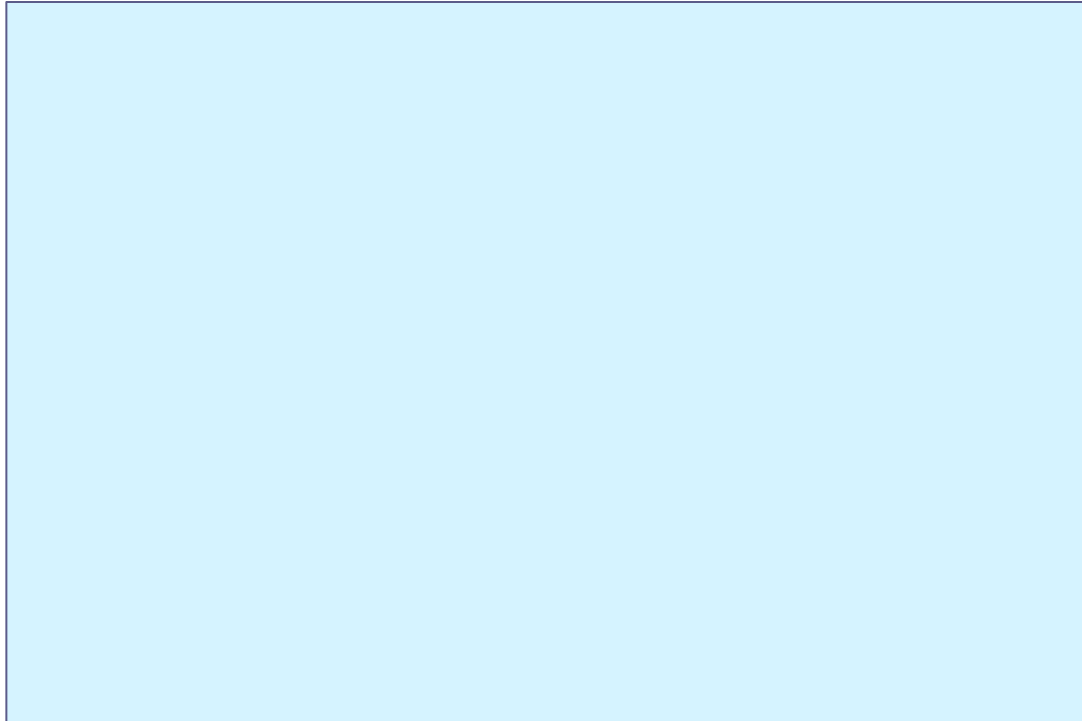
- Resultant change of HF energy

$$\langle i | \hat{V}^{exx} - \hat{V}^{xc} | a \rangle \langle a | \hat{V}^{exx} - \hat{V}^{xc} | i \rangle / (\epsilon_a - \epsilon_i)$$



Hartree-Fock reference (2)

- In 2nd order already 11 diagrams containing \hat{V}_{eff} :

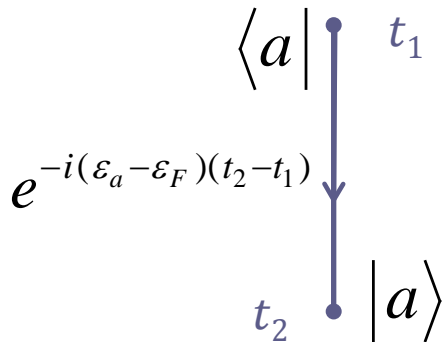


- sign from \hat{V}_{eff} is given explicitly, sign related to topology not
 - in HF: \hat{V}_{eff} cancels all 9 diagrams containing non-propagating connections (on the same Coulomb line), only MP2 remains
- In DFT diagrams need to be included

Diagrams and Green's function

- Straight line = Green's function describing the propagation of an electron or hole from position and time (\mathbf{r}_1, t_1) to (\mathbf{r}_2, t_2)
- Particle propagator $G(1,2) = G(\mathbf{r}_1, \mathbf{r}_2, t_2 - t_1) \quad t_2 > t_1$

time

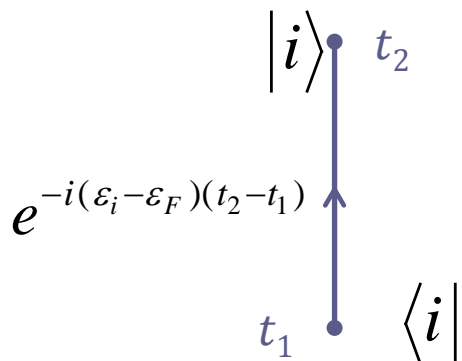


$$G_0(1,2) = \sum_{a \in \text{virt}} \phi_a^*(\mathbf{r}_1) \phi_a(\mathbf{r}_2) e^{-i(\epsilon_a - \epsilon_F)(t_2 - t_1)}$$

- Hole propagator

$$G(1,2) \quad t_2 < t_1$$

QC:
propagation by
unperturbed H

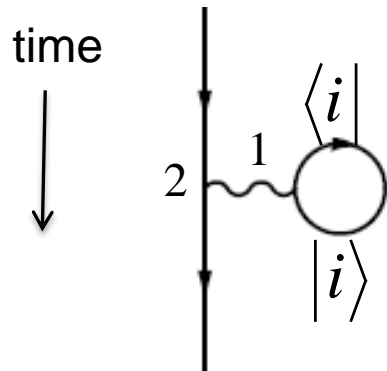


$$G_0(1,2) = - \sum_{i \in \text{OCC.}} \phi_i^*(\mathbf{r}_1) \phi_i(\mathbf{r}_2) e^{-i(\epsilon_i - \epsilon_F)(t_1 - t_2)}$$

Example two simple diagrams

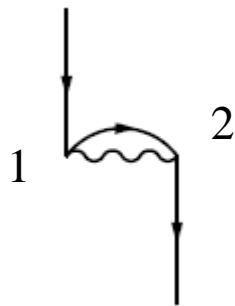
The two first order diagrams (single Coulomb line) yield just the Hartree and exchange energy
(sign depends on # of closed Fermi-loops)

Hartree



$$G(1,1) = \sum_{i \in \text{OCC.}} \phi_i^*(\mathbf{r}_1) \phi_i(\mathbf{r}_1) e^{-i(\varepsilon_i - \varepsilon_F)(t_1 - t_1)} = n(\mathbf{r}_1)$$

$$\int v(\mathbf{r}_2, \mathbf{r}_1) n(\mathbf{r}_1) d\mathbf{r}_1 = \int \frac{n(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1$$



$$G(1,2) = \sum_{i \in \text{OCC.}} \phi_i^*(\mathbf{r}_1) \phi_i(\mathbf{r}_2) e^{-i(\varepsilon_i - \varepsilon_F)(t_1 - t_1)} = \gamma(\mathbf{r}_1, \mathbf{r}_2)$$

$$-G(1,2)v(1,2) = -v(\mathbf{r}_1, \mathbf{r}_2)\gamma(\mathbf{r}_1, \mathbf{r}_2) = -\frac{\gamma(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad t_1 = t_2$$

exchange

2nd order or Møller–Plesset - MP2

Φ_0

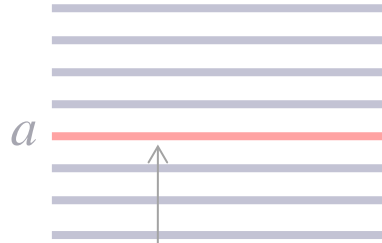


Ground state orbitals:
HF determinant
or KS determinant

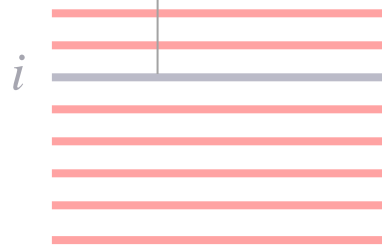
$$\mathbf{h}\phi_n(\mathbf{r}) = \varepsilon_n\phi_n(\mathbf{r})$$



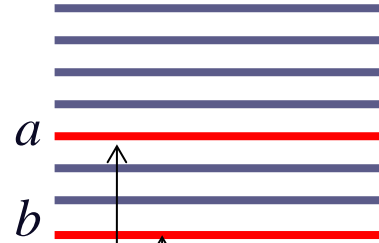
Φ_i^a



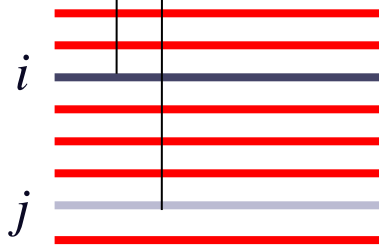
Single
excitation



Φ_{ij}^{ab}



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2nd order: Doubles

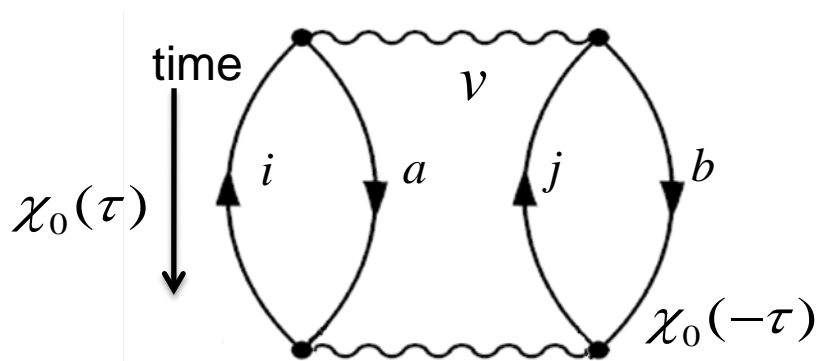
A. Szabo and N. S. Ostlund, Modern Quantum Chemistry (McGraw-Hill, 1989)

- Again standard 2nd order PT
 - Doubles in 2nd order perturbation theory

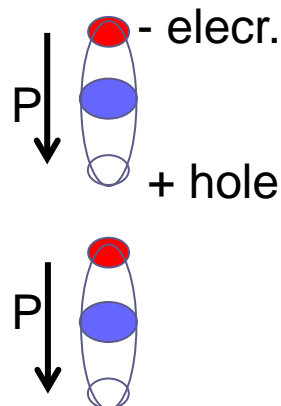
$$E_c^{\text{DE}} = - \sum_{\substack{ab \in \text{virt}, \\ ij \in \text{occ}}} \frac{|\langle \Psi_{ij}^{ab} | \hat{H} - \hat{H}^{\text{mean-field}} | \Psi_0 \rangle|^2}{E_{ab}^{ij} - E_0}$$

- Vacuum fluctuations

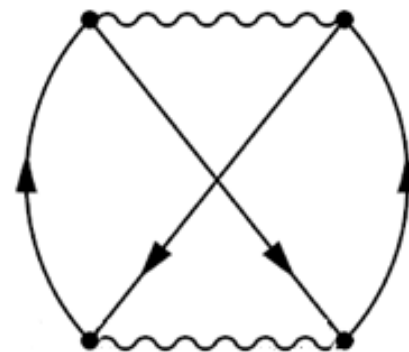
Direct (from Hartree)



$$\text{Tr}[\chi_0 v \chi_0 v] / 2$$



Second order exchange



Hartree-Fock reference (2)

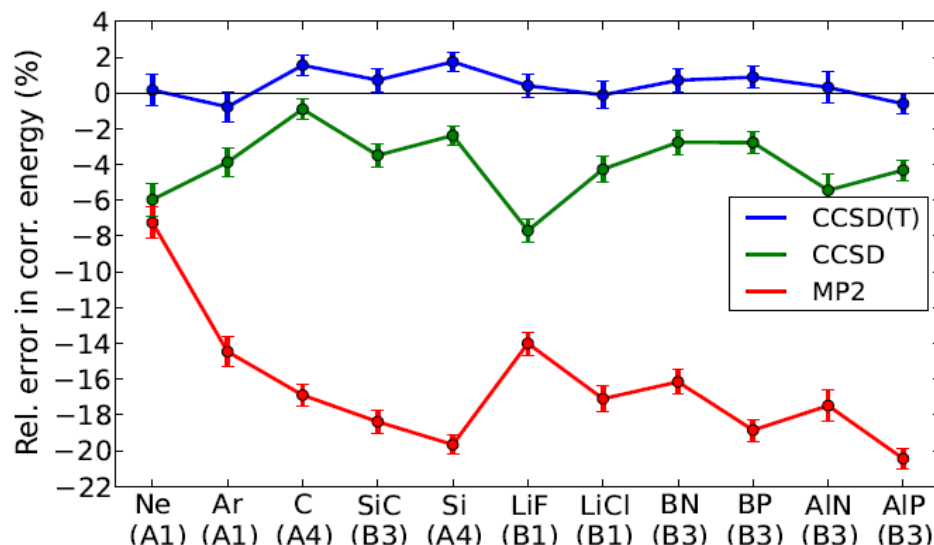
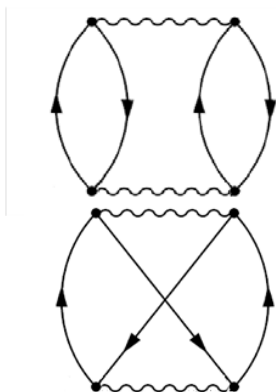
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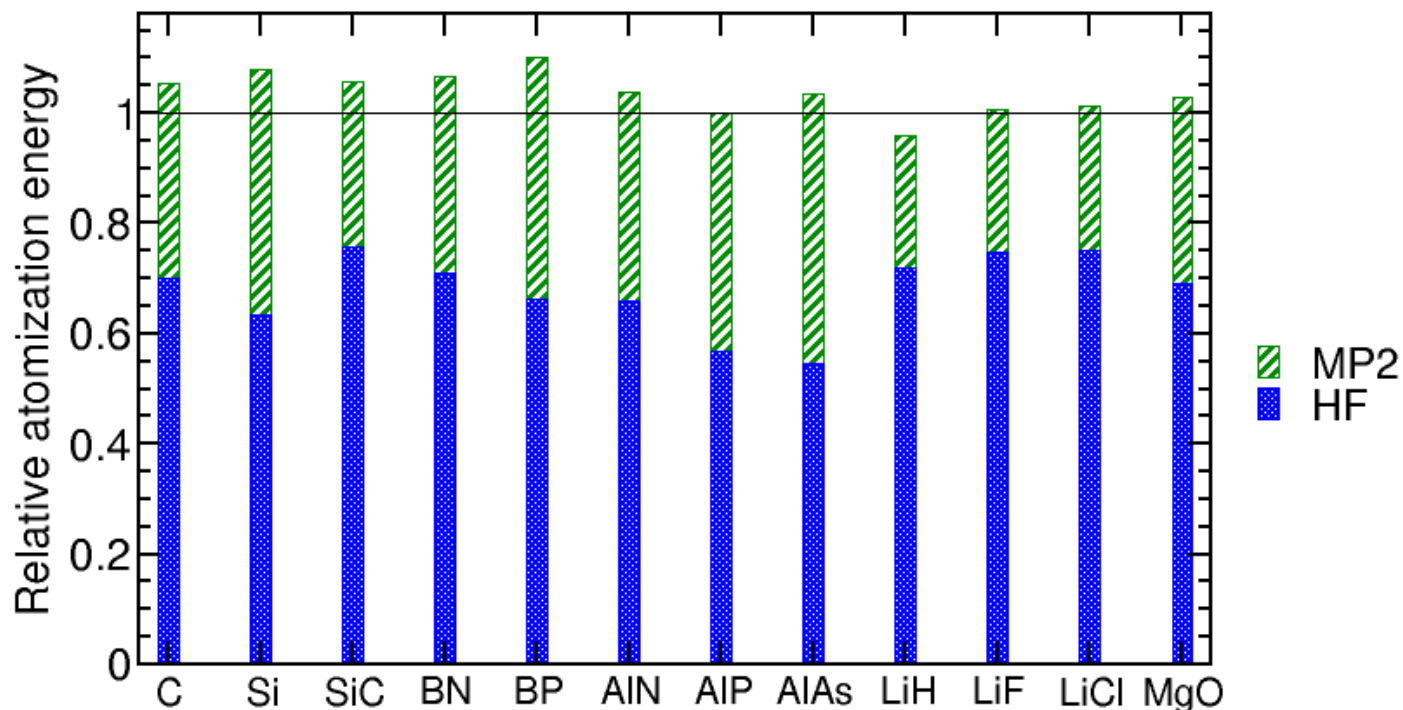
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 - in HF: \hat{V}_{eff} cancels all 9 diagrams containing non-propagating connections (on the same Coulomb line), only MP2 remains
- In DFT diagrams need to be included

How good is Hartree-Fock + MP2

- MP2 can be great for large band gap systems such as water, ice and small molecules
- For solids, low order perturbation theory is however bound to fail as already realized by L. Hedin
- MP2 over- or under-correlates in a non systematic manner



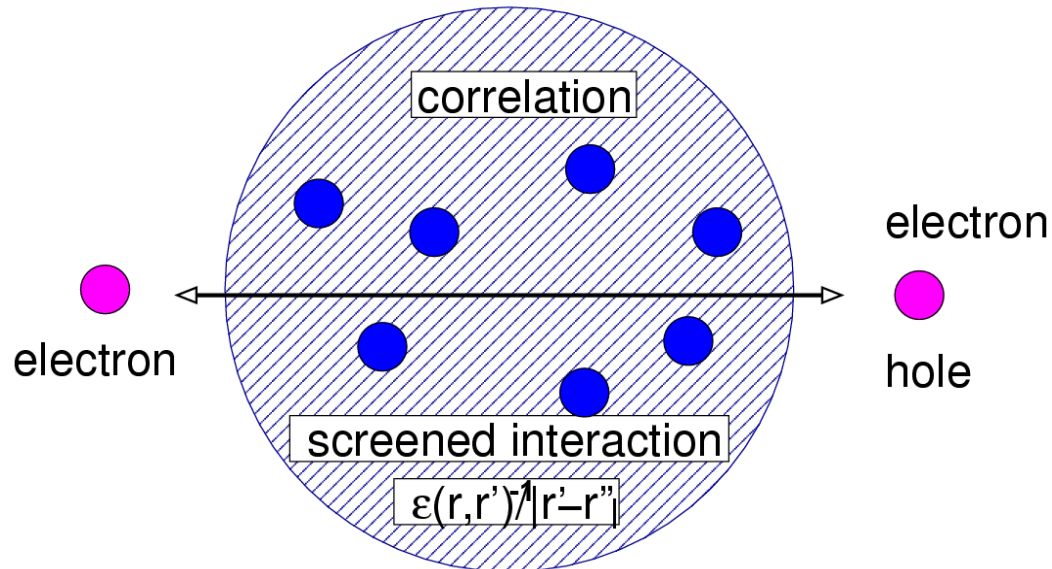
MP2 for solids: Atomization energies



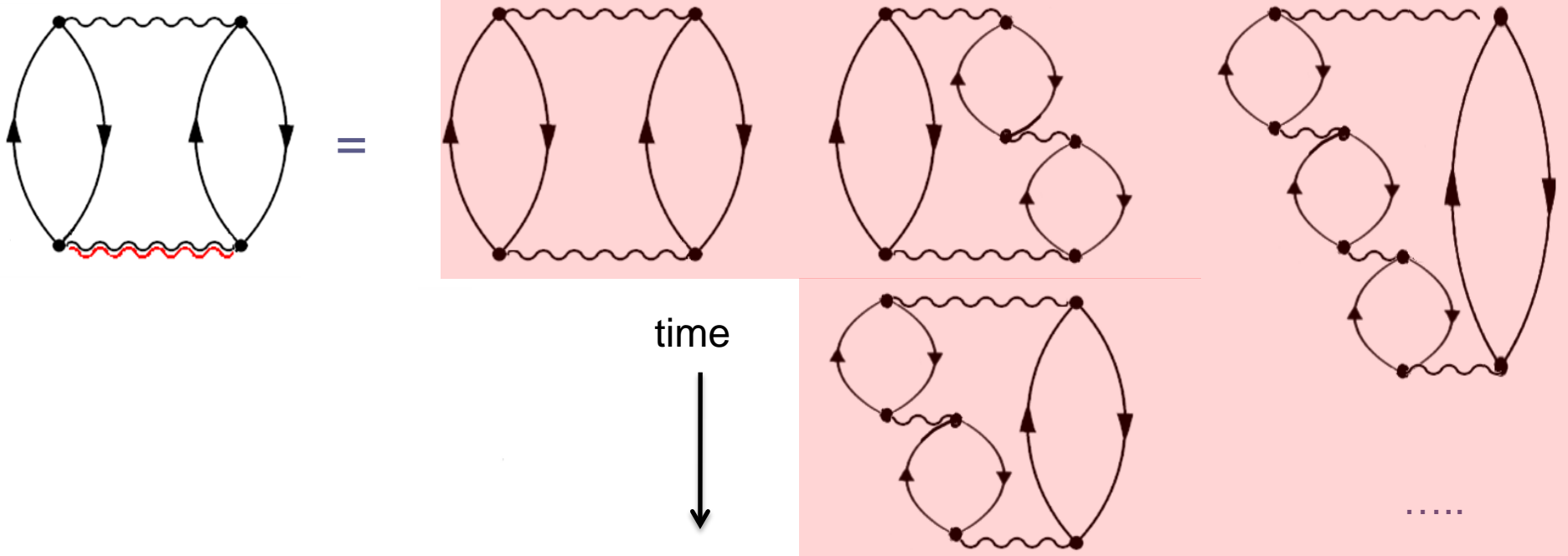
- Not bad
- But universal “trends” not obvious
- Divergent for systems without a gap

In solids the „other“ electrons strongly screen the interaction between any two particles: Nozières and Pines, L. Hedin

Results for small molecules do not prove that a method can be applied to solids



$$W = V + V \chi_0 V + V \chi_0 V \chi_0 V + \dots$$



2.nd order

3.rd order

4.order

$$\ln(1 - v\chi) + v\chi = -\frac{\text{Tr}[\chi v \chi v]}{2} - \frac{\text{Tr}[\chi v \chi v \chi v]}{3} - \frac{\text{Tr}[\chi v \chi v \chi v \chi v]}{4} - \dots$$

Nozières and Pines, Phys. Rev. **111**, 442

Coupled cluster methods

Herman Kümmel, Fritz Coester (nuclear physicists)

Scale only algebraically with systems size

Kümmel (quote from wikipedia):

Considering the fact that the CC method was well understood around the late fifties it looks strange that nothing happened with it until 1966, as Jiří Čížek published his first paper on a quantum chemistry problem. He had looked into the 1957 and 1960 papers published in Nuclear Physics by Fritz and myself. **I always found it quite remarkable that a quantum chemist would open an issue of a nuclear physics journal.** I myself at the time had almost gave up the CC method as not tractable and, of course, I never looked into the quantum chemistry journals. The result was that I learnt about Jiří's work as late as in the early seventies, when he sent me a big parcel with reprints of the many papers he and Joe Paldus had written until then.

Coester & Kümmel; Čížek, J. Chem. Phys 45, 4256 (1966); Monkhorst, Bartlett

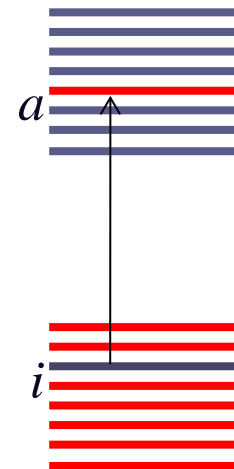
- Sums a subset of infinite many orders & excitations
- Size consistent and consistent with PT
often converges even if PT diverges
groundstate must be close to starting determinant
- Set of linked diagrams (coupled cluster)

$$\text{exp. ansatz: } \Psi = \exp(\mathbf{T})\Psi_0$$

$$\text{yields } \mathbf{H}\exp(\mathbf{T})\Psi_0 = \varepsilon \exp(\mathbf{T})\Psi_0$$

$$\text{CI: } \Psi = (1 + \sum_{i,a} T_i^a \mathbf{a}_a^+ \mathbf{a}_i + \sum_{ij,ab} T_{ij}^{ab} \mathbf{a}_a^+ \mathbf{a}_i \mathbf{a}_b^+ \mathbf{a}_j + \dots) \Psi_0$$

$$\text{CC: } \Psi = \exp(\sum_{i,a} T_i^a \mathbf{a}_a^+ \mathbf{a}_i + \sum_{ij,ab} T_{ij}^{ab} \mathbf{a}_a^+ \mathbf{a}_i \mathbf{a}_b^+ \mathbf{a}_j + \dots) \Psi_0$$



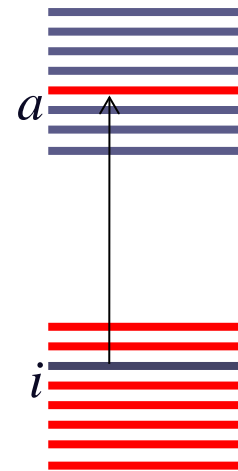
Projected Coupled cluster methods

Čížek, J. Chem. Phys 45, 4256 (1966)

exp. ansatz : $\Psi = \exp(\mathbf{T})\Psi_0$

yields $\mathbf{H}\exp(\mathbf{T})\Psi_0 = \varepsilon \exp(\mathbf{T})\Psi_0$

approx. by $e^{-\mathbf{T}}\mathbf{H}e^{\mathbf{T}}\Psi_0 = \varepsilon\Psi_0$



Coupled cluster equations can not be solved exactly
Instead equation is left multiplied by $e^{-\mathbf{T}}$ and HF,
all single, and all double excited determinants

→ quadratic equation for double amplitudes $\mathbf{T} = \{T_{ij}^{ab}\}$

$$\mathbf{B} + \mathbf{A}\mathbf{T} + \cancel{\mathbf{T}\mathbf{A}} + \underbrace{\cancel{\mathbf{T}\mathbf{B}\mathbf{T}}}_{\text{describes coupling between } +\omega}$$

describes coupling between $+\omega$

Linear coupled cluster doubles (LCCD)

$$\mathbf{B} + (\mathbf{A}' - \mathbf{A}_{diag})\mathbf{T} = 0 \Leftrightarrow \mathbf{A}_{diag}\mathbf{T} = \mathbf{B} + \mathbf{A}'\mathbf{T}$$

Jacobi iteration $\mathbf{T} = \mathbf{A}_{diag}^{-1}(\mathbf{B} + \mathbf{A}'\mathbf{T})$

$$\mathbf{T}_0 = 0$$

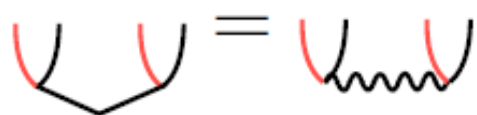
$$\mathbf{T}_1 = \mathbf{A}_{diag}^{-1}\mathbf{B}$$

$$\mathbf{T}_2 = \mathbf{A}_{diag}^{-1}(\mathbf{B} + \mathbf{A}'\mathbf{A}_{diag}^{-1}\mathbf{B})$$

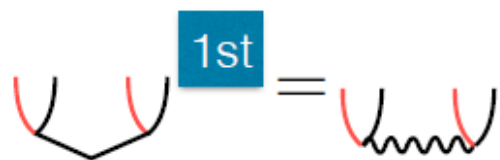
$$\mathbf{T}_3 = \mathbf{A}_{diag}^{-1}(\mathbf{B} + \mathbf{A}'\mathbf{A}_{diag}^{-1}\mathbf{B} + \mathbf{A}'\mathbf{A}_{diag}^{-1}\mathbf{A}'\mathbf{A}_{diag}^{-1}\mathbf{B})$$

Linear CCD: diagrammatic representation

By means of this equation all bubble and ladder diagrams (p-h, p-p, h-h) are summed to infinity

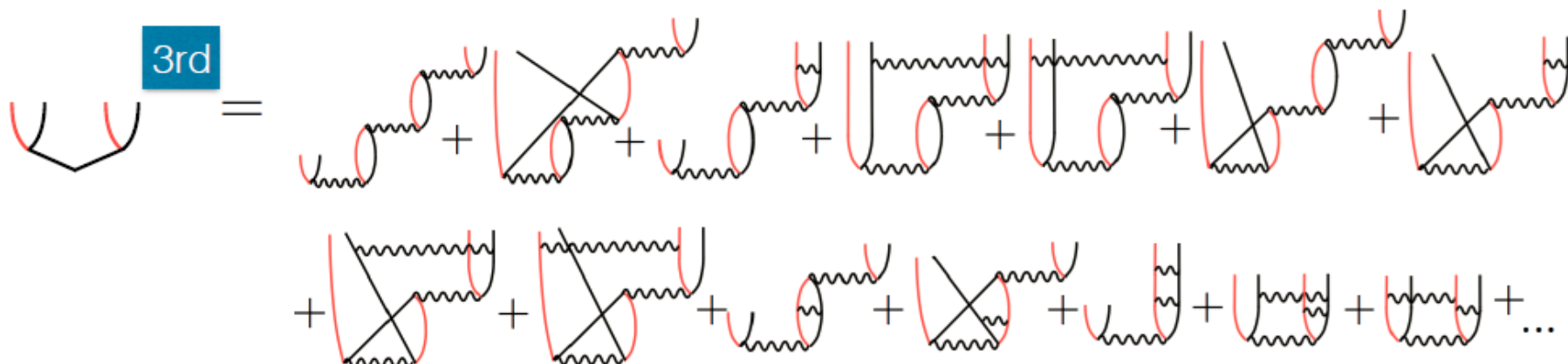


$$\mathbf{T}_0 = \mathbf{A}_{diag}^{-1} \mathbf{B} = (\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j)^{-1} \langle aj | ib \rangle$$

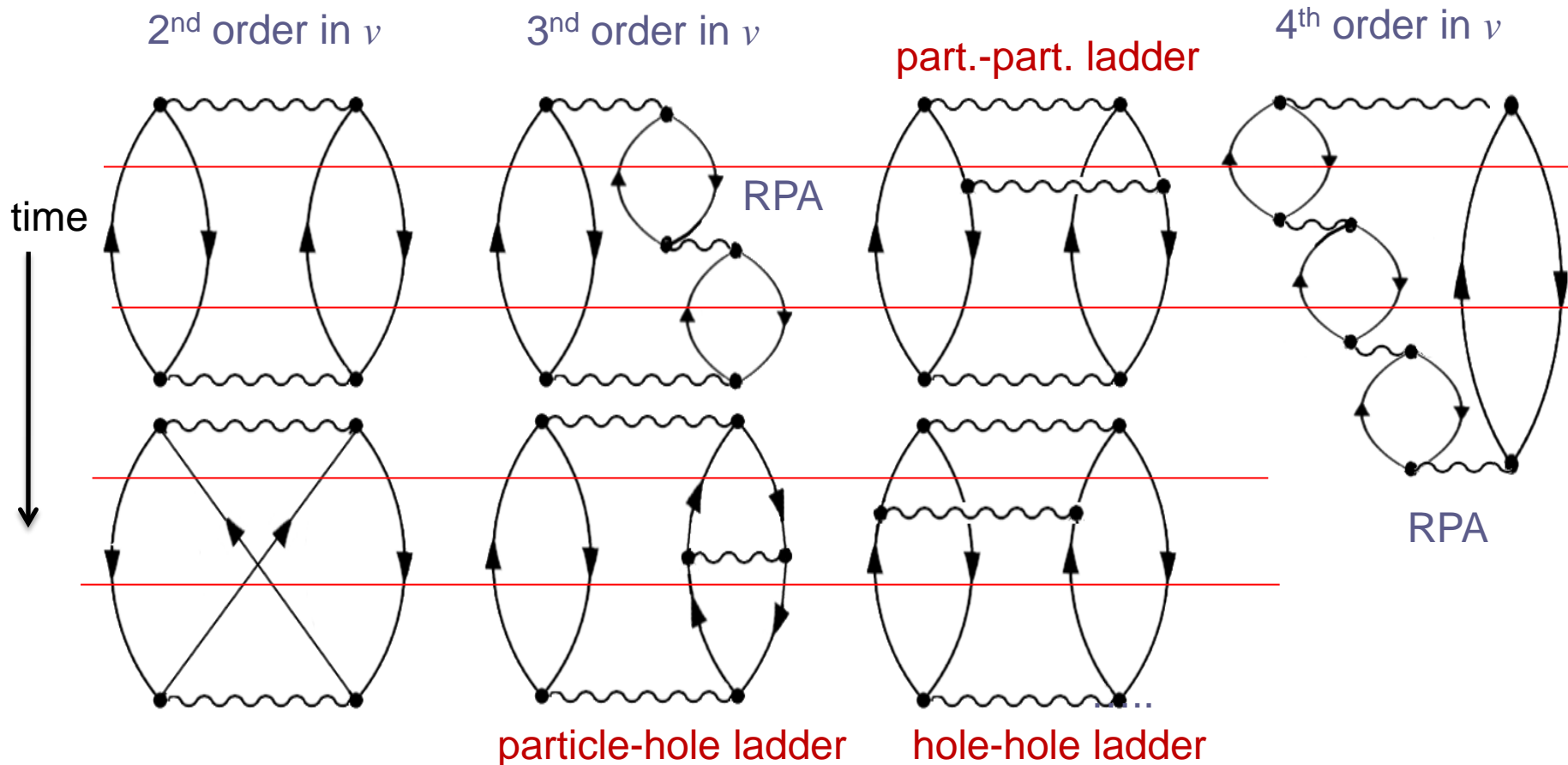


$$E_c^{MP2} = \text{bubble diagram} + \text{crossed diagram}$$

$$\mathbf{A}_{diag}^{-1} \mathbf{A}' \mathbf{T}_0$$



LCCD: all diagrams with two particle-hole pairs

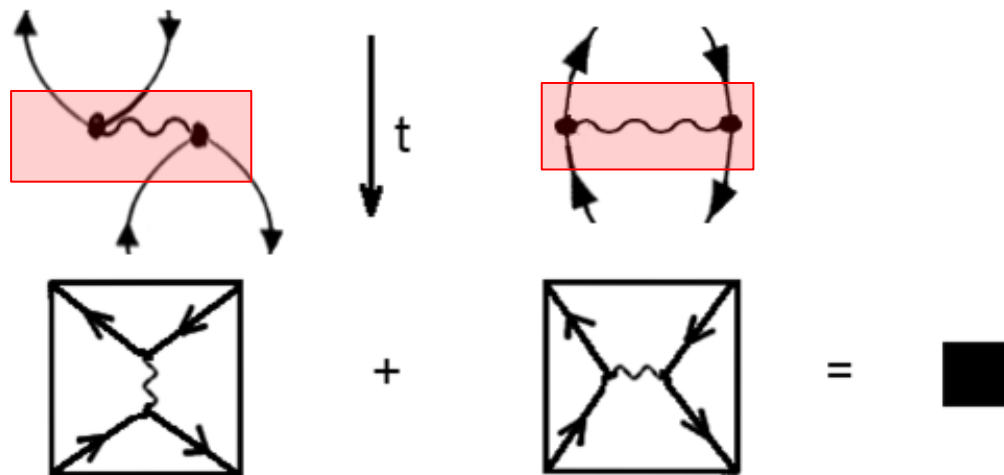


Goldstone diagrams with two particle-hole pairs at any time point

- Includes RPA
- Includes particle-hole RPA of W. Yang, t-matrix

Anti-symmetry and particle-particle ladders

- All involved four orbital integrals are always anti-symmetrized, **particle-hole** ladders are bare in CCSD



- Particle-particle and hole-hole ladder diagrams are also included (with bare Coulomb interaction)
- Screened ladders enter in CCSDT and to **2nd order** in CCSD(T)

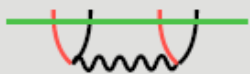
The coupled cluster hierarchy (rank)

MP2 theory

$$\hat{T} = \hat{T}_2$$

- Exact to 2nd-order PT

$$O(N^5)$$



CCSD theory

$$\hat{T} = \hat{T}_1 + \hat{T}_2$$

- Exact to 3rd-order PT
- ph-RPA, pp-RPA, hh-RPA
- Exact for 2e systems

$$O(N^6)$$



$$\text{[Diagram]} = \text{[Diagram]} + \text{[Diagram]} + \text{[Diagram]} + \text{[Diagram]} + \text{[Diagram]} + \dots$$

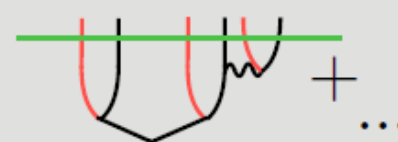
CCSD(T) theory

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$$

\hat{T}_3 in perturbative manner

- Exact to 4th-order PT
- “Chemical Accuracy”
- Exact for 2e systems

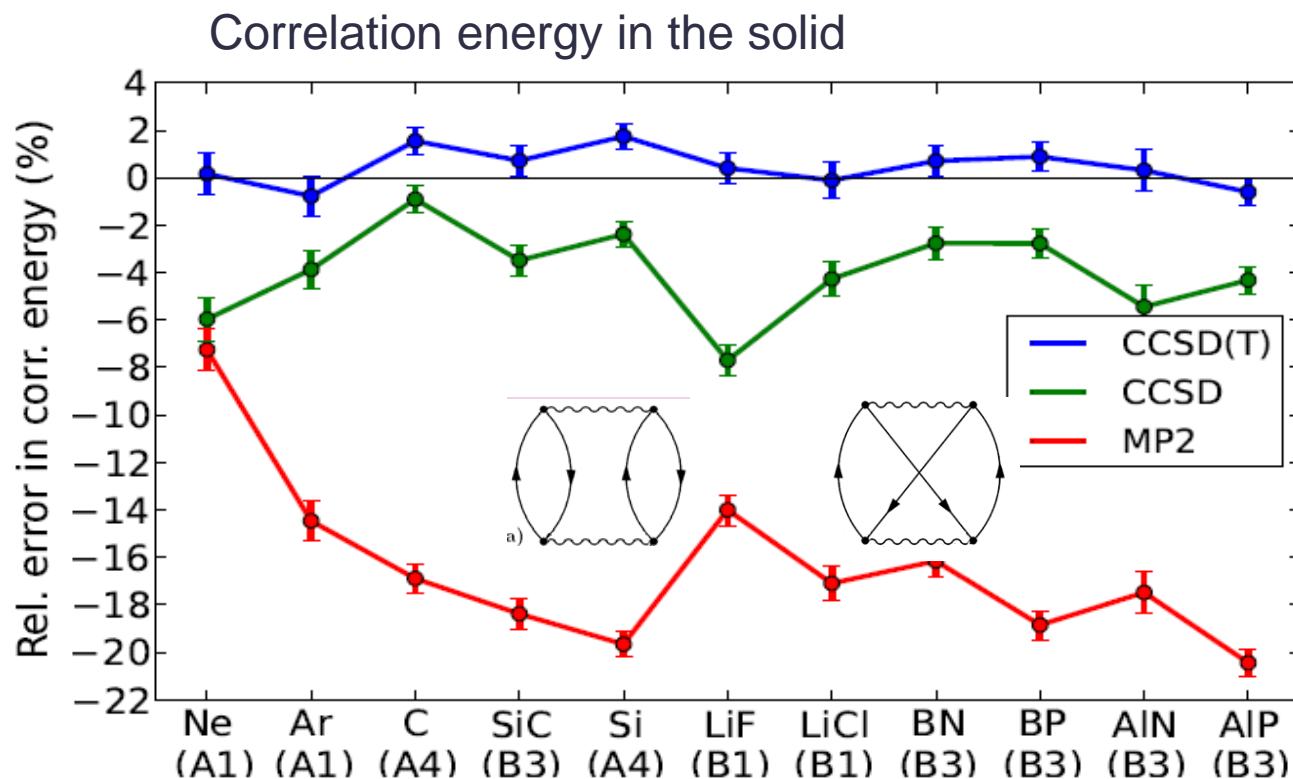
$$O(N^7)$$



Full CI versus MP2, CCSD and CCSD(T)

Booth, A. Grüneis, G. Kresse, and A. Alavi, Nature 493, 365-370 (2013)

To make FCI possible
8 orbitals and
(2x2x2) k-points

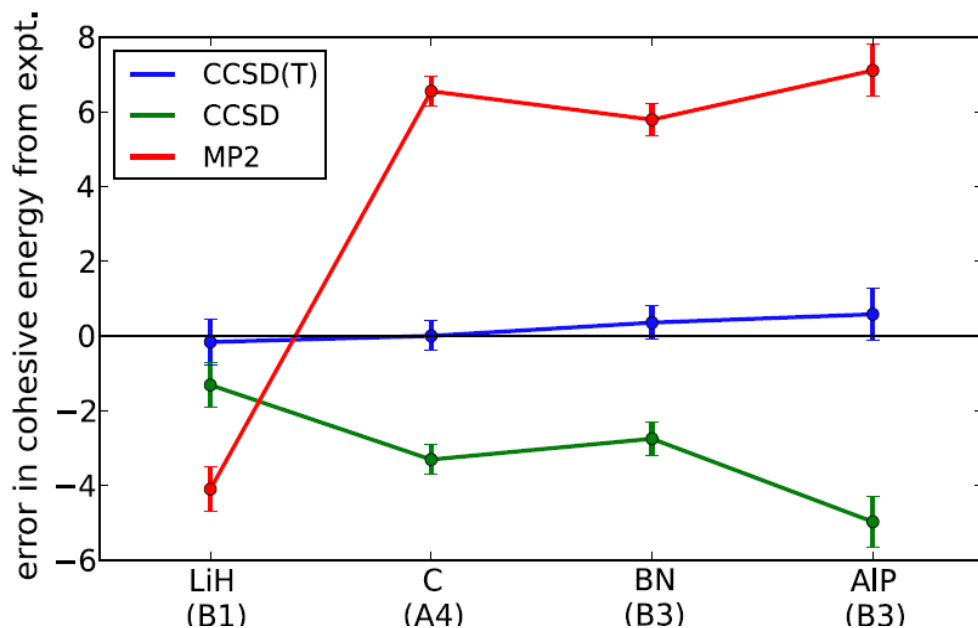


- MP2 underestimates correlation energies by 20 %
- CCSD lacks correlation energy by 5 %
- CCSD(T) over-correlates with maximum deviations of 2 %

CCSD(T) at the basis set limit

CCSD(T) at basis set limit compared to experiment

Booth, A. Grüneis, G. Kresse, and A. Alavi, Nature 493, 365-370 (2013)



LiH	kJ/mol
HF	346.3
MP2	460.3
CCSD	474.6
CCSD(T)	479.5
CCSDT ¹	480.7*
Exp.	479.0

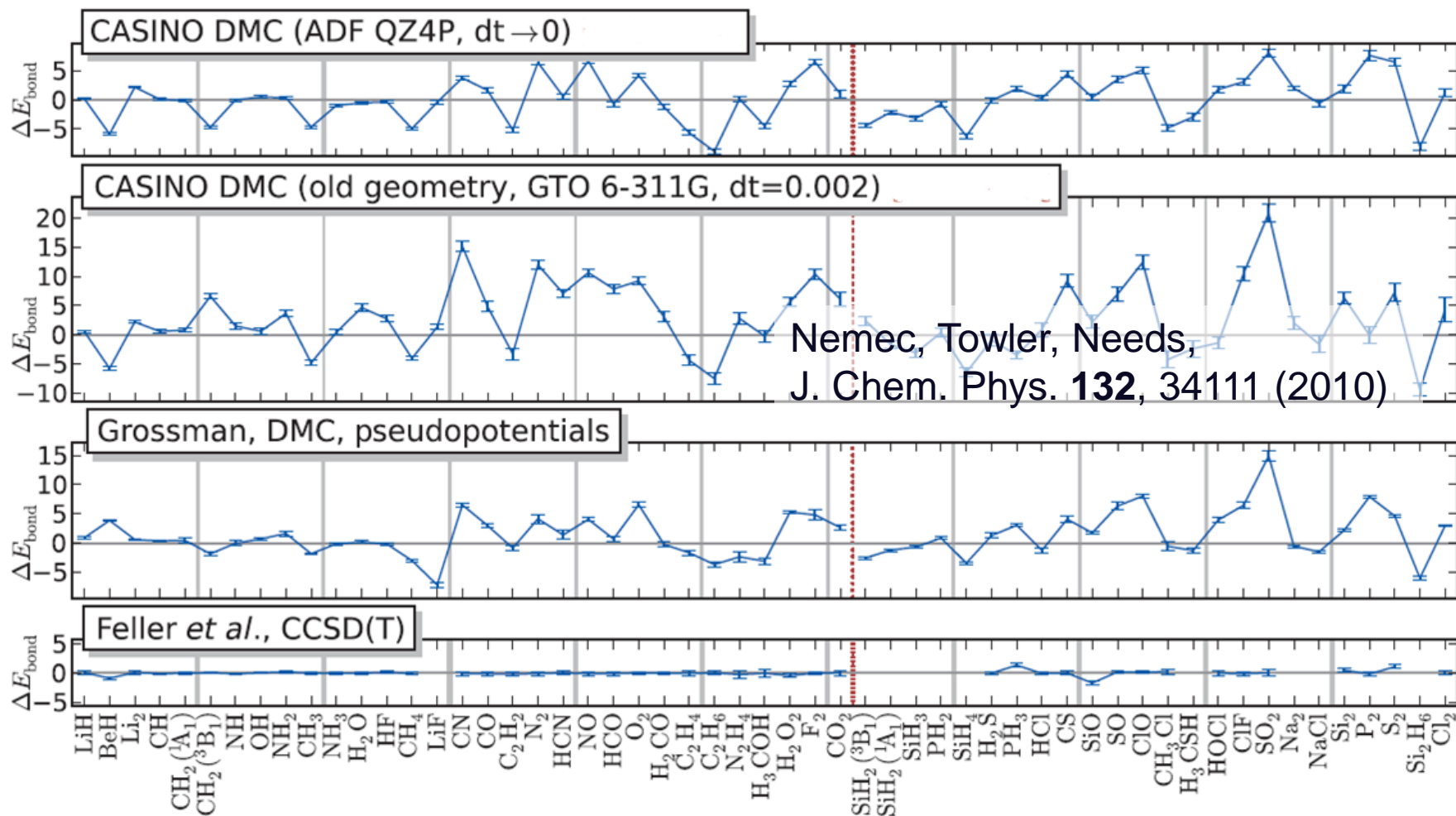
¹ hierarchical approach using clusters:

Nolan, Gillan, Alfe, Allan, Manby, PRB 80, 165109 (2009)

Small molecules: CCSD(T) & diffusion MC

Diffusion MC has a “Fermion” sign problem

Fixed node approximation: fix nodal surface to HF or DFT determinant and perform Bosonic QMC



What can we do for materials science

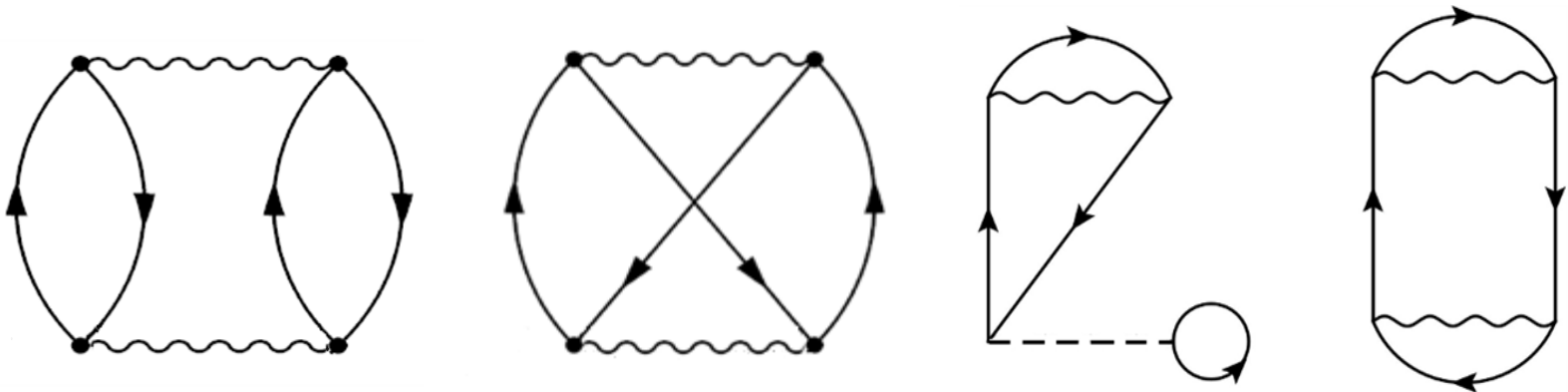
Booth, A. Grüneis, G. Kresse, and A. Alavi, Nature 493, 365-370 (2013)

- Full CI-QMC is extremely powerful, but for the foreseeable future limited to small systems
 - Weakly exponential in the number of electrons $N=50$ diffusion Monte-Carlo can go much larger
- Quantum Chemistry methods CCSD and CCSD(T)
 - Can be very accurate 1 kcal/mol
 - Unfavorable scaling with system size N^6 - N^7
 - Unoccupied orbitals $N^4_{\text{unoccupied}}$
20.000 hours for two atoms in the unit cell
 - f_{12} methods and RI, Jastrow factor (Andreas Grüneis)
 - Chose selected diagrams
 - We absolutely need poor's man methods

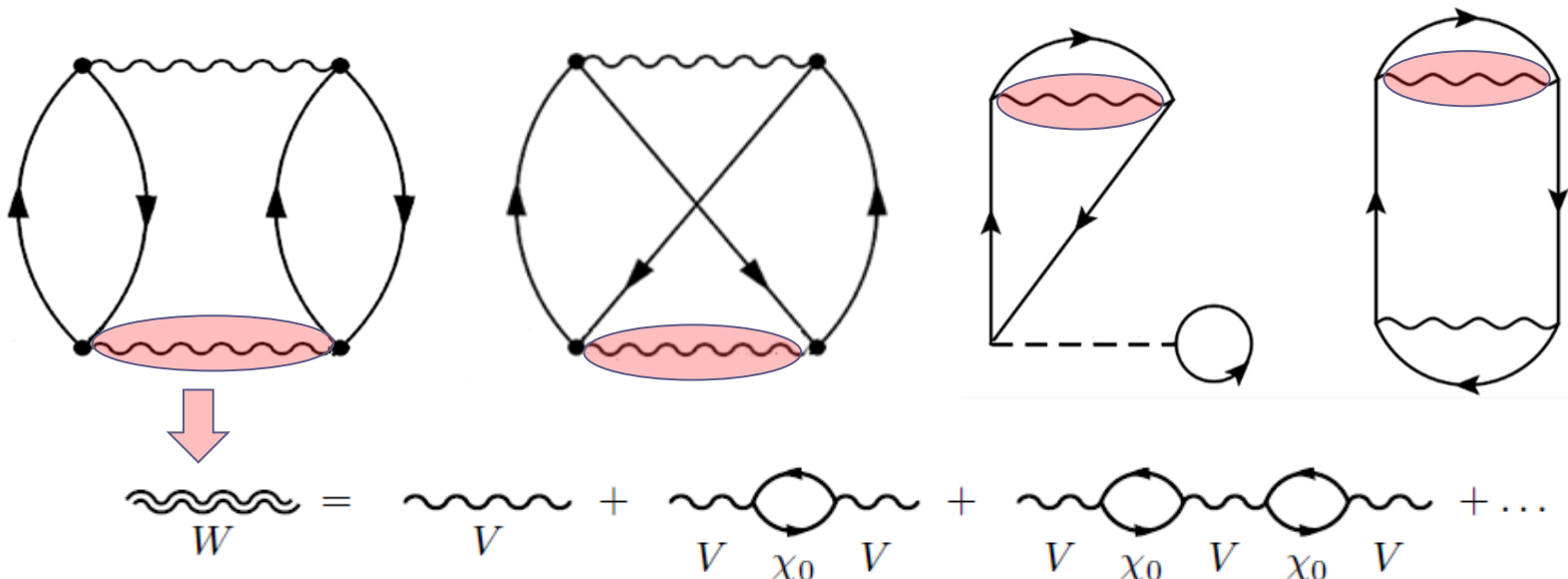
Outline

- Motivation: why do we need methods beyond DFT
- An introduction to quantum chemistry methods
 - Diagrams and Green's functions
 - Full Configuration Interaction (Full CI)
 - Perturbational: CI singles and doubles
 - Resummation: coupled cluster methods
 - Simplified methods: RPA + SOSEX + singles
- Results:
 - Validation of coupled cluster methods for solids
 - Simplified methods: RPA + SOSEX + singles
- Outlook: the many things that remain to be done

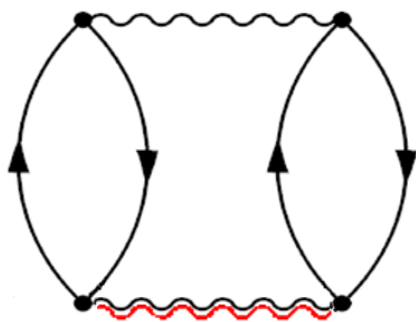
- Standard Quantum Chemistry: Hartree-Fock add correlation
 - The mean field approximation is Hartree-Fock
 - Add fluctuations from second order diagrams
- DFT is, in principle, an exact mean field approximation and should provide a better starting point than HF
- Try to add the most relevant diagrams



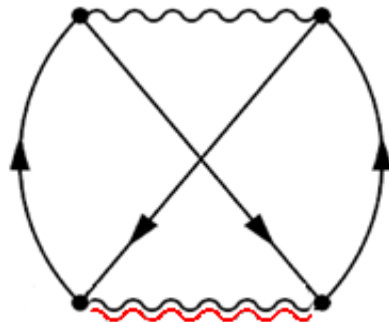
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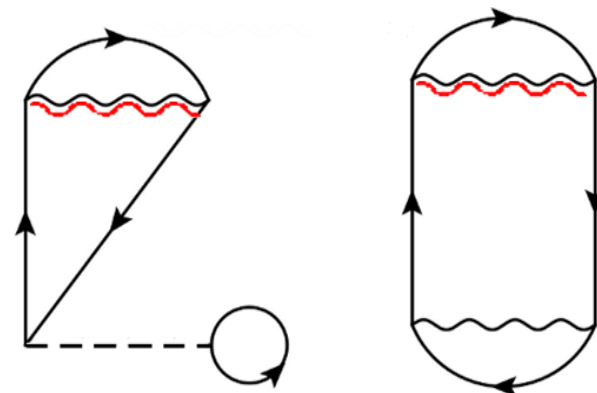
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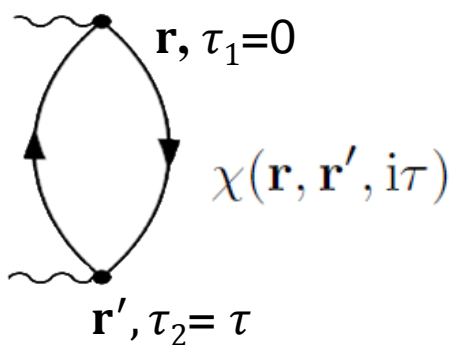
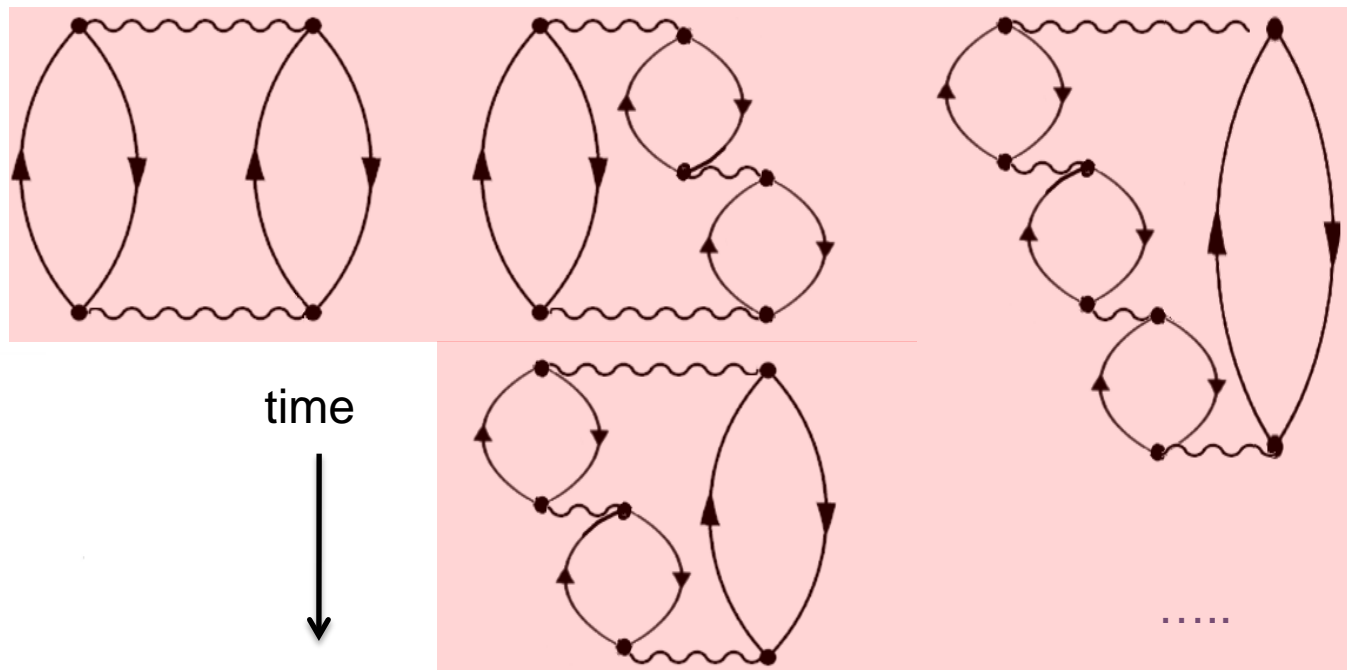
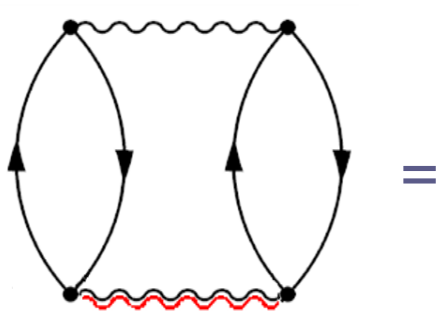
RPA



SOSEX



Singles



time
↓

2.nd order

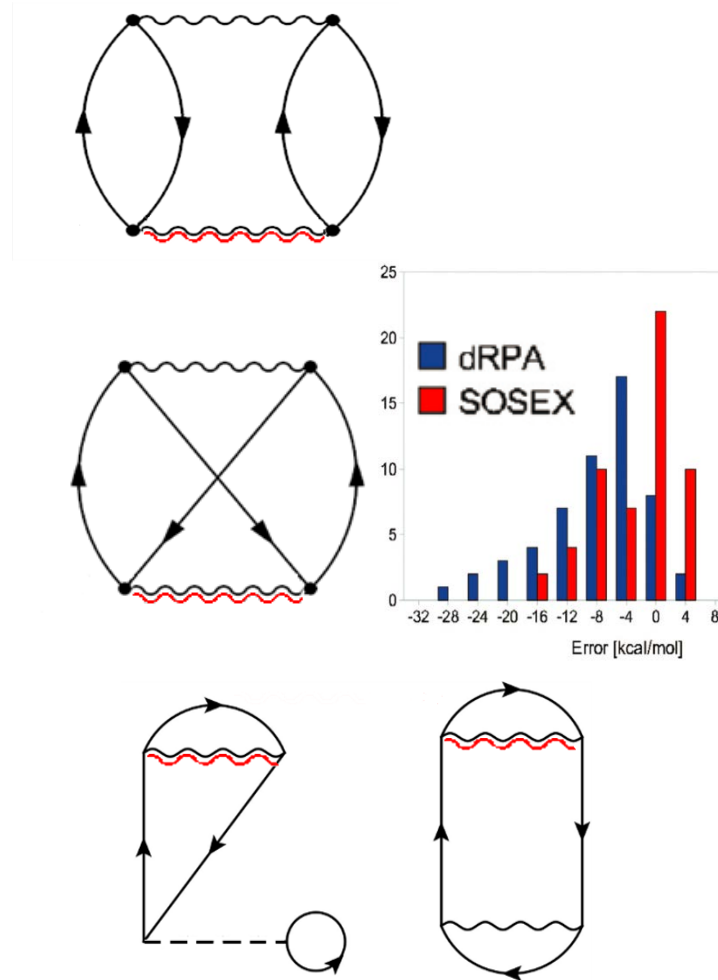
3.rd order

4.order

$$\ln(1 - v\chi) + v\chi = -\frac{\text{Tr}[\chi v \chi v]}{2} - \frac{\text{Tr}[\chi v \chi v \chi v]}{3} - \frac{\text{Tr}[\chi v \chi v \chi v \chi v]}{4} - \dots$$



What do the individual diagrams do

- RPA is the main contribution; it accounts for
 - Covalent
 - Metallic
 - VdW bonding
- SOSEX reduces corr. energy by 30 %
 - Reduces spin-polarization energy
 - Stabilizes non-magnetic solutions
- Singles
 - Contract the charge density compared to DFT and reduce the Pauli repulsion
 - Important for the description of weak interactions



Here the crux starts

- RPA is reasonably good using DFT one electron orbitals
- But how to deal „best“ with exchange diagrams and singles contribution is still a matter of debate
 - For small molecules one might not need to screen exchange since HF+MP2 is excellent (use V^{ex} instead of W) (Ren, Görling)
 - Or approximate exchange by DFT (Olsen-Thyngensen)
- Do all terms efficiently: little point in N^5 - N^6 methods

	Standard	Best
RPA	N^4	N^3 
Screened-EX (SOSEX)	N^5	$N^3 - N^4$
Singles	N^4	N^3 

in progress

- DFT calculation with your favourite functional (PBE)
- Calculate polarizability using auxiliary basis set

$$\chi(\mathbf{r}, \mathbf{r}', i\omega) = \sum_{ia} \langle i|\mathbf{r}\rangle \langle \mathbf{r}|a\rangle \langle a|\mathbf{r}'\rangle \langle \mathbf{r}'|i\rangle \times$$

$$\times \left(\frac{1}{\epsilon_a - \epsilon_i - i\omega_k} + \frac{1}{\epsilon_a - \epsilon_i + i\omega_k} \right)$$

resonant part
poles at positive
frequencies

anti-resonant part
poles at negative
frequencies

$$N_\omega$$

$$N_{\text{occ}} N_{\text{virt}}$$

$$N_r N_r$$

- Calculate correlation energy using plasmon formula

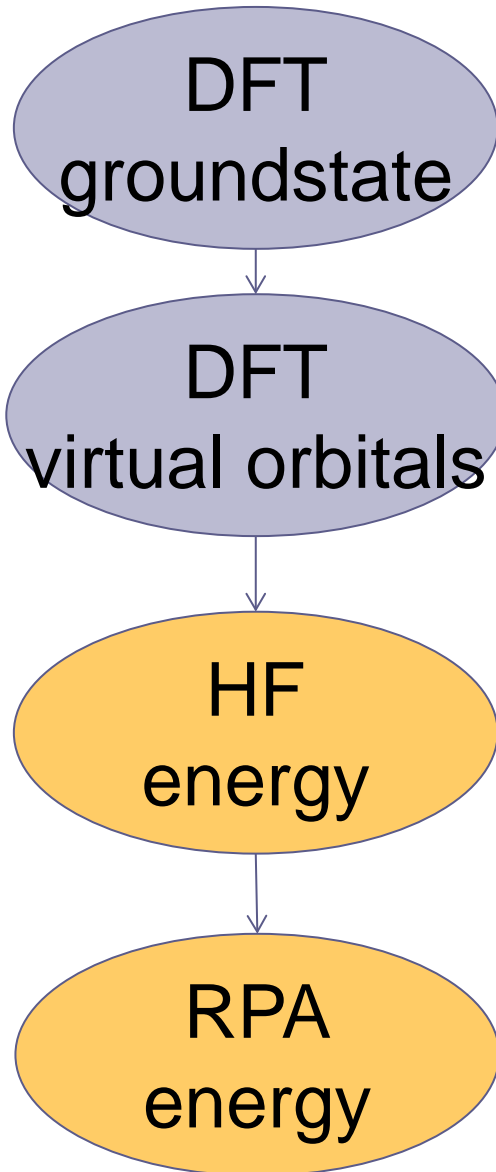
$$E^{\text{RPA}} = \int_0^\infty \frac{d\omega}{2\pi} \text{Tr} \{ \ln [1 - \chi(i\omega)\nu] + \chi(i\omega)\nu \}$$

$$N_\omega$$

$$N_r^3$$

Nozières P and Pines D, 1958, PR **111**, 442; Gonze and Fuchs, PRB **65**, 235109

RPA flow chart



EDIFF = 1E-8
ISMEAR = 0 ; SIGMA = 0.1

NBANDS = maximum # of plane waves
ALGO = Exact ; NELM = 1
ISMEAR = 0 ; SIGMA = 0.1
LOPTICS = .TRUE.

ALGO = Eigenval ; NELM = 1
LWAVE = .FALSE.
LHFCALC = .TRUE. ; AEXX= 1.0
ISMEAR = 0 ; SIGMA = 0.1

NBANDS = maximum # of plane waves
ALGO = ACFDT or ACFDTR
NOMEGA = 12-16

Alternative calculation of polarizability

Rojas, Godby, and Needs (1995), PRL 74, 1827

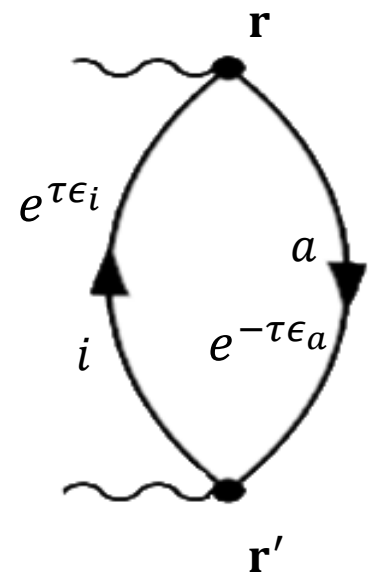
- Polarizability in real space for a set of imag. frequencies

$$\chi(\mathbf{r}, \mathbf{r}', i\omega) = \sum_{ia} \langle i|\mathbf{r}\rangle \langle \mathbf{r}|a\rangle \langle a|\mathbf{r}'\rangle \langle \mathbf{r}'|i\rangle \times \begin{matrix} N_{\text{occ}} N_{\text{virt}} \\ N_{\mathbf{r}} N_{\mathbf{r}'} \end{matrix} \times \left(\frac{1}{\epsilon_a - \epsilon_i - i\omega_k} + \frac{1}{\epsilon_a - \epsilon_i + i\omega_k} \right)$$

- Fourier transform polarizability to imaginary time

$$\chi(\mathbf{r}, \mathbf{r}', i\tau) = \sum_{ia} \langle i|\mathbf{r}\rangle \langle \mathbf{r}|a\rangle \langle a|\mathbf{r}'\rangle \langle \mathbf{r}'|i\rangle e^{-\tau(\epsilon_a - \epsilon_i)}$$

$$\chi(\mathbf{r}, \mathbf{r}', i\tau) = \sum_i e^{\tau(\epsilon_i - \mu)} \langle \mathbf{r}'|i\rangle \langle i|\mathbf{r}\rangle \sum_a e^{\tau(\mu - \epsilon_a)} \langle \mathbf{r}|a\rangle \langle a|\mathbf{r}'\rangle$$



IP polarizability = $G G$

Rojas, Godby, and Needs (1995), PRL 74, 1827

- Fourier transform polarizability to imaginary time and rearrange

$$\chi(\mathbf{r}, \mathbf{r}', i\tau) = \sum_i e^{\tau(\epsilon_i - \mu)} \langle \mathbf{r}' | i \rangle \langle i | \mathbf{r} \rangle \sum_a e^{\tau(\mu - \epsilon_a)} \langle \mathbf{r} | a \rangle \langle a | \mathbf{r}' \rangle$$

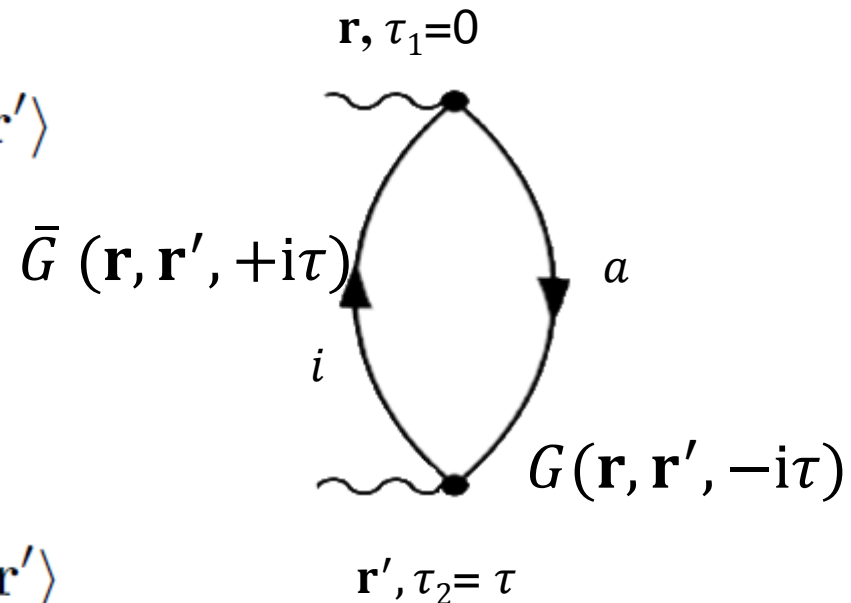
- And defining (Hedin)

$$\bar{G}(\mathbf{r}, \mathbf{r}', i\tau) = \sum_i \langle \mathbf{r} | i \rangle e^{\tau(\epsilon_i - \mu)} \langle i | \mathbf{r}' \rangle$$

$$\underline{G}(\mathbf{r}, \mathbf{r}', -i\tau) = \sum_a \langle \mathbf{r} | a \rangle e^{-\tau(\epsilon_a - \mu)} \langle a | \mathbf{r}' \rangle$$

$$\chi(\mathbf{r}, \mathbf{r}', i\tau) = \bar{G}(\mathbf{r}', \mathbf{r}, i\tau) \underline{G}(\mathbf{r}, \mathbf{r}', -i\tau)$$

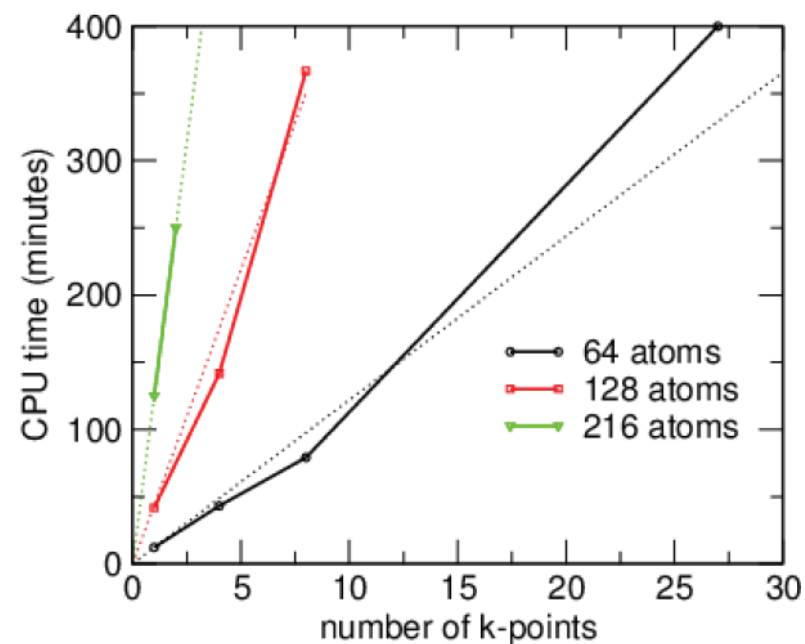
$$\frac{N_{\text{occ}} N_{\text{virt}}}{N_{\mathbf{r}} N_{\mathbf{r}'}} \longrightarrow \frac{(N_{\text{occ}} + N_{\text{virt}})}{N_{\mathbf{r}} N_{\mathbf{r}'}}$$



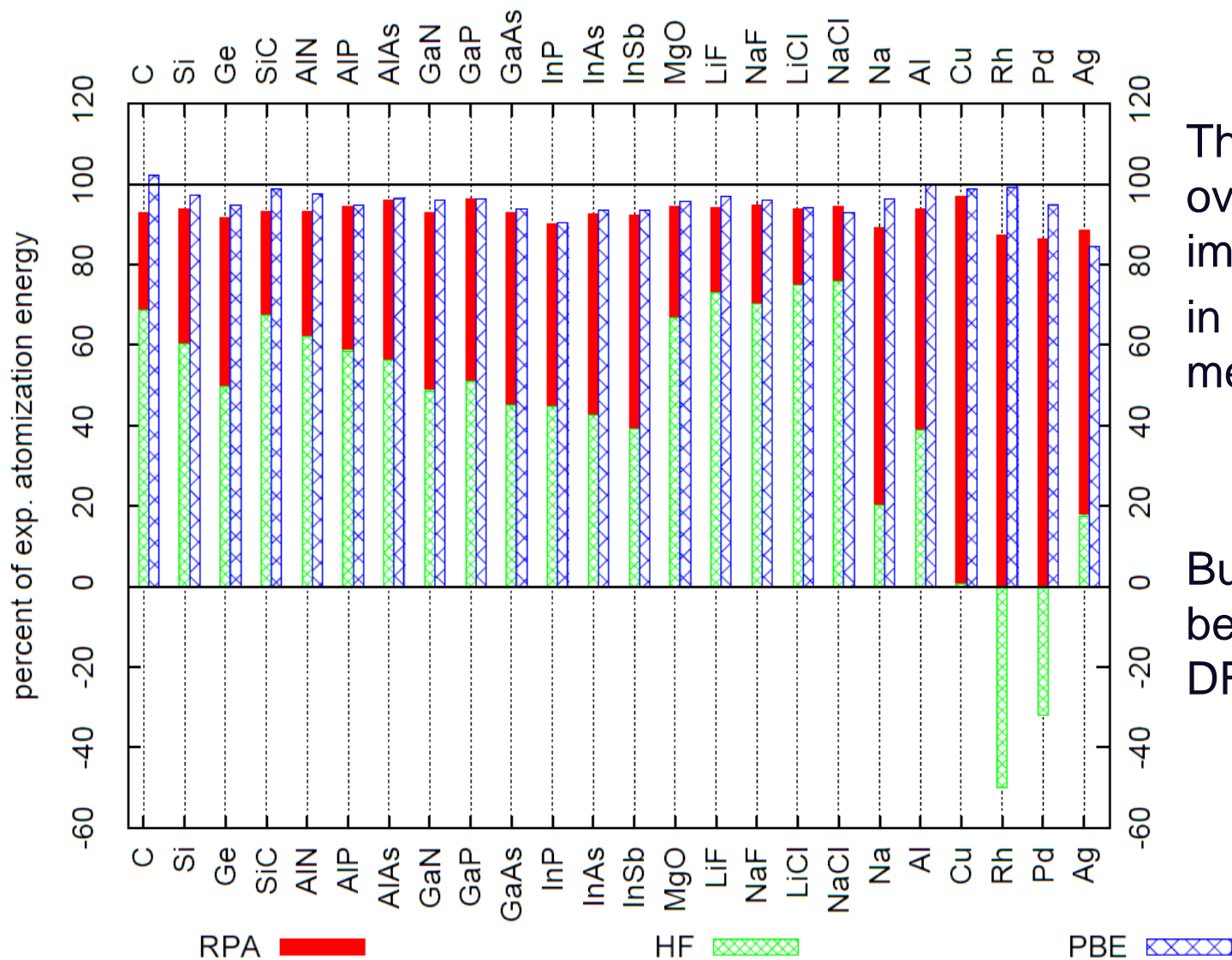
Hedin L. (1965), Phys. Rev. 139, A796.

- New RPA code is available
Kaltak M., Klimeš J., Kresse G. ,
JCTC 10, 2498 (2014).
- Scales linearly in the number of k-points (as DFT)
 - Instead of quadratically as for conventional RPA and hybrid functionals
- Scales cubically in system size (as DFT)
- Pre-factors are much larger than in DFT (of course), but calculations for 200 atoms take less than 1 hour (128 cores)

Si defect calculations
64-216 atoms



RPA how good is it ?



The improvement over HF is impressive in particular for metals

But not much better than best DFT functionals

J. Harl, G. Kresse, PRL 103, 056401 (2009), PRB (2010)

Heats of formation (dRPA)

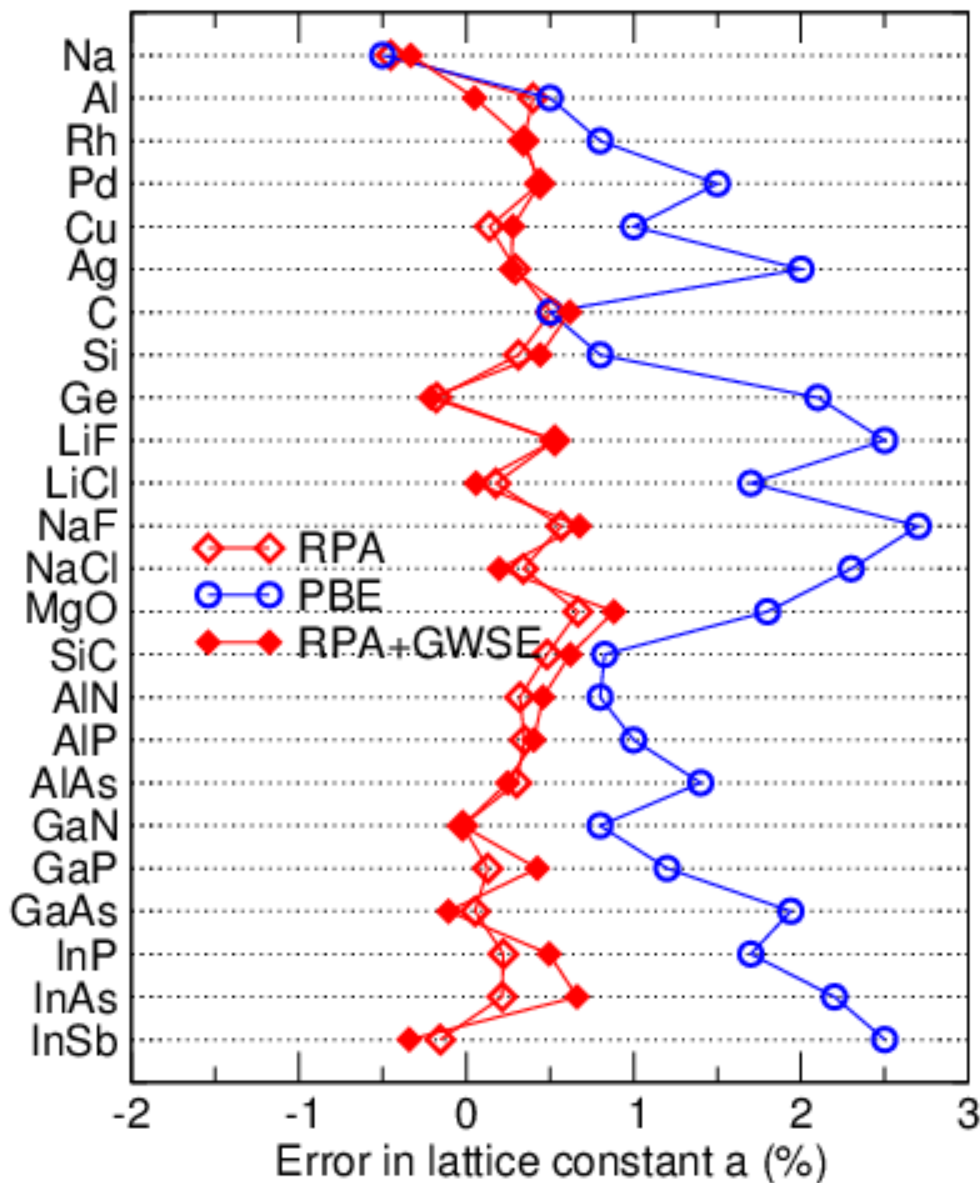
Heats of formation w.r.t normal state at ambient conditions
in kJ/mol



kJ/mol	PBE	RPA	EXP
$\text{Li} + \text{F}_2 \rightarrow \text{LiF}$	570	609	621
$\text{Mg} + \text{O}_2 \rightarrow \text{MgO}$	516	577	604
$\text{Mg} + \text{H}_2 \rightarrow \text{MgH}_2$	52	72	78
$\text{Al} + \text{N}_2 \rightarrow \text{AlN}$	262	291	321
$\text{Si} + \text{C} \rightarrow \text{SiC}$	51	64	69
$\text{CO}@ \text{Rh}$	183	139	144

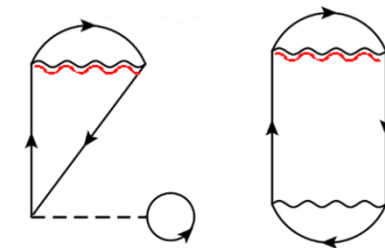
J. Harl, G. Kresse, PRL 103, 056401 (2009)

Lattice constants: metals and covalent solids



- Improvements compared to PBE are substantial

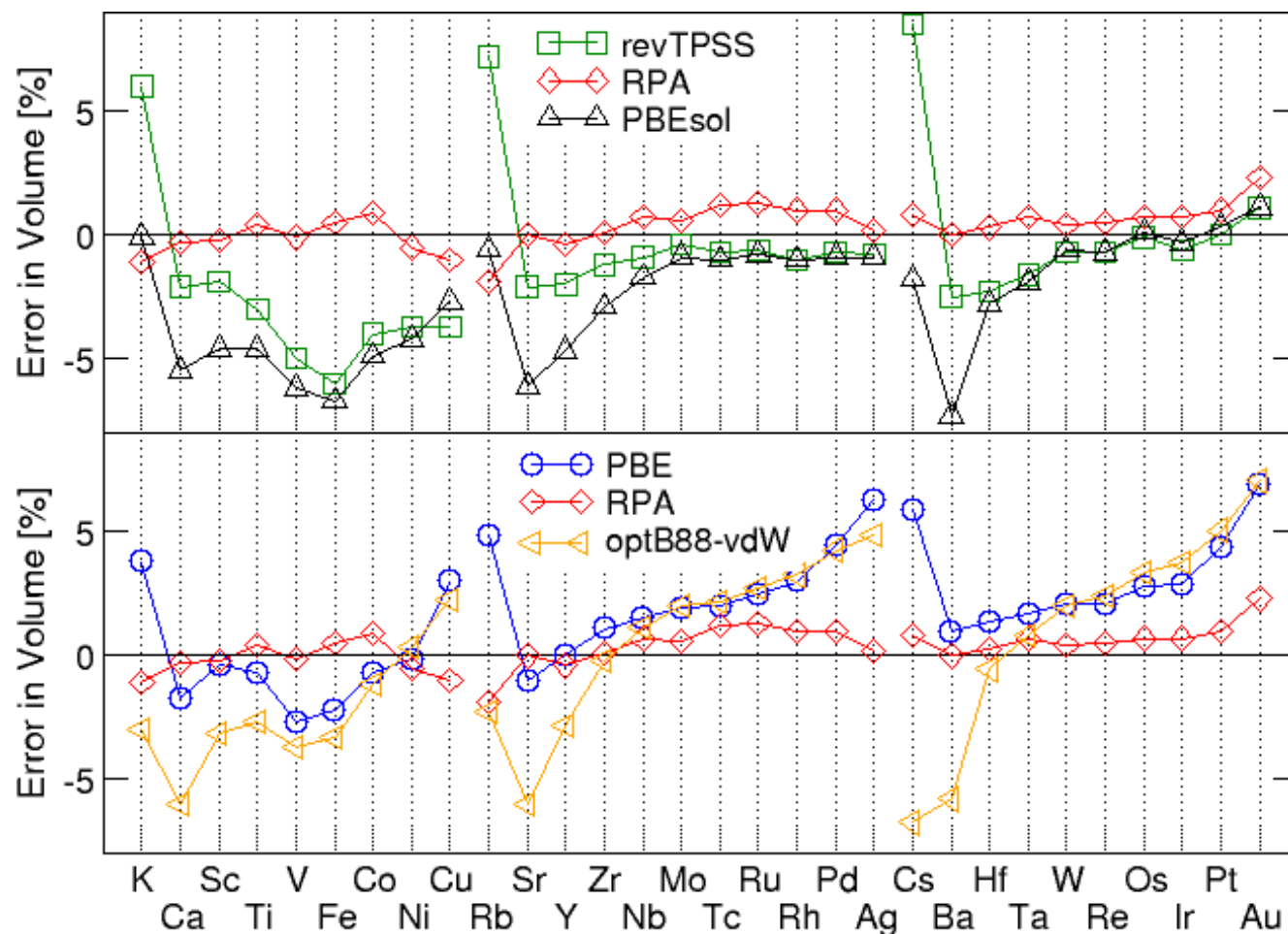
- Here results for a refined treatment beyond RPA are also shown (Singles)



Klimes, Kaltak, Maggio, Kresse, JCP in print

Lattice constants of transition metals: NC PAW

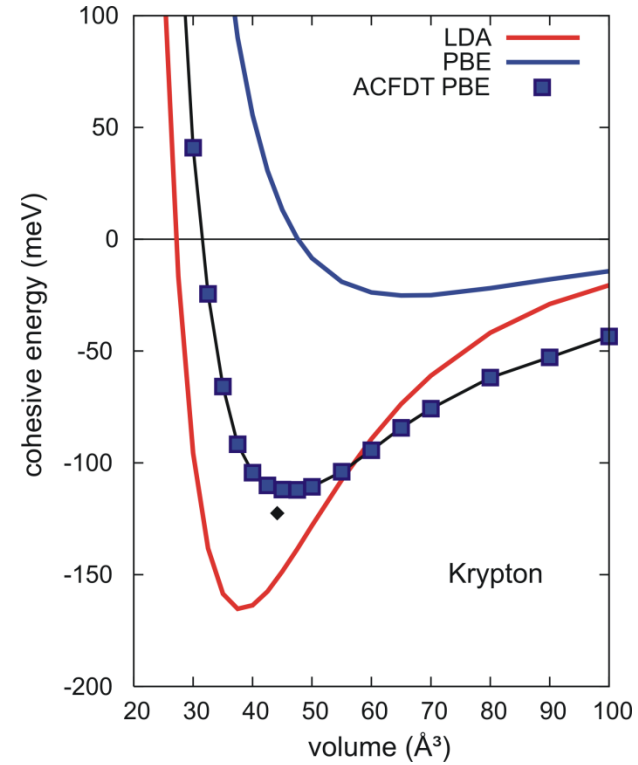
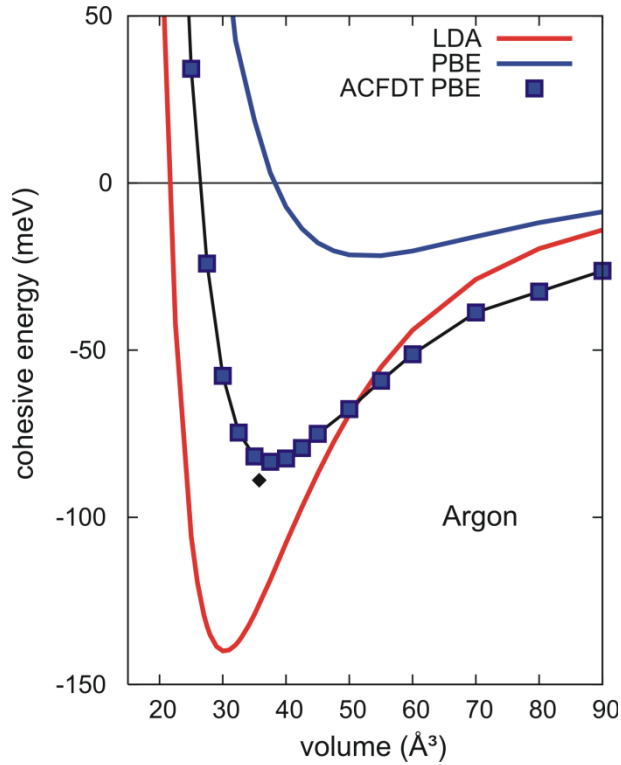
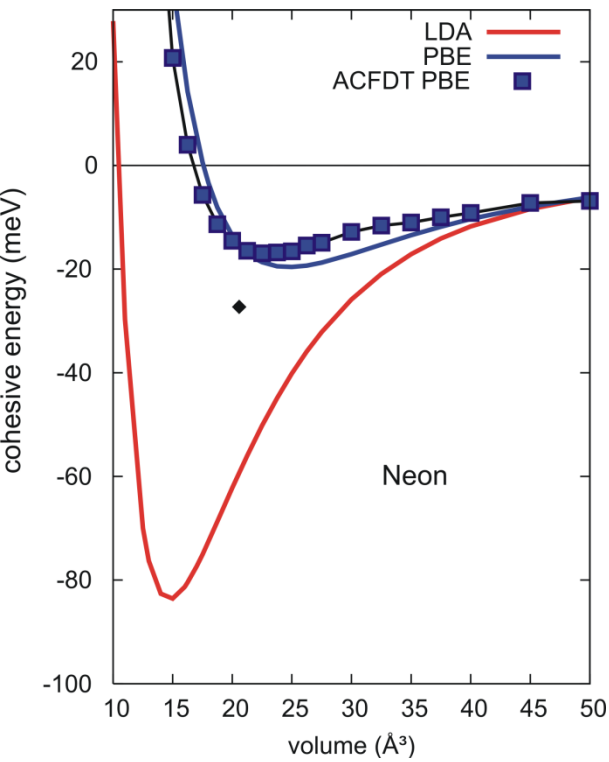
Phys. Rev. B 87, 214102 (2013), Klimes, Kaltak, Kresse, PRB90, 075125 (2014)



Lattice constants are consistently good for 3d, 4d and 5d metals

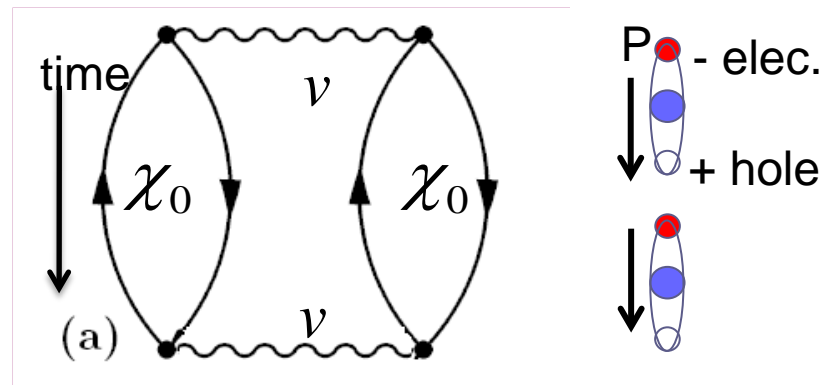
All DFT flavours underestimate 3d lattice constants and most overestimate 4d and 5d

RPA for rare-gas solids: Ne, Ar and Kr



J. Harl and G.Kresse, PRB 77, 045136 (2008).

Klimes, Kaltak, Maggio, Kresse, JCP in print



Singles for rare-gas solids: Ne, Ar and Kr

Rare gas solids: CCSDT Rosciszewski, PRB 62, 5482 (2000)

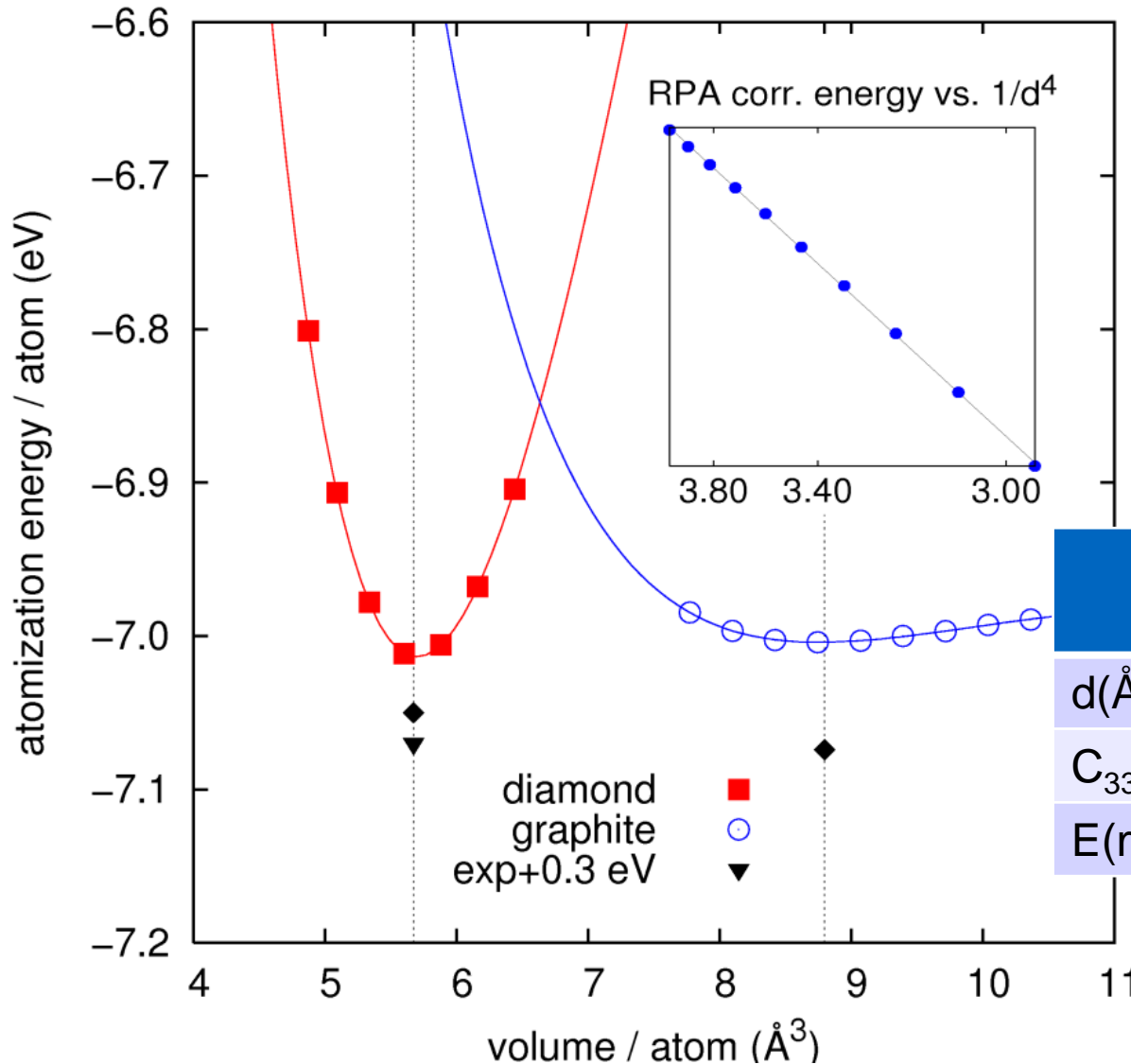
No difference between +rSE and GWSE

Except for Ne, the results are excellent

Latt. Const.	EXX+RPA	+GWSE	EXP
Ne	4.35	4.38	4.30
Ar	5.33	5.25	5.25
Kr	5.68	5.61	5.63
energies			
Ne	19	30	26.2
Ar	66	87	87.9
Kr	97	119	121.8

Klimes, Kaltak, Maggio, Kresse, JCP in print

Covalent versus Van der Waals: Carbon



Graphite versus
Diamond
 $1/d^4$ behavior at short
distances

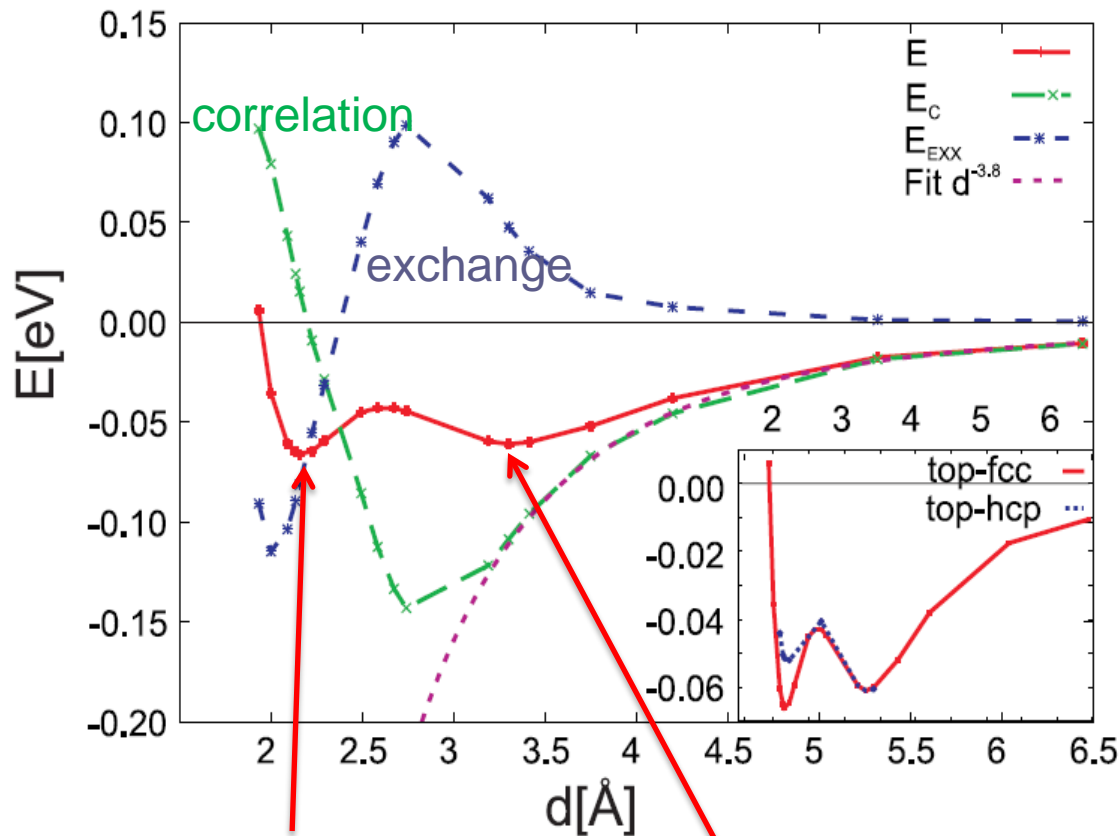
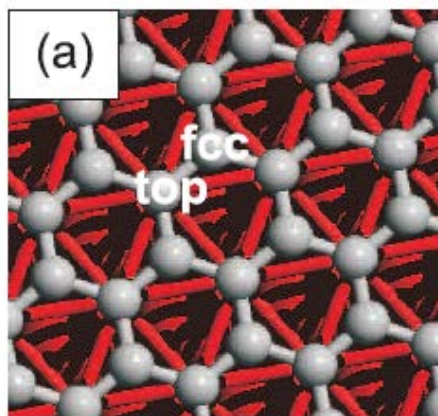
	QMC (Galli)	RPA	EXP
$d(\text{\AA})$	3.426	3.34	3.34
C_{33}		36	36-40
$E(\text{meV})$	56	48	43-50

PRL 103, 056401 (2009).
S. Lebeque, et al.,
PRL 105, 196401 (2010).

Graphene adsorbed on Ni: RPA energetics

Olsen, ..., Thygesen, PRL **107**, 156401.

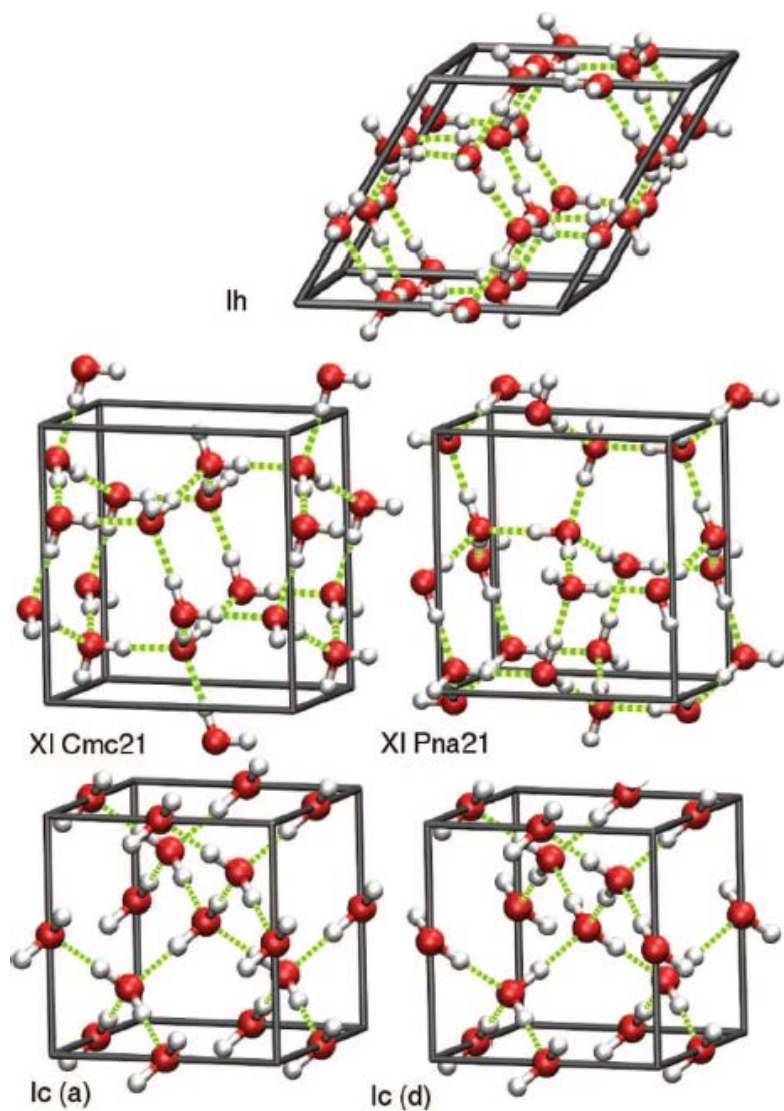
Mittendorfer, ..., Kresse, PRB **84**, 201401.



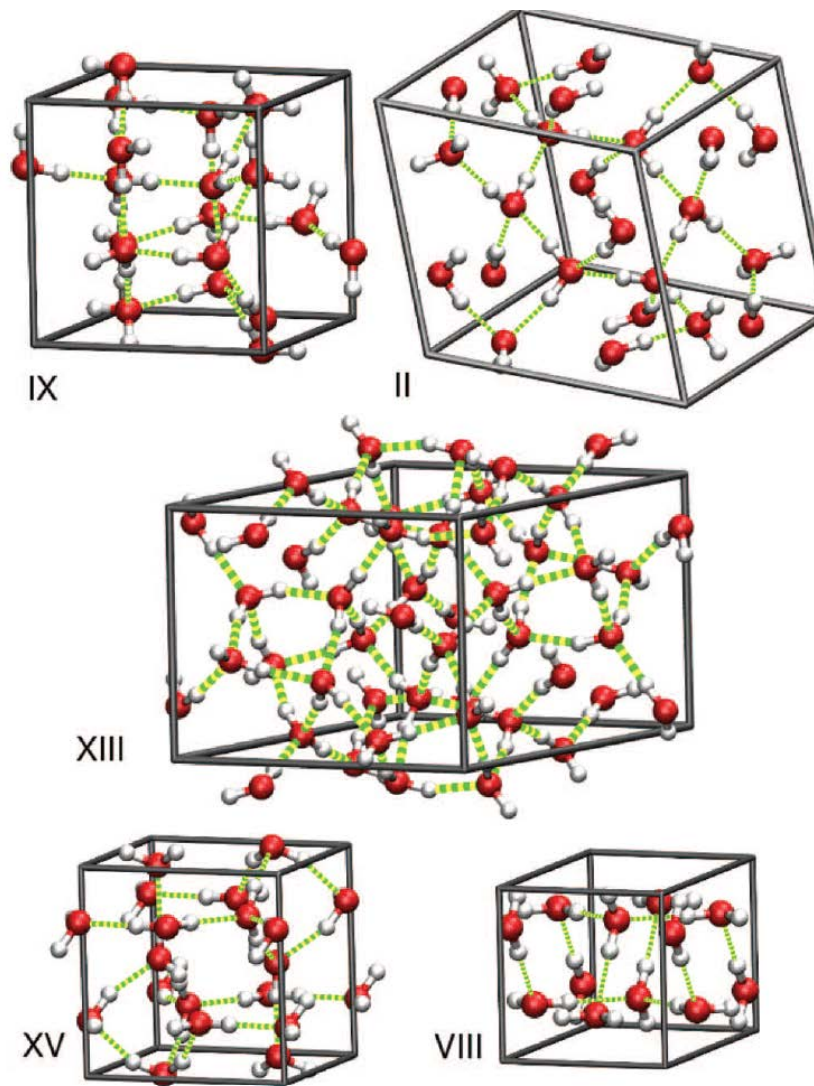
„Chemisorption minimum“
65 meV at 2.1 Å

Physisorption minimum
60 meV at 3.3 Å

Low pressure phases



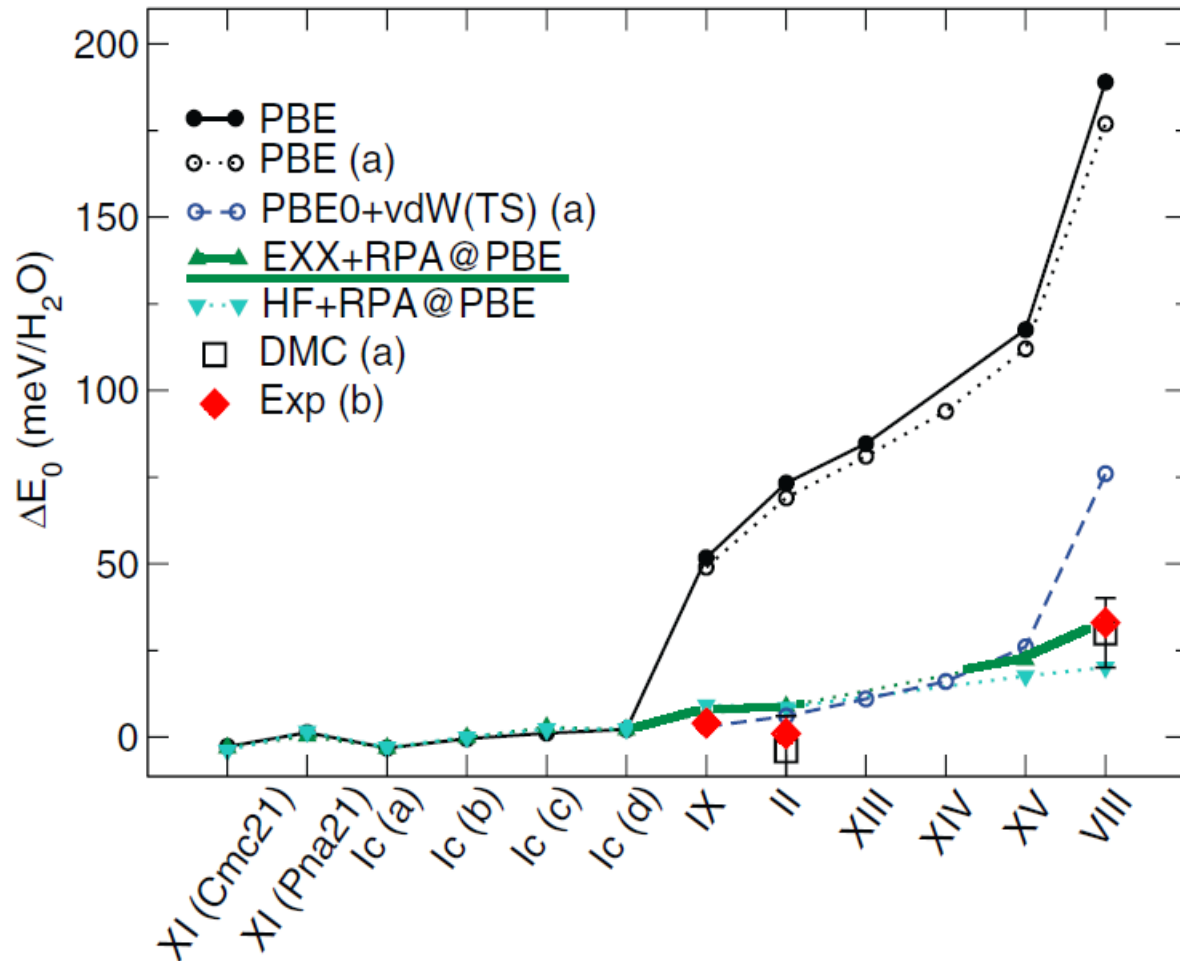
high pressure phases



Issues to describe energetics under pressure

Macher M., Klimeš J., Franchini C., Kresse G. (2014), JCP 140, 084502.

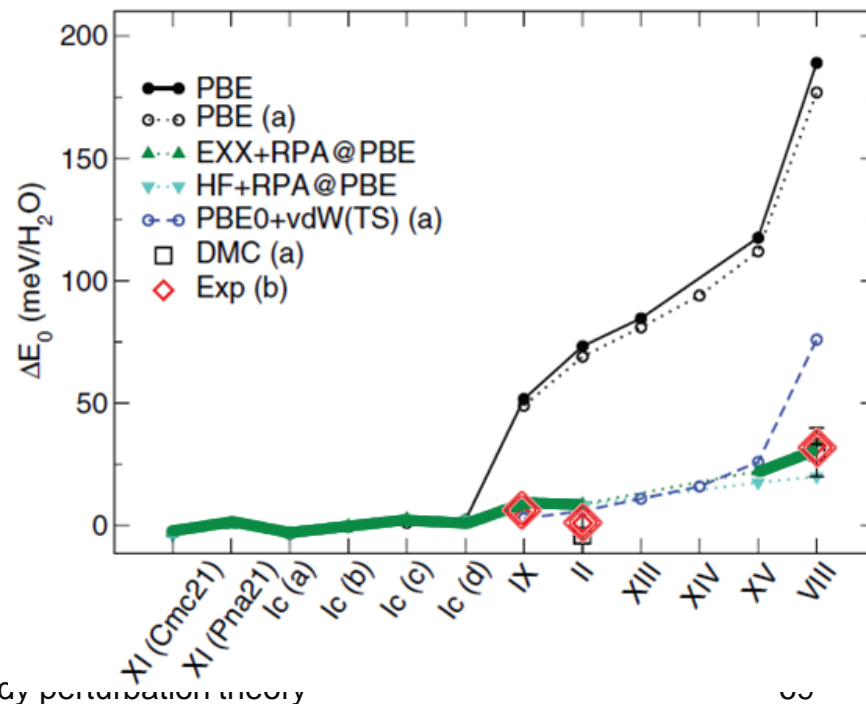
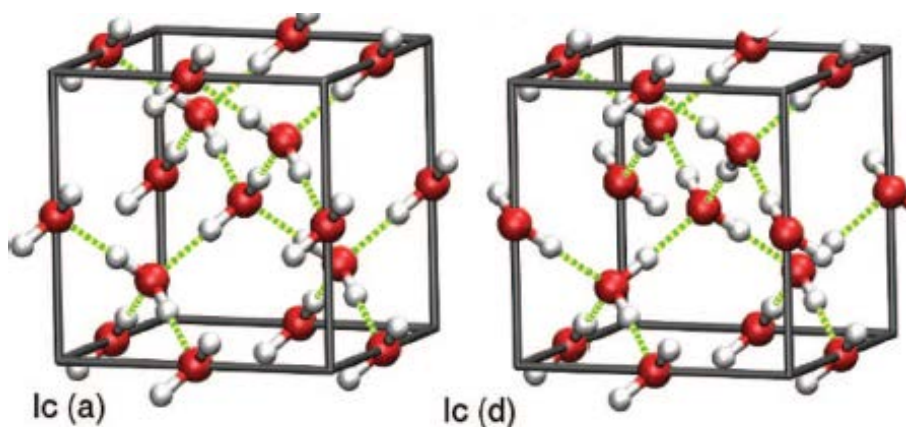
- RPA is very close to DMC (diffusion MC)
- For ice VIII, markedly better agreement with DMC than PBE0+vdW(TS)



Ice: at ambient and high pressure

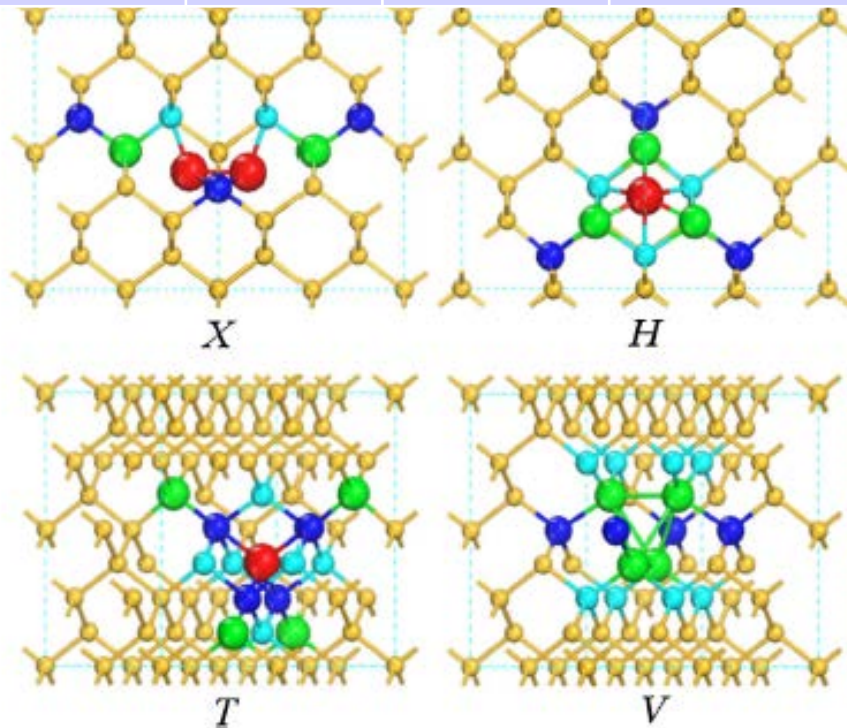
Macher M., Klimeš J., Franchini C., Kresse G. (2014), JCP 140, 084502.
 Klimes, Kaltak, Maggio, Kresse, JCP in print

	EXX+RPA	RPA+GWSE	EXP
volume	32.9	32.0	32.1
energy	536	620	610



Energetics of Si interstitials and vacancies

	PBE	HSE	HSE/vdW	QMC	RPA	rsRPA	GW
Dumbbell X	3.56	4.43	4.41	4.4(1)	4.20	4.50	4.46
Hollow H	3.62	4.49	4.40	4.7(1)	4.33	4.65	4.51
Tetragonal T	3.79	4.74	4.51	5.1(1)	4.93		
Vacancy	3.65	4.19	4.38		4.33	4.24	
Diff.Barrier		0.50	0.29		0.35	0.49	



200 atoms in about 1 hour on 256 cores

Kaltak M., Klimeš J., Kresse G.
PRB 90, 054115 (2014).

HSE, HSE+vdW & Pictures:


Gao, Tkatchenko, PRL 111, 45501

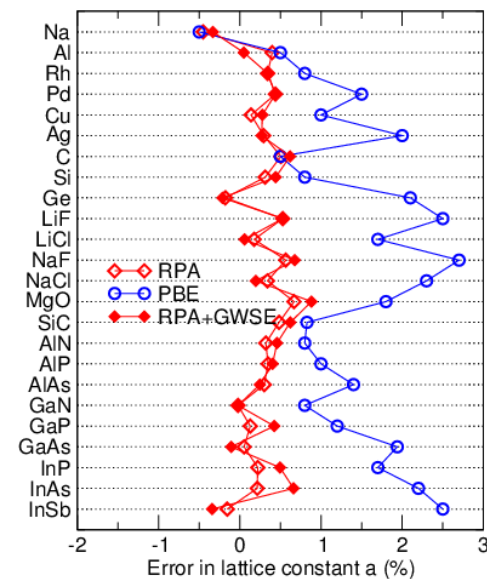
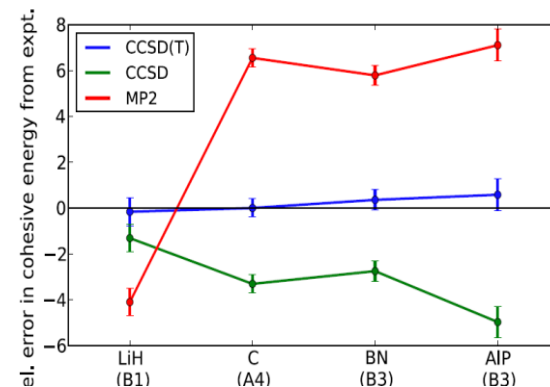
QMC: Parker, Wilkins, Hennig,
Phys. Status Solidi B 248, 267 (2011).

rsRPA: Bruneval, PRL 108, 256403 (2012).

GW: Rinke, PRL 102, 026402 (2009).

Quantum Chemistry methods have a future

- DFT will remain the workhorse method
- 👍 Full CI for solids is possible
 - FCI-QMC operating in the Slater determinant space
- 👍 Quantum Chemistry for solids
 - CCSD(T) seems to be pretty much exact
- 👍 RPA in combination with PBE orbitals
 - A lot of very promising results for a wide variety of systems
 - Forces soon to come in 
- The field is exciting and thriving
 - We need more people to work on codes



QC Issues to be solved in future

- The slow basis set convergence is really a killer
- Coupled cluster methods (CCD) involve terms scaling like

$$N_{virt}^4 N_{occ}^2$$

- One needs to model the inter-electron CUSP condition explicitly using e.g. Jastrow factors (f_{12} method + RI)
- Rely on locality principle
 - RPA correlation stemming from symmetric part of wavefunction is long ranged, but fast to evaluate
 - Correlations related to anti-symmetry (e.g. second order exchange) are shortranged
Locality principle can be exploited
 - Encouraging results for molecules: Werner, F. Neese **ORCA**
- RPA is good for prime time
CC needs another 5-10 years in solids



Acknowledgement

FWF for financial support
The group for their
great work

You for listening

