Advanced Electronic Structure Theory

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Overview

These lectures introduce theoretical methods designed for computing electronic energies of molecular systems. You will learn about the challenges that electron correlation presents and the extent to which state-of-the-art techniques meet these challenges.

1.1 Exact conditions

1.2 Hartree-Fock Theory

1.3 Configuration Interaction Theory

2.1 Coupled-cluster Theory

2.2 Explicit electron correlation

2.3 Multi-reference Theory

Primary Goal

We aim to solve the electronic Schrödinger equation for as many of the particles involved in the processes under investigation as necessary/possible, to as high accuracy as necessary/possible

$$\hat{H}\Psi = E\Psi \qquad\qquad \Psi(\mathbf{r}_1, s_1, \ldots, \mathbf{r}_n, s_n)$$

$$\hat{H} = -\sum_i \frac{1}{2}\nabla_i^2 - \sum_{iI} \frac{Z_j}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\hbar = 4\pi\epsilon_0 = m_e = e = 1$$

This is a prerequisite for studying the thermodynamics and kinetics of the system (e.g. Transition State Theory or Direct Dynamics) and is often the starting point for more accurate treatments that incorporate relativistic and non-adiabatic effects.

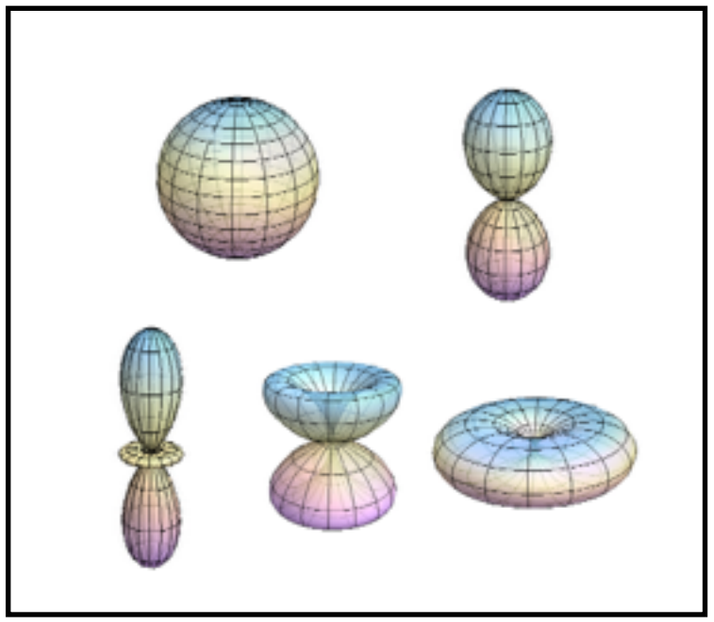
An exact solution : the hydrogen atom

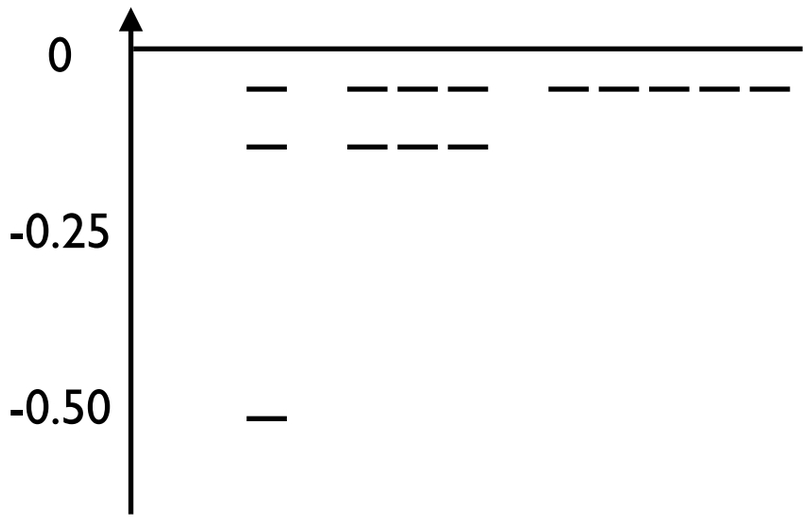
The Schrödinger equation for the H atom can be solved exactly using spherical polar coordinates.

The solutions are the atomic orbitals and have quantum numbers n,l,m_l,m_s which gives rise to the shell structure of excited states of hydrogen. The electronic wave function is the product of a spatial part (the AO) and a spin part for spin up or spin down electrons

$$\phi(\mathbf{r}, s) = \varphi(\mathbf{r})\sigma(s)$$

$1s$
$2s\ 2p$
$3s\ 3p\ 3d$
$4s\ 4p\ 4d\ 4f$
…





Exact conditions I

The exact wave function is also an eigenfunction of any operator that commutes with the Hamiltonian

$$\text{If} \quad \hat{H}\Psi = E\Psi \quad \text{and} \quad [\hat{A}, \hat{H}] = 0, \quad \text{then} \quad \hat{A}\Psi = a\Psi$$

This includes:

- $\hat{S}^2$ Spin is a good quantum number $\hat{S}^2\Psi = S(S+1)\Psi$
- $\hat{S}_z$ $\hat{S}_z\Psi = M_s\Psi$
- $\hat{C}_n, \hat{\sigma}_v \ldots$ Molecular point group symmetry is obeyed
- $\hat{\pi}_\mu$ Fermionic antisymmetry is satisfied

Note: $\hat{H}$ is independent of spin and is invariant to permutations among electron coordinates and among nuclear coordinates

$$\hat{H} = -\sum_i \frac{1}{2}\nabla_i^2 - \sum_{iI} \frac{Z_j}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Exact conditions 2

The local energy is constant $$E_{\rm loc}(\mathbf{r},\sigma) \equiv \frac{\hat{H}\Psi(\mathbf{r},\sigma)}{\Psi(\mathbf{r},\sigma)} = E$$

Aside: This still holds at points infinitesimally close to nodal planes where $\Psi(\mathbf{r},\sigma) = 0$

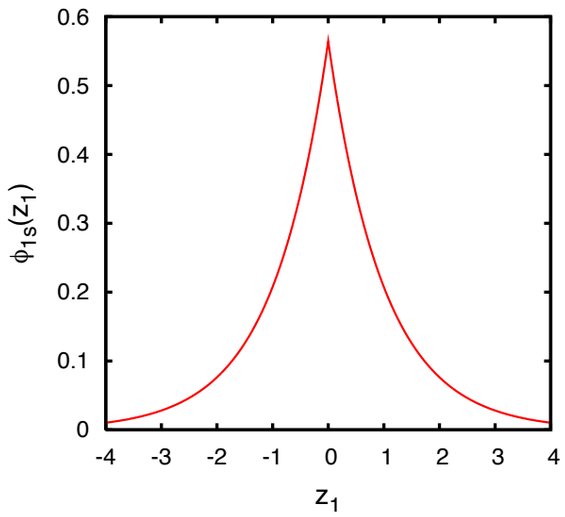
The Coulomb energy diverges when an electron and nucleus meet

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{Z_1}{|\mathbf{R}_1 - \mathbf{r}_1|} + \hat{O}\right)\Psi(\mathbf{r},\sigma)|_{\mathbf{r}_1=\mathbf{R}_1} = E\Psi(\mathbf{r},\sigma)|_{\mathbf{r}_1=\mathbf{R}_1}$$

The kinetic energy must exactly cancel this singularity.
This imposes a universal nuclear cusp condition:

$$\left.\frac{\partial\Psi}{\partial r}\right|_{r=0} = -Z\Psi_{r=0}$$

$$\Psi = \Psi_{r=0}(1 - Zr + \dots)$$



Exact conditions 3

Consider the regions where one electron is far away from the molecular framework and the rest are close. The wave function is then an antisymmetrised product of that of the *cation* and a *distant electron*

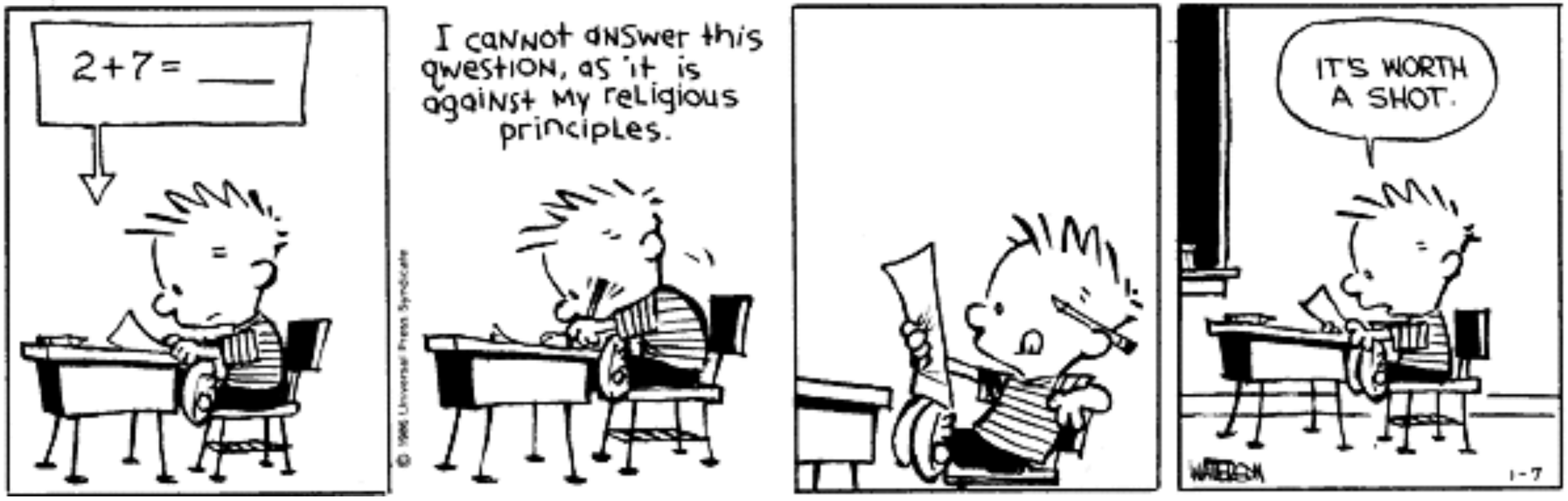
$$\Psi(\mathbf{x}) = \hat{A}[\Psi^e(\mathbf{x}_1)\Psi^{M^+}(\mathbf{x}_2 \ldots \mathbf{x}_n)]$$

The local energy is the sum of the energies of the cation and the distant electron

$$E = E^e + E^{M^+} \qquad \text{so} \quad E^e = E_{IP}$$

The long-range behaviour of $\Psi^e(\mathbf{x})$ is therefore that of a hydrogen-like $1s$ orbital with effective charge $\sqrt{2E_{IP}}$

$$\Psi^e(\mathbf{x}) \to e^{-\sqrt{2E_{IP}}\, r}$$


2+7= ___
I CANNOT ANSWER THIS QWESTION, AS IT IS AGAINST MY RELIGIOUS PRINCIPLES.
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IT'S WORTH A SHOT.
WATTERSON
1-7


HEY, DAD, WILL YOU BUY ME A FLAME THROWER?
OF COURSE NOT. DON'T BE SILLY.
WATTERSON
EVEN IF I DIDN'T USE IT IN THE HOUSE?

The variational principle and trial wave functions

According to the Rayleigh-Ritz variational principal the energy of a trial wave function is never below the exact energy.

$$E_{\text{exact}} \leq \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

In a numerical approximation the unknown n-electron exact wave function is expanded as a linear combination of known n-electron functions (n-electron basis functions).

$$\Psi = \sum_P C_P \Psi_P \qquad\qquad \Psi_P(\mathbf{r}_1, \ldots, \mathbf{r}_n, \sigma_1, \ldots, \sigma_n; \gamma)$$

The expansion has *linear expansion coefficients* C_P and the basis functions contain *non-linear parameters* γ . Either or both can be optimised by minimising the energy to obtain the best possible trial wave function using that set of functions.

Molecular Orbital Theory (Hartree-Fock)

By assuming that the electrons are independent, we approximate the n-electron wavefunction as a product of molecular orbitals.

The valid n-electron wave function satisfying Fermi antisymmetry is an antisymmetrised product of one-electron spin-orbitals

$$\Psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \cdots & \phi_n(1) \\ \phi_1(2) & \phi_2(2) & \cdots & \phi_n(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(n) & \phi_2(n) & \cdots & \phi_n(n) \end{vmatrix}$$

$$= \frac{1}{\sqrt{n!}} \hat{A}(\phi_1(1)\phi_2(2)\cdots\phi_n(n))$$

$$= |\phi_1\phi_2\cdots\phi_n\rangle$$

The theory that optimises the orbitals to minimise the energy is Hartree-Fock theory.

The HF energy

The HF orbitals are orthonormal $\langle\phi_i|\phi_j\rangle = \delta_{ij}$ so that $\langle\Psi|\Psi\rangle = 1$

The energy is therefore

$$E = \langle\Psi|\hat{H}|\Psi\rangle \quad = \langle\Psi|\sum_i \hat{h}_i|\Psi\rangle + \langle\Psi|\sum_{i<j} \hat{V}_{ij}|\Psi\rangle$$

It contains a one-electron term and a two-electron term

$$\hat{h}_i = -\frac{1}{2}\nabla_i^2 - \sum_I \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \qquad \hat{V}_{ij} = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} = \frac{1}{r_{ij}}$$

Using the Slater-Condon rules, the energy expression simplifies into integrals involving at most two orbitals at a time.

$$E = \sum_i \langle\phi_i|\hat{h}|\phi_i\rangle + \frac{1}{2}\sum_{ij}\langle\phi_i\phi_j|\hat{V}|\phi_i\phi_j - \phi_j\phi_i\rangle$$

The HF equations

Minimising the energy with respect to orthonormal orbitals leads to a set of coupled orbital equations, known as the Fock equations

$$(\hat{h} + \hat{J} - \hat{K})\phi_i = \epsilon_i \phi_i$$

where

$$\hat{J} = \sum_j \int d2\, \phi_j(2) r_{12}^{-1} \phi_j(2)$$ Coulomb operator

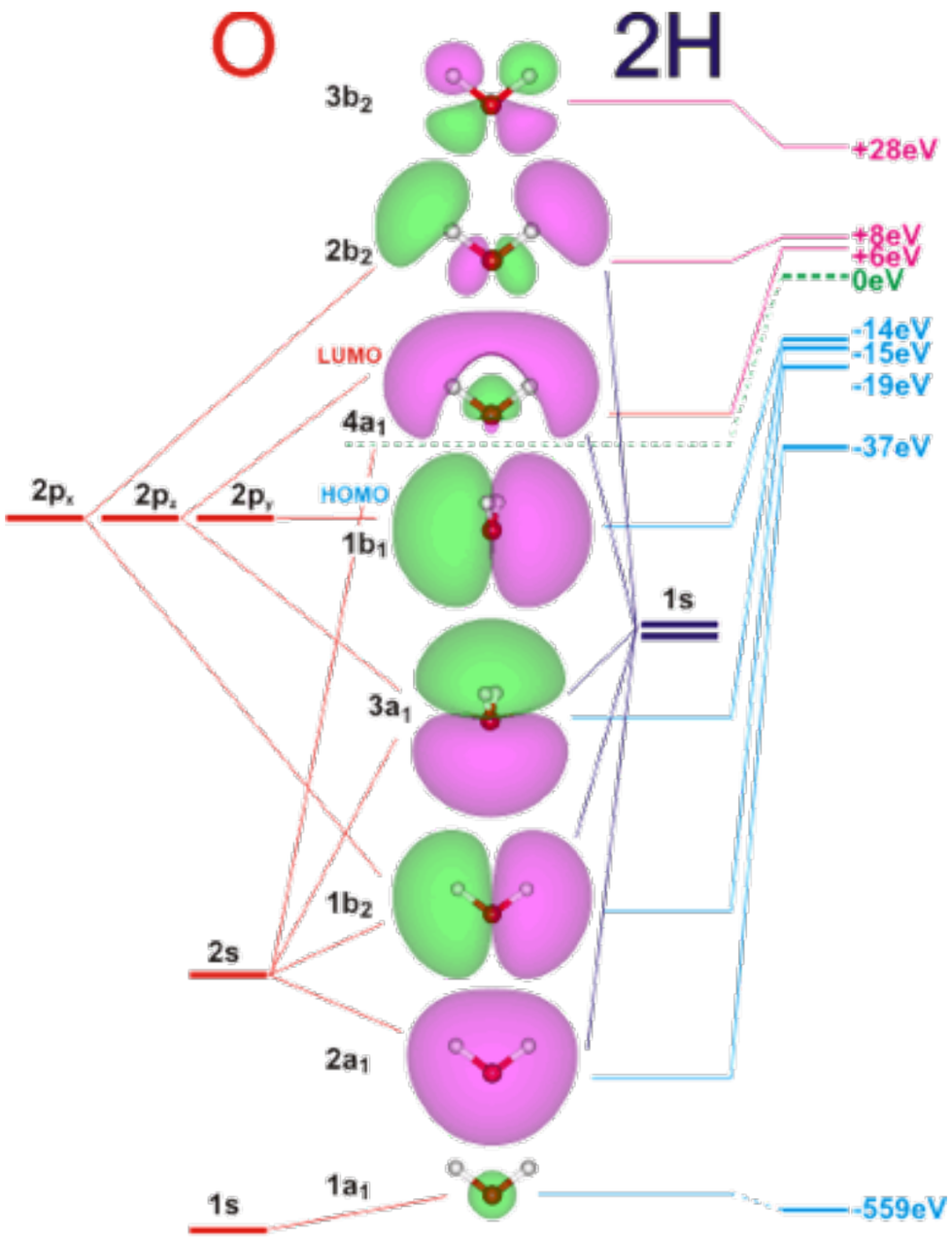
$$\hat{K} = \sum_j \int d2\, \phi_j(2) r_{12}^{-1} \hat{\pi}_{12} \phi_j(2)$$ Exchange operator

Each electron experiences an average potential from the others and the equations must be solved iteratively until self-consistency

The eigenvalues ϵ_i are the energies of the orbitals (MO theory)

MO theory

The HF orbitals and energies provide a qualitative description of bonding in molecules. E.g. water



Koopmans theorem:
The energy differences

$$\epsilon_a - \epsilon_i$$

are a good approximation to the excitation energies

Notation:
ϕ_i refers to an occupied MO
ϕ_a refers to an unoccupied MO

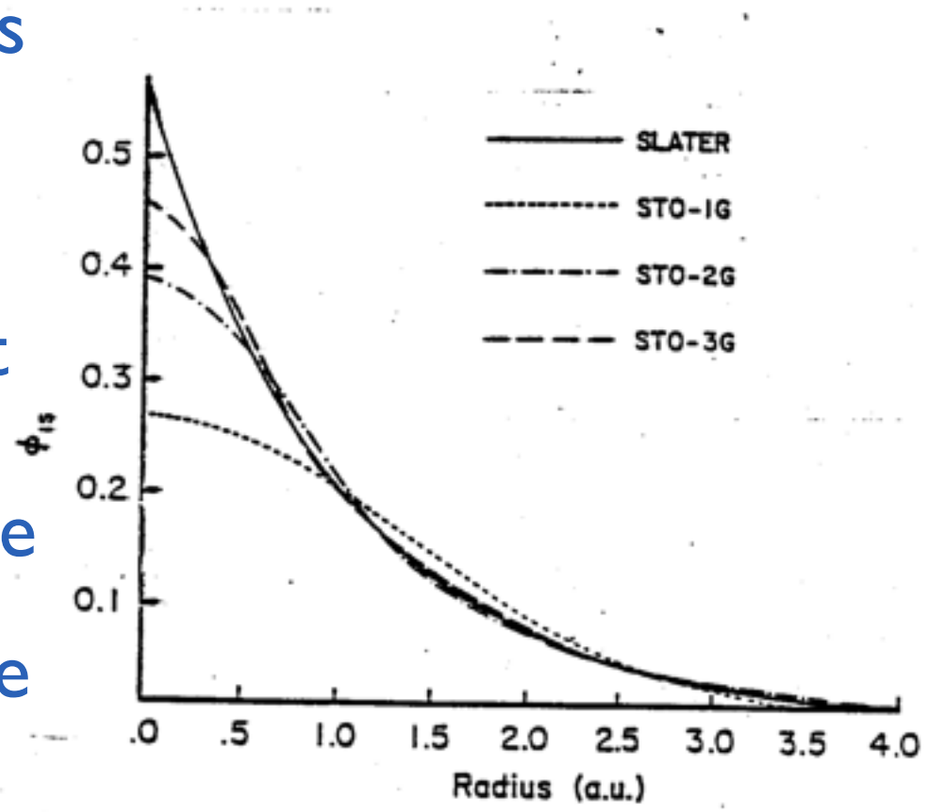
Gaussian-type orbital functions

The orbitals in HF theory are efficiently expressed as a linear combination of atom-centred Gaussian-type orbitals

$$\phi(\mathbf{r}) = \sum_{\mu} C_{\mu}\, \chi_{\mu}(\mathbf{r}) \qquad\qquad \chi^{I}_{nlm}(\mathbf{r} - \mathbf{R}_I) = e^{-\alpha_n r^2} Y_{lm}(\theta, \phi)$$

The index u labels the centre I, the exponent n and the angular function l,m

- Gaussian rather than Slater orbitals are chosen for computational convenience
- Atom-centred functions directly fit the nuclear cusp and can mimic polarised hydrogenic shell structure
- The expansion is formally complete (in fact over-complete if multiple atomic centres are involved)



Gaussian-type orbitals reproducing the hydrogen 1s orbital

Basis sets

We are in the very fortunate position that a number of people have spent an enormous amount of time and energy creating reliable basis sets for every element of the periodic table

SCF basis sets with Cardinal number X have X functions per occupied orbital e.g. for the C atom

DZ : 4s2p TZ : 5s3p QZ : 6s4p

To account for a non-spherical (molecular) environment, polarisation functions are added

DZ : 1d TZ : 2d1f QZ : 3d2f1g

To account for diffuse electron clouds (halogens and anions), the basis is augmented with 1 diffuse function per angular momentum

For post-HF calculations, correlation-consistent basis sets are recommended since they are an optimal compromise between HF and correlation requirements.

Convergence for one-electron systems and the IPM

The GTO expansion is rapidly converging.*

The error in the energy of one-electron systems decays exponentially with the number N of Gaussian functions,* and thus exponentially with the Cardinal number X of the basis set:

$$E(X) = E_{\text{exact}} + A\exp(-BX)$$

The error can thus be reduced through extrapolation

$$E_\infty = \frac{E_Y^2 - E_X E_Z}{2E_Y - E_X - E_Z} \qquad Y = X - 1 \qquad Z = X - 2$$

This exponential convergence is shared by all independent particle models (HF and DFT)

* if the exponents obey a well-tempered sequence

* Be careful! Use polarisation and diffuse functions when needed


UP, UP AND AWAY!
11-22
© 1986 Universal Press Syndicate
KWOOMPH!!
ACKK! KRYPTONITE! KRYPTONITE!
WATTERSON


LOVE THE SINNER HATE THE SIN
UH OH...
© 1993 Watterson Distributed by Universal Uclick
10-11

Electron correlation

In HF theory each electron responds only to the average potential of the other electrons (an independent particle model).

The wavefunction does not account for electron correlation arising from the instantaneous Coulombic repulsions.

- Too small dissociation energies (F_2 is not even bound)
- Much too high reaction barriers
- Dispersion effects completely missing
- Bond lengths 2 pm too short
- Frequencies 10% too large
- Dipole moments 10% too large

HF theory is often qualitatively correct, but inaccurate

Configuration Interaction Theory

The unknown n-electron exact wave function is expanded as a linear combination of known n-electron basis functions : SDs with all possible arrangements of the electrons the HF orbitals

$$\Psi = \sum_P C_P \Psi_P \qquad \Psi_P = |\phi_{P_1}\phi_{P_2}\ldots\phi_{P_n}\rangle$$

The *Secular Equations* that result from applying the variational principal to the CI wave function are particularly simple

$$\sum_Q H_{PQ}C_Q = E\sum_Q S_{PQ}C_Q$$

$$S_{PQ} = \delta_{PQ}$$

$H_{PQ} = 0$ if P and Q differ by more than 2 orbitals

The eigenvalues of H are the ground and excited electronic states

The matrix elements H_{PQ} are 2e-integrals, just like in HF theory

Slater Determinants

Slater Determinants are a very convenient choice for the n-electron basis functions.

$$\Psi = \sum_P C_P \Psi_P \qquad\qquad \Psi_P = |\phi_{P_1}\phi_{P_2}\ldots\phi_{P_n}\rangle$$

The index P labels which spin-orbitals are occupied in each SD function

Each n-elec. basis function individually obeys the exact conditions

- Is a pure spin state with definite S and M_s*
- Obeys the molecular point group symmetry
- Has full antisymmetric permutational symmetry

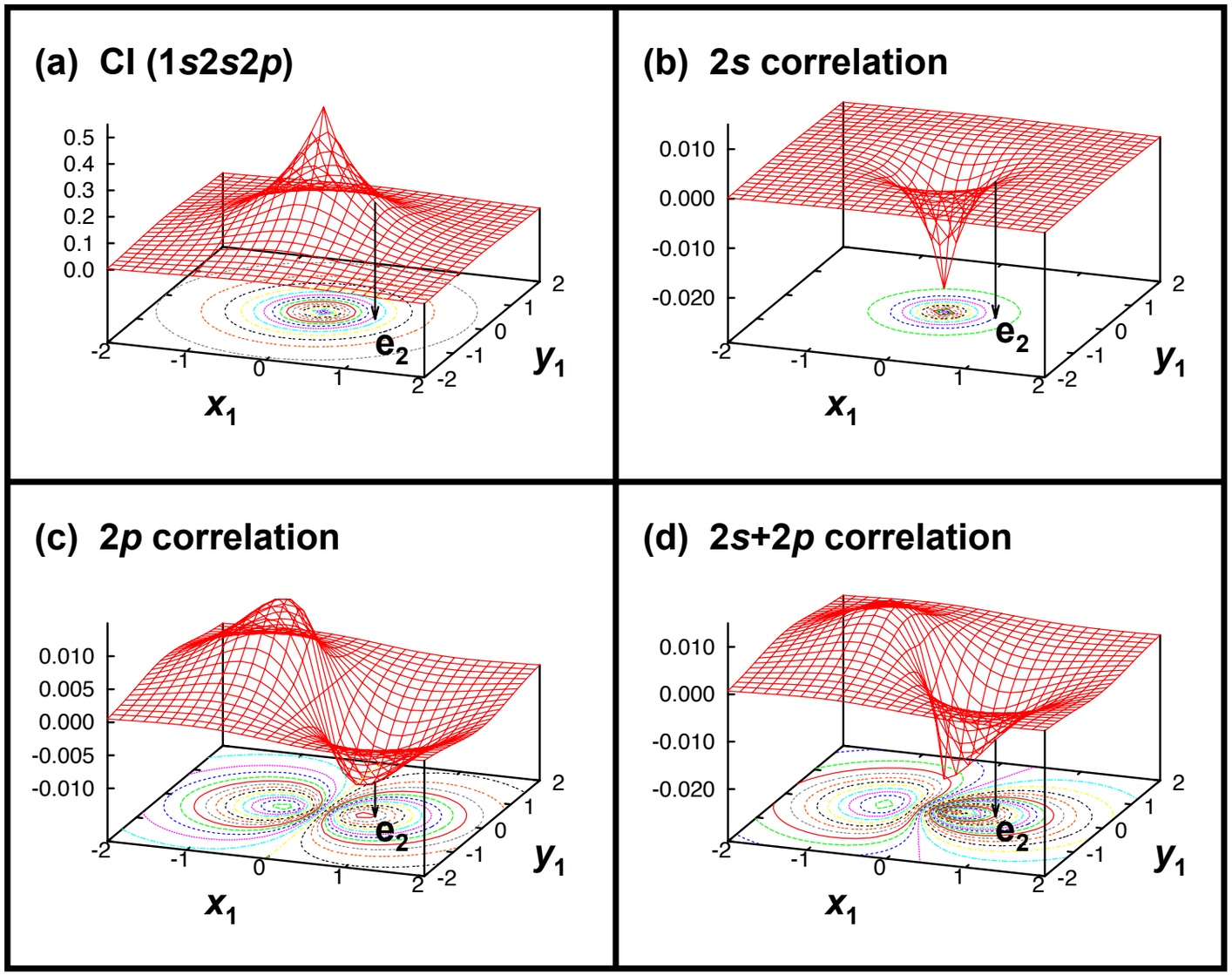
Moreover, an expansion in SDs is *complete* in the limit of a complete set of orbitals (the error can be made arbitrary small by increasing the number of functions in the expansion)

* Some spin states require specific combinations of SDs, called CSFs.

CI wavefunction for helium using 1s, 2s, 2p orbitals

The contribution from the 2s orbitals decreases the probability of the electrons being at the same radius : radial correlation

The contribution from the 2p orbitals decreases the probability of the electrons being on the same side : angular correlation



The cost of CI

Consider the example of the H_2O molecule in a TZVPP basis. There are 59 AOs, and therefore 59 MOs (5 occupied, 54 virtual).

Each configuration (10 electrons in 118 spin-orbitals) can be represented through an occupation number vector

$$\begin{array}{cc} \alpha & \beta \\ \phi_1, \phi_2, \phi_3, \phi_4, \phi_5, \phi_6, \phi_7, \phi_8, \phi_9, \cdots & \phi_1, \phi_2, \phi_3, \phi_4, \phi_5, \phi_6, \phi_7, \phi_8, \phi_9, \cdots \end{array}$$

$$|1,1,1,1,1,0,0,0,0,\cdots , 1,1,1,1,1,0,0,0,0,\cdots\rangle \quad \text{HF}$$

$$|1,1,1,1,0,1,0,0,0,\cdots , 1,1,1,1,1,0,0,0,0,\cdots\rangle \quad \text{1 excitation}$$

$$|1,1,1,1,0,1,0,0,0,\cdots , 1,1,1,1,0,0,1,0,0,\cdots\rangle \quad \text{2 excitations}$$

$$|0,1,0,1,0,1,1,0,1,\cdots , 1,0,1,1,0,0,1,1,0,\cdots\rangle \quad \text{5 excitations}$$

The total number of configurations is $\binom{59}{5} \times \binom{59}{5} = 2.5 \times 10^{13}$

Just storing one CI vector requires 200 Tb of memory!

Truncated CI

Assuming that the HF wavefunction is a good starting point, we can rank the configurations by their degree of difference from the HF reference C_0. Not all configurations are equally important.

Formally, this is revealed through a Krylov subspace expansion

$$K_m = \text{span}\{C_0, HC_0, H^2C_0, \ldots, H^{m-1}C_0\}$$

Since the Hamiltonian is a 2-body operator, HC_0 populates configurations with double excitations from HF. These describe pair correlations and are the most important configurations.

A further application of H generates singles, triples and quadruples, describing orbital relaxation, 3- and 4-electron correlations, etc.

CISD

Truncating the full configuration space to only include single and double excitations results in the CISD method. This wavefunction can describe pair correlations and orbital relaxations.

The CISD wavefunction is

$$|\mathrm{CISD}\rangle = C_0|\mathrm{HF}\rangle + \sum_{ia} C_a^i|_i^a\rangle + \sum_{i<j,a<b} C_{ab}^{ij}|_{ij}^{ab}\rangle$$

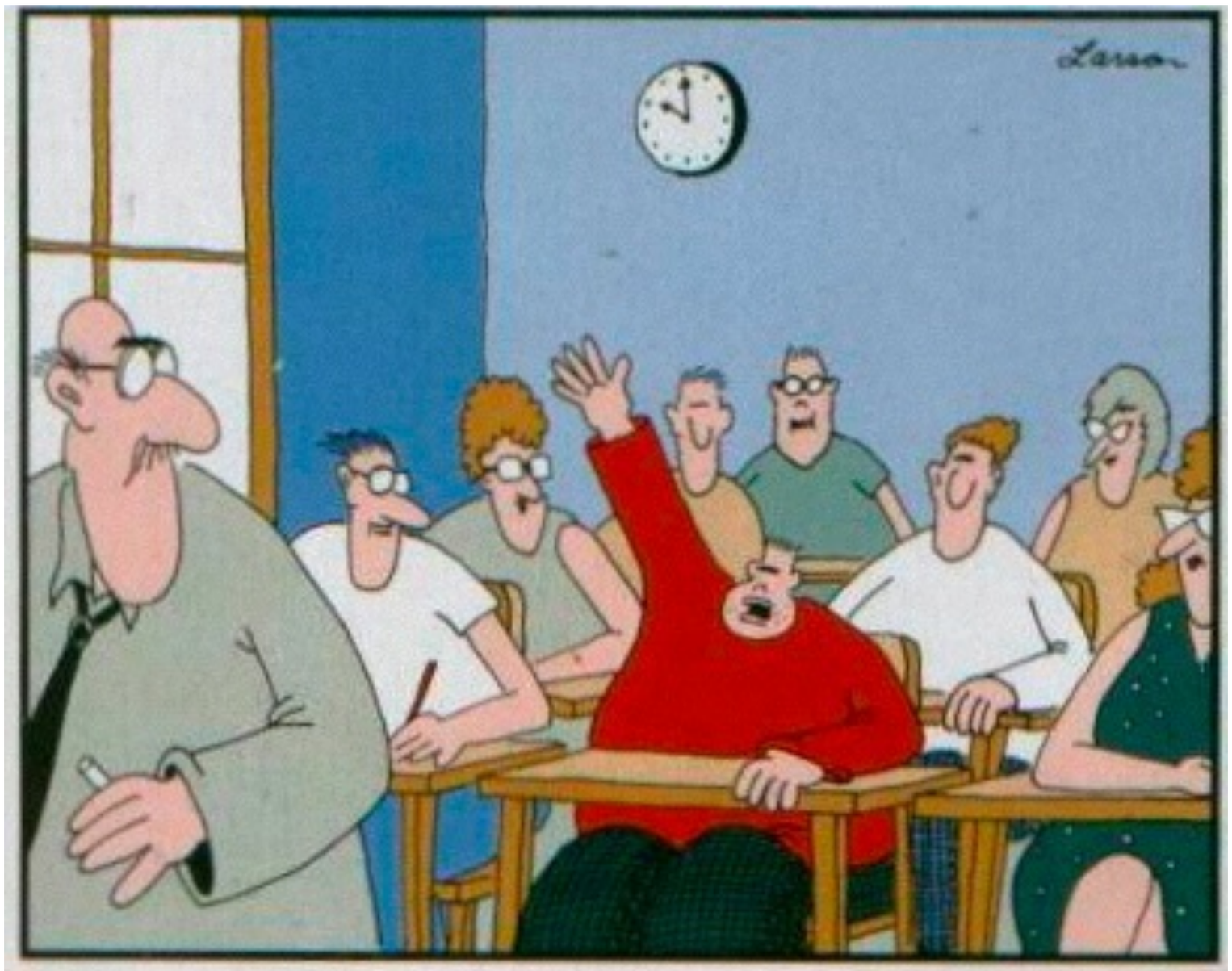
This is obviously extended to give CISDT, CISDTQ…

The same wavefunction in the language of second quantisation is

$$|\mathrm{CISD}\rangle = \left(C_0 + \sum_{ia} C_a^i a_a^\dagger a_i + \sum_{i<j,a<b} C_{ab}^{ij} a_a^\dagger a_b^\dagger a_i a_j\right)|\mathrm{HF}\rangle$$

Where the excitation operators generate a singly and doubly excited configuration from the HF reference

$$|_i^a\rangle = a_a^\dagger a_i|\mathrm{HF}\rangle \qquad |_{ij}^{ab}\rangle = a_a^\dagger a_b^\dagger a_i a_j|\mathrm{HF}\rangle$$



"Mr. Osborne, may I be excused?
My brain is full."

Coupled Cluster theory

In truncated CI theory, the wave function is expanded as e.g.

$$|\mathrm{CISD}\rangle = C_0|\mathrm{HF}\rangle + \sum_{ia} C_a^i|_i^a\rangle + \sum_{i<j,a<b} C_{ab}^{ij}|_{ij}^{ab}\rangle$$

In coupled cluster theory, the CI coefficients of the n-body excitations are generated as products of few-body excitations

$$|\mathrm{CCSD}\rangle = e^{\hat{T}_1+\hat{T}_2}|\mathrm{HF}\rangle$$

$$\hat{T}_1 = \sum_{ia} t_a^i a_a^\dagger a_i$$

$$\hat{T}_2 = \sum_{i<j,a<b} t_{ab}^{ij} a_a^\dagger a_b^\dagger a_i a_j$$

Three-body terms are generated from $\hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3$

Since the CC wave function contains excitations in all orbitals simultaneously, a variational treatment has the same cost as FCI.

Coupled Cluster theory in first quantisation

To better understand coupled cluster theory it is instructive to examine the CCD wave function for an example: helium dimer

He^A … He^B

$$|\mathrm{HF}\rangle = |1s^A_\alpha 1s^A_\beta 1s^B_\alpha 1s^B_\beta\rangle$$

$$\begin{aligned}|\mathrm{CCD}\rangle = {} & |1s^A_\alpha 1s^A_\beta 1s^B_\alpha 1s^B_\beta\rangle \\ & + |\theta^{AA}_{\alpha\beta} 1s^B_\alpha 1s^B_\beta\rangle - |\theta^{AB}_{\alpha\alpha} 1s^A_\beta 1s^B_\beta\rangle + |\theta^{AB}_{\alpha\beta} 1s^A_\beta 1s^B_\alpha\rangle \\ & + |1s^A_\alpha \theta^{AB}_{\beta\alpha} 1s^B_\beta\rangle - |1s^A_\alpha \theta^{AB}_{\beta\beta} 1s^B_\alpha\rangle + |1s^A_\alpha 1s^A_\beta \theta^{BB}_{\alpha\beta}\rangle \\ & + |\theta^{AA}_{\alpha\beta}\theta^{BB}_{\alpha\beta}\rangle - |\theta^{AB}_{\alpha\alpha}\theta^{AB}_{\beta\beta}\rangle + |\theta^{AB}_{\alpha\beta}\theta^{AB}_{\beta\alpha}\rangle\end{aligned}$$

- Every orbital pair $\phi_i\phi_j$ has a correlation function $\theta_{ij} = \sum_{a<b} t^{ij}_{ab}|ab\rangle$
- The wave function contains all possible products of orbitals and correlation functions
- The red terms are those *missing* from the CID wave function and ensure size extensivity:

$$|\mathrm{CCD}\rangle \overset{R=\infty}{\longrightarrow} |\mathrm{CCD}^A\rangle|\mathrm{CCD}^B\rangle$$

The CC working equations

The energy is obtained through projecting the SE with $\langle \mathrm{HF}|$

$$\hat{H}|\mathrm{CC}\rangle \approx E|\mathrm{CC}\rangle \quad \rightarrow \quad E_{\mathrm{CC}} = \langle \mathrm{HF}|\hat{H}|\mathrm{CC}\rangle$$

$$E_{\mathrm{CC}} = E_{\mathrm{HF}} + \sum_{ijab} (t_{ab}^{ij} + t_a^i t_b^j) L_{iajb}$$

This energy is not variational for truncated CC

The amplitudes are obtained through projection with $\langle {}_i^a | e^{-\hat{T}}$

$$\langle {}_i^a | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \mathrm{HF}\rangle = 0 \qquad \text{singles}$$

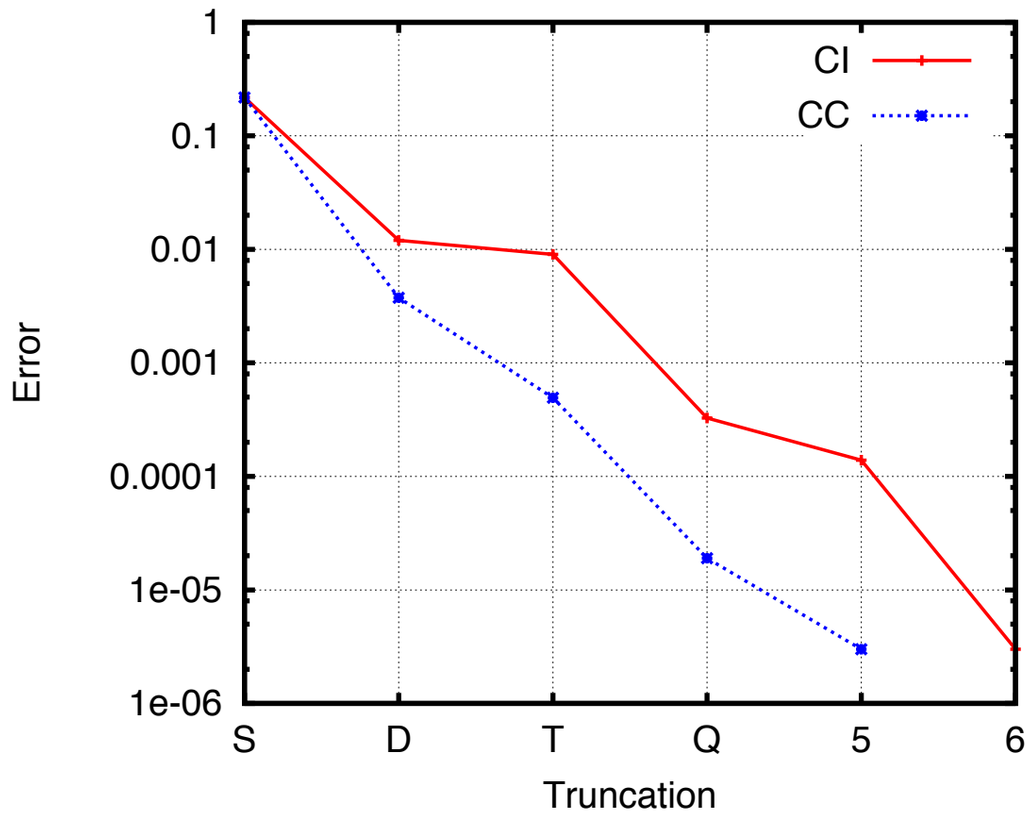
$$\langle {}_{ij}^{ab} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \mathrm{HF}\rangle = 0 \qquad \text{doubles}$$

$e^{-\hat{T}} \hat{H} e^{\hat{T}}$ is the similarity transformed Hamiltonian, which is

$$\hat{H} + [\hat{H}, \hat{T}] + \tfrac{1}{2}[[\hat{H}, \hat{T}], \hat{T}] + \tfrac{1}{6}[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}] + \tfrac{1}{24}[[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}], \hat{T}]$$

The amplitude equations are coupled 4$^{\text{th}}$ order polynomials

Convergence of the CI and CC hierarchies



Excitation	CI	CC
1,2-body	CISD	CCSD
3-body	CISDT	CCSDT
4-body	CISDTQ	CCSDTQ
5-body	CISDTQ5	CCSDTQ5

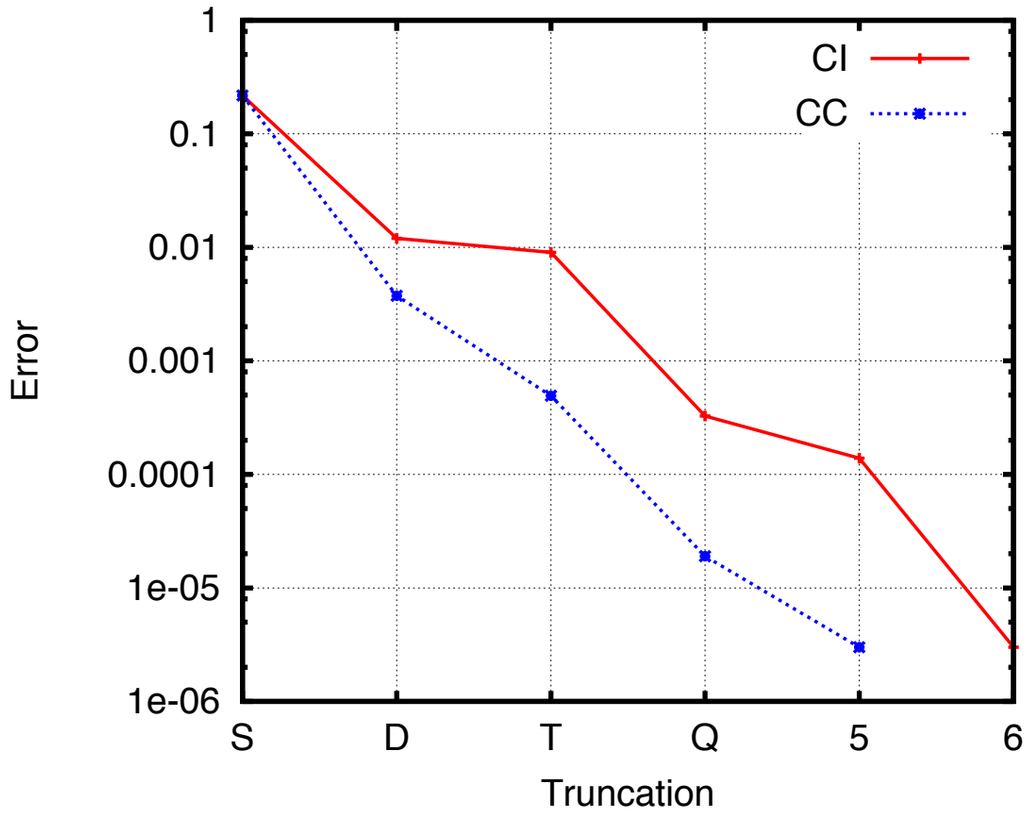
$$\Psi = \sum_P C_P \Psi_P \qquad \Psi = e^{\hat{T}} \Psi_0$$

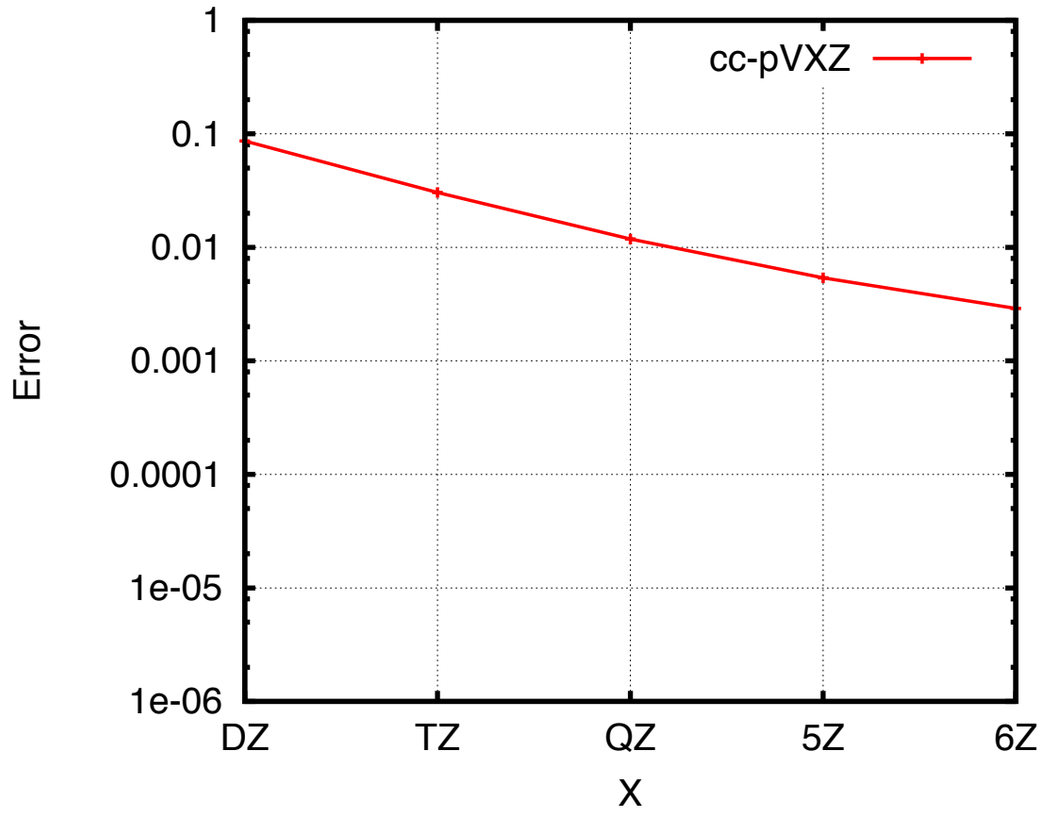
The CI and CC series provide a hierarchy of methods with increasing level of n-body correlation that converge to FCI, where *all* correlation effects are included (within a finite basis set).

The convergence is *exponential* if the IMP is a good starting point.

* plot of error (E_h) w.r.t. FCI for H_2O using cc-pVDZ basis

Comparison of basis set error and truncation error





The *basis set incompleteness error* in the 2-body energy is larger than the error incurred by neglecting 3- and higher-body effects.

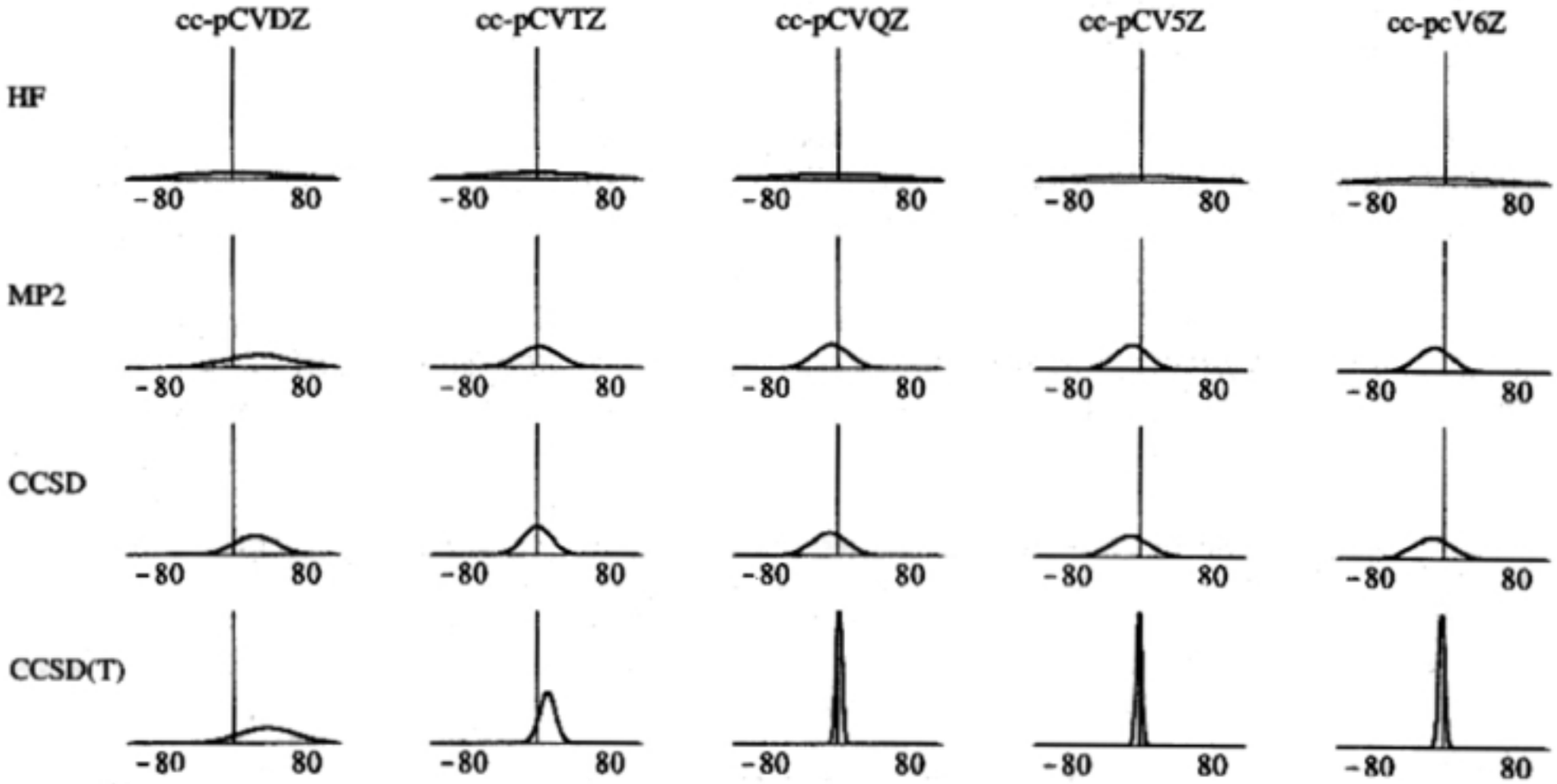
At least a cc-pV5Z basis is required to obtain accurate energies.

(cc-pVQZ for energy differences since is basis set errors cancel to a larger extent than truncation errors).

* plot of error (E_h) w.r.t. CCSD basis set limit for H_2O

Comparison of basis set error and truncation error

Error statistics (kJ/mol) w.r.t experiment for 14 reaction energies of small molecules involving main group elements.



(T) refers to a perturbative approximation to the triples energy

Large basis CCSD(T) calculations return accuracy of ~5 kJ/mol

Comparison to post-FCI contributions

An illustrative example

The electron affinity of oxygen 1.4611 eV

ΔT = CCSDT - CCSD (5Z)

ΔQ = CCSDTQ - CCSDT (TZ)

ΔP = CCSDTQP - CCSDTQ (DZ)

$\Delta CCSD$ = CCSD/CBS - CCSD (5Z)

CCSD	T	Q	P	EA	ΔCCSD	EA
1.2654	0.1727	0.0121	-0.0008	1.4495	0.0197	1.4692

- Mass-Velocity-Darwin (MVD) – 0.0024
- Spin-orbit coupling – 0.0059
- Electron-nucleus dynamic coupling (non-adiabatic effects) + 0.0001

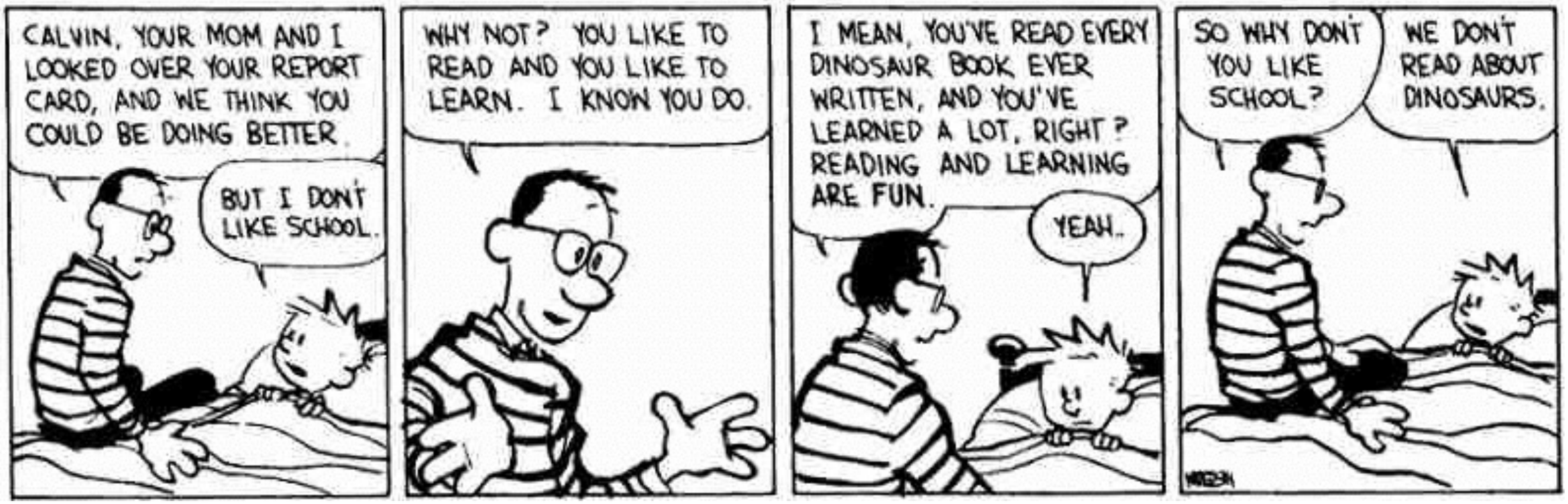
= 1.4610 eV

CCSD basis set incompleteness is larger than post CCSD(T) terms


ATCHOOO!


UH OH.

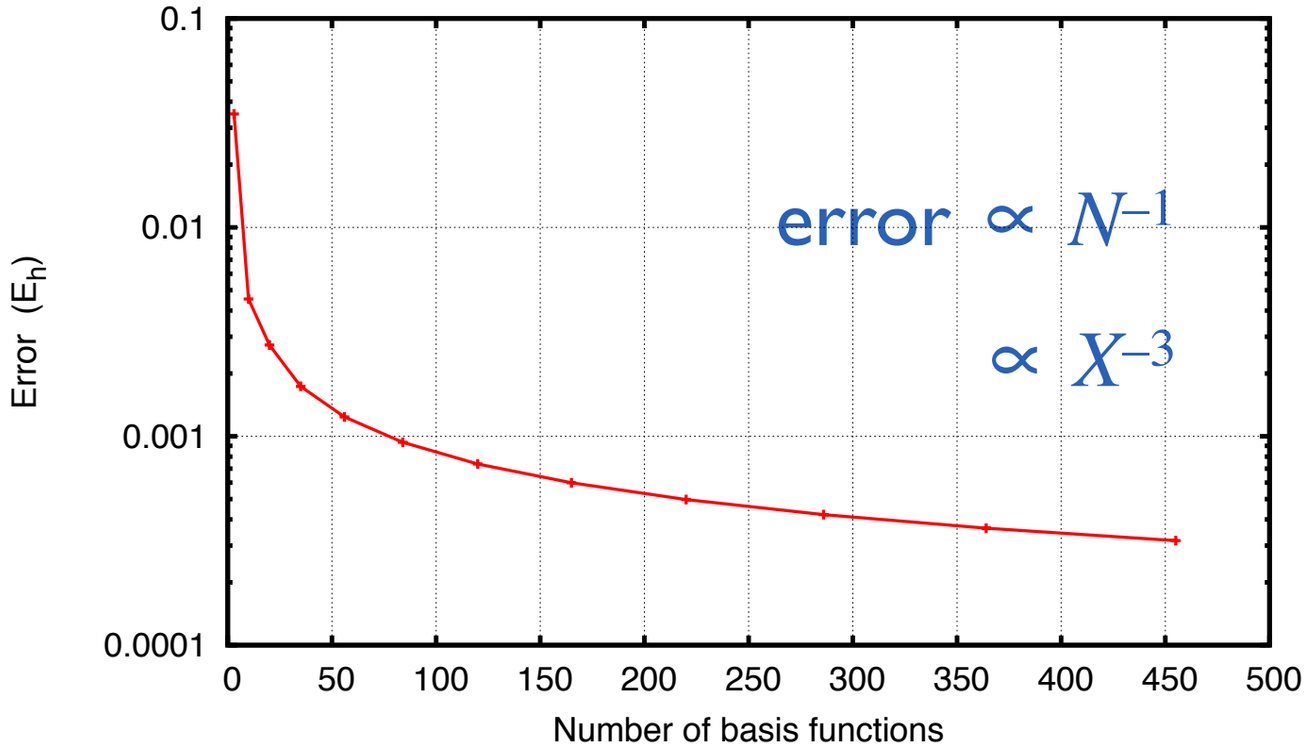

I'M LEAKING BRAIN LUBRICANT.


CALVIN, YOUR MOM AND I LOOKED OVER YOUR REPORT CARD, AND WE THINK YOU COULD BE DOING BETTER.
BUT I DON'T LIKE SCHOOL.
WHY NOT? YOU LIKE TO READ AND YOU LIKE TO LEARN. I KNOW YOU DO.
I MEAN, YOU'VE READ EVERY DINOSAUR BOOK EVER WRITTEN, AND YOU'VE LEARNED A LOT, RIGHT? READING AND LEARNING ARE FUN.
YEAH.
SO WHY DON'T YOU LIKE SCHOOL?
WE DON'T READ ABOUT DINOSAURS.

Electron correlation — lessons from helium

Although the SD expansion for two electron systems is formally complete, it is very slowly converging, even for helium

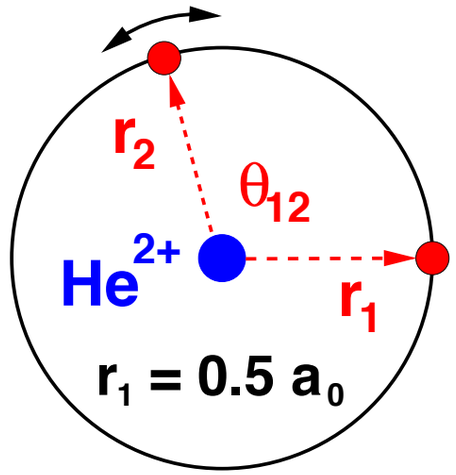
$$\Psi = \sum_P C_P \Psi_P \qquad \Psi_P = |\phi_{P_1} \phi_{P_2}\rangle$$

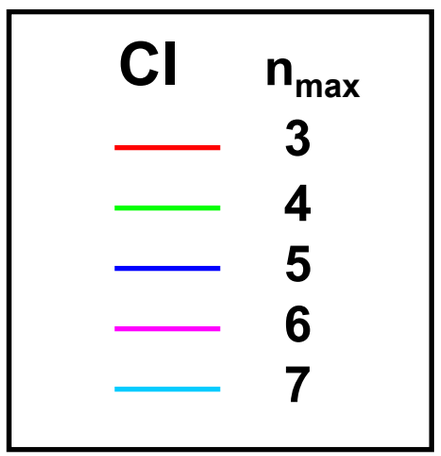


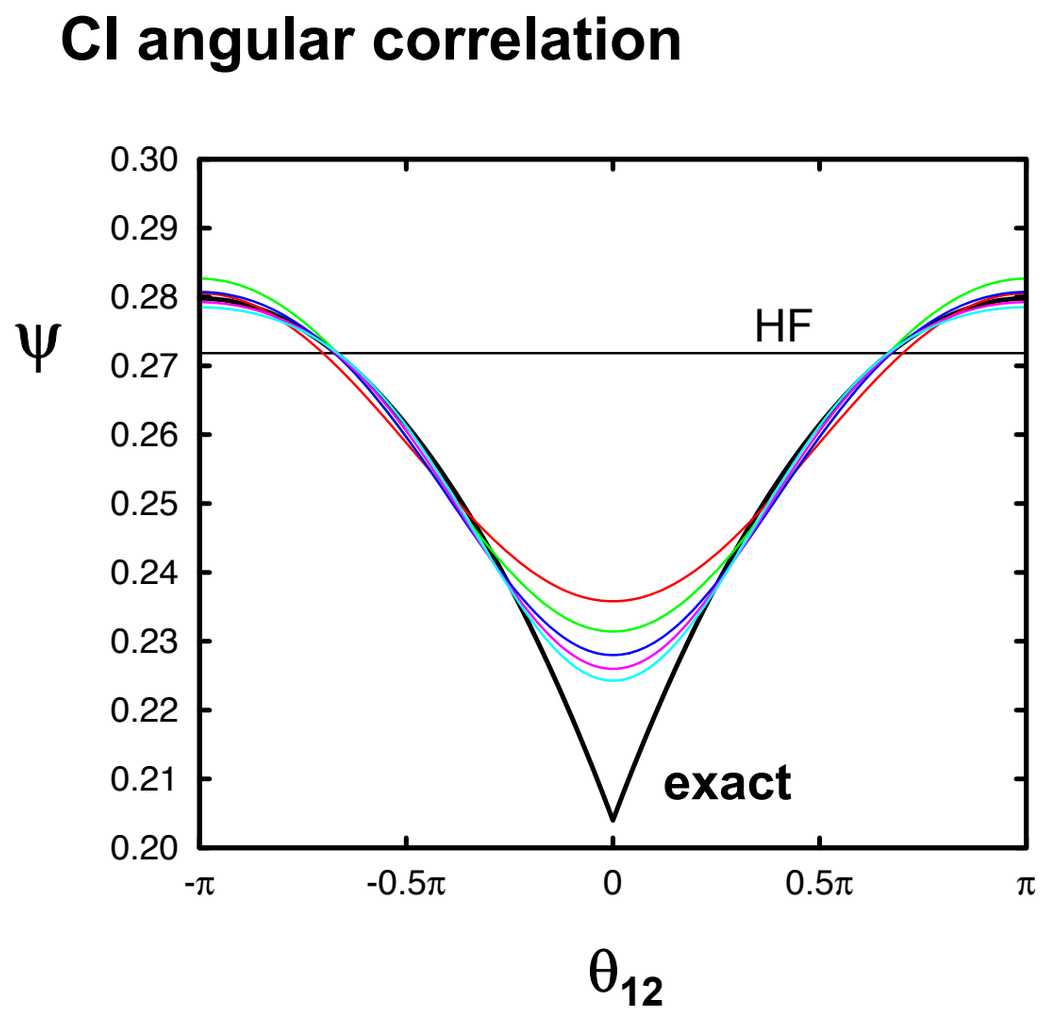
X	IP (eV)
D	24.152
T	24.496
Q	24.555
limit	24.591
exp.	24.587

Extrapolation : $$E_\infty = \frac{X^3 E_X - Y^3 E_Y}{X^3 - Y^3} \qquad Y = X - 1$$

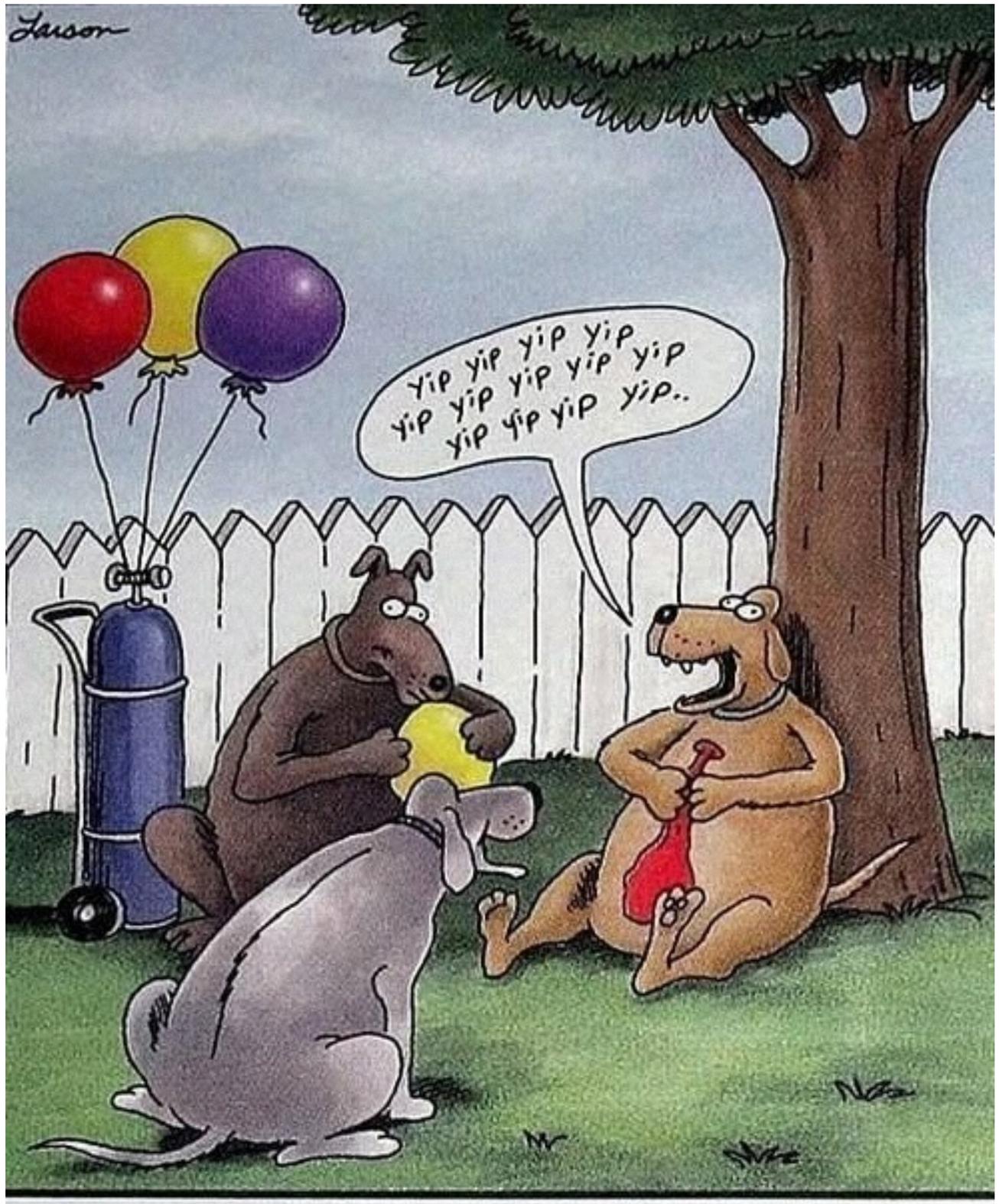
Electron correlation — lessons from helium







Consider a cut of the wave function where both electrons are at a radius of $0.5\ a_0$. The exact wave function has a *cusp* when the two electrons coalesce. The smooth orbitals used in the SD expansion are unable to represent this sharp correlation cusp efficiently.



Big dogs having fun with helium

R12/F12 theory

Kutzelnigg's observations:

1. Only the *short-range* part of the pair correlation function is problematic—the standard expansion is sufficient for the medium and long-range correlation.
2. The 3-, 4- and 5-electron integrals that arise can be *approximated* to sufficient accuracy using only 2-electron integrals by employing a RI technique.

In F12 theory the pair function is expanded as*

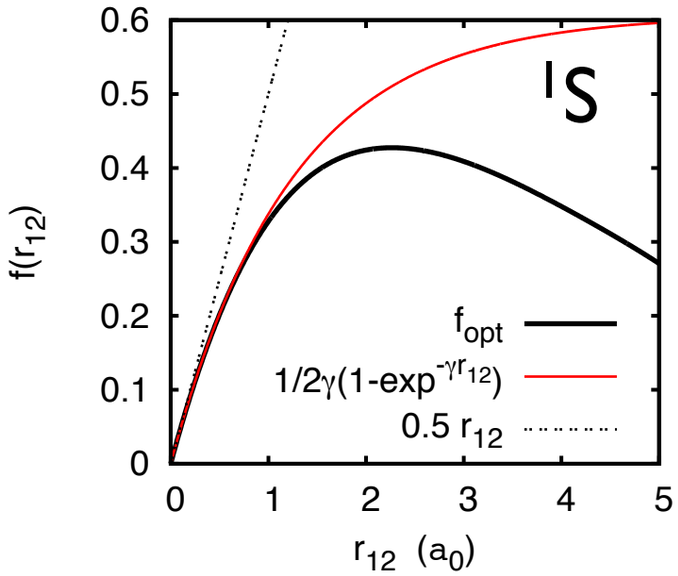
$$|\theta_{ij}\rangle = \sum_{ab} t_{ab}^{ij} |\phi_a \phi_b\rangle + \tfrac{1}{2}\hat{Q}_{12} f(r_{12}) |\phi_i \phi_j\rangle$$

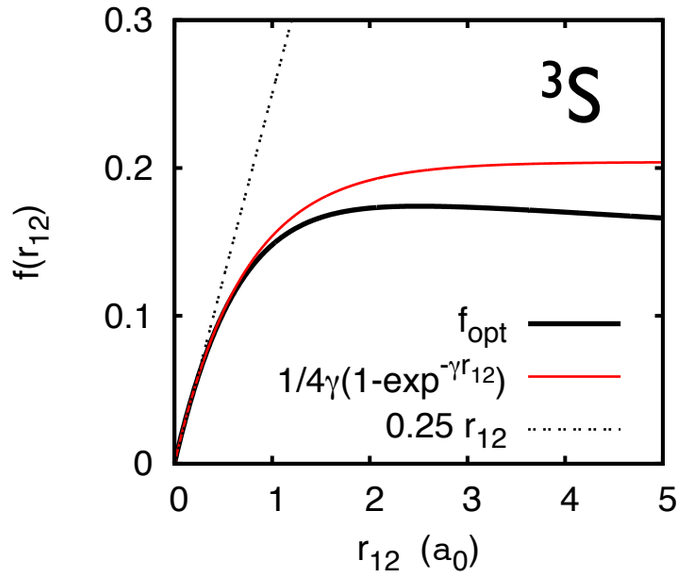
The standard orbital expansion is augmented with a *single fixed term* that explicitly satisfies the cusp ($\frac{1}{4}$ is used for triplet pairs).

* In the original R12 theory $f(r_{12}) = r_{12}$

The correlation factor $f(r_{12})$

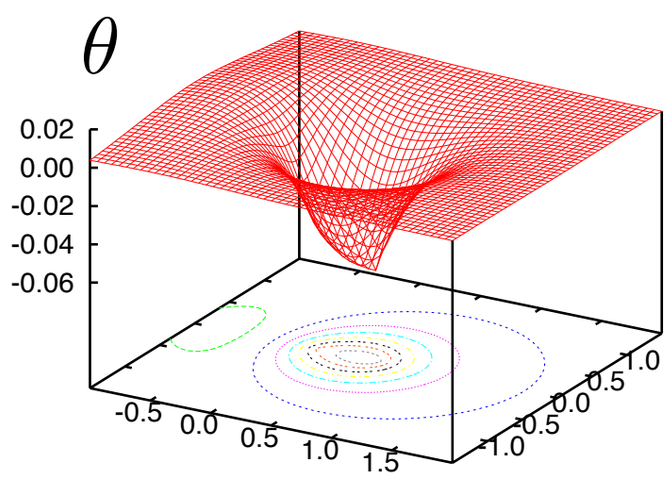
For ortho and para helium it is possible to compute the optimum correlation factor in $|\theta_{ij}\rangle = \sum_{ab} t_{ab}^{ij} |\phi_a \phi_b\rangle + \frac{1}{2}\hat{Q}_{12} f(r_{12}) \hat{S} |\phi_i \phi_j\rangle$

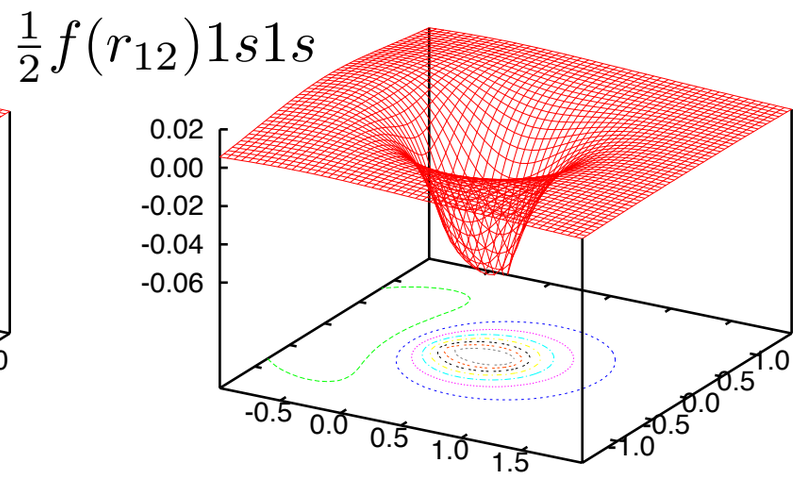


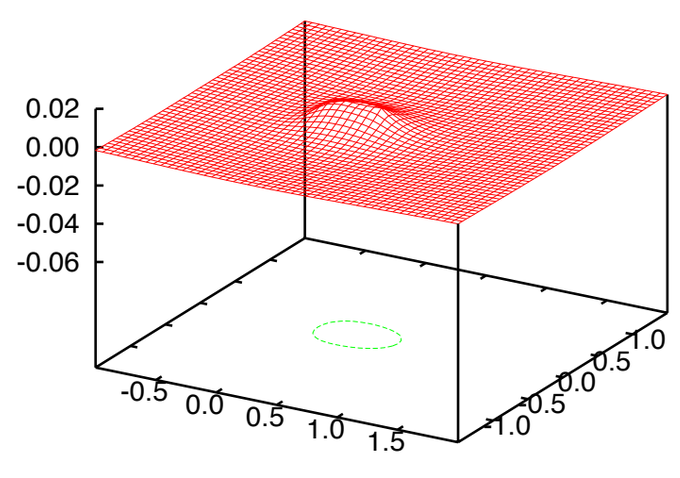


	γ
Valance	0.8-1.4
Core-Val.	1.8-2.6
Core	1.8-2.6

The function $\frac{1}{\gamma}(1 - e^{-\gamma r_{12}})$ reproduces the short- and medium-range correlation hole very closely. γ is a length-scale parameter.







F12 Theory

F12 doubles appear alongside standard doubles in the equations

$$|\text{CCSD-F12}\rangle = e^{\hat{T}_1+\hat{T}_2+\hat{T}_{2'}}|\text{HF}\rangle$$

$$\hat{T}_1 = \sum_{ia} t_a^i \hat{\tau}_i^a$$

$$\hat{\tau}_i^a|\text{HF}\rangle = |{}_i^a\rangle$$

$$\hat{T}_2 = \frac{1}{4}\sum_{ijab} t_{ab}^{ij} \hat{\tau}_{ij}^{ab}$$

$$\hat{\tau}_{ij}^{ab}|\text{HF}\rangle = |{}_{ij}^{ab}\rangle$$

$$\frac{1}{2}\sum_{\kappa\lambda} R_{\kappa\lambda}^{ij}\tau_{ij}^{\kappa\lambda}|\text{HF}\rangle = |{}_{ij}^{f_{12}}\rangle$$

$$\hat{T}_{2'} = \frac{1}{4}\sum_{ij\kappa\lambda} R_{\kappa\lambda}^{ij} \hat{\tau}_{ij}^{\kappa\lambda}$$

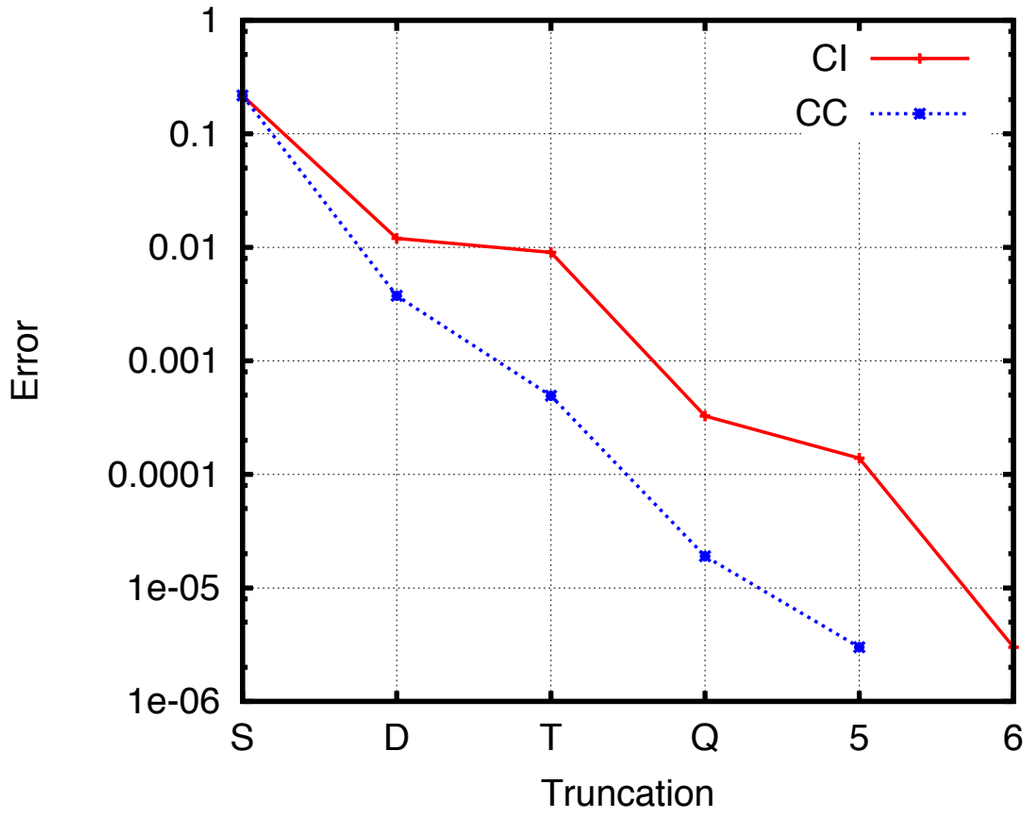
There are no additional amplitude equations, but the (non-zero) F12 residual is added as an energy correction (~Lagrangian)

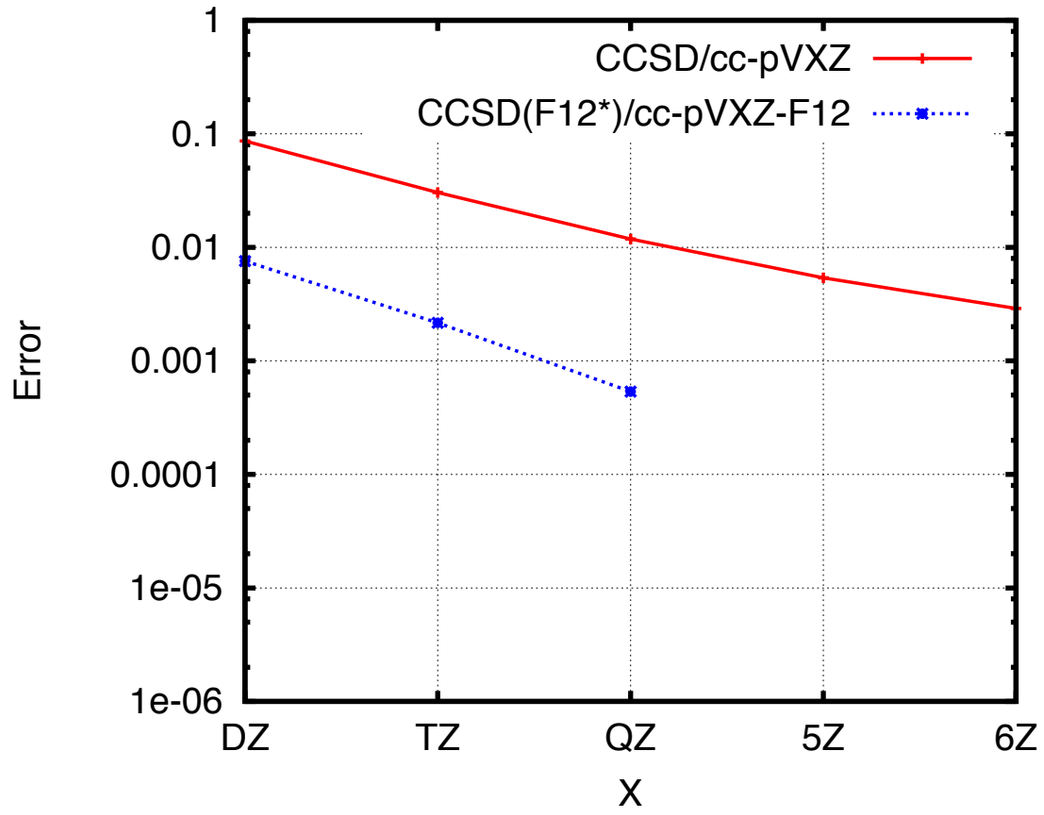
$$E_{\text{CC-F12}} = \langle\text{HF}|\hat{H}|\text{CC-F12}\rangle + \frac{1}{2}\sum_{ij}\langle {}_{ij}^{f_{12}}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\text{HF}\rangle$$

$\langle {}_i^a|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\text{HF}\rangle = 0$ singles

$\langle {}_{ij}^{ab}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\text{HF}\rangle = 0$ doubles

Performance





The *basis set incompleteness error* in the 2-body energy is now smaller than the error incurred by neglecting 3- and higher-body effects, even when small (cc-pVDZ-F12) basis sets are used.

CCSD(T)-F12 is now a standard method in quantum chemistry

TURBOMOLE, MOLPRO, DALTON, ORCA, GELLAN

Other explicitly correlated methods

Strategies for explicit r_{12} dependence in pair functions

- Use functions with simple integral formulae and introduce a high degree of flexibility
- Use physically motivated basis functions and rely on mathematical ingenuity for the many-electron integration

Method	Scaling	Accuracy	Max. Size
Hyl-CI	n!	nE_h	5 electrons
EGC	n!	nE_h	4 electrons
VMC	n^3	85% E_{corr}	500 atoms
DMC	n^3	90-98% E_{corr}	500 atoms
CCSD-GTG	n^7	uE_h	5 atoms
CCSD(T)/5Z	n^7	99.8% E_{corr}	10 atoms
CCSD(T)-F12/DZ	n^7	99.8% E_{corr}	30 atoms


WAP WAP WAP
CALVIN! WHAT ARE YOU DOING TO THE COFFEE TABLE?!?
*
IS THIS SOME SORT OF TRICK QUESTION, OR WHAT?
12-27


Oh please, oh please...
CAT FUD
CAT FUD
CAT FUD

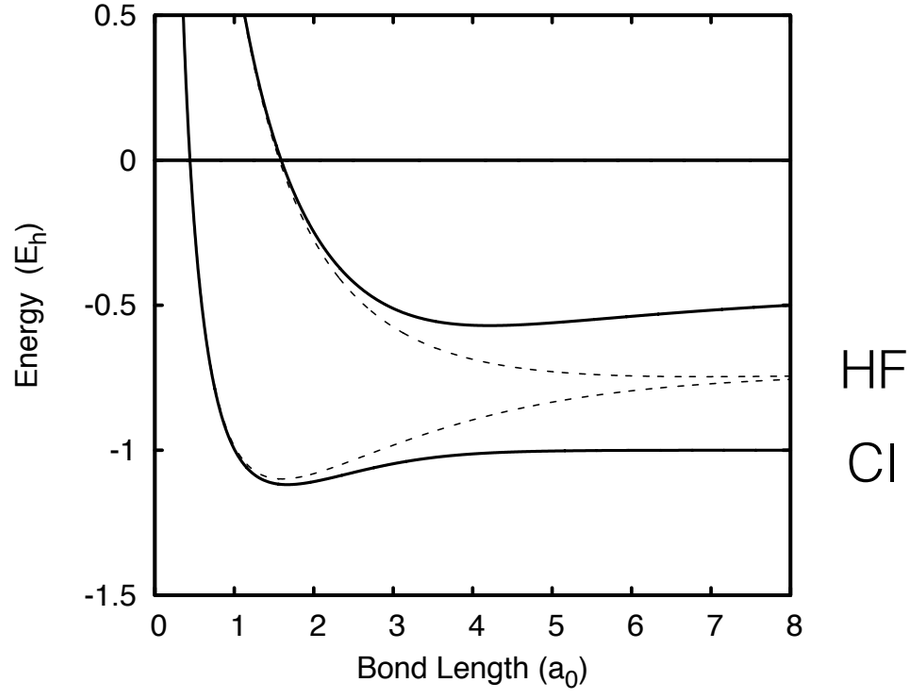
Strong correlation

The CCSD(T) method works well when the HF reference is a good starting point.

Consider the example of the H_2 molecule in the basis of $1s$ orbitals

$$|\mathrm{HF}\rangle = |\sigma_g \alpha \sigma_g \beta\rangle$$

$$|\mathrm{CI}\rangle = c_0 |\sigma_g \alpha \sigma_g \beta\rangle + c_1 |\sigma_u \alpha \sigma_u \beta\rangle$$

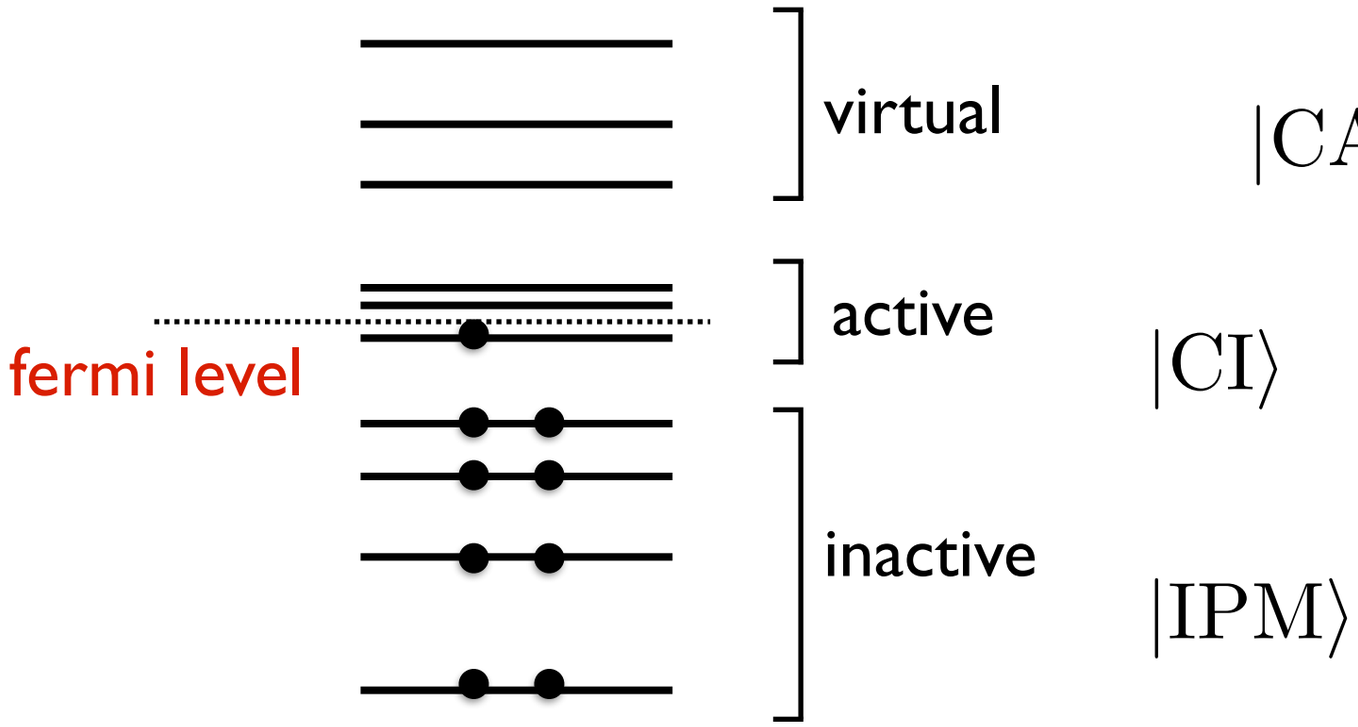


The HF reference is qualitatively wrong when there are two or more interacting states close in energy : strong correlation

prevalent in stretched bonds, transition metals, radicals

CASSCF

The generalisation of the HF method to the situation where more than one SD is required for a qualitatively correct description of the electronic structure is called complete active space self-consistent-field (CASSCF).



$$|\mathrm{CASSCF}\rangle = \hat{A}|\mathrm{CI}\rangle|\mathrm{IPM}\rangle$$

$|\mathrm{CI}\rangle$

$|\mathrm{IPM}\rangle$

A CI calculation is performed in the configurations of n active electrons in m active orbitals, with an associated optimisation of all of the orbitals involved. Scales exponentially with the size of the active space, but cubically with the size of the system.

DMRG and FCI-QMC

The CASSCF method is very appealing, but the pragmatic decisions imposed by the exponential cost of increasing the active space often makes it very difficult to define consistent orbital spaces across reaction pathways, particularly if several electronic states are traversed.

In Density Matrix Renormalisation Group (DMRG) the CI vector is approximated as a tensor train with one tensor per orbital, reducing cost of storage and manipulation

$$|\Psi\rangle = \sum_P C_P |P\rangle \qquad C_P \simeq \sum_{l_1,l_2,\ldots,l_m} C^1_{l_1} C^2_{l_2} \ldots C^m_{l_m}$$

In FCI-QMC, the CI vector is sampled by a Monte-Carlo dynamic where energies are extracted through time averaging

$$|\Psi\rangle \simeq \{|P\rangle\}_{\mathrm{av}}$$

Diffusion Monte Carlo

In DMC the Metropolis method is used to directly sample the *exact wave* function where the MC walkers follow the dynamics of the imaginary time Schrödinger equation:

Consider the time dependent Schrödinger equation

$$i\frac{\partial \Psi}{\partial t}(\mathbf{x},t) = \hat{H}\Psi(\mathbf{x},t)$$

The formal time-dependent solutions are

$$\Psi(\mathbf{x},t) = \sum_{n=0}^{\infty} C_n \Psi_n(\mathbf{x}) \exp(-iE_n t)$$

$$\hat{H}\Psi_n(\mathbf{x}) = E_n \Psi_n(\mathbf{x})$$

An arbitrary trial wave function is a linear combination of the time-independent eigenstates $\Psi_n(\mathbf{x})$, which rotate in the complex plane with a frequency proportional to E_n

Diffusion Monte Carlo

If we transform to imaginary time $\tau = it$ then

$$\frac{\partial \Psi}{\partial \tau}(\mathbf{x}, \tau) = -\hat{H}\Psi(\mathbf{x}, \tau)$$

$$\Psi(\mathbf{x}, \tau) = \sum_{n=0}^{\infty} C_n \Psi_n(\mathbf{x}) \exp(-E_n \tau)$$

As τ propagates in imaginary time the states all decay exponentially. Since excited states decay faster than the ground state, $\Psi(\mathbf{x}, \tau)$ collapses to the ground state!

Diffusion Monte Carlo is a stochastic realisation of the imaginary time-evolution. $\Psi(\mathbf{x}, \tau)$ is represented as a population of walkers that evolves with time according to the Hamiltonian

- Position representation : density of walkers maps to $\Psi(\mathbf{x}, \tau)$
- SD representation : density of walkers maps to $C_P(\tau)$ in

$$\Psi(\tau) = \sum_P C_P(\tau) \Psi_P$$

Diffusion Monte Carlo

Compare

$$\frac{\partial \Psi}{\partial \tau}(\mathbf{x}, \tau) = \frac{1}{2}\nabla^2 \Psi(\mathbf{x}, \tau) - V(\mathbf{x})\Psi(\mathbf{x}, \tau) \qquad \text{(I)}$$

$$\frac{\partial [A]}{\partial t}(\mathbf{x}, t) = D\nabla^2 [A](\mathbf{x}, t) - k[A](\mathbf{x}, t) \qquad \text{(II)}$$

The SE (I) is similar to the *diffusion equation* of a species A undergoing a *first order reaction* (II).

- $\Psi(\mathbf{x}, \tau)$ is equivalent to the concentration of the species
- $V(\mathbf{x})$ acts as a source or sink of species concentration

In FCI QMC, the equations become

$$-\frac{\partial C_i}{\partial \tau} = (H_{ii} - E_0 - S)C_i + \sum_{j \neq i} H_{ij} C_j$$

Diagonal Hamiltonian elements act as the source or sink and the off diagonal elements diffuse the population of walkers

Summary

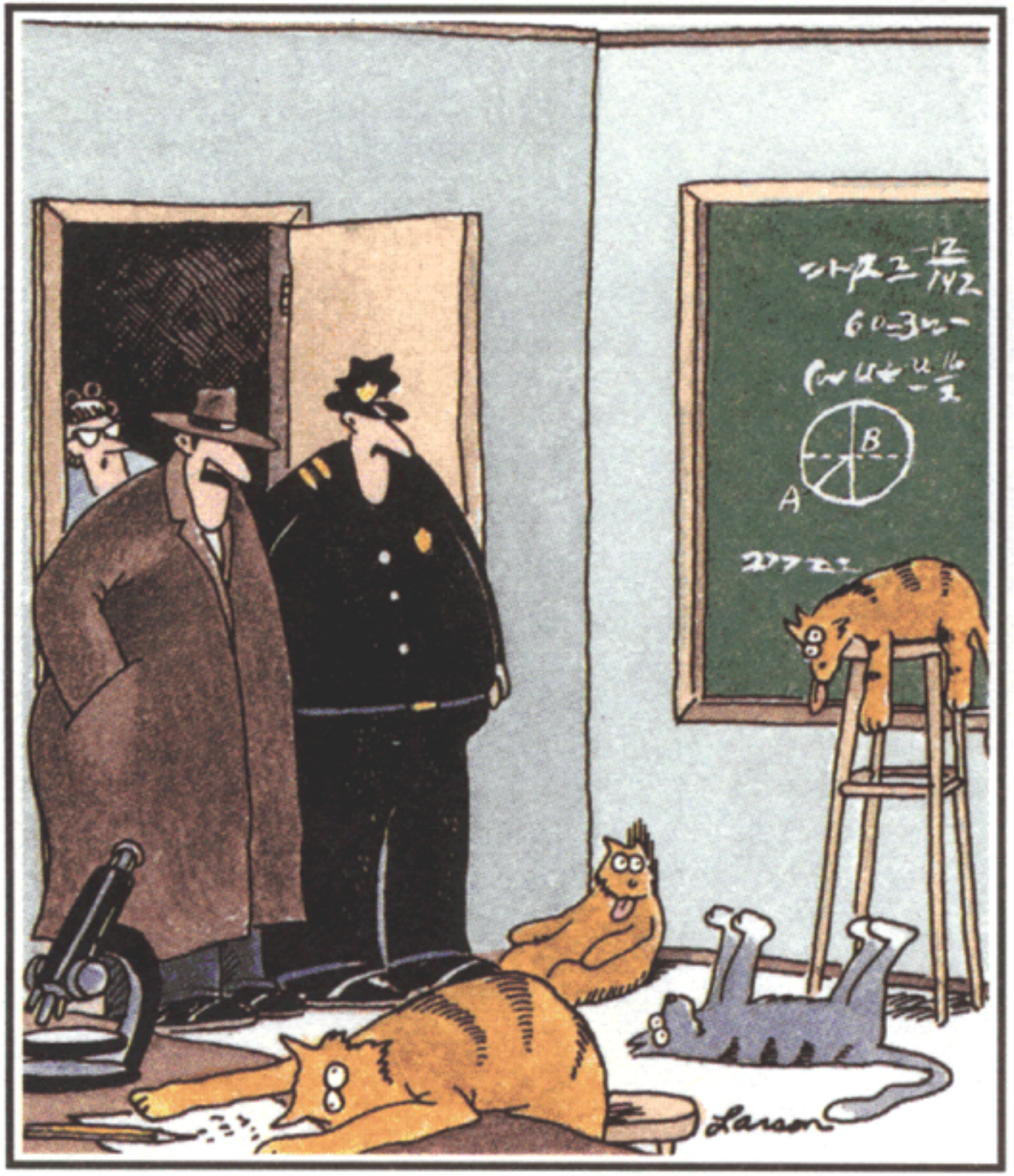
98+% of electronic structure calculations use DFT because it is cheap, often qualitatively accurate and implemented in many easy-to-use programs together with nuclear gradients and many other molecular properties.

When you want the right answer for the right reason, wave function methods can be used:

CCSD(T)-F12 for energies, gradients, molecular properties of molecules up to 30 atoms (linear scaling versions of this are under development for 200+ atoms)

CASSCF-based treatments for strongly correlated systems


GO AHEAD DOWN. YOU'LL MISS ALL THOSE TREES.
YOU CAN DO IT. YOU'LL STOP BEFORE YOU GO OVER THAT LEDGE AT THE BOTTOM.
YOU WON'T GO INTO THAT POND. BESIDES, THE ICE IS PROBABLY REAL THICK ANYWAY. GO AHEAD DOWN.
MY BRAIN IS TRYING TO KILL ME.
© 1987 Universal Press Syndicate
WATTERSON
1-9



"Notice all the computations, theoretical scribblings, and lab equipment, Norm. ... Yes, curiosity killed these cats."