Convergence enhancement in Rayleigh-Schrödinger Perturbation Theory: Quantum Chemical Applications

Péter R. Surján, Zsuzsanna Mihálka, and Ágnes Szabados

Eötvös University, Faculty of Science
Institute of Chemistry, Laboratory of Theoretical Chemistry

Budapest, Hungary

Content

- Introduction
  - RSPT
  - The Problem of Convergence in RSPT
- Partitioning in PT
- Minimizing $||QW||$
- Simple examples
- Dissociation curves with SR 0^{th} order

Perturbation Theory (RSPT)

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

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{W}$$

$$\Psi = \sum_n \lambda^n\, \Psi^{(n)}$$

$$E = \sum_n \lambda^n\, E^{(n)}$$

RSPT — unknown convergence conditions

Reduced resolvent, $\hat{Q}$

$$\hat{Q}\left(H^{(0)} - E^{(0)}\right) = 1 - |\Psi^{(0)}\rangle\langle\Psi^{(0)}|$$

$$(\hat{H}^{(0)} + \hat{W})\Psi \;=\; (E^{(0)} + \Delta E)\Psi$$

$$(\hat{H}^{(0)} - E^{(0)})\Psi \;=\; (\Delta E - \hat{W})\Psi$$

Reduced resolvent, $\hat{Q}$

$$\hat{Q}\left(H^{(0)} - E^{(0)}\right) = 1 - |\Psi^{(0)}\rangle\langle\Psi^{(0)}|$$

$$(\hat{H}^{(0)} + \hat{W})\Psi \;=\; (E^{(0)} + \Delta E)\Psi$$

$$\hat{Q}(\hat{H}^{(0)} - E^{(0)})\Psi \;=\; \hat{Q}(\Delta E - \hat{W})\Psi$$

Reduced resolvent, $\hat{Q}$

$$\hat{Q}\left(H^{(0)} - E^{(0)}\right) = 1 - |\Psi^{(0)}\rangle\langle\Psi^{(0)}|$$

$$(\hat{H}^{(0)} + \hat{W})\Psi \;=\; (E^{(0)} + \Delta E)\Psi$$

$$\underbrace{\hat{Q}(\hat{H}^{(0)} - E^{(0)})}_{1-|\Psi^{(0)}\rangle\langle\Psi^{(0)}|}\Psi \;=\; \hat{Q}(\Delta E - \hat{W})\Psi$$

Reduced resolvent, $\hat{Q}$

$$\hat{Q}\left(H^{(0)} - E^{(0)}\right) = 1 - |\Psi^{(0)}\rangle\langle\Psi^{(0)}|$$

$$(\hat{H}^{(0)} + \hat{W})\Psi \;=\; (E^{(0)} + \Delta E)\Psi$$

$$\underbrace{\hat{Q}(\hat{H}^{(0)} - E^{(0)})}_{1-|\Psi^{(0)}\rangle\langle\Psi^{(0)}|}\Psi \;=\; \hat{Q}(\Delta E - \hat{W})\Psi$$

$$\Psi \;=\; \Psi^{(0)} \;+\; \hat{Q}(\Delta E - \hat{W})\Psi$$

iterative form

$$E^{(n)} = \langle \Psi^{(0)} | \hat{W} | \Psi^{(n-1)} \rangle$$

$$\Psi^{(1)} = -\hat{Q}\hat{W}|\Psi^{(0)}\rangle$$

$$\begin{aligned} \Psi^{(2)} &= \hat{Q}(\hat{W} - E^{(1)})\hat{Q}\hat{W}|\Psi^{(0)}\rangle \\ &= \left(\hat{Q}\,\hat{W}\right)_c \hat{Q}\hat{W}|\Psi^{(0)}\rangle \end{aligned}$$

$$\Psi^{(n)} = \pm \left(\hat{Q}\,\hat{W}\right)_c^{(n-1)} \hat{Q}\hat{W}|\Psi^{(0)}\rangle$$

The Problem of Convergence in RSPT: Kato's approach

$$\hat{G}(z) = \left(z - \hat{H}\right)^{-1}$$

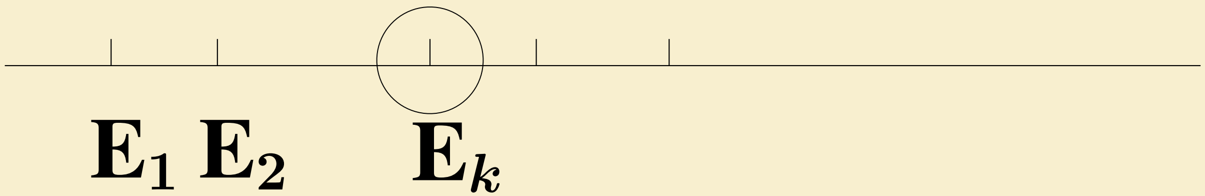
$$\hat{G}^{(0)}(z) = \left(z - \hat{H}^{(0)}\right)^{-1}$$

$$\hat{G}(z) = \hat{G}^{(0)}(z) + \hat{G}^{(0)}(z)\hat{W}\hat{G}(z)$$

— Dyson equation

Energies from $\hat{G}(z)$

$$E_k = \frac{1}{2\pi i} \oint z \, \mathrm{Tr} \; \hat{G}(z) \, dz$$



$$G(z) \; = \; \sum_k \frac{1}{z - E_k} \, |\Psi_k\rangle\langle\Psi_k|$$

$$\oint \frac{z}{z - E_k} dz \; = \; 2\pi i \; E_k$$

$$\hat{G}(z) \;=\; \hat{G}^{(0)}(z) + \hat{G}^{(0)}(z)\hat{W}\hat{G}(z)$$

— Dyson equation

$$\hat{G}(z) \;=\; \left(1 \;-\; \hat{G}^{(0)}(z)\,\hat{W}\right)^{-1}\,\hat{G}^{(0)}(z)$$

expanded as

$$\hat{G}(z) = \left(1 + \hat{G}^{(0)}\hat{W} + \hat{G}^{(0)}\hat{W}\hat{G}^{(0)}\hat{W} + \ldots\right)\hat{G}^{(0)}(z)$$

$$\hat{G}(z) = \left(\hat{G}^{(0)} + \hat{G}^{(0)}\hat{W}\hat{G}^{(0)} + \hat{G}^{(0)}\hat{W}\hat{G}^{(0)}\hat{W}\hat{G}^{(0)} + \dots\right)$$

$$\underbrace{\oint z\mathrm{Tr}\,\hat{G}(z)dz}_{2\pi i E} = \underbrace{\oint z\mathrm{Tr}\,\hat{G}^{(0)}dz}_{2\pi i E^{(0)}} + \underbrace{\oint z\mathrm{Tr}\,\hat{G}^{(0)}\hat{W}\hat{G}^{(0)}dz}_{2\pi i E^{(1)}} + \underbrace{\oint zTr\hat{G}^{(0)}\hat{W}\hat{G}^{(0)}\hat{W}\hat{G}^{(0)}dz}_{2\pi i E^{(2)}}$$

convergent iff $||\hat{G}^{(0)}(z)\hat{W}|| < 1,$

for all z in the integration path.

Partitioning in PT

$$\hat{H} = \hat{H}^0 + \hat{W}$$

Two conflicting points:

- **The smaller is $\hat{W}$, the better**
- **The easier to solve $\hat{H}^0$, the better**

LEVEL SHIFTS: repartitioning by a diagonal operator

$$\hat{H}^0 \rightarrow \hat{H}^0 + \sum_k \eta_k \, |k\rangle\langle k|$$

Examples to repartitionings

- **MP $\rightarrow$ EN**
- **Feenberg-scaling**
- **Optimized partitioning: (MR) CEPA-0**
- $||\hat{W}||$ **minimization**
- $||\hat{Q}\hat{W}||$ **minimization**

$||\hat{Q}\hat{W}||$ minimization

Analogy to Kato's idea:

$$\hat{G}^0(z) = \frac{1}{z - \hat{H}^0}$$

$$\hat{Q} = \frac{1 - |\Psi^0\rangle\langle\Psi^0|}{\hat{H}^0 - E^0}$$

$$||\hat{G}^0\hat{W}|| \Rightarrow ||\hat{Q}\hat{W}||$$

$||\hat{Q}\hat{W}||$ minimization

$$\hat{H} = \underbrace{\hat{H}^0 + \sum_k \eta_k |k\rangle\langle k|}_{H^{0\prime}} + \underbrace{\hat{W} - \sum_k \eta_k |k\rangle\langle k|}_{W'(\eta)}$$

$$\hat{Q}'(\eta) = \frac{1 - |\Psi^0\rangle\langle\Psi^0|}{\hat{H}^0 + \sum_k \eta_k |k\rangle\langle k| - E^0}$$

$||\hat{Q}\hat{W}||$ minimization

$$||\hat{Q}\hat{W}||^2 = \mathbf{Tr}\,[QW(QW)^\dagger] = \mathbf{Tr}\,[WQ^2W]$$

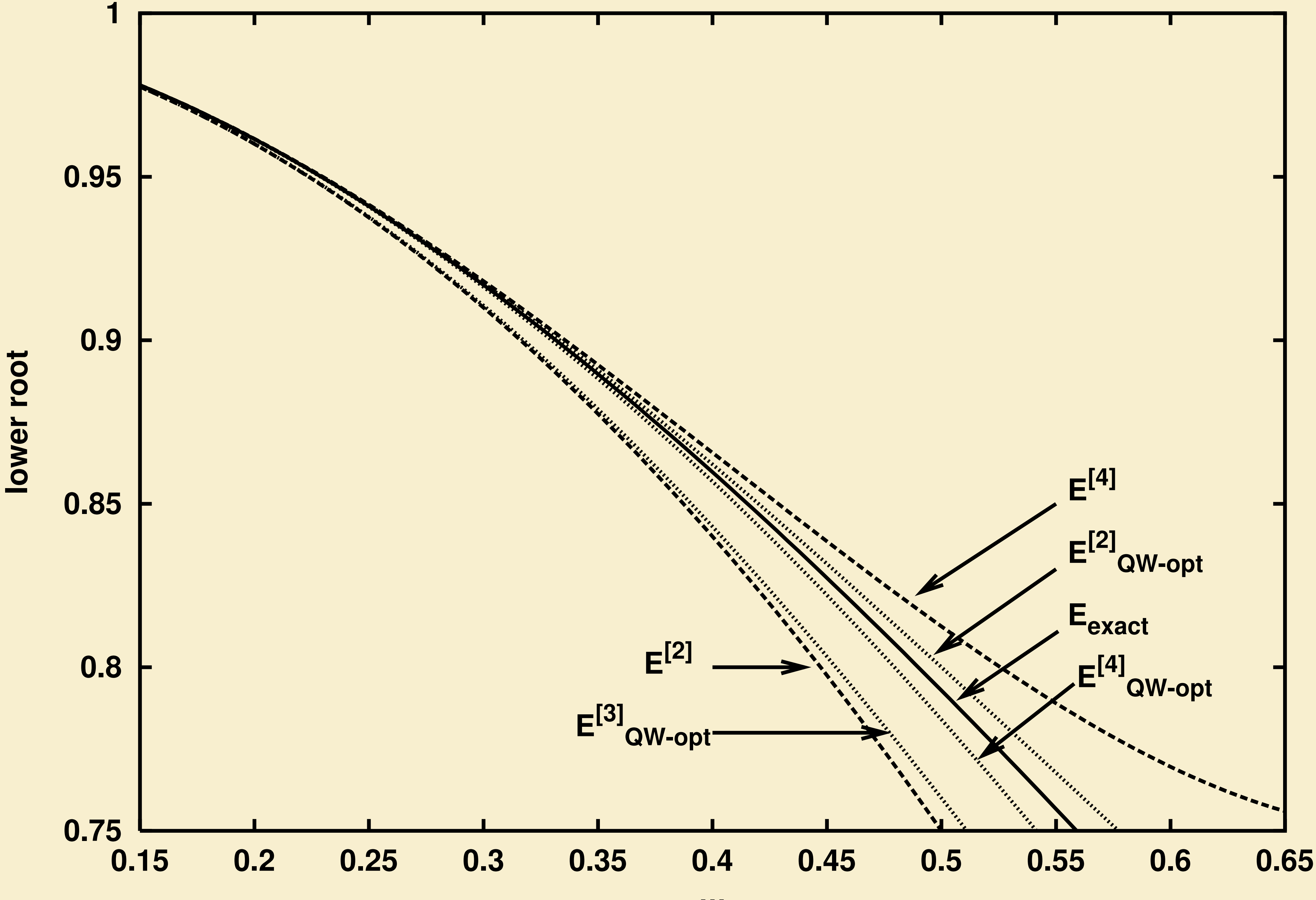
$$\frac{\partial}{\partial \eta_k}\,||\hat{Q}\hat{W}||^2 = 0$$

$$\eta_k = \frac{\langle k|W^2|k\rangle + \langle k|W|k\rangle(E_k^{(0)} - E_0^{(0)})}{\langle k|W|k\rangle + (E_k^{(0)} - E_0^{(0)})}$$

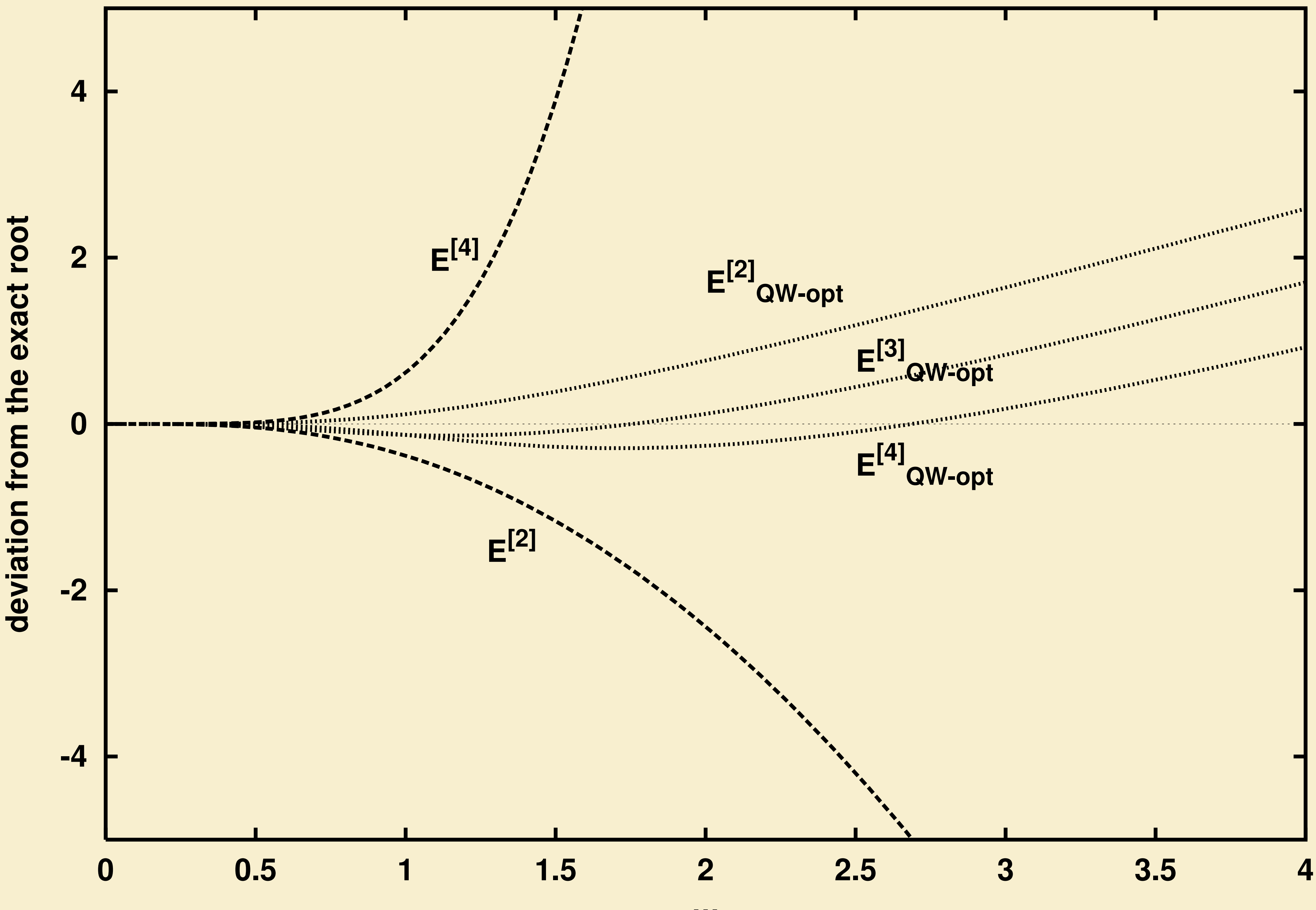
Matrix example

$$\boldsymbol{H} = \begin{pmatrix} a & w \\ w & b \end{pmatrix} = \underbrace{\begin{pmatrix} a & 0 \\ 0 & b+\eta \end{pmatrix}}_{H^{(0)}} + \underbrace{\begin{pmatrix} 0 & w \\ w & -\eta \end{pmatrix}}_{W}.$$

$$||QW||^2 = \textbf{mini} \quad \Rightarrow \quad \eta = \frac{w^2}{b-a}$$



lower root
1
0.95
0.9
0.85
0.8
0.75
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
0.55
0.6
0.65
$E^{[4]}$
$E^{[2]}_{QW\text{-}opt}$
E_{exact}
$E^{[4]}_{QW\text{-}opt}$
$E^{[2]}$
$E^{[3]}_{QW\text{-}opt}$



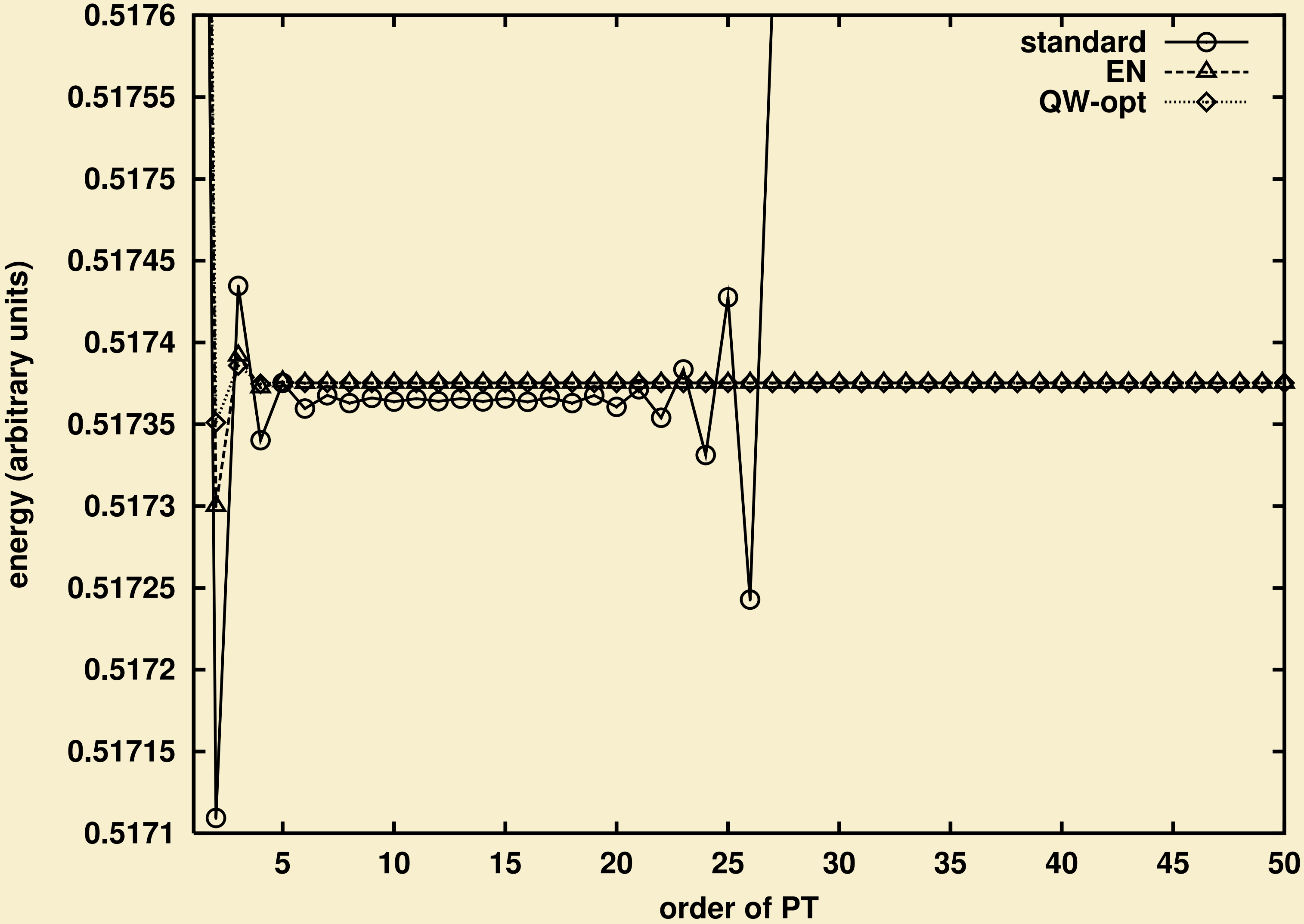
deviation from the exact root
4
2
0
-2
-4
0
0.5
1
1.5
2
2.5
3
3.5
4
E[4]
E[2]
E[2]QW-opt
E[3]QW-opt
E[4]QW-opt

Quartic Anharmonic Oscillator

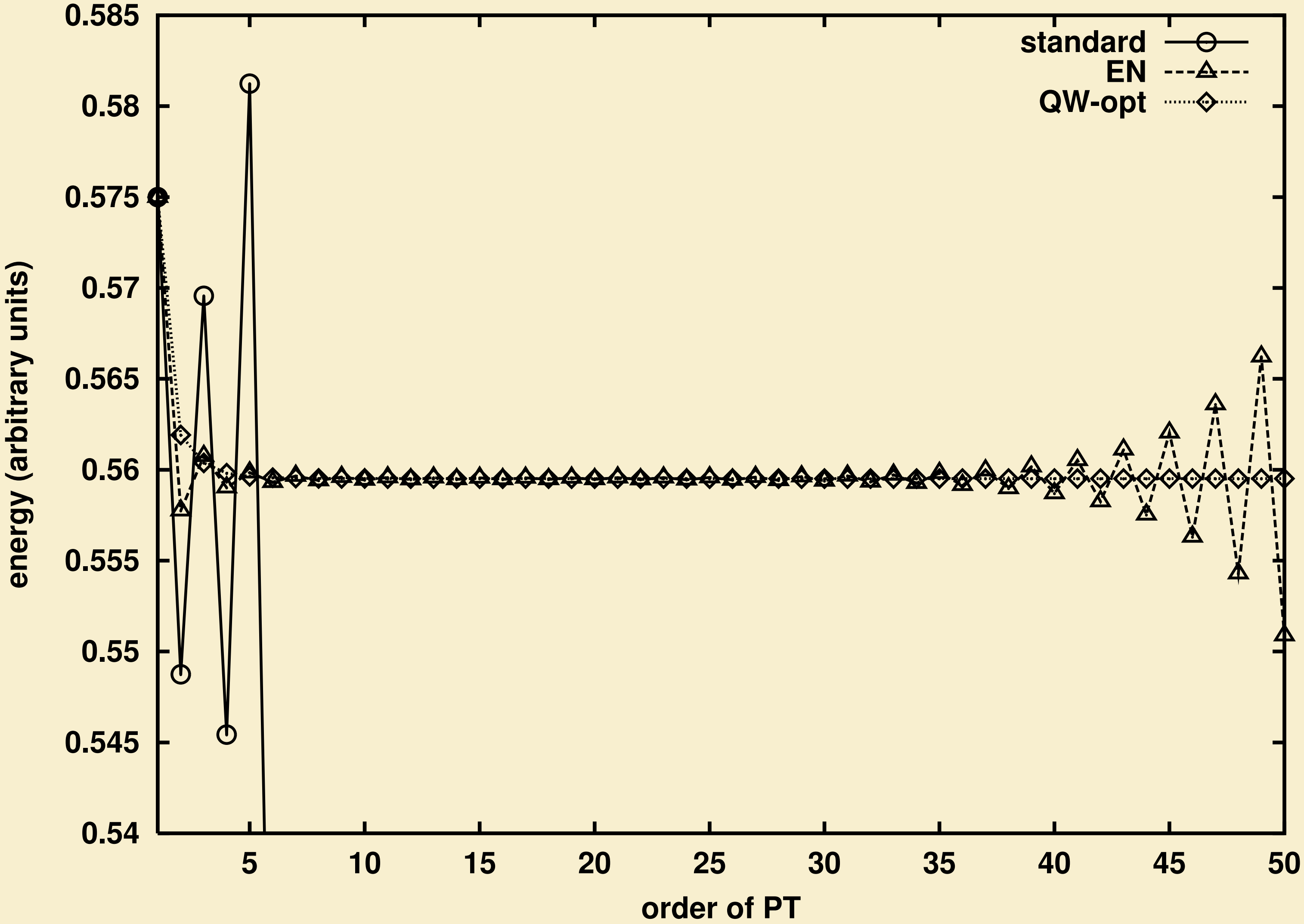
$$\hat{H} = -\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}x^2 + \gamma x^4,$$

RSPT convergence radius wrt γ : 0

$\gamma = \mathbf{0.025}$

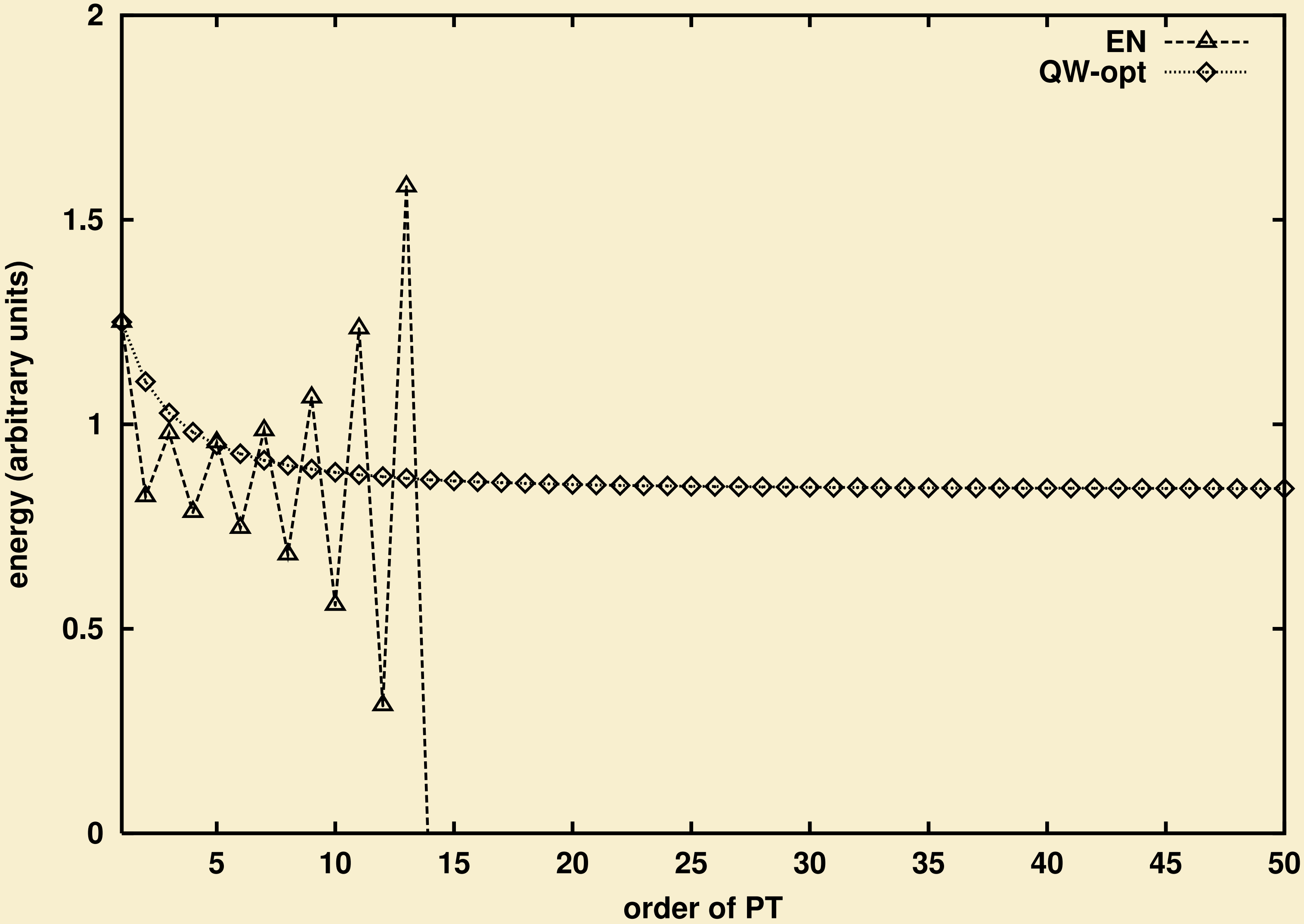


$$\gamma = 0.1$$



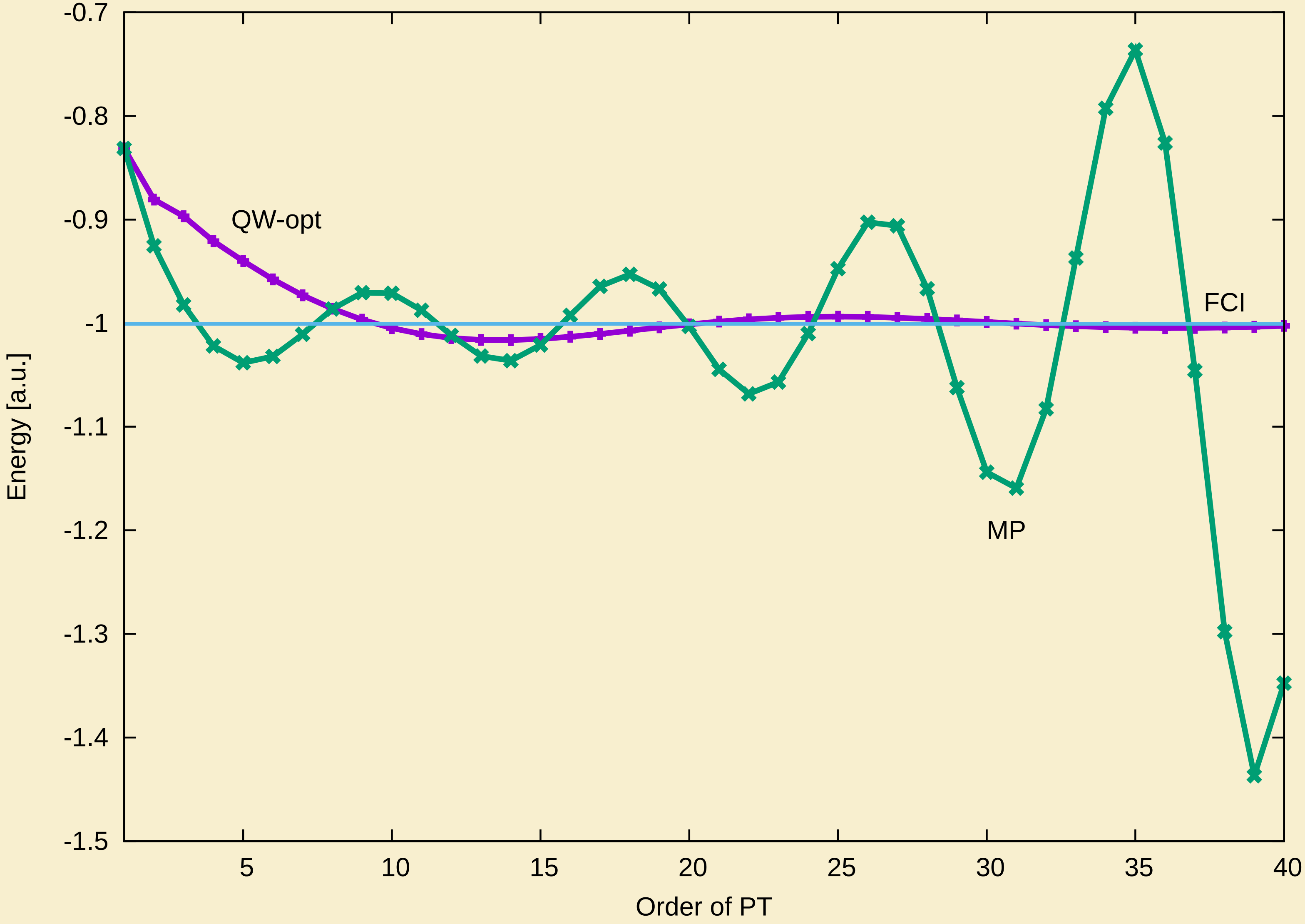
standard
EN
QW-opt
energy (arbitrary units)
order of PT
0.585
0.58
0.575
0.57
0.565
0.56
0.555
0.55
0.545
0.54
5
10
15
20
25
30
35
40
45
50

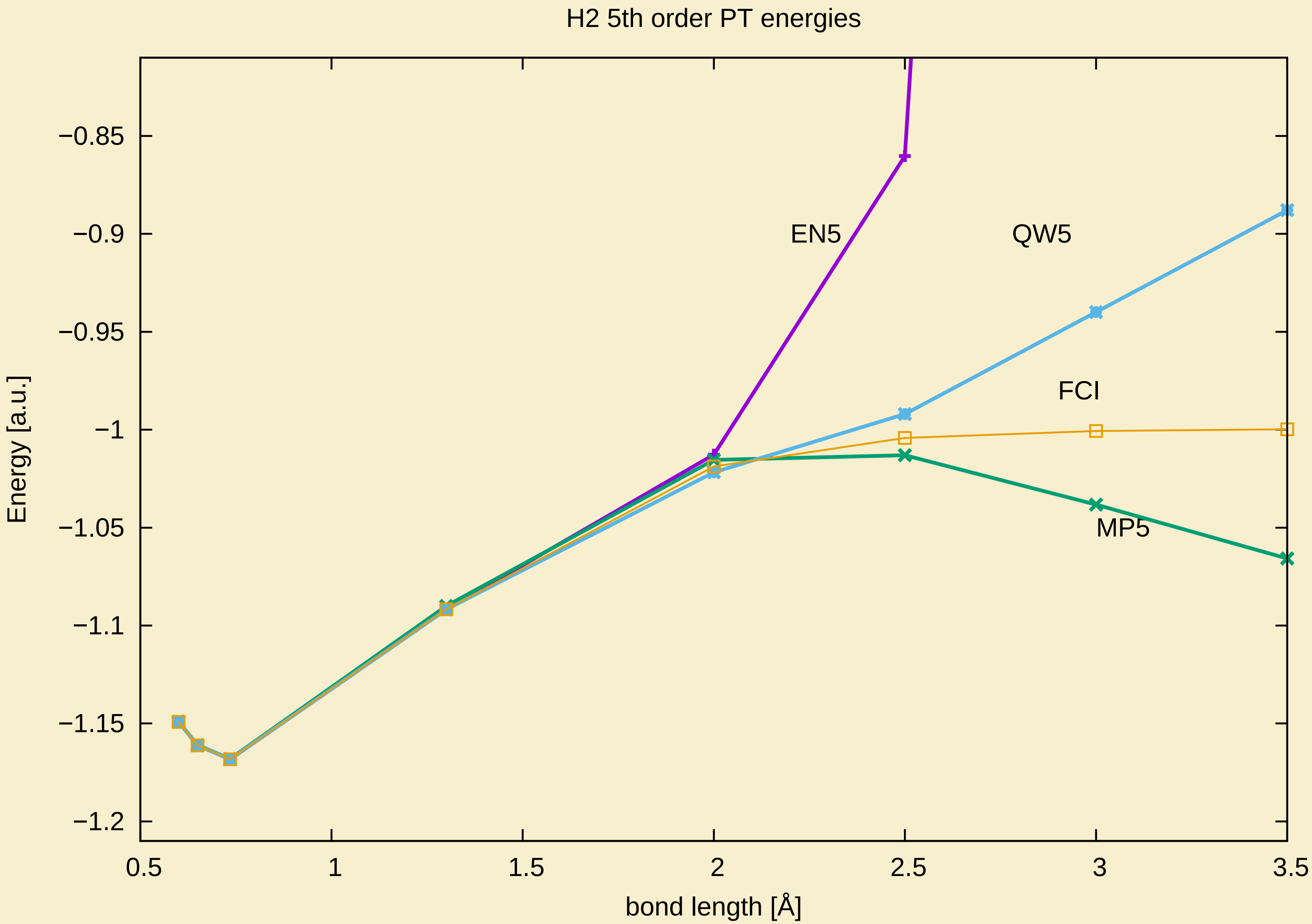
$$\gamma = 1.0$$

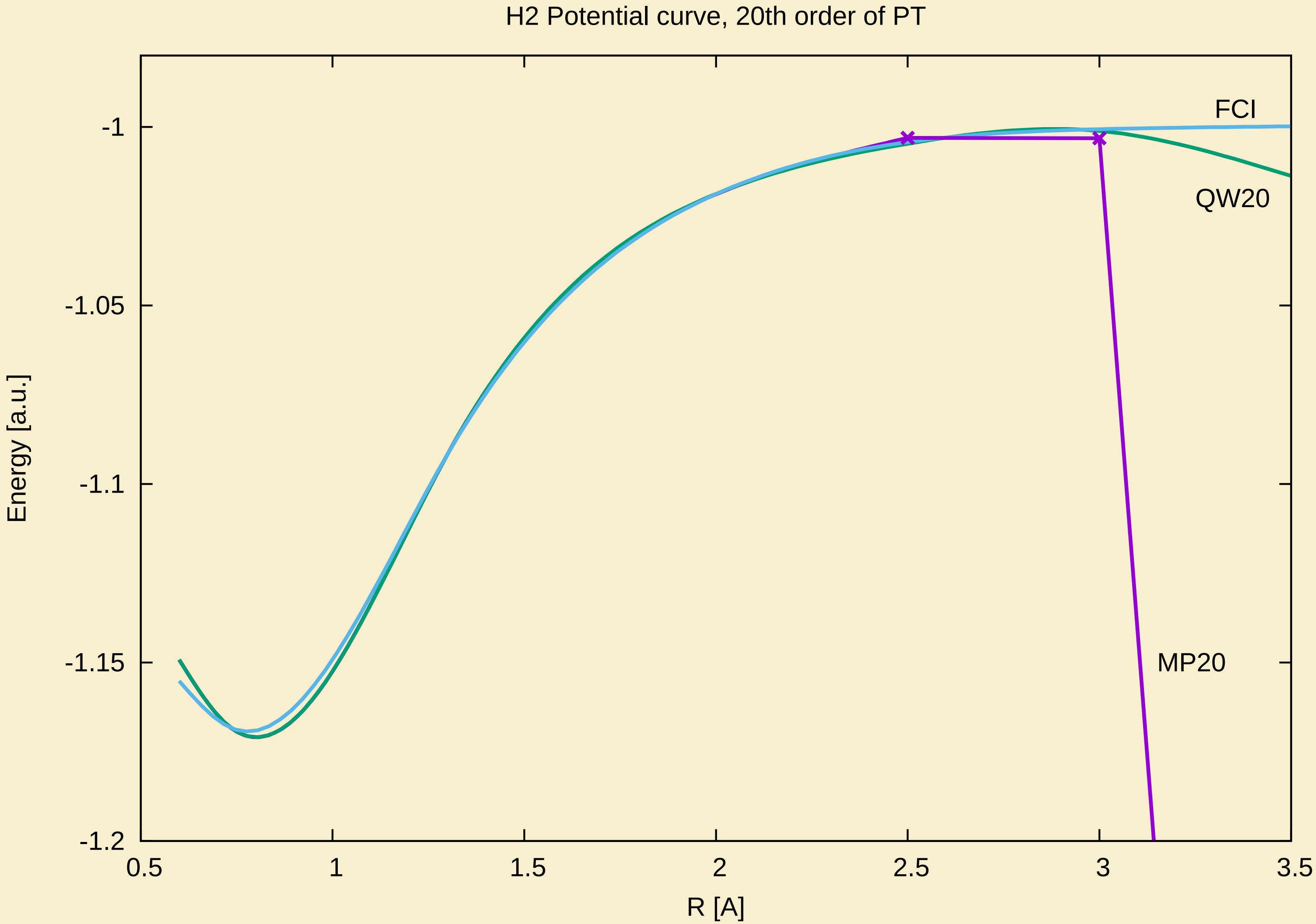


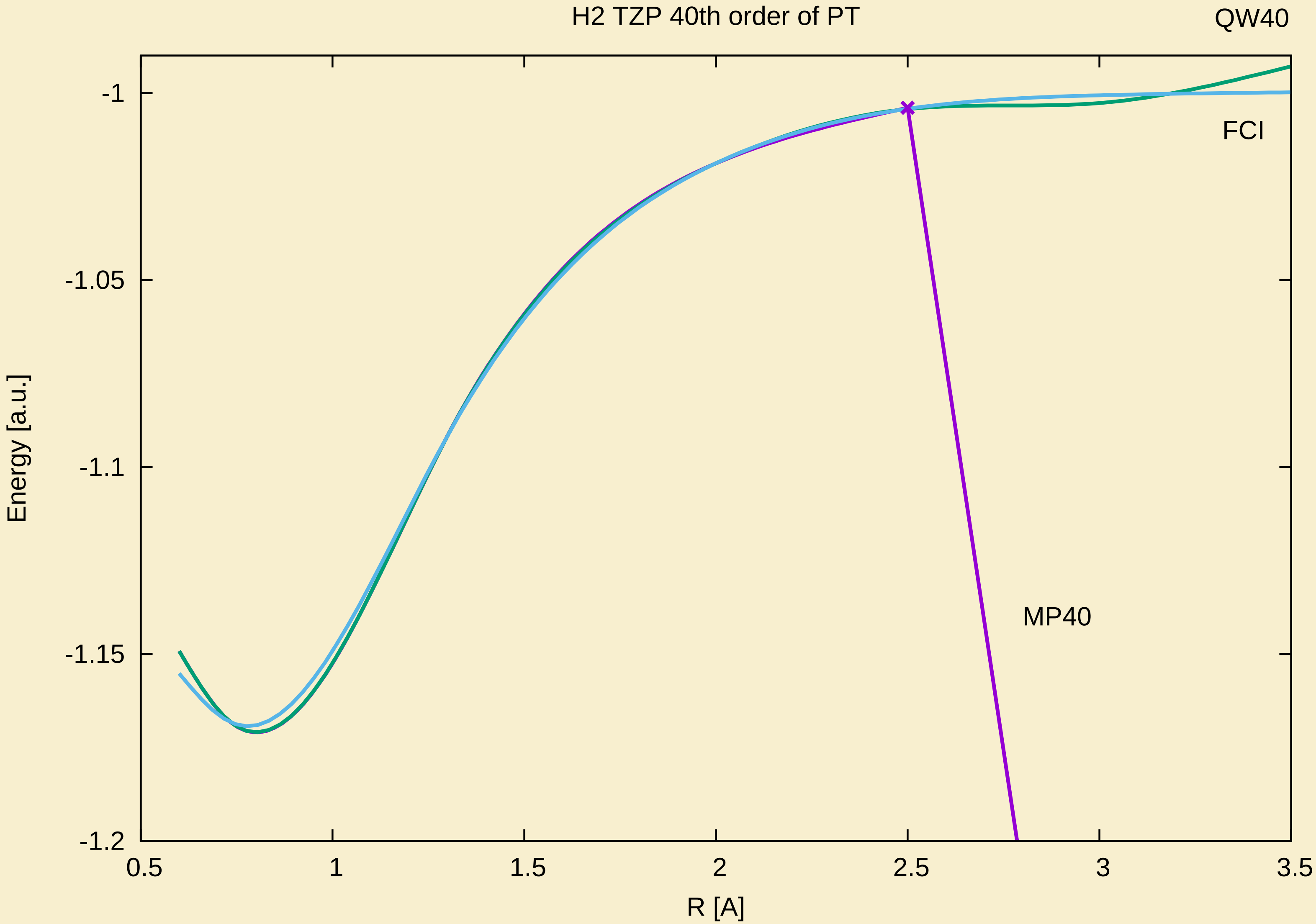
EN
QW-opt
energy (arbitrary units)
order of PT
2
1.5
1
0.5
0
5
10
15
20
25
30
35
40
45
50

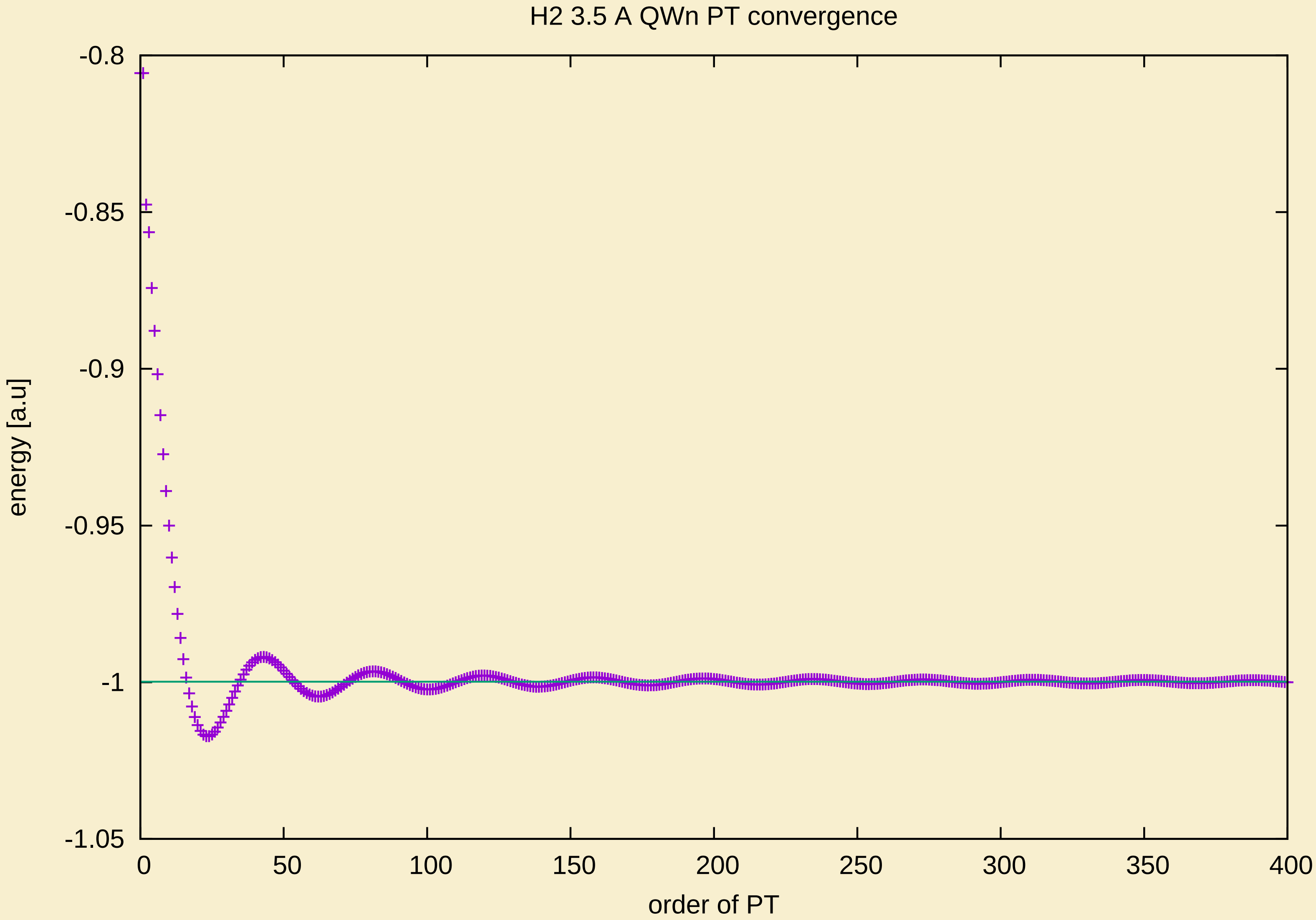
SR Potential Curve H_2 TZP 3.0 Å

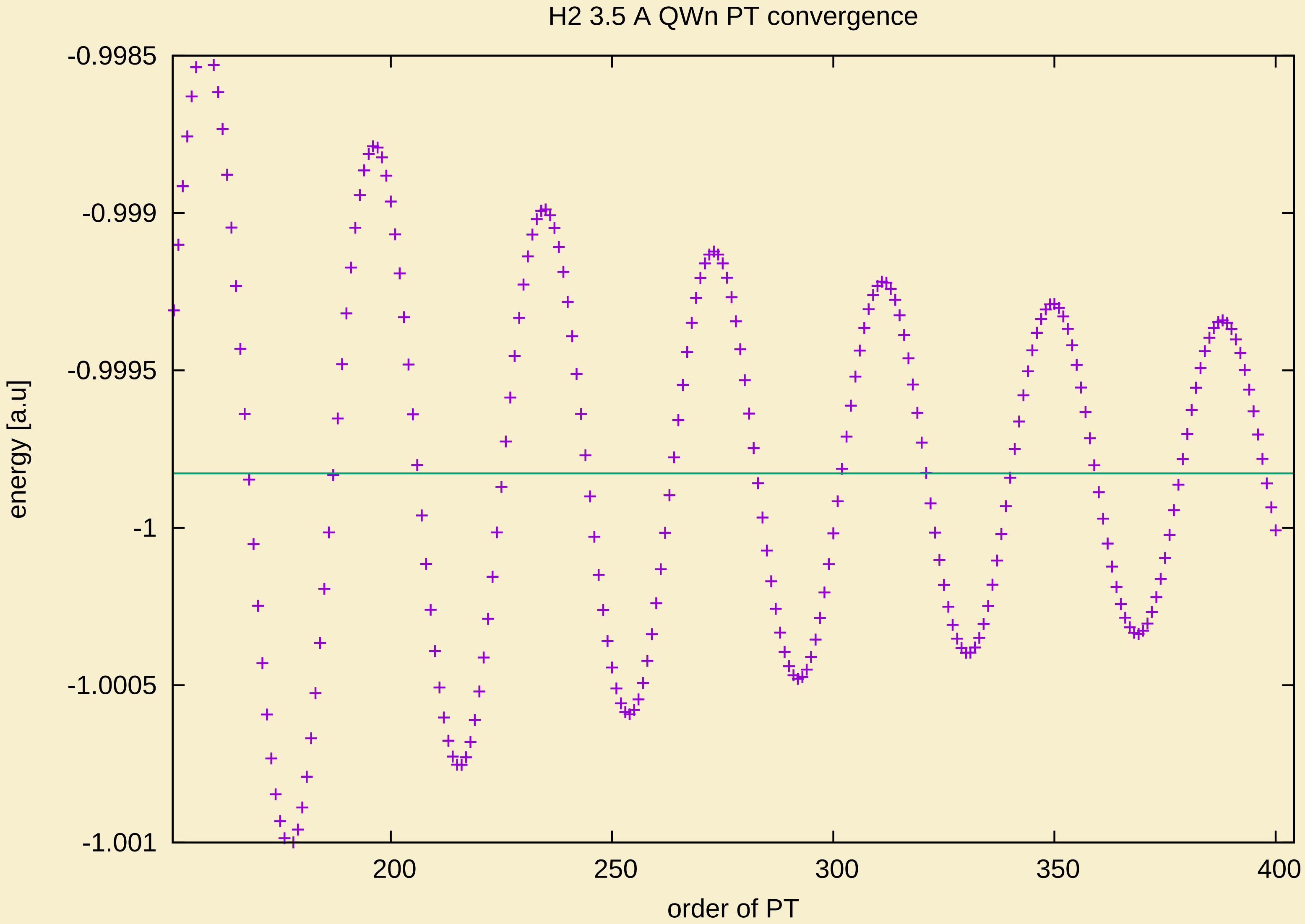


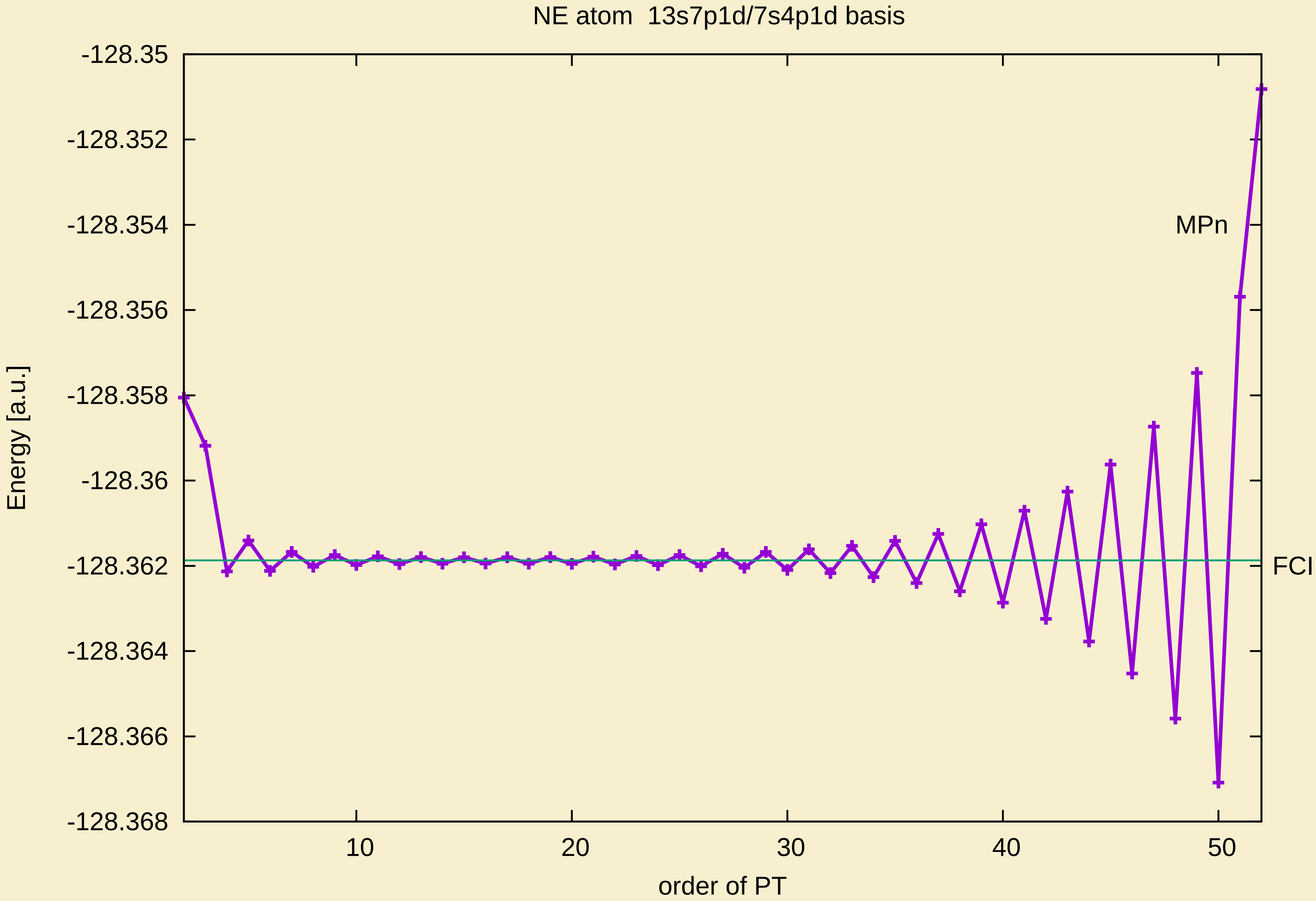

H2 5th order PT energies
Energy [a.u.]
−0.85
−0.9
−0.95
−1
−1.05
−1.1
−1.15
−1.2
0.5
1
1.5
2
2.5
3
3.5
bond length [Å]
EN5
QW5
FCI
MP5

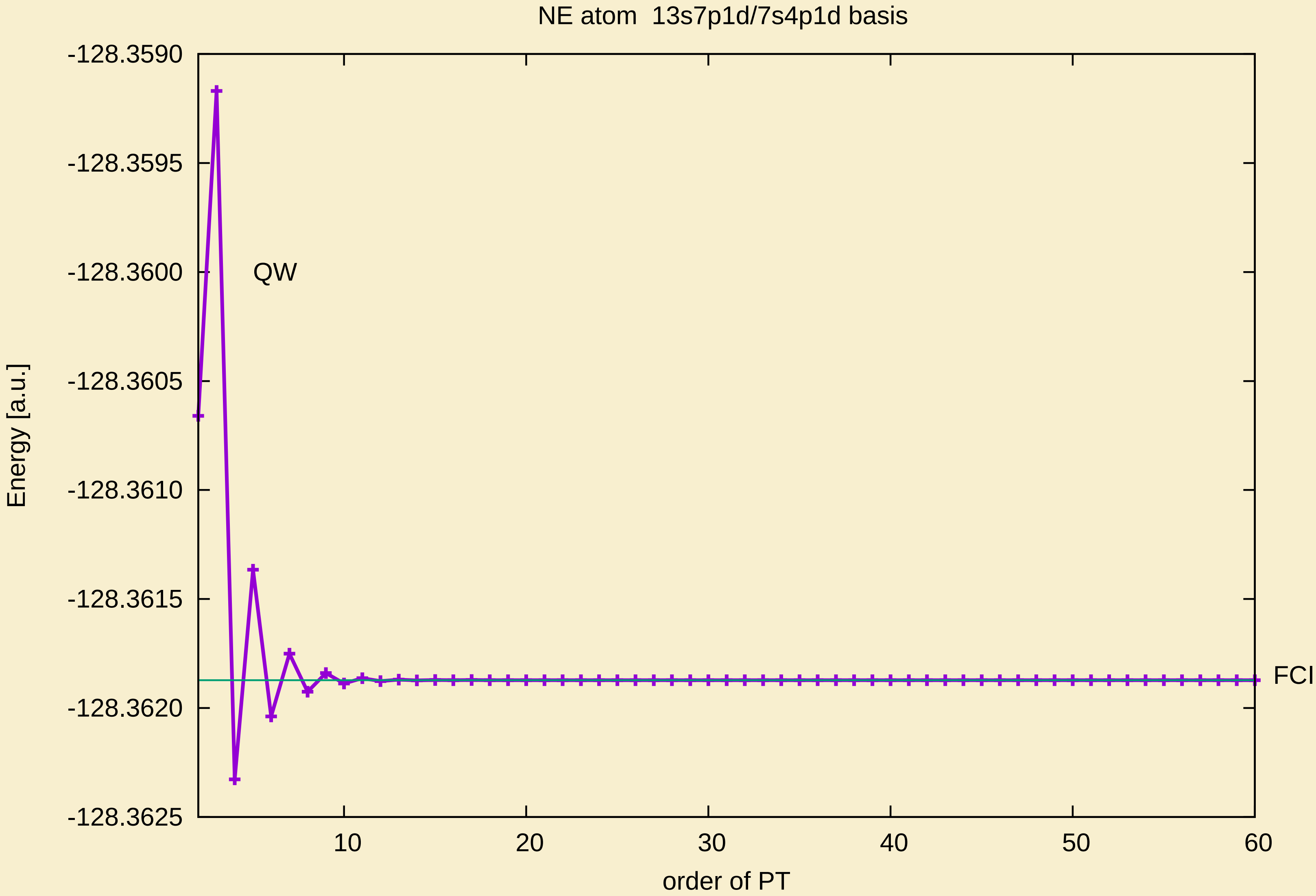

H2 Potential curve, 20th order of PT
Energy [a.u.]
-1
-1.05
-1.1
-1.15
-1.2
0.5
1
1.5
2
2.5
3
3.5
R [A]
FCI
QW20
MP20

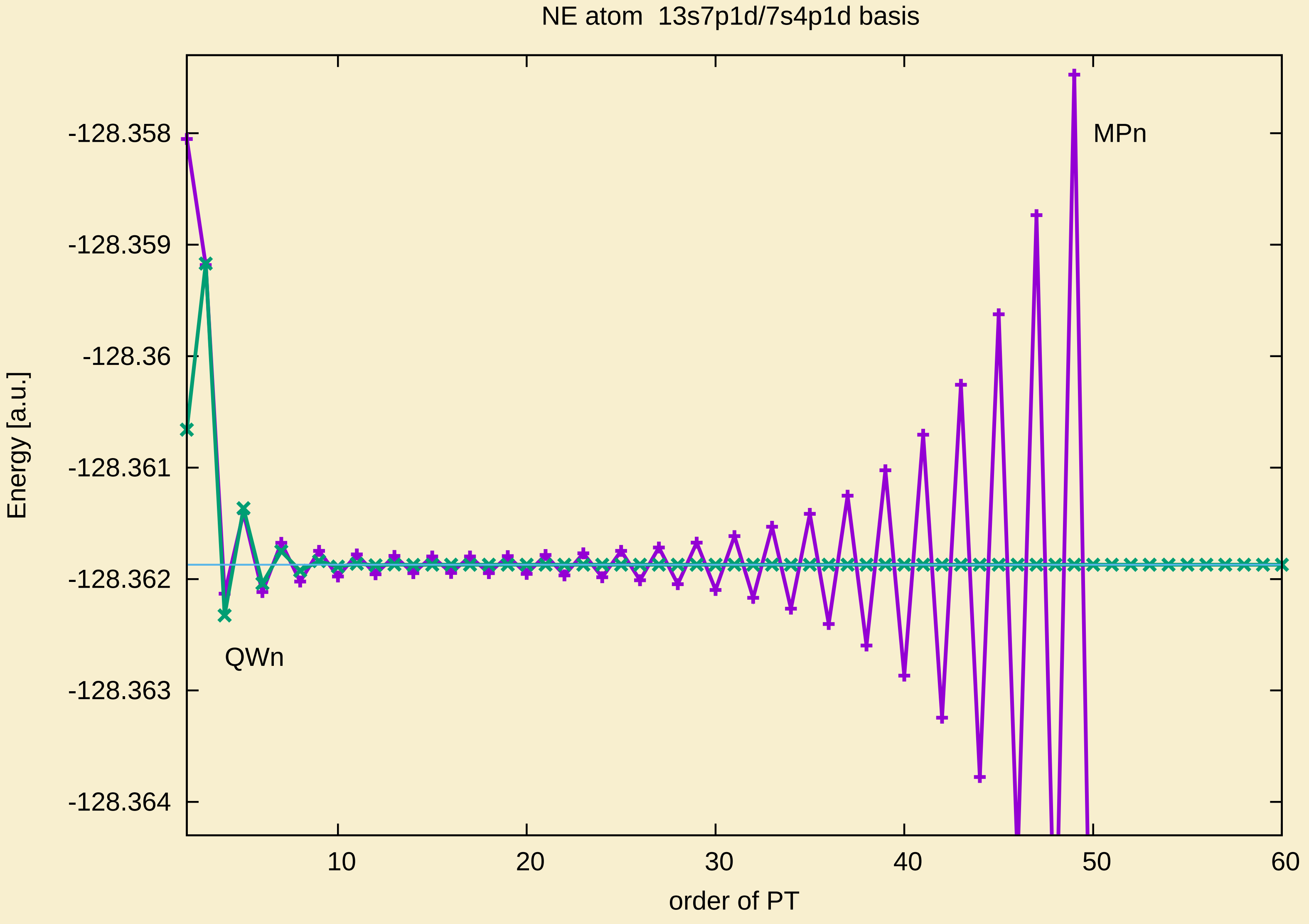

H2 TZP 40th order of PT
QW40
FCI
MP40
Energy [a.u.]
R [A]
-1
-1.05
-1.1
-1.15
-1.2
0.5
1
1.5
2
2.5
3
3.5


H2 3.5 A QWn PT convergence
energy [a.u]
order of PT
-0.8
-0.85
-0.9
-0.95
-1
-1.05
0
50
100
150
200
250
300
350
400


H2 3.5 A QWn PT convergence
-0.9985
-0.999
-0.9995
-1
-1.0005
-1.001
energy [a.u]
200
250
300
350
400
order of PT


NE atom 13s7p1d/7s4p1d basis
-128.35
-128.352
-128.354
-128.356
-128.358
-128.36
-128.362
-128.364
-128.366
-128.368
Energy [a.u.]
10
20
30
40
50
order of PT
MPn
FCI


NE atom 13s7p1d/7s4p1d basis
-128.3590
-128.3595
-128.3600
-128.3605
-128.3610
-128.3615
-128.3620
-128.3625
Energy [a.u.]
QW
FCI
10
20
30
40
50
60
order of PT


NE atom 13s7p1d/7s4p1d basis
Energy [a.u.]
-128.358
-128.359
-128.36
-128.361
-128.362
-128.363
-128.364
10
20
30
40
50
60
order of PT
MPn
QWn

— THE END —

Analytic continuation approach to the resummation of divergent series in Rayleigh-Schrödinger perturbation theory

E. Zs. Mihálka and Péter R. Surján

February 21, 2018

SZTE, ELMÉLETI FIZKAI TANSZÉK, 2018.2.22.

$$\hat{H}(z) = \hat{H}^{(0)} \; + \; z \, \hat{W}. \tag{1}$$

$$\hat{H}(z) \; \Psi(z) = E(z) \; \Psi(z), \tag{2}$$

$$E(z) \; = \; \sum_n \; z^n E^{(n)} \tag{3}$$

LINEAR PADÉ APPROXIMANT

$$q(z)E_{[NM]}(z) = p(z) \tag{4}$$

$$E_{[NM]}(z) = \frac{p(z)}{q(z)} \tag{5}$$

QUADRATIC PADÉ APPROXIMANT

$$r(z)E^2_{[NMR]}(z) + q(z)E_{[NMR]}(z) = p(z) \tag{6}$$

$$E_{[NMR]}(z) = \frac{-q(z) \pm \sqrt{q(z)^2 + 4r(z)p(z)}}{2r(z)} \tag{7}$$

A trivial example

$1 - 2 + 4 - 8 + 16 - 32 \pm \ldots$: — Taylor expansion of $1/(1+2x)$ at x=1

Scaling by $0 < \mu < 1/2$: convergent. E.g., for $\mu = 0.4$:

$$f(0.4) = 1 - 0.8 + 0.64 - 0.512 + 0.410 - 0.327 \pm \ldots = 0.55\dot{5}.$$

No singularities in the real axis, so:

- draw $f(\mu)$
- use a Padé approximant to extrapolate
- $[0,1]$ Padé fits exactly: gives $1/(1+2) = 1/3$, at $\mu = 1$.

Anharmonic oscillator

$$\hat{H} = -\frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{2}\omega x^2 + \gamma x^4. \tag{8}$$

PT contributions (EN partitioning, $\gamma = 0.1$):

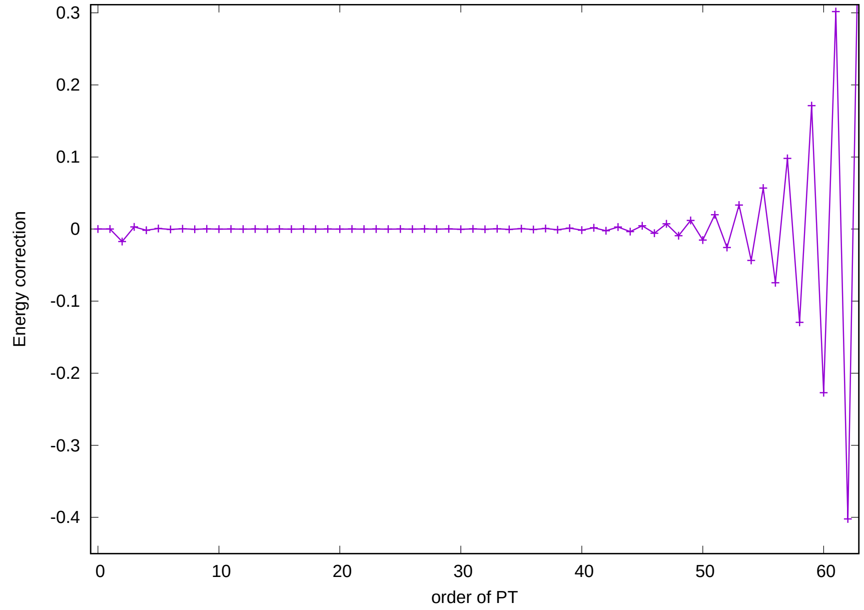
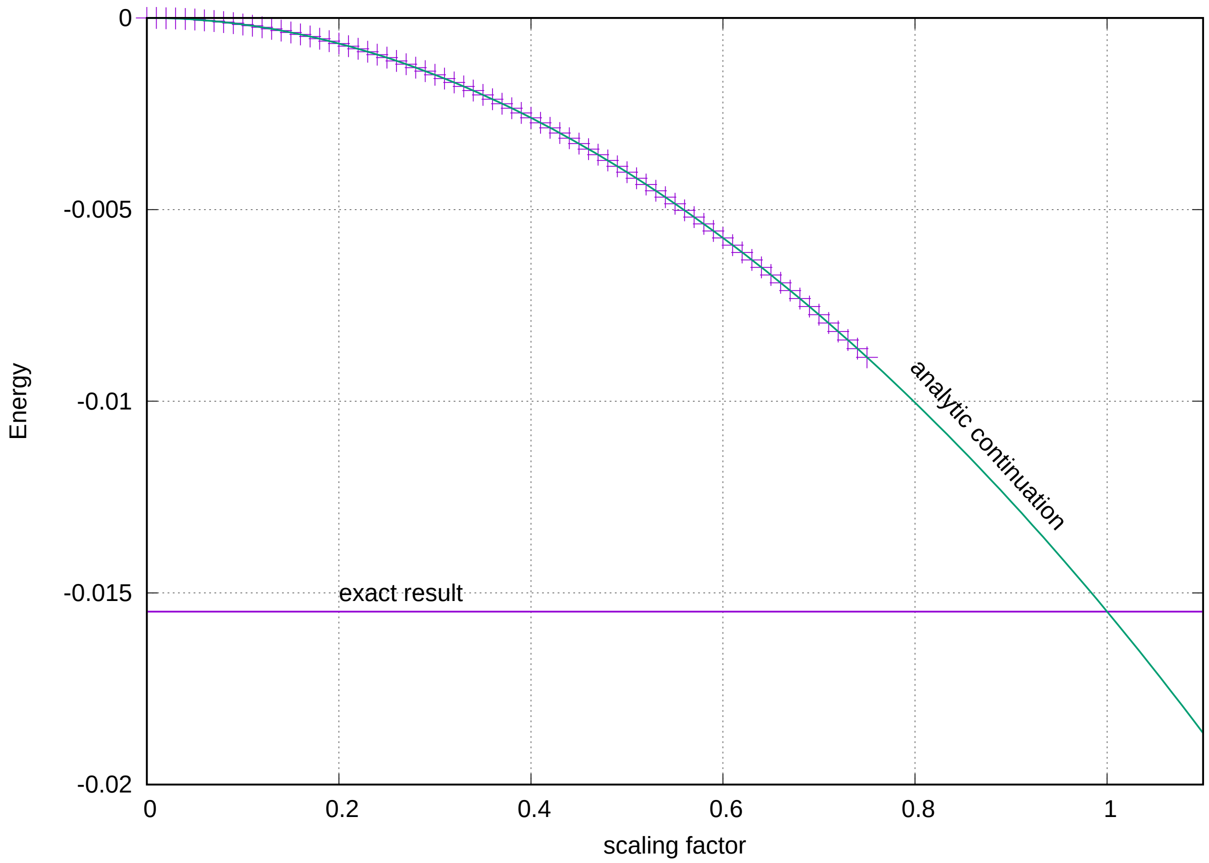


Table 1: Perturbational energy contributions for the quartic anharmonic oscillator

	energy correction [a.u.]			
order	original	scaled		
n	μ =1.0	μ =0.2	μ =0.4	μ =0.6
0	0.0	0.000000	0.000000	0.000000
1	0.0	0.000000	0.000000	0.000000
2	-0.017660	-0.000706	-0.002826	-0.006358
3	0.003103	0.000025	0.000199	0.000670
4	-0.001817	-0.000003	-0.000047	-0.000236
5	0.000873	0.000000	0.000009	0.000068
6	-0.000567	-0.000000	-0.000002	-0.000026
7	0.000372	0.000000	0.000001	0.000010
...				
40	-0.001651	-0.000000	-0.000000	-0.000000
...				
50	-0.017227	-0.000000	-0.000000	-0.000000
SUM	∞	-0.000684	-0.002666	-0.005876



Analytic continuation of the energy of the quartic anharmonic oscillator

Table 2: Predicted values for the energy of quartic anharmonic oscillator with coupling constant γ=0.1 as obtained from analytic continuation.

method of continuation	energy [a.u.]
polynomial of order 2	-0.016352
polynomial of order 4	-0.015866
polynomial of order 6	-0.015853
$[2,2]$ linear Padé approximation	-0.015854
$[4,4]$ linear Padé approximation	-0.015853
$[6,6]$ linear Padé approximation	-0.015855
$[2,2,2]$ quadratic Padé approximation	-0.015858
$[4,4,4]$ quadratic Padé approximation	-0.015853
$[6,6,6]$ quadratic Padé approximation	-0.015853
exact solution	-0.015854

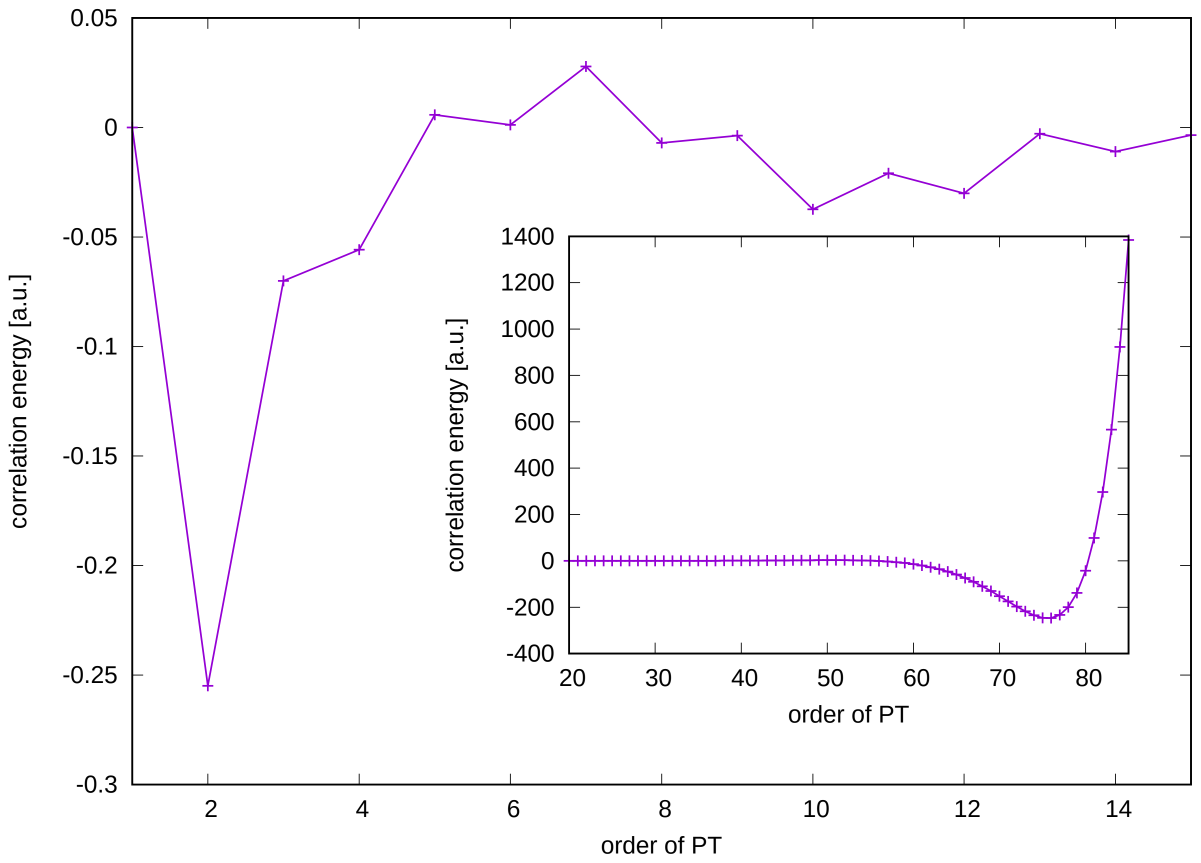
Table 3: Dependence of the predicted energies as obtained by fitting [6,6,6] quadratic Padé approximants for the anharmonic oscillator from the size of the fitting region.

fitting region	$E_{[6,6,6]}$	number of orders used
$[0-0.4]$	0.015868	6
$[0-0.5]$	0.015850	8
$[0-0.6]$	0.015851	10
$[0-0.7]$	0.015853	24
exact result	0.015854	∞

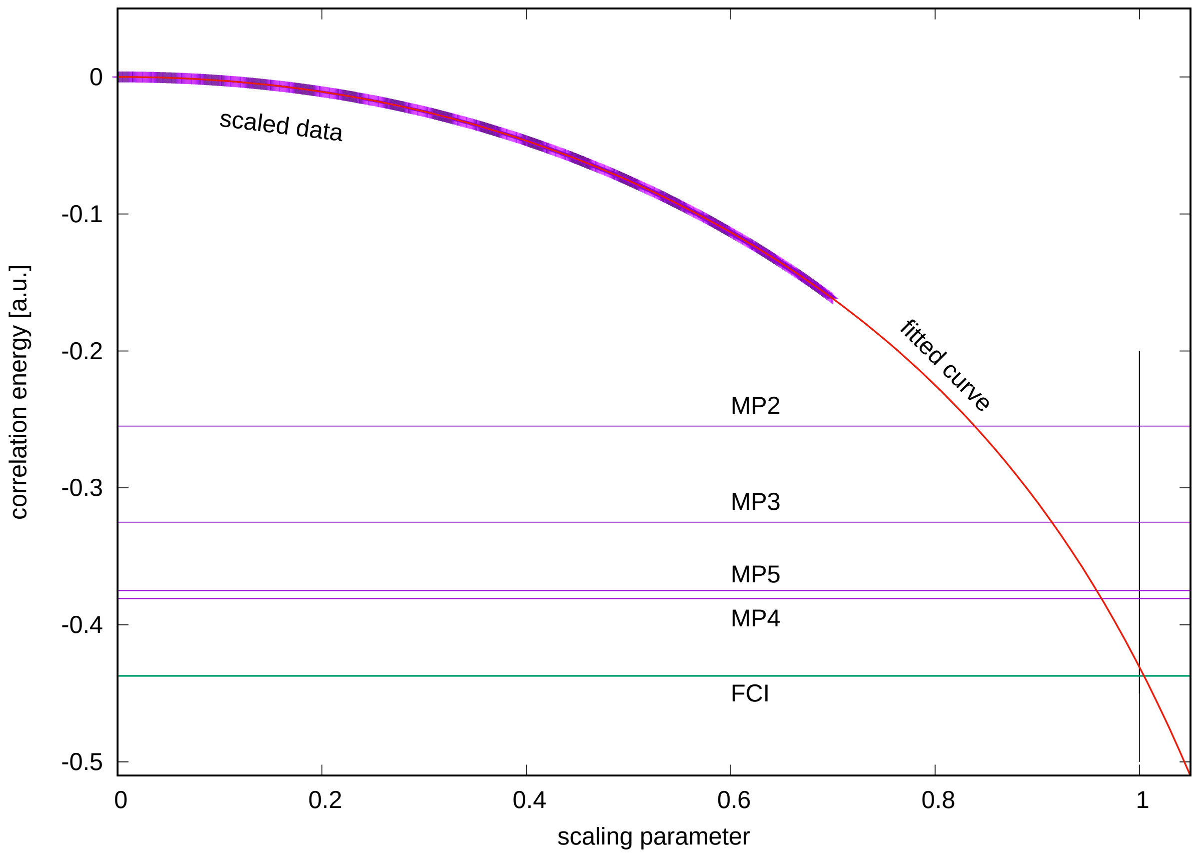
Correlation energy

Table 4: Correlation energy of dissociating water

	energy correction [a.u.]			
order	original	scaled		
n	$\mu = 1$	$\mu = 0.3$	$\mu = 0.2$	$\mu = 0.1$
2	-0.254895	-0.022941	-0.010196	-0.002549
3	-0.070076	-0.001892	-0.000561	-0.000070
4	-0.055826	-0.000452	-0.000089	-0.000006
5	0.005759	0.000014	0.000002	0.000000
6	0.001211	0.000001	0.000000	0.000000
7	0.027852	0.000006	0.000000	0.000000
∞		-0.025264	-0.010844	-0.002625



Correlation energy of water in MP partitioning.

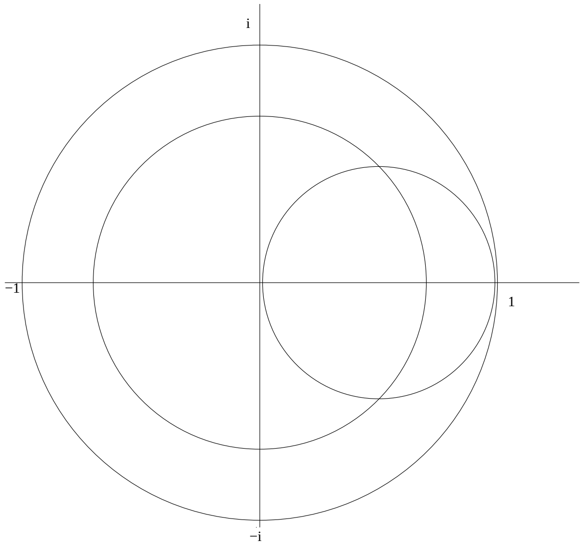


0
-0.1
-0.2
-0.3
-0.4
-0.5
correlation energy [a.u.]
0
0.2
0.4
0.6
0.8
1
scaling parameter
scaled data
fitted curve
MP2
MP3
MP5
MP4
FCI

Table 5: Correlation energy of the water molecule at 2.5 equilibrium distance predicted by analytic continuation

method of continuation	correlation energy [a.u.]
polynomial of order [6]	-0.43266
$[6, 6]$ linear Padé approximation	-0.43715
exact (full-CI) result	-0.43725

Inverz peremérték feladat

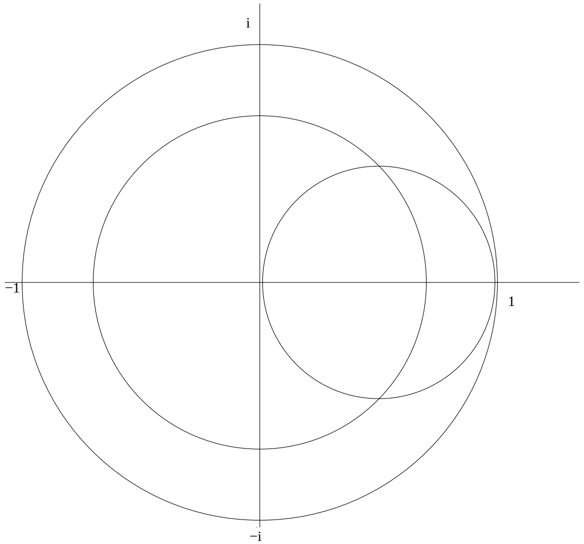


$$E(z) = u(x,y) + i\,v(x,y)$$

$$\Delta u(x,y) = 0$$

Mik azok a peremértékek, amik képesek reprodukálni a "trusted" régió exact értékeit?

Cauchy integrál formula



$$\oint \frac{E(z)}{z-z_0}\, dz \;=\; 2\pi i E(z_0)$$

Teszt számítás a

$$f(z) = \frac{z^2}{1 + 2z^2}$$

függvényre: