Variational vs. Perturbational

$$\Psi = \sum_i c_i \Phi_i$$

$H\Psi = E\Psi \rightarrow \mathbf{HC} = \mathbf{EC}$

Linear Variational calculus

All in one step

$E_i \geq E_i^{exact}$

Variational Theorem

Simple/Stable/Big

$H = H^0 + V$

$H^0 \Psi^0 = E^0 \Psi^0$

$\Psi = \Psi^0 + \Psi^{(1)} + \cdots$

$E = E^0 + E^{(1)} + \cdots$

well defined order

no variational theorem

no guaranteed convergence

Perturbation Theory

$H = H^0 + V$ Start with ....

$H^0\Psi^0 = E^0\Psi^0$

$H = H^{0+} + \lambda V$ Expand H,Ψ and E in orders of λ

$\Psi = \Psi^{(0)} + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)} + \lambda^3\Psi^{(3)} + \cdots$

$$\left(H^0 + \lambda V\right)\left(\Psi^{(0)} + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)} + \lambda^3\Psi^{(3)} + \cdots\right) = \qquad \text{H}\Psi\text{=E}\Psi$$

$$\left(E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + \cdots\right)\left(\Psi^{(0)} + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)} + \lambda^3\Psi^{(3)} + \cdots\right)$$

λ 0 $H^0\Psi^{(0)} = E^{(0)}\Psi^{(0)}$ Gather terms with same power of λ

λ 1 $H^0\Psi^{(1)} + V\Psi^{(0)} = E^{(0)}\Psi^{(1)} + E^{(1)}\Psi^{(0)}$

λ 2 $H^0\Psi^{2)} + V\Psi^{(1)} = E^{(0)}\Psi^{(2)} + E^{(1)}\Psi^{(1)} + E^{(2)}\Psi^{(0)}$

......

λ 1 $H^0\Psi^{(1)} + V\Psi^{(0)} = E^{(0)}\Psi^{(1)} + E^{(1)}\Psi^{(0)}$

λ 2 $H^0\Psi^{(2)} + V\Psi^{(1)} = E^{(0)}\Psi^{(2)} + E^{(1)}\Psi^{(1)} + E^{(2)}\Psi^{(0)}$

λ 3 $H^0\Psi^{(3)} + V\Psi^{(2)} = E^{(0)}\Psi^{(3)} + E^{(1)}\Psi^{(2)} + E^{(2)}\Psi^{(1)} + E^{(3)}\Psi^{(0)}$

......

$E^{(1)} = \left\langle \Psi^{(0)} \middle| V \middle| \Psi^{(0)} \right\rangle$

$E^{(2)} = \left\langle \Psi^{(0)} \middle| V \middle| \Psi^{(1)} \right\rangle$ from λ=1,2,3 by left mult.
by $\Psi(0)$ and integrating

$E^{(3)} = \left\langle \Psi^{(0)} \middle| V \middle| \Psi^{(2)} \right\rangle$

$E^{(3)} = \left\langle \Psi^{(2)} \middle| V \middle| \Psi^{(0)} \right\rangle$ Hermitian and real

Check $E^{(1)}$ and $E^{(3)}$ **(3x)**

What causes it not to be an expectation value?

$V\Psi^{(0)} = -\left(H^0 - E^{(0)}\right)\Psi^{(1)} + E^{(1)}\Psi^{(0)}$ from λ=1

$E^{(3)} = \left\langle \Psi^{(2)} \middle| -\left(H^0 - E^{(0)}\right) \middle| \Psi^{(1)} \right\rangle + E^{(1)}\left\langle \Psi^{(2)} \middle| \cancel{\Psi^{(0)}} \right\rangle = \left\langle \Psi^{(1)} \middle| -\left(H^0 - E^{(0)}\right) \middle| \Psi^{(2)} \right\rangle$

$\left(H^0 - E^{(0)}\right)\Psi^{(2)} = E^{(1)}\Psi^{(1)} + E^{(2)}\Psi^{(0)} - V\Psi^{(1)}$ from λ=2

$E^{(3)} = \left\langle \Psi^{(1)} \middle| -\left(E^{(1)} - V\right) \middle| \Psi^{(1)} \right\rangle + \left\langle \Psi^{(1)} \middle| -\cancel{\left(E^{(2)}\right)} \middle| \Psi^{(0)} \right\rangle = \left\langle \Psi^{(1)} \middle| V - E^{(1)} \middle| \Psi^{(1)} \right\rangle$

Almost expectation value

For $E^{(3)}$, one requires $\Psi^{(1)}$; In general $\Psi^{(n)} \Rightarrow E^{(2n+1)}$

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How to find $\Psi^{(1)}$

$$\lambda = 1: \quad H^0 \Psi^{(1)} + V \Psi^{(0)} = E^{(0)} \Psi^{(1)} + E^{(1)} \Psi^{(0)}$$

$$\left(H^0 - E^{(0)} \right) \Psi^{(1)} = \left(-V + E^{(1)} \right) \Psi^{(0)}$$

$$\Psi^{(1)} = \frac{1}{\left(H^0 - E^{(0)} \right)} \left(-V + E^{(1)} \right) \Psi^{(0)}$$

$$Diagonal: \frac{1}{\begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}} = \begin{pmatrix} \frac{1}{a} & 0 & 0 \\ 0 & \frac{1}{b} & 0 \\ 0 & 0 & \frac{1}{c} \end{pmatrix}$$

Conjugate gradient

$$\Psi^{(1)} = \frac{1}{M} V' \Psi^{(0)}$$

$$\left(M + D - D \right) \Psi^{(1)} = V' \Psi^{(0)}$$

$$D \Psi^{(1)'} = -\left(M - D \right) \Psi^{(1)} + V' \Psi^{(0)}$$

$$\Psi^{(1)'} = \frac{1}{D} \left(D - M \right) \Psi^{(1)} + \frac{1}{D} V' \Psi^{(0)}$$

$$\Psi^{(1)'} = \Psi^{(1)} + \frac{1}{D} \left(V' \Psi^{(0)} - M \Psi^{(1)} \right)$$

Pre-conditioner

Residue

- Iterative

- D own choice
  Level shifting
  D→D+ Const

- Dim. M ~ CI

- possible use for
  eigenvectors

Use Conjugate Gradient for your own set of linear equations Does the convergence rate depend on the dimension? Conclusion ?

$$H^0 = \sum_i f(i)$$

Møller *Plesset*

$$V = H - \sum_i f(i)$$

Single Reference

Canonical H^0 (diagonal)

What is E_{MP0} ?

What is $E_{MP0} + E_{MP1}$

$$E^{(2)} = - \sum_{i<j}^{occ} \sum_{a<b}^{virt} \frac{\left| (ia|jb) - (ib|ja) \right|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}$$

What is interpretation of E_{MP2} ?

$$MP2 \sim n_{occ} n^4 \quad MP3 \sim n^5$$

$$MP4(SDQ) \sim n^6 \quad MP4(SDTQ) \sim n^7$$

$$MP5(SDTQ) \sim n^8 \quad MP4(SDTQ56) \sim n^9$$

Local MP2(Pulay, Werner)
non-diagonal

$$C_2H_4 + 2H_2 \rightarrow 2CH_4$$

From W.J.Hehre, L.Radom, P.v.R. Schleyer en J.A.Pople,
Ab Initio Molecular Orbital Theory , (Wiley, New York) (1986)
p. 91. Calculations are with 6-31G** basis at HF/6-31G* geometries.
Frozen core approximation used throughout. Exp 57.2 kcal/mol

Method	Energy Ethene (Hartree)	heat of reaction (kcal/mol)
Hartree-Fock	-78.03884	-64.0
MP2	-78.31682	-60.9
MP3	-78.33998	-62.4
MP4	-78.35306	-59.7

Improve on this

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Molecular Potential

$$H^0 = f \qquad V = -\frac{1}{r} + \sum_A \frac{Z_A}{r_A}$$

$$E(r) = \left\langle \Psi \left| \frac{1}{r} \right| \Psi \right\rangle + \sum_A \frac{Z_A}{R_A}$$

Energy of a positive charge
$\Rightarrow$ where an electrofiel attack
$\Rightarrow$ where a nucleofiel does not attack
Cheap => many points - color coded map (see MOLDEN)

Used in Computer Aided Drug Design + Density => repulsion

Multi-Reference Perturbation Theory

$$\Psi_0 = \sum_i^n c_i \Phi_i$$

Multi reference

CASPT2 (Roos) MRPT2
Size consistent
for proper choice of H^0

$$H^0 = |\Psi_0\rangle\langle\Psi_0| \left(\sum_i f(i)\right) \Psi_0\rangle\langle\Psi_0| + |S\rangle\langle S| \left(\sum_i f(i)\right) S\rangle\langle S| + \cdots$$

To get Eigenfunction

Size consistency errors for different choices of H^0 for O(^{3}P) ... O^{3}P (Huub van Dam)

CASCI		0.32532498
CASCI+Q		0.05535859
CASCEPA		0.02005912

Werner	CASMP2	-0.00034
	CASMP3	0.00084
$H0(1)$	CASMP2	-0.00046151
	CASMP3	0.00112953
$H0(2)$	CASMP2	-0.00023489
	CASMP3	0.00007136
$H0(3)$	CASMP2	0.00000000
	CASMP3	0.00000000

Convergence of MP series

If the excitation level is not raised a convergence study is quite possible
(H.J.J. van Dam, Thesis, Utrecht (1997)

Table I: Zeroth-order and first-order energies for single- and multi-reference calculations on the nitrogen molecule.

		$E^{(0)}$	$E^{(1)}$
		(hartree)	(hartree)
SR	$R = 2.1$ bohr	-70.91866361	-38.04781784
MR	$R = 2.1$ bohr	-70.38351456	-38.72366820
SR	$R = 5.0$ bohr	-69.62628236	-38.46756589
MR	$R = 5.0$ bohr	-67.38477070	-41.40496354

Figure III: MPPT calculations on H_2O in C_{2v} symmetry at R_{OH} is 0.967 Å and θ_{HOH} is 107.6°

SR PT SDCI-space
E=-76.012873 Hartree
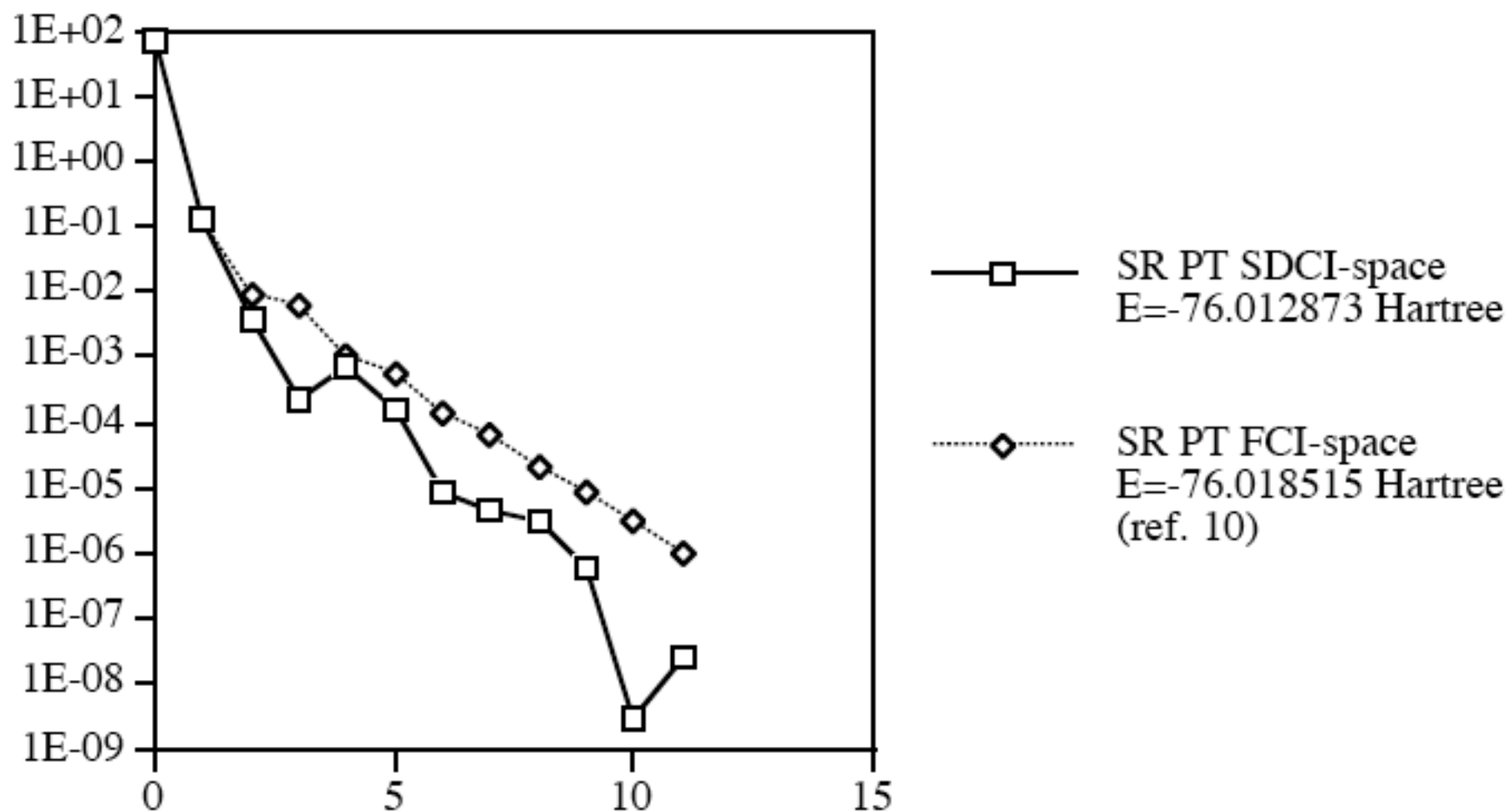
SR PT FCI-space
E=-76.018515 Hartree
(ref. 10)

Figure V: Convergence behaviour of the MPPT series of the nitrogen molecule at R_{NN} is 2.1 bohr

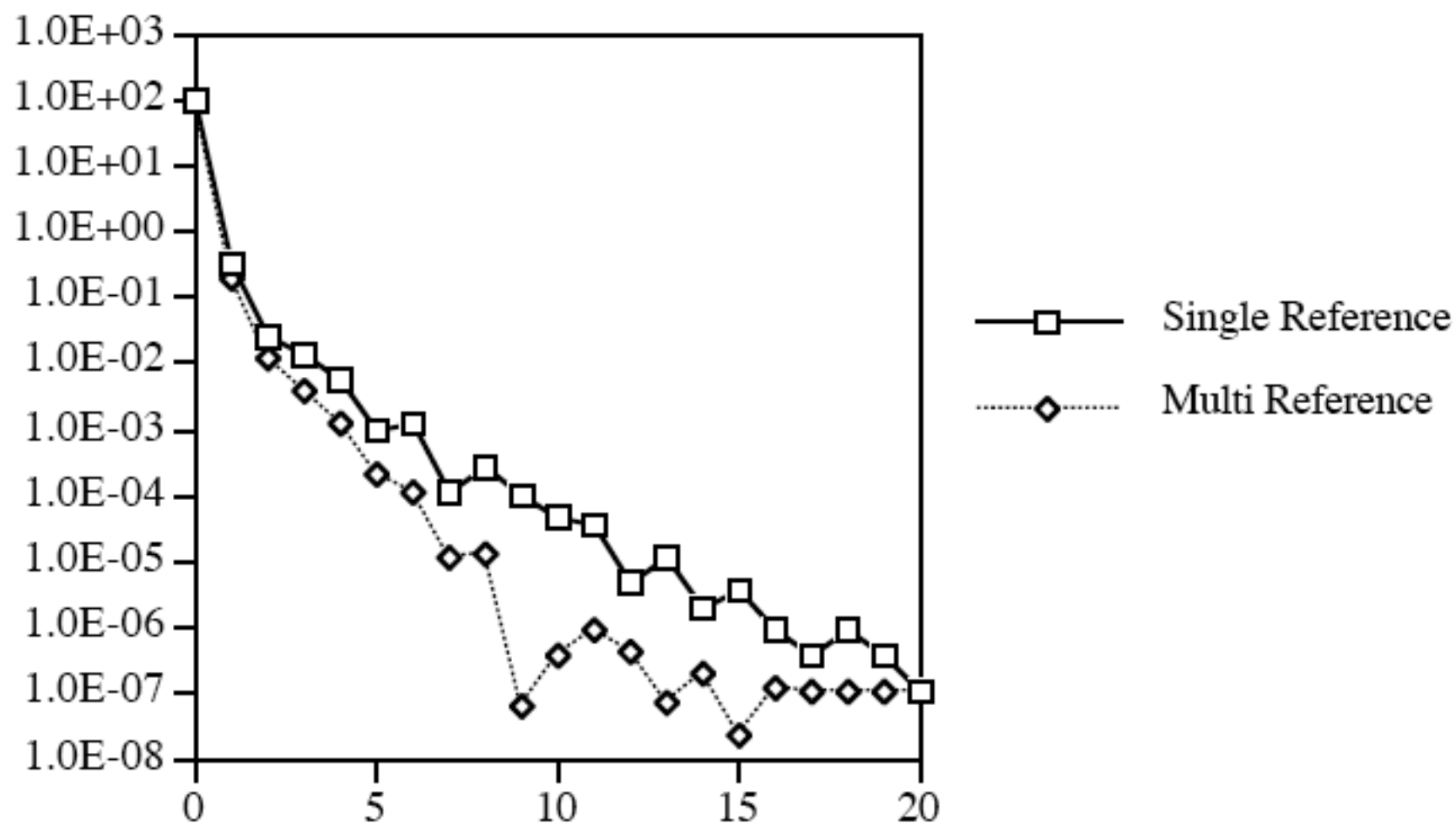**Figure VI:** Convergence behaviour of the MPPT series of the nitrogen molecule at R_{NN} is 5.0 bohr

Convergence3

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