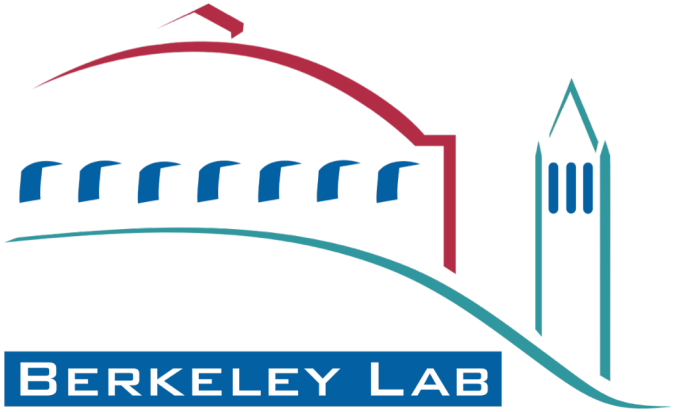
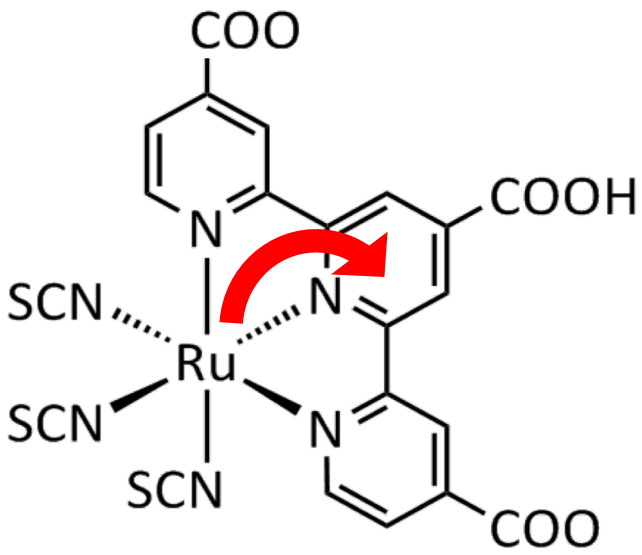
Variational Monte Carlo Optimization and Excited States

Eric Neuscamman

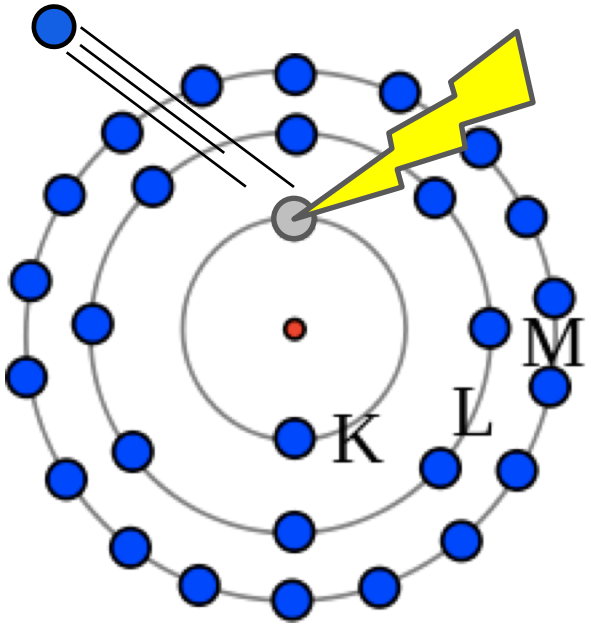
August 9, 2018



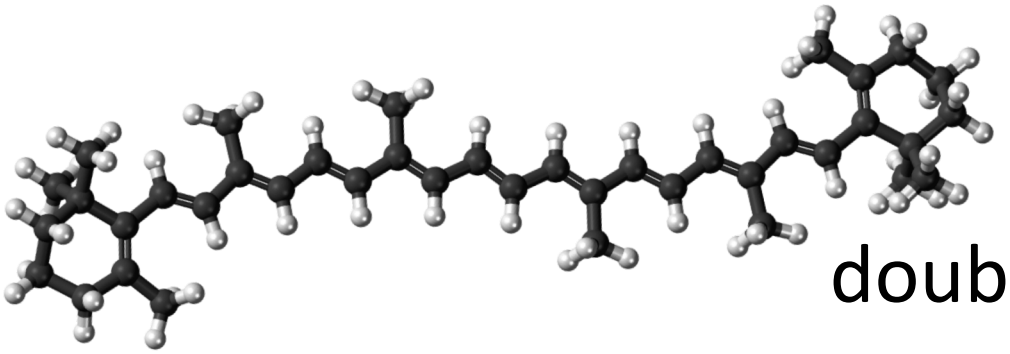
motivation



charge transfer



core spectroscopy



double excitations

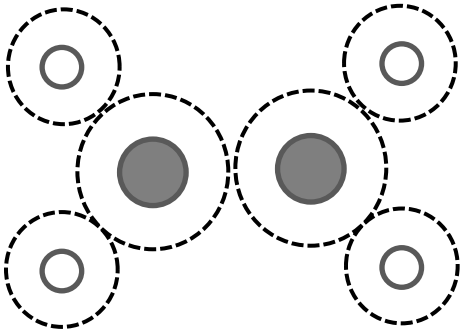
the menu

aperitif: number counting Jastrows

main course: excited states with QMC

dessert: optimization methods

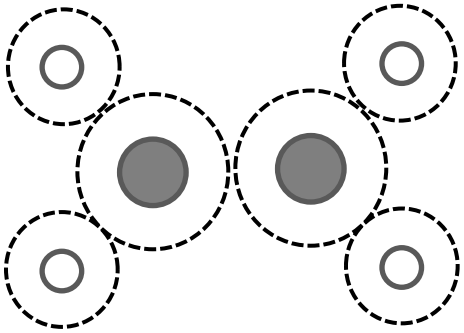
number counting Jastrow factors



$$C_i(\vec{r}) = 1 \text{ if } \vec{r} \text{ in region } i$$
$$= 0 \text{ otherwise}$$

Van Der Goetz & Neuscamman, JCTC 2017

number counting Jastrow factors



$$\mathrm{C_i}(\vec{\mathrm{r}}) = 1 \text{ if } \vec{\mathrm{r}} \text{ in region } i$$
$$= 0 \text{ otherwise}$$

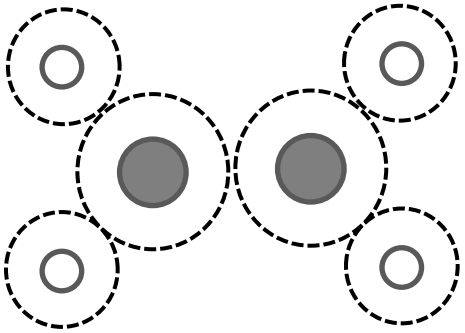
$$\exp\left(-\alpha\left(N - \sum_k \mathrm{C_i}(\vec{\mathrm{r}}_k)\right)^2\right)$$

modifies the balance between these configs:

$\mathrm{C}\,\mathrm{C}$ $\quad$ $\mathrm{C}^+\mathrm{C}^-$ $\quad$ $\mathrm{C}^-\mathrm{C}^+$

Van Der Goetz & Neuscamman, JCTC 2017

number counting Jastrow factors



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modifies the balance between these configs:

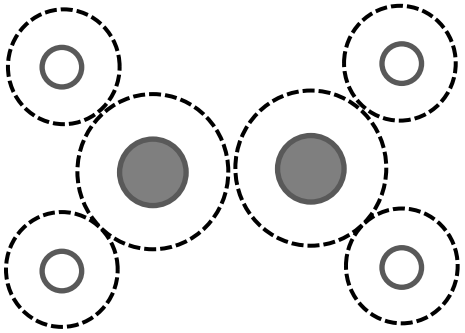
$\mathrm{C}\,\mathrm{C}$ $\quad$ $\mathrm{C}^+\mathrm{C}^-$ $\quad$ $\mathrm{C}^-\mathrm{C}^+$

general form:

$$\exp\left(\sum_{ijkl} \mathrm{F_{ij}}\ \mathrm{C_i}(\vec{\mathrm{r}}_k)\ \mathrm{C_j}(\vec{\mathrm{r}}_l)\right)$$

Van Der Goetz & Neuscamman, JCTC 2017

number counting Jastrow factors



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$$= 0 \text{ otherwise}$$

$$\exp\left(-\alpha\left(N - \sum_k C_i(\vec{r}_k)\right)^2\right)$$

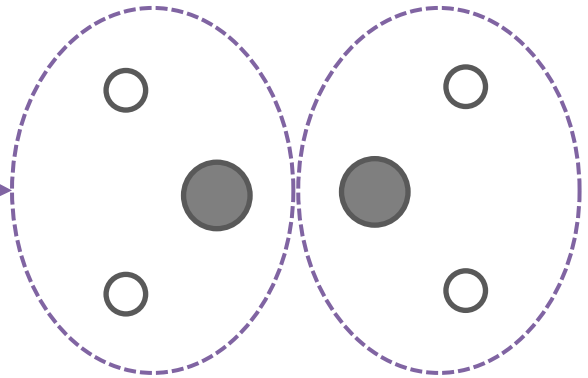
modifies the balance between these configs:

$C\,C$ $\quad$ C^+C^- $\quad$ C^-C^+

general form:

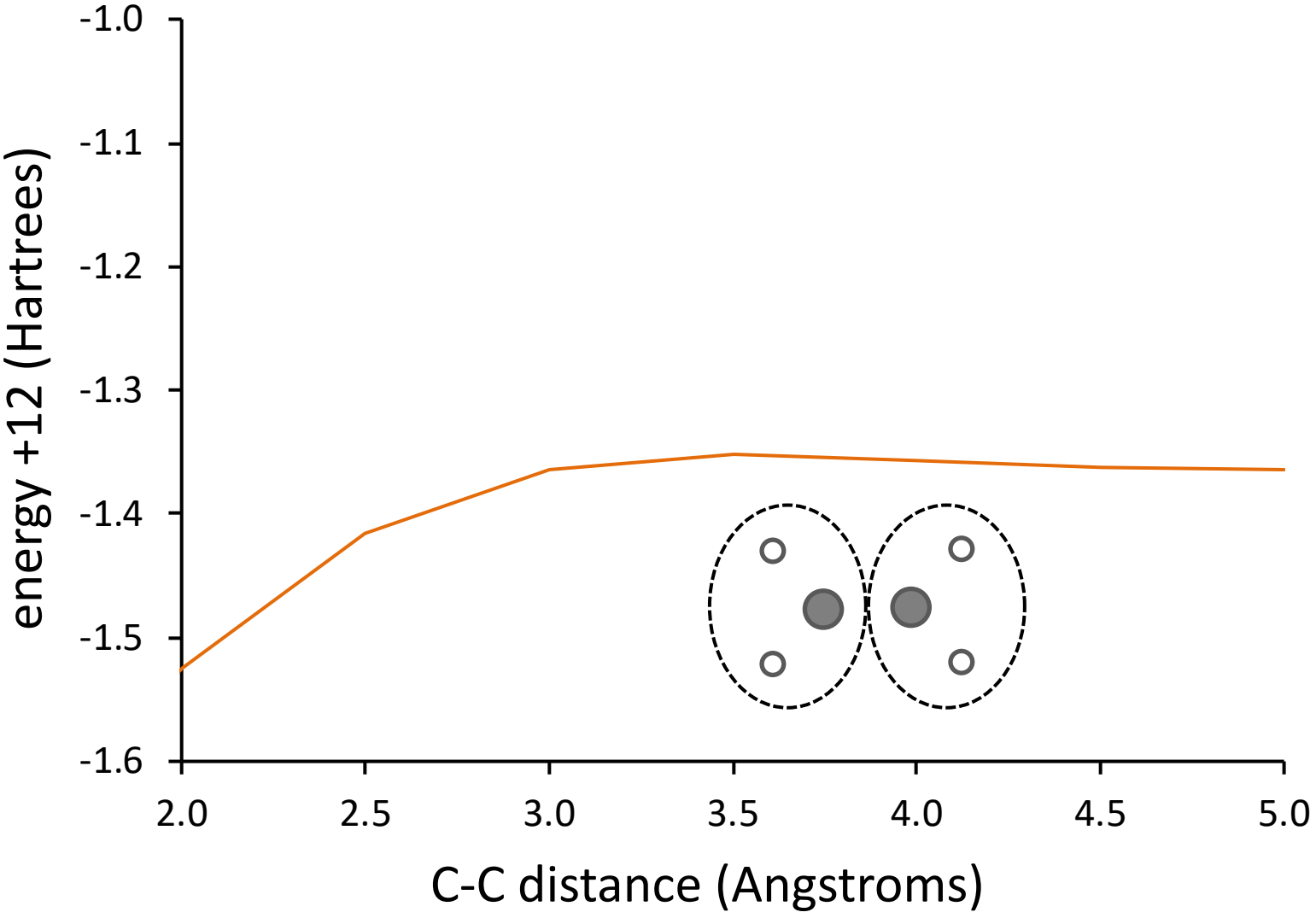
$$\exp\left(\sum_{ijkl} F_{ij}\, C_i(\vec{r}_k) C_j(\vec{r}_l)\right)$$

linear combinations?



Van Der Goetz & Neuscamman, JCTC 2017

clean additivity



Van Der Goetz & Neuscamman, JCTC 2017

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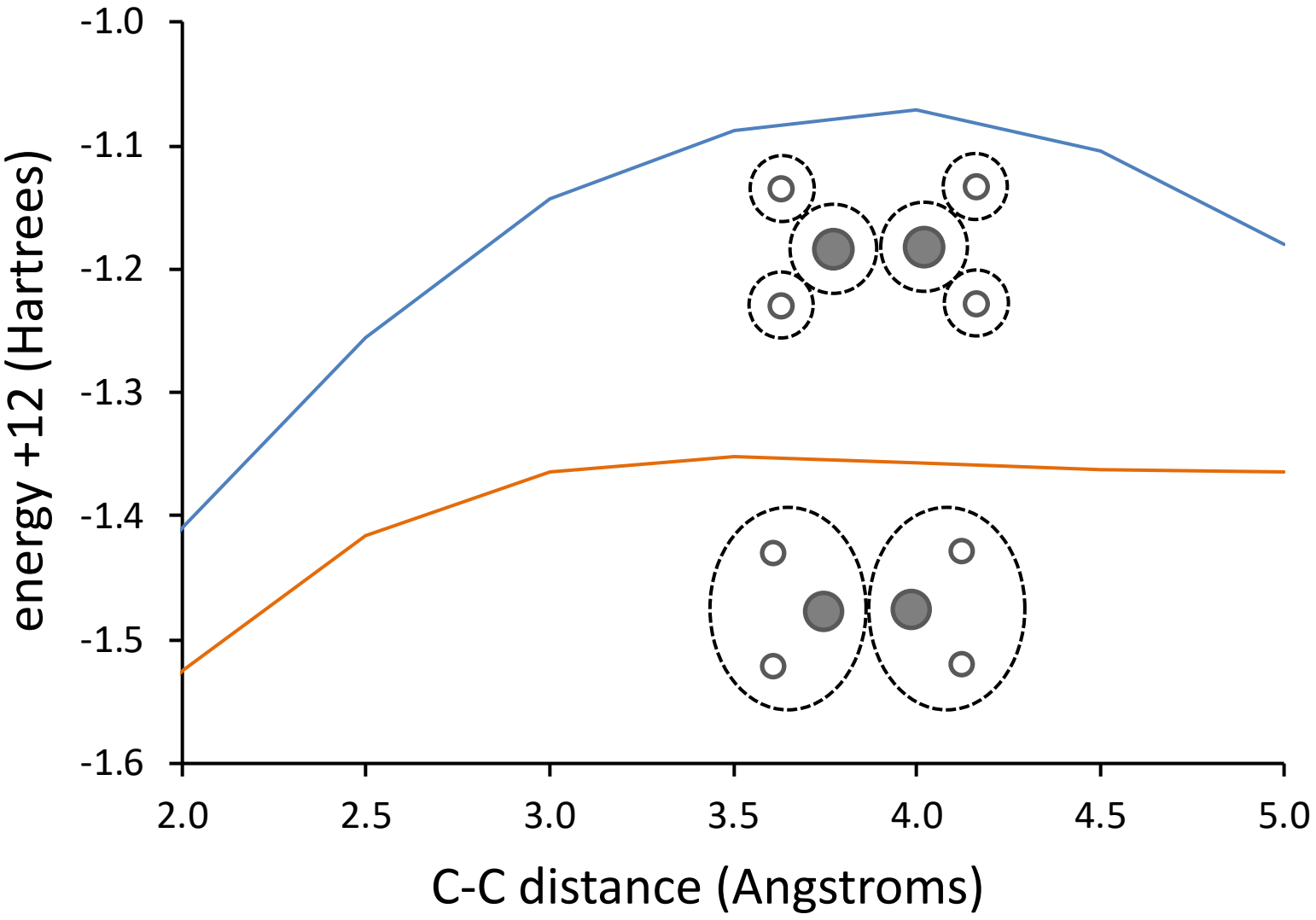

Van Der Goetz & Neuscamman, JCTC 2017

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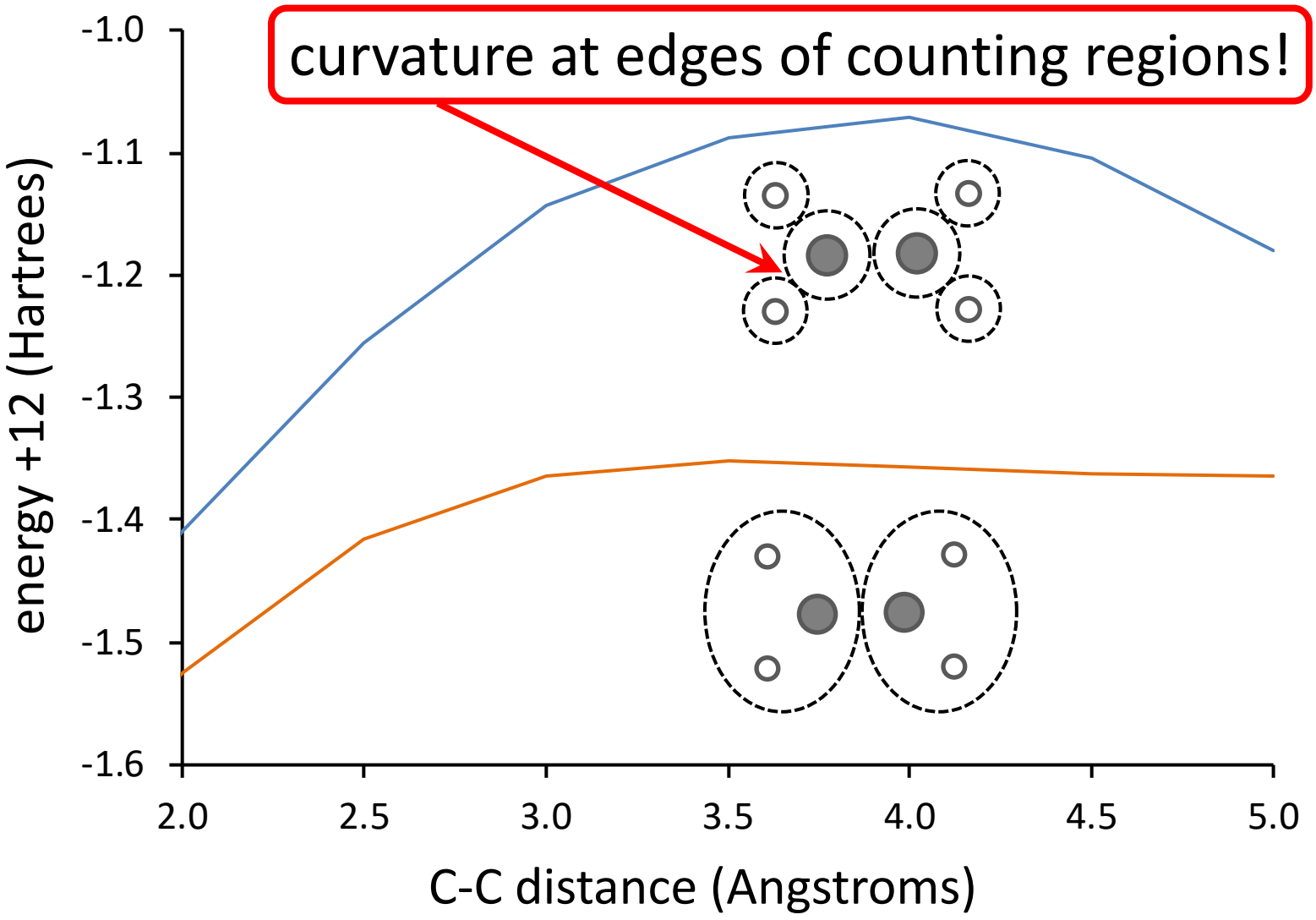

Van Der Goetz & Neuscamman, JCTC 2017

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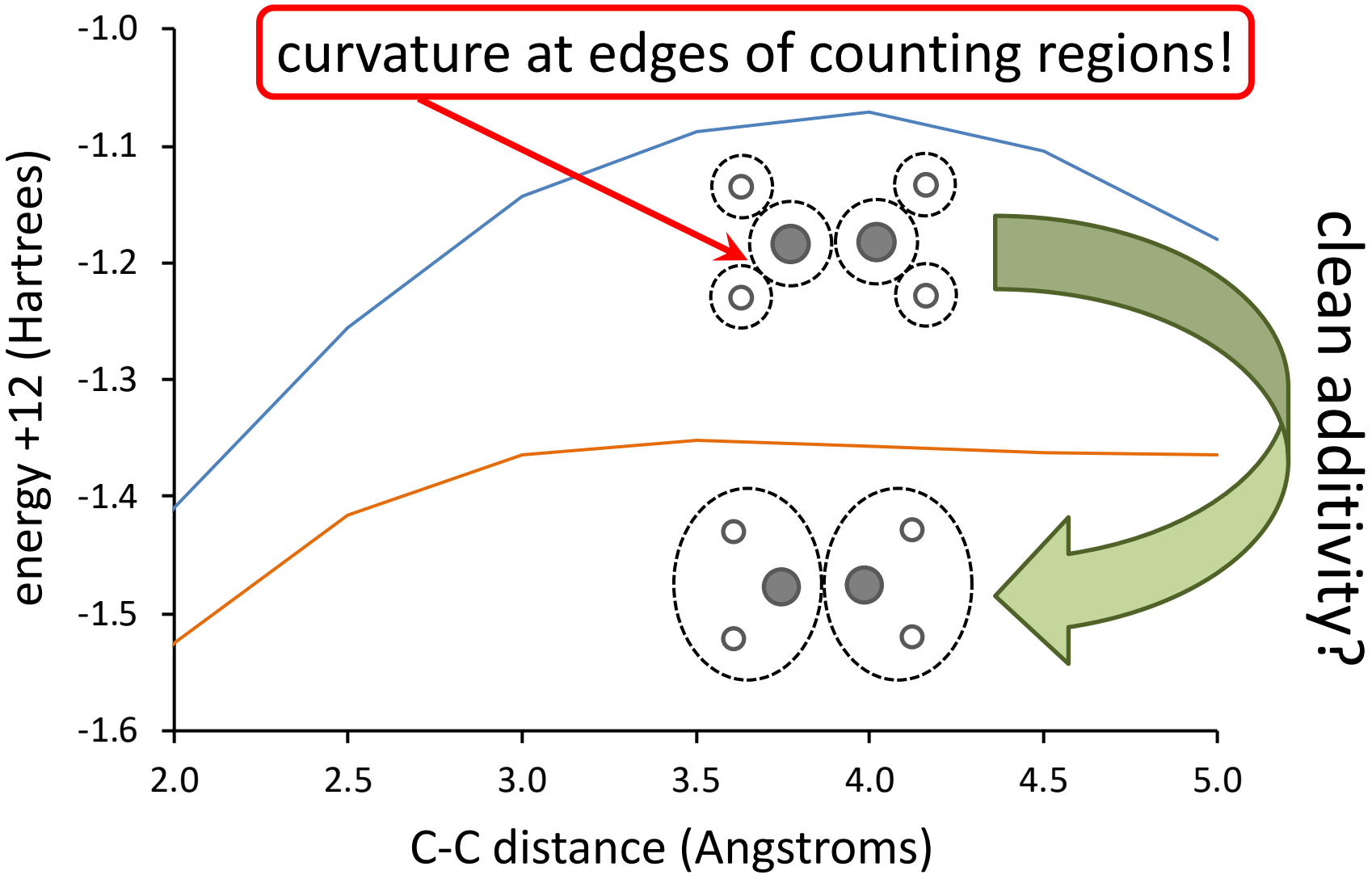

Van Der Goetz & Neuscamman, JCTC 2017

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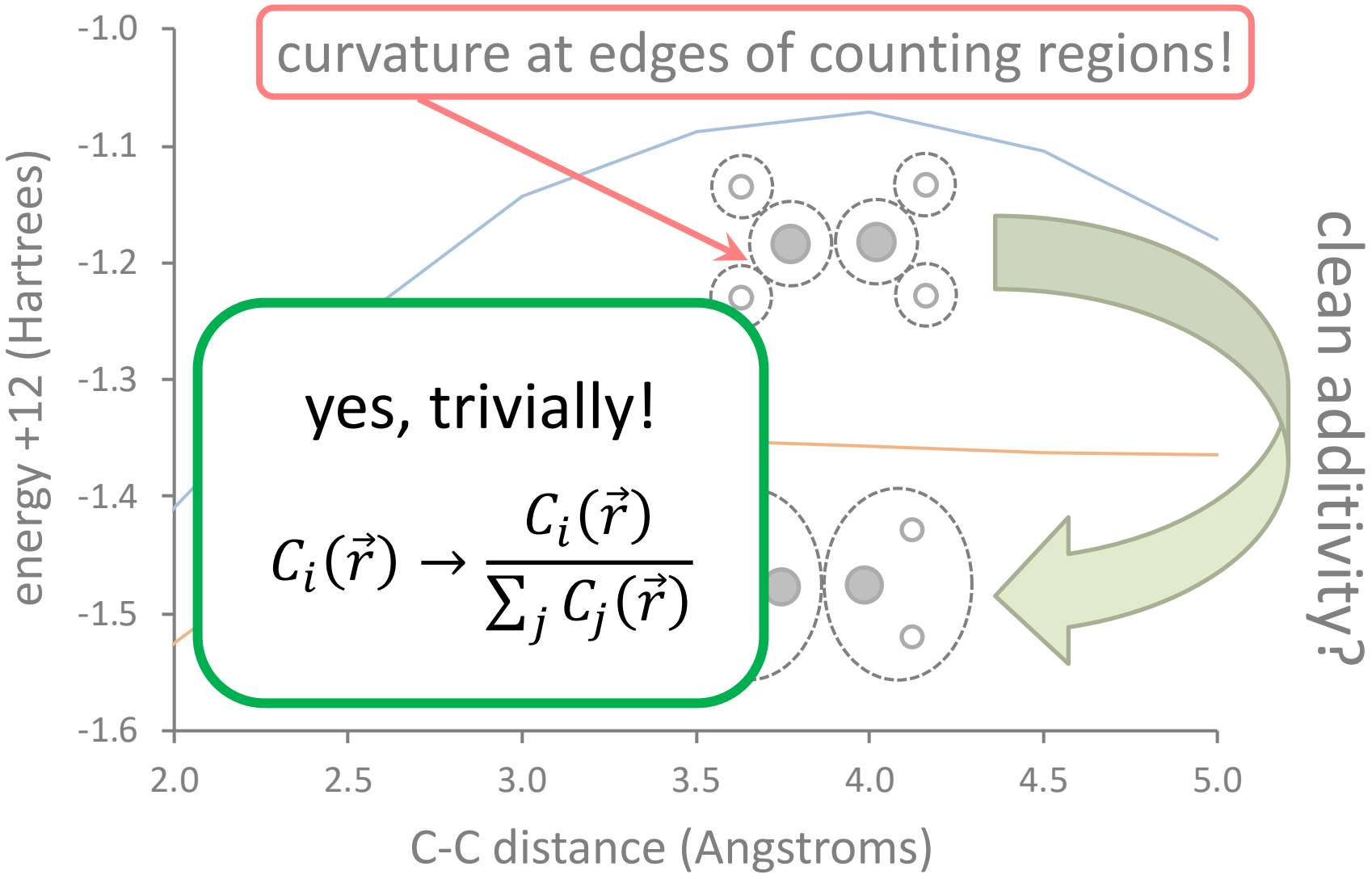
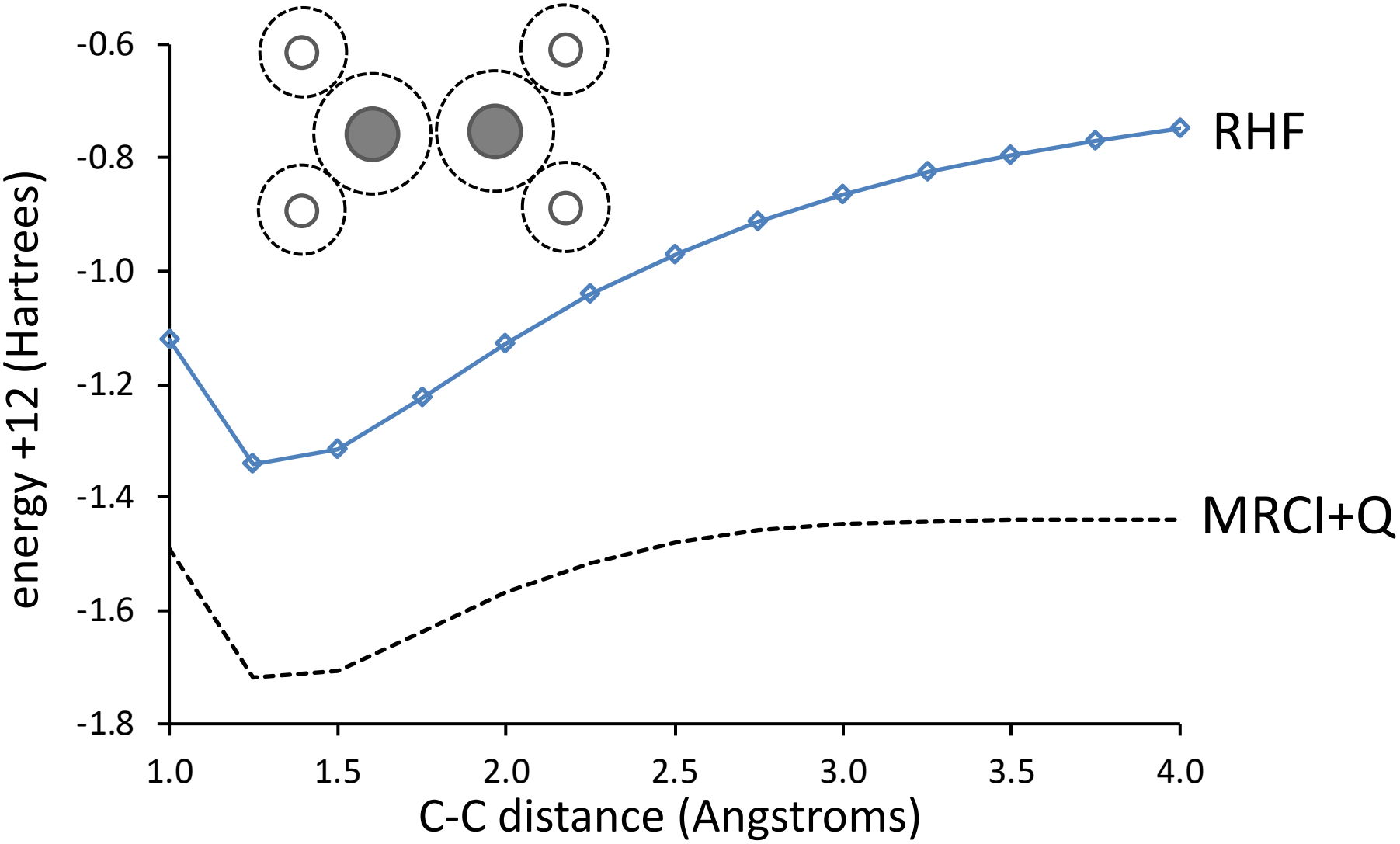


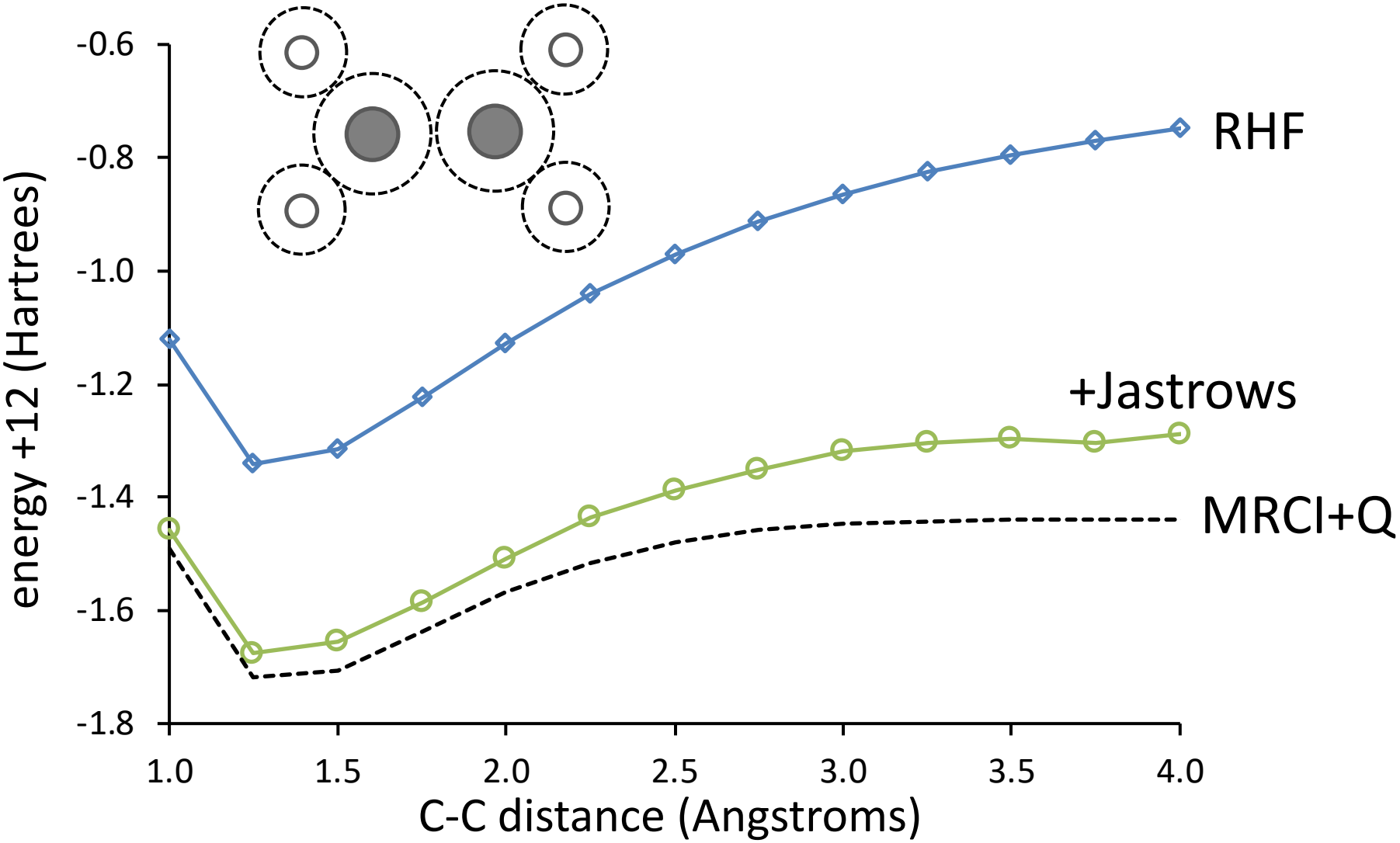
Van Der Goetz & Neuscamman, JCTC 2017

clean additivity works



Van Der Goetz & Neuscamman, in preparation

clean additivity works



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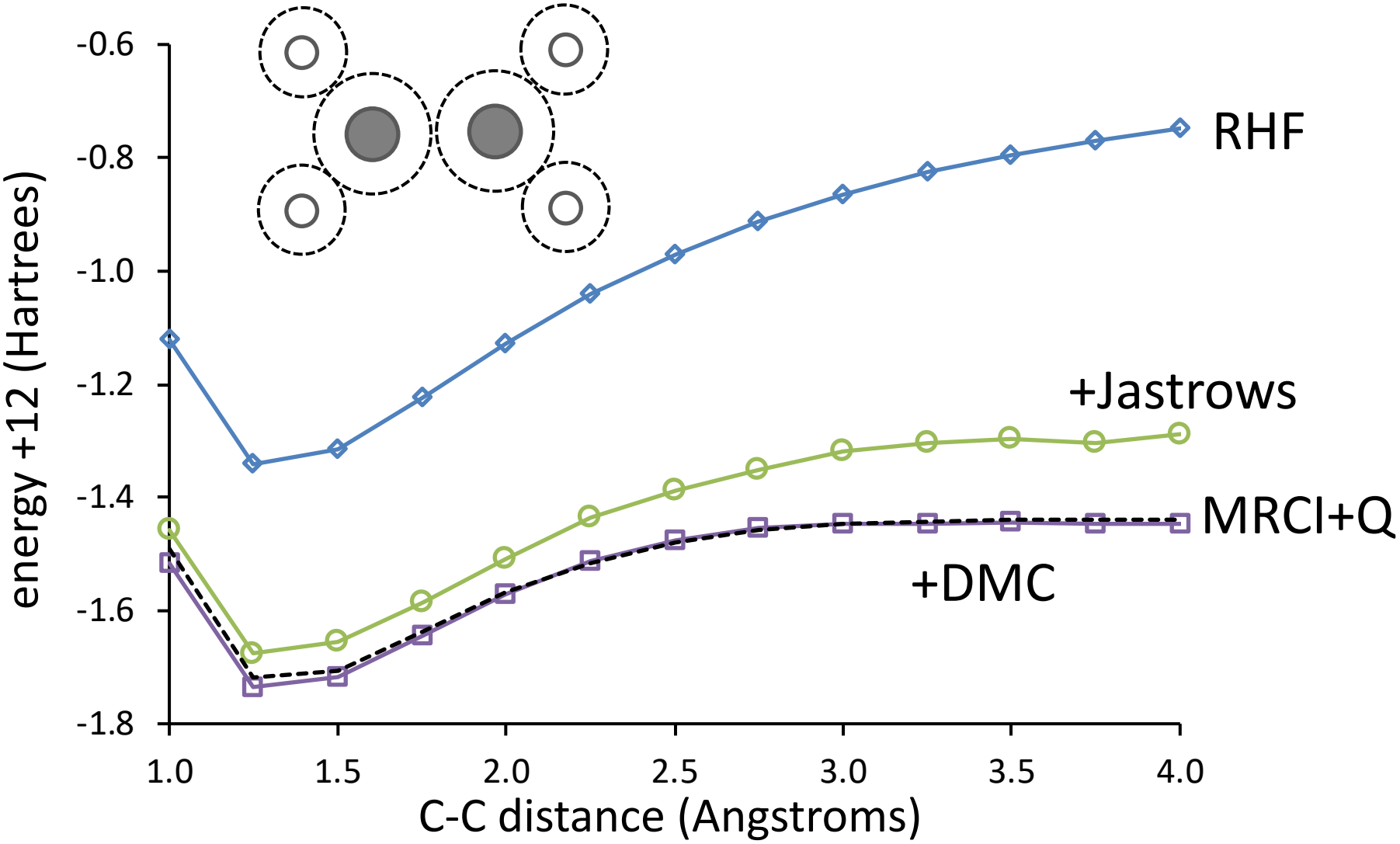

Van Der Goetz & Neuscamman, in preparation

the menu

aperitif: number counting Jastrows

main course: excited states with QMC

dessert: optimization methods

variational principles

ground state

$$\frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

any eigenstate

$$\frac{\langle\Psi|(H-E)^2|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

Umrigar, Filippi, others

state near ω

$$\frac{\langle\Psi|(\omega-H)^2|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

Choi, Lebeda, & Messmer, CPL 1970

Van Voorhis et al, JCP 2017

state above ω

$$\frac{\langle\Psi|(\omega-H)|\Psi\rangle}{\langle\Psi|(\omega-H)^2|\Psi\rangle}$$

Zhao & Neuscamman, JCTC 2016, 2017

Shea & Neuscamman, JCTC 2017

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evaluate $\langle H^2\rangle$ by Monte Carlo integration

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Choi, Lebeda, & Messmer, CPL 1970

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Zhao & Neuscamman, JCTC 2016, 2017

Shea & Neuscamman, JCTC 2017

poor properties

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not specific

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Zhao & Neuscamman, JCTC 2016, 2017

Shea & Neuscamman, JCTC 2017

not size-consistent

interconversion

ground state

$$\frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

any eigenstate

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Umrigar, Filippi, others

$\omega \to E$

$\omega \to E - \sigma$

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Zhao & Neuscamman, JCTC 2016, 2017

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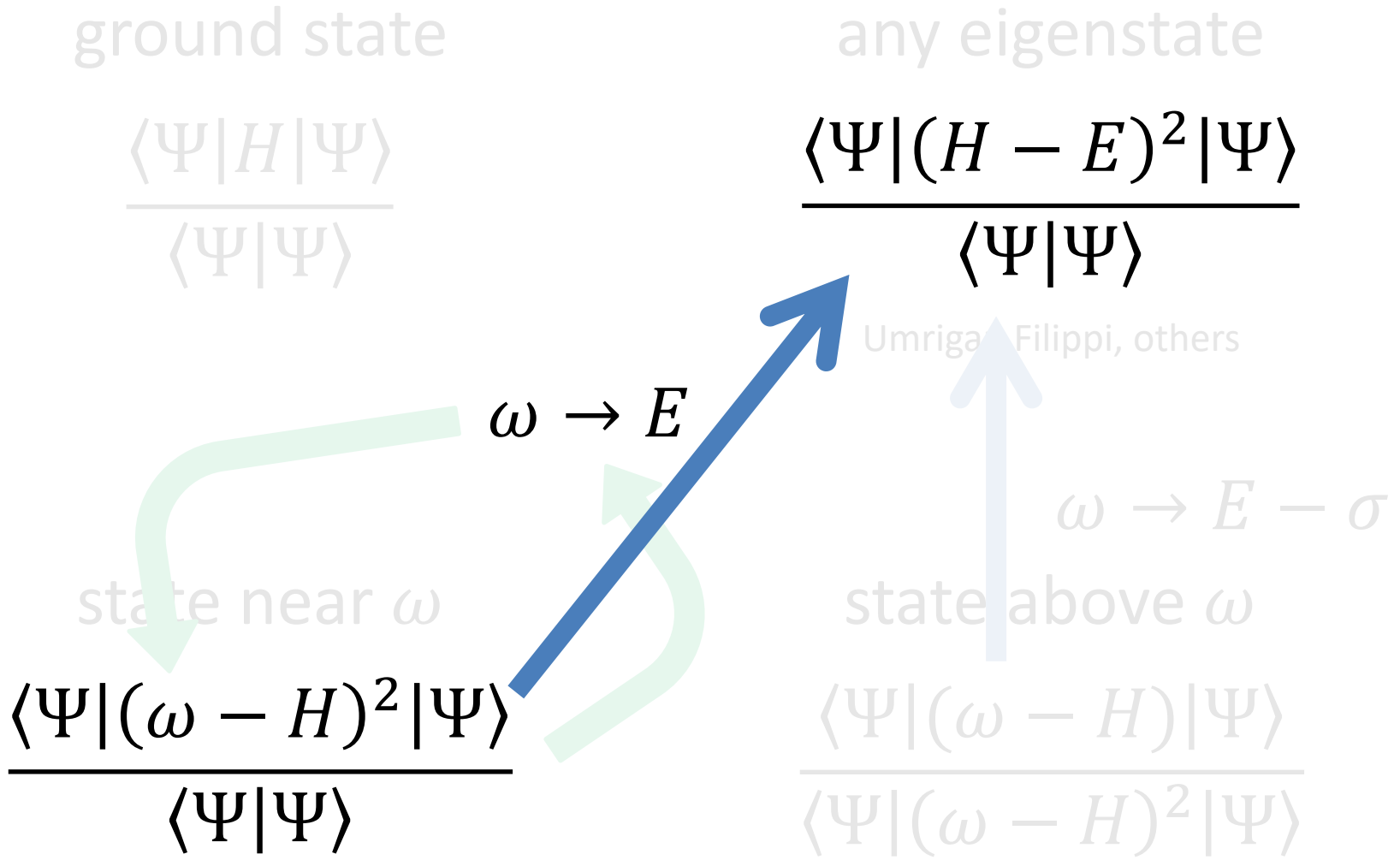
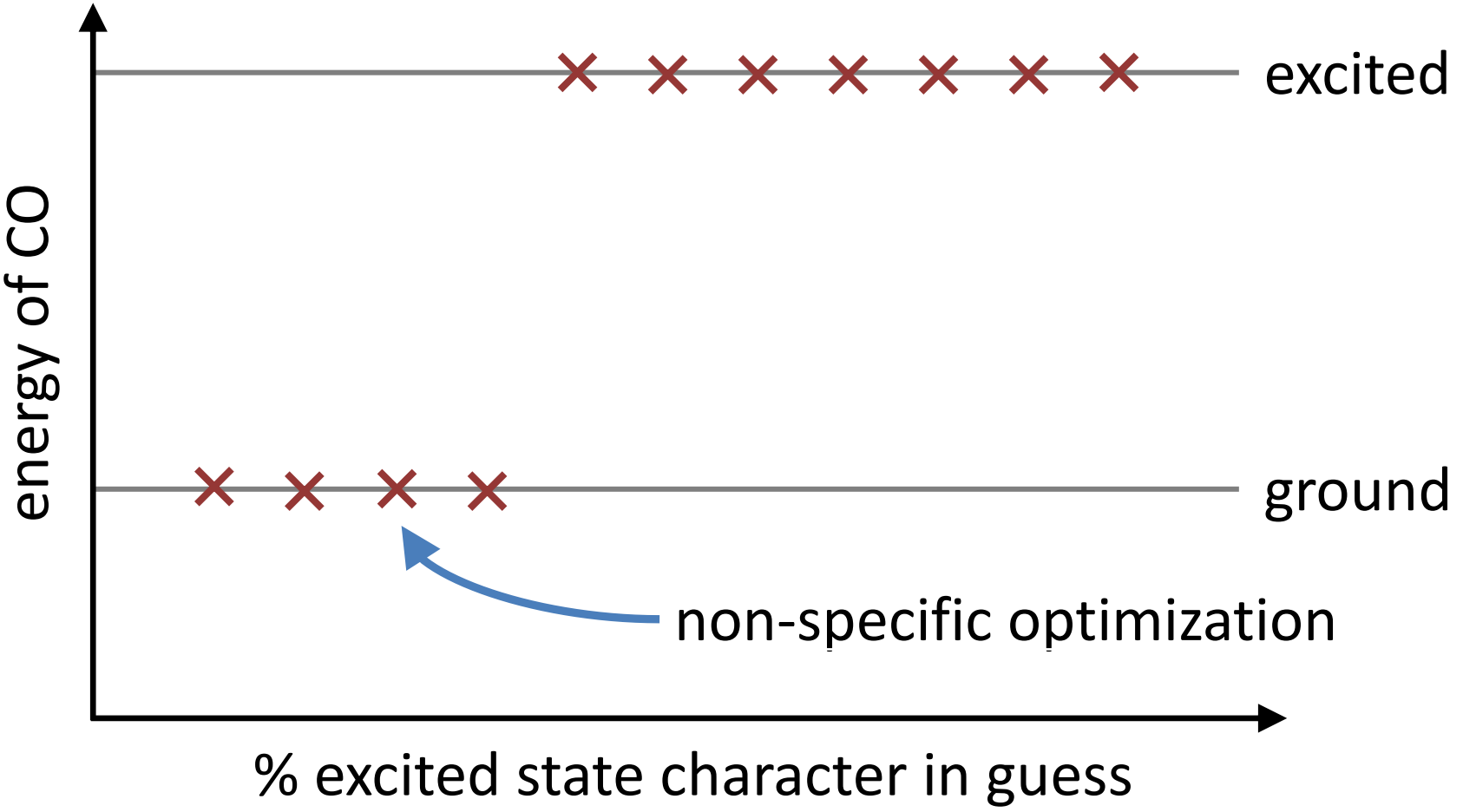


having it both ways



Shea & Neuscamman, JCTC 2017

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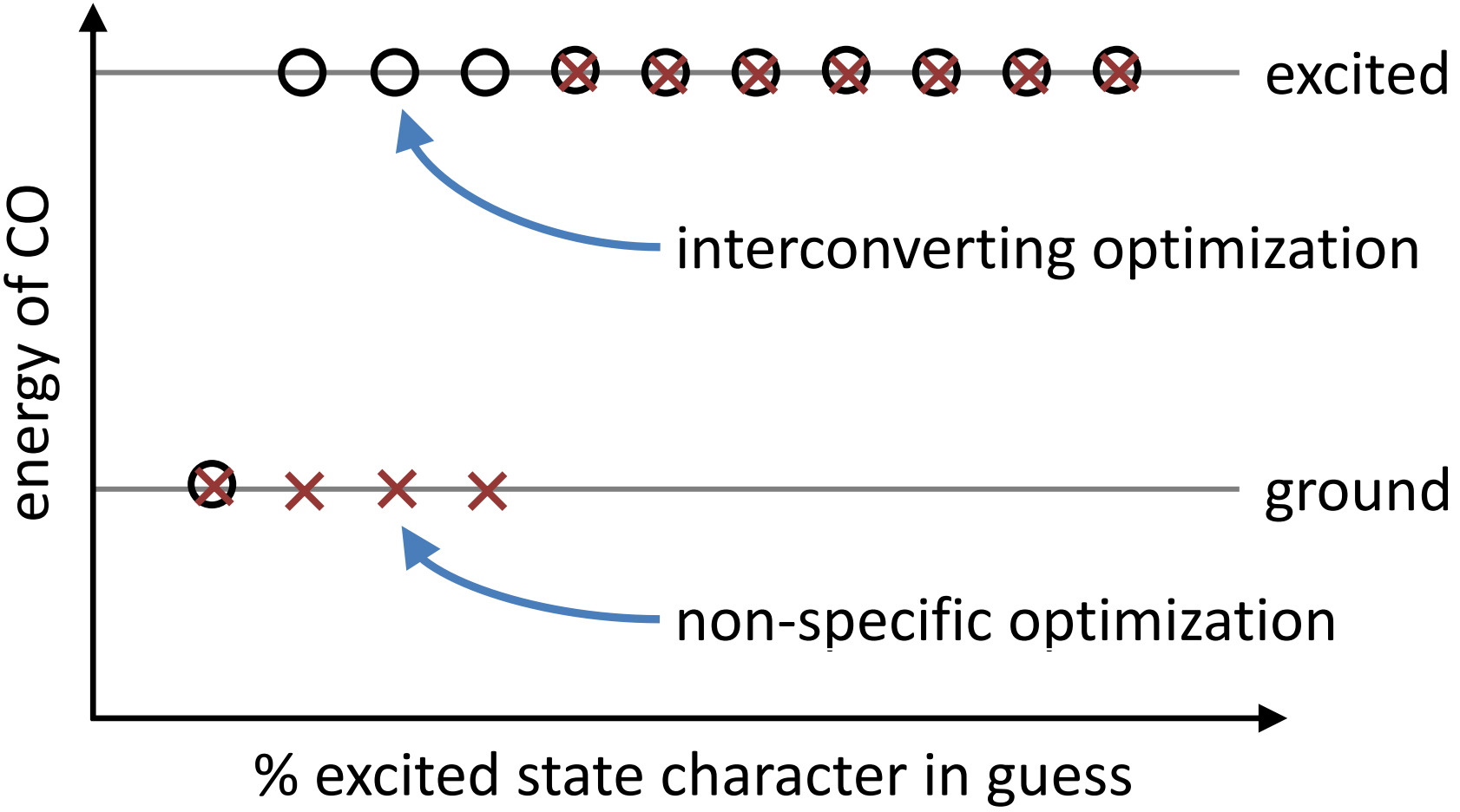

Shea & Neuscamman, JCTC 2017

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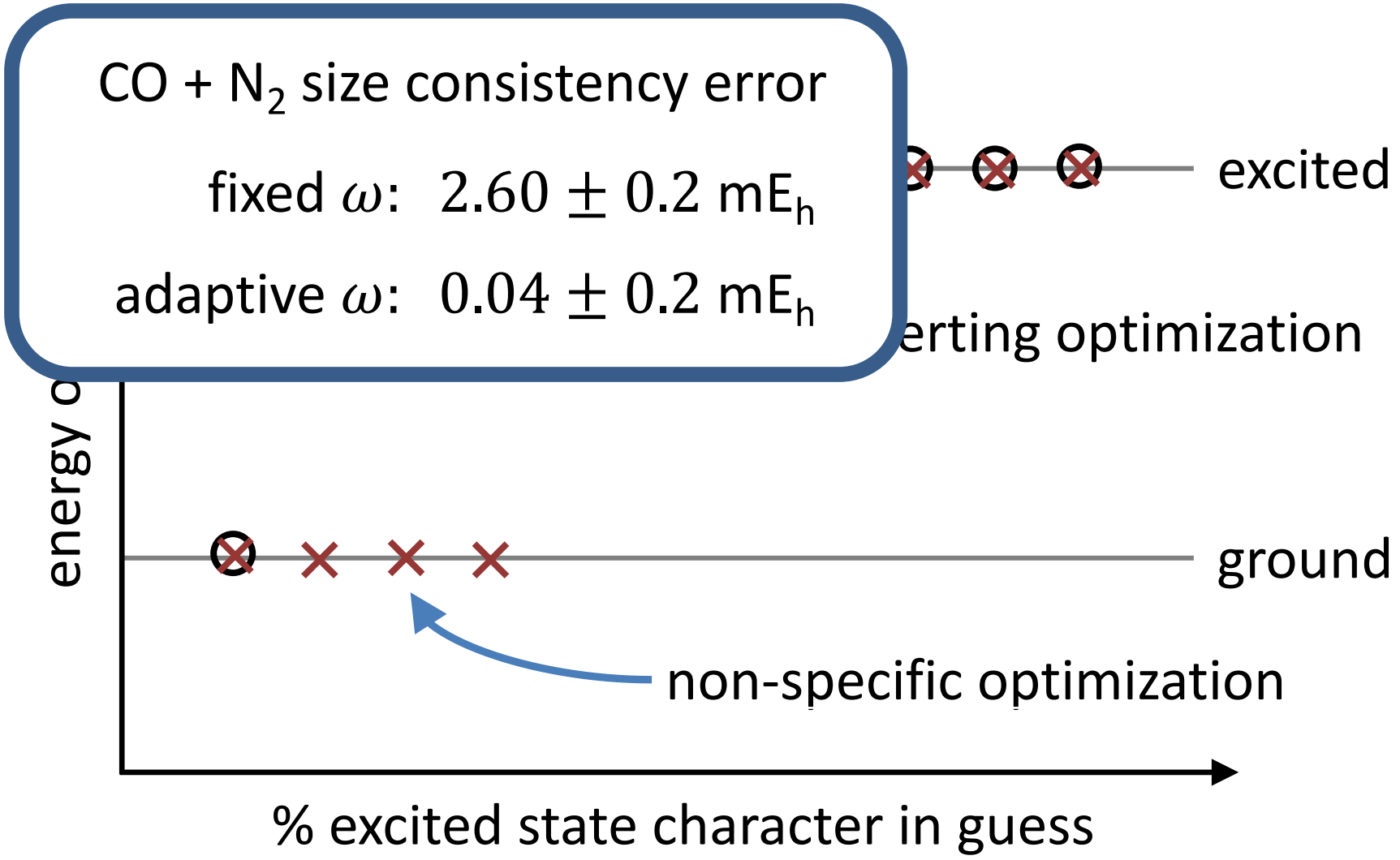


Shea & Neuscamman, JCTC 2017

charge transfer orbital relaxation

state-averaged CASSCF:

2.7 eV to 5.9 eV (yikes!)

state-averaged CASPT2:

intruder states

state-specific CASSCF:

4.4 eV

state-specific CASPT2:

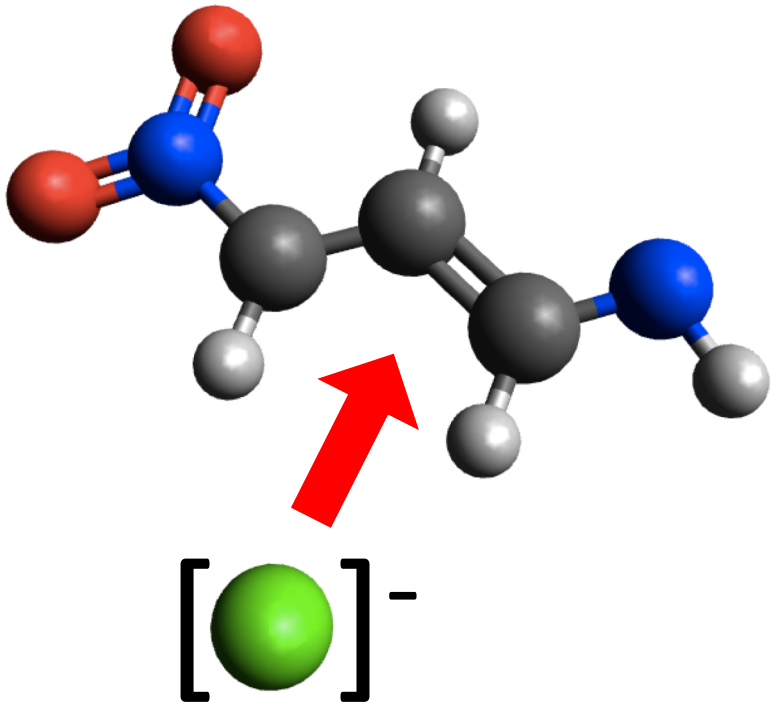
3.5 eV

EOM-CCSD:

3.8 eV

σ^2-matched VMC:

3.8 eV

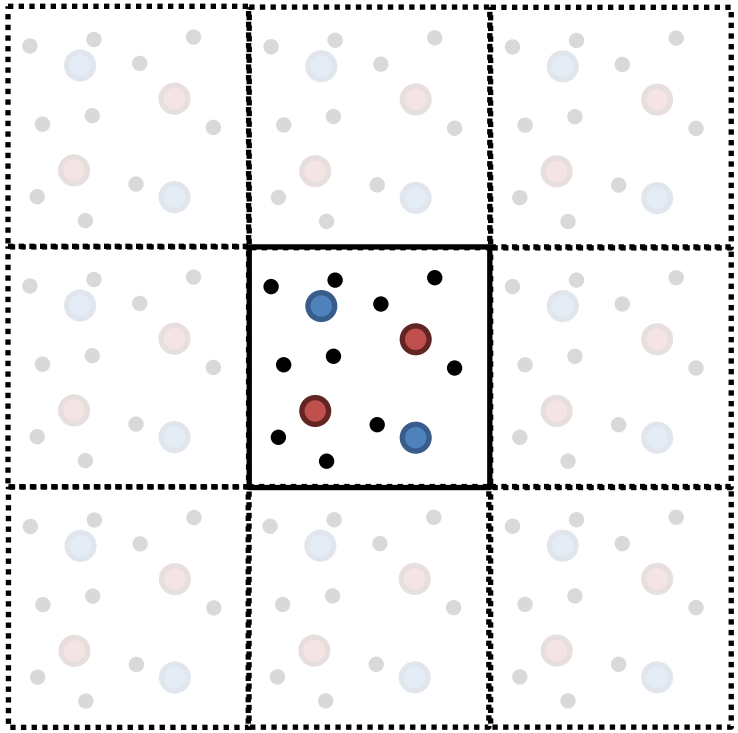


Ψ_0 = multi-Slater from CISPI

Pineda Flores & Neuscamman, in preparation

solids

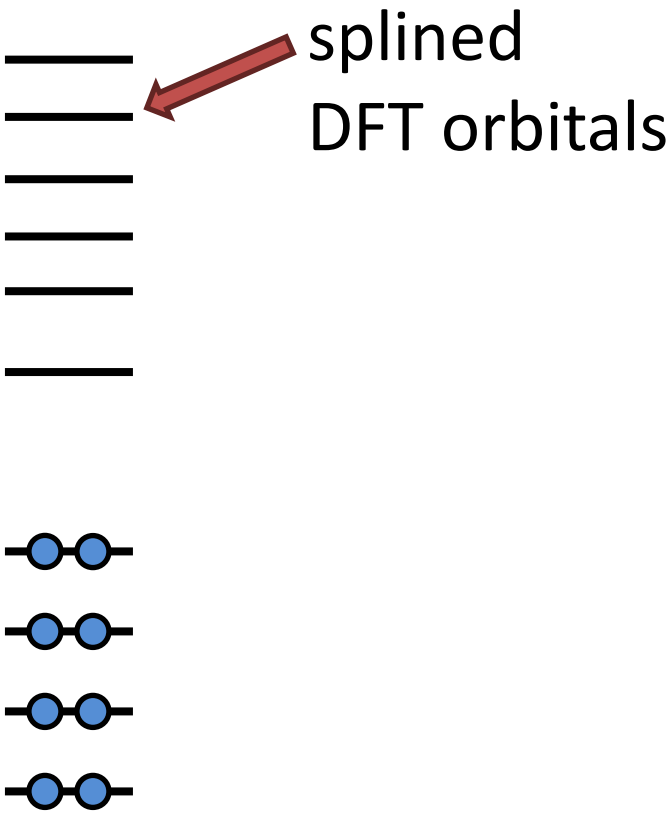
in QMC, solids are molecules with funny electrons



$$H = T + \underbrace{V_{nn} + V_{en} + V_{ee}}$$

periodic sums, but still
a finite number of particles

the wave function



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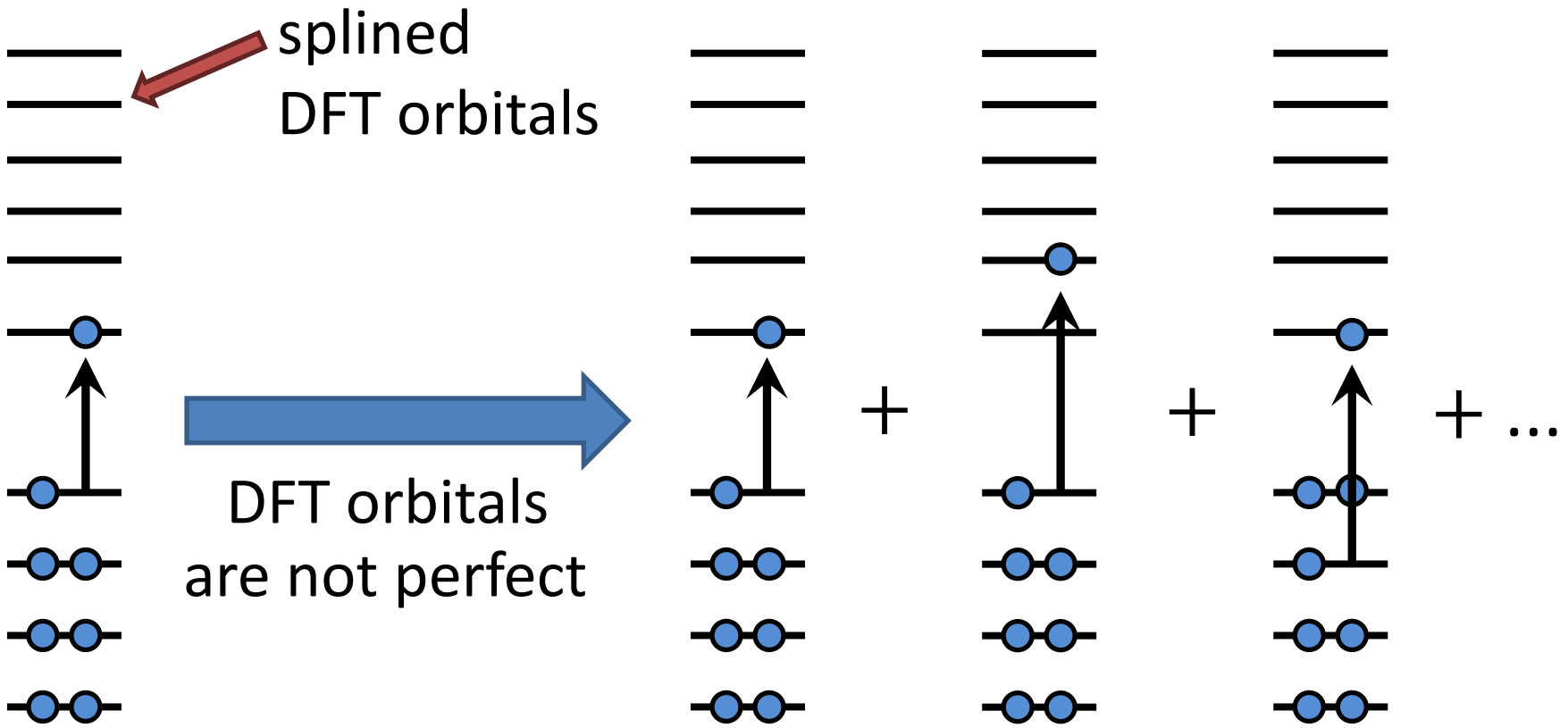

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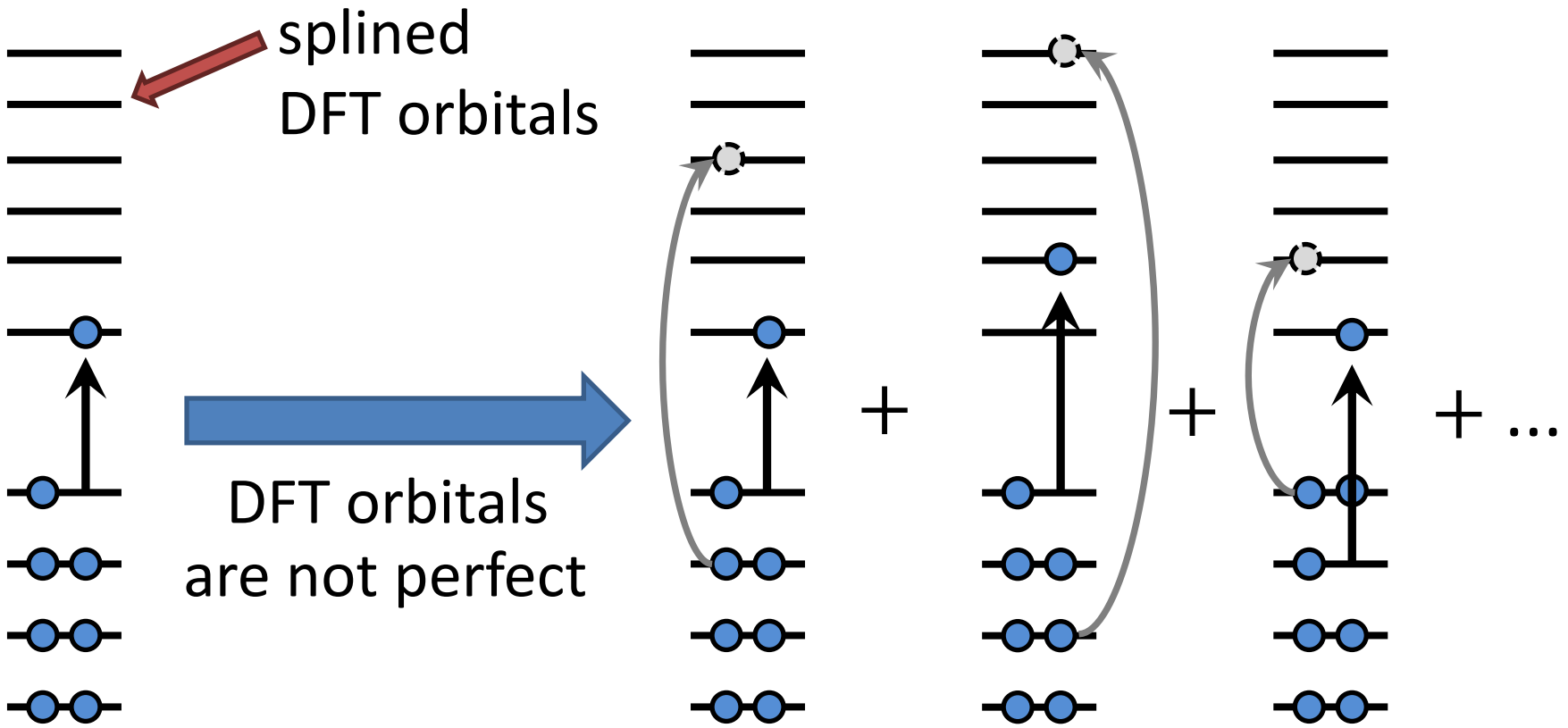
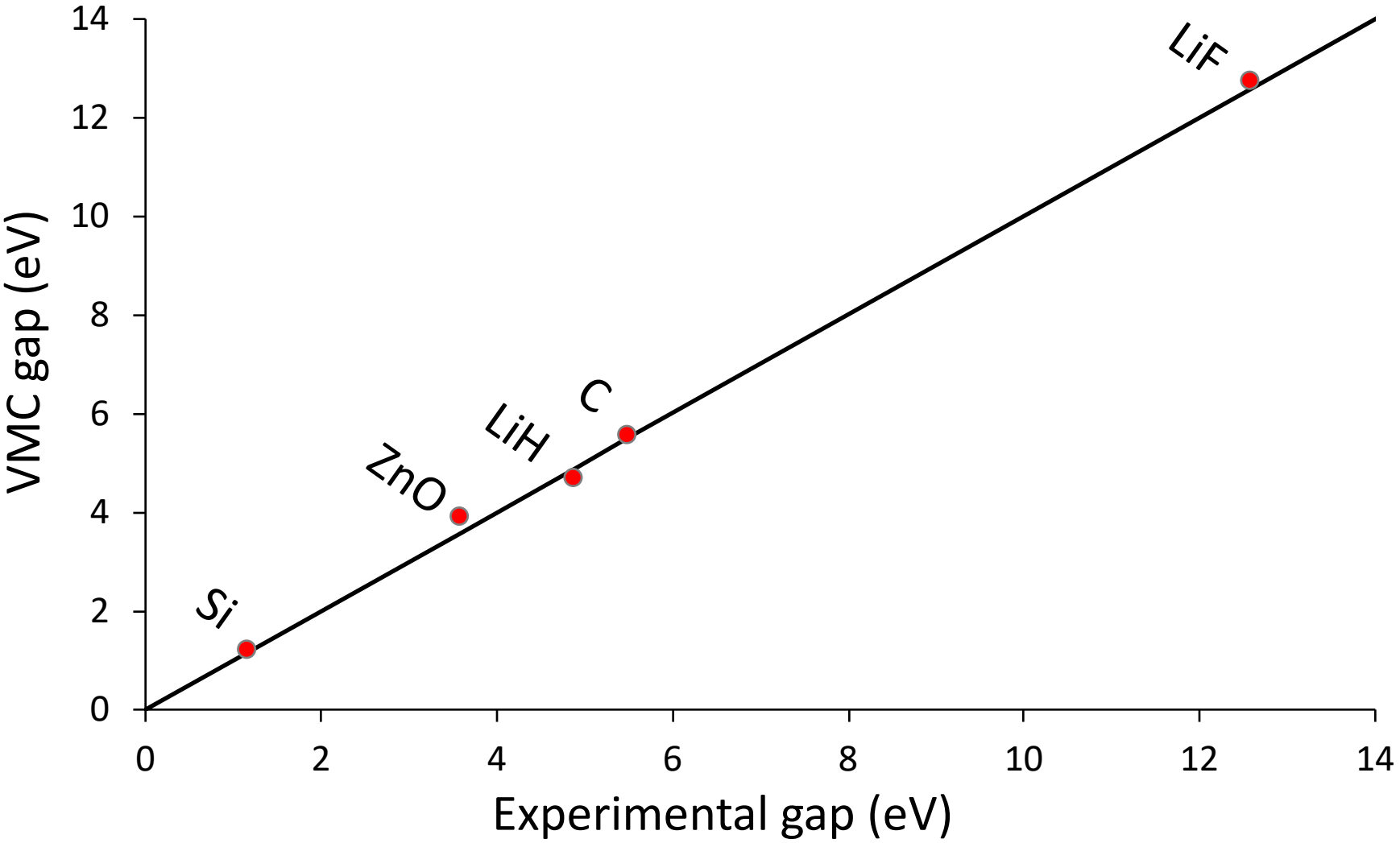


Ψ = all singles + doubles on important singles

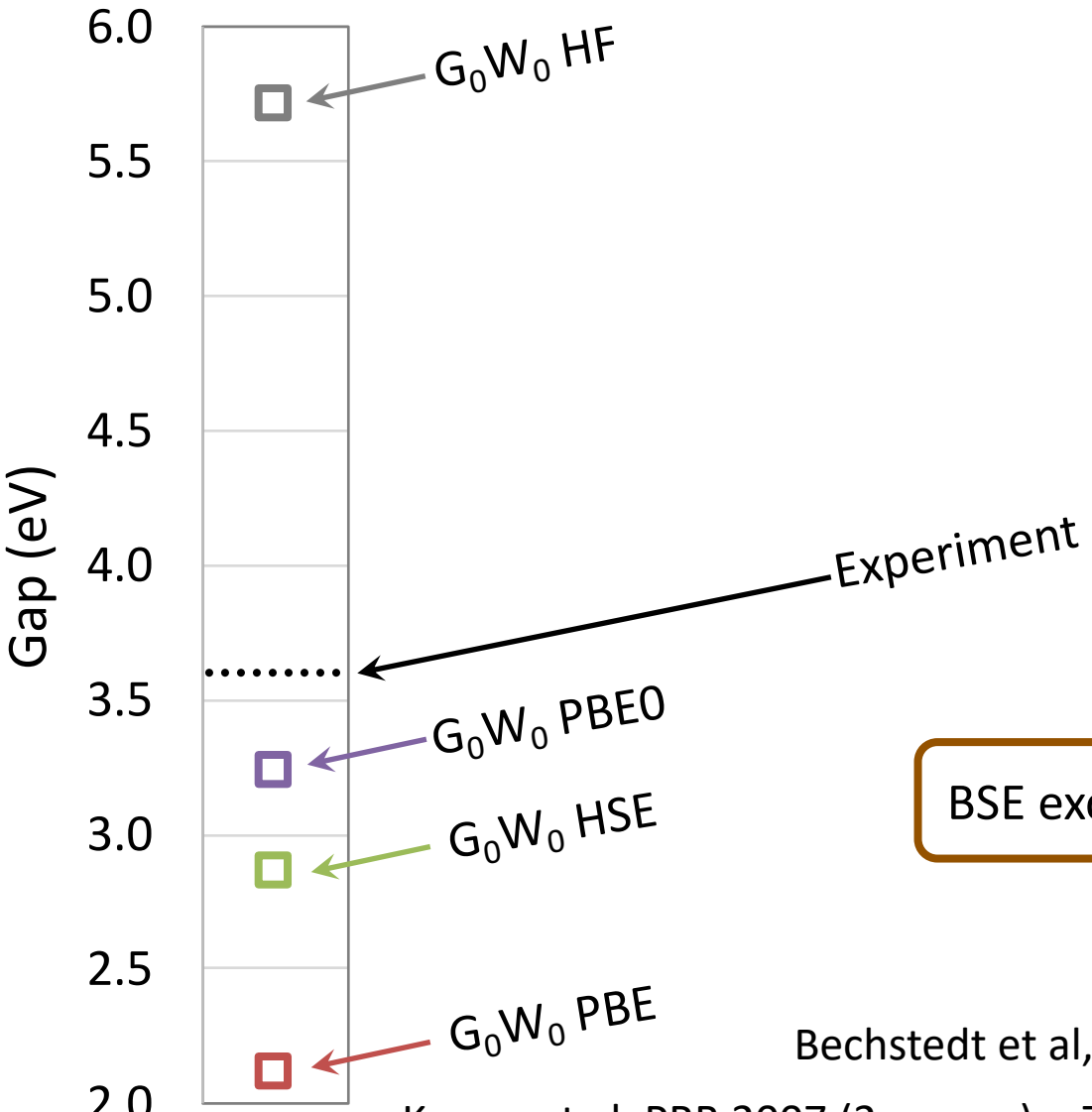
(then cut off small singles to variance match)

optical gaps



Zhao & Neuscamman, arXiv 1804.09663

Zinc Oxide



BSE exciton binding ~ 0.06 eV

Bechstedt et al, PRB 2009

Pulci et al, PRB 2010

Kresse et al, PRB 2007 (2 papers)

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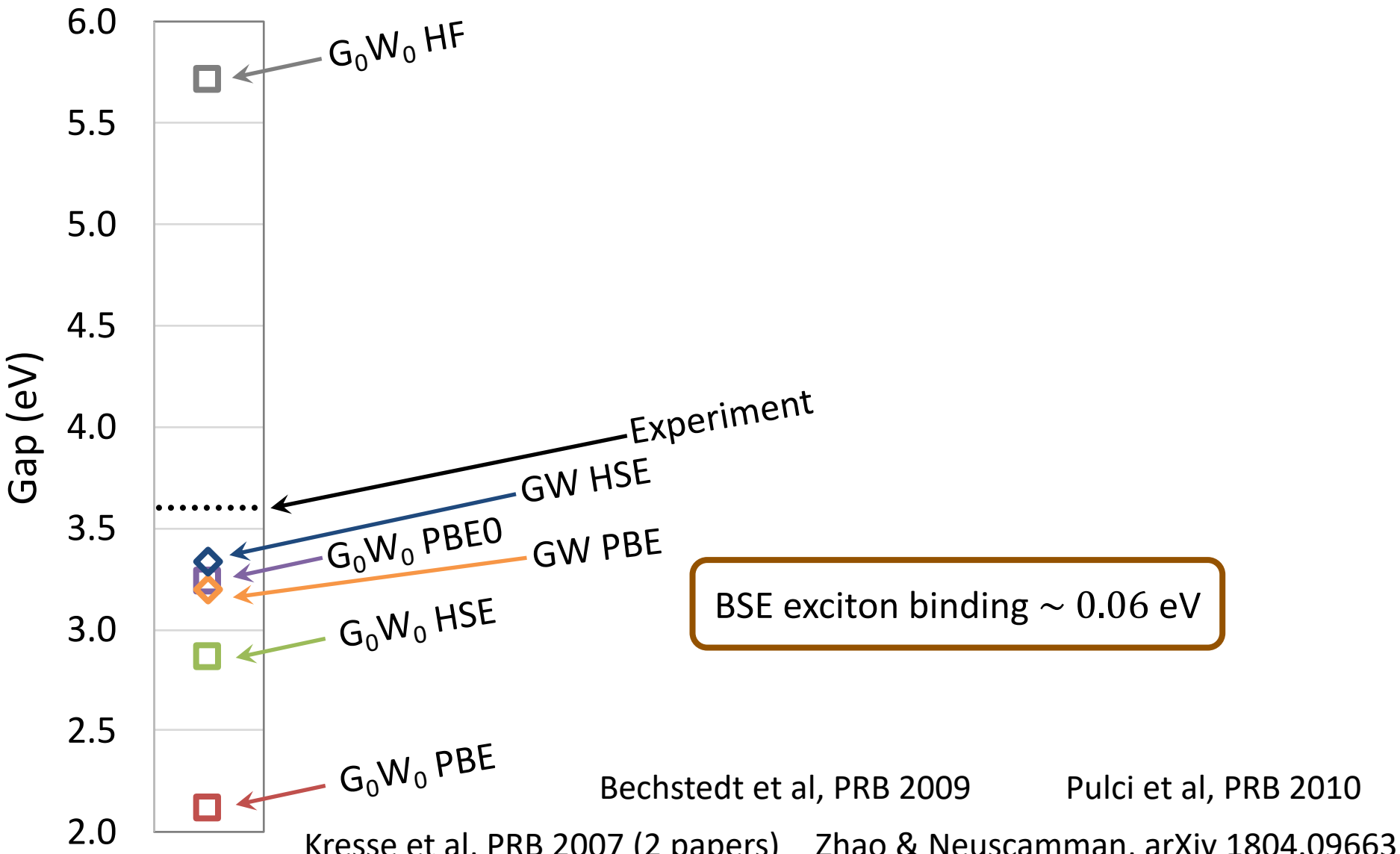
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Gap (eV)
G_0W_0 HF
Experiment
GW HSE
G_0W_0 PBE0
GW PBE
G_0W_0 HSE
G_0W_0 PBE
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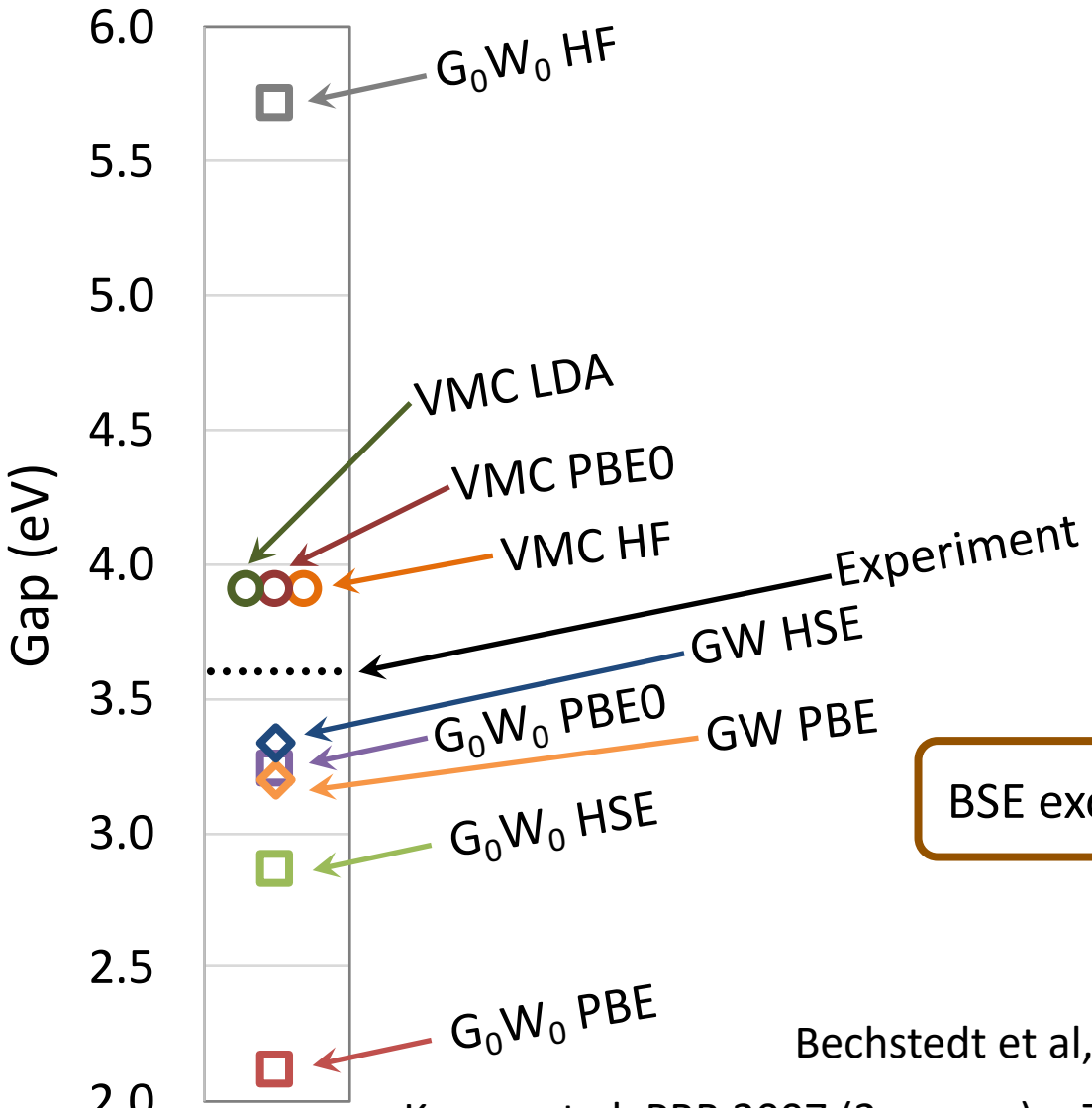

VMC-HF
90% HOMO → LUMO

VMC-PBE0
85% HOMO → LUMO

VMC-LDA
80% HOMO → LUMO

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Pulci et al, PRB 2010

Kresse et al, PRB 2007 (2 papers)

Zhao & Neuscamman, arXiv 1804.09663

the menu

aperitif: number counting Jastrows

main course: excited states with QMC

dessert: optimization methods

the linear method

$$\Psi(\vec{c}) \rightarrow \mathrm{a}_0 \Psi(\vec{c}) + \sum_{i=1}^{N} a_i \frac{\partial \Psi}{\partial c_i}$$

minimize E w.r.t. $\vec{a}$, or, in other words, solve

$$\mathbf{H}\,\vec{a} = E\,\mathbf{S}\,\vec{a}$$

good:

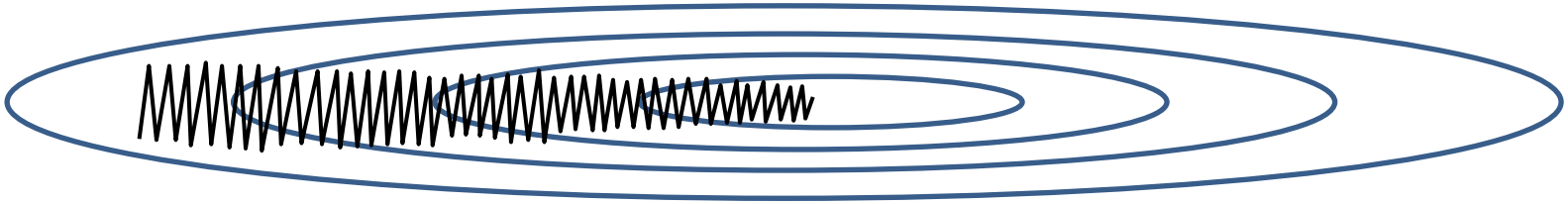
- fast convergence
- well established

bad:

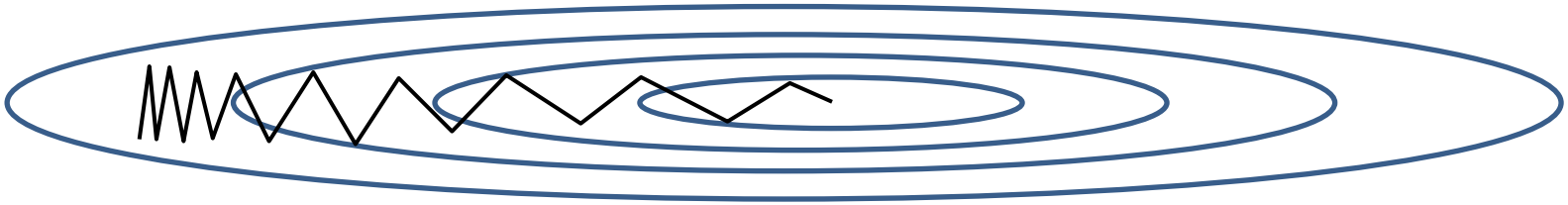
- matrices get huge
- highly nonlinear

Umrigar, Toulouse, Filippi, Sorella, Hennig, PRL 2007

accelerated descent



remember the average movement and add momentum…



good:

- low memory
- nearly linear

bad:

- first order method
- little VMC data so far

Schwarz, Alavi, Booth, PRL 2017

Sabzevari & Sharma, arXiv 1807.10633

blocked linear method

$\Psi(\vec{c})$ with $\vec{c} = \{c_1, \ldots, c_n, c_{n+1}, \cdots, c_{2n}, c_{2n+1}, \cdots, c_{3n}, \cdots\}$

do linear method for first set…

Zhao & Neuscamman, JCTC 2017

blocked linear method

$\Psi(\vec{c})$ with $\vec{c} = \{c_1, \ldots, c_n, c_{n+1}, \ldots, c_{2n}, c_{2n+1}, \ldots, c_{3n}, \ldots\}$

do linear method for first set…

then second set…

Zhao & Neuscamman, JCTC 2017

blocked linear method

$\Psi(\vec{c})$ with $\vec{c} = \{c_1, \ldots, c_n, c_{n+1}, \ldots, c_{2n}, c_{2n+1}, \ldots, c_{3n}, \ldots\}$

do linear method for first set…

then second set… then third set…

Zhao & Neuscamman, JCTC 2017

blocked linear method

$\Psi(\vec{c})$ with $\vec{c} = \{c_1, \ldots, c_n, c_{n+1}, \ldots, c_{2n}, c_{2n+1}, \ldots, c_{3n}, \ldots\}$

do linear method for first set…

then second set… then third set…

now restrict variables to best directions from each set

do LM on $\Psi(\vec{c}) \rightarrow \Psi(\vec{z})$ with $\vec{z}$ much shorter than $\vec{c}$

good:

- fast convergence
- low memory

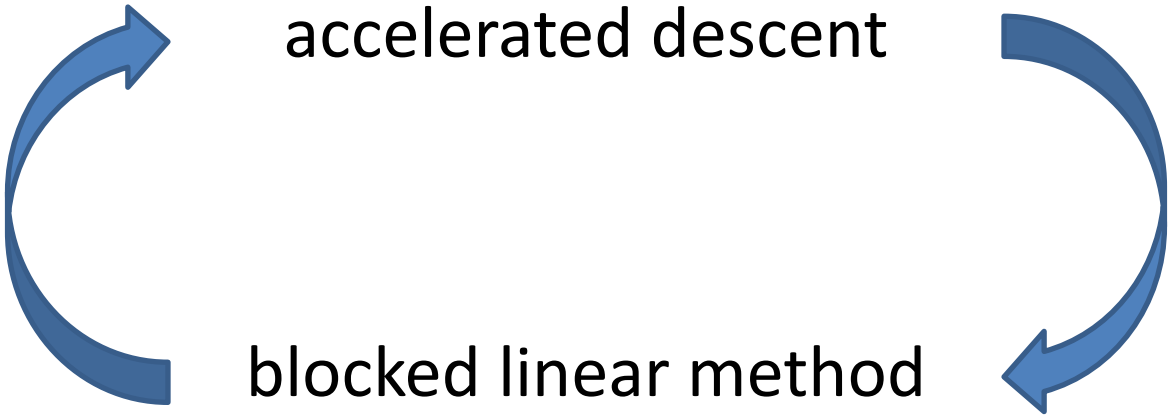
bad:

- extra samples
- little VMC data so far

Zhao & Neuscamman, JCTC 2017

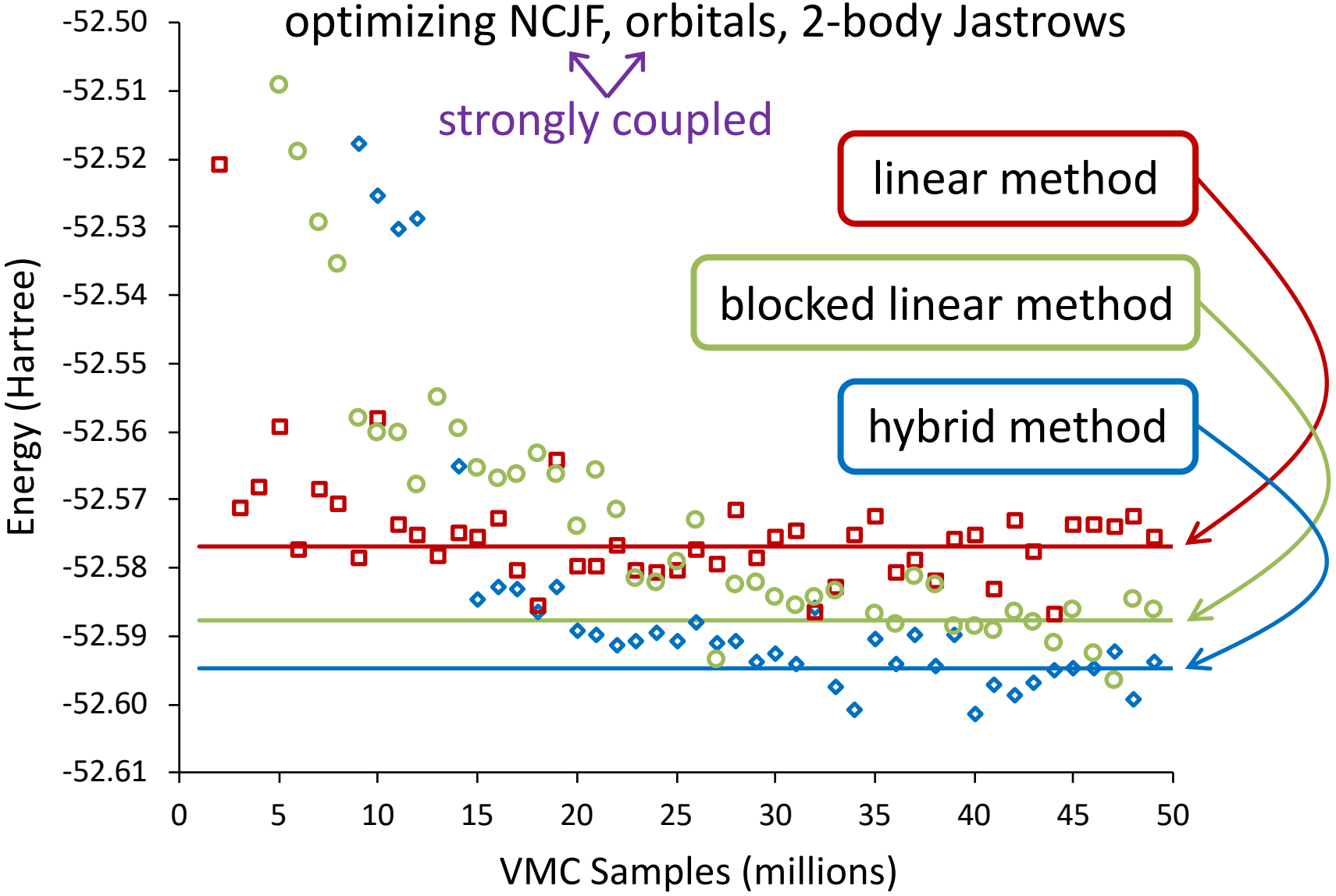
hybrid method?

hard to couple stiff parameters w/o 2nd order derivatives



needs info about other blocks to get coupling right

comparing methods in CaO



future directions

oo-MSJ in solids

core excitations

selective CI → VMC → DMC

black-box hybrid optimizer

acknowledgements

CPSFM | Center for Predictive Simulation of Functional Materials

NERSC

- Gas Phase Chemical Physics
- Computational & Theoretical Chemistry