Gluing Coupled Cluster to Geminal Powers with Quantum Monte Carlo

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&

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outline

motivation

geminals

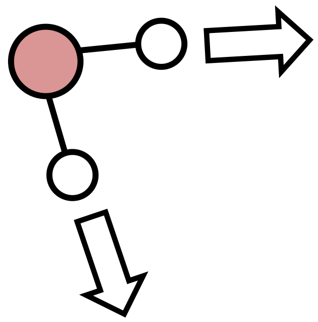
coupled cluster

results

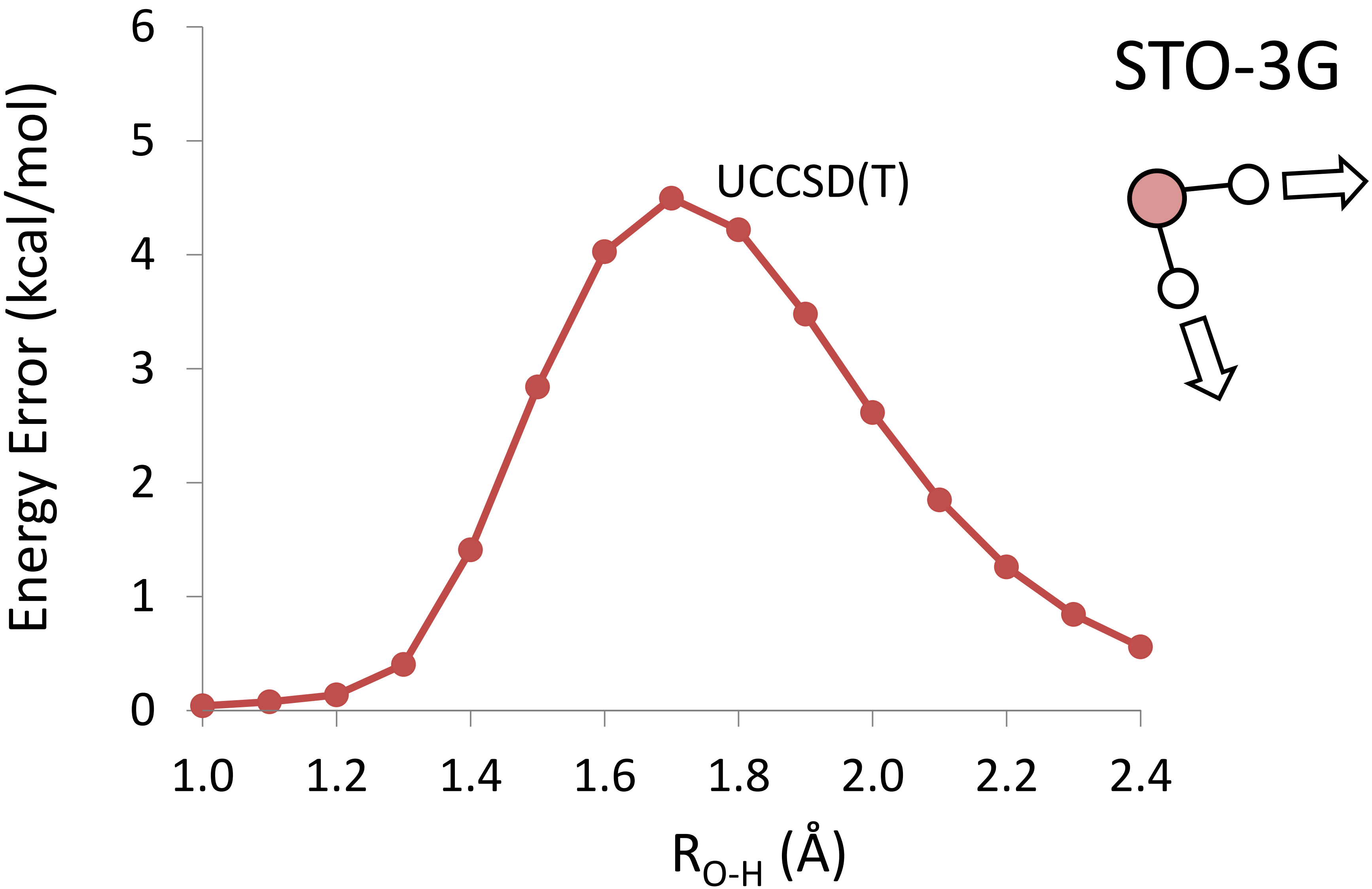
conclusions

wetting one's appetite

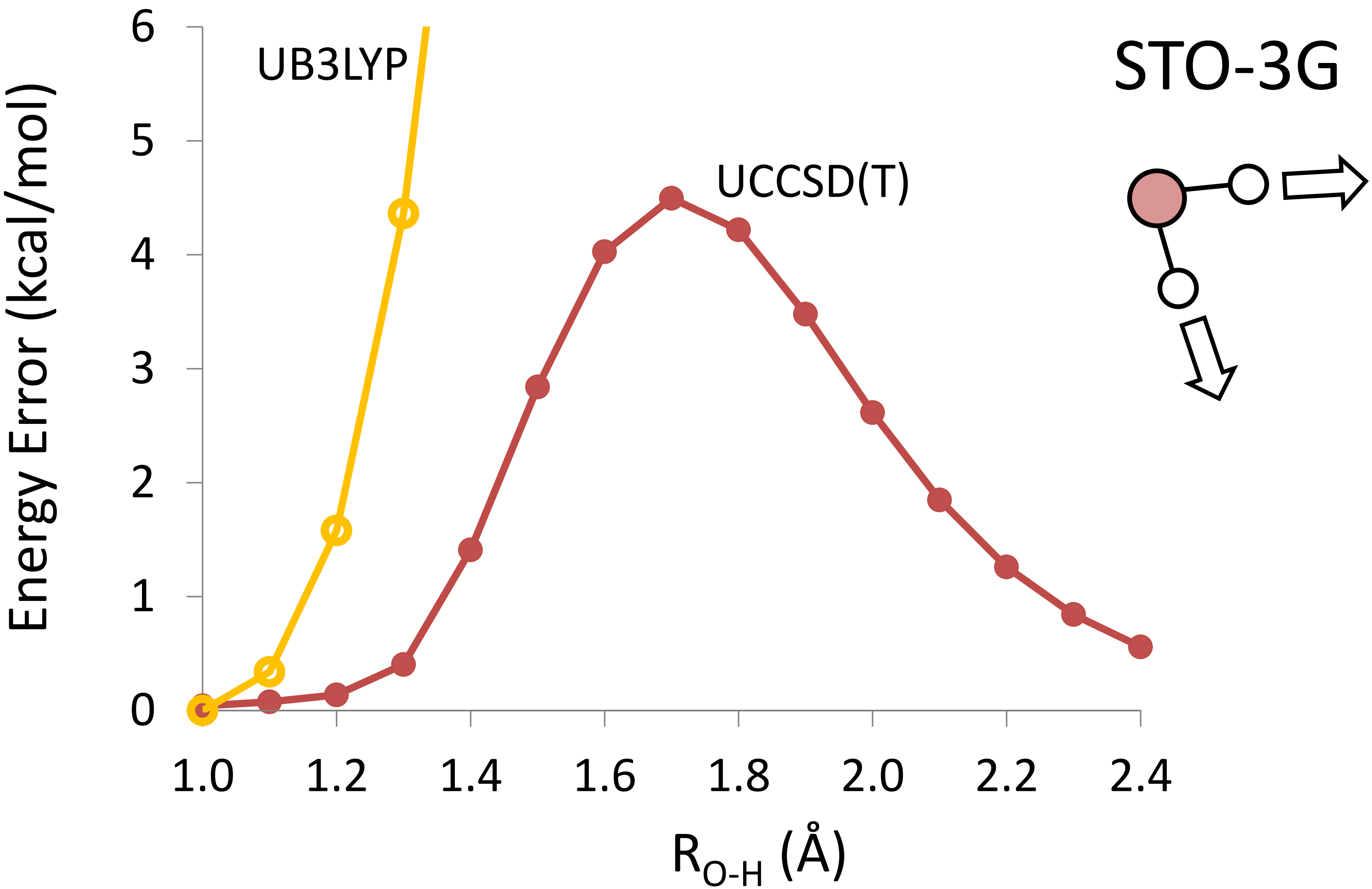
STO-3G



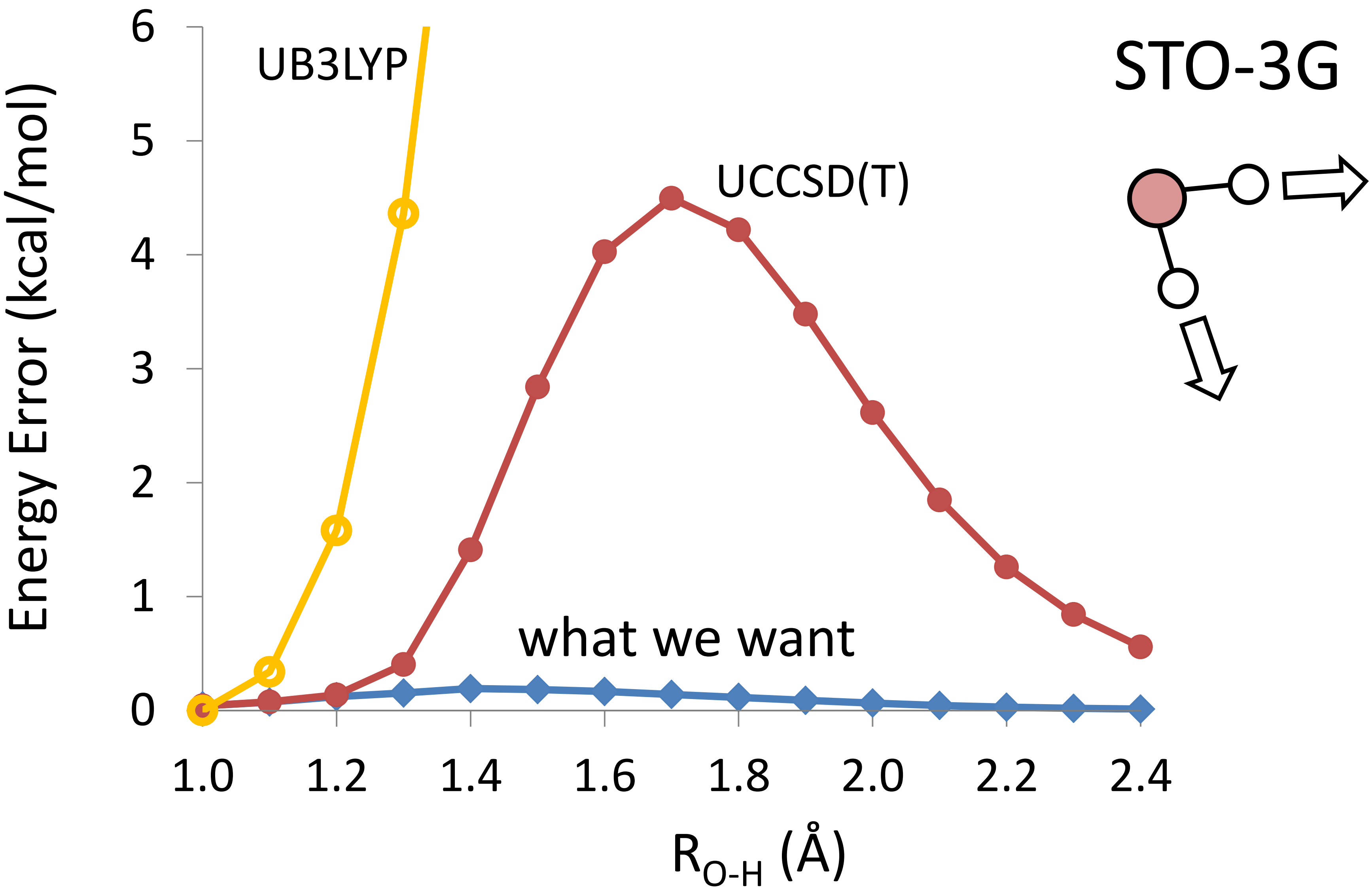
wetting one's appetite



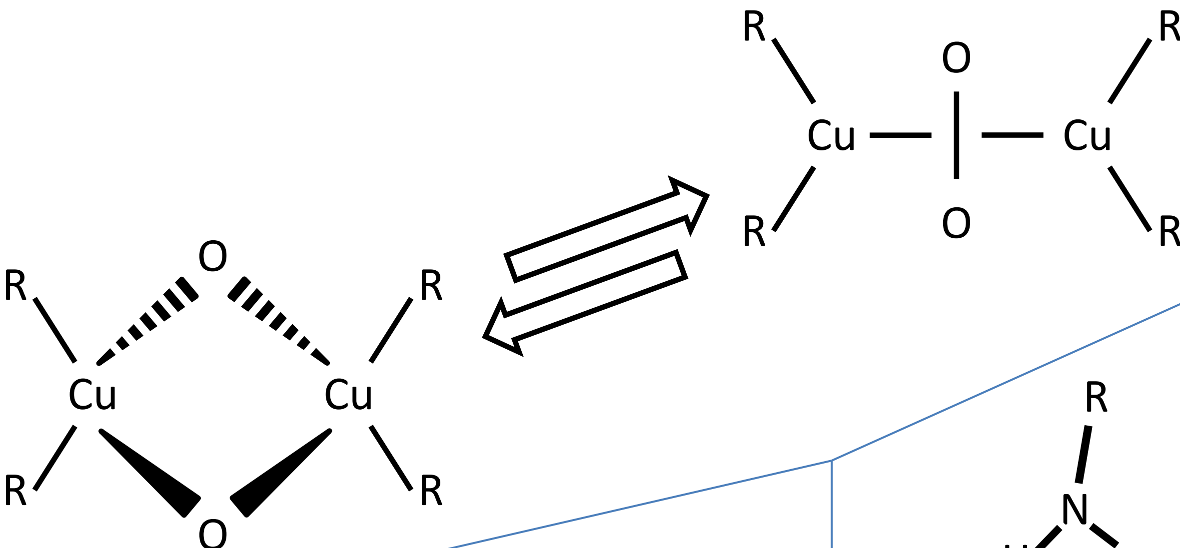
wetting one's appetite

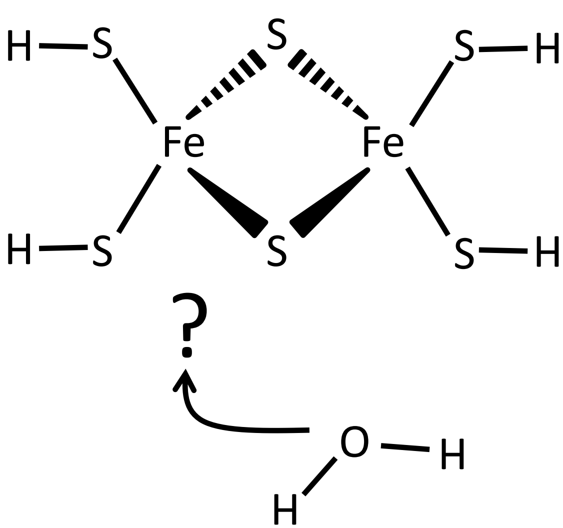


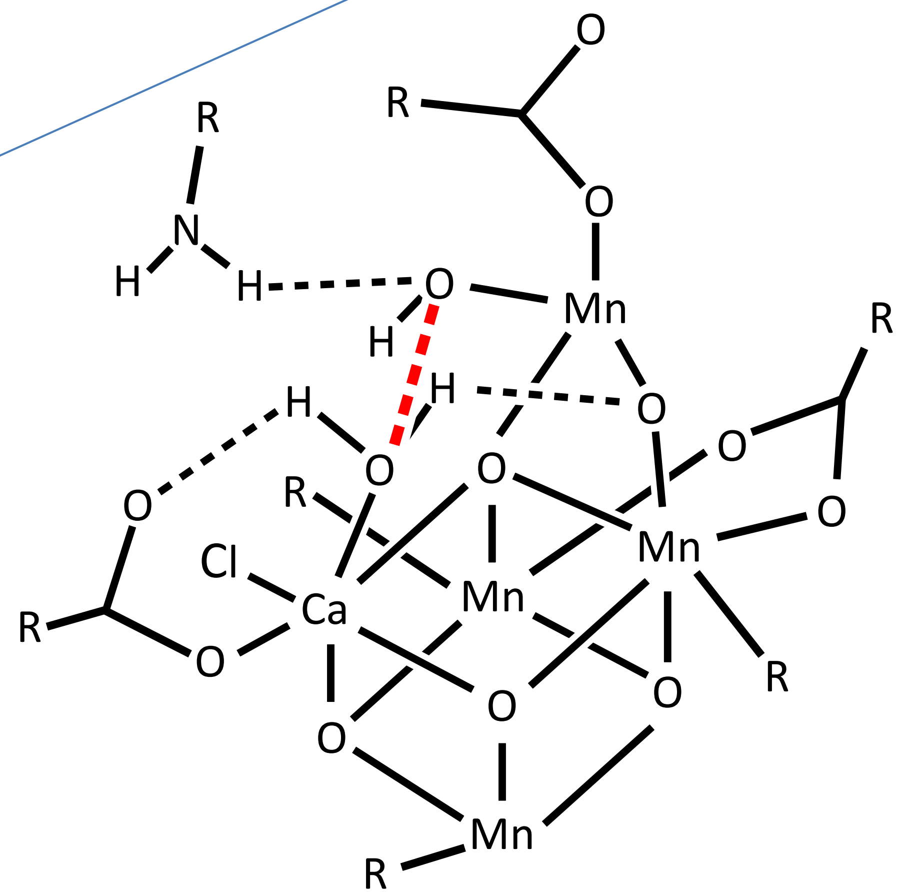
wetting one's appetite



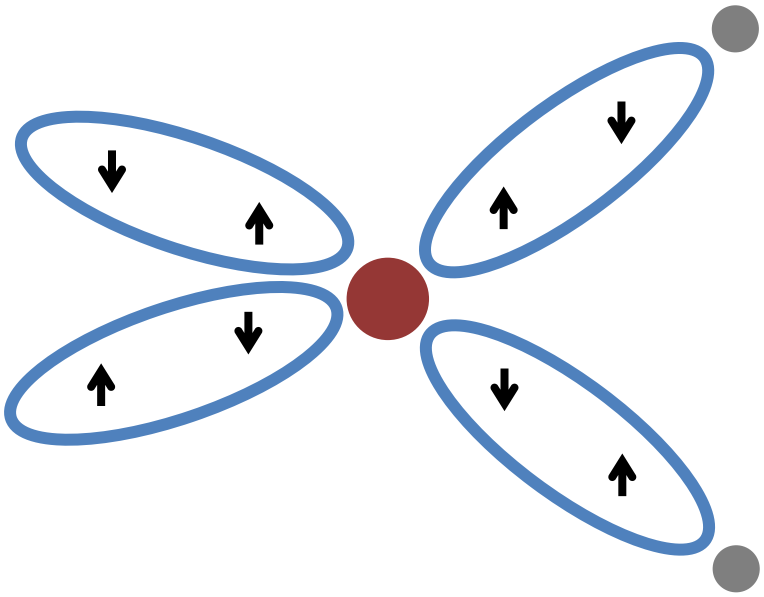
stuff real chemists care about







geminals: two electron building blocks



$$\hat{\mathcal{A}}\,[\phi_1\phi_2\phi_3\phi_4 \dots]$$

geminals: two electron building blocks

$\hat{\mathcal{A}}\,[\phi_{12}\,\phi_{34}\,\dots]$

~~exponential scaling!~~

PP/Q/H	Head–Gordon
PMF	Scuseria
QMC	Sorella, Bajdich, Schmidt, others...

size consistent/extensive

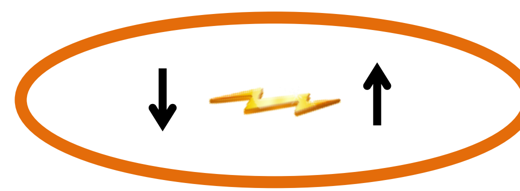
$$1+1+1\ldots\propto N$$

variational

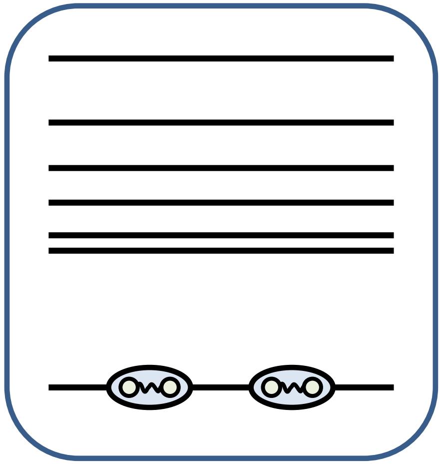
$$1+1>0$$

accurate

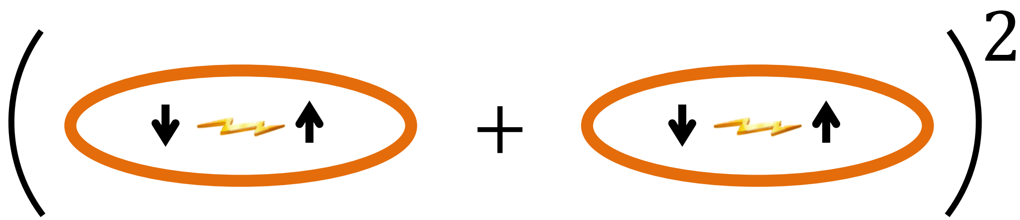
$$1+1=2$$

e^{T} 

the antisymmetric geminal power



$$\Psi = \phi_{\mathrm{A}}(\vec{r}_1, \vec{r}_2) \times \phi_{\mathrm{B}}(\vec{r}_3, \vec{r}_4)$$



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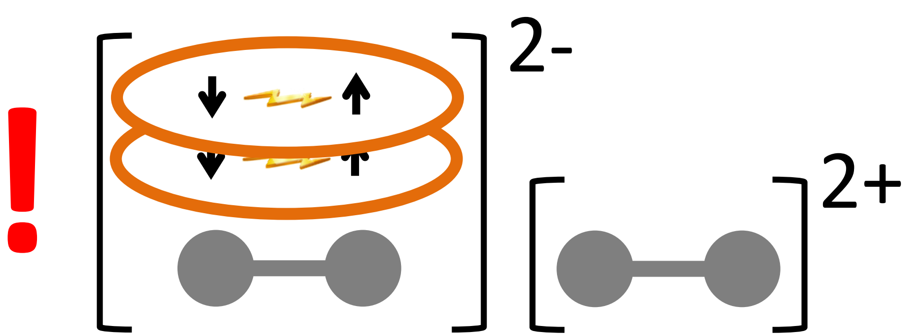

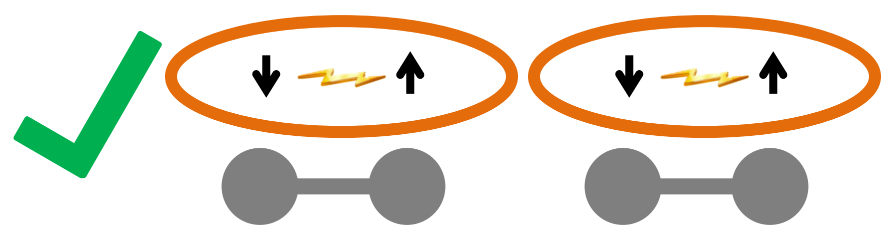

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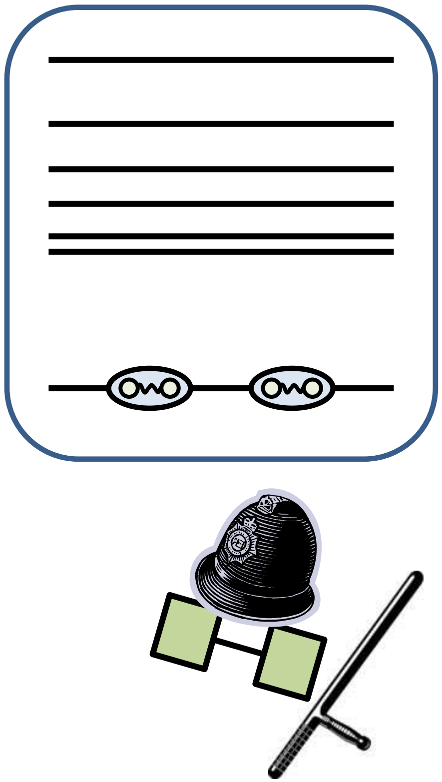

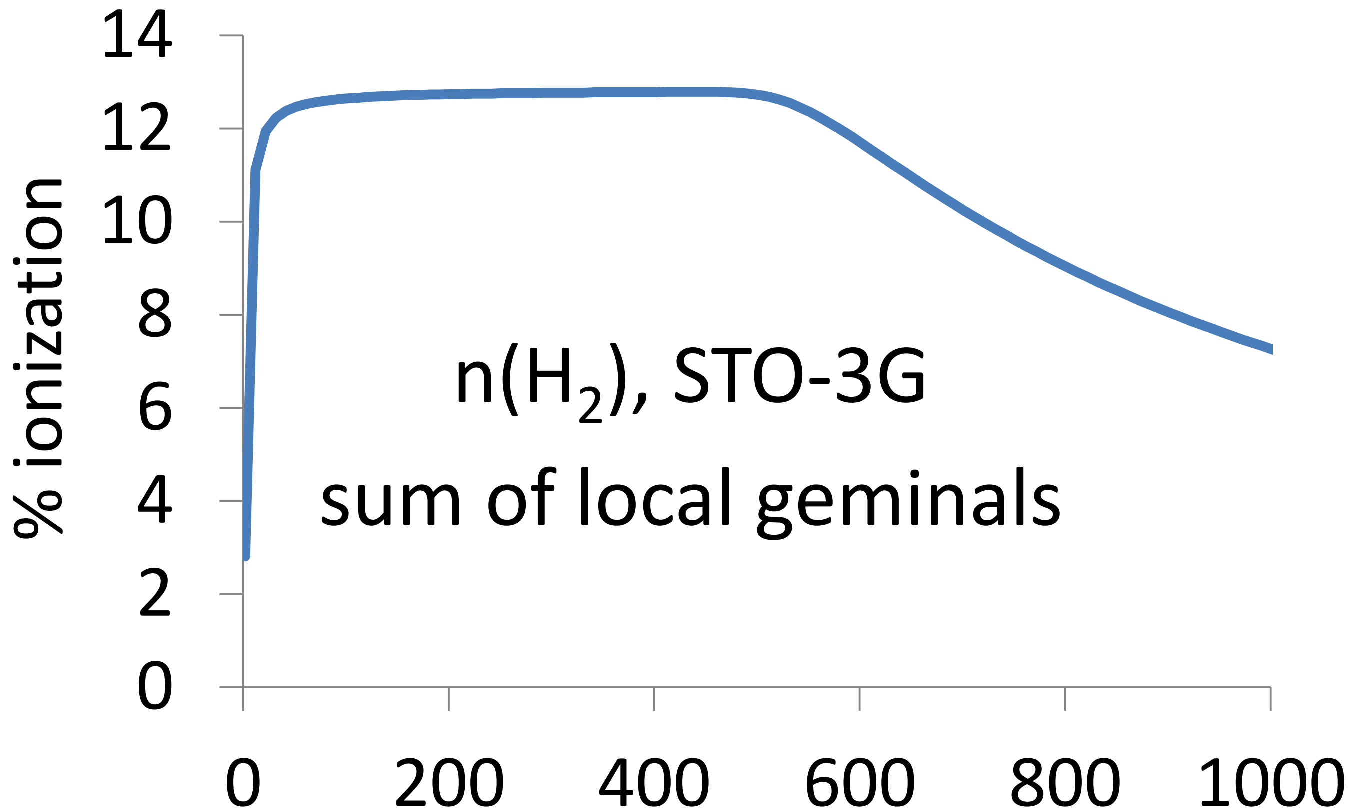

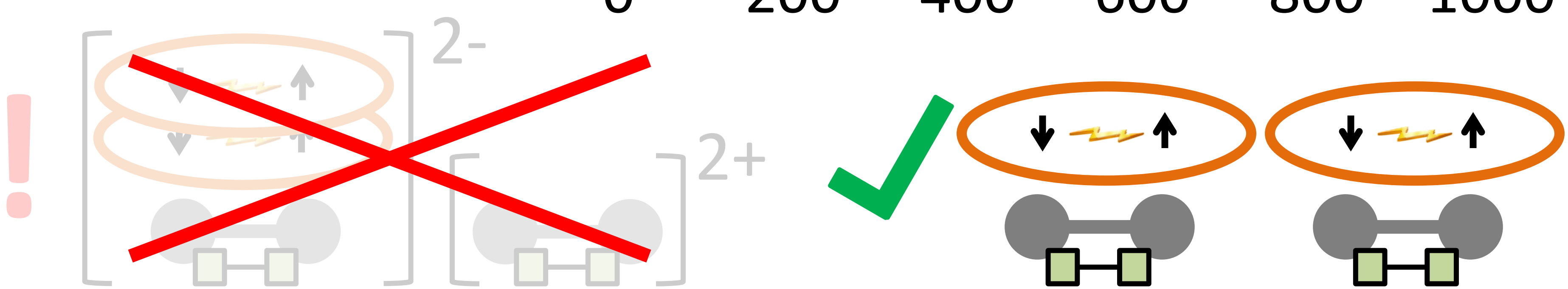

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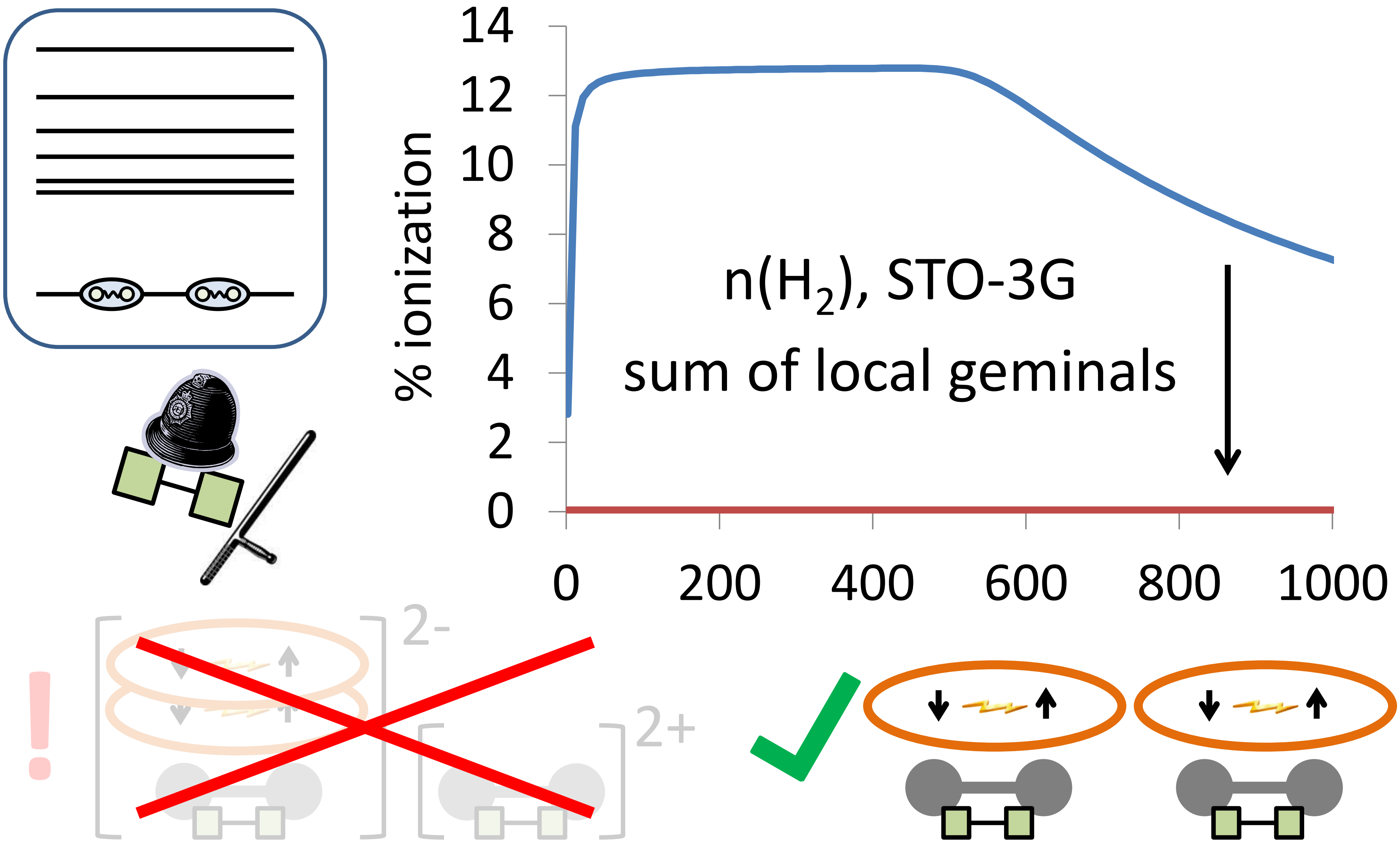

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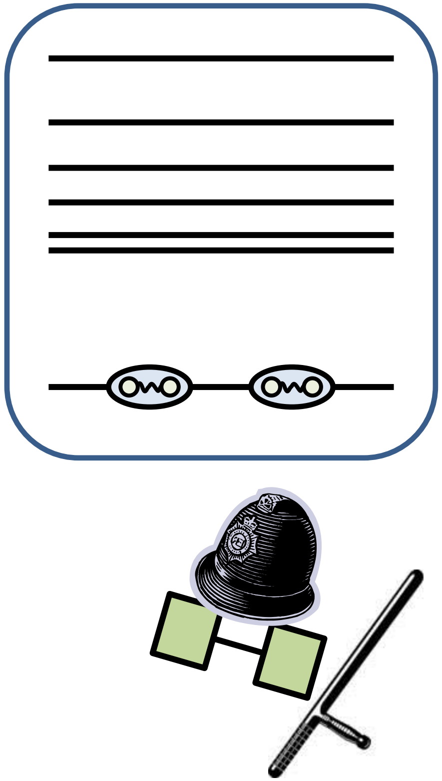

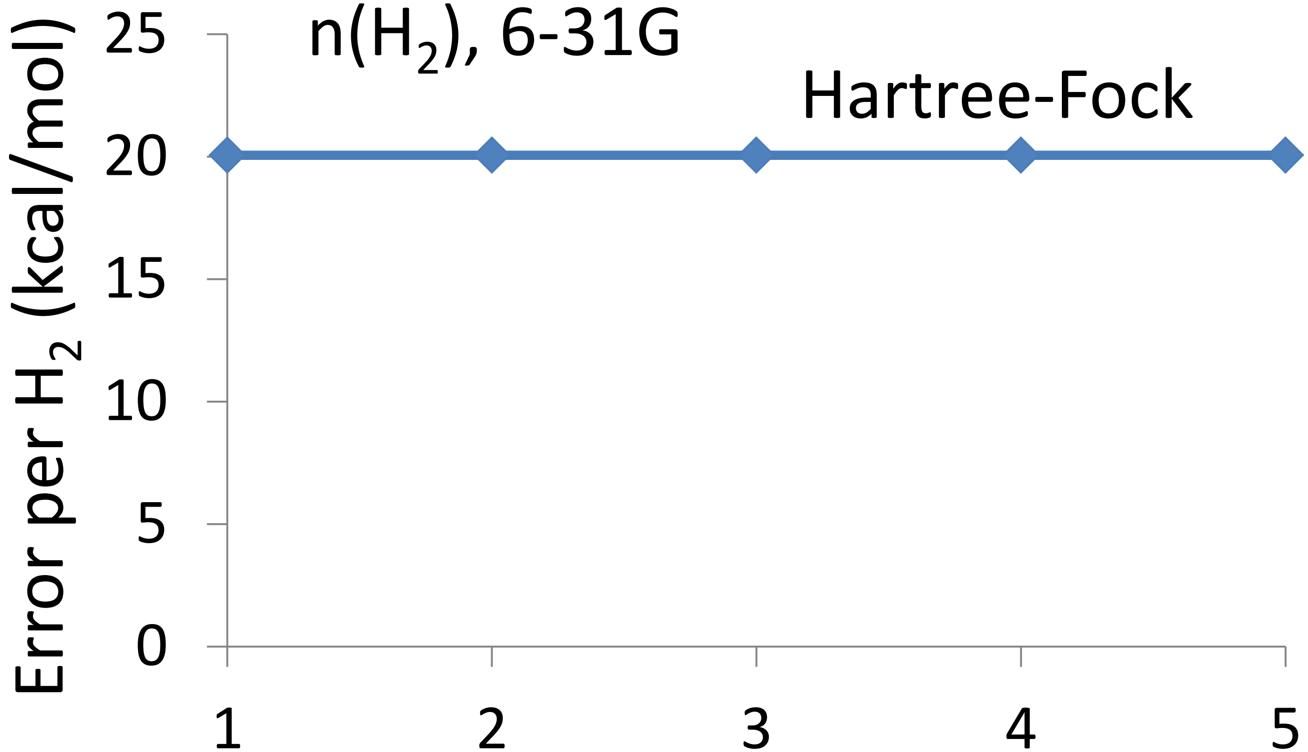

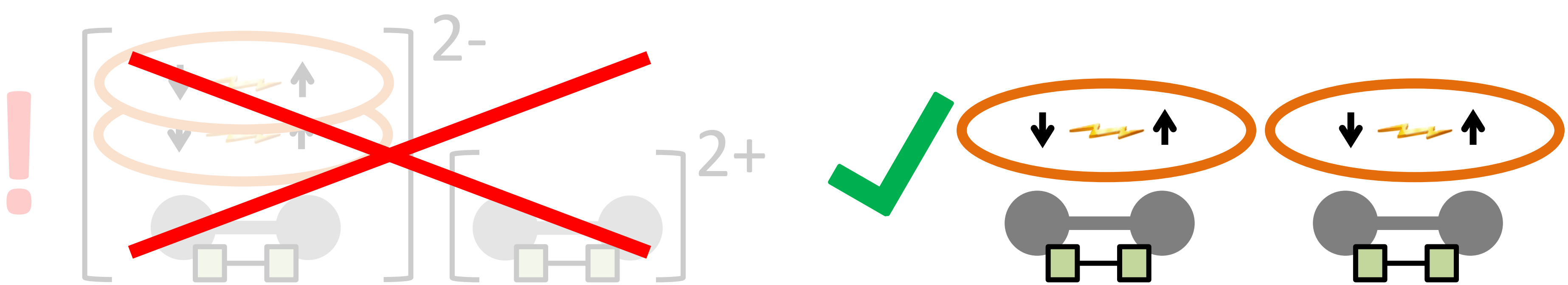

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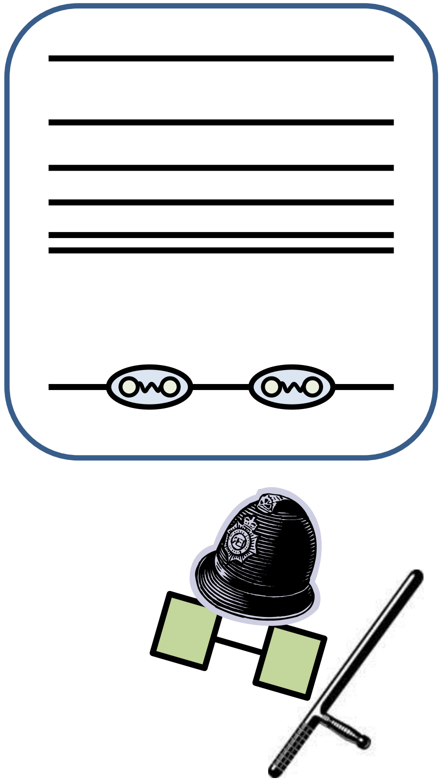

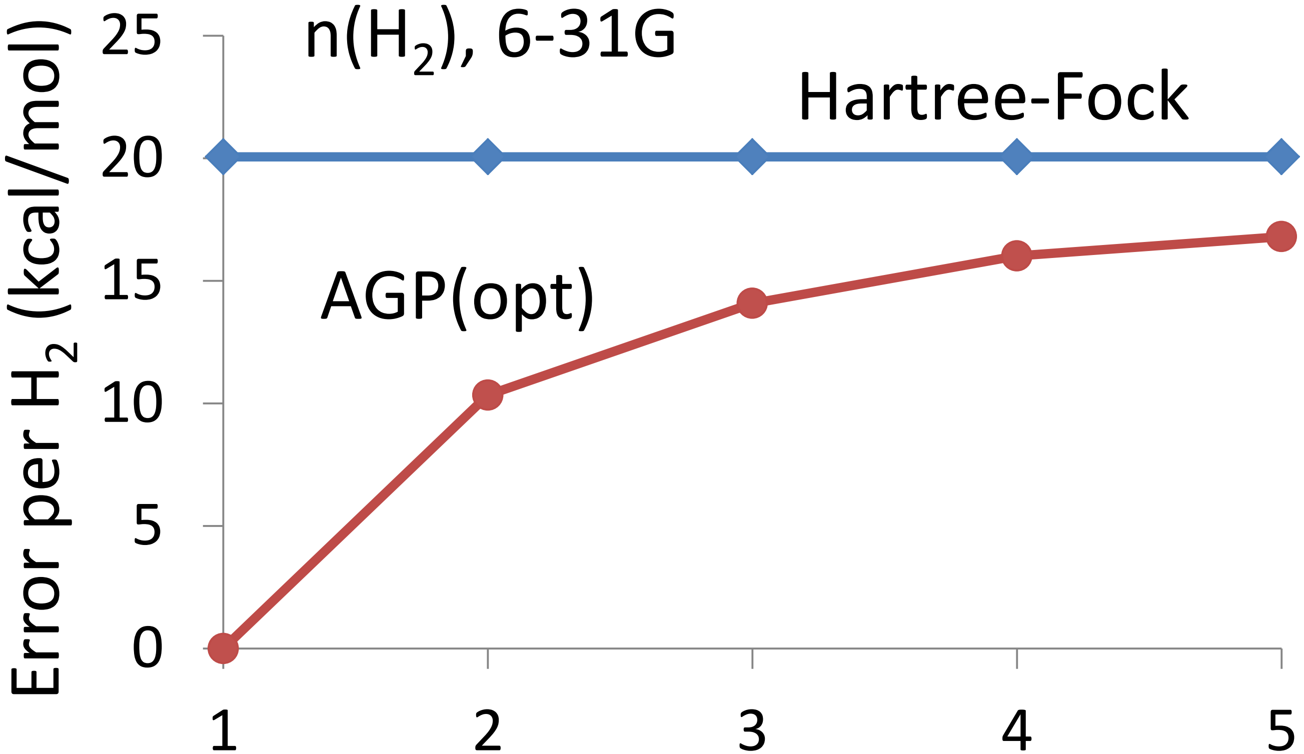

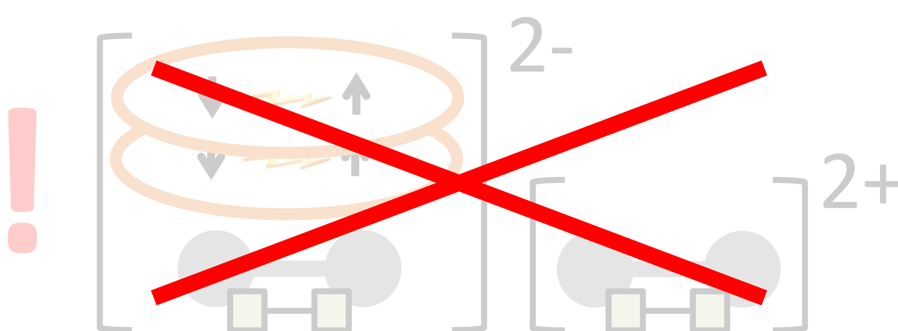

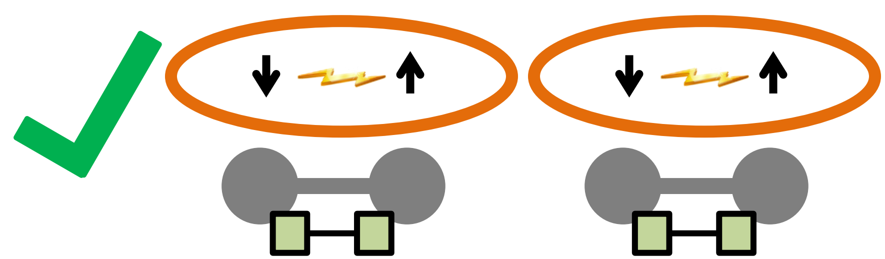

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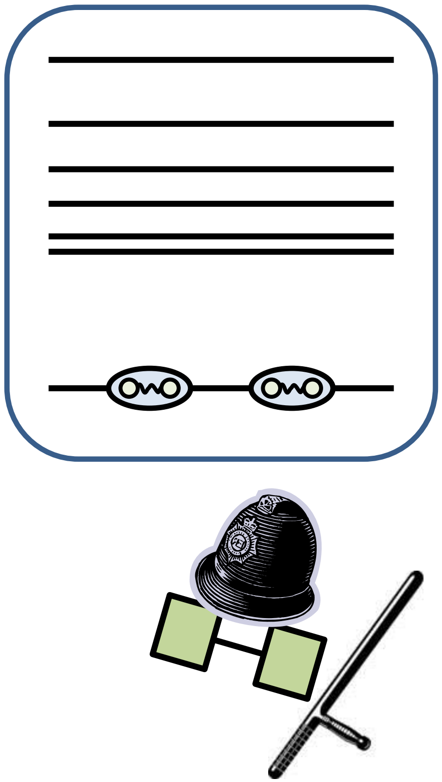

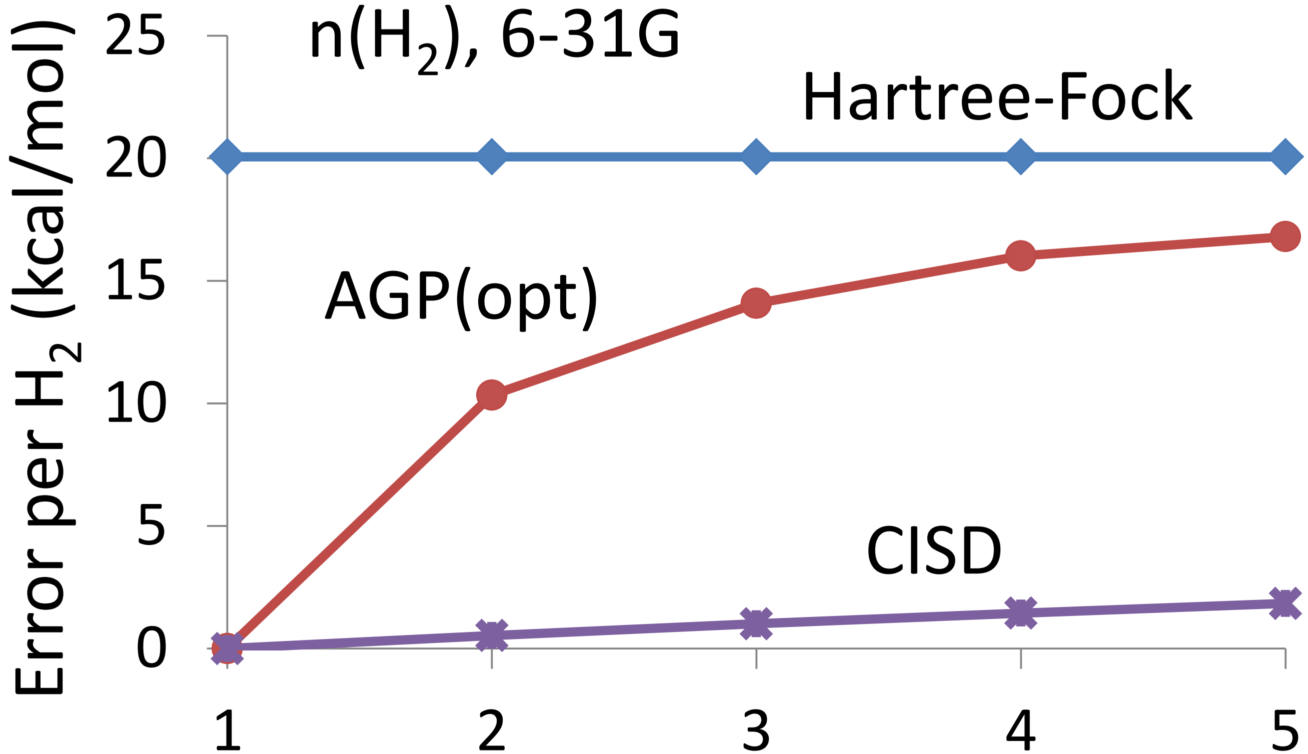

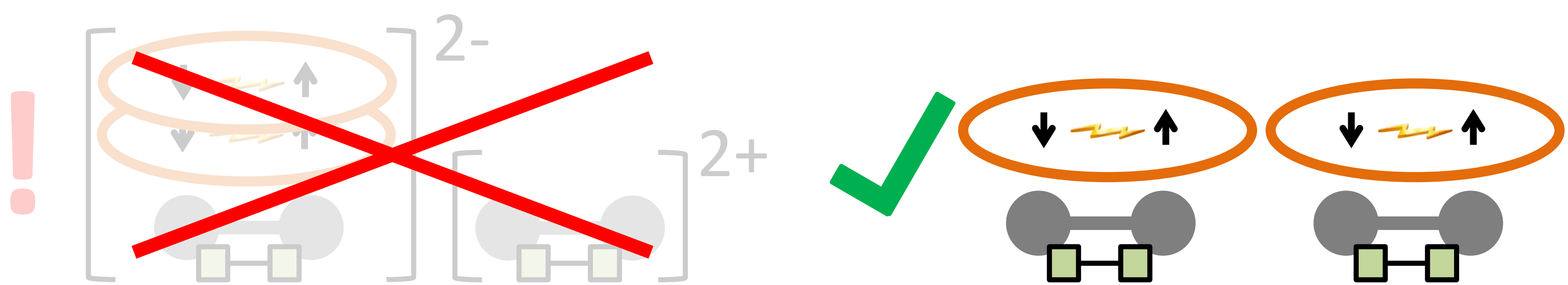

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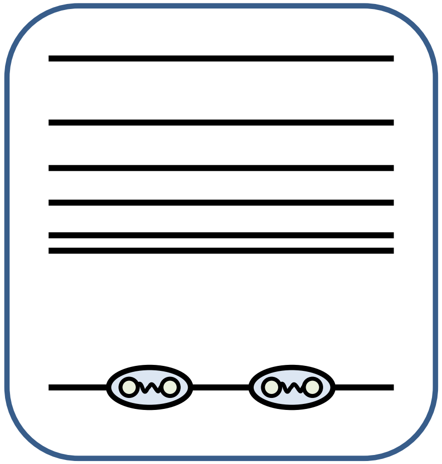
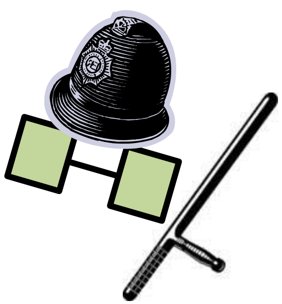
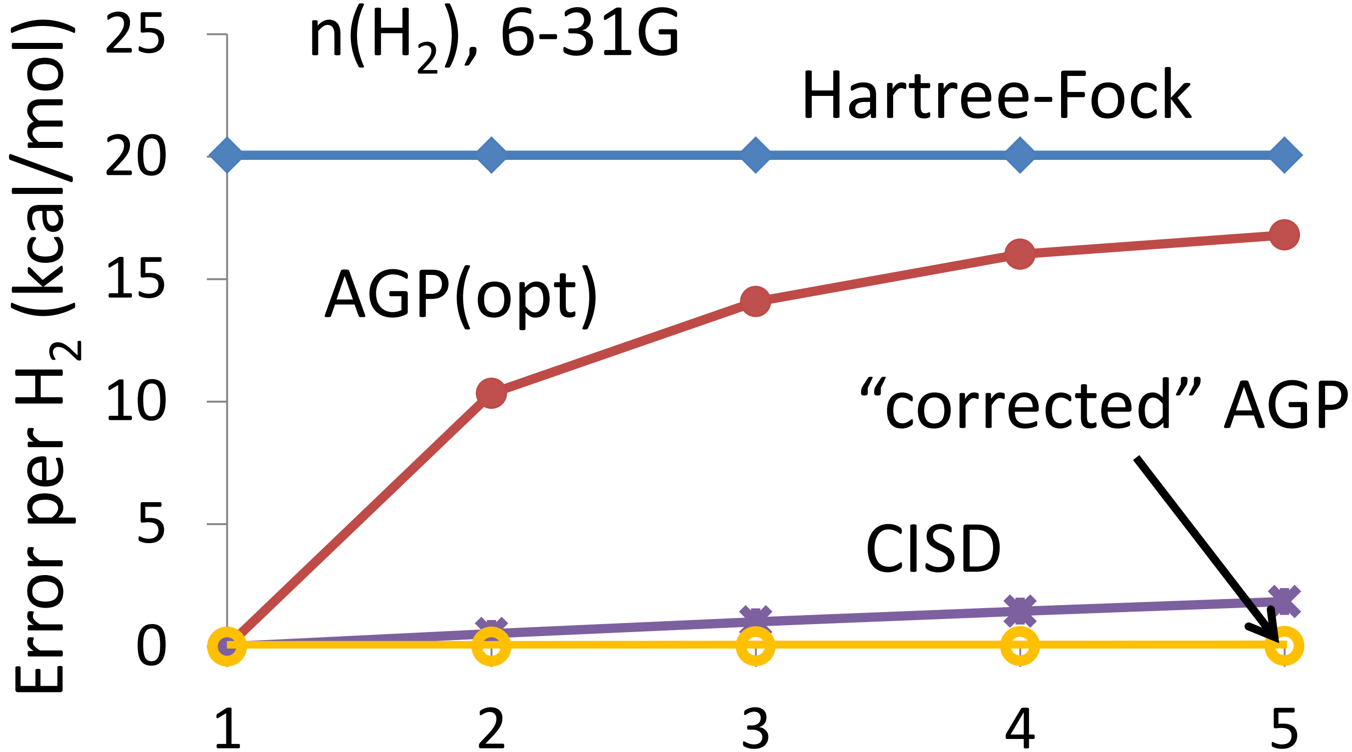
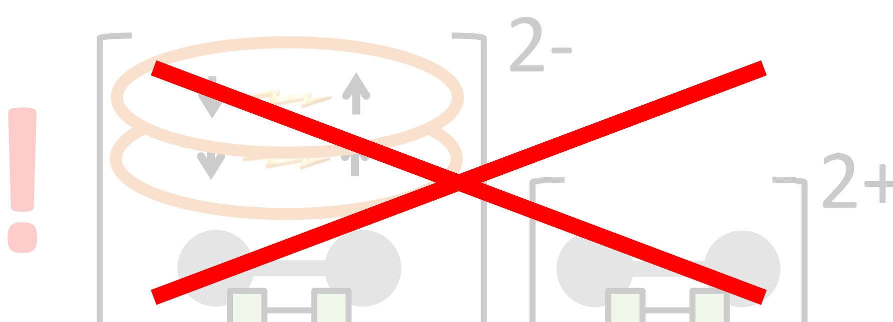
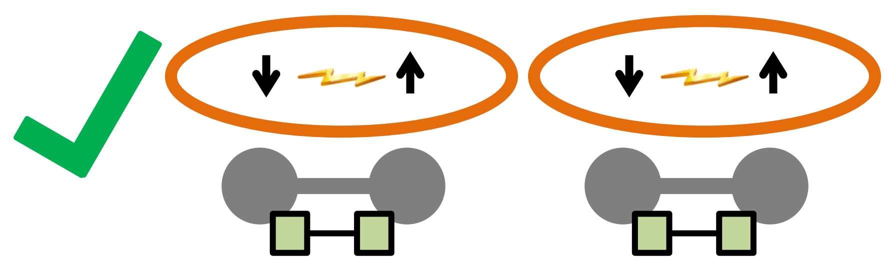




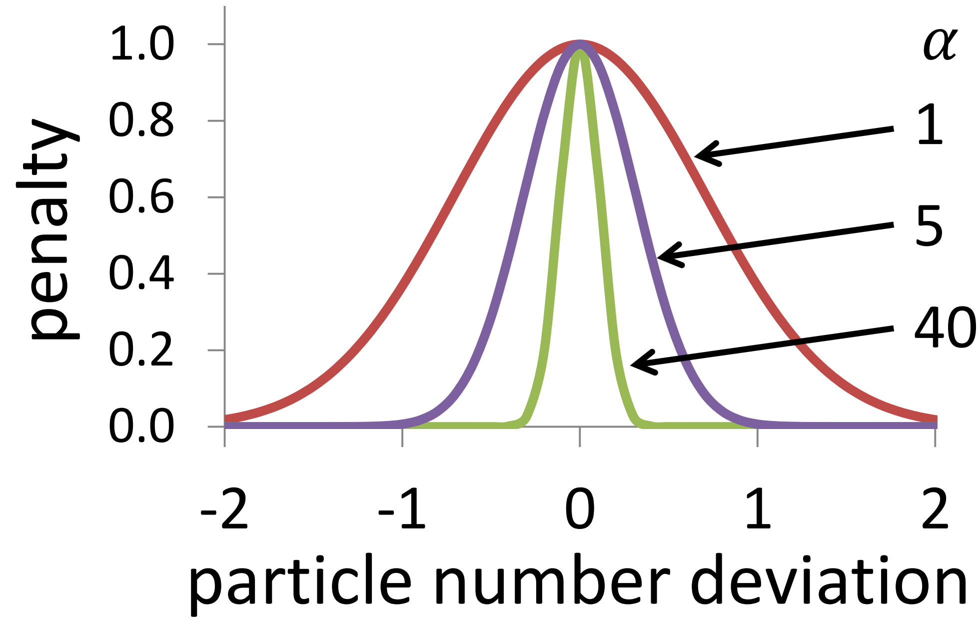




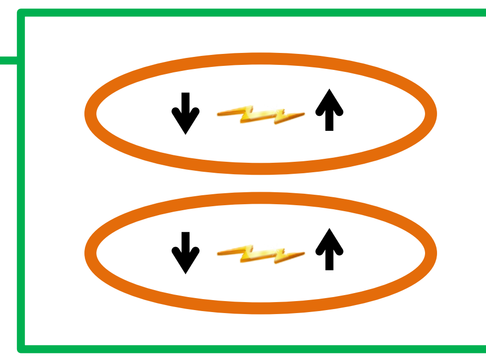


Hilbert space Jastrow factors

$$\exp\left[-\alpha\left(M-\sum_i \hat{n}_i\right)^2\right]|\Psi\rangle$$



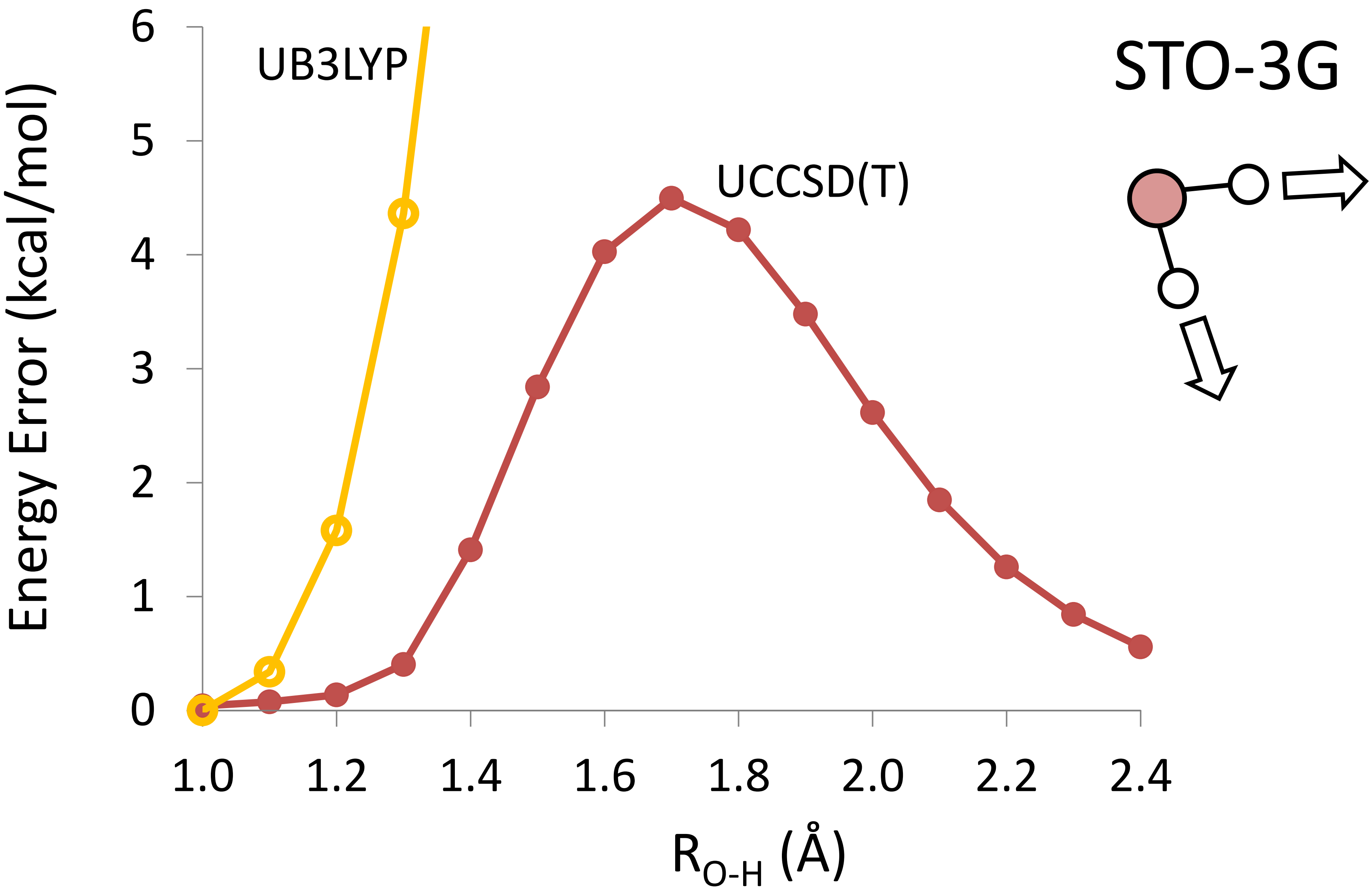
$$|\Psi_{\mathrm{JAGP}}\rangle = \exp\left[\sum_{ij} J_{ij}\hat{n}_i\hat{n}_j\right]\left(\sum_{pq}\phi_{pq}a_p^+a_q^+\right)^{\frac{N}{2}}|0\rangle$$



The (Hilbert space) JAGP Ansatz

EN, PRL 2012

getting closer



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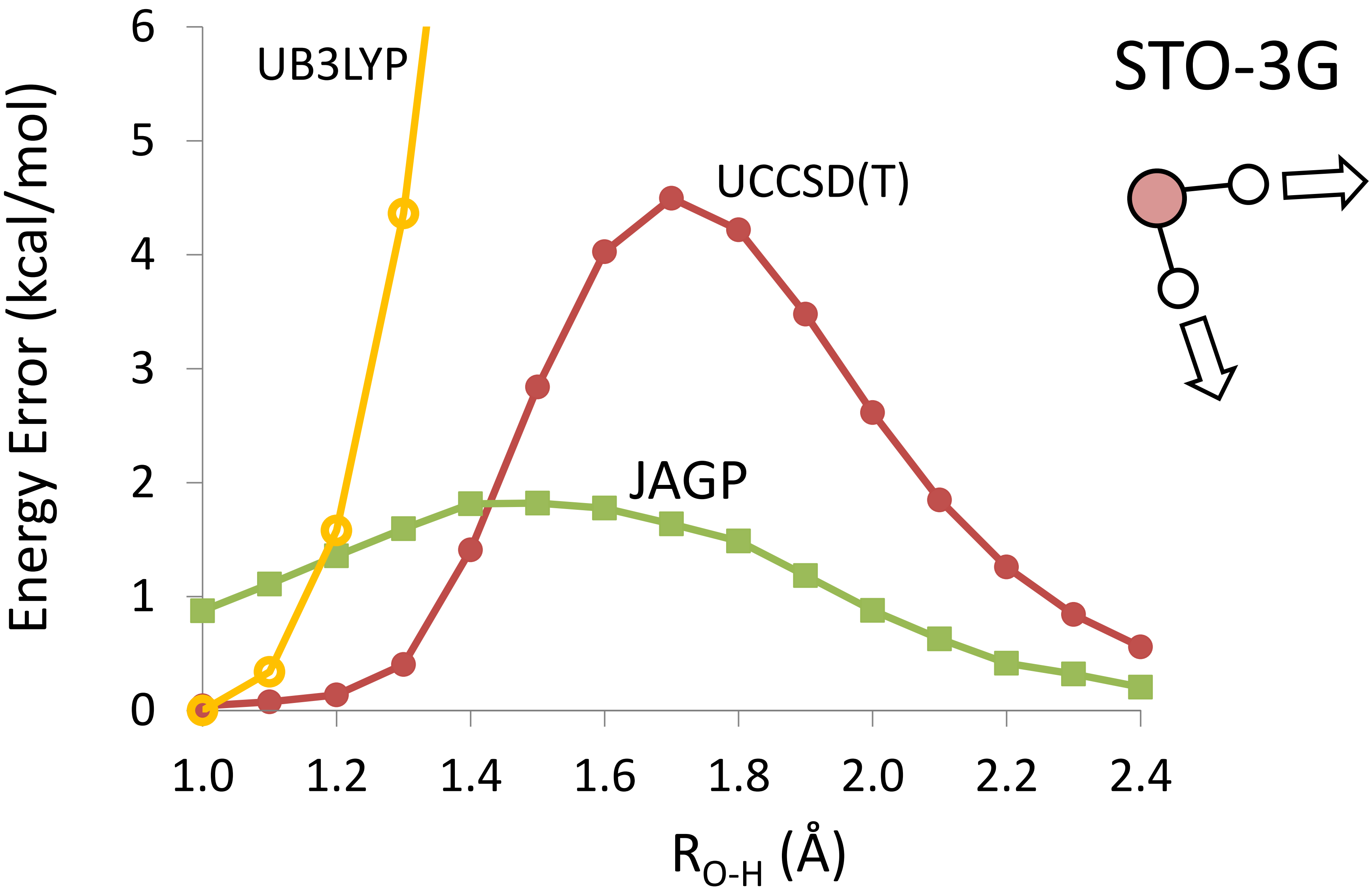
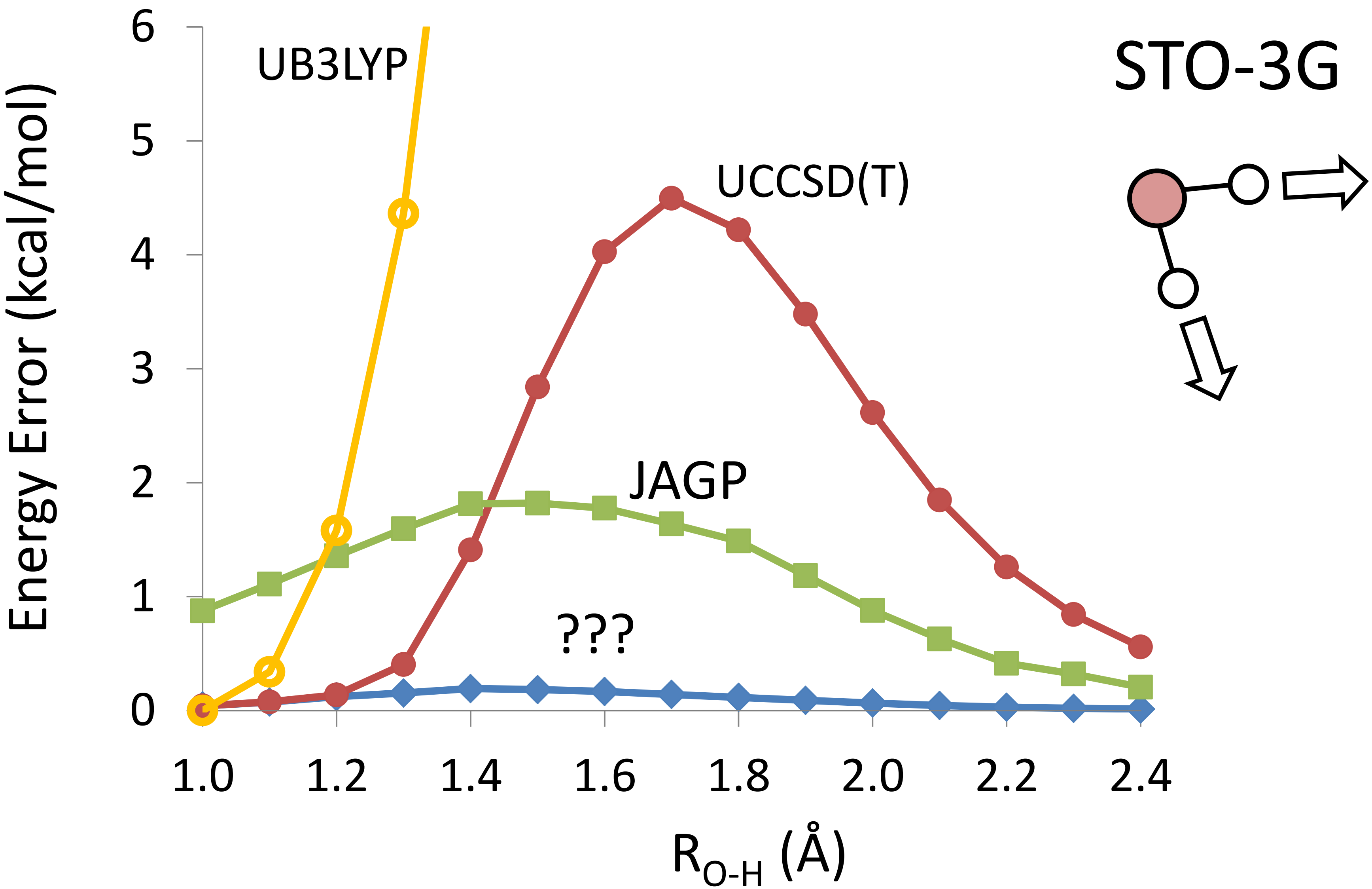


getting closer



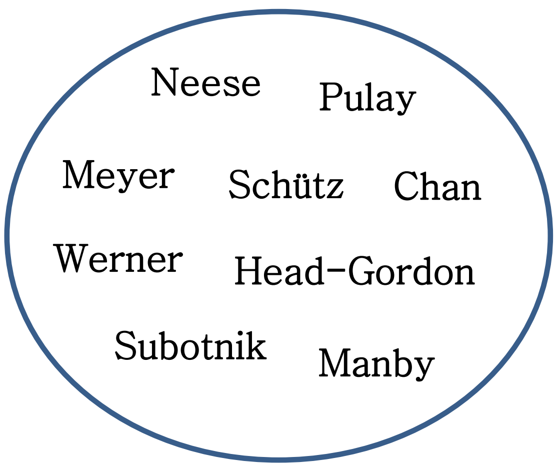
coupled cluster theory

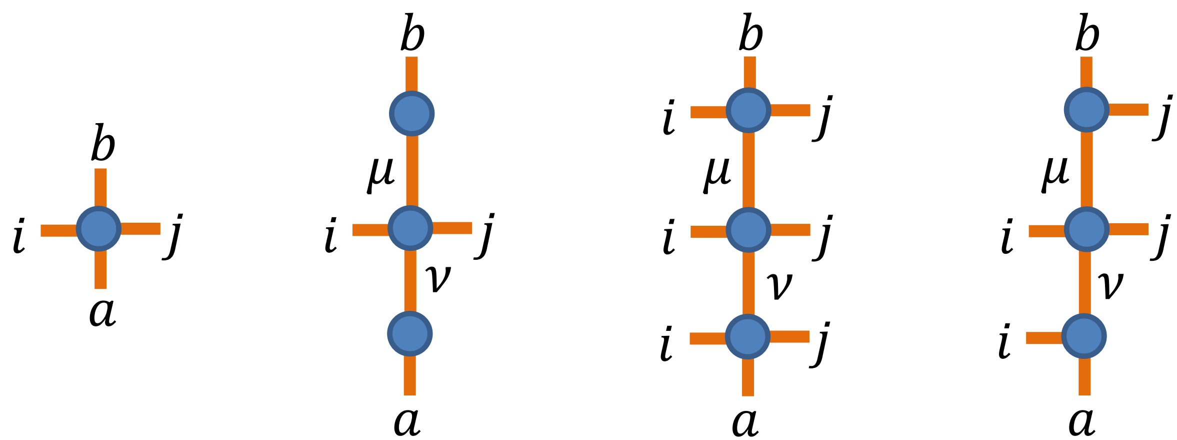
$$\exp\left[\sum_{iajb} T_{ij}^{ab} a_a^{+} a_i a_b^{+} a_j\right]$$

$$\left(\langle\vec{n}| = \langle 010011010|\right)$$

$$\langle\vec{n}|\, e^{T} |\Phi\rangle$$

exponential cost





full T PAO PNO OSV

Yang et al, JCP 2011

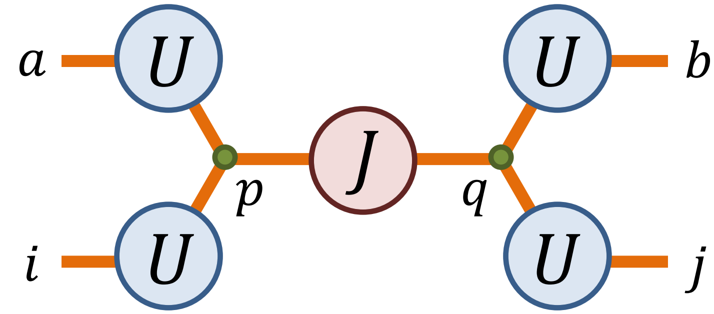
the Jastrow cluster operator

$$\sum_{pq} a_p^+ a_p \, J_{pq} \, a_q^+ a_q$$

orbital rotation with unitary U

$$\sum_{pq} \sum_{iajb} (U_{pa}^* a_a^+)(U_{pi} a_i) \, J_{pq} (U_{qb}^* a_b^+)(U_{qj} a_j)$$

$$T_{ij}^{ab} \approx$$



$$\sum_{iajb} T_{ij}^{ab} a_a^+ a_i a_b^+ a_j$$

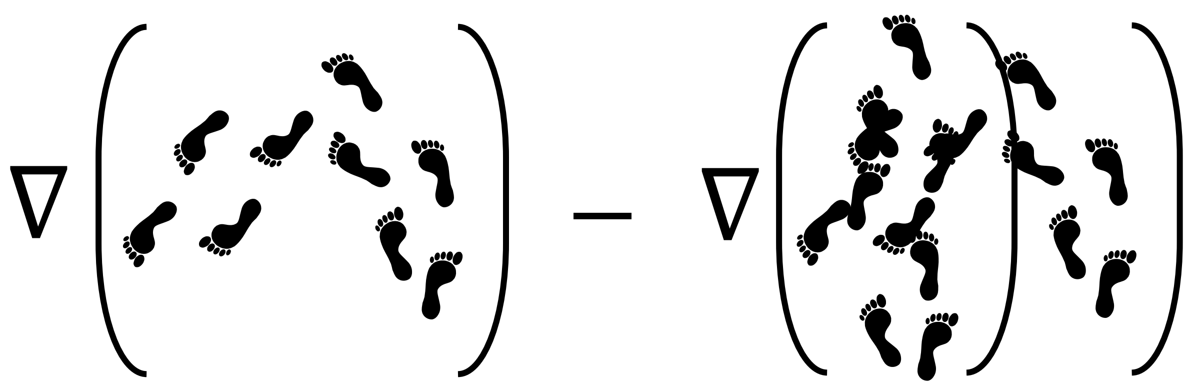
optimization

$$\langle\Phi|e^{T^+}He^{T}|\Phi\rangle \xrightarrow{T \approx U^+JU} \left[\langle\tilde{\Phi}|\right]e^{J^+}\left[\tilde{H}\right]e^{J}\left[|\tilde{\Phi}\rangle\right]$$

$$\boldsymbol{U} = e^{\boldsymbol{K}-\boldsymbol{K}^+}$$

$$\frac{\partial E}{\partial \mathrm{K_{pq}}} = \sum_{ij}\frac{\partial E}{\partial \tilde{t}_{ij}}\frac{\partial \tilde{t}_{ij}}{\partial \mathrm{K_{pq}}} + \sum_{ijkl}\frac{\partial E}{\partial \tilde{V}_{ijkl}}\frac{\partial \tilde{V}_{ijkl}}{\partial \mathrm{K_{pq}}}$$

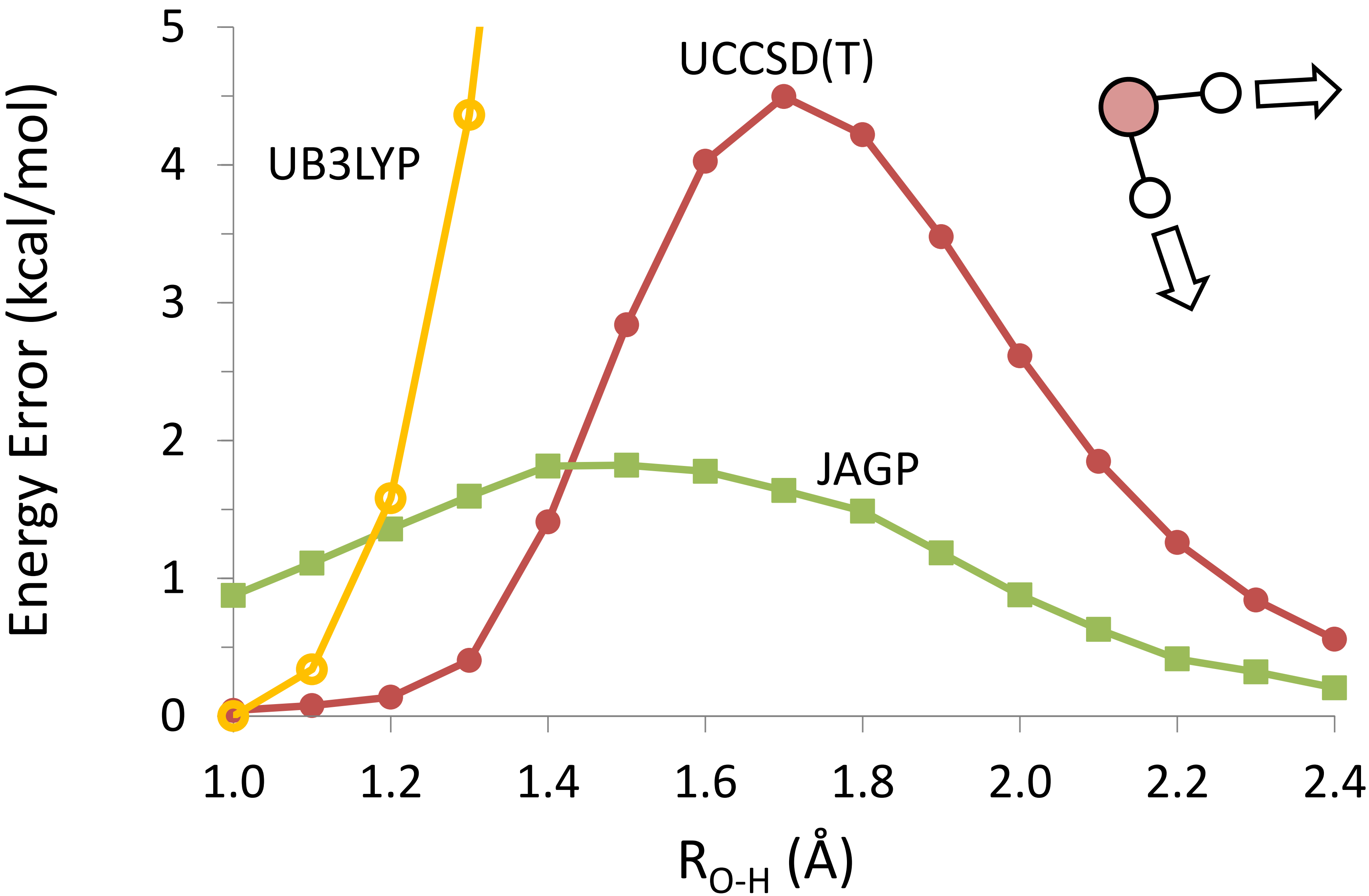
correlated sampling



derivatives ✓

quasi-Newton ?✓

strong correlation (H_2O, STO-3G)



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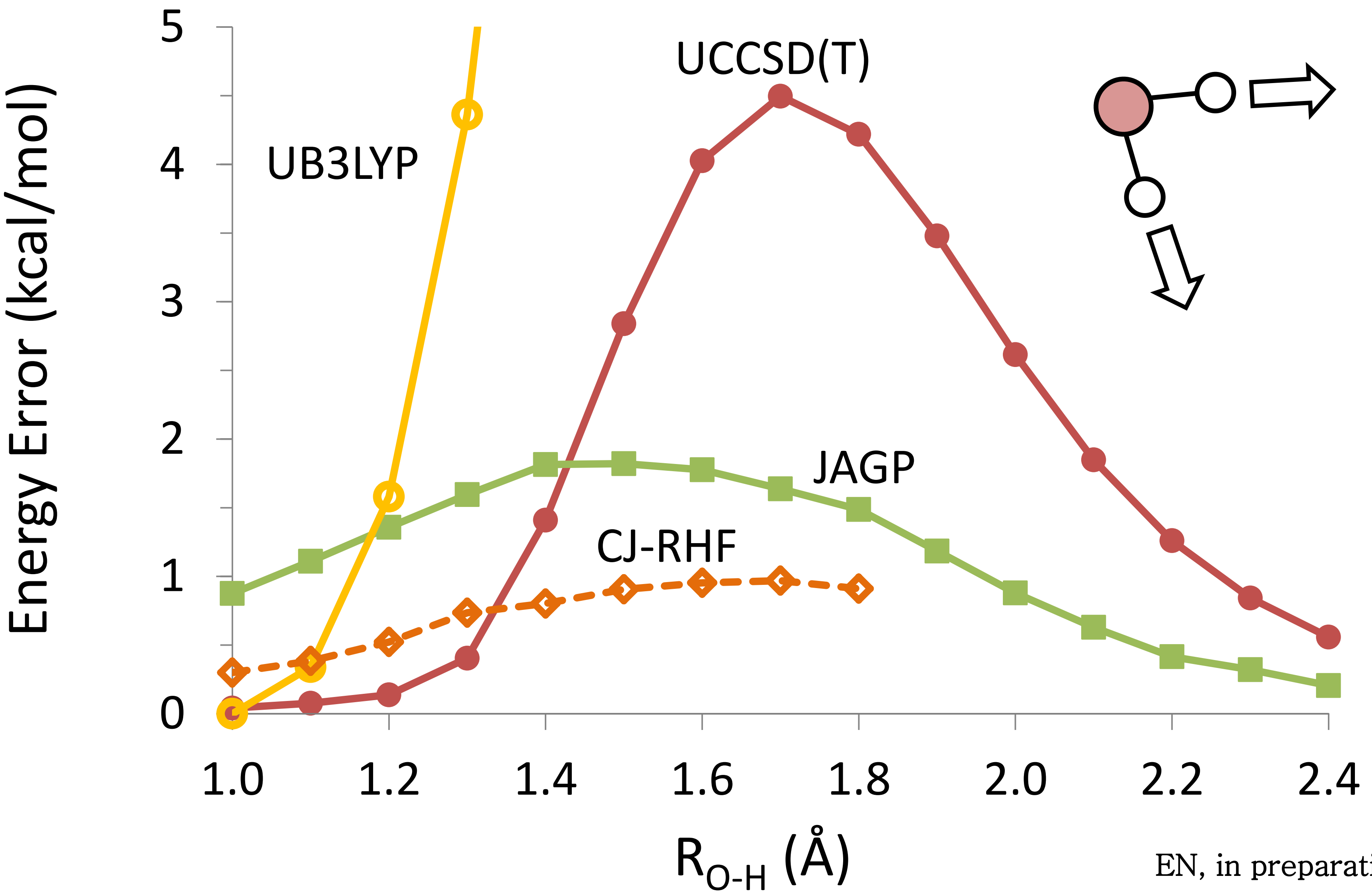
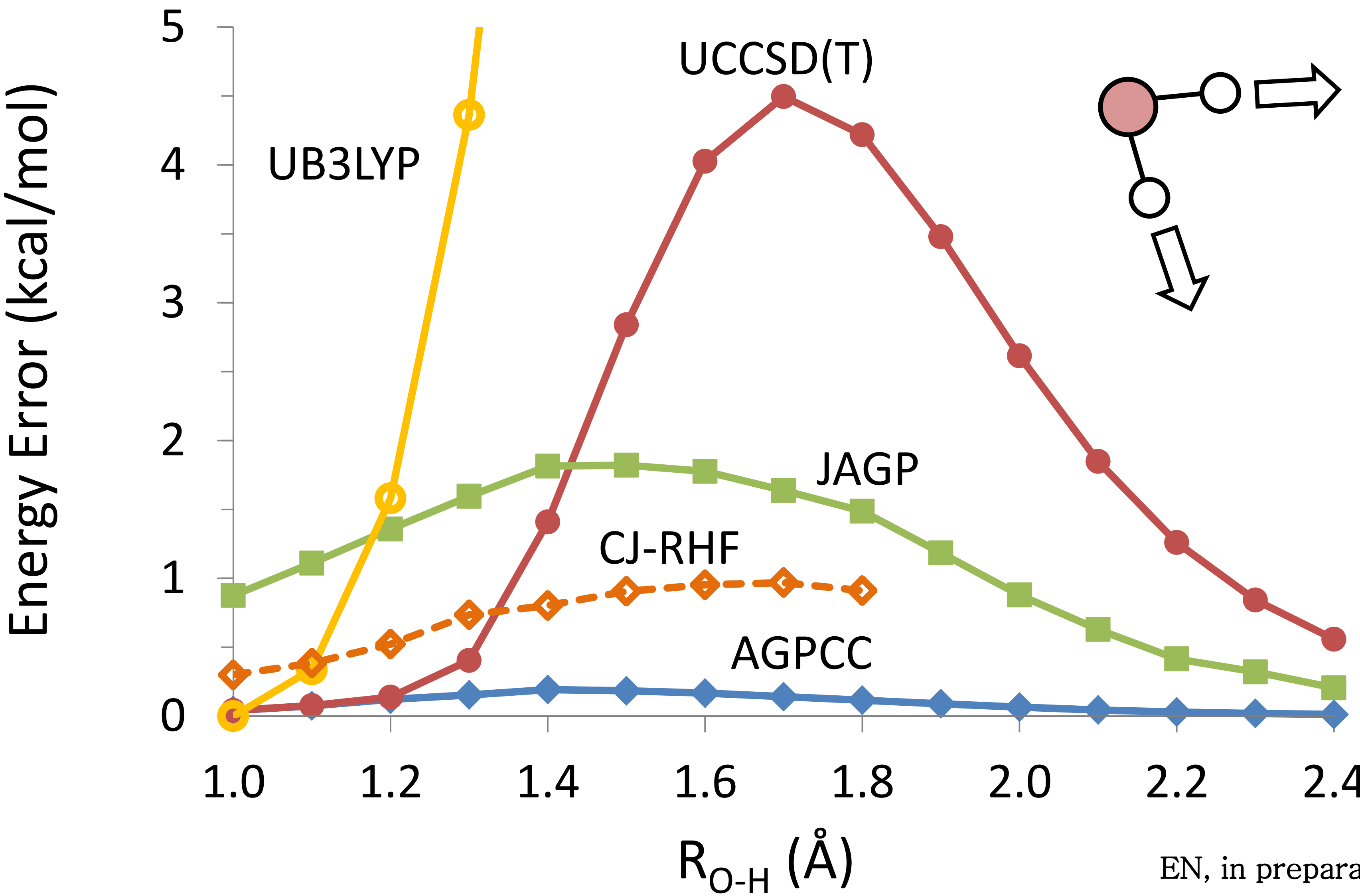


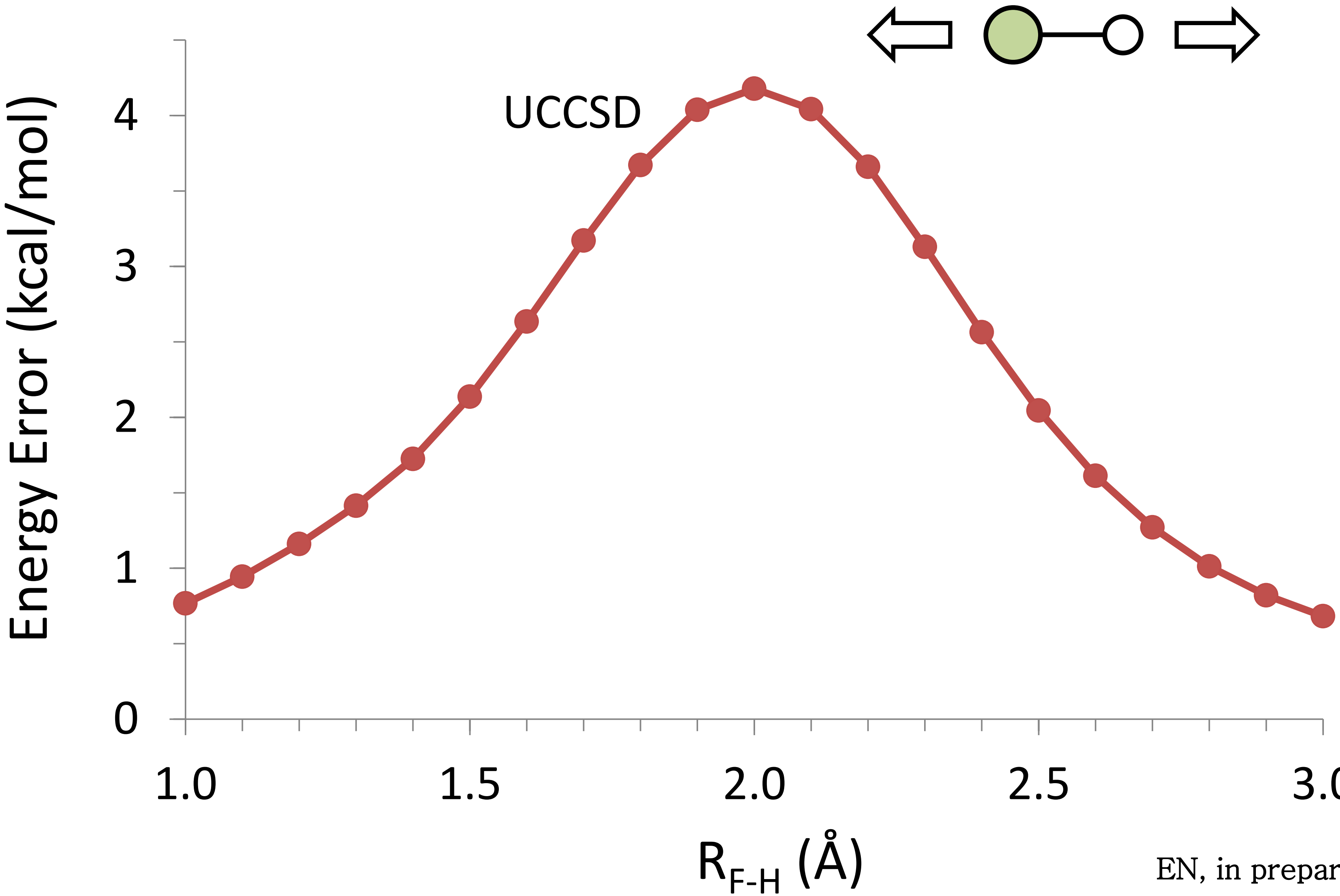
EN, in preparation

strong correlation (H_2O, STO-3G)



EN, in preparation

strong and weak (HF, 6-31G)



EN, in preparation

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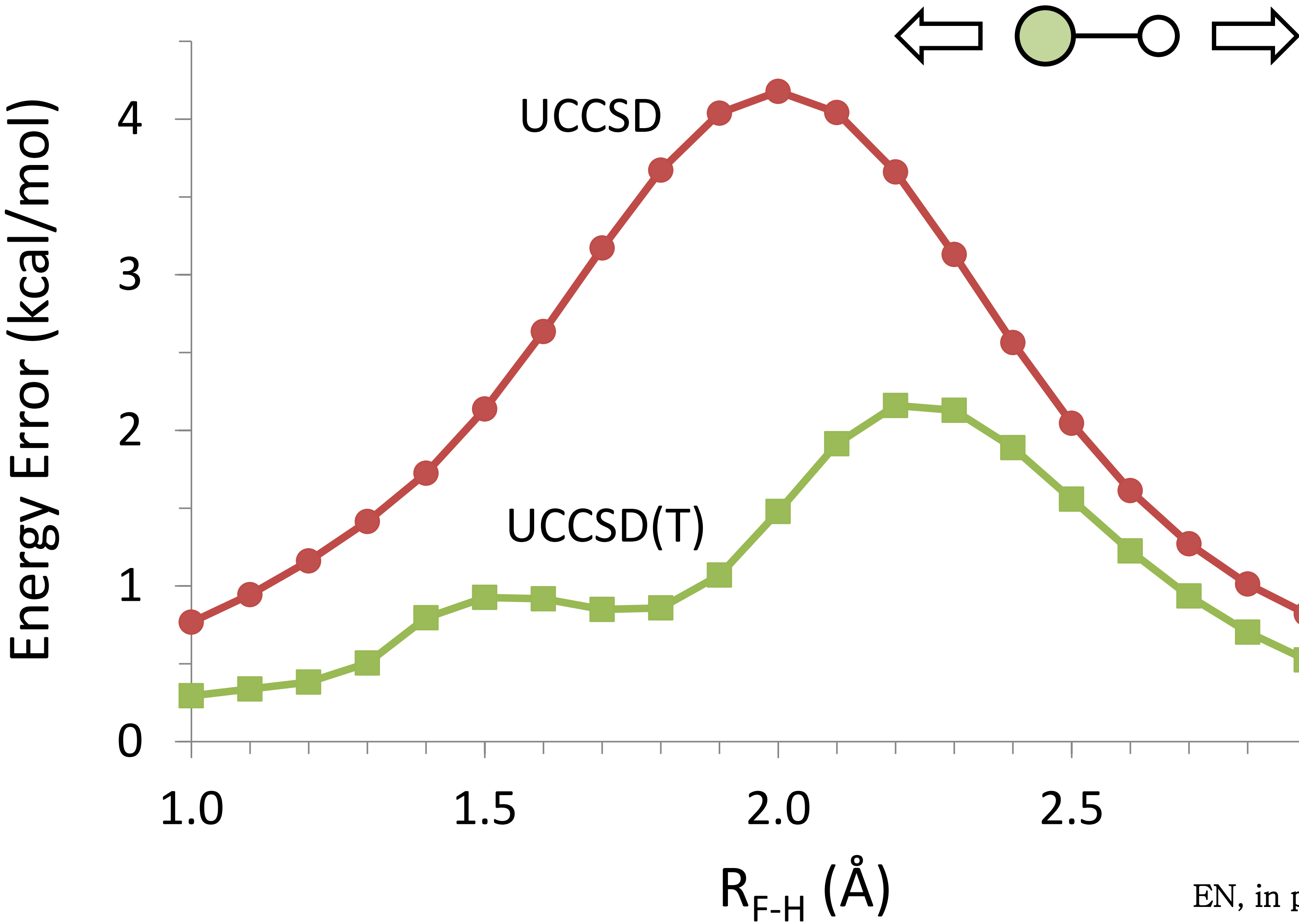

EN, in preparation

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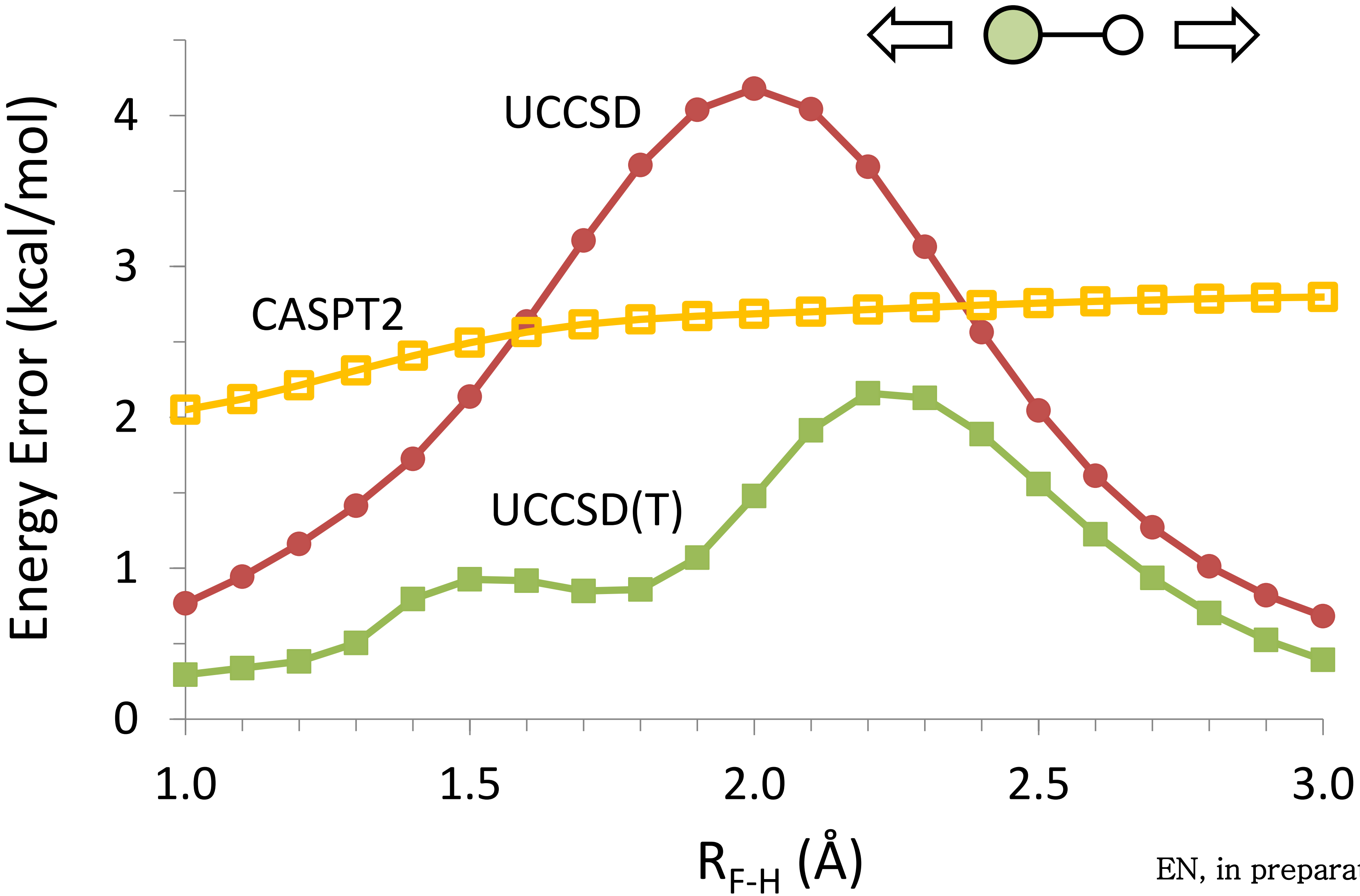

EN, in preparation

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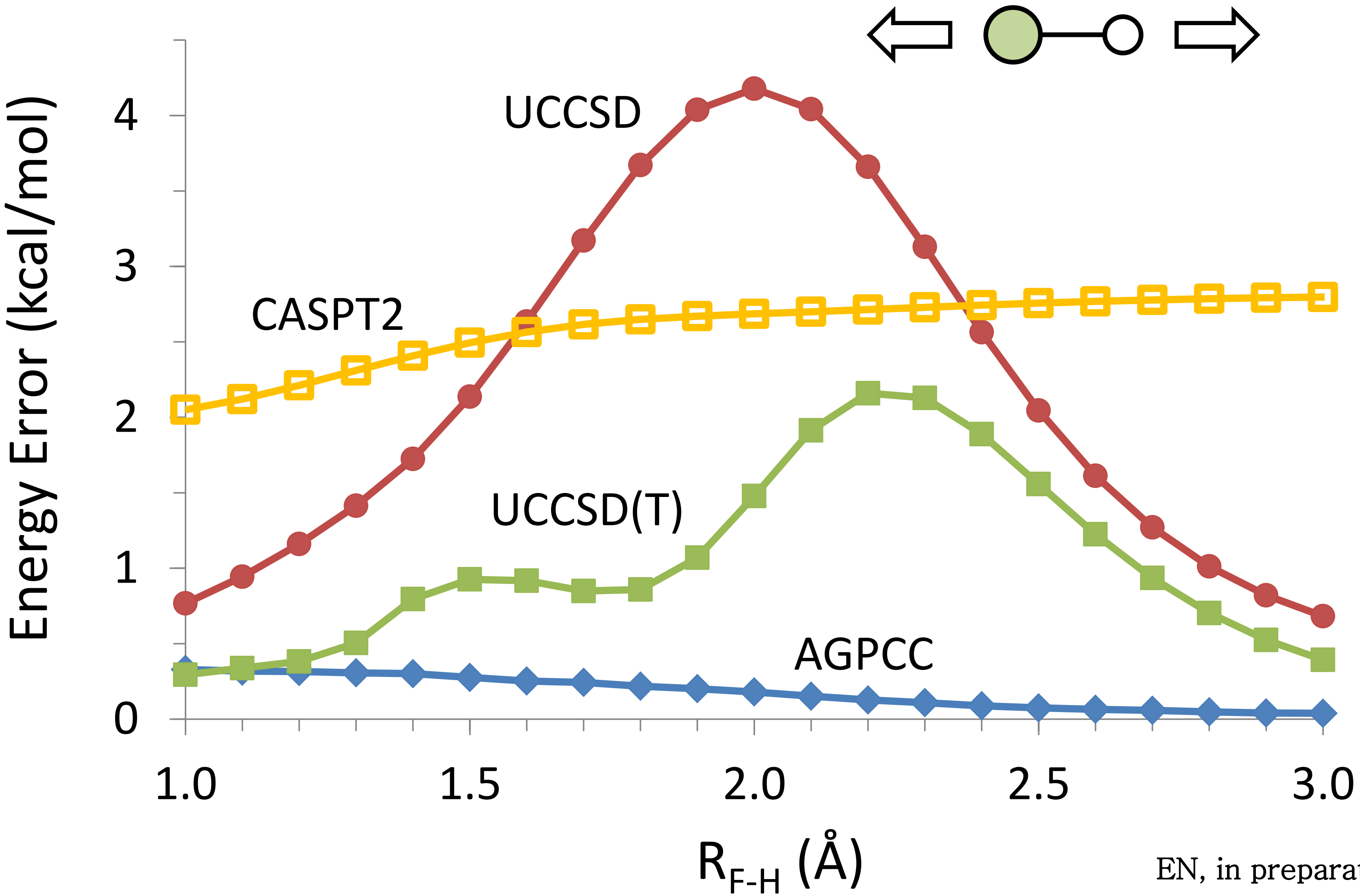

EN, in preparation

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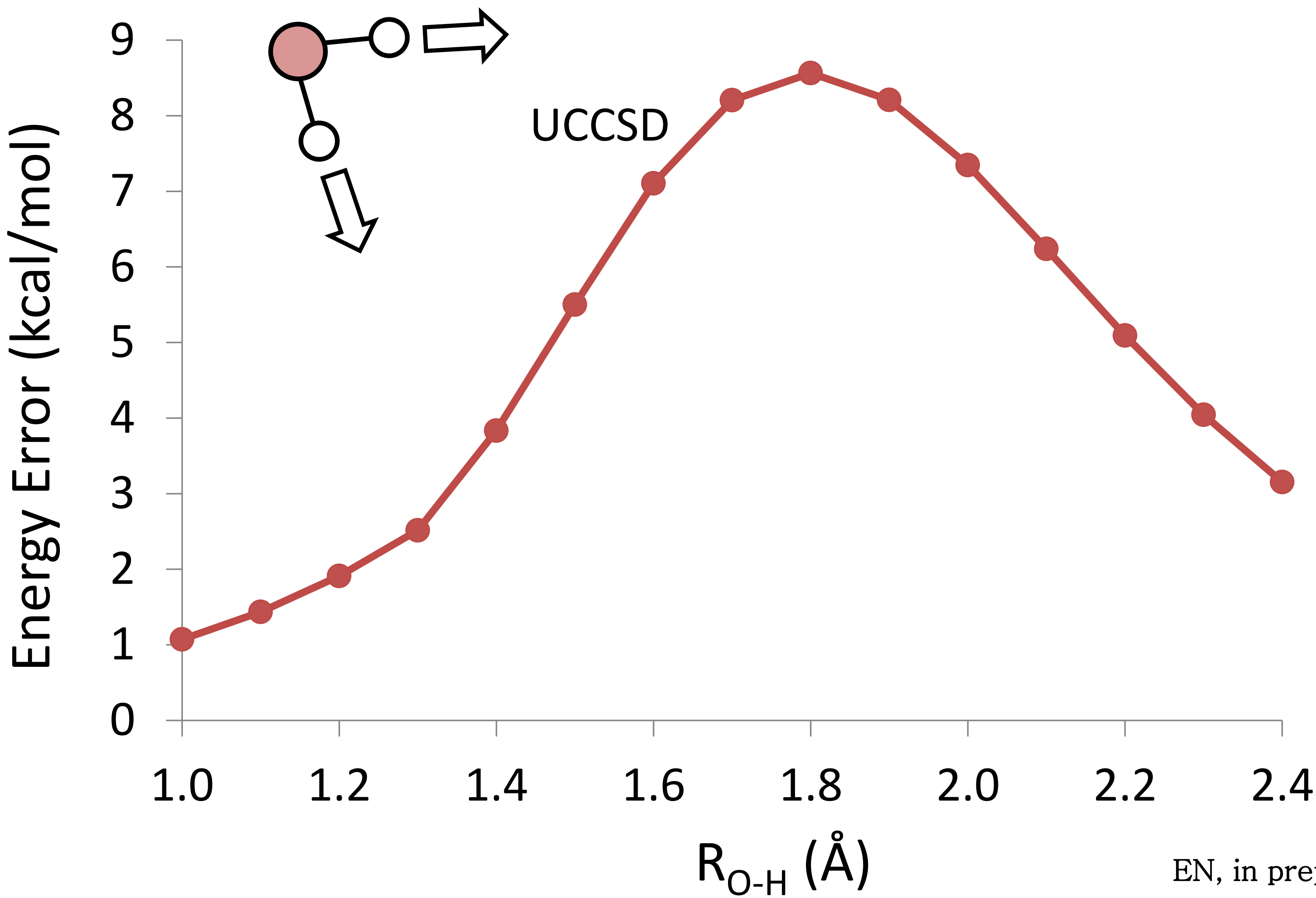

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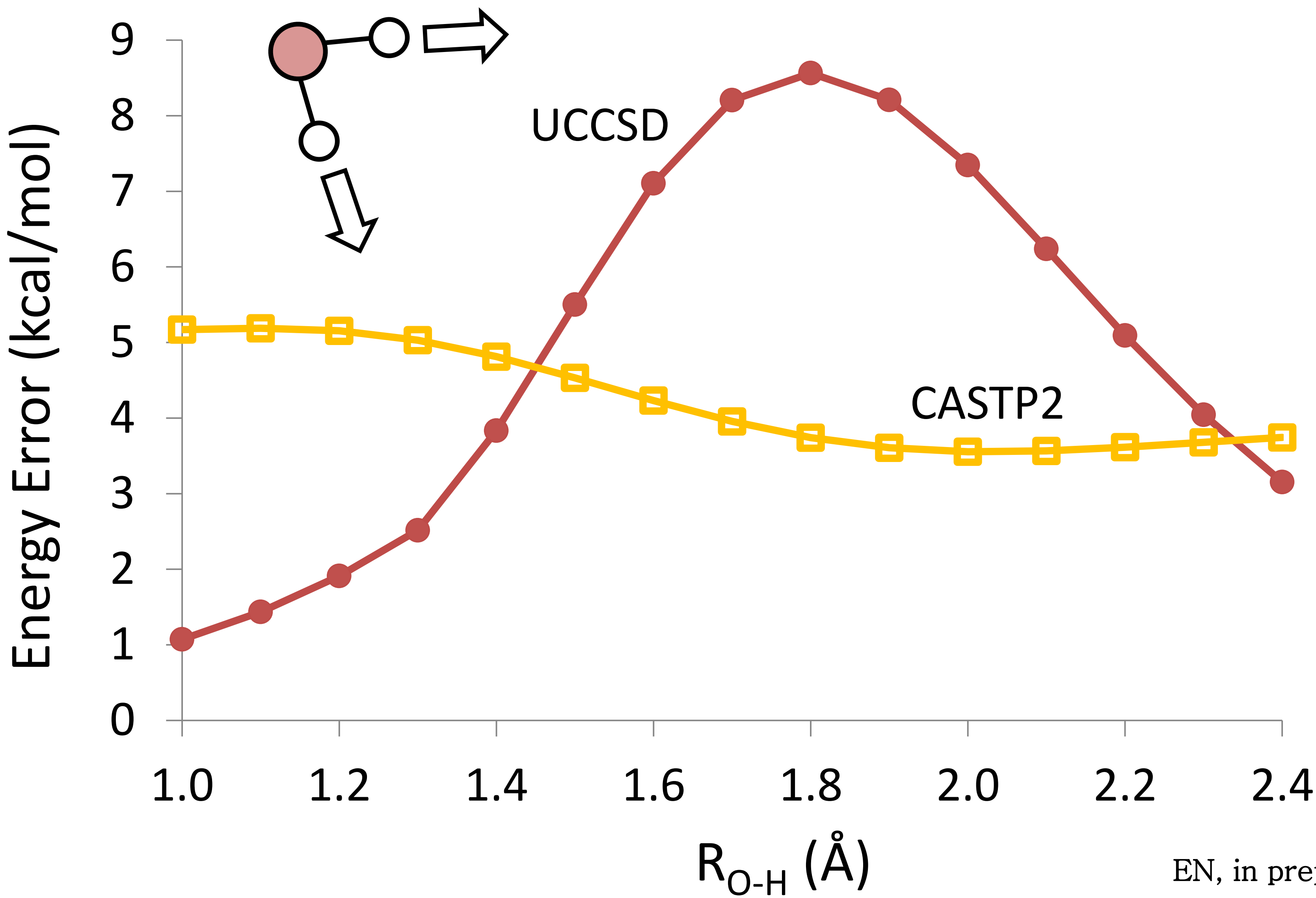

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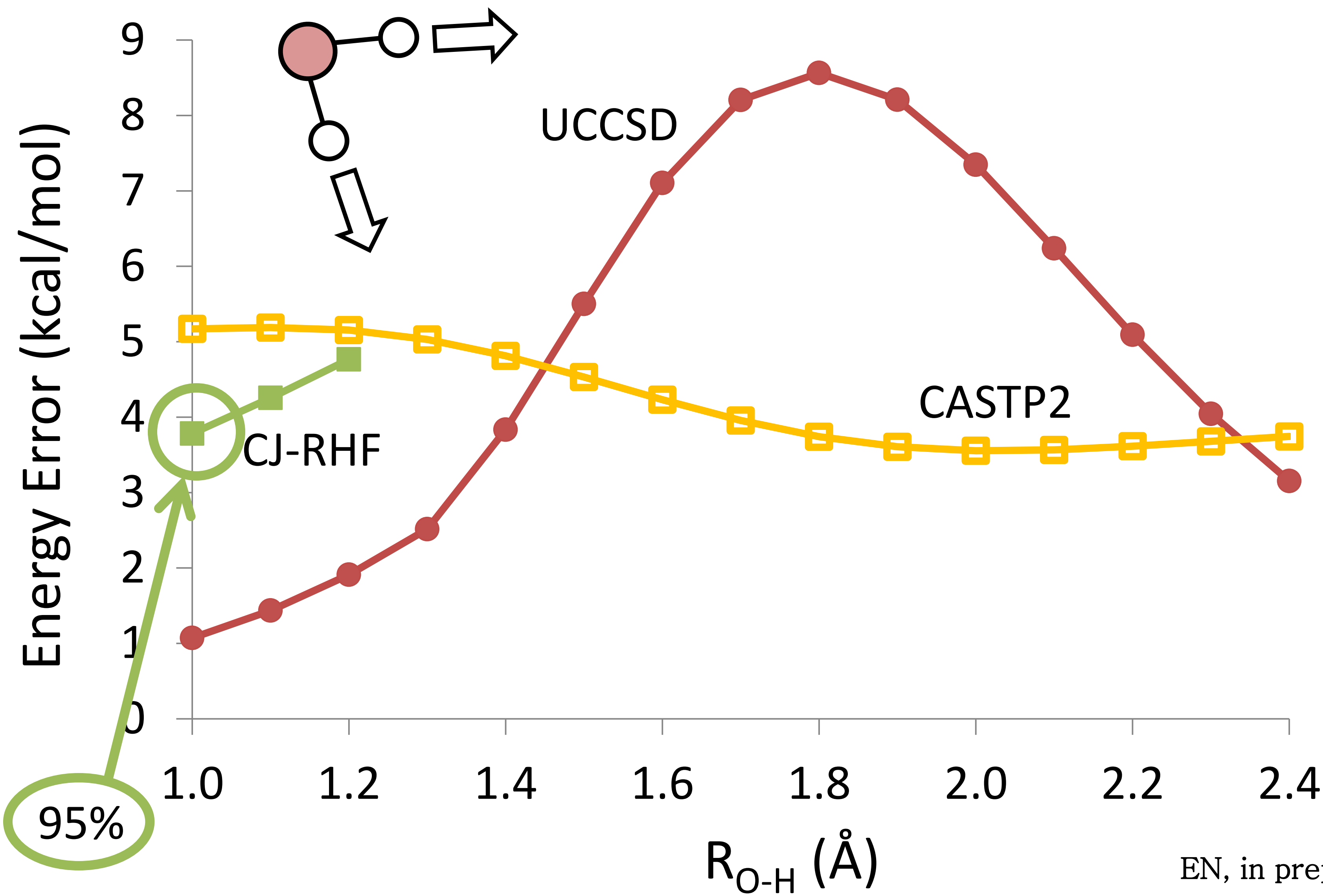

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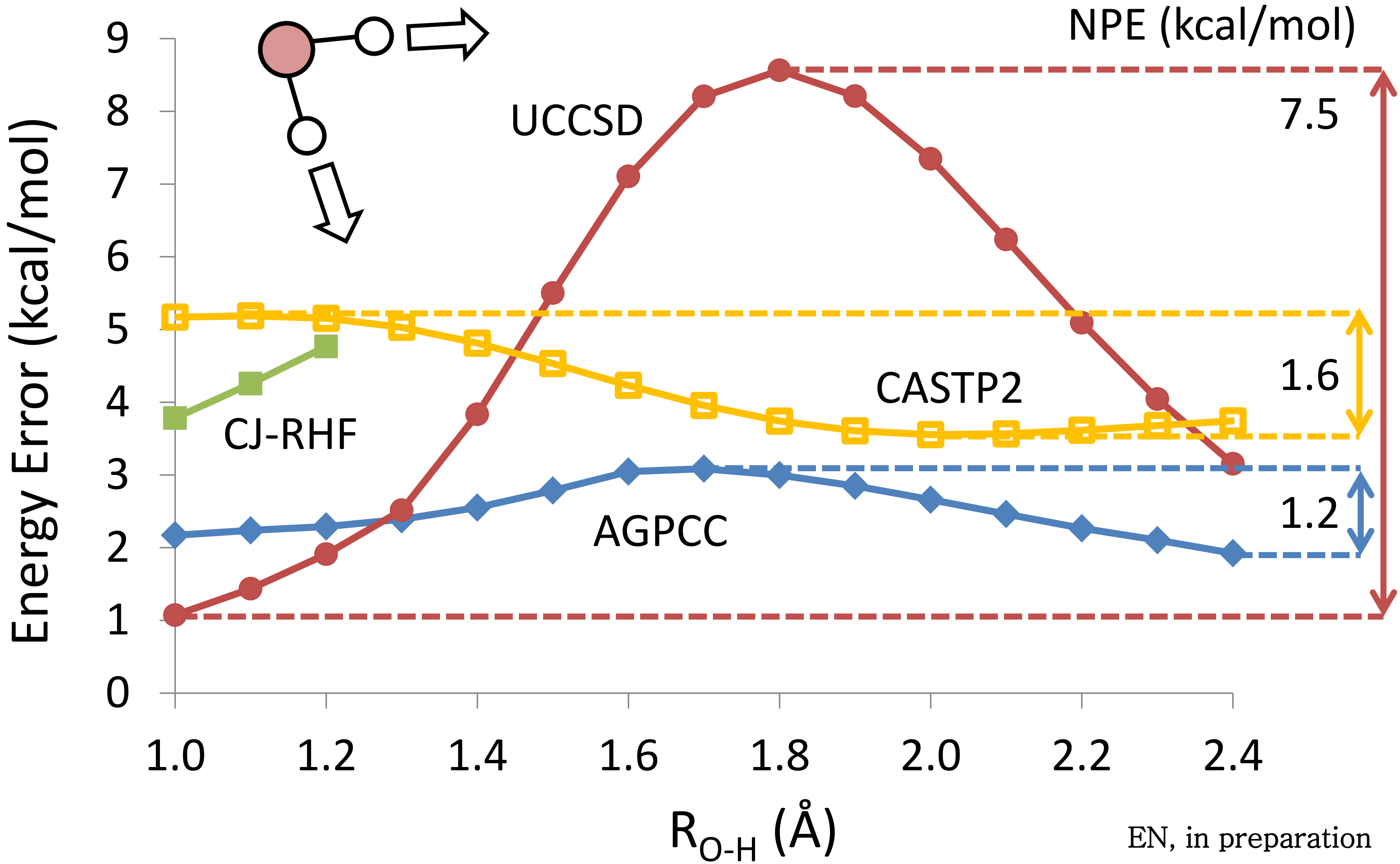

EN, in preparation

a word on cost

accurate (strong & weak)

$$1 + 1 = 2$$

size consistent/extensive

$$1 + 1 + 1 \ldots \propto N$$

variational

$$1 + 1 > 0$$

e^T 

$$\text{cost} = \mathrm{C} \times N^5$$

very large (10^8)

quasi-Newton ∇ 

analytic Hessian

acknowledgements

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