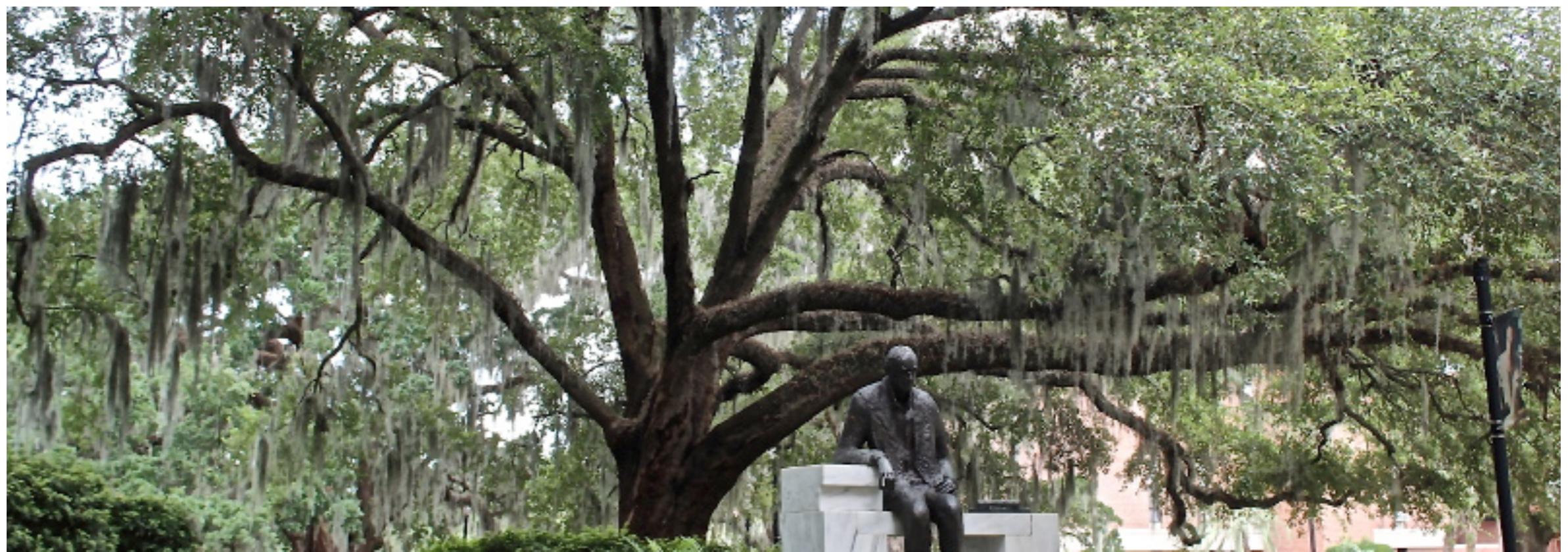


Electronic structure theory





“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus **completely known**, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

Paul A. M. Dirac, 1929



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the Schrödinger equation: $-i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$ or $\hat{H}\Psi = E\Psi$

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It therefore becomes desirable that **approximate practical methods** of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems **without too much computation.**”

Paul A. M. Dirac, 1929

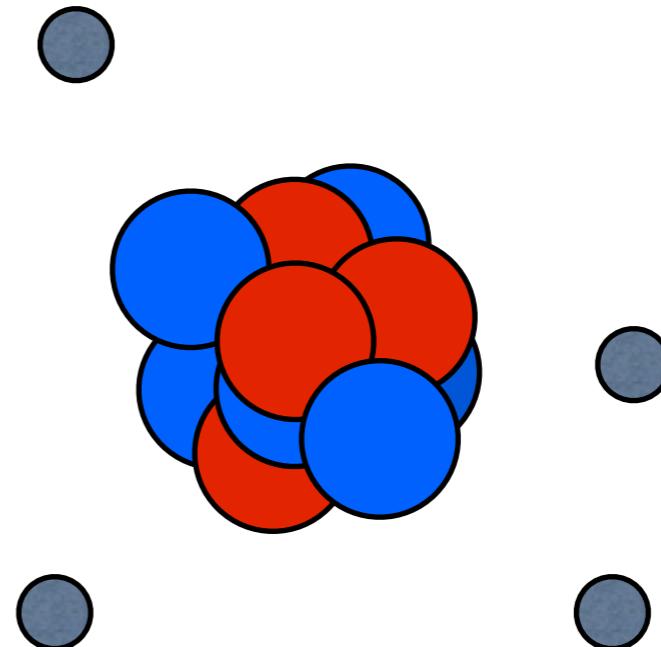
many electron atoms

the full Hamiltonian is a function of the nuclear and electronic coordinates

but within the Born-Oppenheimer approximation, we assume that the motion of nuclei is negligible relative to that of electrons, since they are so much heavier. So, for many-electron atoms, we typically concern ourselves only with the electronic wave function

$$\psi(1, 2, 3, 4)$$

the wave function is a function of electrons
1, 2, 3, and 4

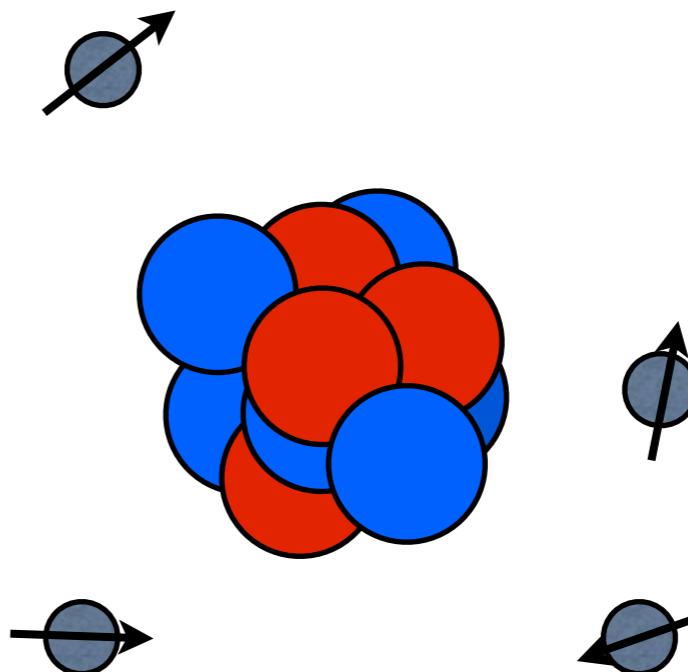


many electron atoms

what goes into electronic Hamiltonian?

$$\hat{H} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2$$

- kinetic energy of electrons

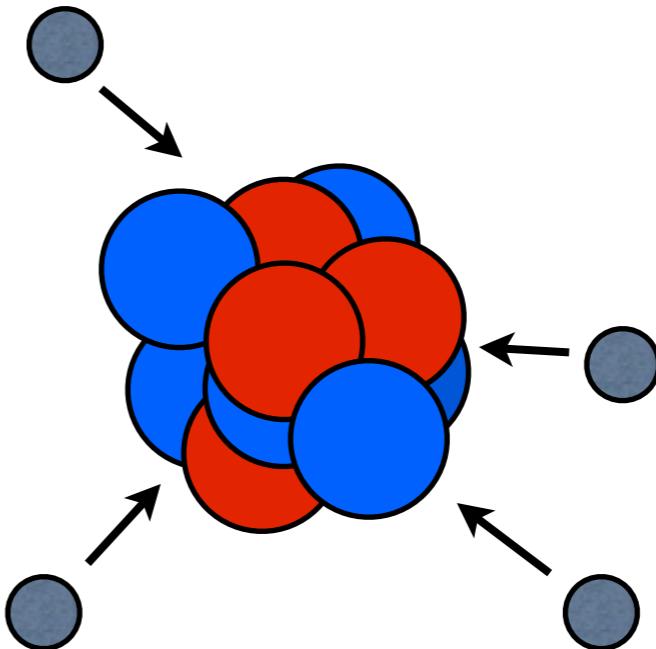


many electron atoms

what goes into electronic Hamiltonian?

$$\hat{H} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_i \frac{Ze^2}{4\pi\epsilon_0 r_i}$$

- kinetic energy of electrons
- electron-nuclear attraction

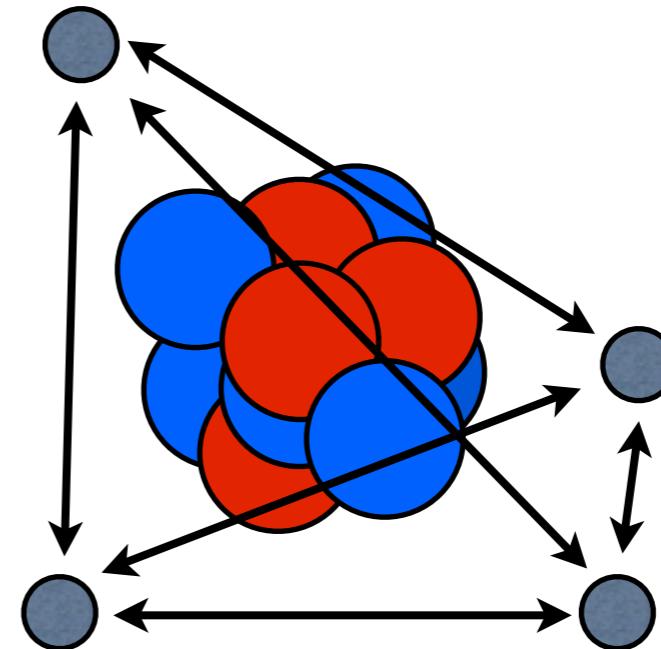


many electron atoms

what goes into electronic Hamiltonian?

$$\hat{H} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_i \frac{Ze^2}{4\pi\epsilon_0 r_i} + \sum_{i < j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

- kinetic energy of electrons
- electron-nuclear attraction
- electron-electron repulsion

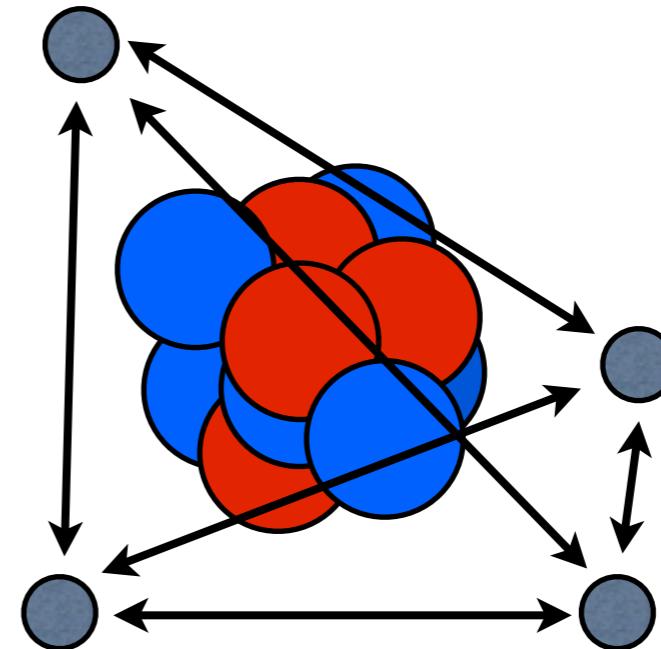


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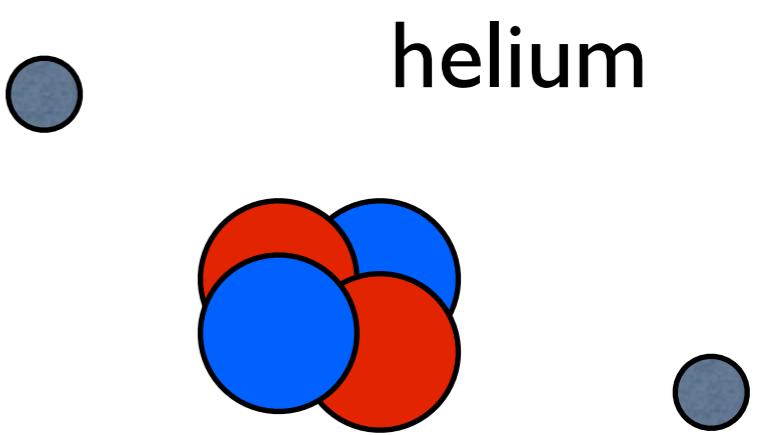
- kinetic energy of electrons
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this problem is way too complicated to solve exactly,
so we must make some approximations

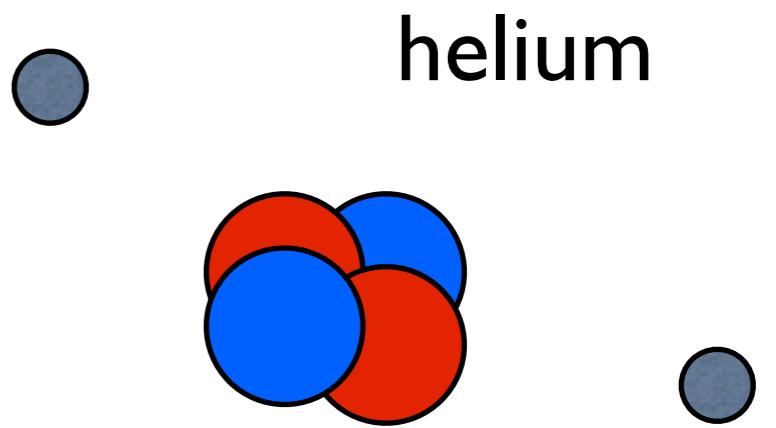
the orbital approximation

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1}$$
$$-\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$



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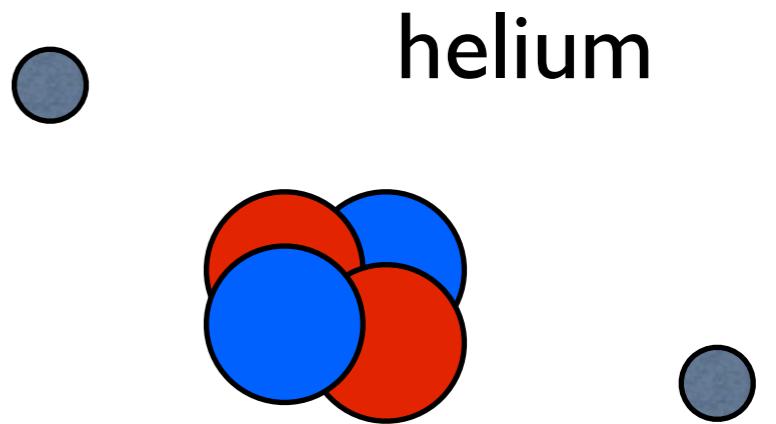


If there was no electron-electron repulsion, then the Hamiltonian would be separable, and we could write the wave function as a product of wave functions for electrons one and two.

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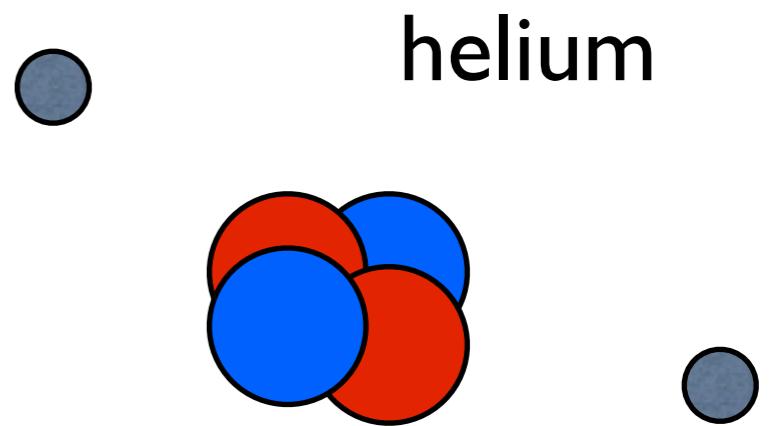


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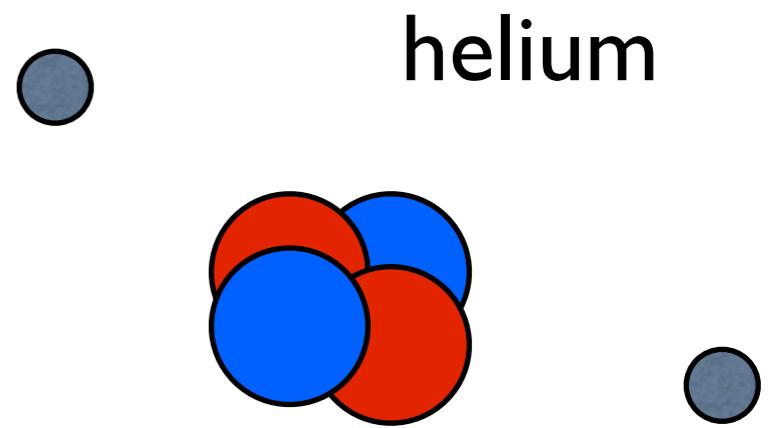
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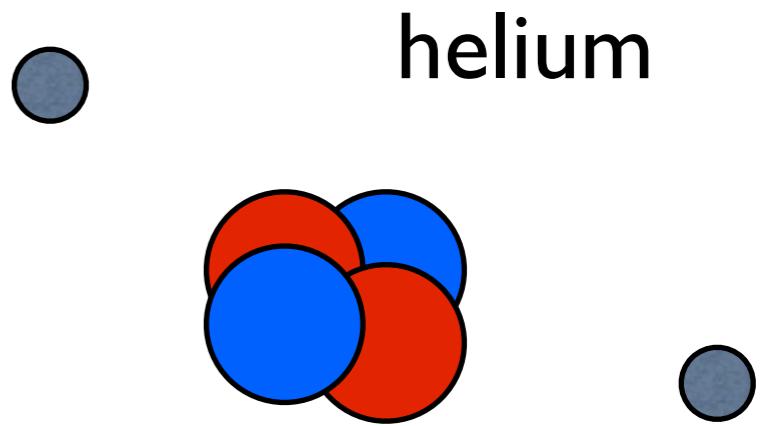
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$$\psi(1, 2) = \psi_1(1)\psi_2(2)$$



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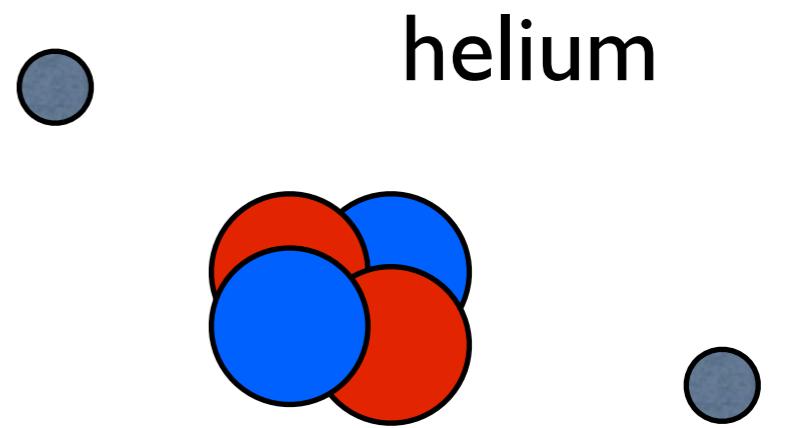


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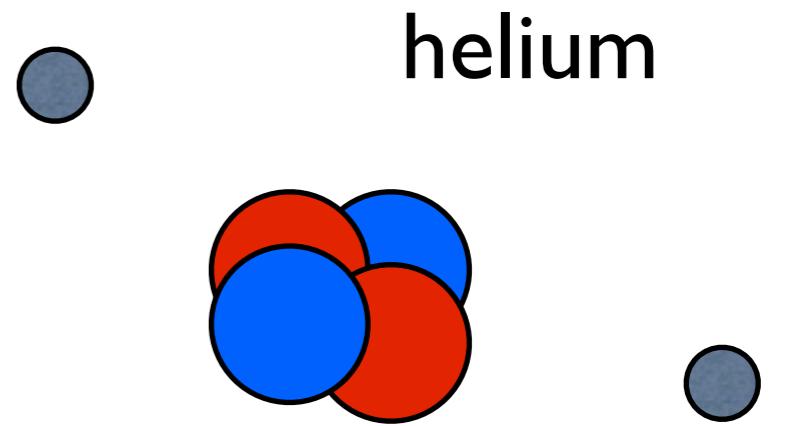
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however, this wave function (a “Hartree product”) doesn’t satisfy the antisymmetry principle

Antisymmetry principle

the wave function for a system of identical fermions is antisymmetric with respect to the exchange of the coordinates of two particles

$$\psi(1, 2) = -\psi(2, 1)$$

electrons are fermions, so an electronic wave function must be antisymmetric with respect to the exchange of the indices of any two electrons.

Pauli exclusion principle

the Pauli exclusion principle is a consequence of the antisymmetry principle. It states that two fermions cannot occupy the same spin orbital.

Slater determinants

Constructing a proper fermionic wave function can be tedious. Thankfully, John Slater* noted that a determinant has all of the antisymmetry properties we seek in a fermionic wave function. For a two-electron system:

$$\Psi(1, 2) = \frac{1}{2^{1/2}} \begin{vmatrix} \psi_{1s}(1)\alpha(1) & \psi_{1s}(2)\alpha(2) \\ \psi_{1s}(1)\beta(1) & \psi_{1s}(2)\beta(2) \end{vmatrix}.$$

It is a bit easier to discuss the properties of Slater determinants if we use spin orbitals

$$\Psi(1, 2) = \frac{1}{2^{1/2}} \begin{vmatrix} \chi_1(1) & \chi_1(2) \\ \chi_2(1) & \chi_2(2) \end{vmatrix} = \frac{1}{2^{1/2}} [\chi_1(1)\chi_2(2) - \chi_2(1)\chi_1(2)].$$

if we exchange the indices of particles one and two

$$\Psi(2, 1) = \frac{1}{2^{1/2}} \begin{vmatrix} \chi_1(2) & \chi_1(1) \\ \chi_2(2) & \chi_2(1) \end{vmatrix} = \frac{1}{2^{1/2}} [\chi_1(2)\chi_2(1) - \chi_2(2)\chi_1(1)] = -\Psi(1, 2)$$

in terms of the determinant, swapping the coordinates of electrons 1 and 2 amounts to swapping two columns of the determinant. For any determinants, swapping any two columns changes the sign of the determinant. In this way, Slater determinants enforce the antisymmetry principle.

*Heisenberg, Dirac separately used determinants to represent many-electron wave functions

Slater determinants

Slater determinants also enforce the Pauli exclusion principle. If two electrons occupy the same spin orbital, then two rows of the Slater determinant will be identical

$$\Psi(1, 2) = \frac{1}{2^{1/2}} \begin{vmatrix} \chi_1(1) & \chi_1(2) \\ \chi_1(1) & \chi_1(2) \end{vmatrix} = \frac{1}{2^{1/2}} [\chi_1(1)\chi_1(2) - \chi_1(1)\chi_1(2)] = 0$$

It is a general property of determinants that, if any two rows of the determinant are identical, then the determinant vanishes.

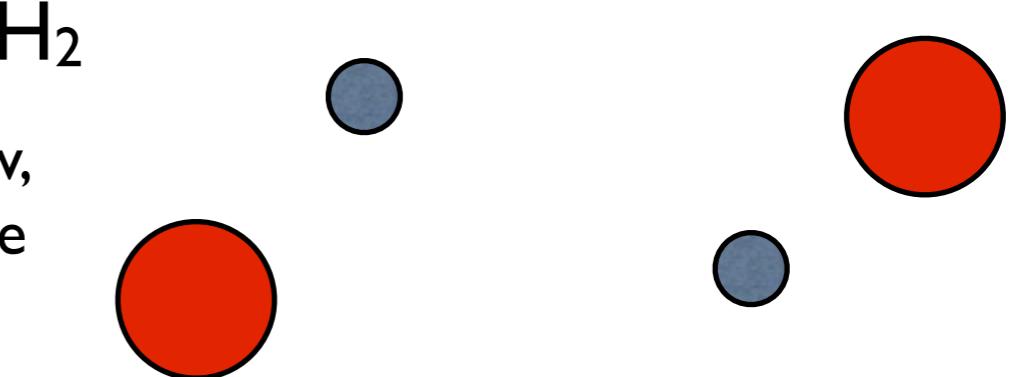
General notation:

$$\Psi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} |\phi_1(1)\phi_2(2)\dots\phi_N(N)|$$

molecules

again, we invoke the Born-Oppenheimer approximation. Nuclei are heavier than electrons, so their motion is much slower and can be neglected. We solve the electronic Schrodinger equation where the electrons experience the potential due to the fixed nuclei

we can also invoke the orbital approximation, but now, electrons occupy molecular orbitals, which are delocalized over the entire molecule.

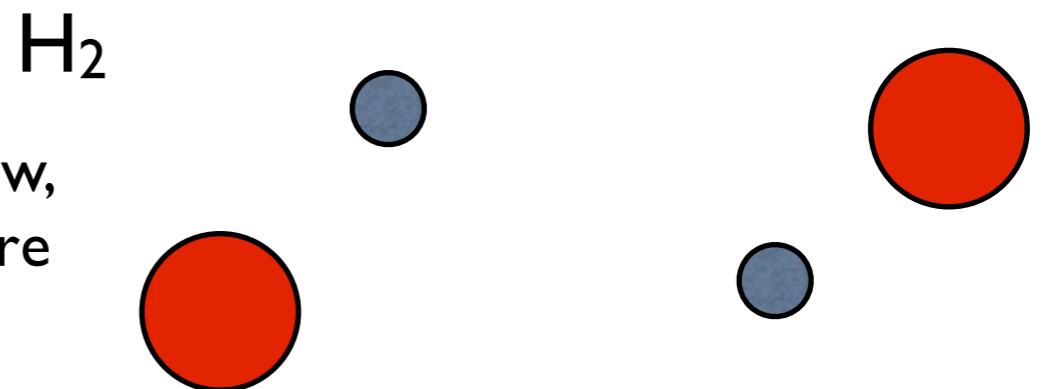


we can form molecular orbitals from a linear combination of atomic orbitals (LCAO-MO)

$$\phi = c_1 \chi_1 + c_2 \chi_2$$

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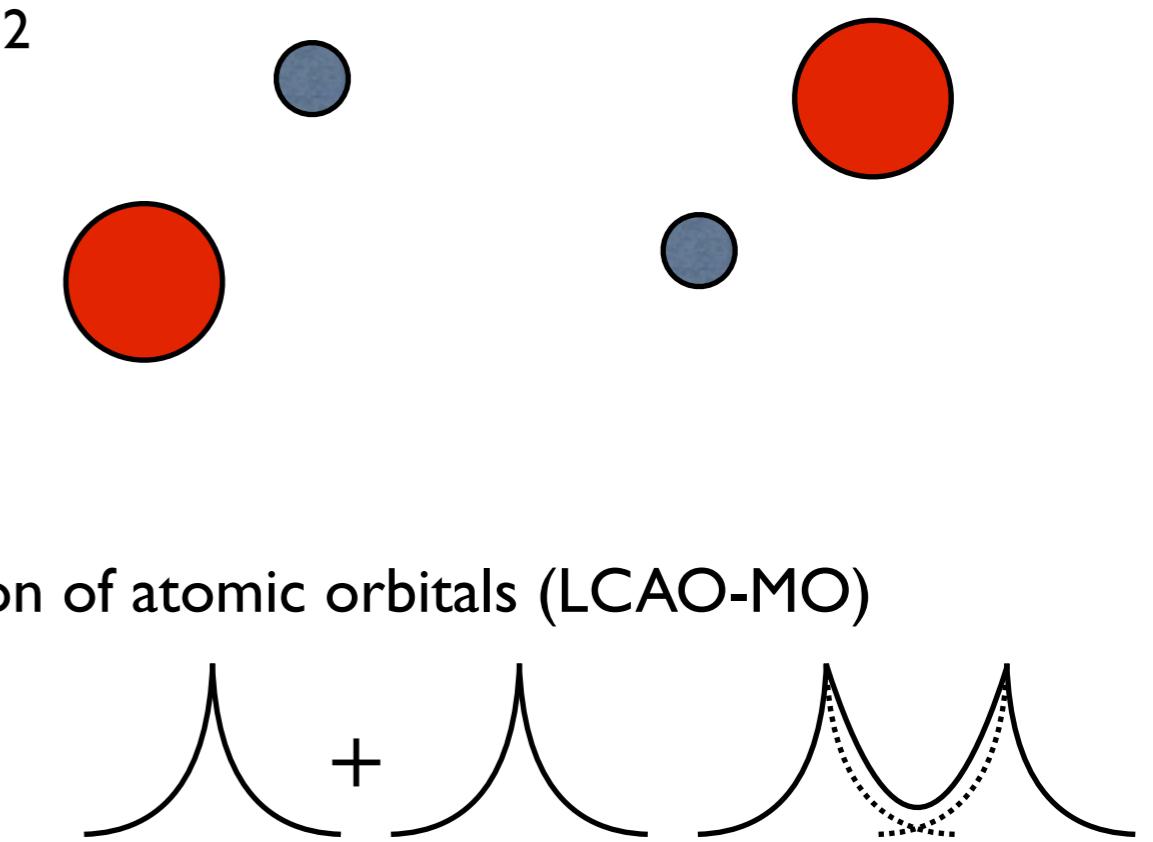
$$\phi_{\sigma_g} = \frac{1}{\sqrt{2}}(\chi_{1s,A} + \chi_{1s,B}) \text{ bonding}$$

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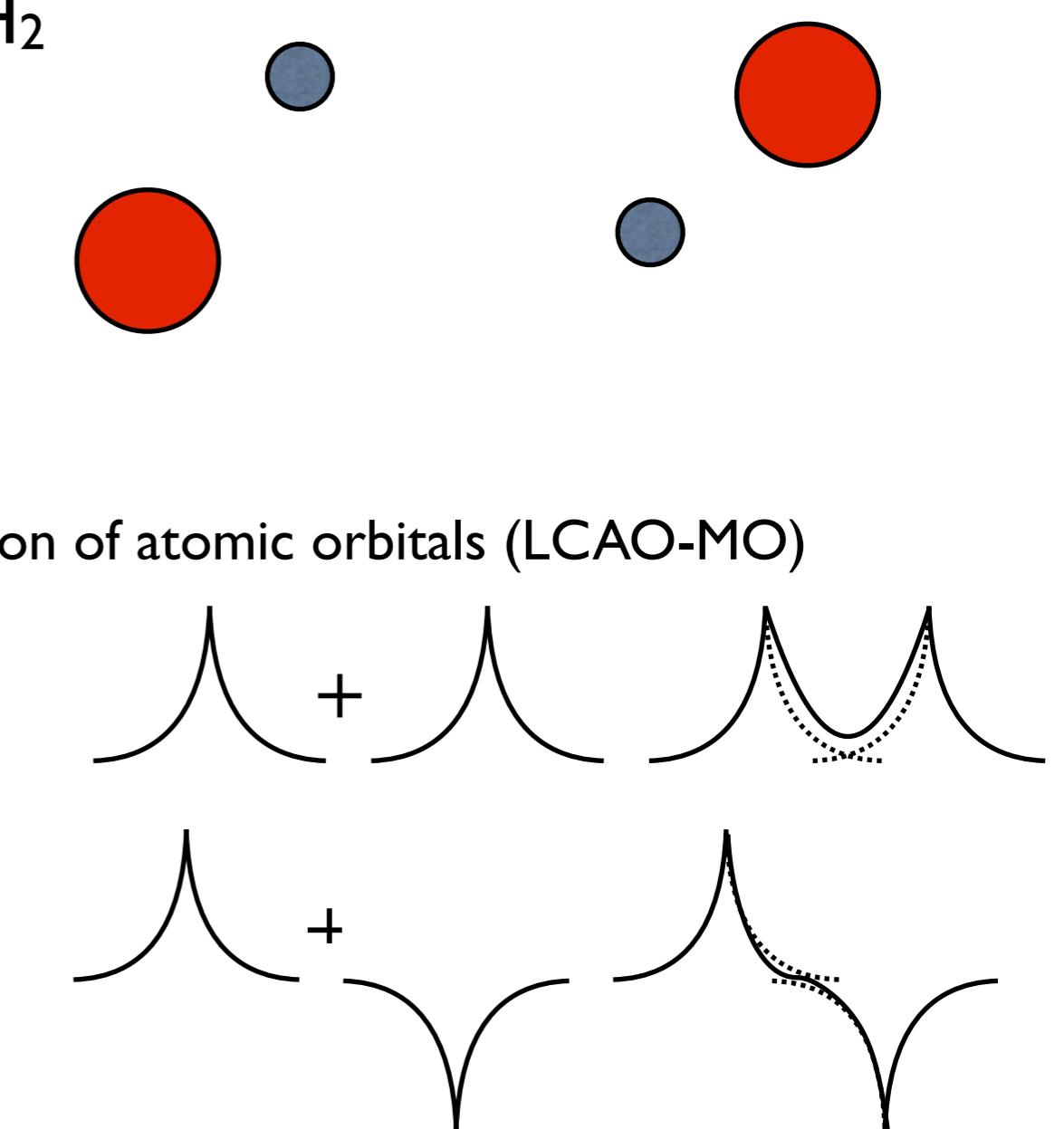
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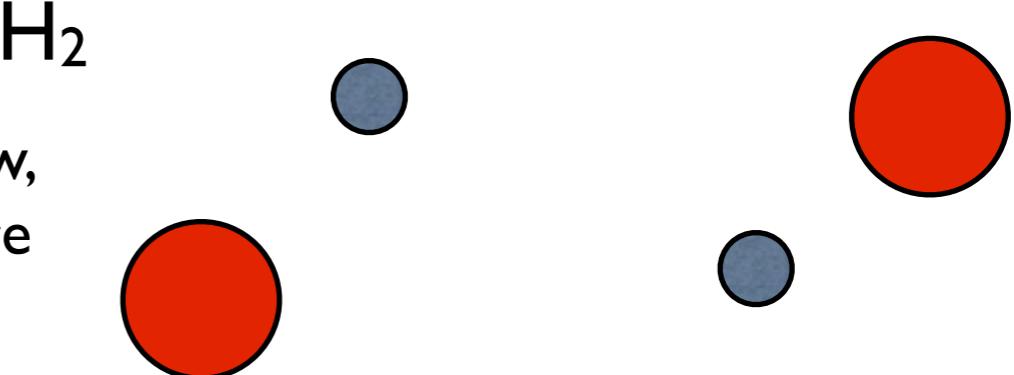
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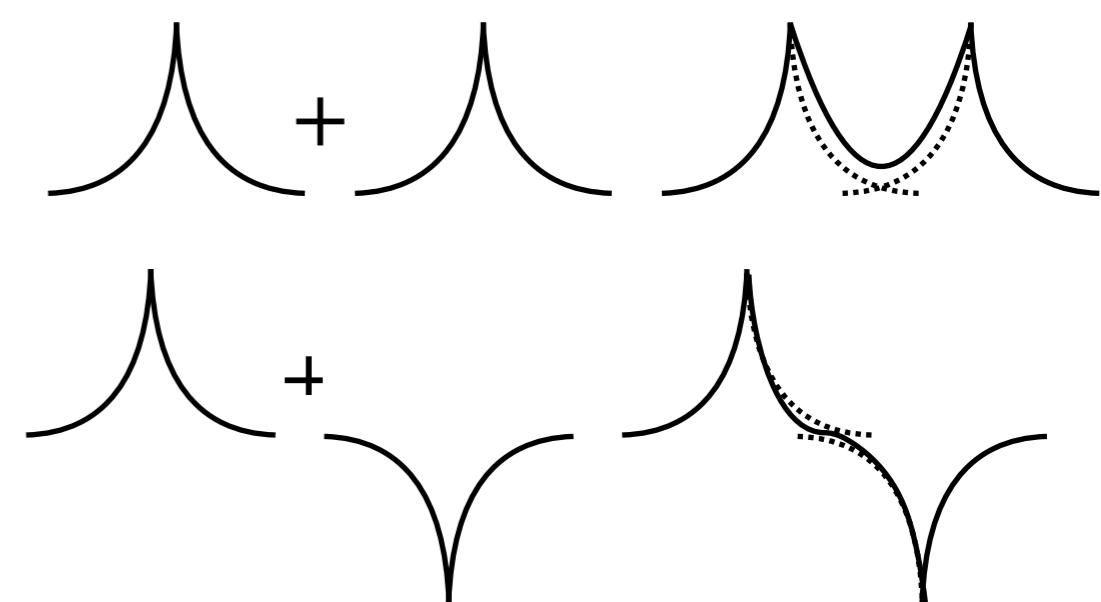


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where do these coefficients actually come from?



the variational principle

the energy of an approximate wave function is always an upper bound to the true energy

$$\hat{H}\Psi = E\Psi$$

$$E = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} \geq E_{\text{true}}$$

why is this important?

the variational principle

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why is this important? well, think about the orbital approximation:

$$\Psi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} |\phi_1(1)\phi_2(2)\dots\phi_N(N)|$$

and LCAO molecular orbitals

$$\phi_i = \sum_{i\mu} c_{i\mu} \chi_\mu$$

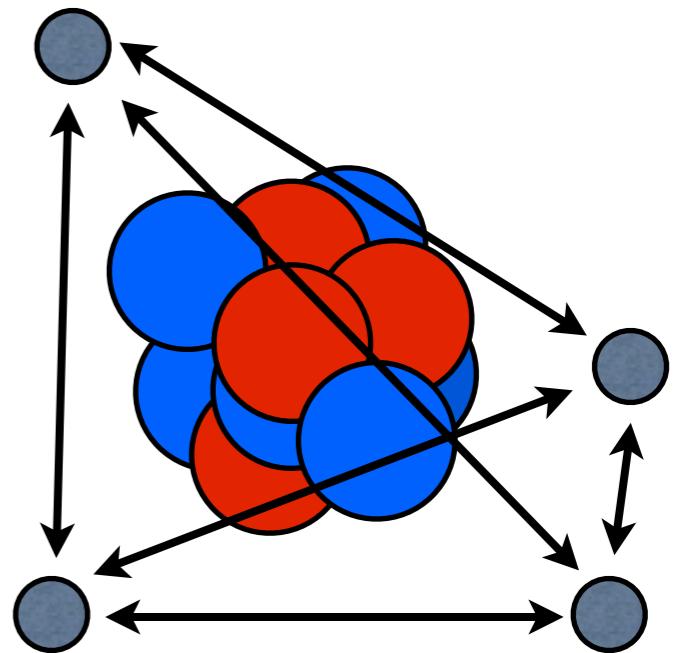
what are the coefficients? the variational theorem tells us that we can vary them to minimize the total energy, and the lower the energy, the closer we are to the true result!

The variational theorem is one of the most important concepts in quantum chemistry.
It gives us a way to numerically determine wave functions!

the Hartree-Fock method

the energy of an approximate wave function is always an upper bound to the true energy

$$\hat{H}\Psi = E\Psi \quad \text{take wave function to be Slater determinant of LCAO-MOs}$$

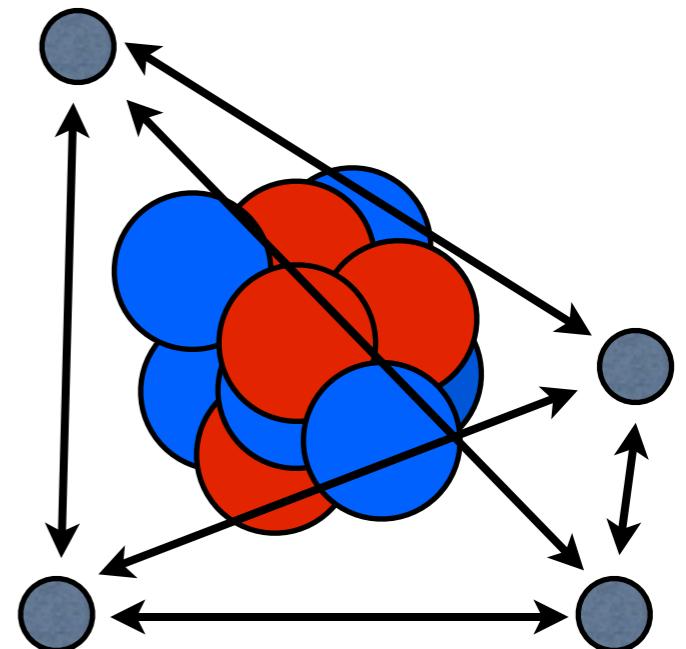


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minimize energy with respect to expansion coefficients ($c_{i\mu}$)
subject to constraint that the MOs form an orthonormal set



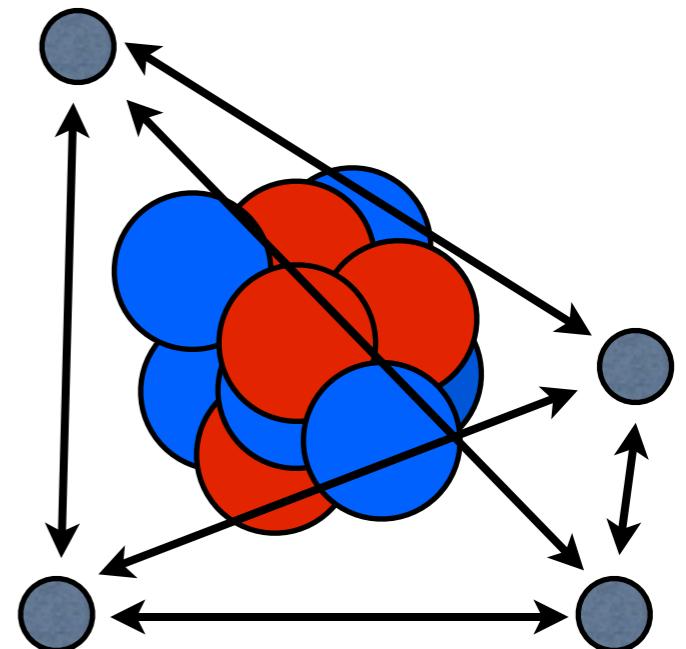
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$$\hat{F}\phi_i = \epsilon_i\phi_i \quad \text{new eigenvalue problem!}$$



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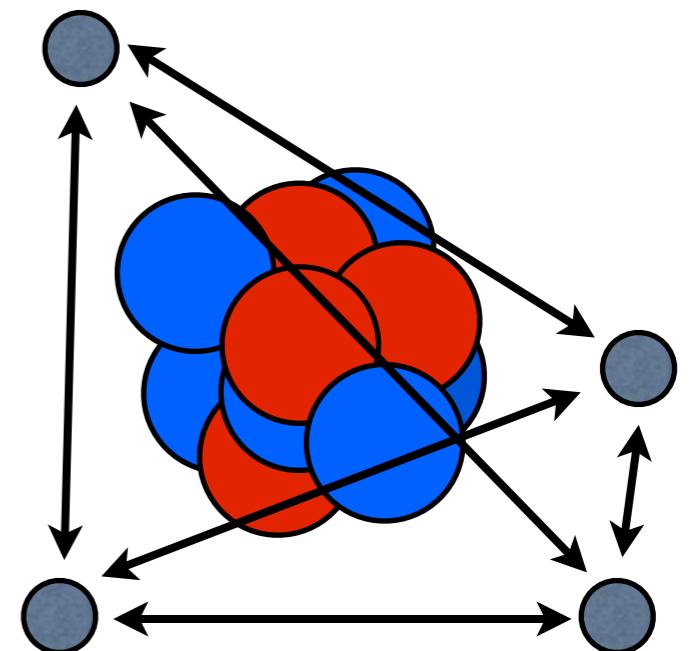
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new eigenvalue problem!
eigenfunctions are *molecular orbitals*
eigenvalues are molecular orbital energies

the Fock operator describes the
interaction of an electron with the
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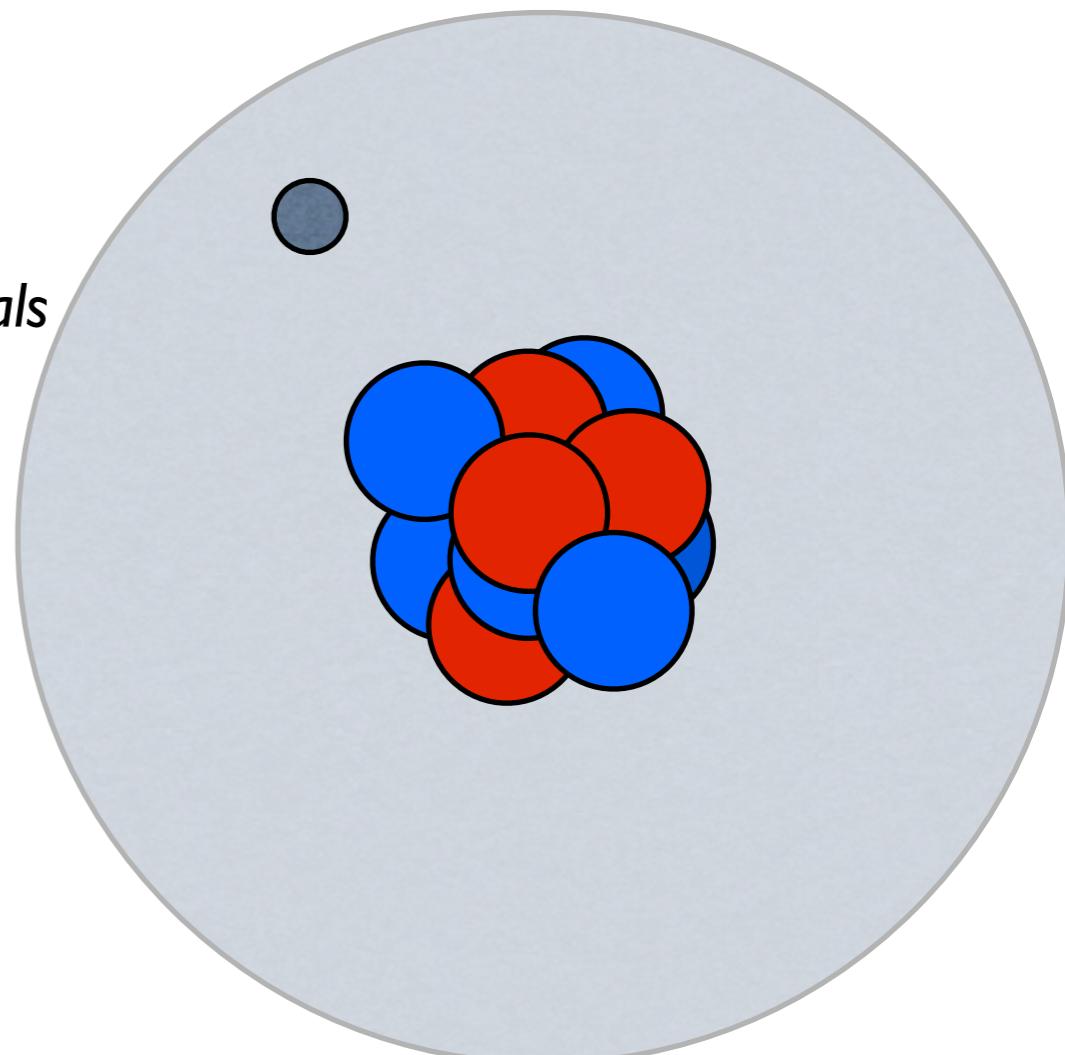
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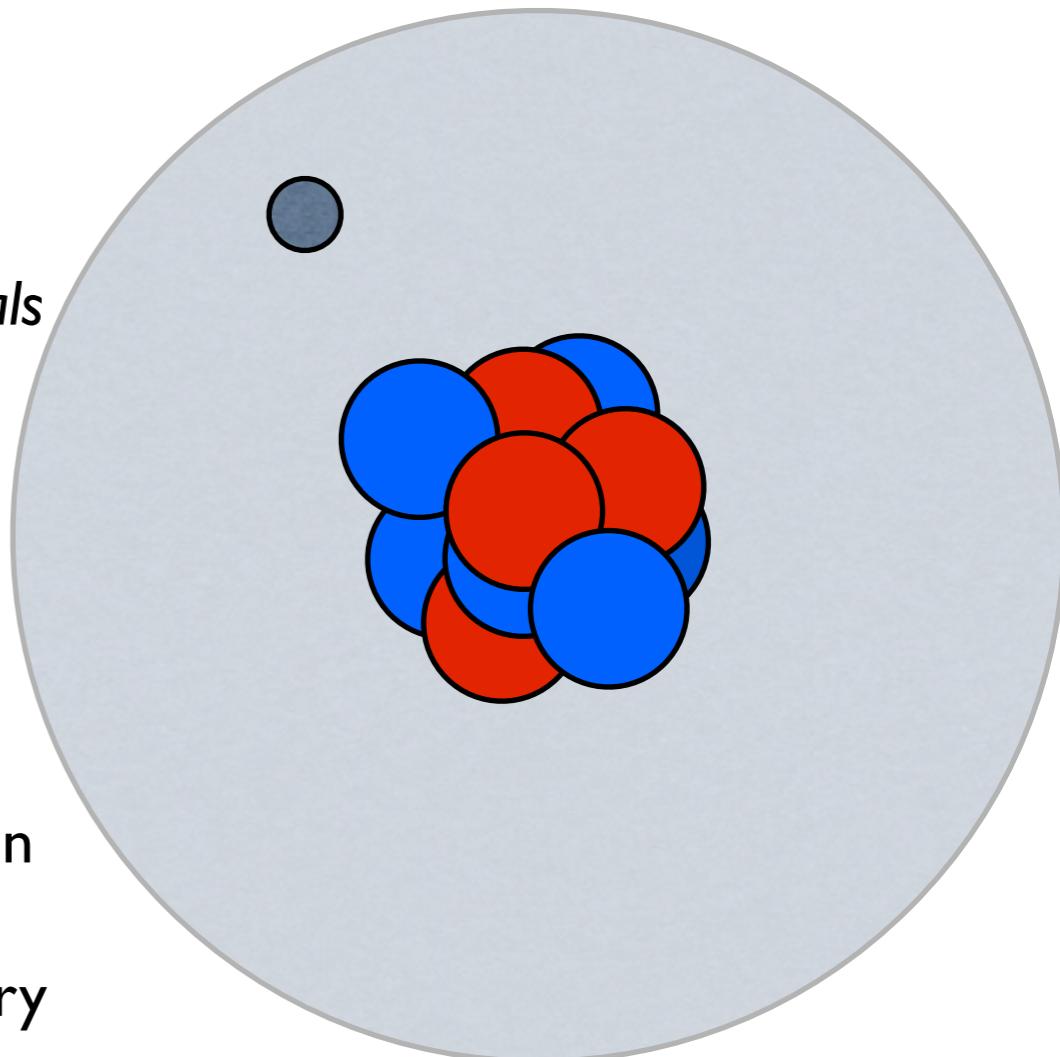
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the Fock operator depends on the orbitals, so this equation
must be solved self consistently. We call this approach
Hartree-Fock theory, or self-consistent field (SCF) theory



Beyond the energy: what can Hartree-Fock tell us?

Once we have obtained the wave function, we can compute a variety of molecular properties:

- molecular orbitals (obtained as part of solving the Hartree-Fock equations)

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Once we have obtained the wave function, we can compute a variety of molecular properties:

- molecular orbitals (obtained as part of solving the Hartree-Fock equations)
- ionization potentials / electron affinities (Koopmans' theorem)
- dipole / quadrupole / octupole / etc.
- Mulliken / Lowdin population analysis (partial charges)
- electrostatic potentials

Koopmans' theorem

The physical interpretation of the occupied orbital energies is that they correspond to the (negative of the) energy required to remove an electron from that orbital (ionization potential) considerations:

- (i) correlation effects
- (ii) orbital relaxation effects

These effects tend to cancel, although it is not always easy to rationalize why.

Note: people tend to use the same ideas in density functional theory (DFT) ... that is, IP/EA are associated with the energies of the Kohn-Sham orbitals

Failures of Hartree-Fock theory

Classic example: the dipole moment in CO

Which way should the dipole point?



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Lone pair puts small negative charge on carbon

Failures of Hartree-Fock theory

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Hartree-Fock dipole moment is backward!
(negative charge on oxygen)

(side note: Mulliken charges do show
negative charge on carbon in large basis)

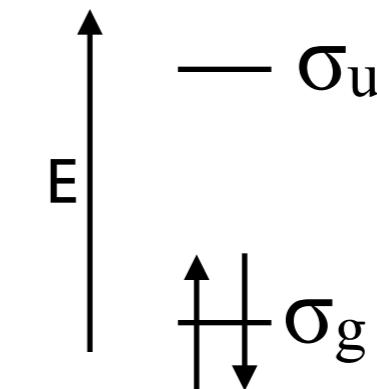
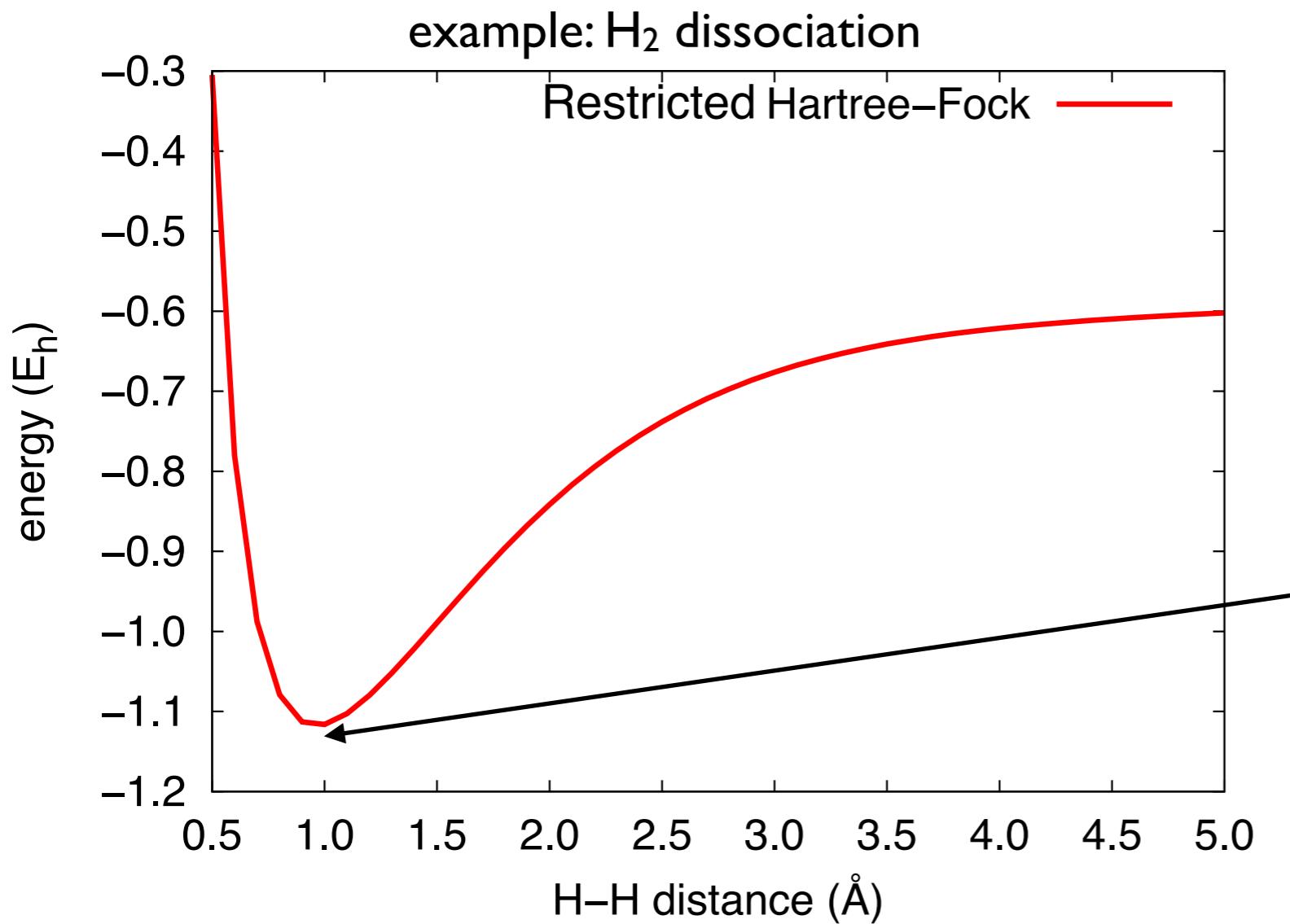
Table 3.24 SCF dipole moment (a.u.) of CO for the standard basis sets. A positive dipole moment corresponds to C⁻O⁺

Basis set	Dipole moment
STO-3G	0.066
4-31G	-0.237
6-31G*	-0.131
Near-HF-limit ^a	-0.110
Experiment	0.044

^a A. D. McLean and M. Yoshimine, *Intern. J. Quantum Chem.* 15: 313 (1967).

Failures of Hartree-Fock: bond breaking

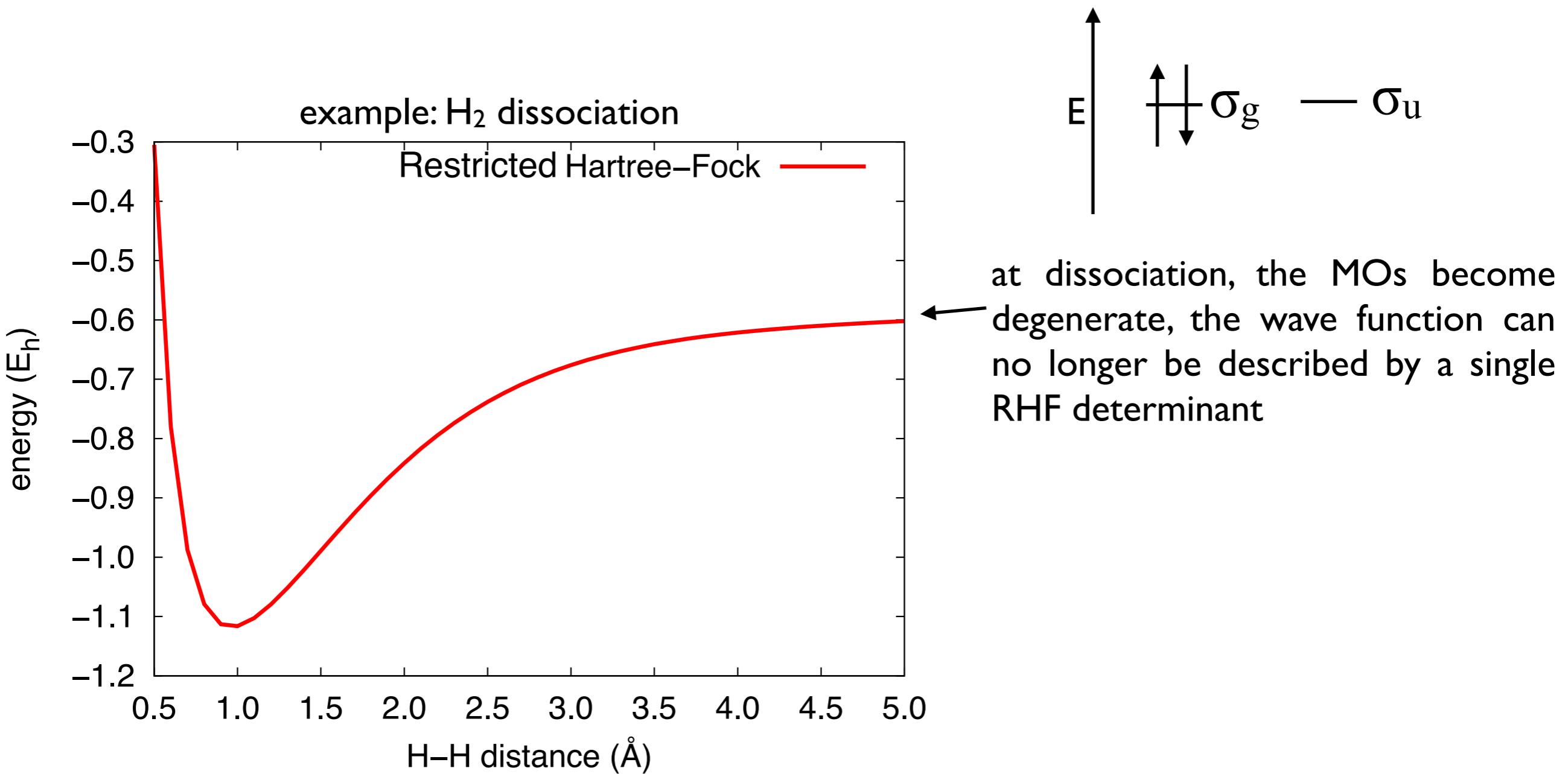
static / strong / non-dynamical / multireference electron correlation



in bonding region, wave function is well-described by a single electronic configuration

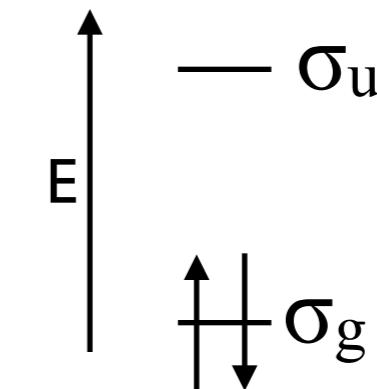
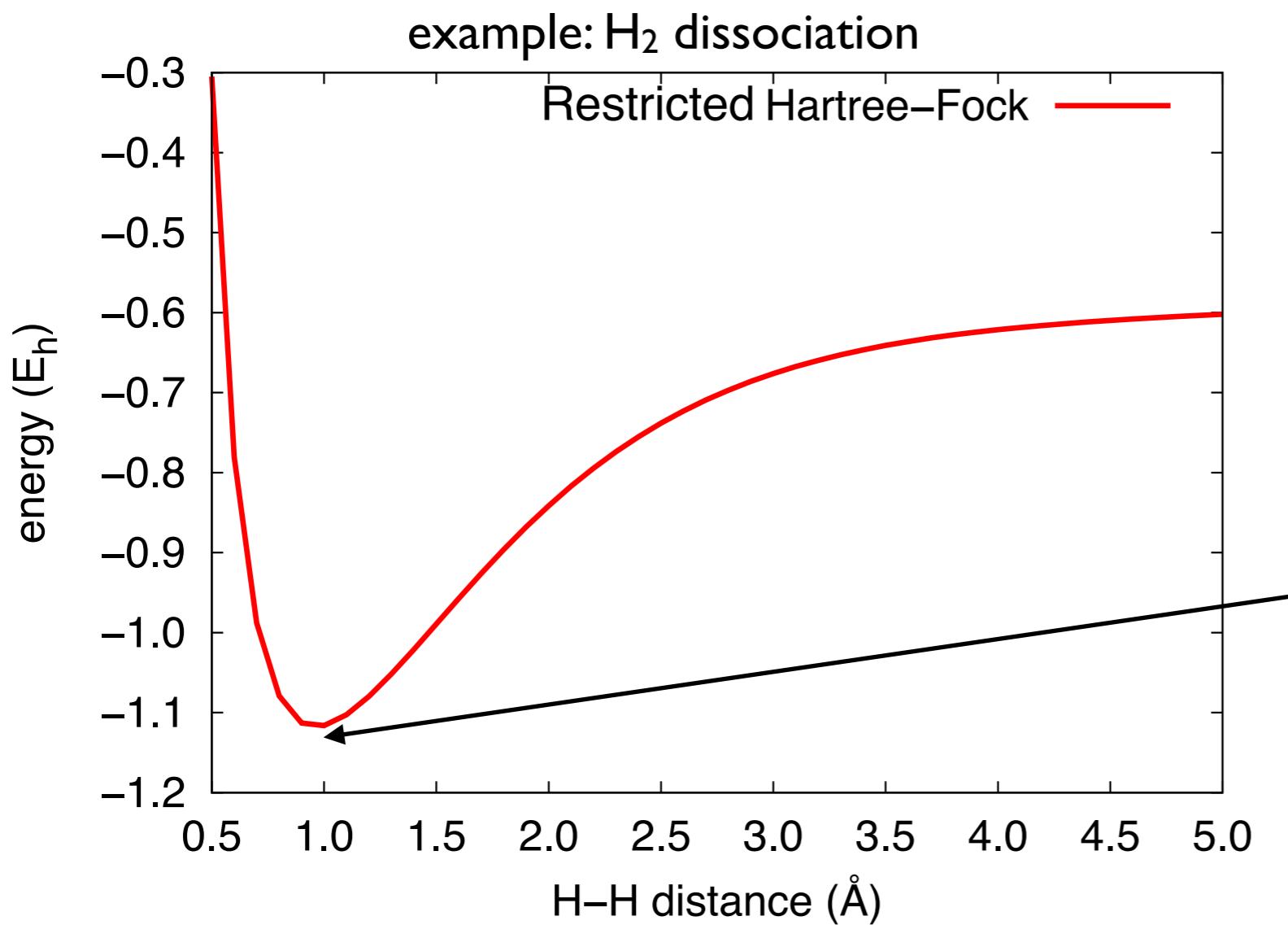
Failures of Hartree-Fock: bond breaking

static / strong / non-dynamical / multireference electron correlation



Failures of Hartree-Fock: bond breaking

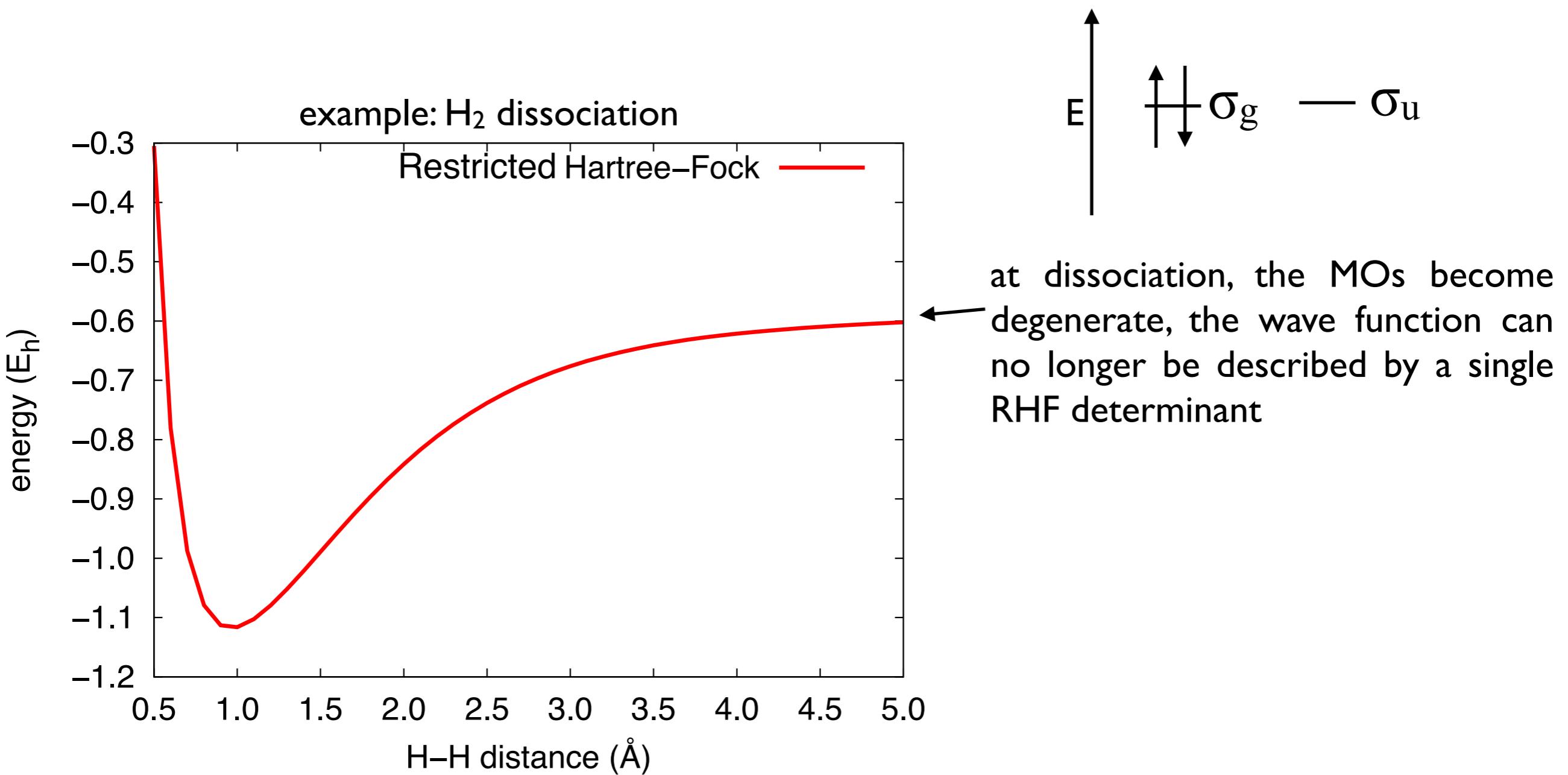
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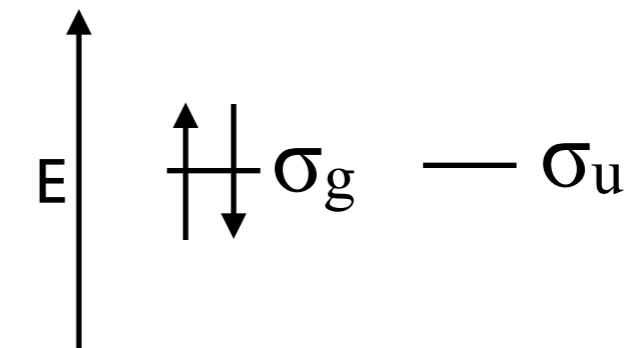
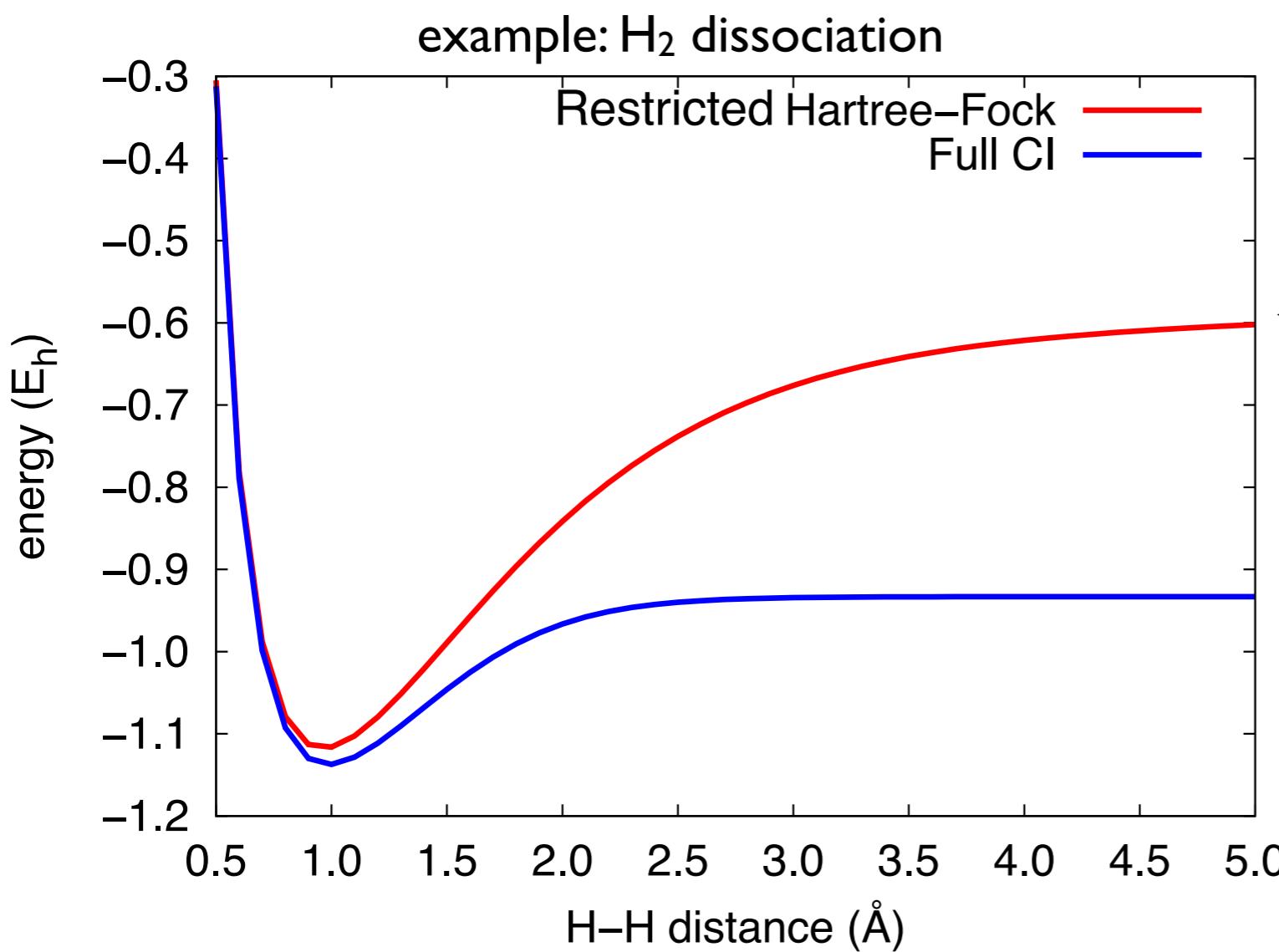
Failures of Hartree-Fock: bond breaking

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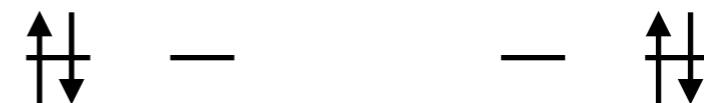


Failures of Hartree-Fock: bond breaking

static / strong / non-dynamical / multireference electron correlation



at dissociation, the MOs become degenerate, the wave function can no longer be described by a single RHF determinant



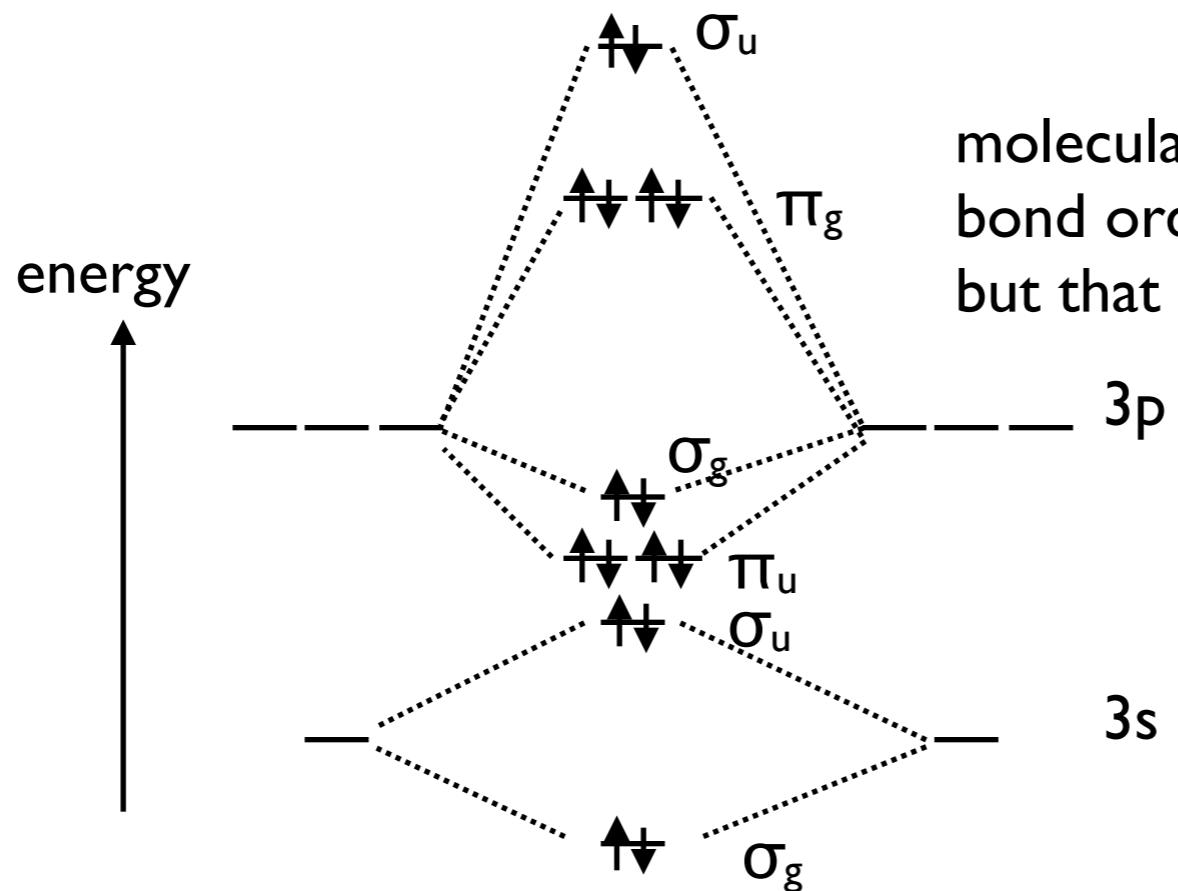
qualitatively correct wave function includes equal contributions from two electronic configurations

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} (\sigma_g^2 - \sigma_u^2)$$

Failures of Hartree-Fock: dispersion

Hartree-Fock theory cannot capture dispersion interactions

example: Argon dimer

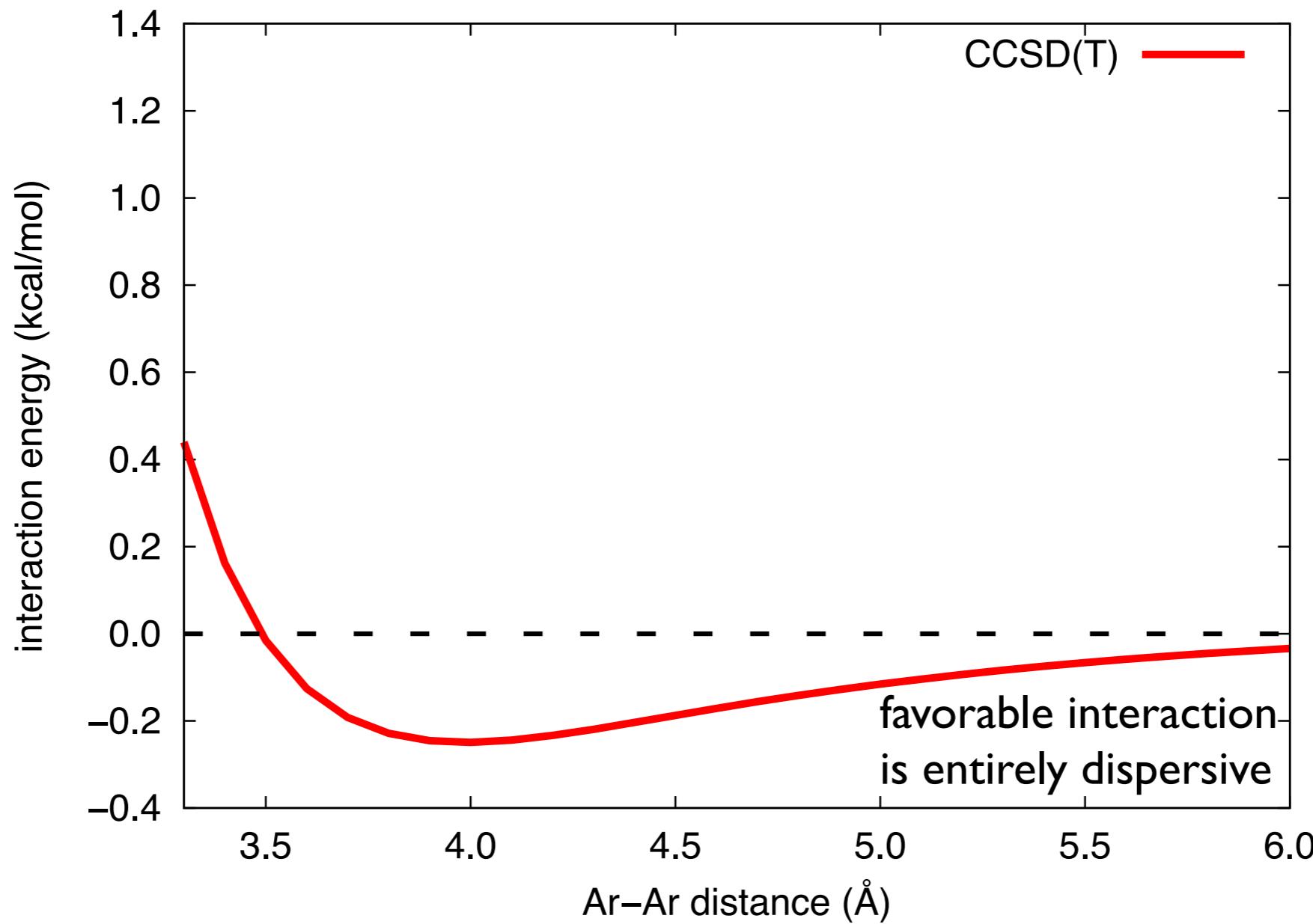


molecular orbital diagram suggests a bond order of 0, so no covalent bond, but that doesn't tell the whole story

Failures of Hartree-Fock: dispersion

Hartree-Fock theory cannot capture dispersion interactions

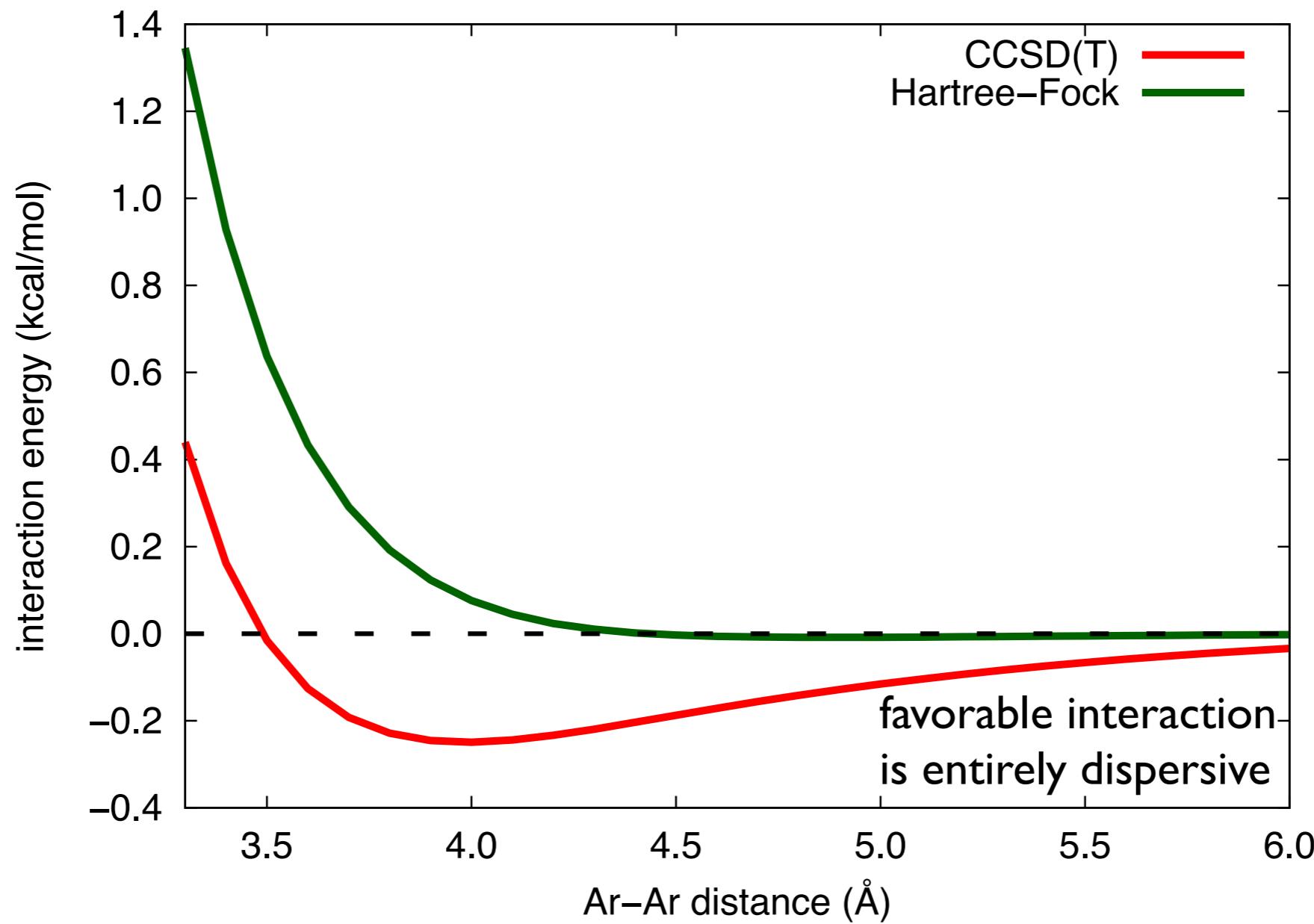
example: Argon dimer



Failures of Hartree-Fock: dispersion

Hartree-Fock theory cannot capture dispersion interactions

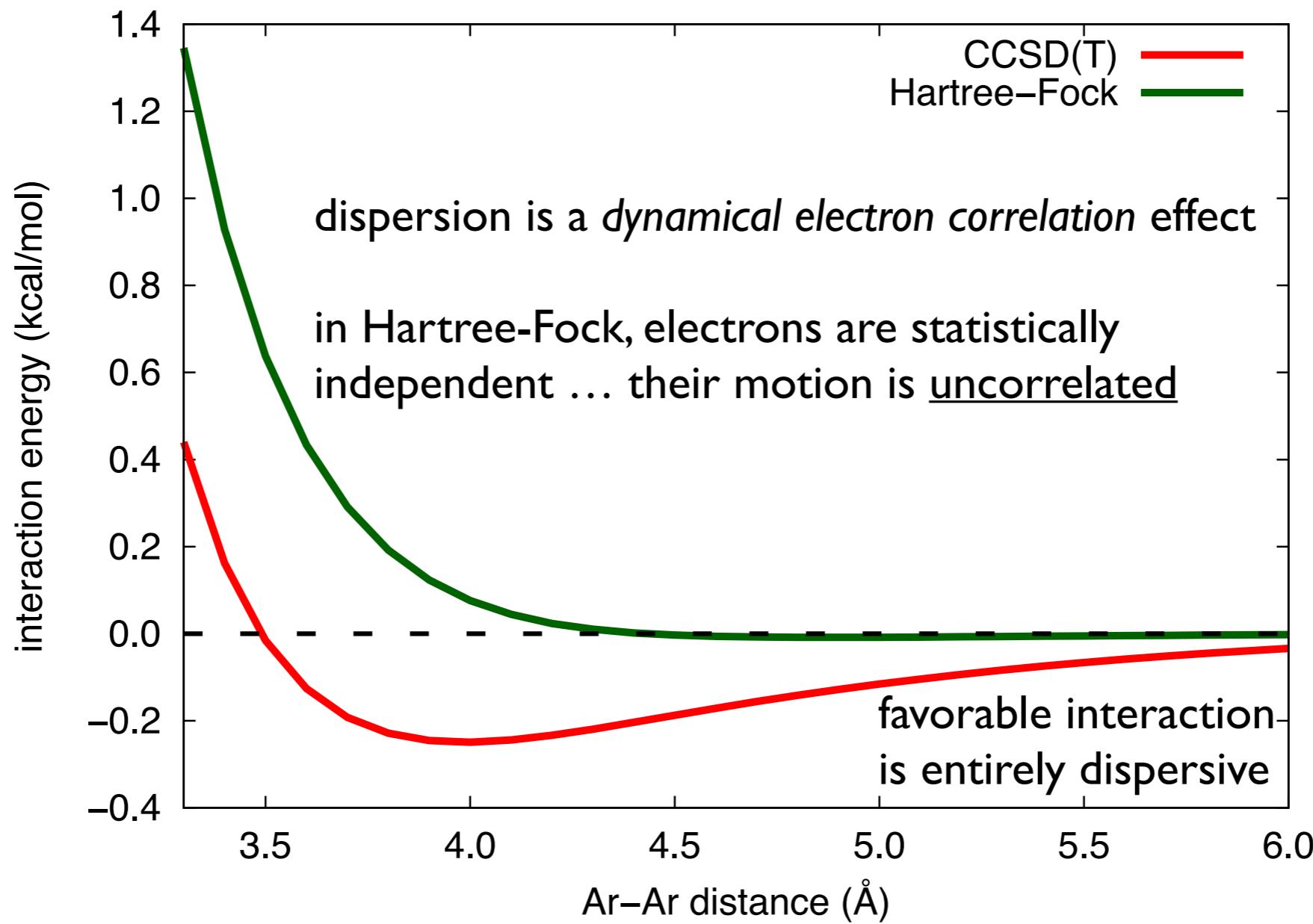
example: Argon dimer



Failures of Hartree-Fock: dispersion

Hartree-Fock theory cannot capture dispersion interactions

example: Argon dimer



Shortcomings of Hartree-Fock theory

Classic example: the dipole moment in CO is backward!

No dispersion: no bound Argon dimer (or methane dimer, or He dimer, ...)

Bond breaking: H₂ doesn't dissociate correctly

IP in N₂ ... incorrect ordering of states (σ/π orbitals ordered incorrectly)

Predicted bond lengths are almost always too short.

How can we clean up Hartree-Fock?

electron correlation

At the Hartree-Fock level, electrons are confined to occupy the lowest-energy orbitals with no consideration for their instantaneous repulsion

In a real molecule, the motion of electrons is *correlated*. We usually refer to two classes of correlation:

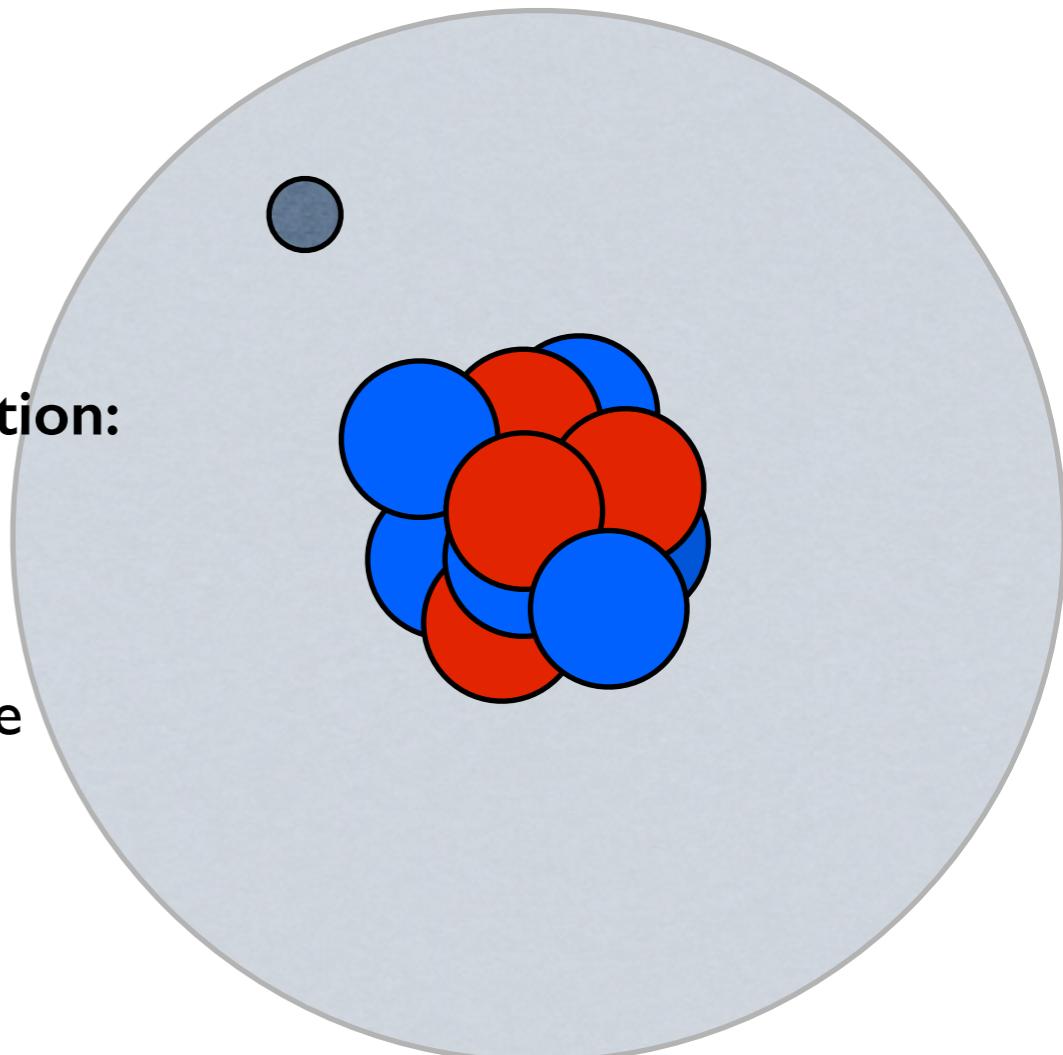
dynamical electron correlation:

instantaneous repulsion between electron pairs

static / strong / non dynamical / multireference correlation:

something else entirely...

becomes important when multiple electron configurations (determinants) become degenerate



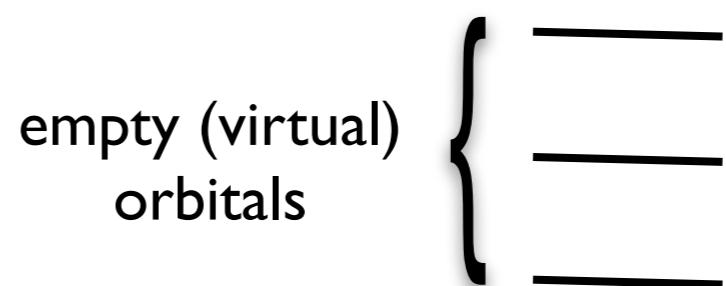
dynamical electron correlation

At the Hartree-Fock level, electrons are confined to occupy the lowest-energy orbitals with no consideration for their instantaneous repulsion

We obtain a better solution if we allow them the flexibility to move (excite) into some of the empty orbitals.

When electrons respond to the instantaneous repulsion of other electrons, we say they are **correlated**. This type of correlated motion is called dynamic electron correlation.

$$|\Psi\rangle =$$



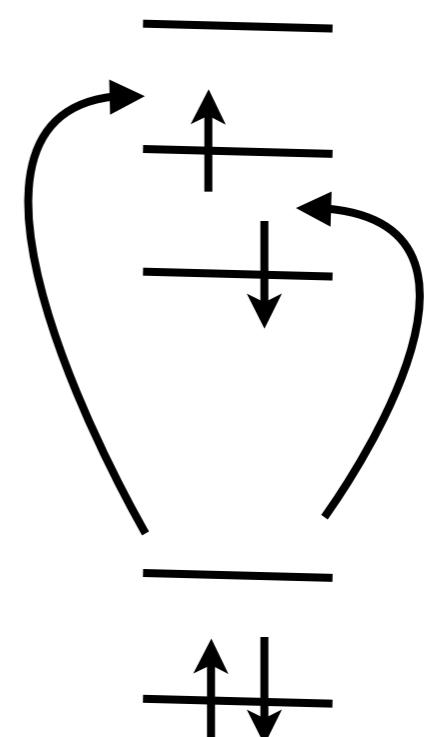
$$|\psi_0\rangle$$

dynamical electron correlation

At the Hartree-Fock level, electrons are confined to occupy the lowest-energy orbitals with no consideration for their instantaneous repulsion

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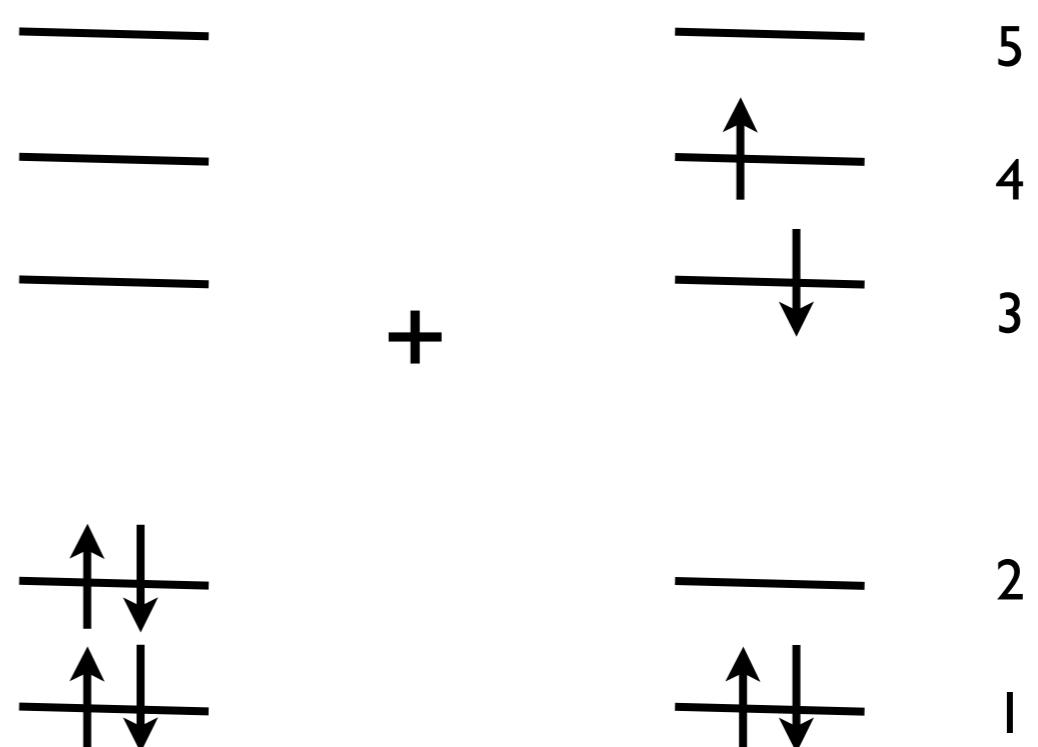
$$|\Psi\rangle = |\psi_0\rangle$$

dynamical electron correlation

At the Hartree-Fock level, electrons are confined to occupy the lowest-energy orbitals with no consideration for their instantaneous repulsion

We obtain a better solution if we allow them the flexibility to move (excite) into some of the empty orbitals.

When electrons respond to the instantaneous repulsion of other electrons, we say they are **correlated**. This type of correlated motion is called dynamic electron correlation.



$$|\Psi\rangle = |\psi_0\rangle + t_{22}^{43}|\psi_{22}^{43}\rangle$$

Now we can solve the SE in the space of this new wave function

What methods should we use and when?

Wave-function-based methods:

Hartree-Fock / self-consistent-field
configuration interaction (full and truncated CI)
perturbation theory (Moller Plesset and symmetry adapted PT)
coupled cluster theory (CCSD, CCSDT, CCSD(T), etc.)

Density-based methods:

Density functional theory (DFT)
- B3LYP, PBE0, B97, M06-2X, and a zillion other acronyms

Dispersion-corrected density functional theory:

- take a popular DFT method and add correction to account for dispersion (“-D”)
- e.g. B97-D

What methods should we use and when?

Wave-function-based methods:

Hartree-Fock / self-consistent-field

- wave function is a single Slater determinant
- very cheap method: $O(N^4)$
- no electron correlation
- no dispersion
- cannot break bonds

When to use it?

- never.
- ... and always. Hartree-Fock is the starting point for many other popular (and useful) electronic structure methods

What methods should we use and when?

Wave-function-based methods:

Configuration interaction

need a slide describing CI

What methods should we use and when?

Wave-function-based methods:

Configuration interaction

- wave function is a linear combination of Slater determinants
- full configuration interaction is extremely expensive: $O(N!)$
- truncated CI is cheaper. CISD: $O(N^6)$
- CI fixes all of the problems that Hartree-Fock has
- full CI gives the exact result for a many-electron system (within a given basis set)

When to use it?

- full CI? almost never (too expensive).
- truncated CI? almost never (truncated CI is not size extensive).

What methods should we use and when?

Wave-function-based methods:

Configuration interaction

- wave function is a linear combination of Slater determinants
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- CI fixes all of the problems that Hartree-Fock has
- full CI gives the exact result for a many-electron system (within a given basis set)

When to use it?

In cases with strong electronic degeneracies (where 2 or more Slater determinants are very important), you can combine SCF and CI methods into:

- multi-configurational self-consistent-field (**MCSCF**)
- complete active space self-consistent-field (**CASSCF**)

to add dynamic correlation on top of MCSCF, could incorporate all S/D out of this multiconfiguration reference: multi-reference cisd (**MR-CISD**)

What methods should we use and when?

Wave-function-based methods:

Perturbation theory

What methods should we use and when?

Wave-function-based methods:

Perturbation theory - partition Hamiltonian into solvable part, H_0 , and a small perturbation, V

- Moller-Plesset (MP): zeroth-order Hamiltonian is the Fock operator $H = F + V$
- MP2 is pretty cheap: $O(N^5)$
- MP3: $O(N^6)$, MP4: $O(N^7)$
- useful in gauging the accuracy of other methods
 - CISD is complete only to 3rd-order, CCSD(T) is complete to 4th-order
- MP PT is size-extensive at all orders but doesn't obey variational principle
- non-iterative

When to use it?

- MP2:**
- cheapest way to incorporate electron correlation
 - suitable for large molecules where you aren't concerned with quantitative accuracy
 - a good implementation could treat 100's of atoms
 - fails for strongly degenerate systems, but you can do similar things to MR-CISD
 - **MR-PT2, CAS-PT2**
 - fails for bond stretches

What methods should we use and when?

Wave-function-based methods:

Perturbation theory - partition Hamiltonian into solvable part, H_0 , and a small perturbation, V

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- non-iterative

When to use it?

MP3: - never use MP3

What methods should we use and when?

Wave-function-based methods:

Perturbation theory - partition Hamiltonian into solvable part, H_0 , and a small perturbation, V

- Moller-Plesset (MP): zeroth-order Hamiltonian is the Fock operator $H = F + V$
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 - CISD is complete only to 3rd-order, CCSD(T) is complete to 4th-order
- MP PT is size-extensive at all orders but doesn't obey variational principle
- non-iterative

When to use it?

MP4: - much more accurate than MP2, but for the cost (N^7), you are probably better off using coupled cluster theory [CCSD(T): $O(N^7)$]

What methods should we use and when?

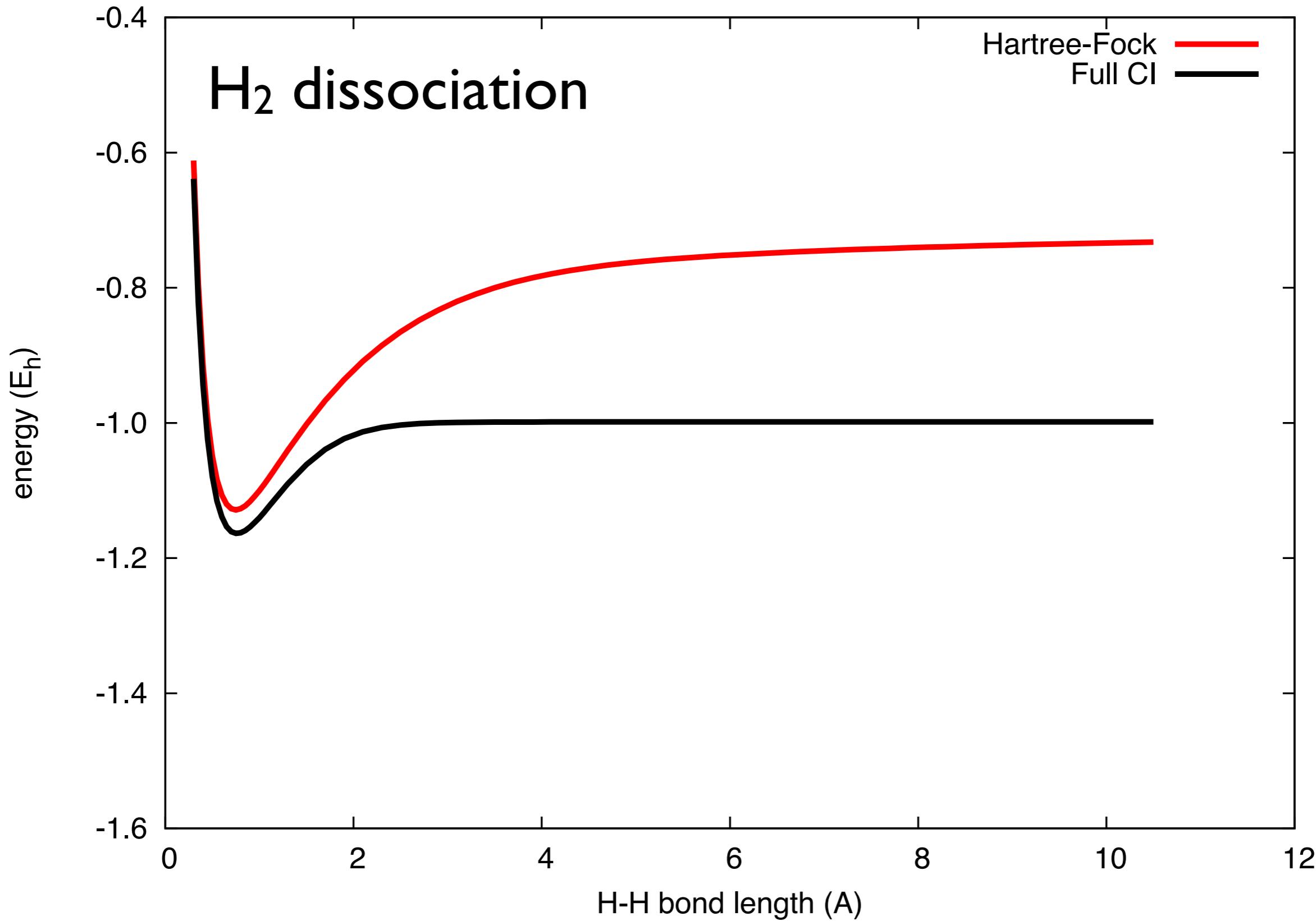
Wave-function-based methods:

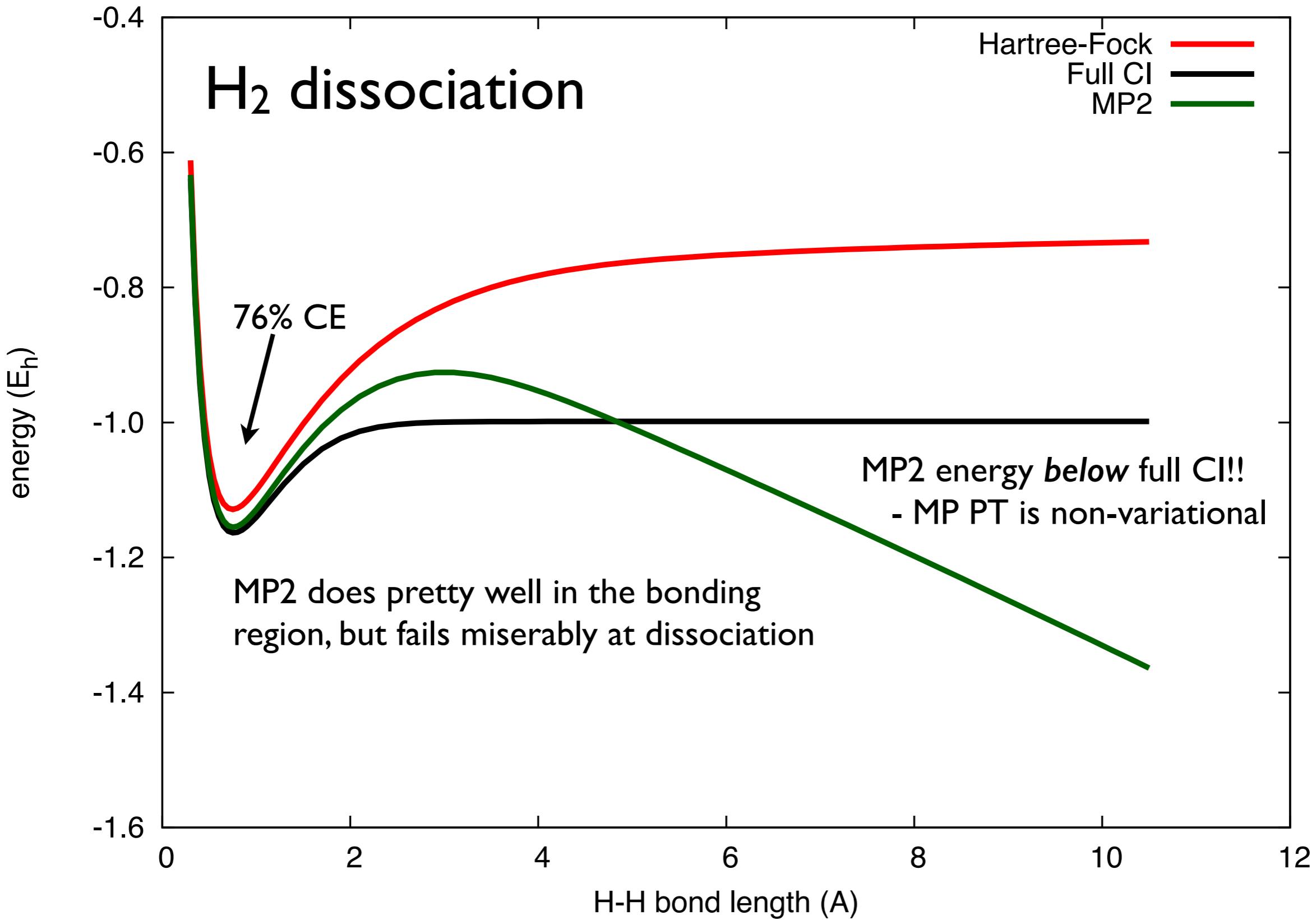
Perturbation theory - partition Hamiltonian into solvable part, H_0 , and a small perturbation, V

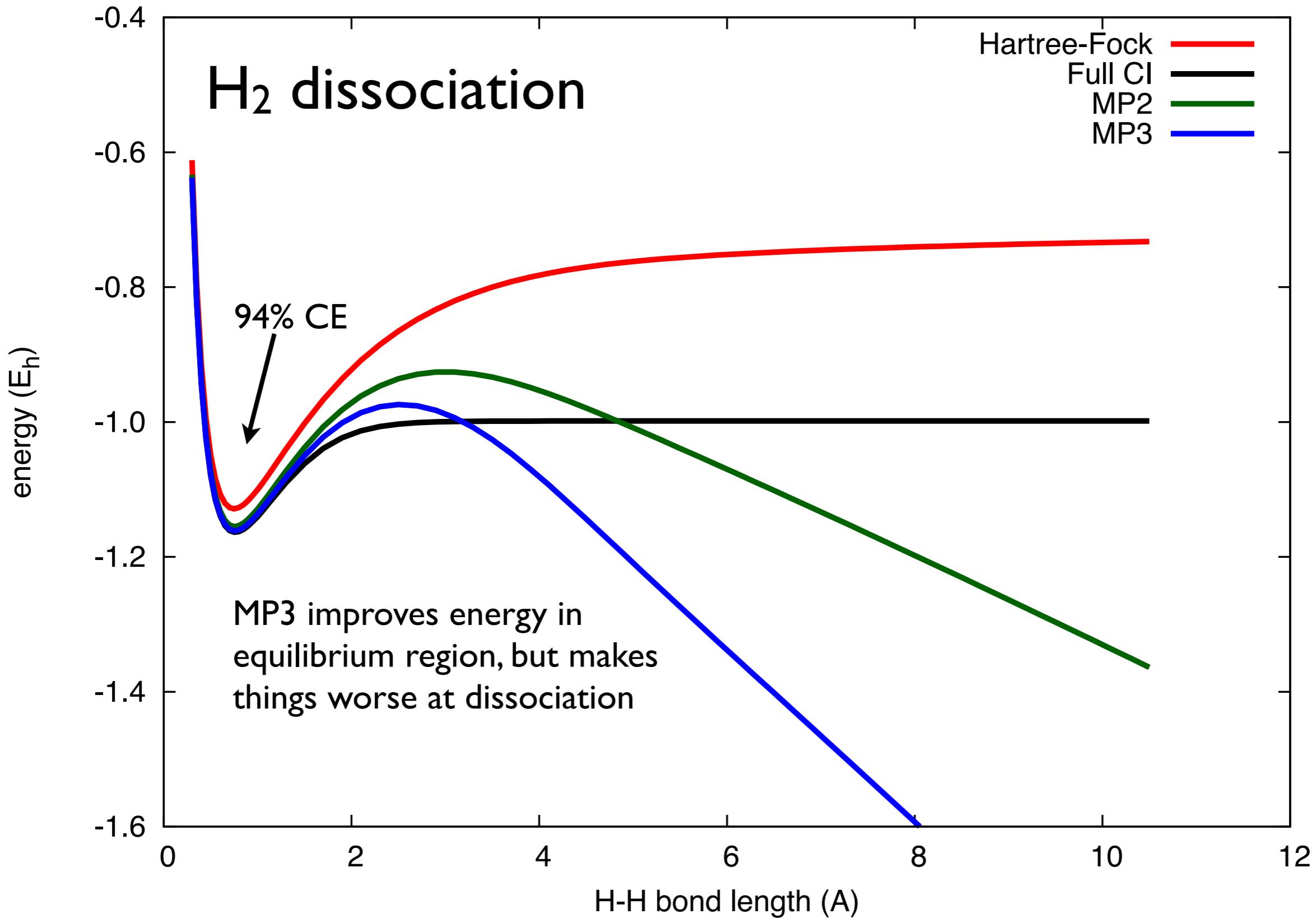
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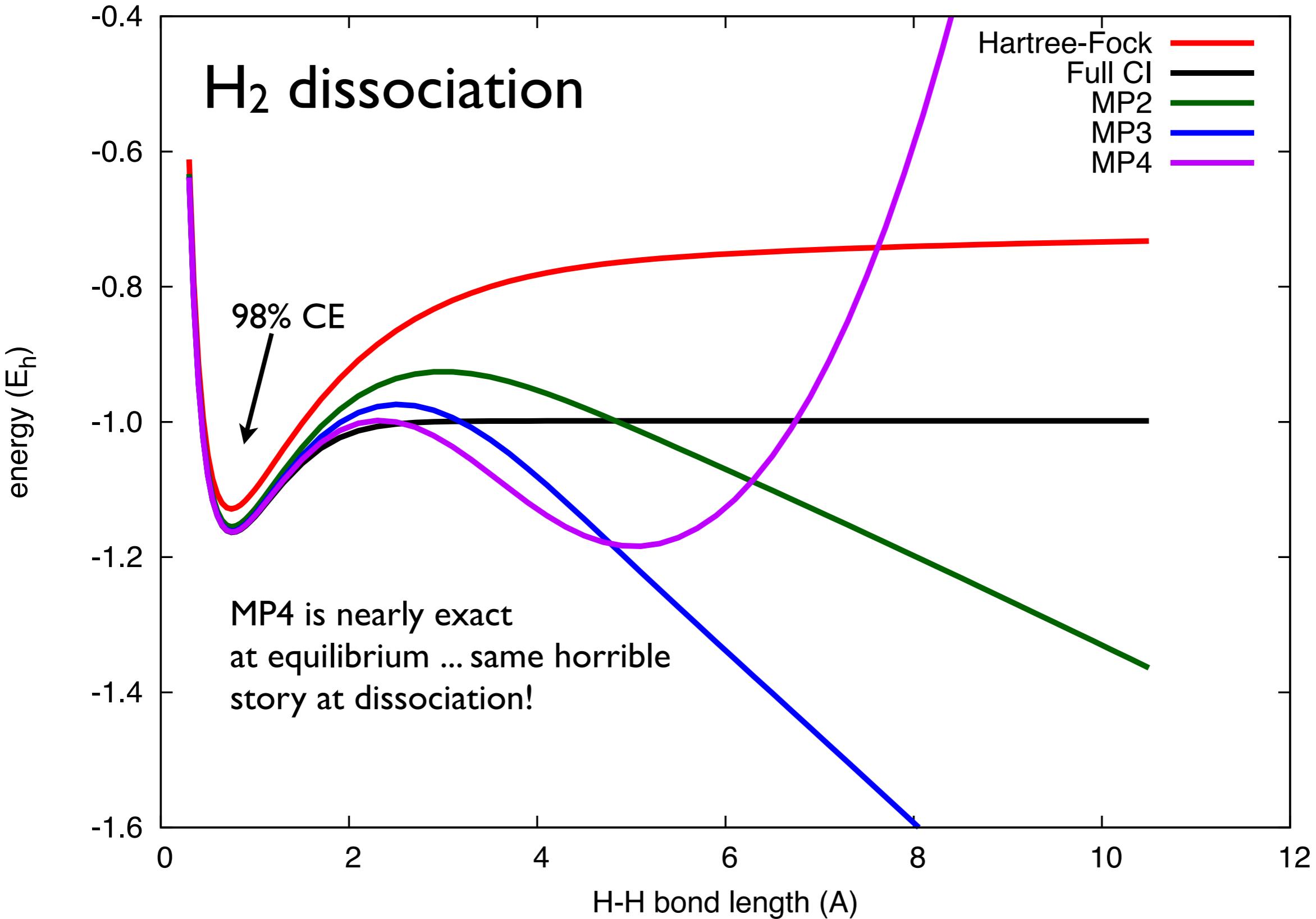
When to use it?

MPn: - there is no guarantee that the PT series will converge to the right answer,
especially far from equilibrium geometries

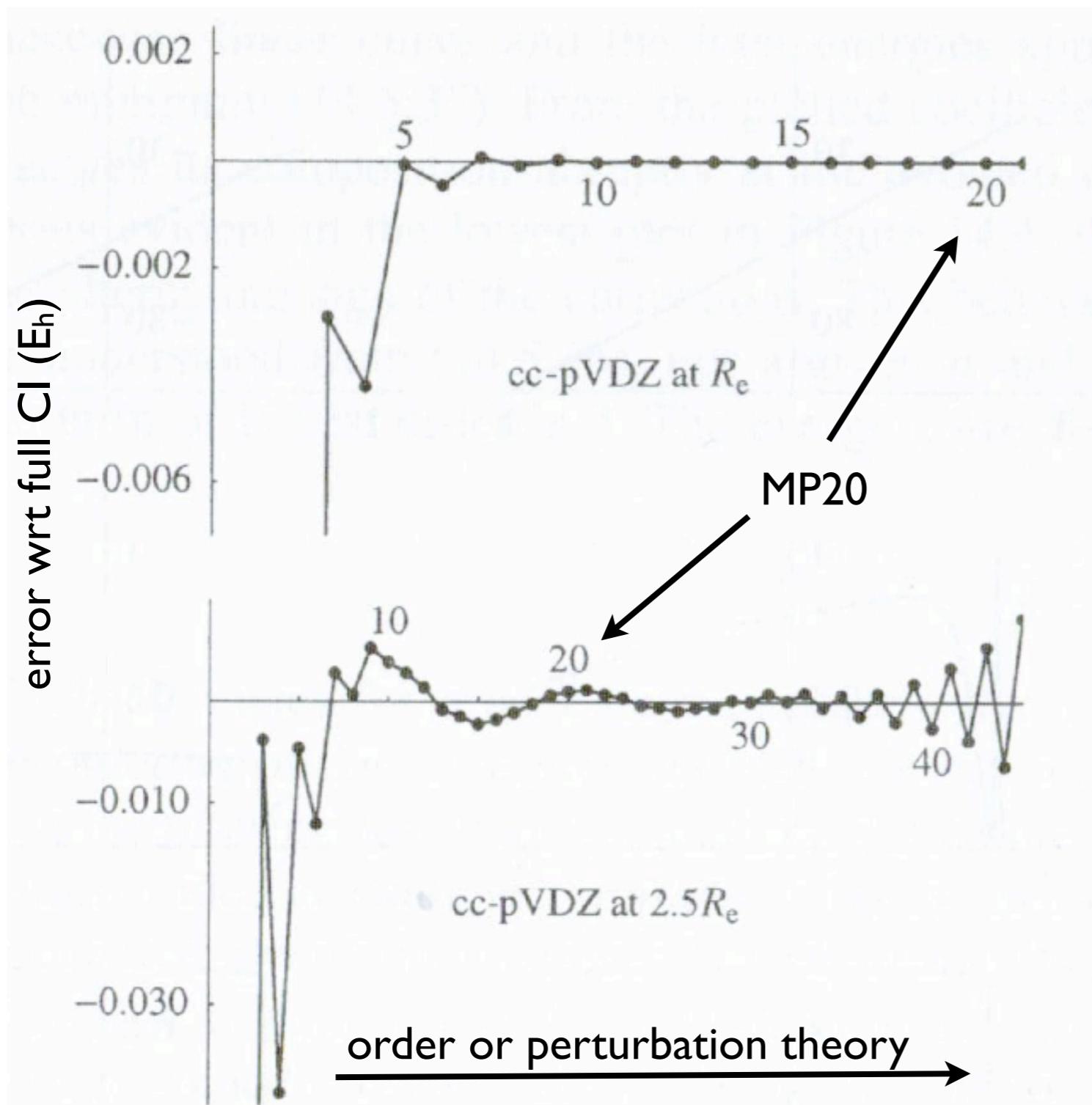








MPn series for water molecule with different O-H bond lengths



near equilibrium, the perturbation series converges nicely to the full CI solution

far from equilibrium, perturbation theory diverges from the full CI solution.

in this situation, the perturbation is not “small” and perturbation theory fails

What methods should we use and when?

Wave-function-based methods:

Symmetry adapted perturbation theory (SAPT)

- intermolecular perturbation theory
- interaction energies by component:
 - electrostatics, dispersion, induction/polarization, exchange-repulsion
- qualitative description of intermolecular forces: SAPT0: $O(N^5)$
- quantitative description: SAPT2+3: $O(N^7)$

When to use it?

SAPT0: applicable to systems with 100's of atoms if you want a qualitative description of nonbonded interactions in your molecule.

- base pair stacking, base pair steps in DNA, protein ligand complexes, etc.

high-order SAPT: need a more quantitative description of noncovalent interactions

- scales just like CCSD(T), but never have to compute total energy for any dimers

What methods should we use and when?

Symmetry adapted perturbation theory (SAPT)

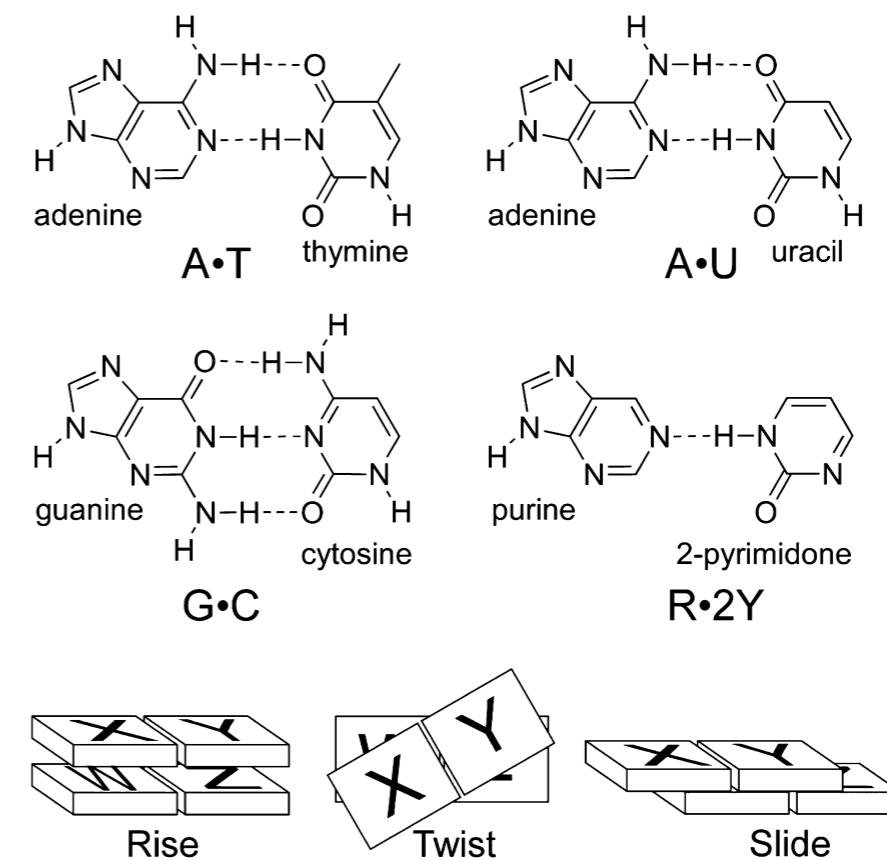
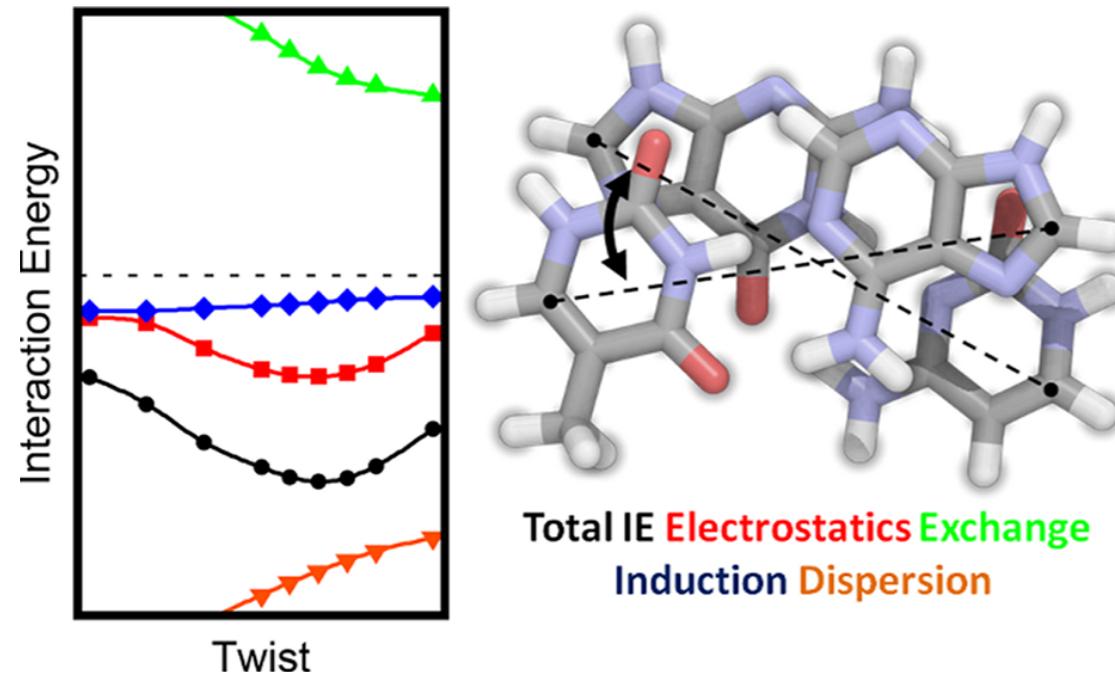


Figure 1. Natural and parent nucleobases considered in the present study and illustrations of the helical parameters Rise, Twist, and Slide.

What methods should we use and when?

Symmetry adapted perturbation theory (SAPT)

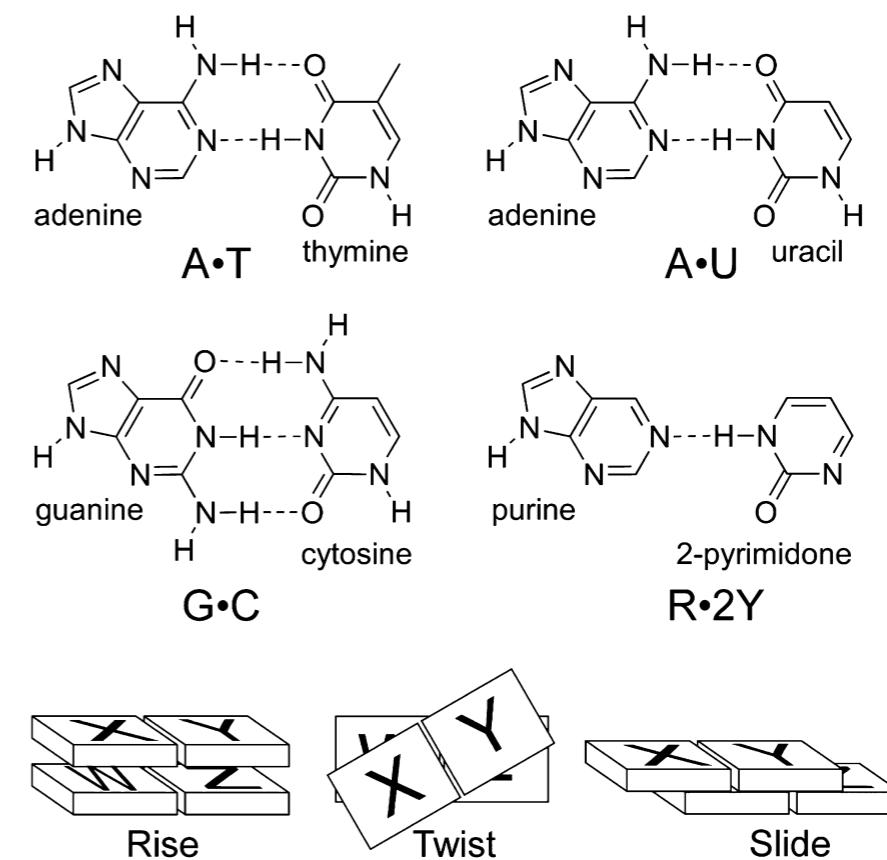
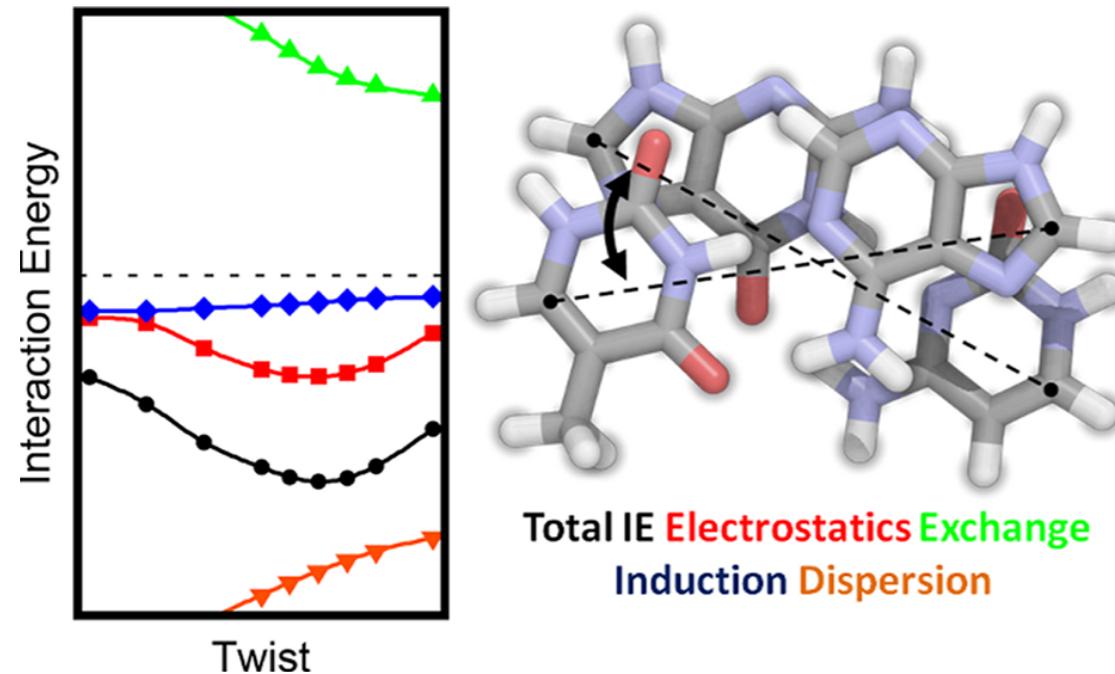


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- stacking interactions between base pairs in DNA/RNA dominated by dispersion

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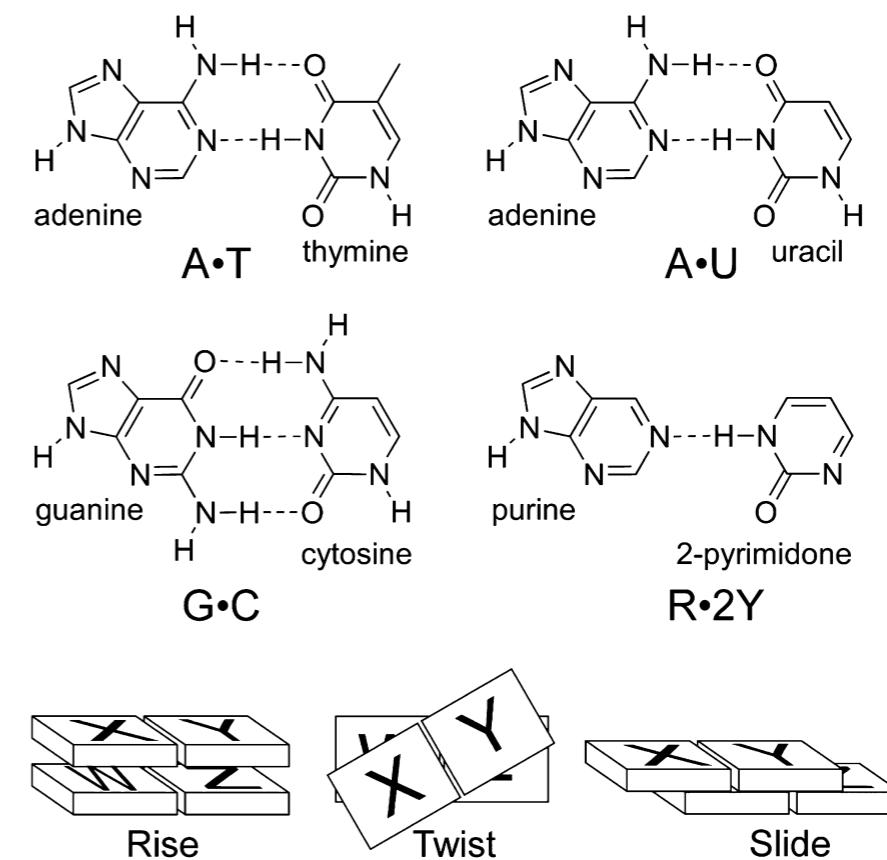
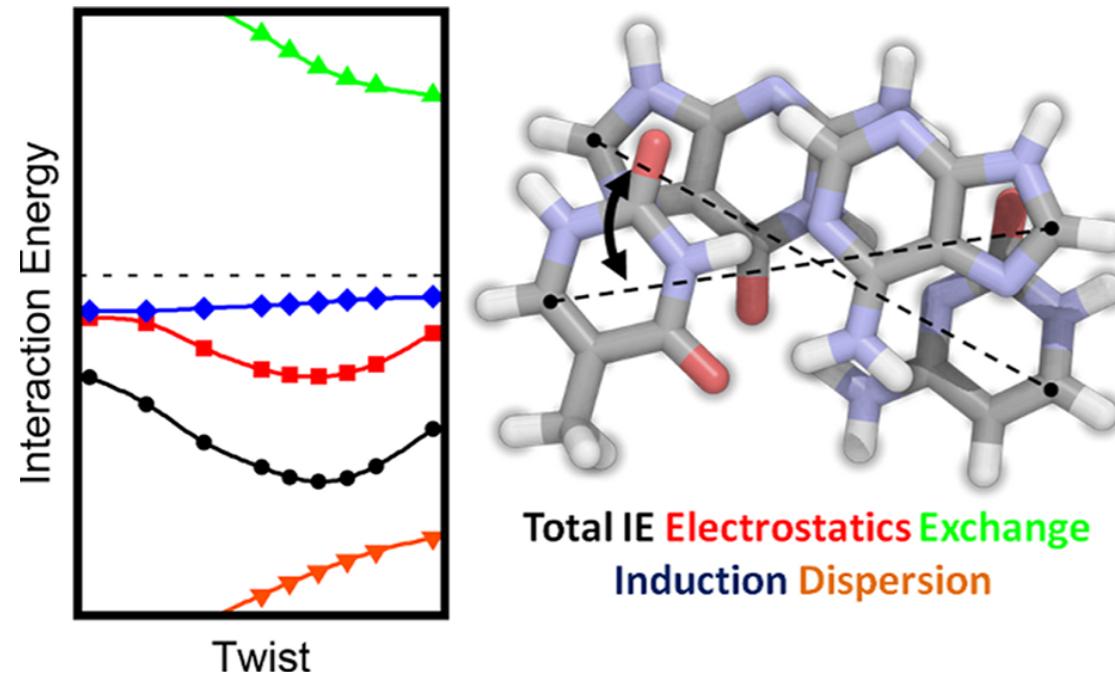


Figure 1. Natural and parent nucleobases considered in the present study and illustrations of the helical parameters Rise, Twist, and Slide.

- stacking interactions between base pairs in DNA/RNA dominated by dispersion

What methods should we use and when?

Wave-function-based methods:

Coupled cluster theory

- formally equivalent to full CI
- truncation of CC wave function:
 - CCSD, CCSDT, CCSDTQ **all are size-extensive. none are variational**
- CC is solved iteratively ... can add non-iterative corrections based on PT
 - CCSD(T): iterative N⁶ (CCSD), non-iterative N⁷ step (T)
- systematically improvable toward full CI limit

When to use it?

- whenever you can!
 - CCSD(T): the “gold-standard” method in QC. the right answer for the right reasons
- quantitative / predictive accuracy
 - non-covalent interactions, accurate descriptions of excited states
 - benchmarking new methods

$$|\Psi_{CC}\rangle = e^{\hat{T}} |\psi_0\rangle$$

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

excitation operators:
singles, doubles, etc.
(just like in CI)

What methods should we use and when?

Density-based methods:

Density functional theory (DFT)

- B3LYP, PBE0, B97, M06-2X, and a zillion other acronyms

Dispersion-corrected density functional theory:

- take a popular DFT method and add correction to account for dispersion (“-D”)
- e.g. B97-D

DFT methods are extremely important in computational chemistry because of a combination of

- (i) how cheap they are: $O(N^4)$, just like Hartree-Fock
- (ii) how (surprisingly) accurate they are for a large portion of computational chemistry

Beware:

- DFT methods fail drastically in for a number of simple cases
- DFT cannot be systematically improved (how do you know how good your answer is?)
- there are many many many density functionals out there. Choose wisely.

DFT functionals offered by QChem

EXCHANGE

Specifies the exchange functional or exchange–correlation functional for hybrid.

TYPE:

STRING

DEFAULT:

No default exchange functional

OPTIONS:

HF	Fock exchange
Slater, S	Slater (Dirac 1930)
Becke, B, B88	Becke 1988
muB88	Short-range Becke exchange, as formulated by Song et al. [65]
Gill96, Gill	Gill 1996
GG99	Gilbert and Gill, 1999
Becke(EDF1), B(EDF1)	Becke (uses EDF1 parameters)
PW91, PW	Perdew
PBE	Perdew-Burke-Ernzerhof 1996
PBE0, PBE1PBE	PBE hybrid with 25% HF exchange
PBEOP	PBE exchange + one-parameter progressive correlation
wPBE	short-range ω PBE exchange, as formulated by Henderson et al. [66]
muPBE	short-range μ PBE exchange, as formulated by Song et al. [65]
B97	Becke97 XC hybrid 1997
B97-1	Becke97 re-optimized by Hamprecht et al. 1998
B97-2	Becke97-1 optimized further by Wilson et al. 2001
B3PW91, Becke3PW91, B3P	B3PW91 hybrid
B3LYP, Becke3LYP	B3LYP hybrid
B3LYP5	B3LYP based on correlation functional #5 of Vosko, Wilk, and Nusair rather than their functional #3
BOP	B88 exchange + one-parameter progressive correlation
EDF1	EDF1
EDF2	EDF2
BMK	BMK hybrid
M05	M05 hybrid
M052X	M05-2X hybrid
M06L	M06-L hybrid
M06HF	M06-HF hybrid
M06	M06 hybrid
M062X	M06-2X hybrid
BR89	Becke-Roussel 1989 represented in analytic form
omegaB97	variations of B97 exchange and(!) correlation
omegaB97X	hybrid including variations of B97 exchange/correlation
omegaB97X-D	hybrid including variations of B97 exchange/correlation and dispersion correction
General, Gen	User defined combination of K, X and C (refer next section).

RECOMMENDATION:

Consult the literature to guide your selection.

CORRELATION

Specifies the correlation functional.

TYPE:

STRING

DEFAULT:

None No correlation.

OPTIONS:

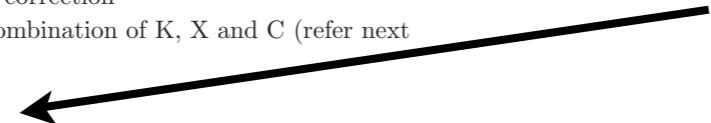
None	No correlation
VWN	Vosko–Wilk–Nusair parameterization #5
LYP	Lee–Yang–Parr (LYP)
PW91, PW	GGA91 (Perdew)
PW92	LSDA 92 (Perdew and Wang) [29]
LYP(EDF1)	LYP(EDF1) parameterization
Perdew86, P86	Perdew 1986
PZ81, PZ	Perdew–Zunger 1981
PBE	Perdew–Burke–Ernzerhof 1996
B94	Becke 1994 correlation represented in analytic form
PK06	Proynov–Kong 2006
(B88)OP	OP correlation, [42] optimized for use with B88 exchange
(PBE)OP	OP correlation, [42] optimized for use with PBE exchange
Wigner	Wigner

RECOMMENDATION:

Consult the literature to guide your selection.

The “exchange-correlation functional” has two parts ...
exchange and correlation

Note QChem’s advice!



Hohenberg-Kohn theorems

- I. The external potential “ $v(r)$, is (to within a constant) a unique functional of $\rho(r)$; since, in turn, $v(r)$ fixes H we see the the full many-particle ground state is a functional of $\rho(r)$.”

Hohenberg-Kohn theorems

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Since Ψ is a functional of $\rho(\mathbf{r})$, so are the electronic kinetic energy and the electron-electron repulsion. We can define a **universal functional** $F[\rho(\mathbf{r})]$ that describes the kinetic energy and e-e interactions and express the *exact electronic energy* as

$$E[\rho(\mathbf{r})] = \int \mathbf{v}(\mathbf{r})\rho(\mathbf{r})d\tau + F[\rho(\mathbf{r})]$$

system dependent
(external potential) system independent
(universal functional)

Hohenberg-Kohn theorems

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$$E[\rho(\mathbf{r})] = \int \mathbf{v}(\mathbf{r})\rho(\mathbf{r})d\tau + F[\rho(\mathbf{r})]$$

- II. The ground state density is the one that minimizes the total energy (variational theorem)

$$\frac{\partial E[\rho(\mathbf{r})]}{\partial \rho(\mathbf{r})} = 0$$

Hohenberg-Kohn theorems

“If $F[\rho(r)]$ were a known and sufficiently simple functional of $\rho(r)$, the problem of determining the ground-state energy and density in a given external potential would be rather easy since it requires merely the minimization of a functional of the three-dimensional density function. The major part of the complexities of the many-electron problems are associated with the determination of the universal functional $F[\rho(r)]$. ”

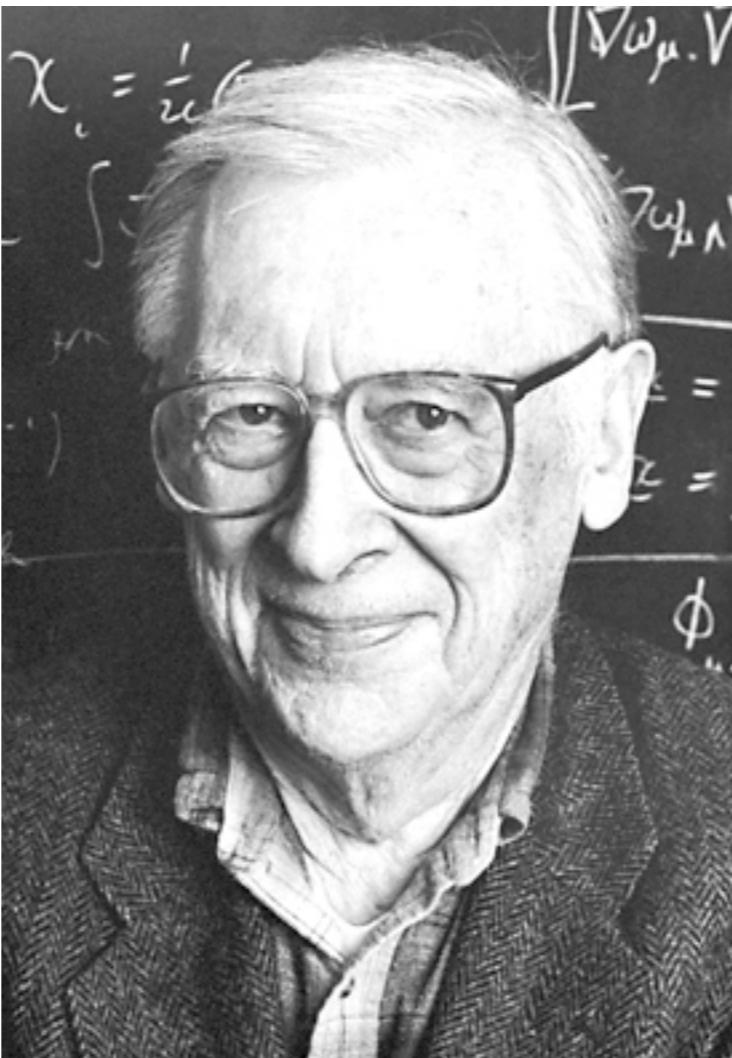
P. Hohenberg and W. Kohn, Phys. Rev. 135, B864 (1964).

Nobel prize



Walter Kohn was awarded the 1998 Nobel Prize in chemistry
“for his development of the density-functional theory”

Nobel prize



Kohn and Pople shared the prize.

Hohenberg-Kohn theorems

“If $F[\rho(r)]$ were a known and sufficiently simple functional of $\rho(r)$, the problem of determining the ground-state energy and density in a given external potential would be rather easy since it requires merely the minimization of a functional of the three-dimensional density function. The major part of the complexities of the many-electron problems are associated with the determination of the universal functional $F[\rho(r)]$.”

P. Hohenberg and W. Kohn, Phys. Rev. 135, B864 (1964).

H-K theorem is an existence theorem. It says F exists, but makes no claims about the form of F . It would be remarkable if we could determine the exact electronic energy using only the density, at a cost comparable to that of Hartree-Fock theory. Remarkable!

The search for this universal functional (or at least a good approximation to it) is at the heart of density functional theory.

How to build a functional

What should go into this universal functional? The density? The gradient of the density?

How to build a functional

What should go into this universal functional? The density? The gradient of the density?

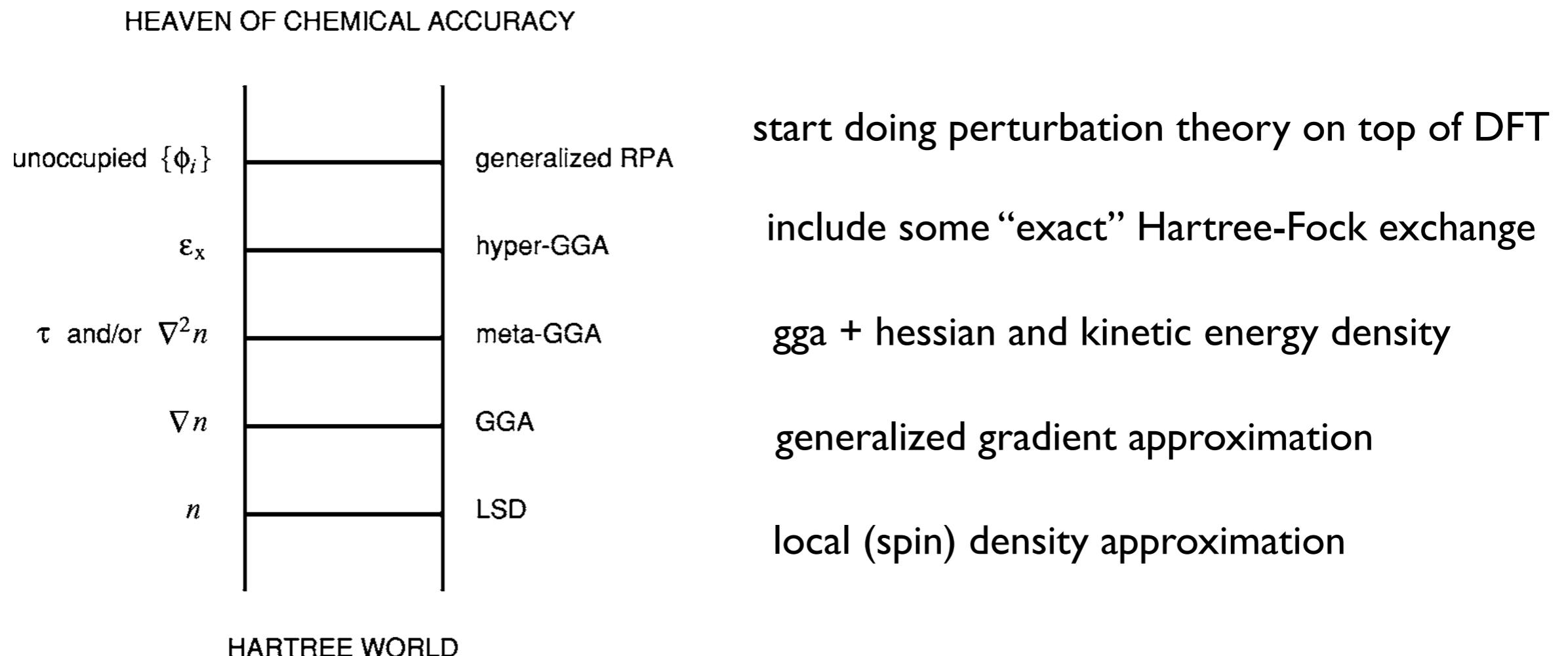


FIG. 1. Jacob’s ladder of density functional approximations to the exchange-correlation energy.

How to build a functional

Once you pick what goes into the functional, you can parametrize it against empirical data

PBE: parameter free

B3LYP: few parameters (I think only 3)

M06-2X and other Minnesota functionals: many parameters (dozens)

DFT successes

With the right functional, DFT provides quite reasonable results

Table 6.1 Comparison of the performance of DFT methods by mean absolute deviations (kcal/mol)

Method	G2	LSDA	B88	BPW91	B3PW91
Atomization Energies	1.2	35.7	3.9	5.7	2.4
Ionization Potentials	1.4	6.3	11.2	4.1	3.8
Proton Affinities	1.0	5.6	2.4	1.5	1.2



“G2” is a composite method that stitches together results from HF, MP2, MP4, and QCISD(T)

DFT successes

With the right functional, DFT provides quite reasonable results

Table 6.2 Comparison of the performance of DFT methods (kcal/mol)

Method	Mean absolute deviation	Maximum absolute deviation
G2	1.6	8.2
G2(MP2)	2.0	10.1
G2(MP2, SVP)	1.9	12.5
SVWN	90.9	228.7
BLYP	7.1	28.4
BPW91	7.9	32.2
B3LYP	3.1	20.1
B3PW91	3.5	21.8

Recall how well B3LYP did for atomization energies? Here it exhibits the best performance of the DFT methods.

G2/97 test set: 125 reaction energies, 148 enthalpies of formation, 88 ionization potentials, 58 electron affinities, and 8 proton affinities.

DFT successes

DFT works remarkably well for thermochemical properties, geometric structure prediction, and harmonic frequency analysis (usually scaled by some value)

B3LYP has emerged as an extremely reliable tool for much of computational chemistry. The go-to-method for experimentalists looking to support their conclusions is

B3LYP / 6-31G*

Be careful, though, there are a number of situations where B3LYP (and DFT in general) fail dramatically. It isn't a silver bullet!

DFT shortcomings

semilocal functionals (LSD/GGA) can't capture dispersion interactions

Empirical corrections (“-D”) have become very common (and reliable). The corrections are basically free, so if you think dispersion interactions may be important in your system, use B3LYP-D or B97-D instead of plain old B3LYP.

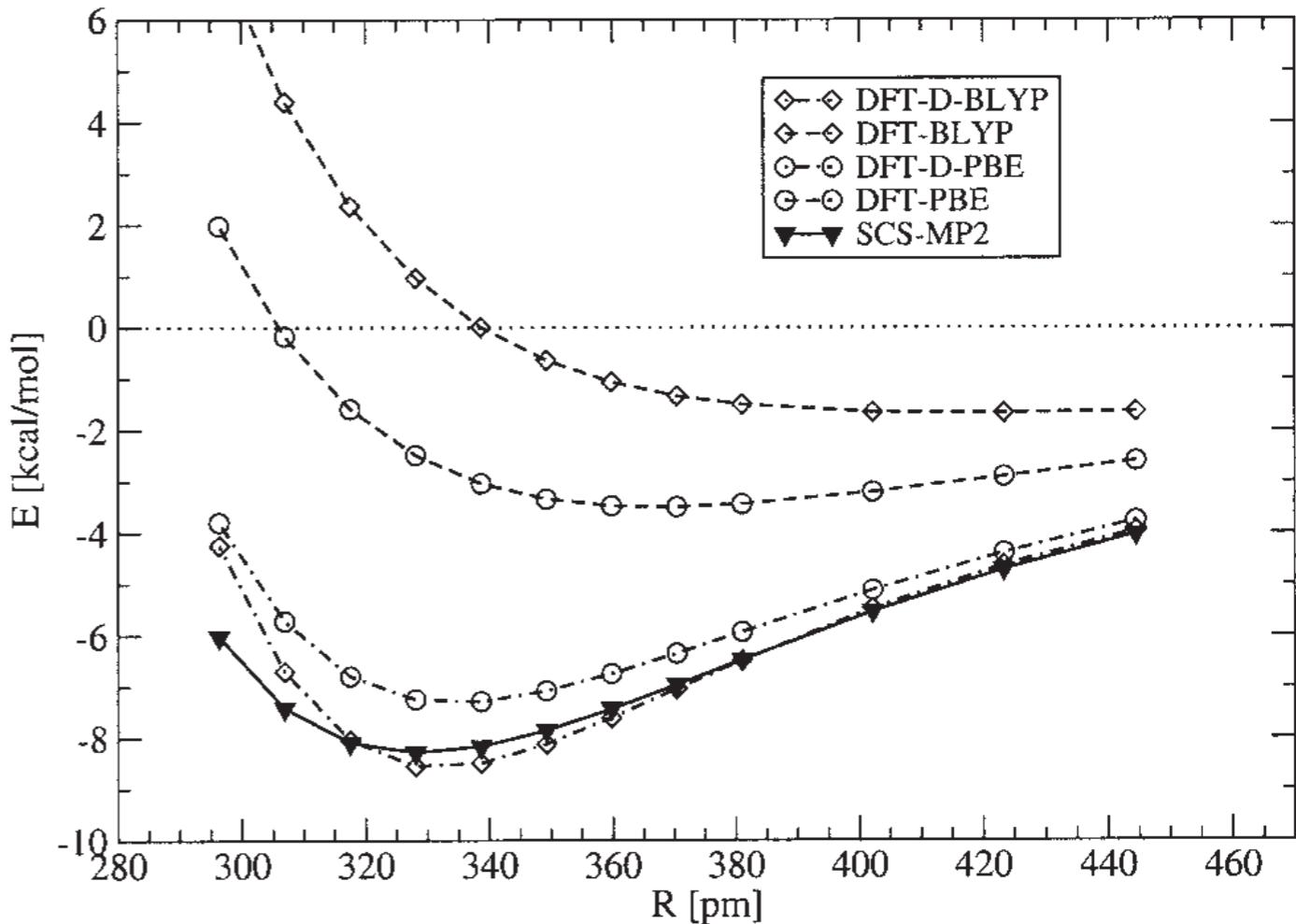


Figure 5. Dependence of the interaction energy on the vertical separation for the cytosine base pair (antiparallel oriented, planar fragments, C_i symmetry, QZV(2df,2dp) AO basis). The counterpoise-corrected SCS-MP2(FC) values are included as reference.

Grimme, *J. Comp. Chem.*, **25**(12), 1463 (2004) [-D1]

Grimme, *J. Comp. Chem.*, **27**(15), 1787 (2006) [-D2]

Grimme, *J. Chem. Phys.*, **132**, 154104 (2010) [-D3]

DFT shortcomings

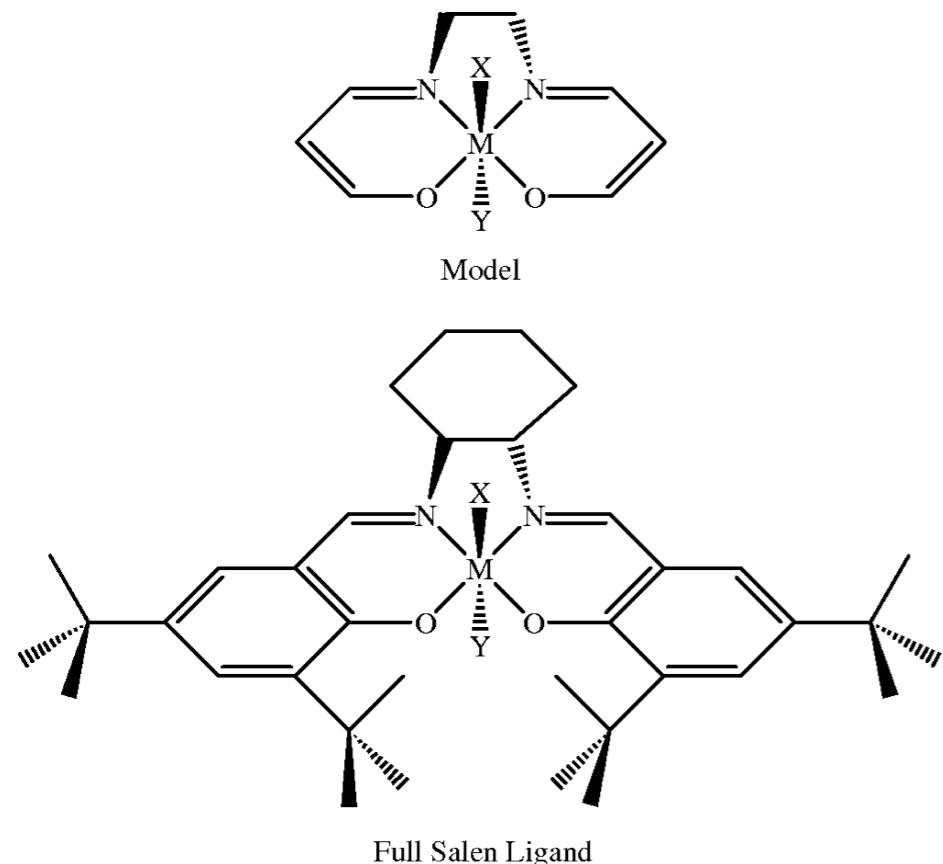


Figure 1. Model system for the metal–salen catalysts and the full salen ligand.

- errors in spin-state splittings are as large as the splittings
- performance is erratic, not systematic
- geometries aren't nearly as bad as energetics

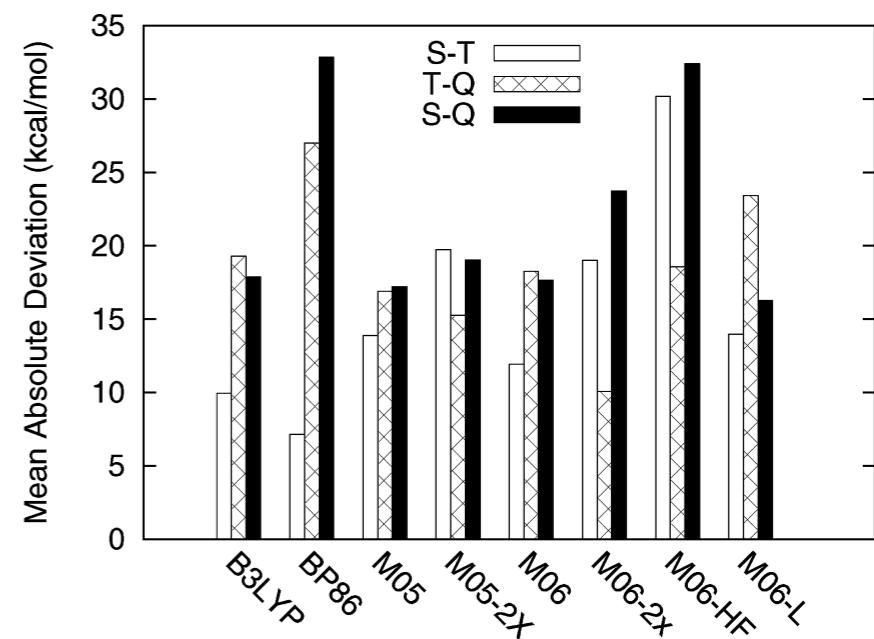


Figure 3. Mean absolute deviations (kcal/mol) for various DFT functionals compared against CASPT3 singlet–triplet (S–T), triplet–quintet (T–Q), and singlet–quintet (S–Q) energy gaps.

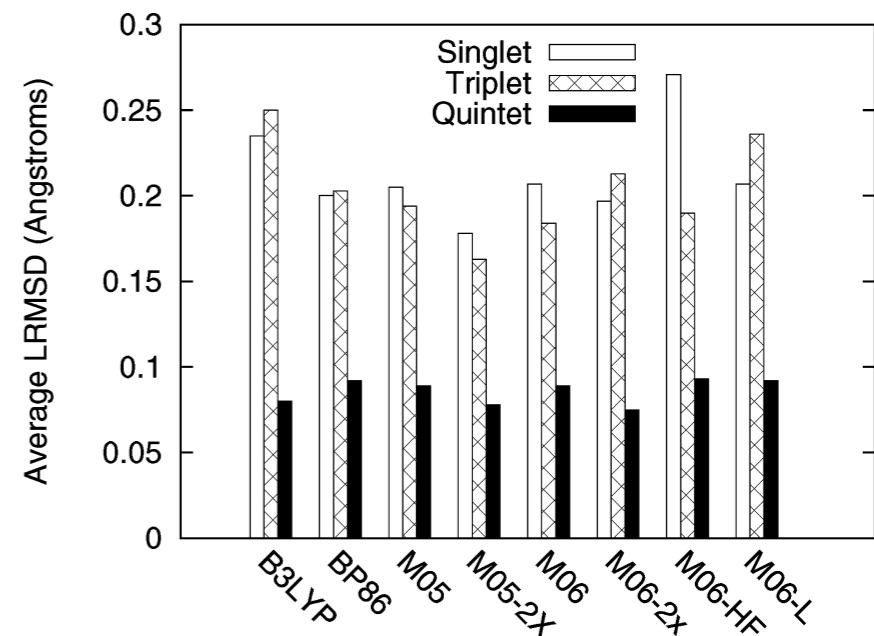


Figure 4. Average LRMSD (\AA) in the 1^1A , 1^3A , and 1^5A state molecular geometries for various DFT functionals compared to CASSCF-optimized geometries.

DFT peculiarities

DFT suffers from “self-interaction error”

Remember the coulomb and exchange terms in Hartree-Fock theory?

$$E_N = \sum_{i=1}^N h_i + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (J_{ij} - K_{ij})$$

bare hamiltonian coulomb operator exchange operator

The diagram shows the mathematical expression for the Hartree-Fock energy E_N . It consists of three main components: a sum over i labeled 'bare hamiltonian', a double sum over i and j labeled 'coulomb operator', and another double sum over i and j labeled 'exchange operator'. Arrows point from each label to its corresponding term in the equation.

In Hartree-Fock, when $i=j$, the coulomb self-repulsion (i is j) term exactly cancels with the exchange term.

In DFT, we have chosen some functional for exchange that is different than in Hartree-Fock, and the terms don't cancel exactly. Electrons repel themselves!

(NOTE: if we knew the true form of the functional, self-interaction error wouldn't be a problem)

DFT peculiarities

DFT suffers from “self-interaction error”

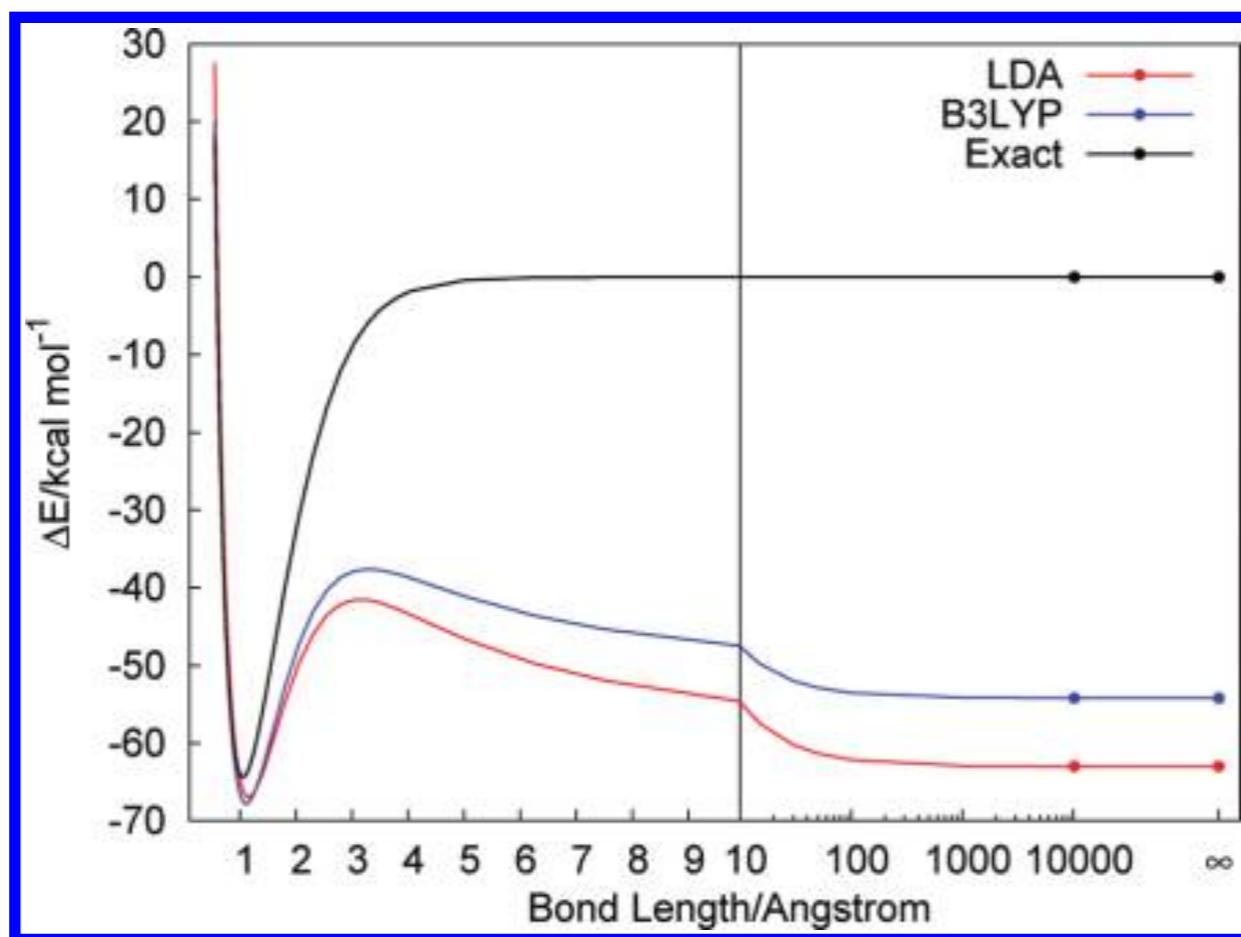


Figure 2. Binding energy curves of stretched H_2^+ , calculated with LDA, B3LYP, and exact (HF). After 10 Å the x axis changes to a logarithmic scale and the final point at infinity is from an explicitly fractional charge calculation ($2 \times \text{H}^{[1/2\alpha, 0]}$).

DFT peculiarities

DFT tends to over delocalize charge

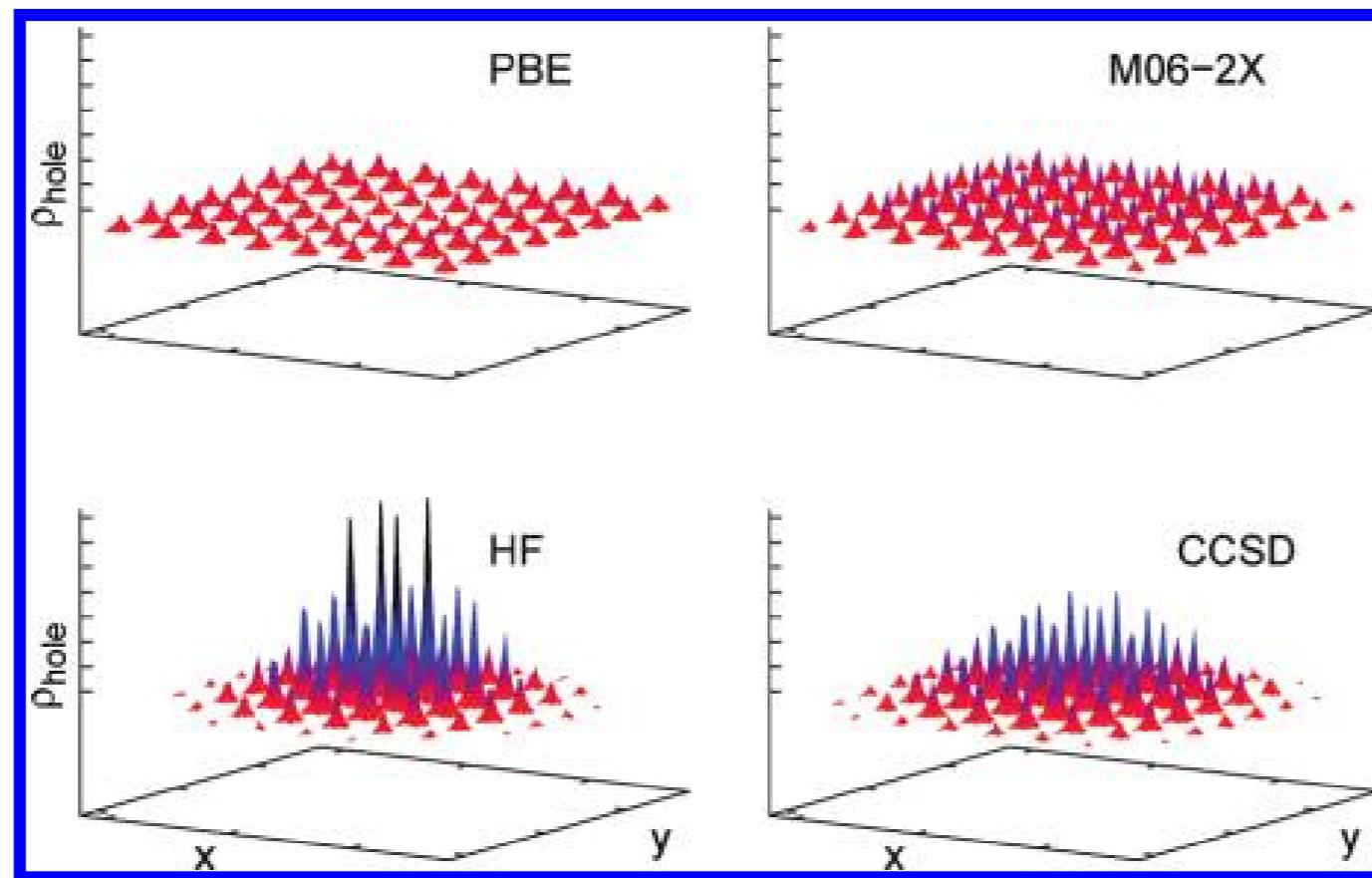


Figure 5. Visualization of the delocalization error: The density difference or hole, $\rho_{\text{hole}} = \rho_N - \rho_{N-1}$, for the ionization process $\text{He}_{64} \rightarrow \text{He}_{64}^+$ is shown for four different methods. CCSD gives a good description of ρ_{hole} in this system. In comparison a GGA functional, such as PBE, overdelocalizes ρ_{hole} , whereas Hartree–Fock overlocalizes ρ_{hole} . A hybrid functional, such as M06-2X, which has quite a large amount of exchange (58%), still does not adequately describe ρ_{hole} .

DFT peculiarities

Grids: many of the integrals involved in DFT cannot be evaluated analytically, so they are evaluated numerically on a grid

That's fine, but not all grids are created equal

- different packages have different default grids
be careful comparing numbers between packages
- can have *grid* superposition error just like BSSE
in the case that your grid is incomplete
- some functionals behave very oddly with incomplete grids

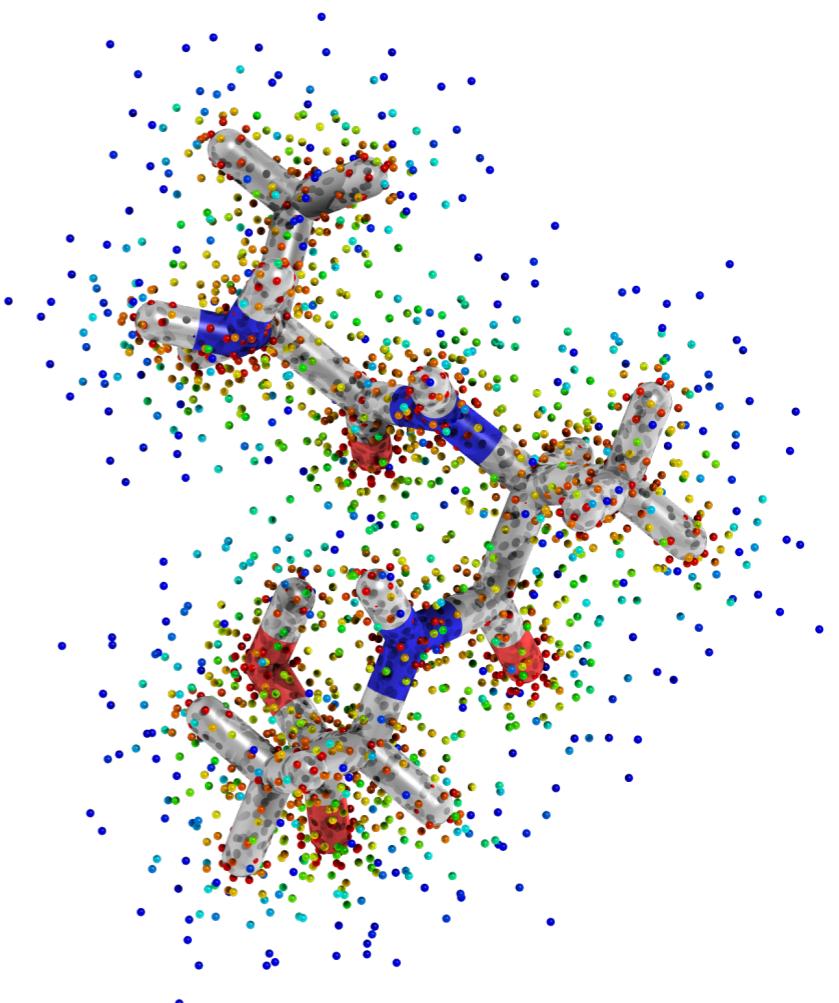


image credit: Rob Parrish, Georgia Tech

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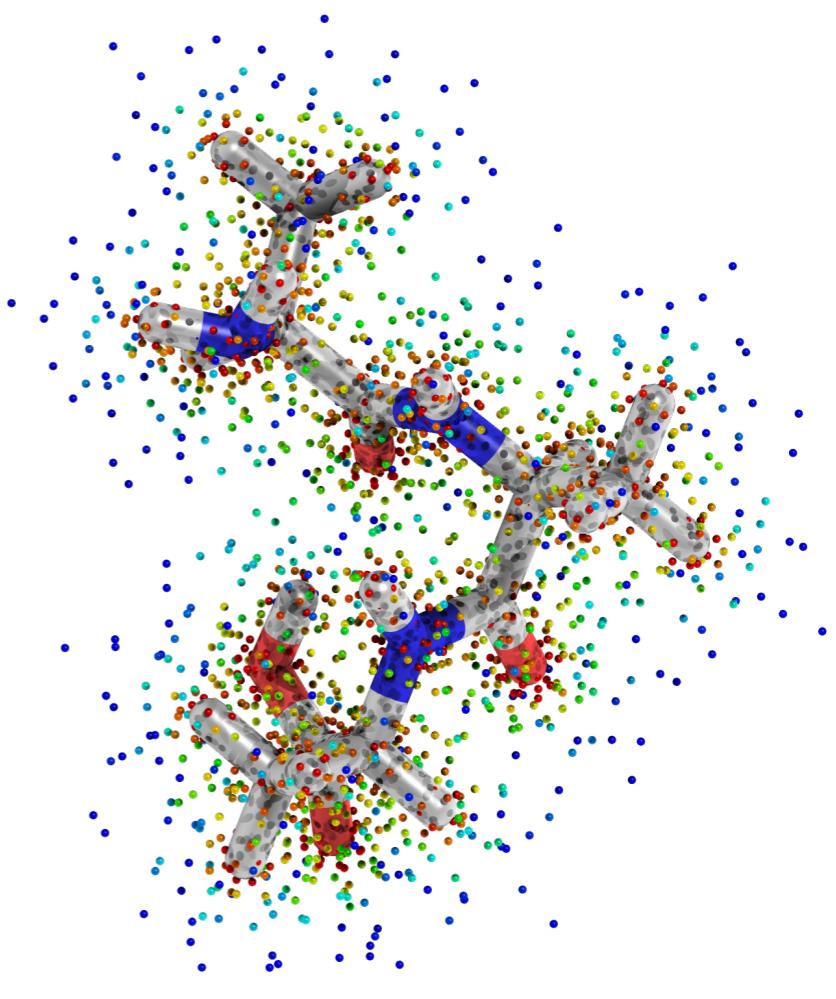
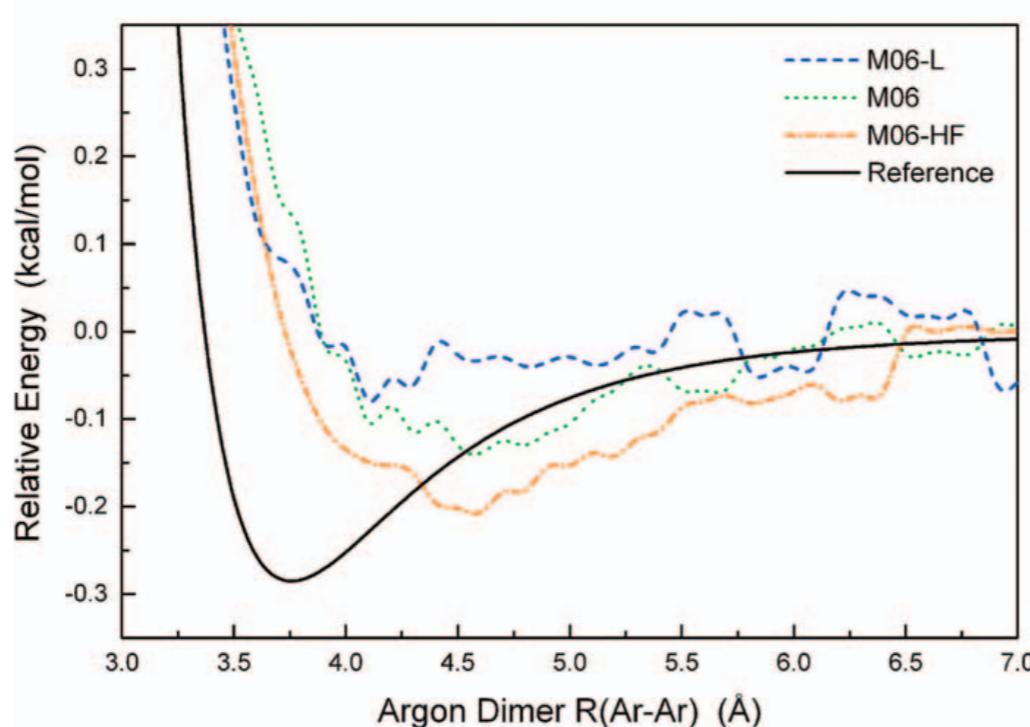


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DFT peculiarities

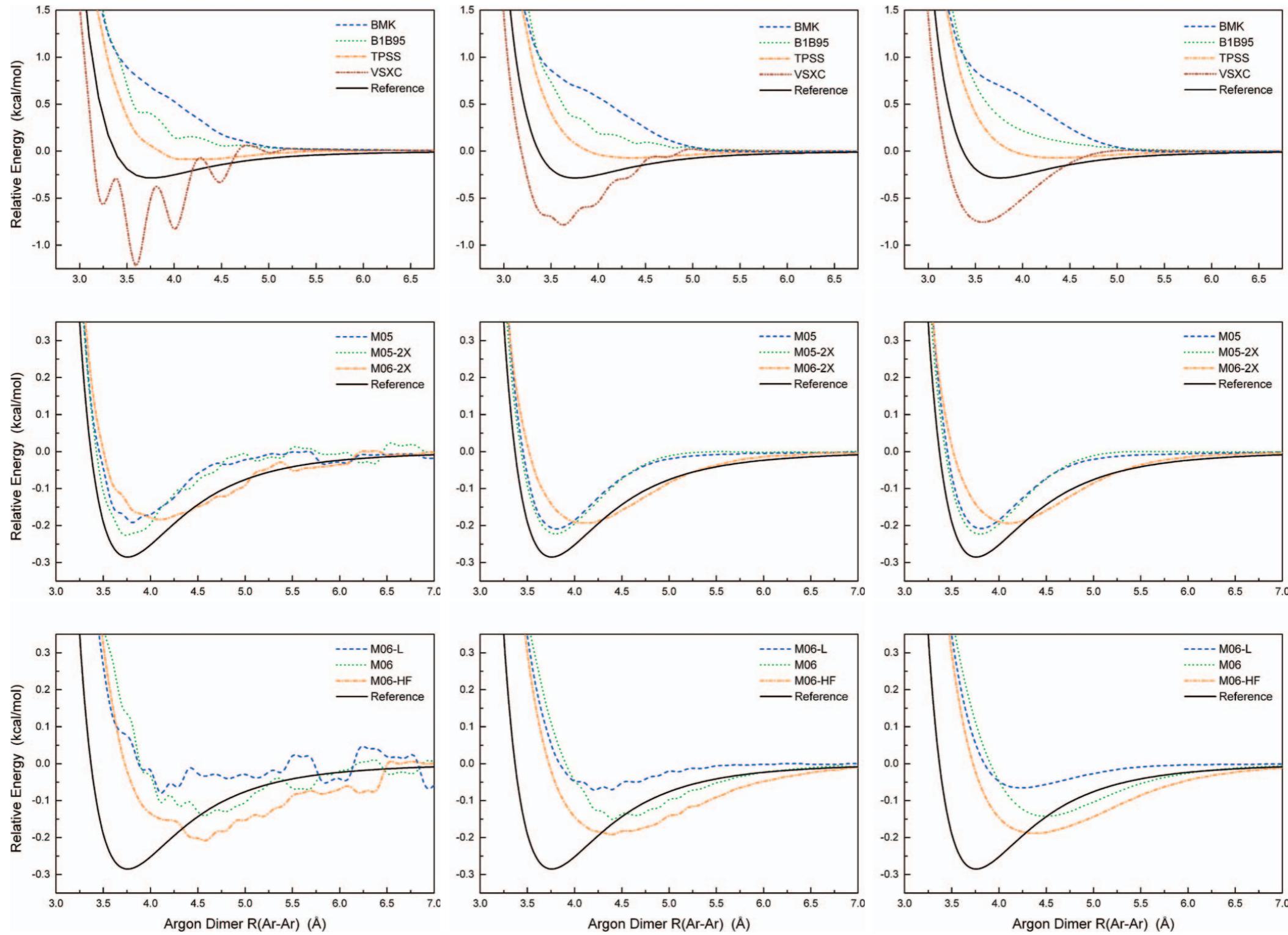
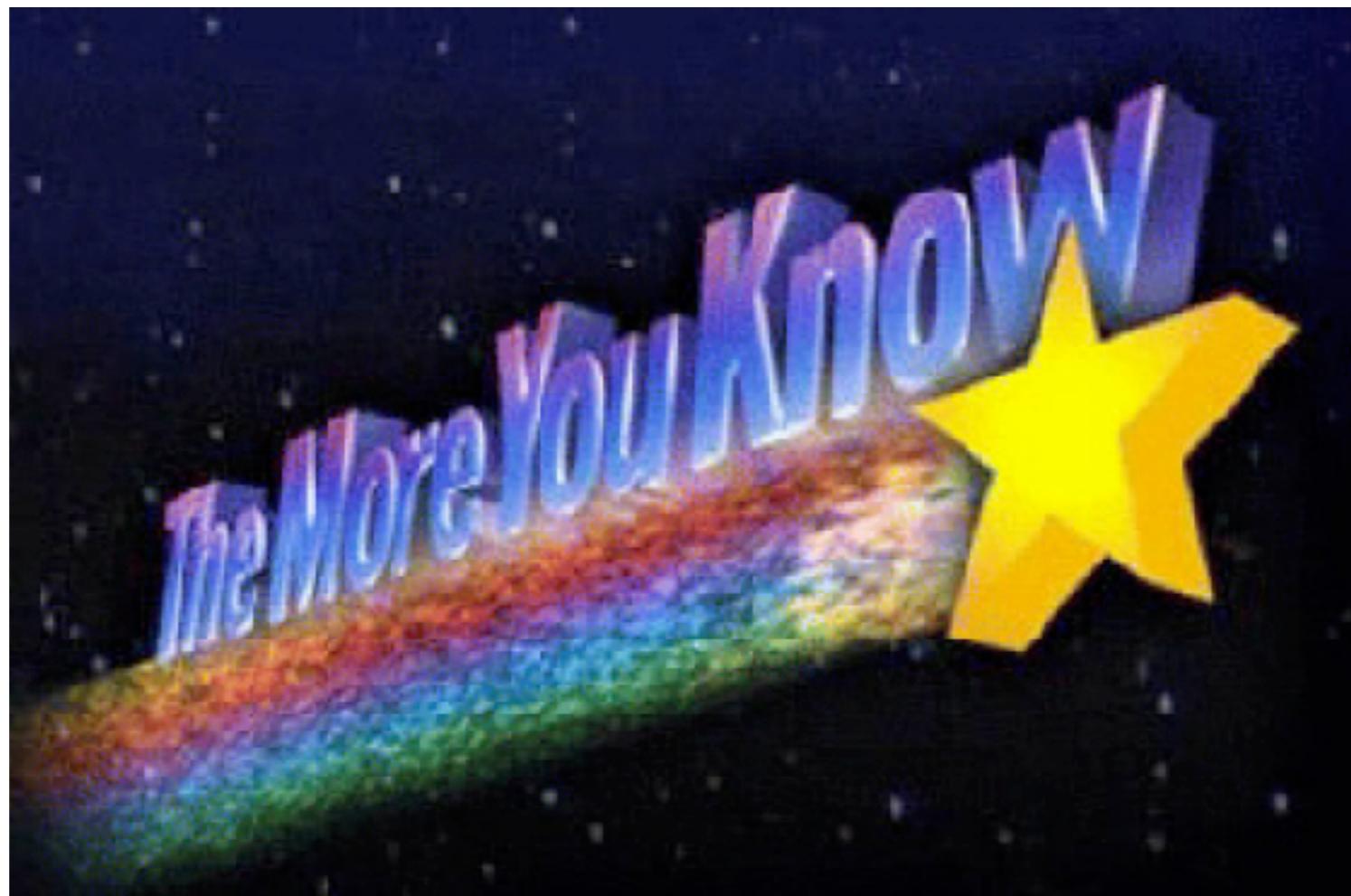


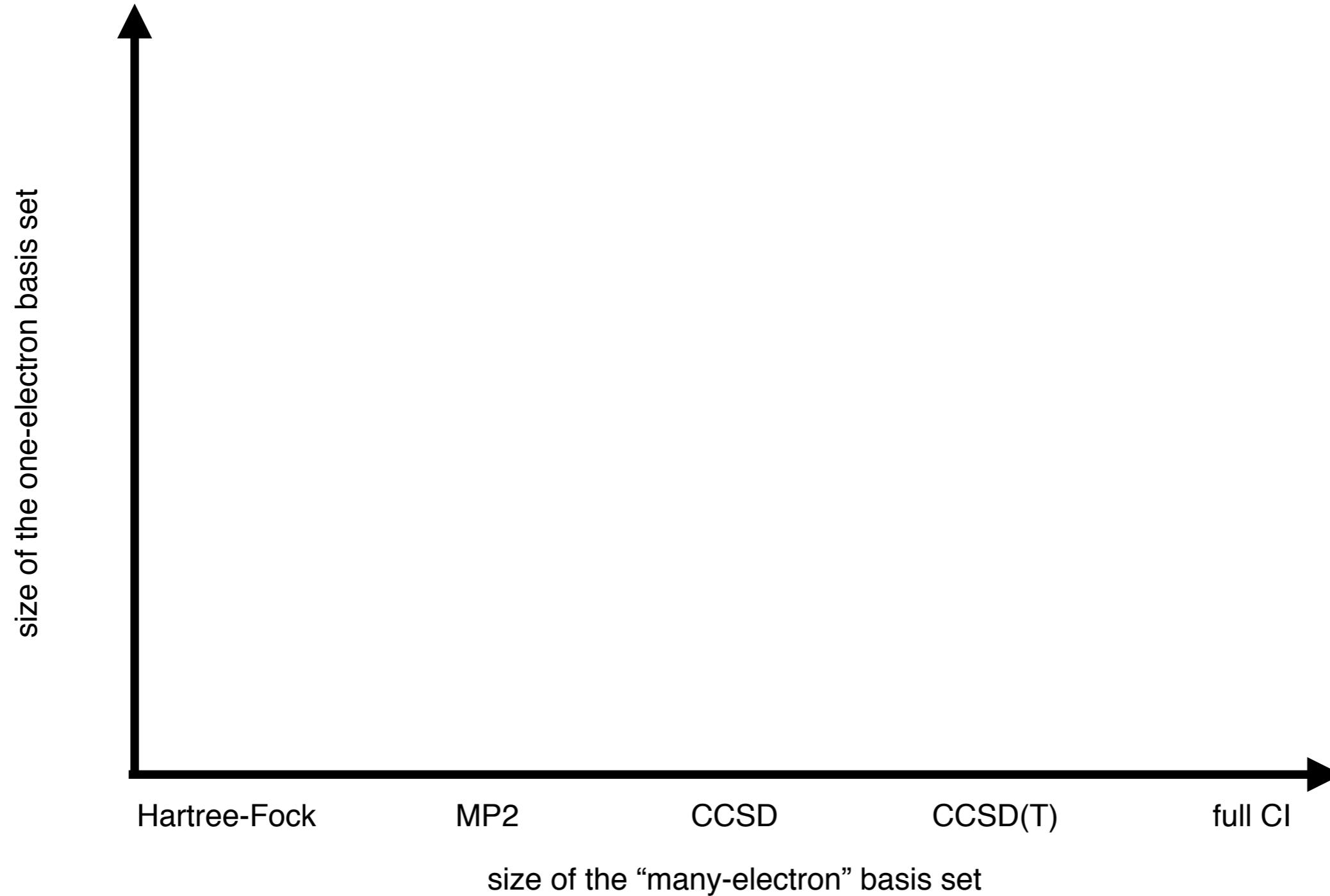
FIG. 1. Potential energy curves for the argon dimer calculated using the $(n_r, n_\ell) = (75, 302)$, $(99, 590)$, and $(250, 590)$ integration grids. The curves on the left are for the coarsest grid and the curves on the right are for the finest grid. The accurate reference potential was obtained from Ref. 30.

“The talk”

I know you are all going to use DFT. It's fun. It's easy. All your friends are doing it.



I just want you to be careful. Get the facts.

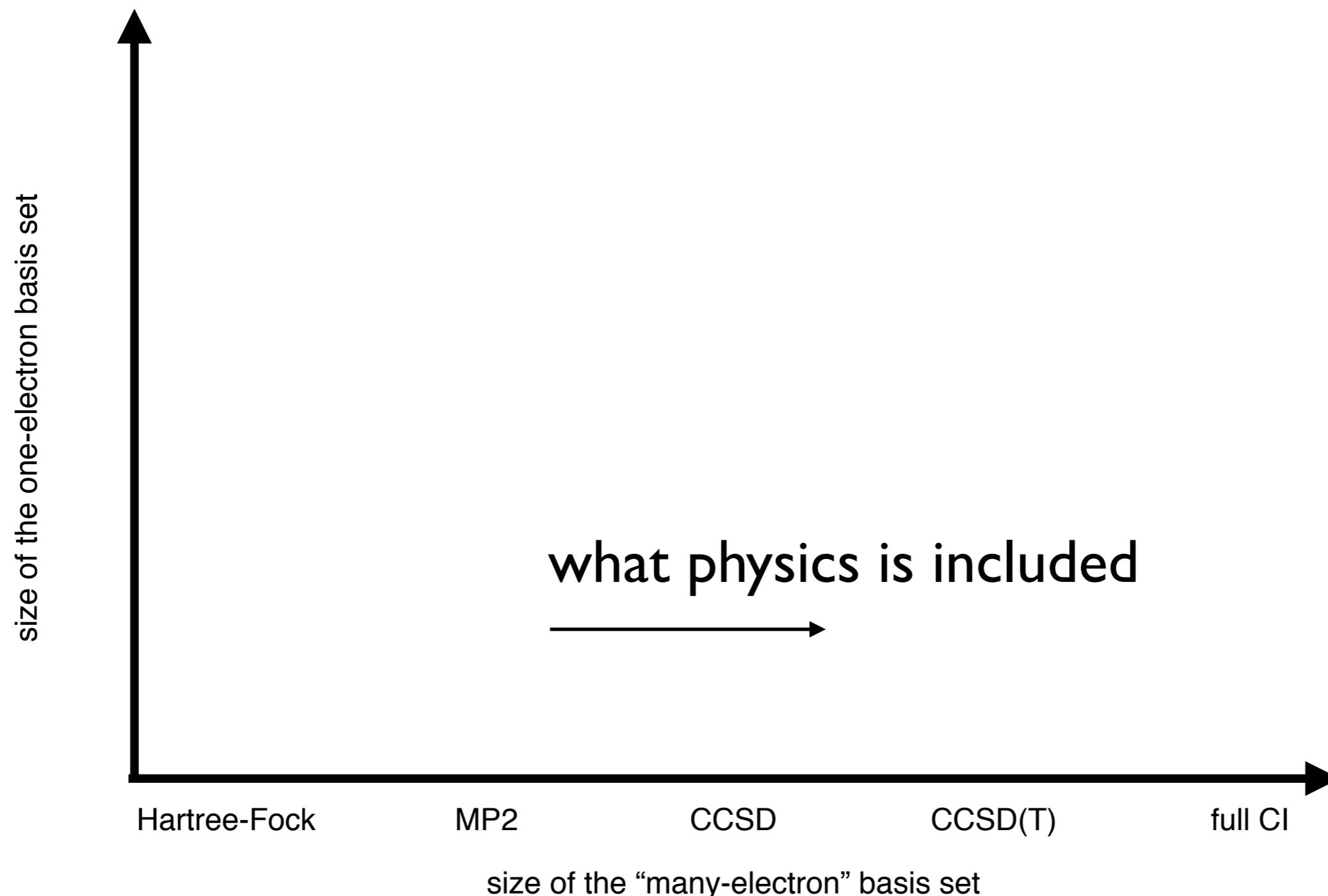


MP2: 2nd-order perturbation theory

CCSD: coupled cluster with single and double excitations

CCSD(T): CCSD + perturbative triplet excitations

full CI: full configuration interaction ... include *all* possible electronic configurations

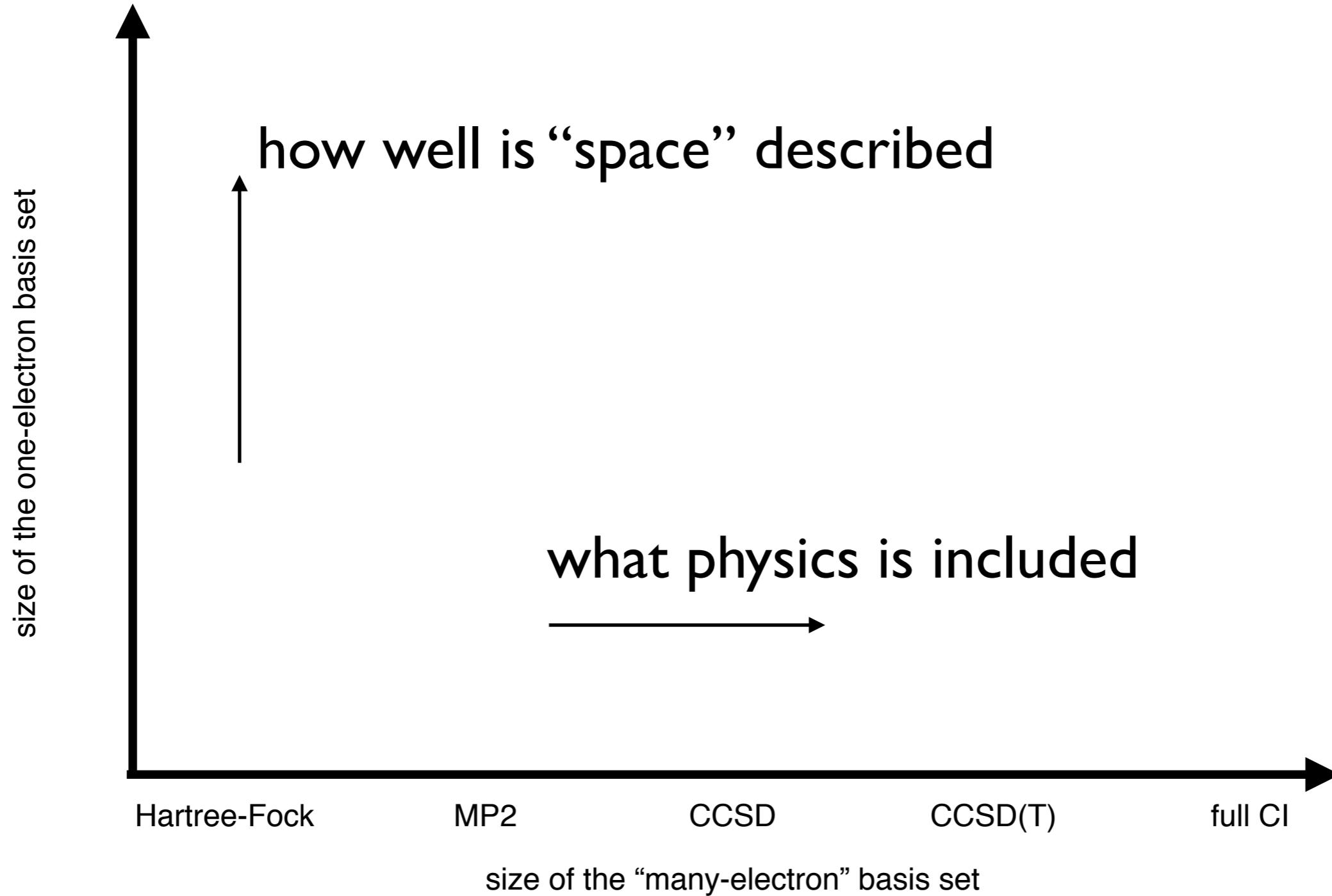


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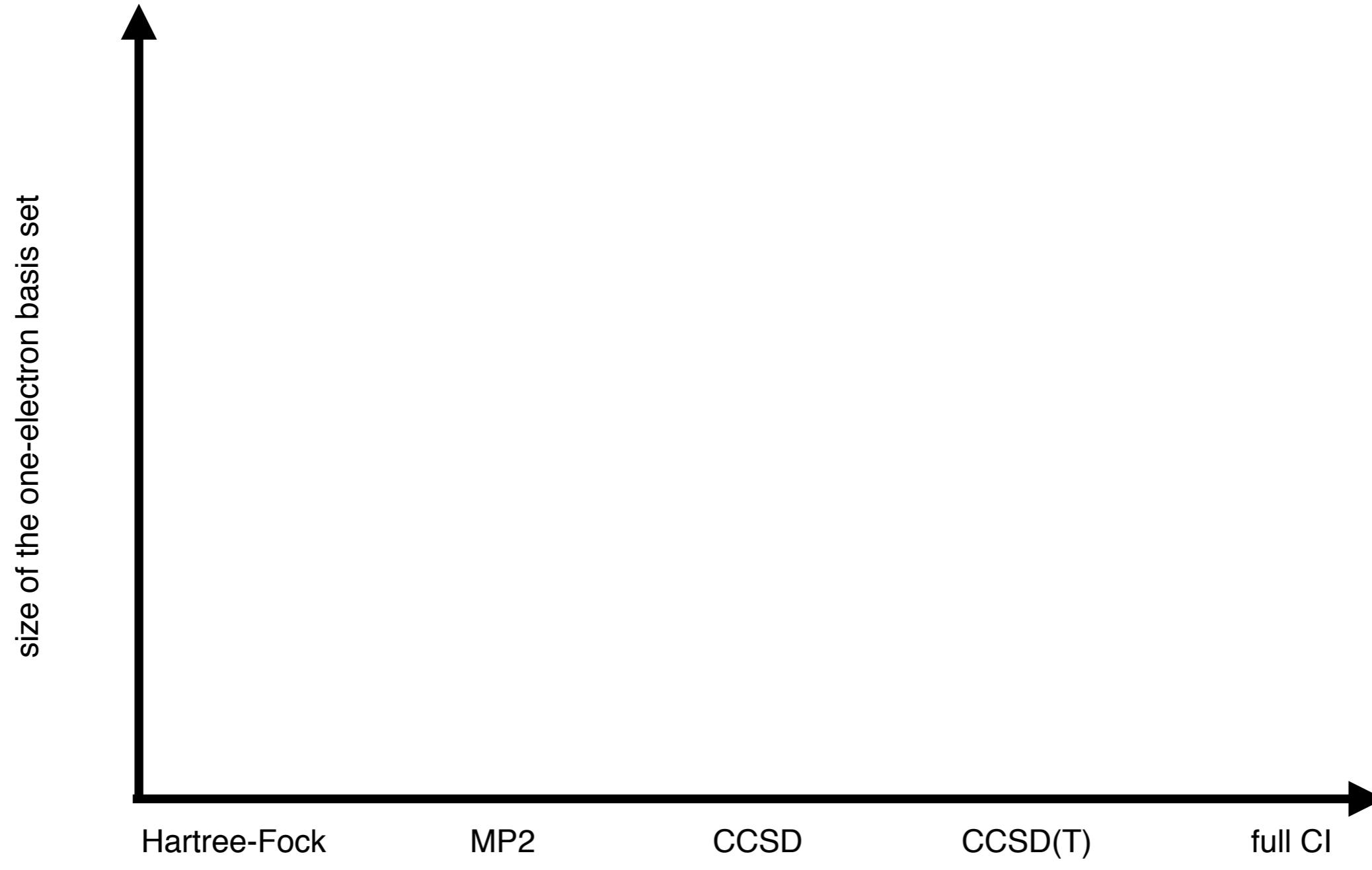


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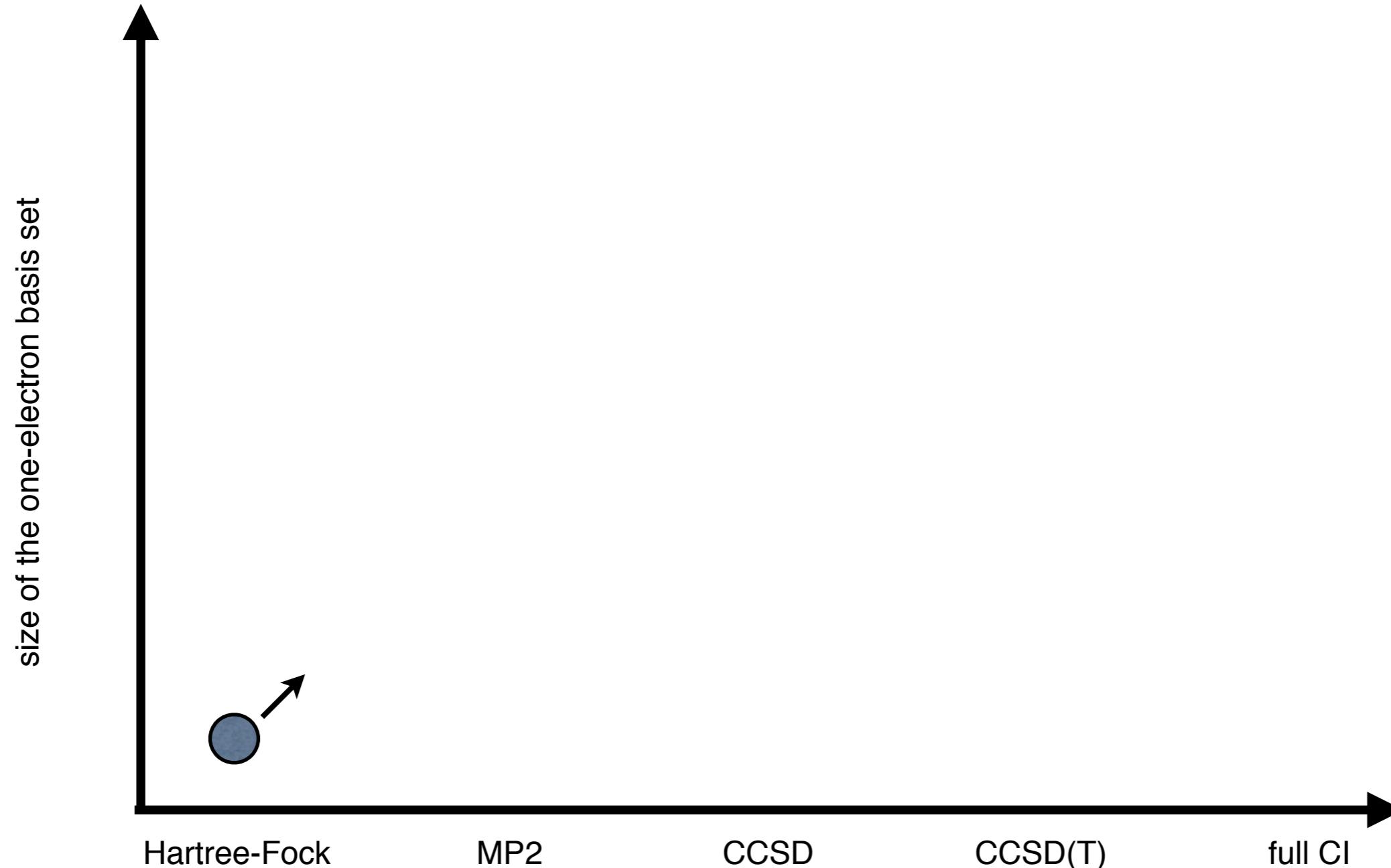
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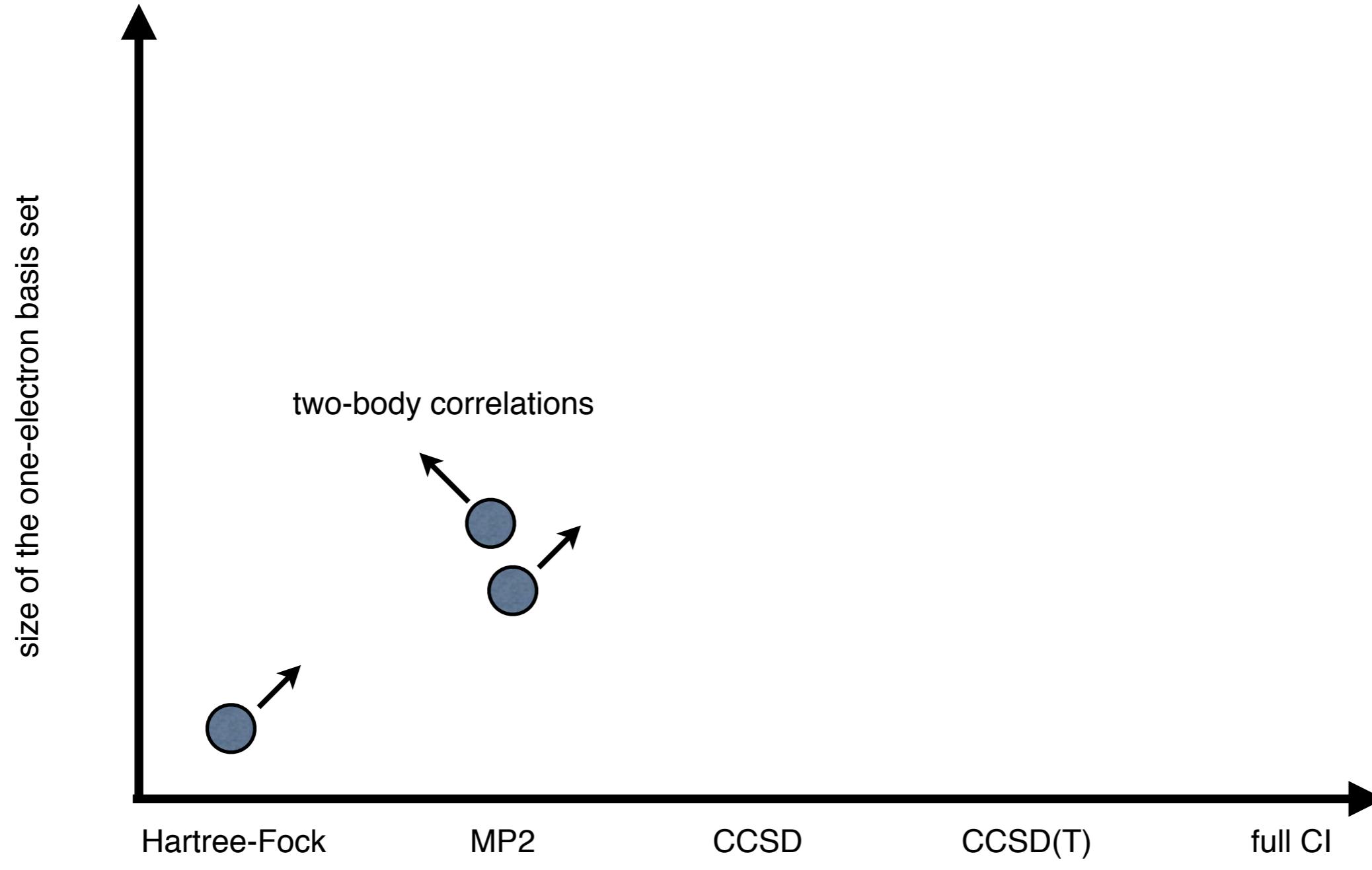
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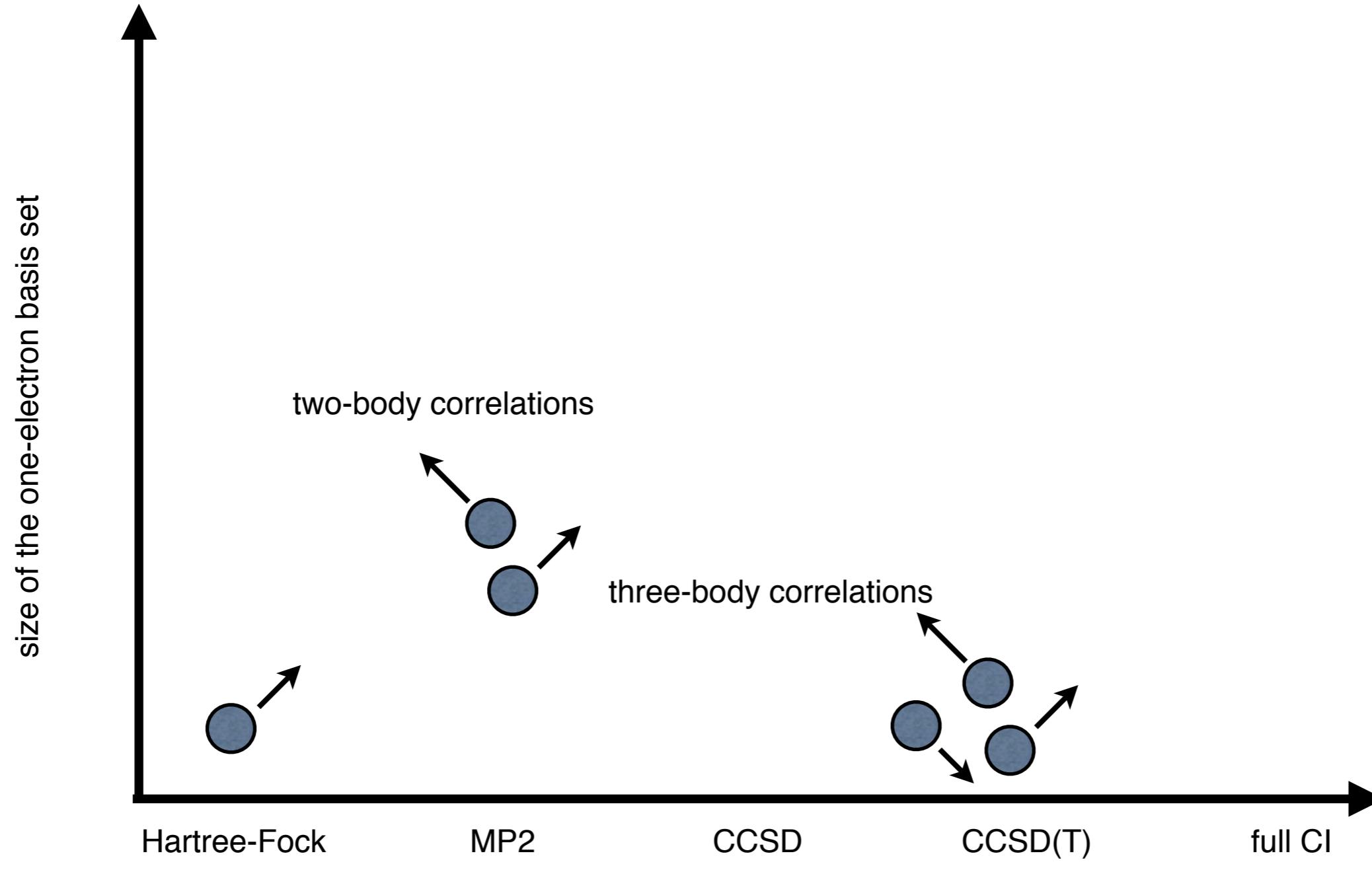
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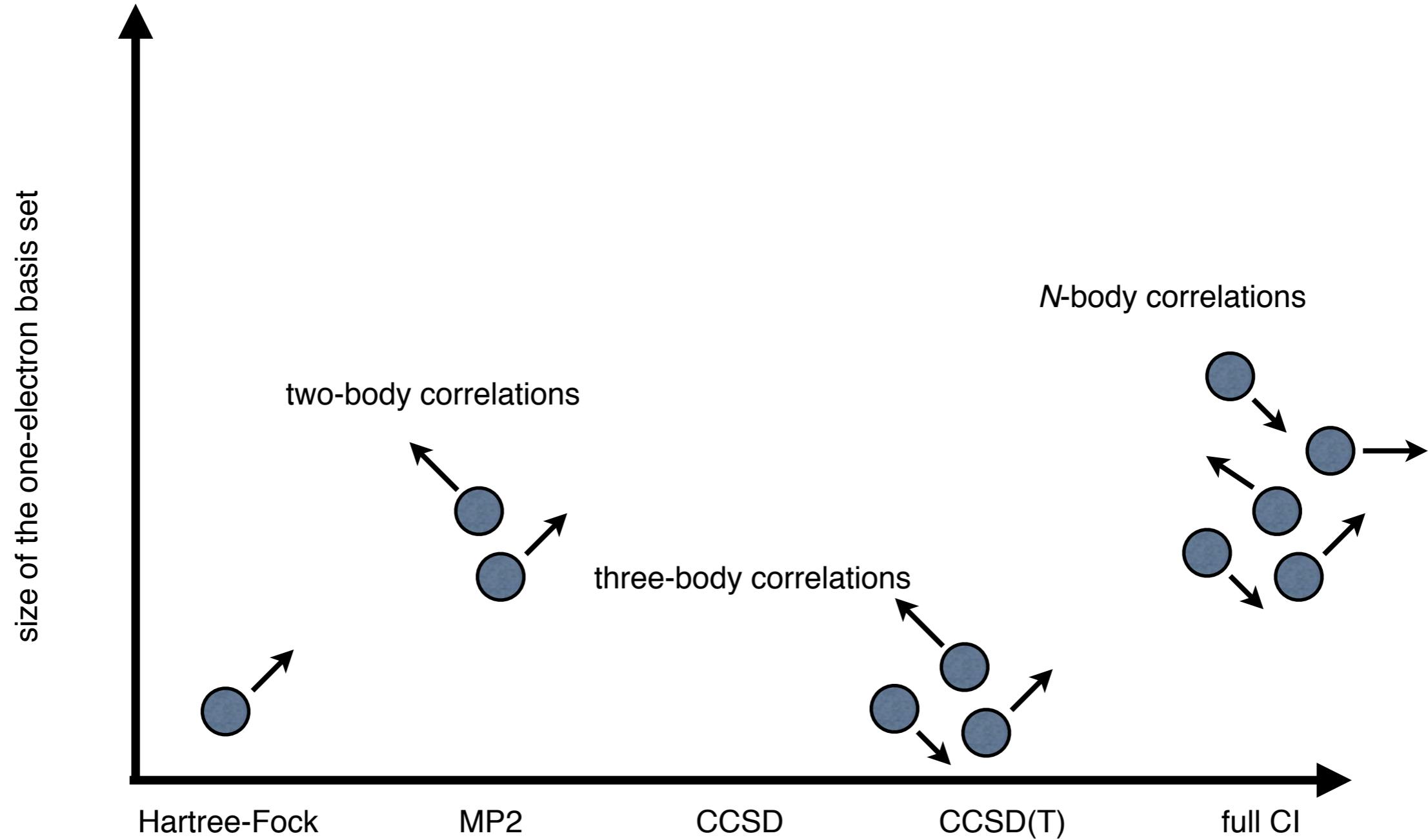
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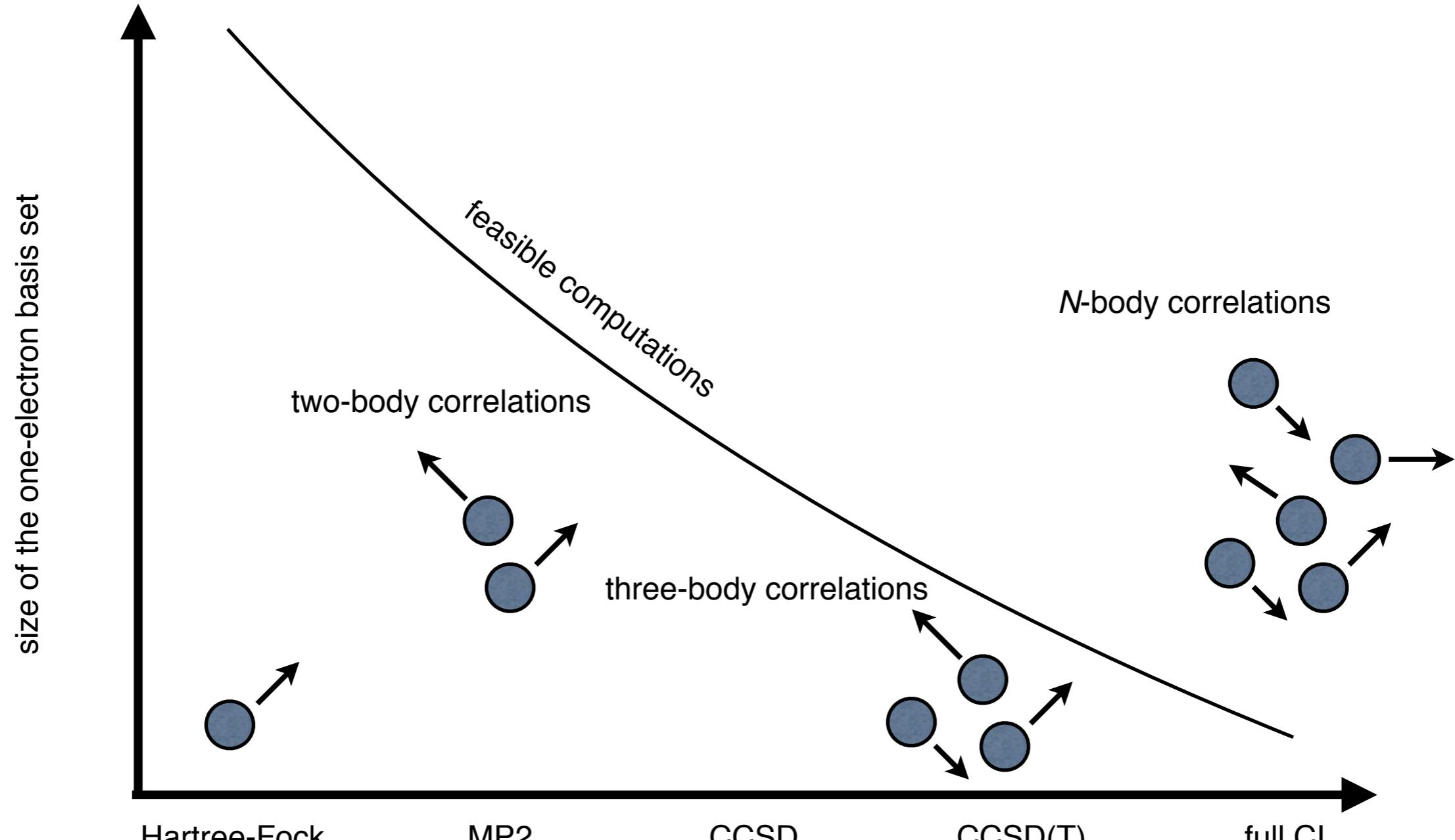
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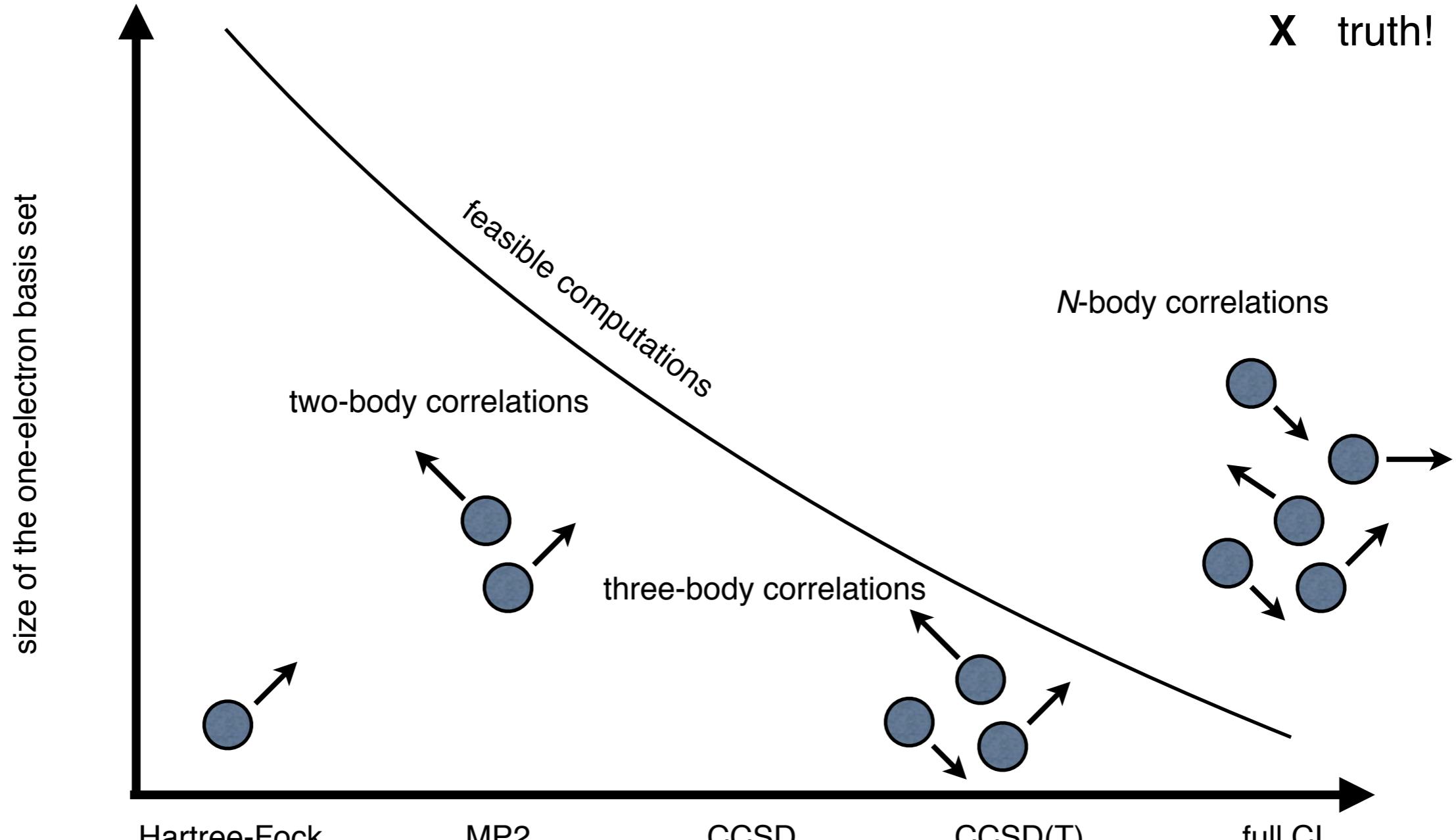
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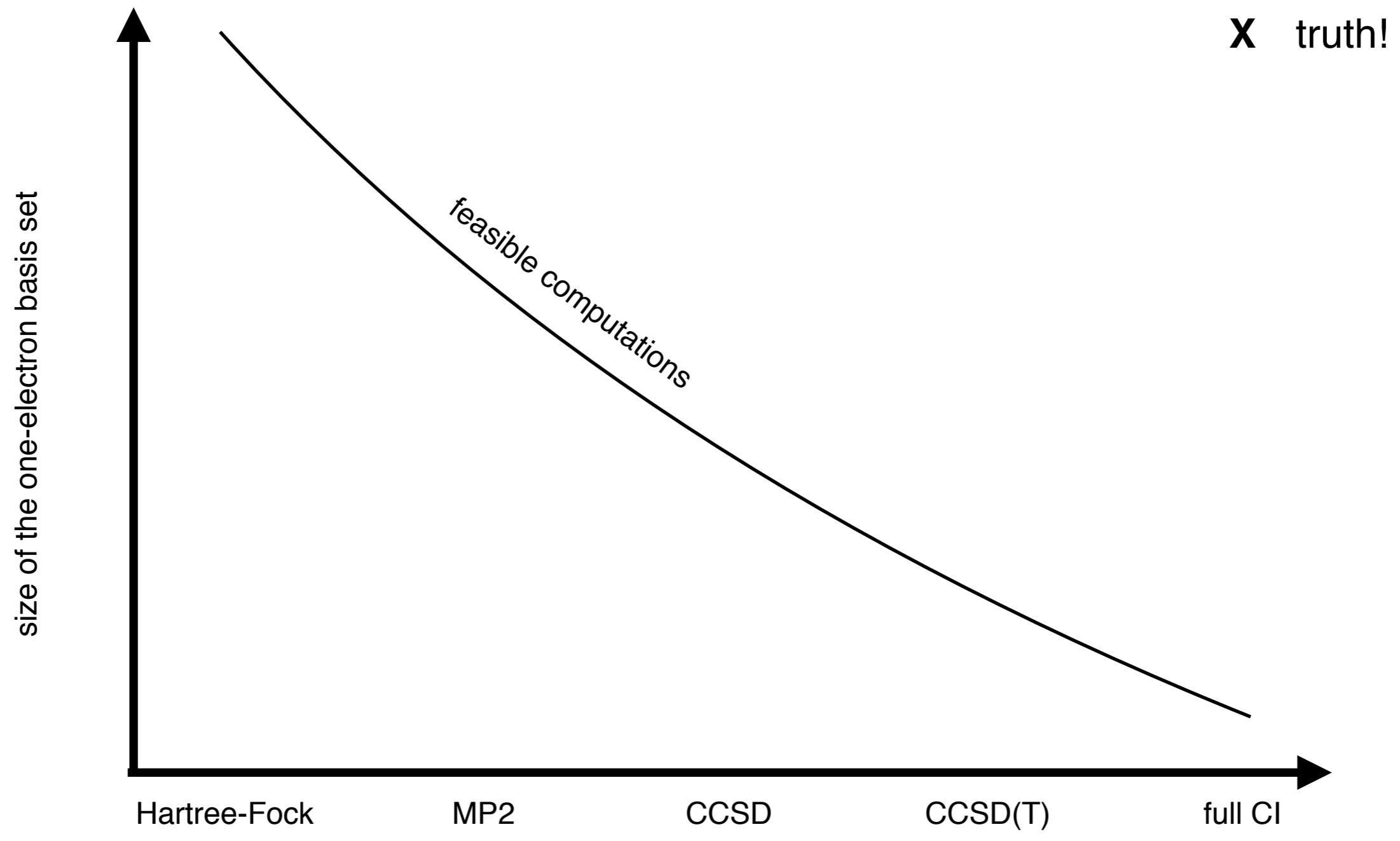
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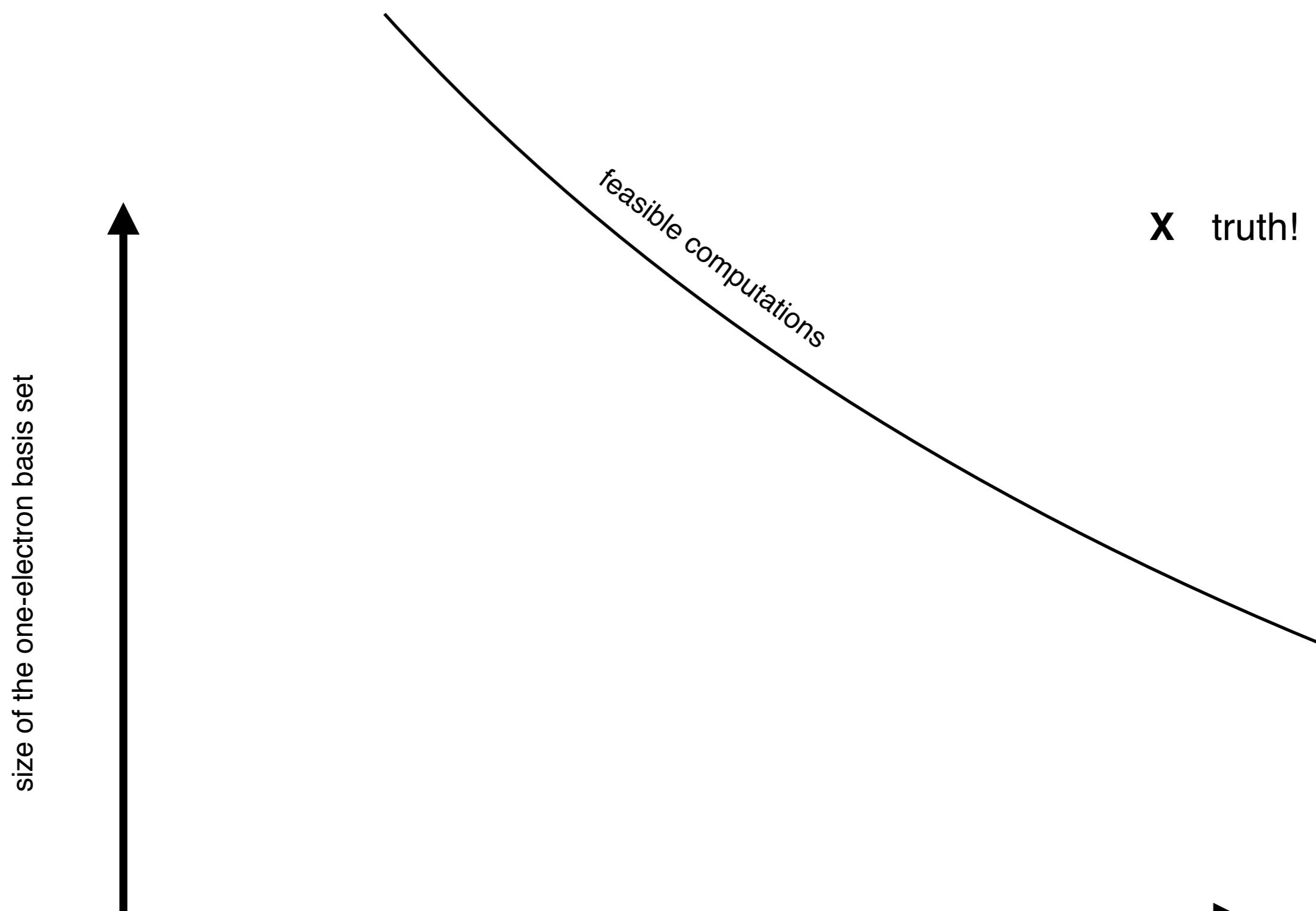
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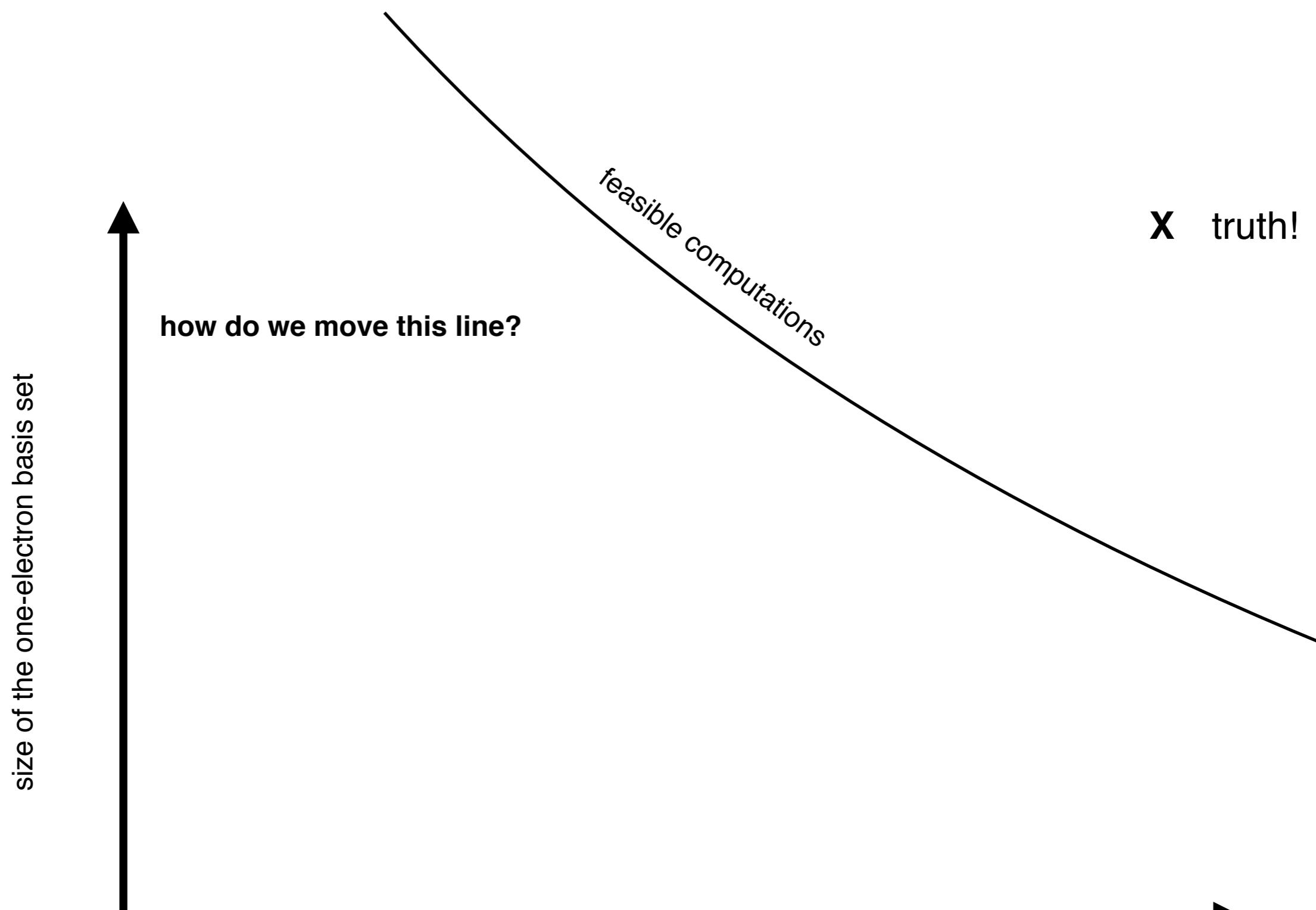


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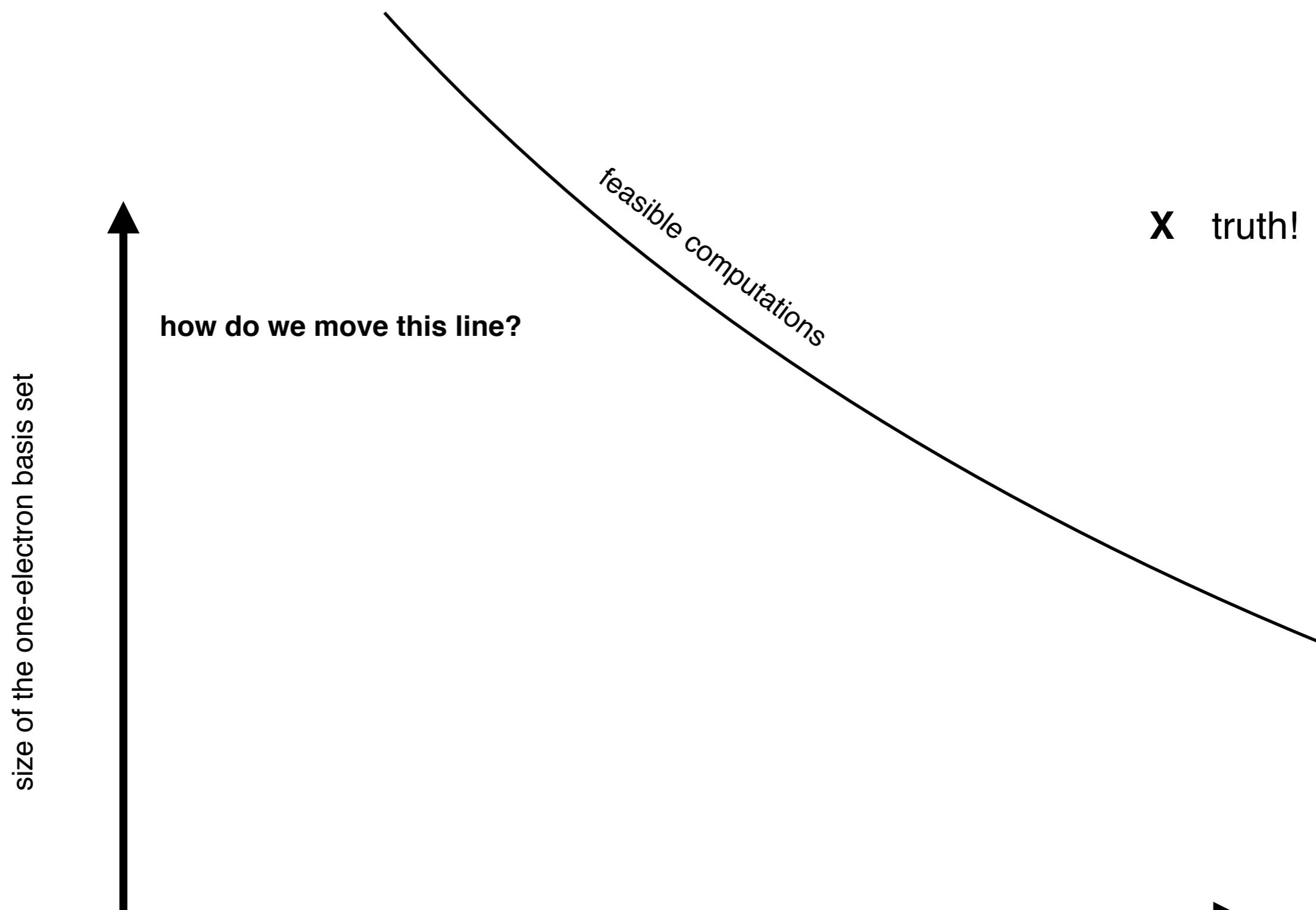
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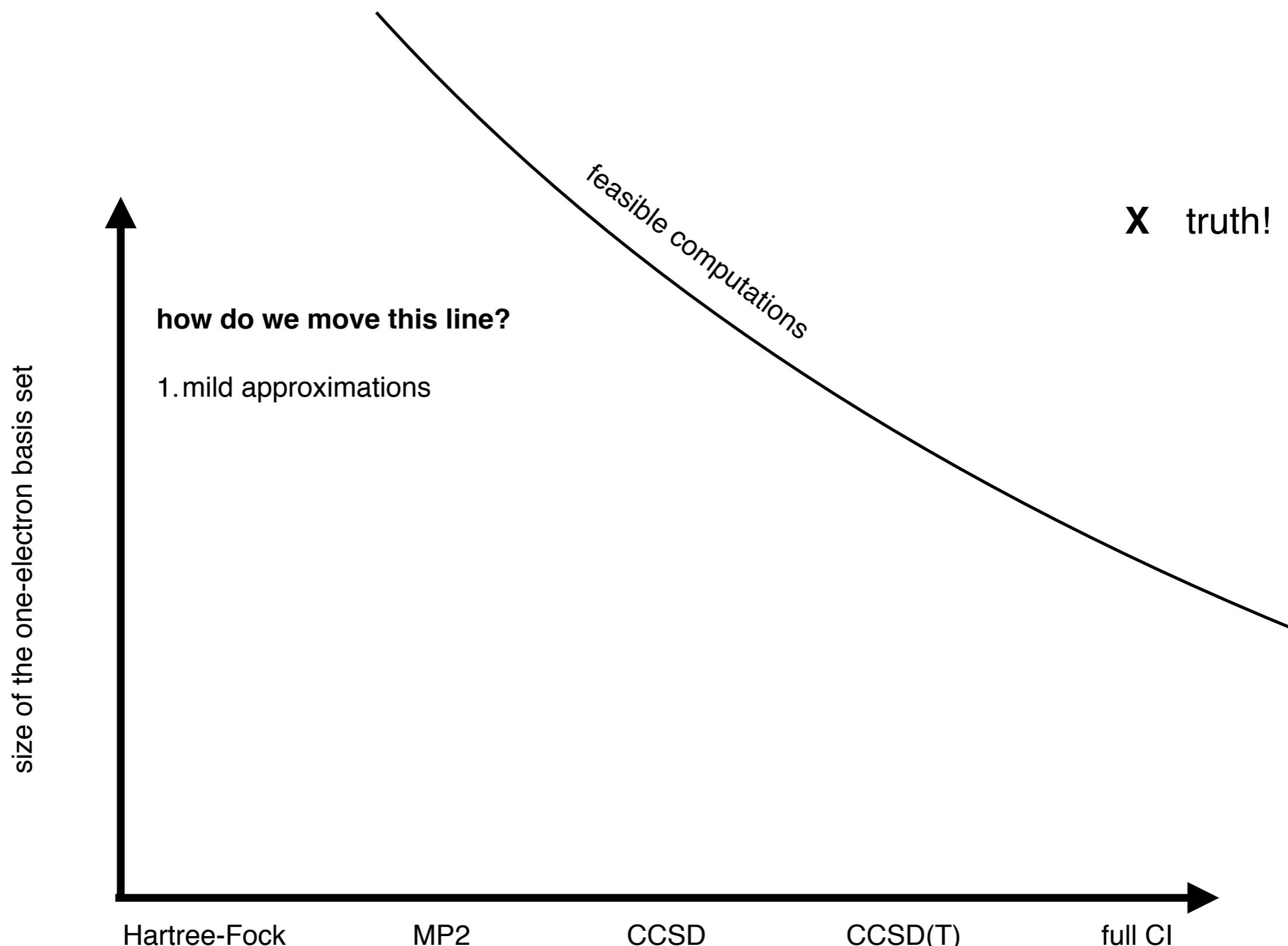
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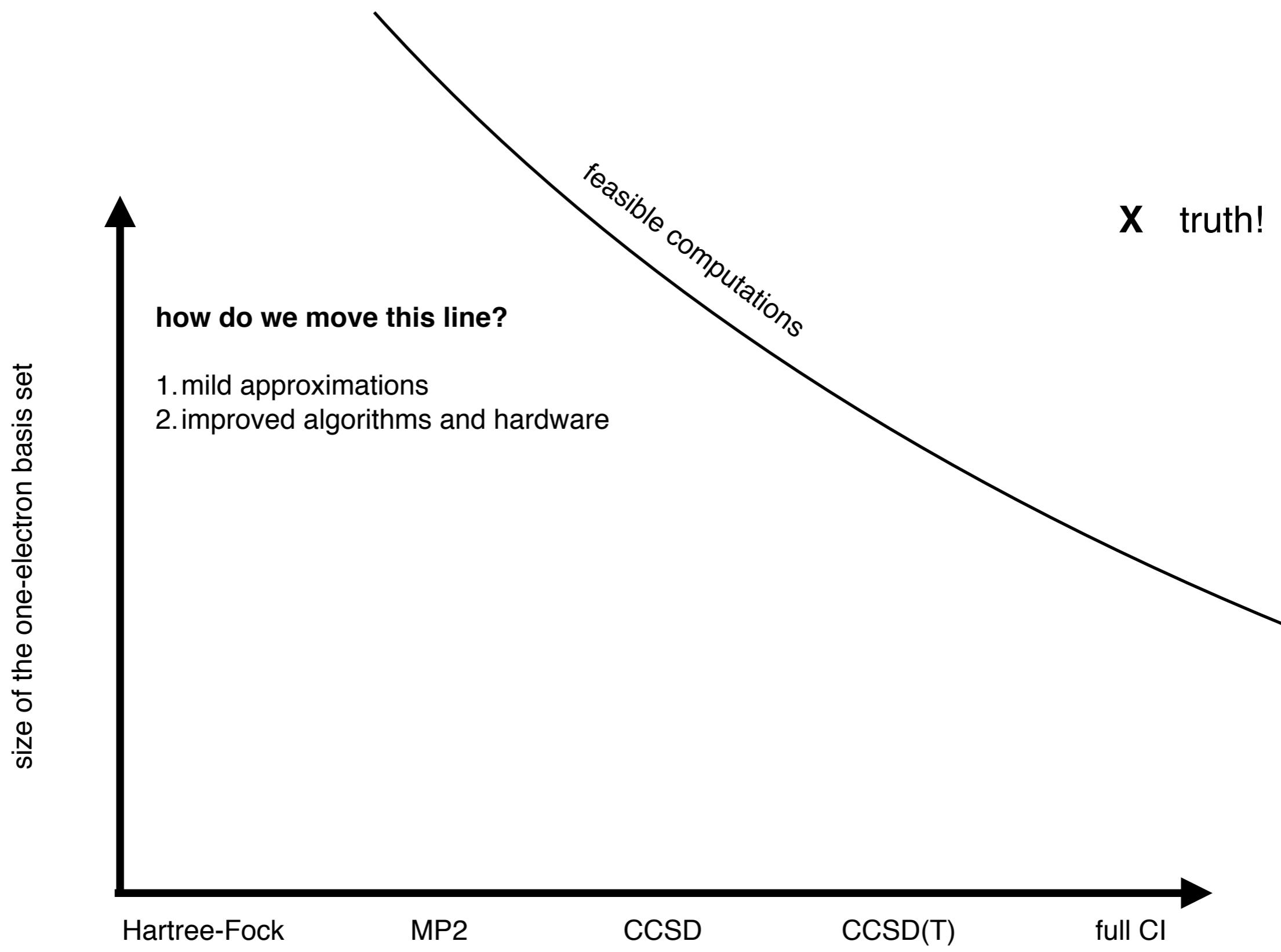


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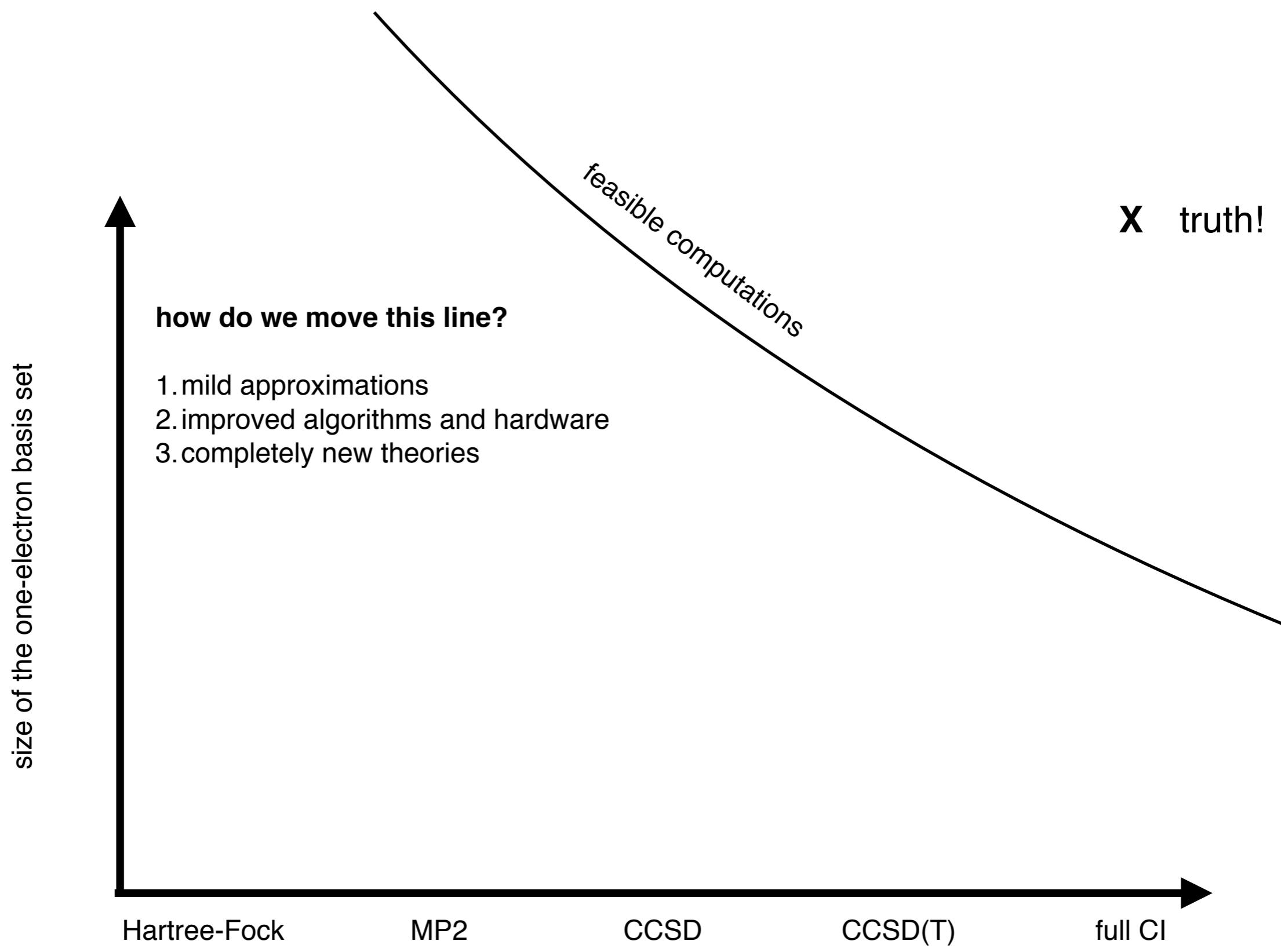
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