Strongly orthogonal geminals and group functions: size-extensive and variational reference states

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CONTENT

I. Nature and properties of geminal-type wave functions

II. Improving geminal wave functions

III. Group functions and the the FLMO approach

INTRODUCTION

Central problems of quantum chemistry:

i. **Small differences of large numbers**

ii. **Lack of simple though reliable models**

— **geminals**

APSG

$$\Psi_{\mathrm{HF}} = \underbrace{\phi^+_{1\uparrow}\ \phi^+_{1\downarrow}}_{\phi^+_1}\ \underbrace{\phi^+_{2\uparrow}\ \phi^+_{2\downarrow}}_{\phi^+_2}\ \cdots\ \underbrace{\phi^+_{\frac{N}{2}\uparrow}\ \phi^+_{\frac{N}{2}\downarrow}}_{\phi^+_{\frac{N}{2}}}\ |vac\rangle$$

$$\Psi_{\mathrm{APSG}} = \psi^+_1 \psi^+_2 \ldots \psi^+_{\frac{N}{2}}\ |vac\rangle$$

$$\psi^+_i = \sum_{q=1}^{M} C^i_q\ \phi^+_{q\uparrow}\ \phi^+_{q\downarrow} \qquad \text{— a geminal}$$

An essential difference between HF and APSG: the algebra

$$[\phi_i^+, \phi_k^-]_- = \delta_{ik}$$

(Grassmann- algebra)

$$[\psi_i^+, \psi_k^-]_+ = \hat{Q}_{ik}$$

(a very complicated algebra)

Under strong orthogonality:

$$[\psi_i^+, \psi_k^-]_+ = \hat{Q}_i \delta_{ik}$$

(somewhat simpler)

$\hat{Q}_{ik}$: Matrix of operators
– an extremely complicated object
(C. Valdemoro, 1985, Surján, 1989)

However:

$$\hat{Q}_i = 1 - \sum_{\mu\nu} P^i_{\mu\nu} a^+_\mu a_\nu$$

thus

$$\hat{Q}_i |vac\rangle = |vac\rangle$$

WICK's theorem remains valid

APSG AS A COUPLED CLUSTER

– Ukrainskii, Cullen, Head-Gordon

A single geminal in exponential form

$$\psi_i^+ = \sum_{q=1}^{M} C_q^i \; \phi_{q\uparrow}^+ \; \phi_{q\downarrow}^+$$

$$= C_1^i \; \phi_{1\uparrow}^+ \; \phi_{1\downarrow}^+ + \sum_{q=2}^{M} C_q^i \; \underbrace{\phi_{q\uparrow}^+ \; \phi_{q\downarrow}^+}$$

$$\phi_{q\uparrow}^+ \; \phi_{q\downarrow}^+ \phi_{1\downarrow}^- \phi_{1\uparrow}^- \; \phi_{1\uparrow}^+ \; \phi_{1\downarrow}^+$$

$$\psi_i^+ = \left[C_1^i + \sum_{q=2}^{M} C_q^i \underbrace{\phi_{q\uparrow}^+ \ \phi_{q\downarrow}^+ \phi_{1\downarrow}^- \phi_{1\uparrow}^-}_{\hat{t}_q} \right] \phi_{1\uparrow}^+ \ \phi_{1\downarrow}^+$$

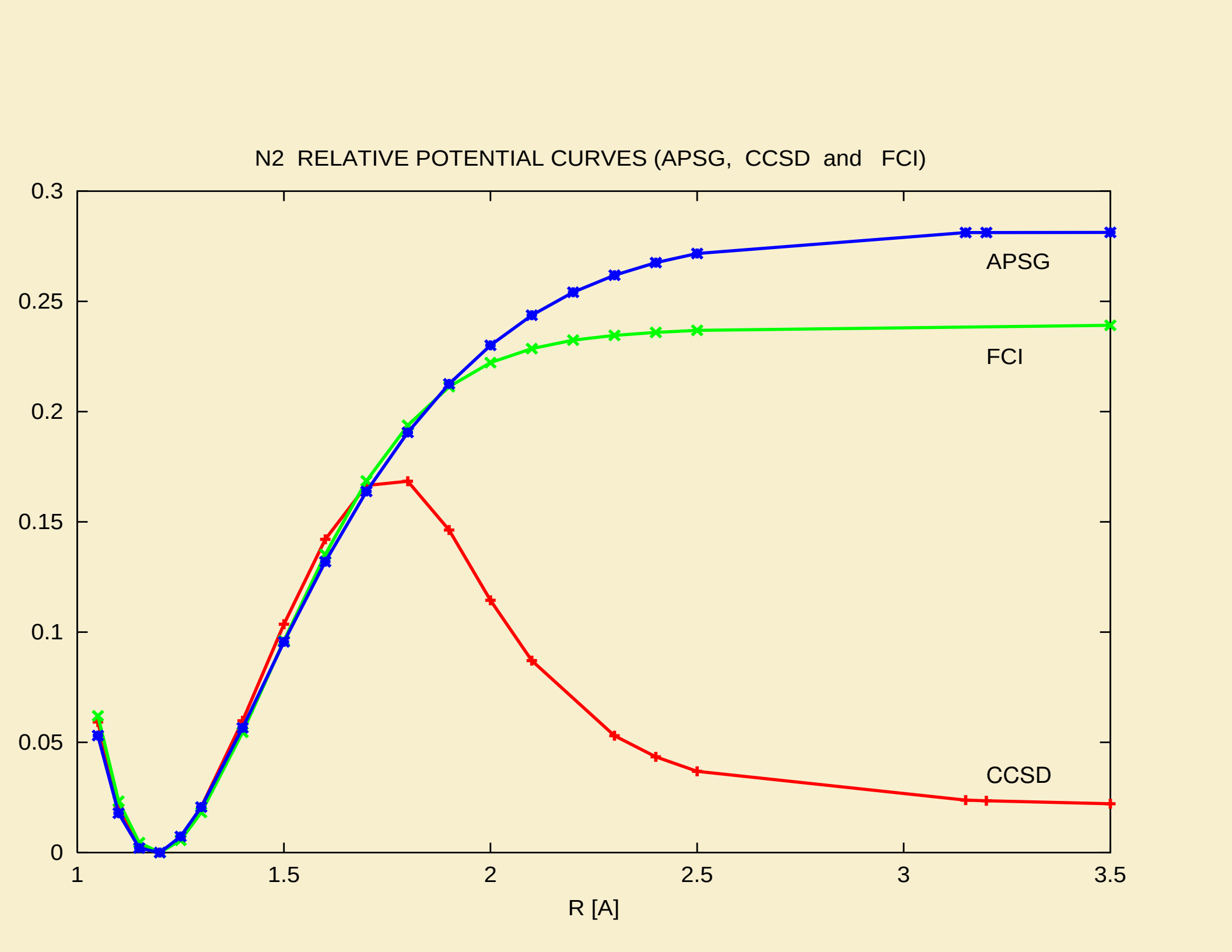
$$\psi_i^+ = C_1^i \underbrace{\left[1 + \underbrace{\sum_{q=2}^{M} \frac{C_q^i}{C_1^i} \hat{t}_q}_{\hat{T}_i} \right]}_{e^{\hat{T}_i}} \phi_{1\uparrow}^+ \ \phi_{1\downarrow}^+$$

$$\textbf{since } \left(\hat{T}_i\right)^2 = 0$$

$$\psi_i^+ = C_1^i \; e^{\hat{T}_i} \; \phi_{1\uparrow}^+ \; \phi_{1\downarrow}^+$$

$$\begin{aligned}
\Psi_{\text{APSG}} &= \psi_1^+ \psi_2^+ \ldots |vac\rangle \\
&= \underbrace{C_1^1 C_1^2 \ldots}_{C_1} \underbrace{e^{\hat{T}_1} e^{\hat{T}_2} \ldots}_{e^{\hat{T}_0}} \underbrace{\phi_{1\uparrow}^+ \; \phi_{1\downarrow}^+ \ldots |vac\rangle}_{|HF\rangle} \\
&= C_0 \; e^{\hat{T}_0} |HF\rangle
\end{aligned}$$

— a restricted CC wave function
($\sim$ Brueckner-type)


N2 RELATIVE POTENTIAL CURVES (APSG, CCSD and FCI)
0.3
0.25
0.2
0.15
0.1
0.05
0
1
1.5
2
2.5
3
3.5
R [A]
APSG
FCI
CCSD

List of advantages

- retain the formal simplicity of HF
- close to the chemists' way of thinking
- Composite quasi-bosonic particles with a a beautiful algebra
- Geminals are easy to deal with
- Exponential cluster operator
- Single-bond dissociation: O.K.
- E(APSG): strict upper bound to E(true)
- Size-extensivity

Disadvantages

1. **Strong orthogonality: severe restriction**
2. **No inter-geminal correlation**
3. **Multiple bond dissociation: incorrect spin state**
4. **Excited states are difficult to handle**
5. **Problems with inherently delocalized objects**
6. **Collective phenomena are not described.**

II. IMPROVING GEMINALS

- **CI (& M. Kállay)**
- **MP2 (& E. Rosta)**
- **MCPT (& Á. Szabados, Z. Rolik)**
- **RS-PT (& V. Rassolov)**
- **MC-CEPA (& D. Mukherjee)**

GEMINAL - CI

CI equations with reference state $|G\rangle$

$$\Psi = \sum_K C_K \ \hat{O}_K |G\rangle$$

$$\hat{O}_K = \quad p^+ i^-, \quad p^+ q^+ i^- k^-, \ldots \text{ etc.}$$

$$\hat{H}\Psi = E\Psi, \qquad \left[e^{\hat{T}}, \hat{O}_K\right] = 0:$$

$$\sum_K \hat{H} e^{\hat{T}} \hat{O}_K |HF\rangle C_K = E \sum_K e^{\hat{T}} \hat{O}_K |HF\rangle C_K$$

Multiplying by $\hat{O}_L^\dagger$ and projecting by $\langle HF|$:

$$\sum_K \underbrace{\langle HF|\hat{O}_L^\dagger \hat{H} e^{\hat{T}} \hat{O}_K|HF\rangle}_{\mathcal{H}_{LK}} C_K$$

$$= E \sum_K \underbrace{\langle HF|\hat{O}_L^\dagger e^{\hat{T}} \hat{O}_K|HF\rangle}_{\mathcal{S}_{LK}} C_K$$

a non-Hermitian generalized eigenvalue problem

Experience: CI improves very well E_0
inaccurate for excited states

MP2

The APSG-MP2 method

(1) Do an APSG calculation
(2) Do a standard MP2 with canonical MOs
(3) Do a localized MP2 but only for intra-bond correlation
(4) Compute the energy as the difference

$$E = E_{APSG} + E_{MP2} - E_{MP2}^{intrabond}$$

Umbrella inversion in NH_3

6-311G**	Total E [H] SCF-opt. geom.	Barrier [kJ/mol]
APSG	-56.244226	29.47
APSG-MP2	-56.432732	25.69
MP2	-56.427023	24.39
CCSD	-56.441739	25.31
CCSDT	-56.446775	25.71

Inversion barrier of H_2O

Method	Total E [H]	Barrier [kJ/mol]
6-311G**		
APSG	-76.091310	163.30
APSG-MP2	-76.290340	148.54
MP2	-76.282235	145.85
CCSD	-76.289946	147.99
CCSDT	-76.294652	148.89
3-21G		
MP2	-75.705525	145.96
APSG	-75.619001	131.72
APSG-MP2	-75.713986	146.22
CCSD	-75.712642	148.81
CCSDT	-75.713897	149.63
frozen-core FCI	-75.712484	156.14

A General MCPT formalism

$|0\rangle$ **multiconfigurational reference state**

$\hat{O} = |0\rangle\langle 0|$ **projector**

$\hat{P} = 1 - \hat{O}$ **orthogonal complement**

$|k\rangle = a_p^+ a_i |HF\rangle$ **excited determinants**

$|k'\rangle = \hat{P}|k\rangle$ **projected determinants:**

$$\hat{O}|k'\rangle = 0$$

$$\boldsymbol{\mathcal{S}} = \begin{bmatrix} \langle 0|0\rangle & \langle 0|\hat{P}|l\rangle \\ \langle k|\hat{P}|0\rangle & \langle k|\hat{P}|l\rangle \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & S \end{bmatrix}$$

$$S_{kl} = \langle k'|l'\rangle = \langle k|\hat{P}|l\rangle = \delta_{kl} - \underbrace{\langle k|0\rangle}_{C_k^0}\underbrace{\langle 0|l\rangle}_{C_l^0}$$

Matrix S is easily invertable:

$$(S^{-1})_{kl} = \delta_{kl} + \frac{C_k^0 C_l^0}{1 - \sum_j (C_j^0)^2}$$

Biorthogonal determinants:

$$\langle \tilde{k'}| = \sum_j (S^{-1})_{kj} \langle j'|$$

Zero order Hamiltonian for MCPT:

$$\hat{H}^0 = E_0 \hat{O} + \sum_k E_k |k'\rangle\langle \tilde{k'}|$$

$$\hat{H}^0|0\rangle = E_0|0\rangle \qquad \hat{H}^0|k'\rangle = E_k|k'\rangle$$

Perturbation corrections:

$$E^1 = \langle 0|\hat{W}|0\rangle$$

$$E^2 = -\sum_k \frac{\langle 0|\hat{W}|k'\rangle\langle\tilde{k}'|\hat{W}|0\rangle}{E_k^0 - E_0^0}, \text{etc.}$$

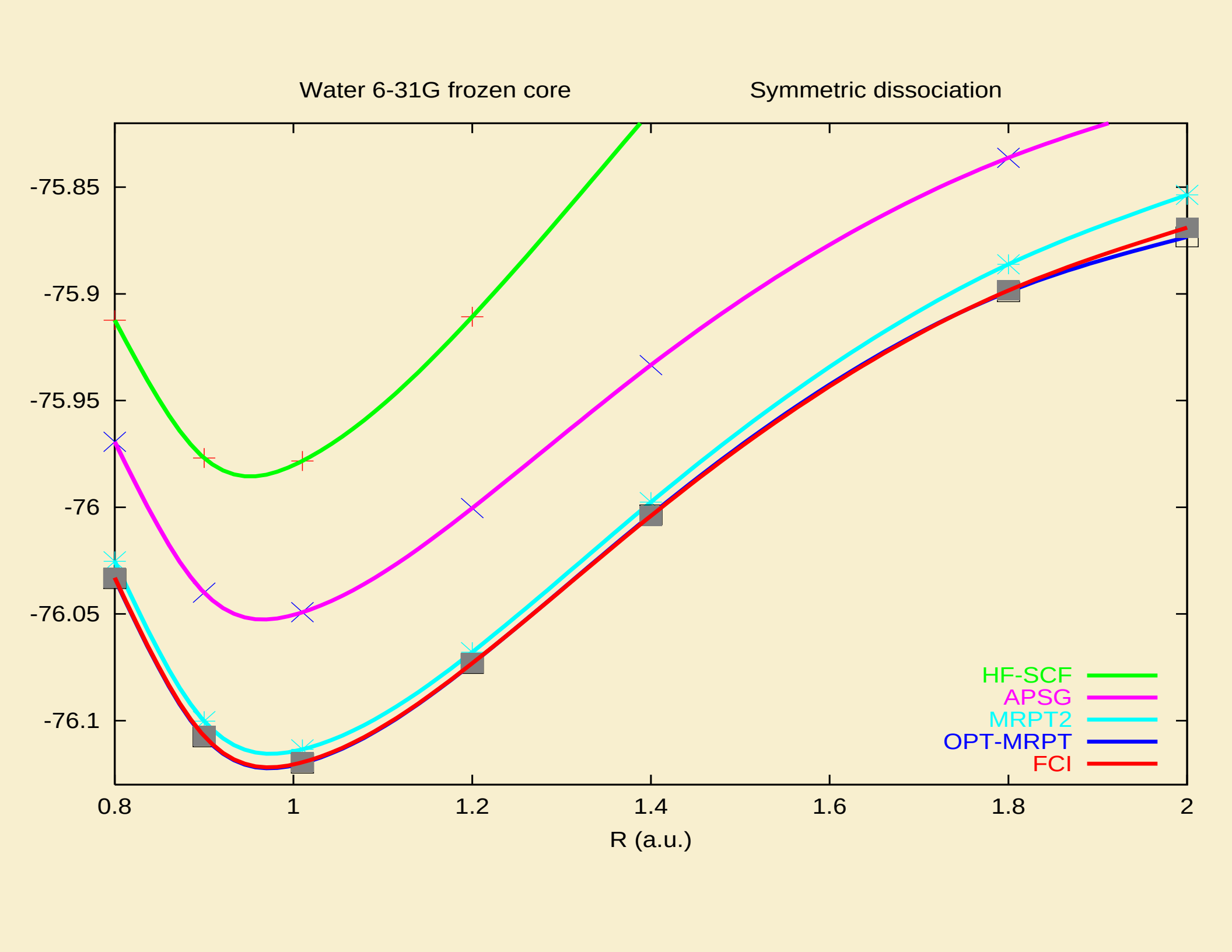
E_k^0**-s:**

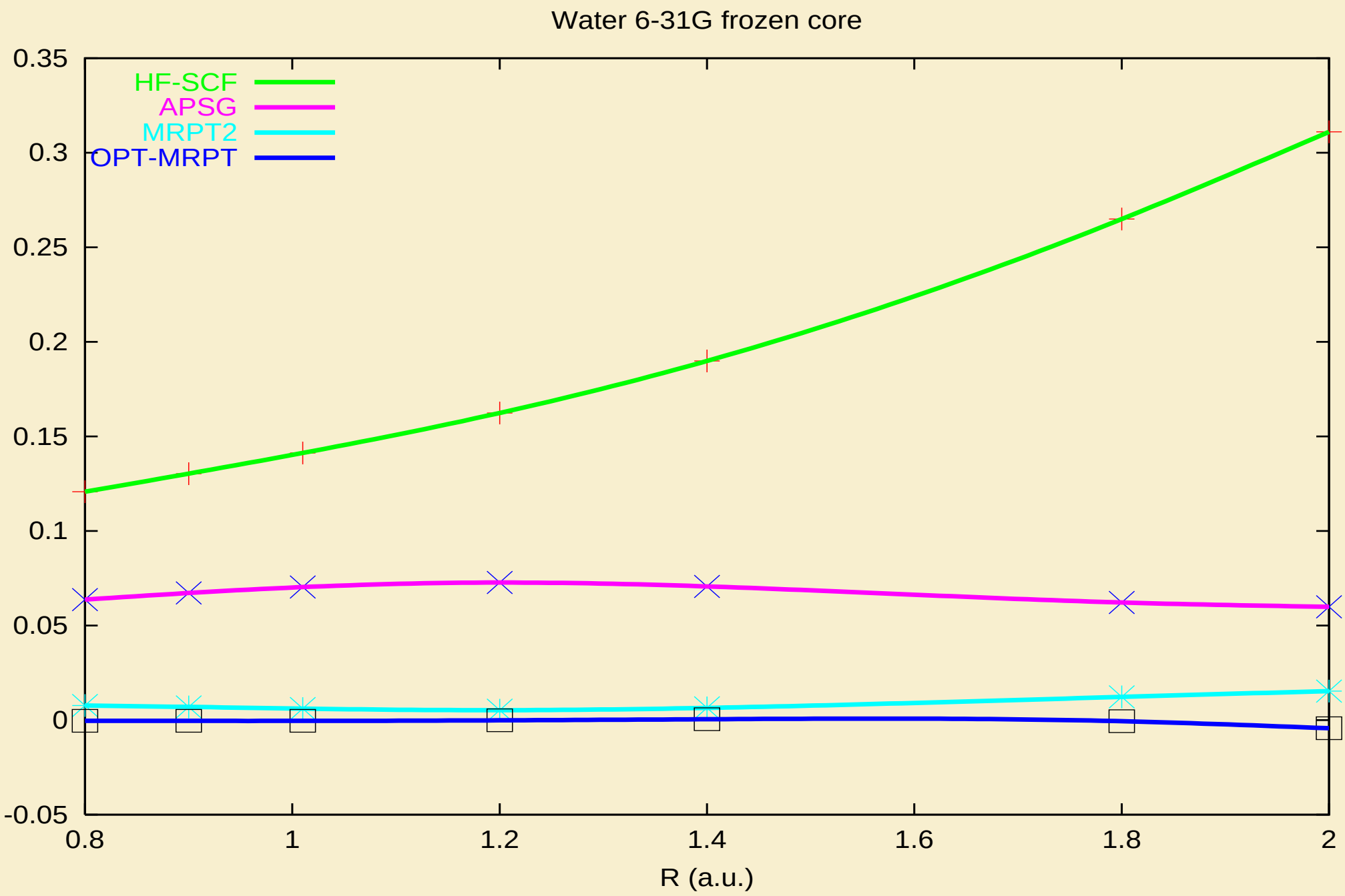
from canonical ε_i**-s,**
from optimized ε_i**-s,**
or fully optimized

MCPT and OPT-MCPT RESULTS

Ne atom pVTZ (6-311G**)

	E_{tot} (a.u.)
HF-SCF	-128.522553
APSG	-128.584315
CISD	-128.725623
MP-MCPT-2	-128.731305
OPT-MCPT-2	-128.733816
fc-FCI	-128.735214


Water 6-31G frozen core
Symmetric dissociation
-75.85
-75.9
-75.95
-76
-76.05
-76.1
0.8
1
1.2
1.4
1.6
1.8
2
R (a.u.)
HF-SCF
APSG
MRPT2
OPT-MRPT
FCI


Water 6-31G frozen core
HF-SCF
APSG
MRPT2
OPT-MRPT
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
-0.05
0.8
1
1.2
1.4
1.6
1.8
2
R (a.u.)

Constant denominator approximation

$$\hat{H}^0 = E^0 \hat{O} + \nu \hat{P}$$

$$E = \underbrace{\langle \Phi | \hat{H} | \Phi \rangle}_{E^0 + E^1} + \underbrace{\frac{\langle \Phi | \hat{V} \hat{P} \hat{V} | \Phi \rangle}{E^0 - \nu}}_{E^2} + \mathcal{O}(3)$$

ν : where from?

OPTIMIZED PARTITIONING:

$$\nu = E^0 + \frac{\langle \hat{H}^3 \rangle_c}{\langle \hat{H}^2 \rangle_c}$$

yielding

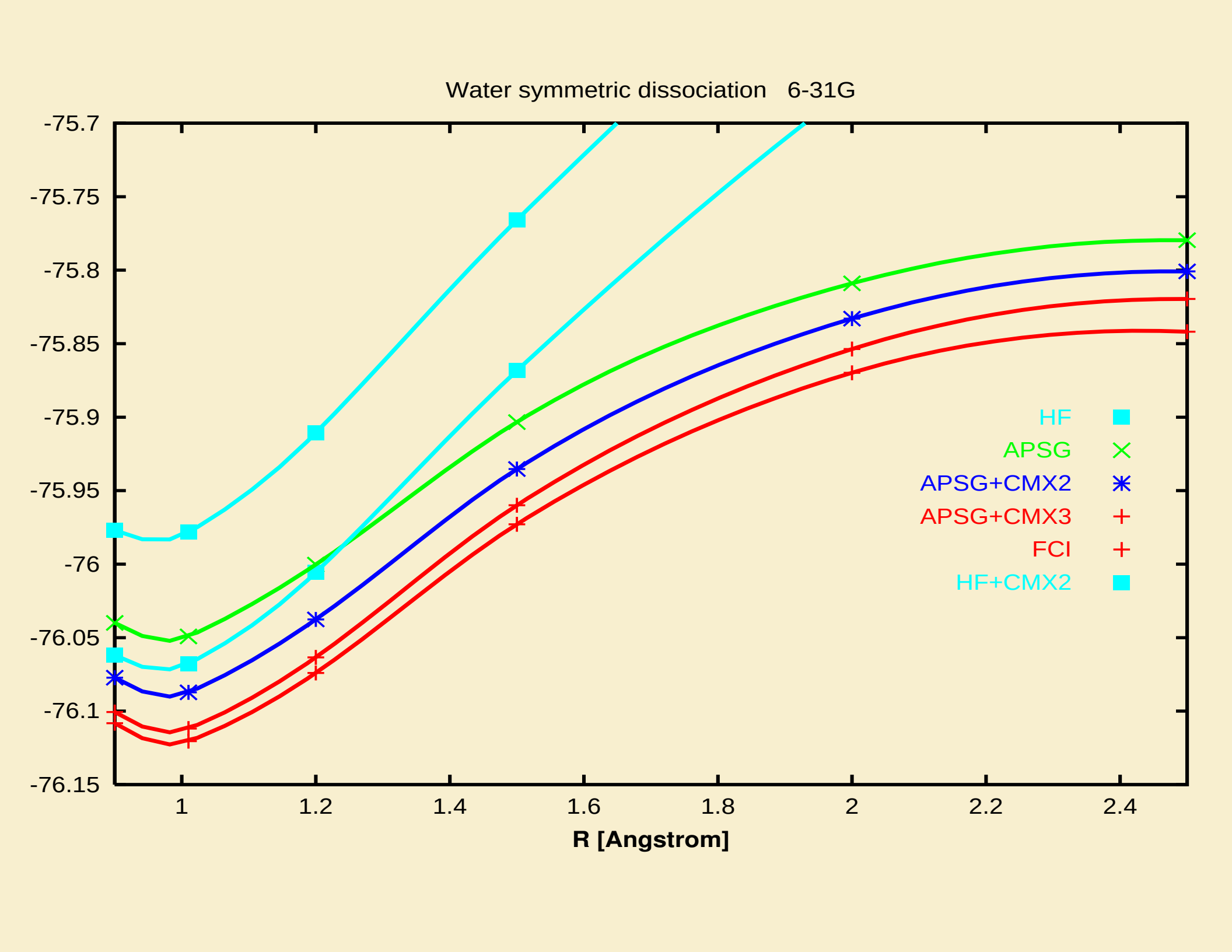
$$E^{(2)}_{opt} = -\frac{\langle \hat{H}^2 \rangle_c^2}{\langle \hat{H}^3 \rangle_c} = E^{(2)}_{CMX}$$

$$E^{(3)}_{opt} = 0$$

MR-CMX RESULTS

Be atom

	6-311G**
HF-SCF	-14.57187
MP2	-14.59847
APSG	-14.61734
APSG + CMX2	-14.63210
APSG + CMX3	-14.63323
FCI	-14.63338


Water symmetric dissociation 6-31G
-75.7
-75.75
-75.8
-75.85
-75.9
-75.95
-76
-76.05
-76.1
-76.15
1
1.2
1.4
1.6
1.8
2
2.2
2.4
R [Angstrom]
HF
APSG
APSG+CMX2
APSG+CMX3
FCI
HF+CMX2

MC-CEPA – a new theory?

reference state:

$$|\Phi\rangle = c_{HF}|HF\rangle + \sum c_\mu |\mu\rangle$$

Ansatz:

$$|\Psi\rangle = c_{HF}|HF\rangle + \sum_\mu d_\mu |\mu\rangle + \sum_k d_k |k\rangle$$

$$H\Psi = E\Psi$$

Define $\langle\tilde{\nu}| = \langle\nu| - \frac{d_\nu}{c_{\mathrm{HF}}}\langle HF|$

satisfying $\langle\tilde{\nu}|\Psi\rangle = 0$.

From $\langle\tilde{\nu}|H - E|\Psi\rangle = 0$:

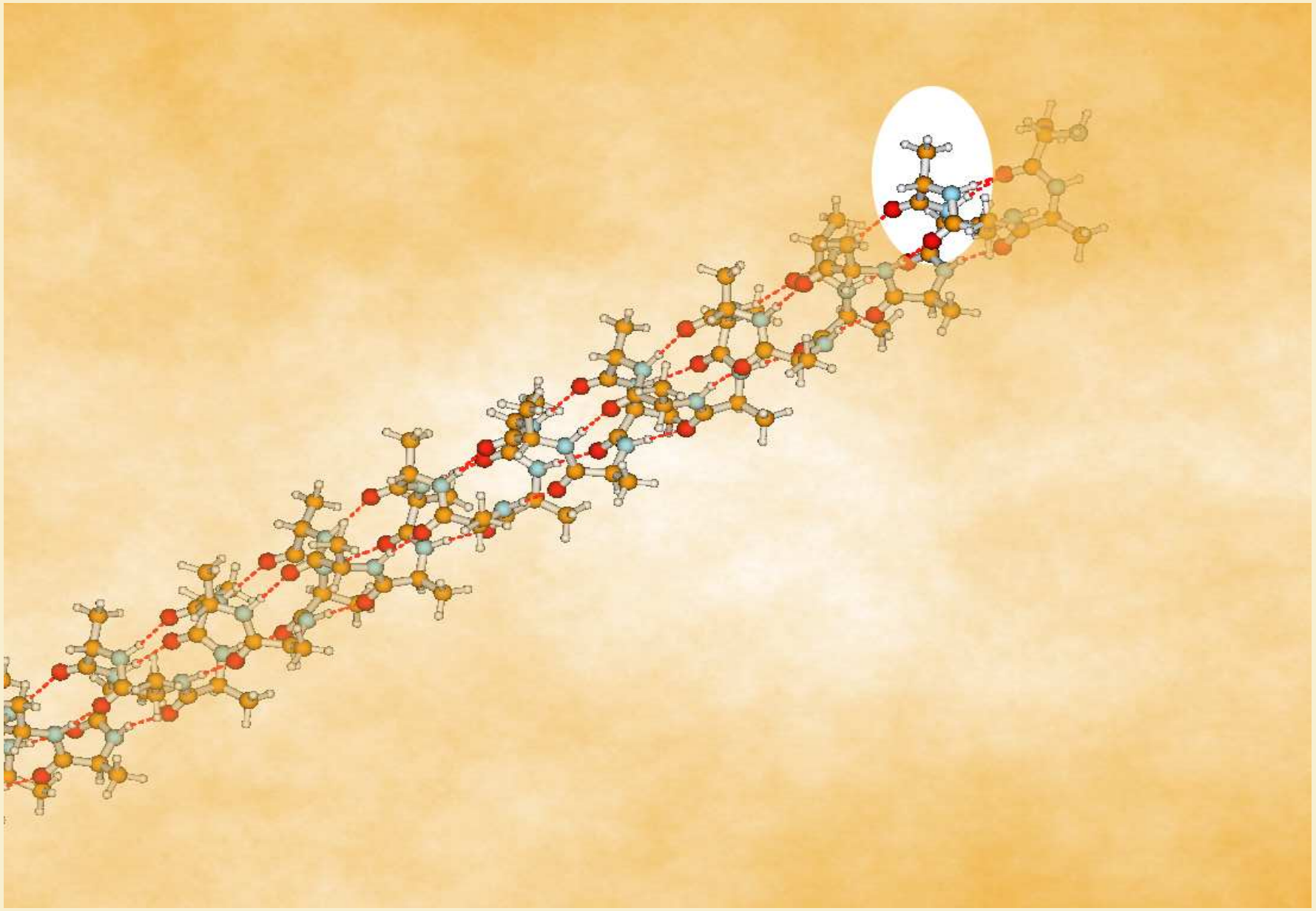
$$H_{\nu\,\mathrm{HF}}\ c_{\mathrm{HF}} \quad + \quad \sum_\mu H_{\nu\mu}\ d_\mu$$

$$-E_{\mathrm{HF}}\ d_\nu \quad + \quad \sum_l H_{\nu l}\ d_l - \sum_\mu H_{\mathrm{HF}\mu}\ \frac{d_\nu d_\mu}{c_{\mathrm{HF}}}$$

$$-\sum_l H_{\mathrm{HF}l}\ \frac{d_\nu d_l}{c_{\mathrm{HF}}} = \ 0$$

analysis of connectedness (cf. Malrieu)

FLMOS — Polyalanin



Electron correlation in the active part

$$H = \sum_{ij} H_{ij}^{\mathrm{eff}} a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl} [ij|kl] a_i^\dagger a_j^\dagger a_l a_k$$

$$i, j, k, l \in \text{active}$$

$$H_{ij}^{\mathrm{eff}} = \sum_{\mu\nu} C_{\mu i}^{\mathrm{LMO}} \; H_{\mu\nu}^{\mathrm{eff}} \; C_{\nu j}^{\mathrm{LMO}}$$

$$P = P^{\mathbf{frozen}} + P^{\mathbf{active}}$$

$$\begin{aligned} H^{\mathbf{eff}}_{\mu\nu} &= H_{\mu\nu} + \sum_{\lambda\sigma} P^{\mathbf{frozen}}_{\lambda\sigma}[\mu\lambda||\nu\sigma] \\ &= \underbrace{H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}[\mu\lambda||\nu\sigma]}_{F_{\mu\nu}} \\ &\quad - \sum_{\lambda\sigma} P^{\mathbf{active}}_{\lambda\sigma}[\mu\lambda||\nu\sigma] \end{aligned}$$

$$P^{\mathbf{active}}_{\lambda\sigma} = \sum_{i} C^{\mathbf{LMO}}_{\lambda i} C^{\mathbf{LMO}}_{\sigma i}$$

Active Fockian:

$$F_{ij} = \sum_{\mu\nu} C_{\mu i} F_{\mu\nu} C_{\nu j}$$

Canonization of active MOs:

— diagonalize F

Use any correlational method

(FCI, CC, MRPT, MCPT, MP2 . . .)

MP2 : localized, but noniterative!

Note: Frozen LMOS are never explicitly

constructed!

NaCl cluster – bond length prolongation

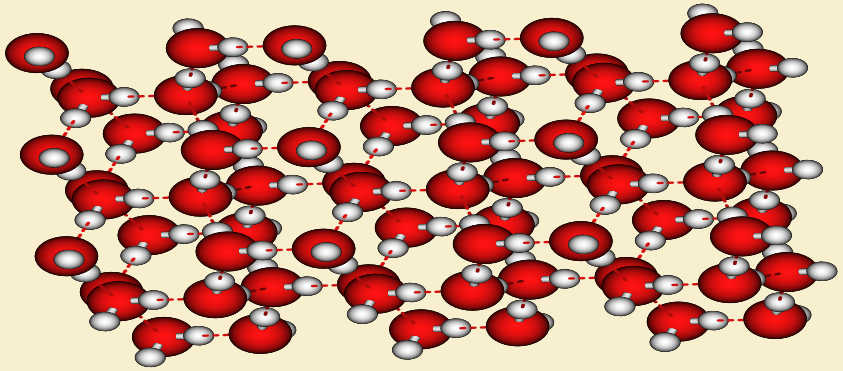
Relative CCSD energies E(R)-E(Re) [mH]

	Nbasis	R=2R_e 4.59 Å	R=3R_e 6.88 Å	CPU
monomer	18	151.0	189.6	
FLMO	21	113.8	140.3	10 sec
	39	113.9	140.5	
	57	114.0	140.6	10 min
	...			
full	90	114.2	140.8	10 hrs

$R_e = 2.293$ Å

Linear-tetrahedral barrier of a water molecule in a cluster of

ice



	barrier [mH]	error [mH]
tests on water dimer		
one water molecule		
MP2	127.294	-10.102
MP3	130.402	-10.151
two water molecules – FLMO		
MP2	117.400	-0.208
MP3	120.334	-0.083
two water molecules		
MP2	117.192	
MP3	120.251	
ice cluster – FLMO with 1 active water		
MP2	117.358	
MP3	120.237	

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