

# Variational vs. Perturbational

$$\Psi = \sum c_i \Phi_i$$

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

Linear Variational calculus

All in one step

$$E_i \geq E_i^{exact}$$

Variational Theorem

Simple/Stable/Big

$$H = H^0 + V$$

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

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

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

well defined order

no variational theorem

no guaranteed convergence

# Perturbation Theory

$$H = H^0 + V \quad \text{Start with ....}$$

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

$$H = H^{0+} + \lambda V$$

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

Expand H,  $\Psi$  and E  
in orders of  $\lambda$

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

$$(E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + \dots)(\Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \lambda^3 \Psi^{(3)} + \dots)$$

$$\lambda^0 \quad H^0 \Psi^{(0)} = E^{(0)} \Psi^{(0)}$$

Gather terms with same power of  $\lambda$

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

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

.....

$$\begin{aligned} \lambda \ 1 \quad & H^0 \Psi^{(1)} + V \Psi^{(0)} = E^{(0)} \Psi^{(1)} + E^{(1)} \Psi^{(0)} \\ \lambda \ 2 \quad & H^0 \Psi^{(2)} + V \Psi^{(1)} = E^{(0)} \Psi^{(2)} + E^{(1)} \Psi^{(1)} + E^{(2)} \Psi^{(0)} \\ \lambda \ 3 \quad & H^0 \Psi^{(3)} + V \Psi^{(2)} = E^{(0)} \Psi^{(3)} + E^{(1)} \Psi^{(2)} + E^{(2)} \Psi^{(1)} + E^{(3)} \Psi^{(0)} \end{aligned}$$

.....

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

$$E^{(2)} = \langle \Psi^{(0)} | V | \Psi^{(1)} \rangle$$

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

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

from  $\lambda=1,2,3$  by left mult. by  $\Psi^{(0)}$  and integrating

Hermitian and real

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

*What causes it not to be an expectation value?*

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

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

$$(H^0 - E^{(0)}) \Psi^{(2)} = E^{(1)} \Psi^{(1)} + E^{(2)} \Psi^{(0)} - V \Psi^{(1)} \quad \text{from } \lambda=2$$

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

Almost expectation value

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

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

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

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

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

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

# Conjugate gradient

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

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

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

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

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

Pre-conditioner  $\nearrow$

Residue  $\nwarrow$

- Iterative
- D own choice  
Level shifting  
 $D \rightarrow D + \text{Const}$
- Dim.  $M \sim \text{CI}$
- possible use for eigenvectors

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

$$H^0 = \sum_i f(i) \quad \text{Møller Plesset} \quad V = H - \sum_i f(i)$$

*Single Reference*

Canonical  $H^0$  (diagonal)

$$E^{(2)} = - \sum_{i < j}^{\text{occ}} \sum_{a < b}^{\text{virt}} \frac{|(ia|jb) - (ib|ja)|^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}$$

*What is  $E_{MP0}$ ?*

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

*What is interpretation of  $E_{MP2}$ ?*

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

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

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

Local MP2(Pulay, Werner)  
non-diagonal



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

# Molecular Potential

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

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

Energy of a positive charge

⇒ where an electrofiel attack

⇒ 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

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

Multi reference

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

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

To get Eigenfunction

**Size consistency errors for different choices of  $H^0$  for  $O(^3P) \dots O(^3P)$  (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

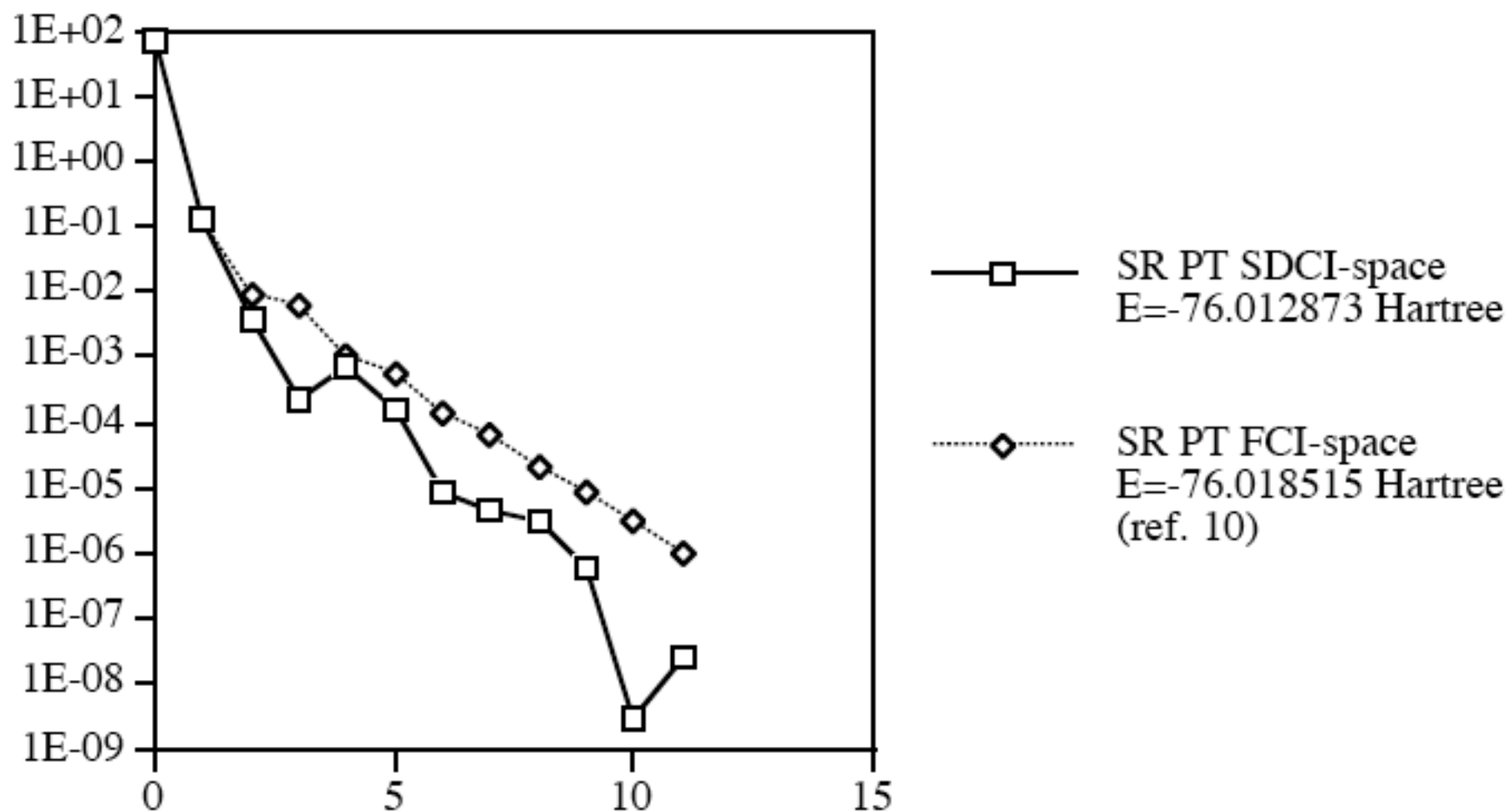
# Convergence of MP series

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

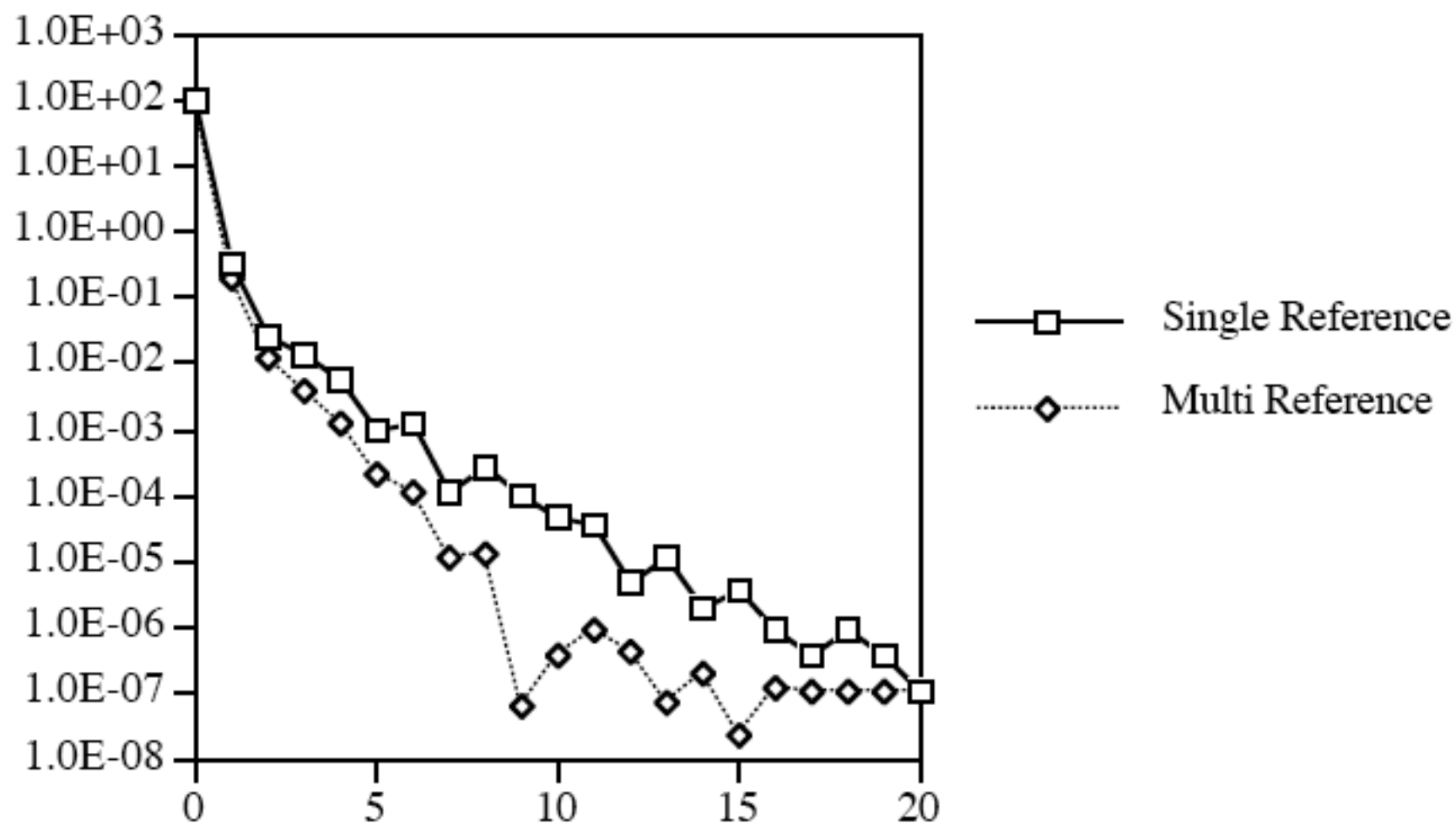
**Table I:** Zeroth-order and first-order energies for single- and multi-reference calculations on the nitrogen molecule.

		$E^{(0)}$	$E^{(1)}$
		(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<sub>2</sub>O in C<sub>2v</sub> symmetry at  $R_{\text{OH}}$  is 0.967 Å and  $\theta_{\text{HOH}}$  is 107.6°



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



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

Convergence3

