COPING WITH DIVERGENT PERTURBATION SERIES

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Content

- The Basic Problem of Quantum Chemistry
- Perturbation Theory
- Improving Convergence
- Determining Convergence: Singularity Analysis
- Regularizing Divergent Series

INTRODUCTION
The Basic Problem of Quantum Chemistry

$$H\,\Psi_k \;=\; E_k\,\Psi_k \qquad\quad k = 0, 1, \ldots$$

$$H = -\frac{1}{2}\,\Delta_{3N} \;+ \sum_{i=1}^{N} V_i + \sum_{i<j}^{N} V(i,j)$$

$$\Psi = \Psi(x_1, y_1, z_1, x_2, y_2, \cdots x_N, y_N, z_N)$$

INTRODUCTION
Perturbation Theory

$$H = H^0 + \lambda W$$

$$H^0 \, \Psi_k^0 \; = \; E_k^0 \, \Psi_k^0 \qquad k = 0, 1, \ldots$$

$$\Psi = \sum_{\mu=0}^{\infty} \lambda^\mu \, \Psi^{(\mu)} \qquad E = \sum_{\mu=0}^{\infty} \lambda^\mu \, E^{(\mu)}$$

Rayleigh–Schrödinger **Brillouin–Wigner** **Béla Szőkefalvi-Nagy**

PT from iterative Schrödinger eq.

$$\left(H^0 + W\right)\Psi \;=\; \left(E^0 + \Delta E\right)\Psi$$
$$\left(H^0 - E^0\right)\Psi \;=\; \left(\Delta E - W\right)\Psi$$

Define Q: $$Q\left(H^0 - E^0\right) \;=\; P \;:=\; 1 - P^0$$

where $$P^0\Psi \;=\; \Psi^0$$

$$\underbrace{Q\left(H^0 - E^0\right)\Psi}_{(1-P^0)\Psi \;=\; \Psi-\Psi^0} \;=\; Q\left(\Delta E - W\right)\Psi$$

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

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

Iterative solution, starting with Ψ^0:

$$\Psi^1 = -\,Q\,W\Psi^0 + \ldots$$

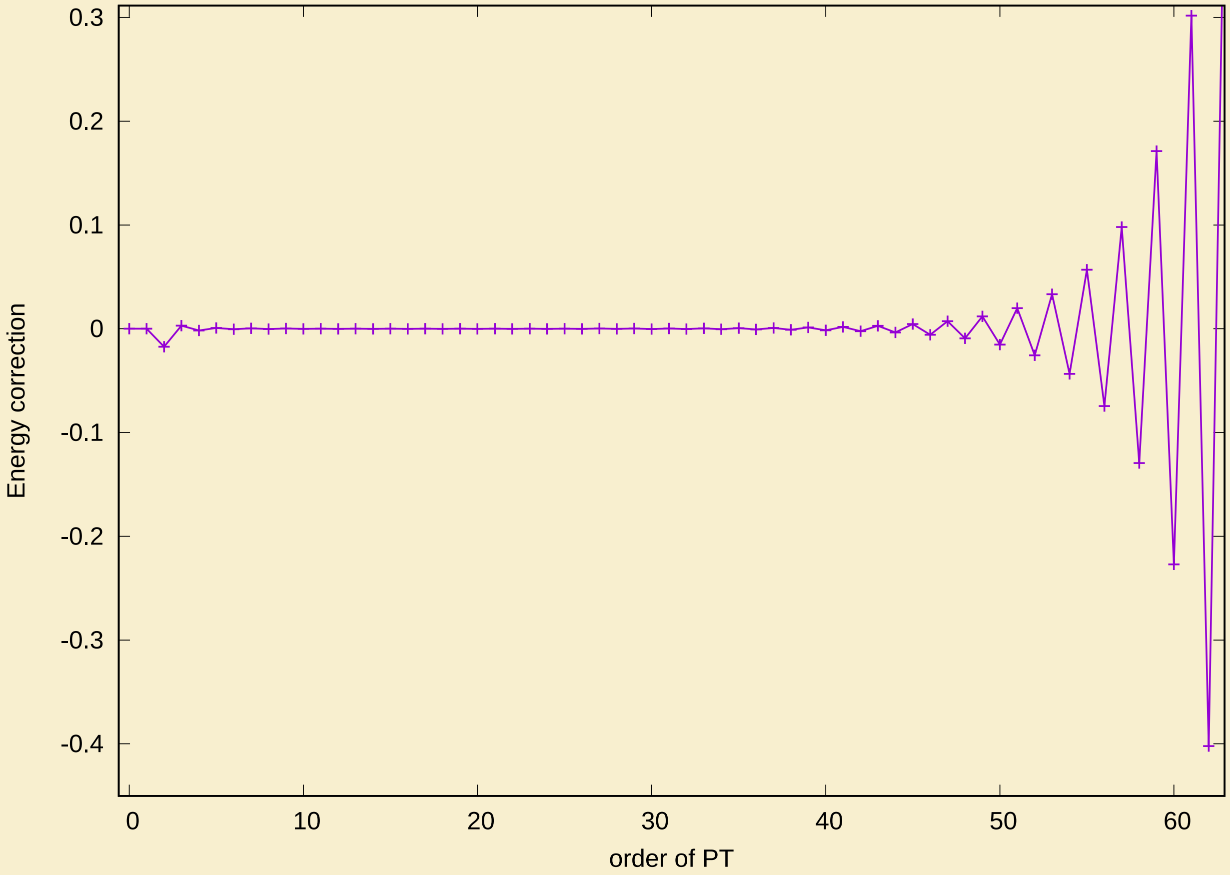
$$\Psi^2 = QWQ\,W\Psi^0 + \ldots$$

$$\Psi^n = \pm\,Q\,\overset{\underset{\smile}{1}}{W}\,Q\,\overset{\underset{\smile}{2}}{W}\,\cdots Q\,\overset{\underset{\smile}{\mathrm{n}}}{W}\,\Psi^0 + \ldots$$

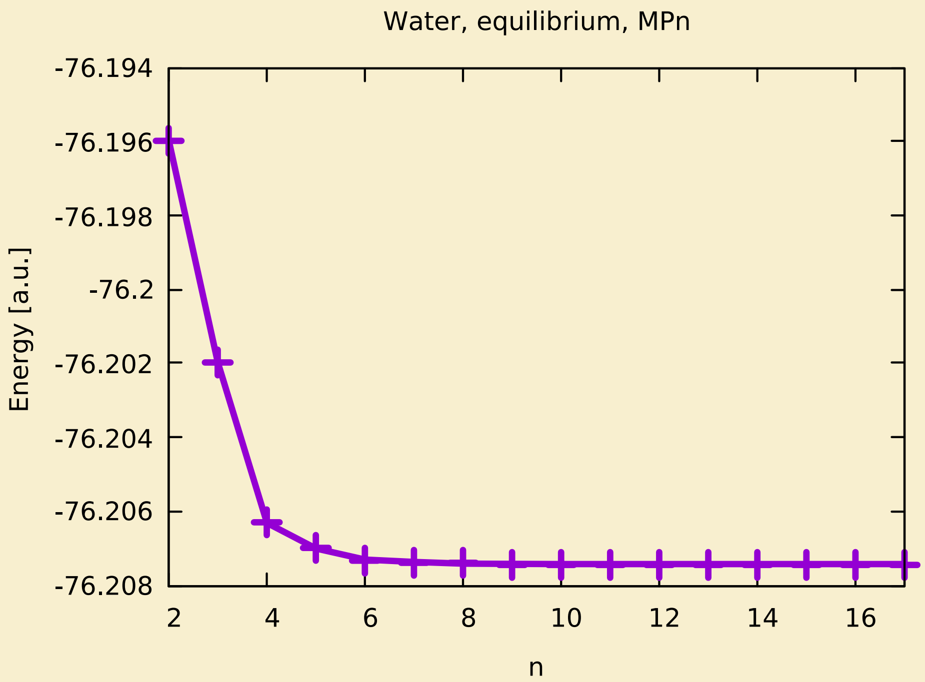
$$E^n = \langle \Psi^0 | W \Psi^{n-1} \rangle$$

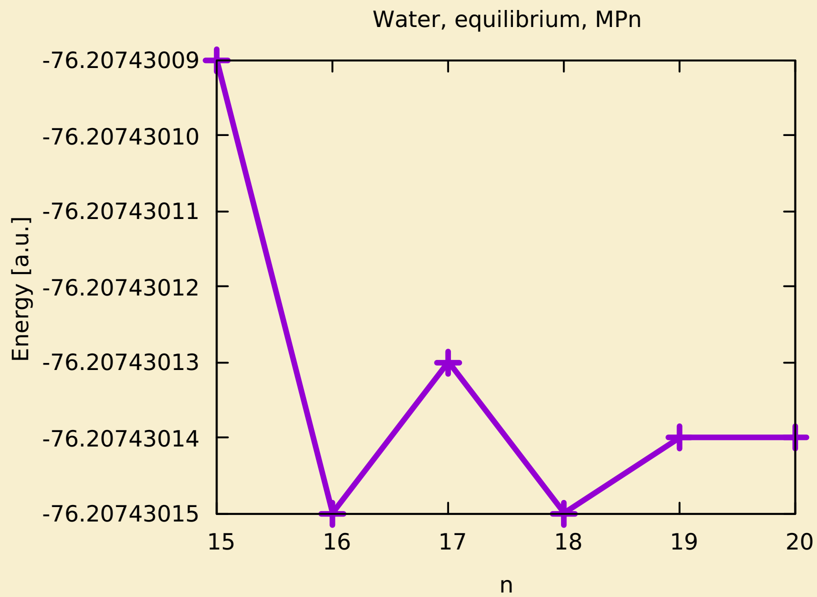
Examples

Anharmonic oscillator

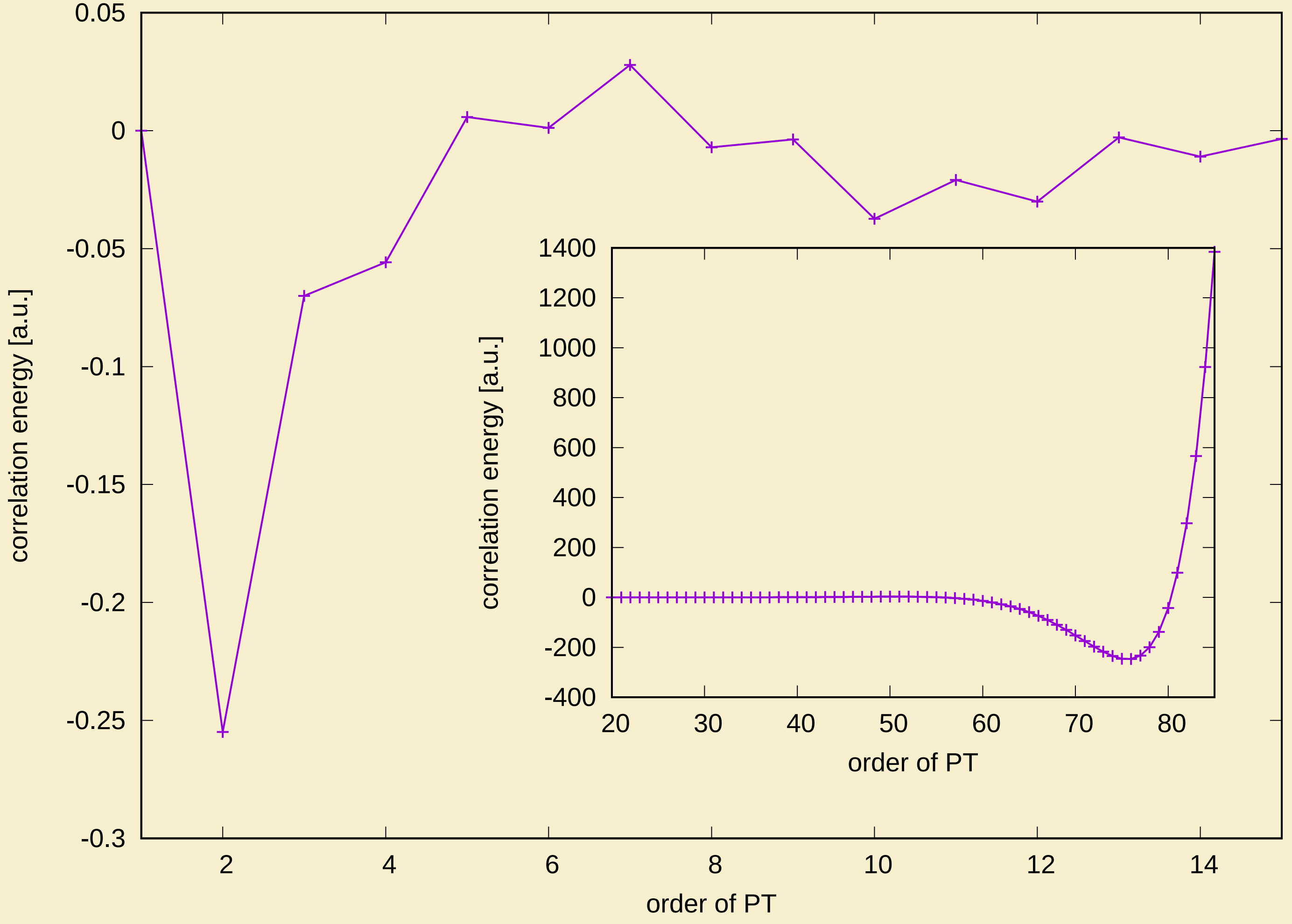


Water molecule – at equilibrium





Water molecule – prolongated R(O—H)



strongly divergent after some maelstrom

Simple extrapolation/damping techniques

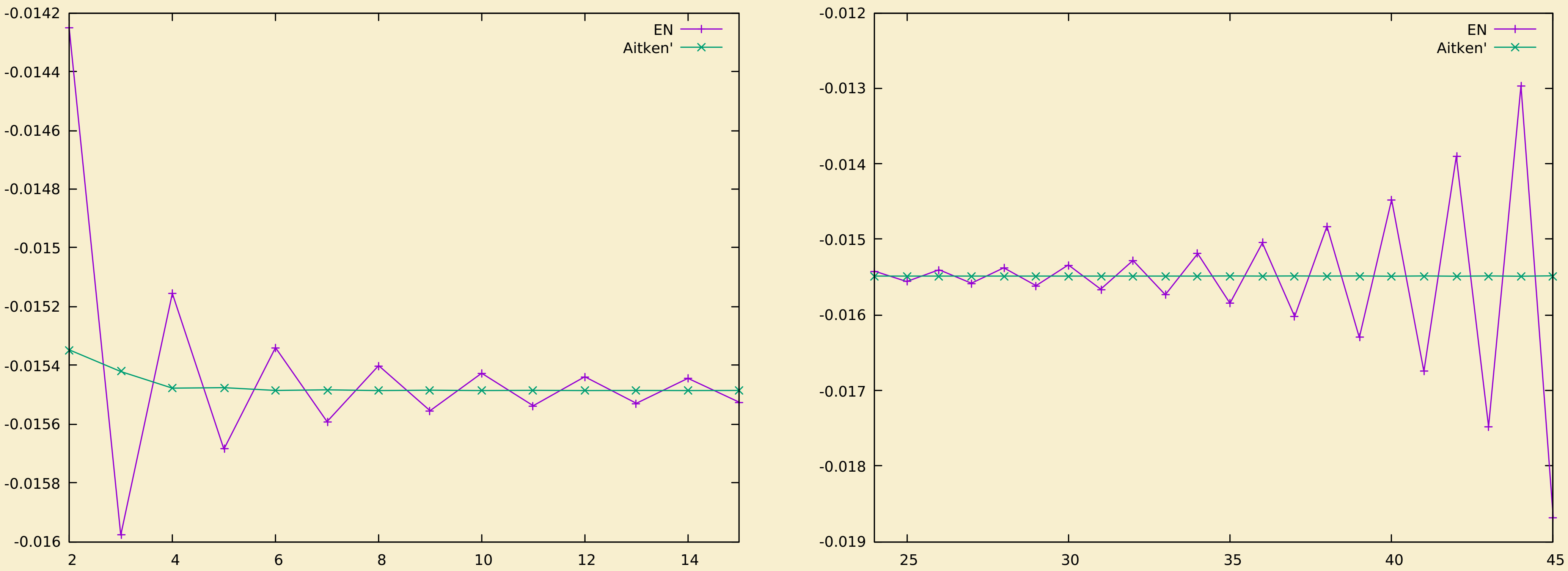
Aitken (Wynn, Shanks) 3-point extrapolation

$$S_n = \sum_{k=0}^{n} a_k$$

$$T_n = \frac{S_{n+1}S_{n-1} - S_n^2}{S_{n+1} - 2S_n^2 + S_{n-1}}$$

Derivation: geometric convergence is assumed.

Anharmonic oscillator



...helps very rarely

Resummation of Divergent Series: a Toy Example

$$1 + 2 + 4 + 8 + 16 + \cdots \; = ???$$

Resummation of Divergent Series: a Toy Example

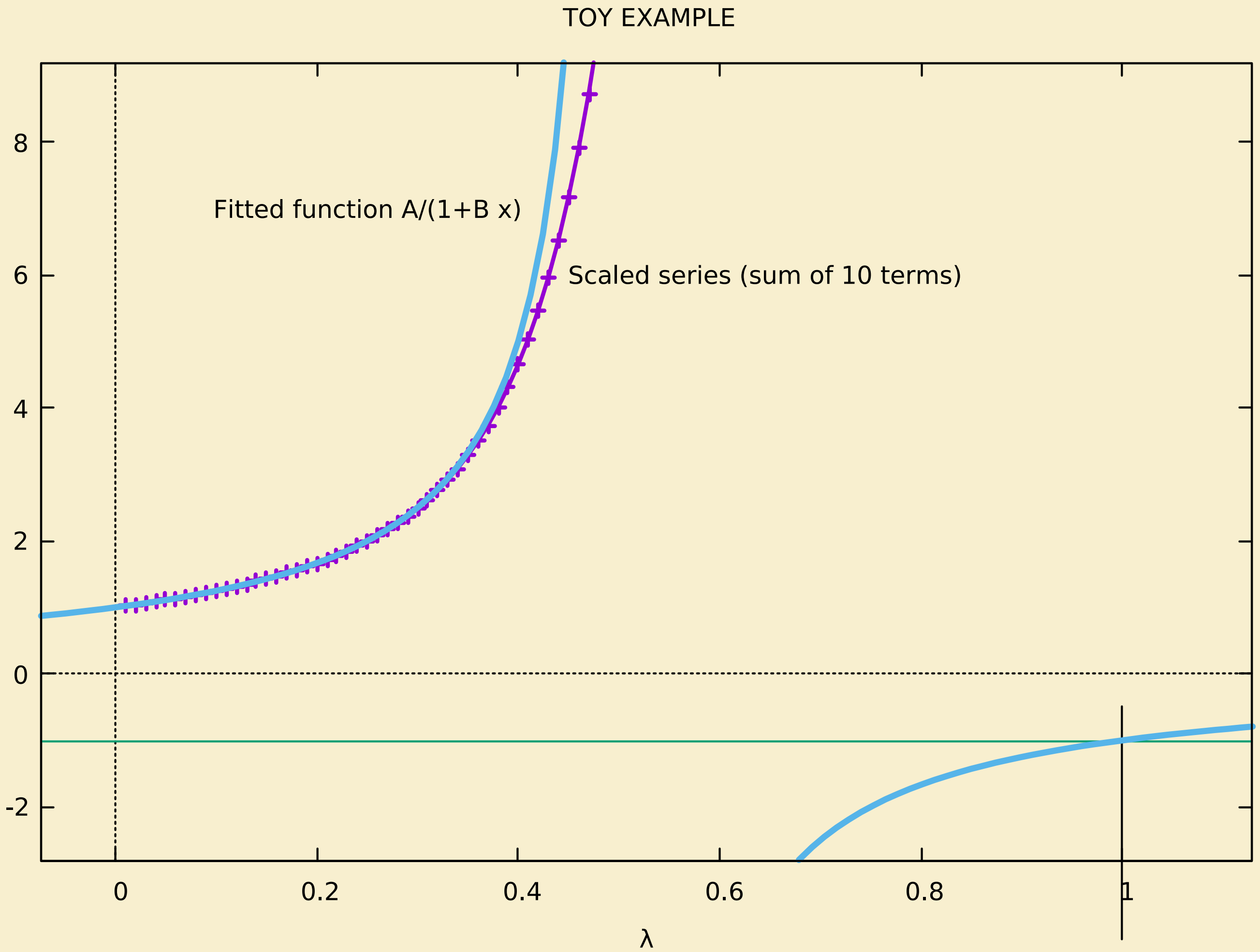
$$\mathbf{1 + 2 + 4 + 8 + 16 + \cdots \; = \; -1.}$$

Resummation of Divergent Series: a Toy Example

$$1+2+4+8+16+\cdots = \sum_{k=0}^{\infty} 2^k \Rightarrow \sum_{k=0}^{\infty} (2\lambda)^k$$

$$\sum_{k}^{\infty} x^k = \frac{1}{1-x} = -1 \quad \textbf{for} \;\; x = 2.$$

$$\sum_{k}^{\infty} (2\lambda)^k = \frac{1}{1-2\lambda} = -1 \quad \textbf{for} \;\; \lambda = 1.$$


TOY EXAMPLE
Fitted function A/(1+B x)
Scaled series (sum of 10 terms)
8
6
4
2
0
-2
0
0.2
0.4
0.6
0.8
1
λ

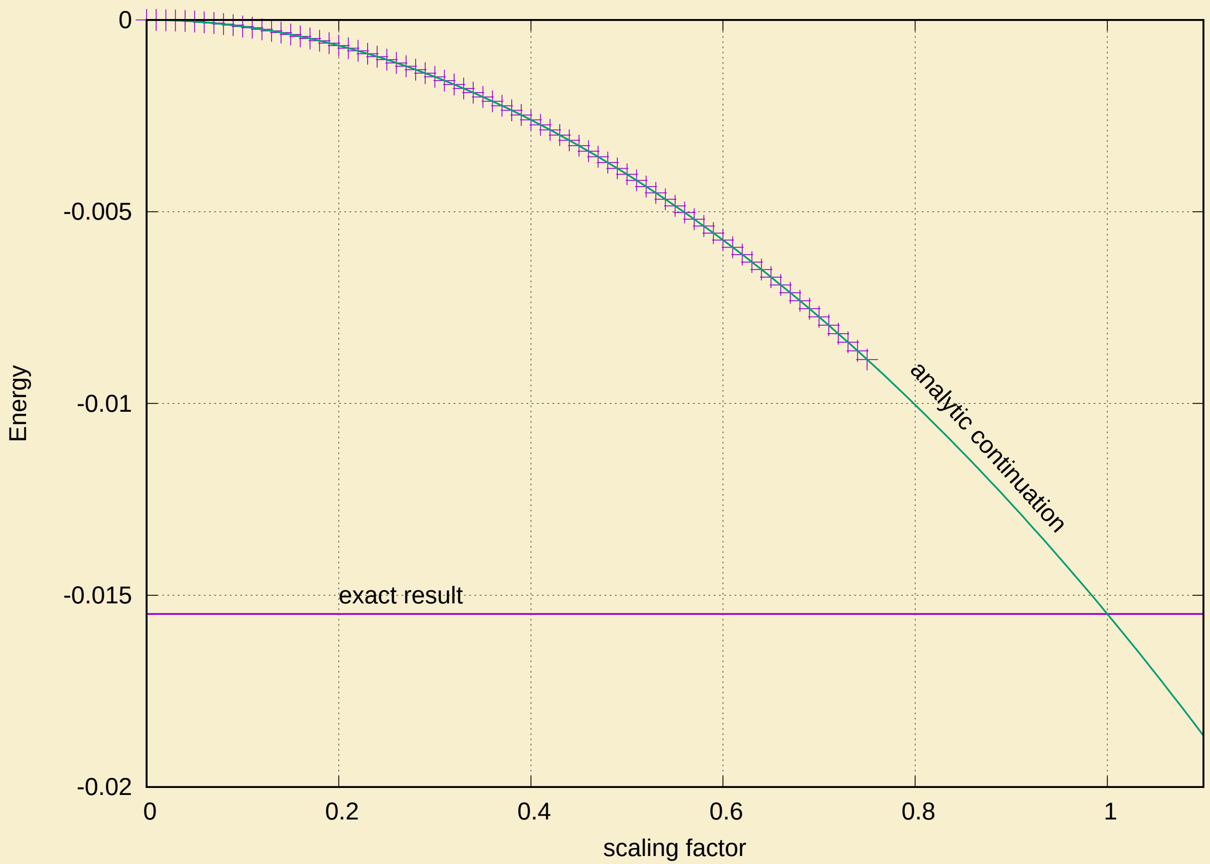
Scaling on the real axis

Anharmonic oscillator

$$H = \underbrace{-\frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{2}\omega x^2}_{H^0} + \lambda\, x^4$$

Perturbational energy contributions for the quartic anharmonic oscillator

	energy correction [a.u.]			
order	original	scaled		
n	λ =1.0	λ =0.2	λ =0.4	λ =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



Extrapolation — a chapter in numerical mathematics?

Extrapolation techniques

- **simple polynomial fit** $E_N(\lambda) = p_N(\lambda)$
- **Padé approximant** $q_M(\lambda)E_{[NM]}(\lambda) = p_N(\lambda)$

$$E_{[NM]}(\lambda) = \frac{p_N(\lambda)}{q_M(\lambda)}$$ ← **can simulate poles**

- **Quadratic Padé approximant** ← **simulates branches**

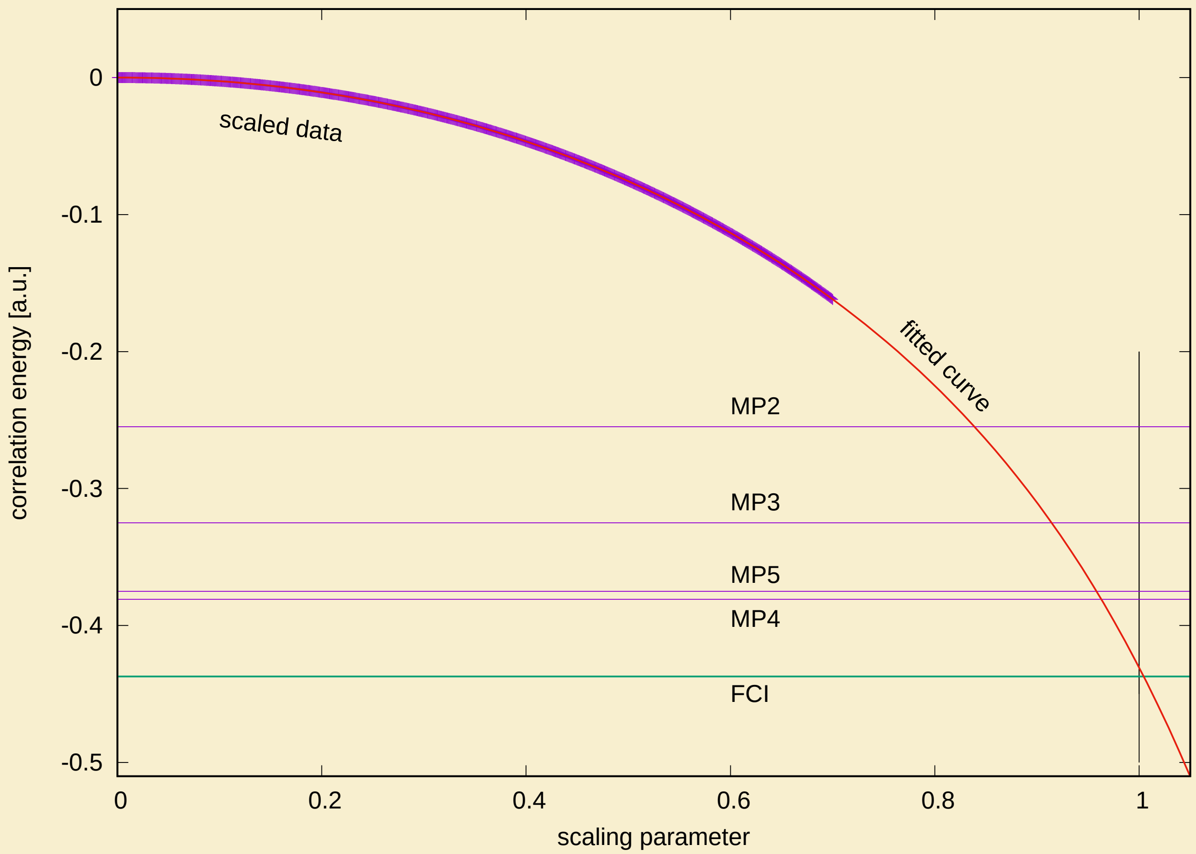
$$r(\lambda)E^2_{[NMR]}(\lambda) + q(\lambda)E_{[NMR]}(\lambda) = p(\lambda)$$

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

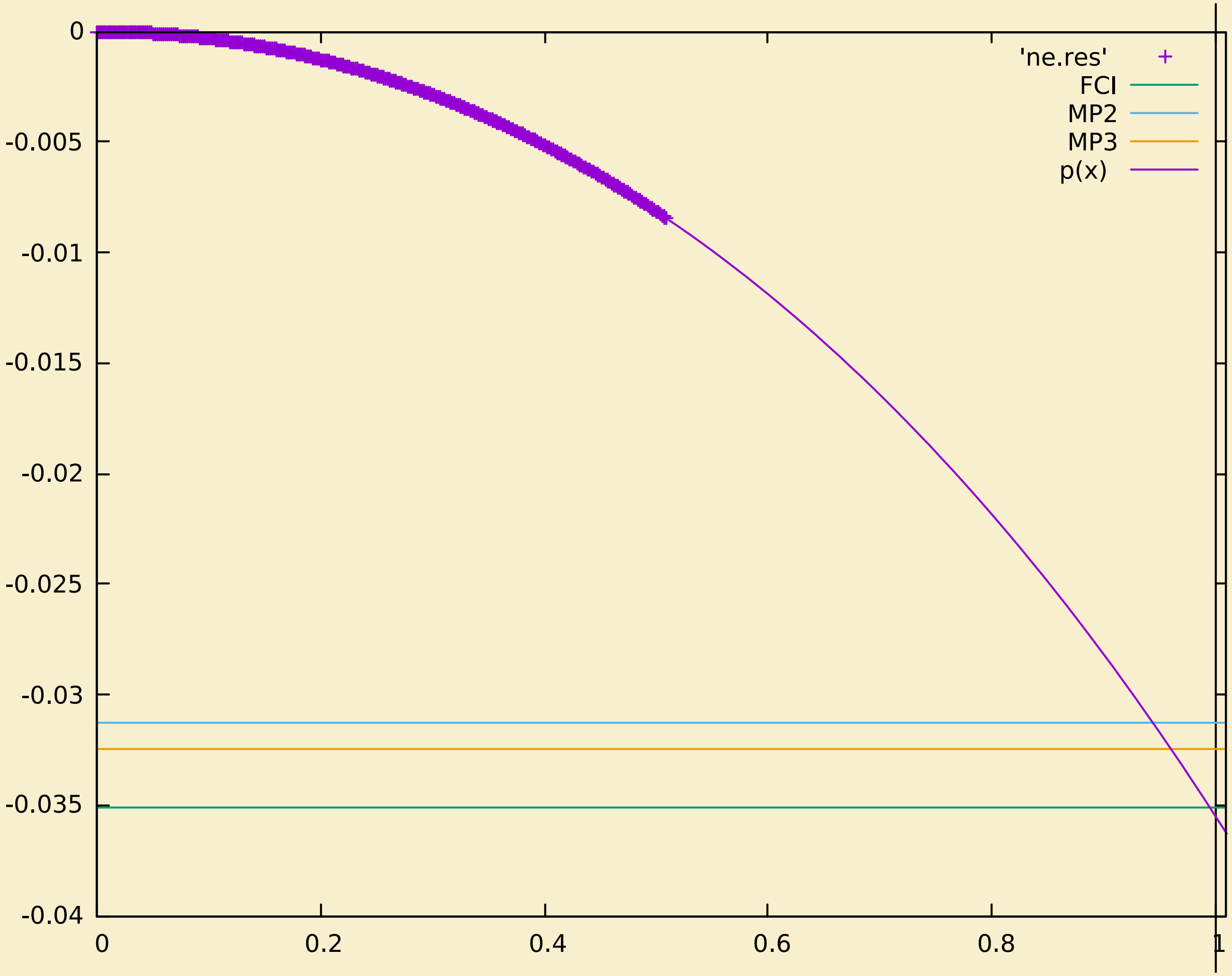
Predicted values for the energy of quartic anharmonic oscillator with coupling constant γ=0.1 as obtained from analytic continuation.

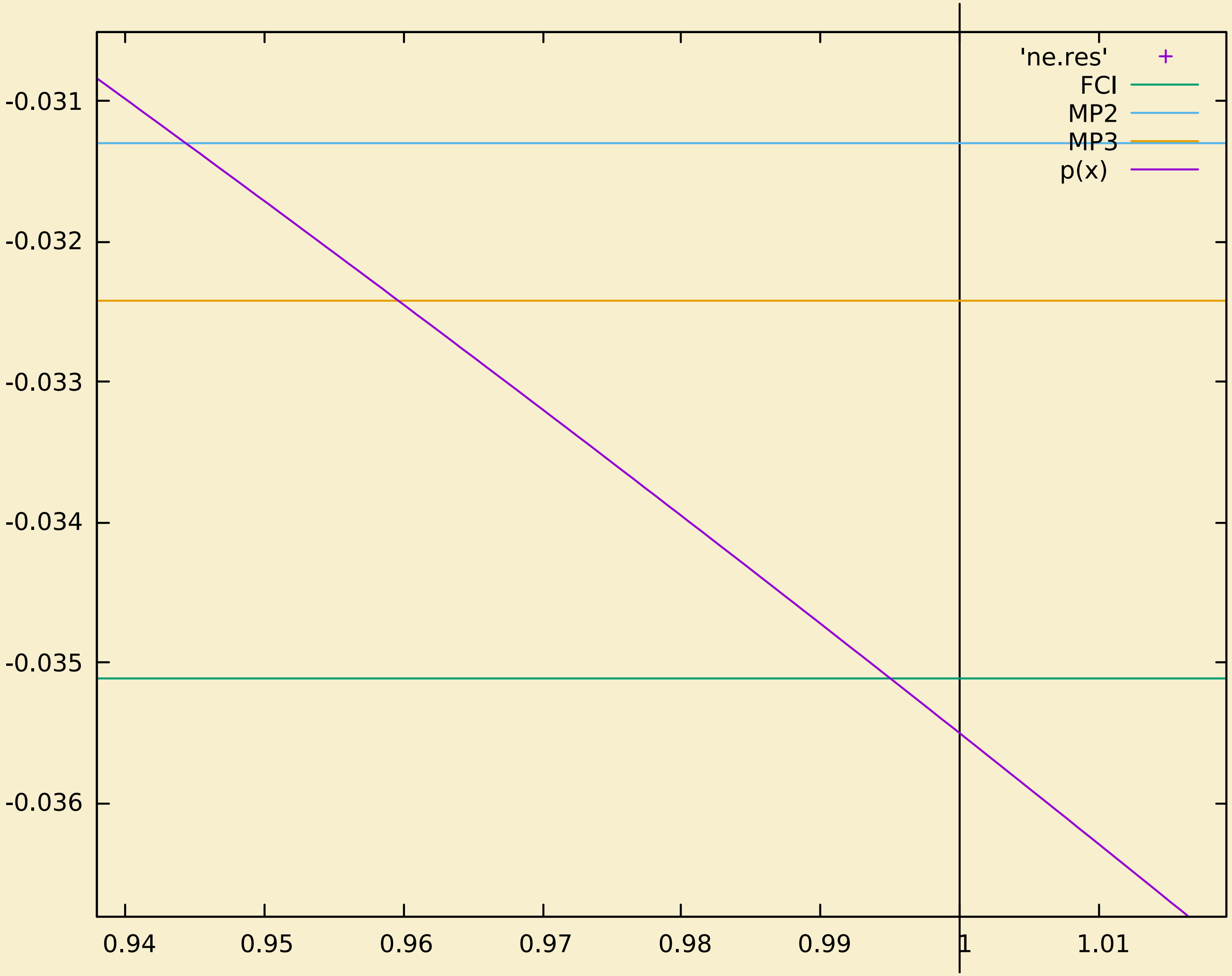
method of continuation	energy [a.u.]
polynomial of order 2	-0.016352
polynomial of order 4	-0.015866
polynomial of order 6	-0.015853
[2, 2] linear Padé approximation	-0.015854
[4, 4] linear Padé approximation	-0.015853
[6, 6] linear Padé approximation	-0.015855
[2, 2, 2] quadratic Padé approximation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

Water correlation energy

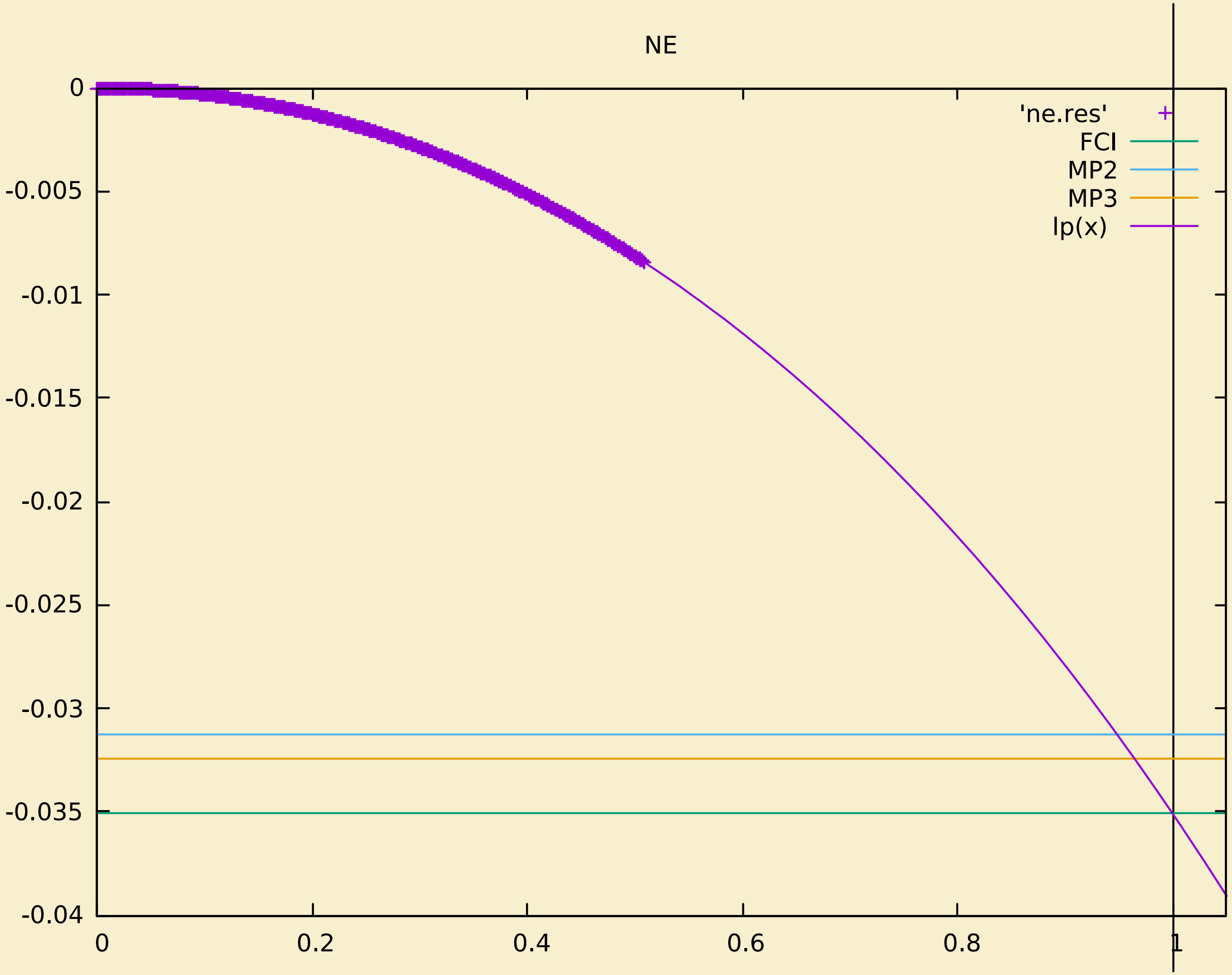


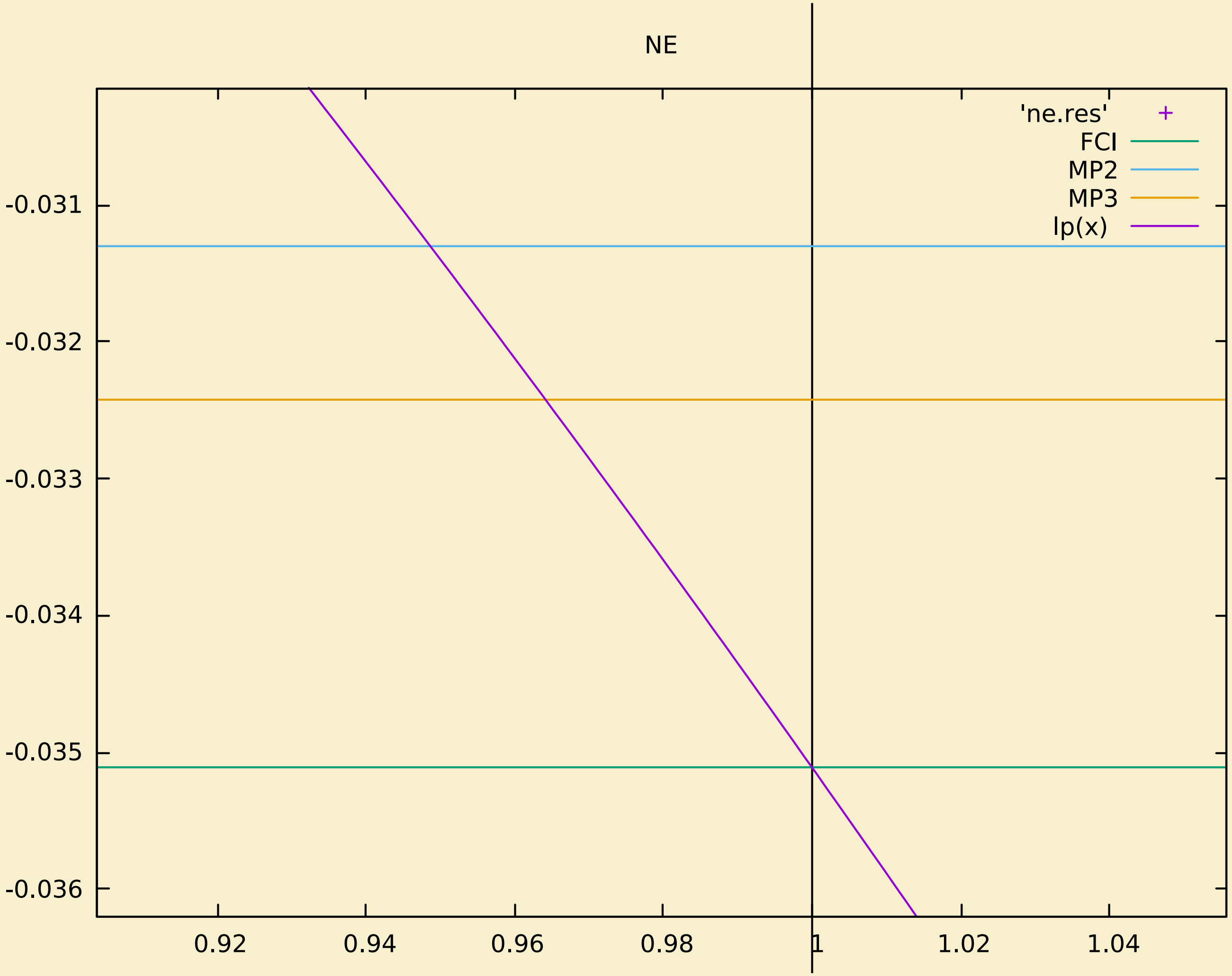
Neon atom:
Analitic continuation with polynomials

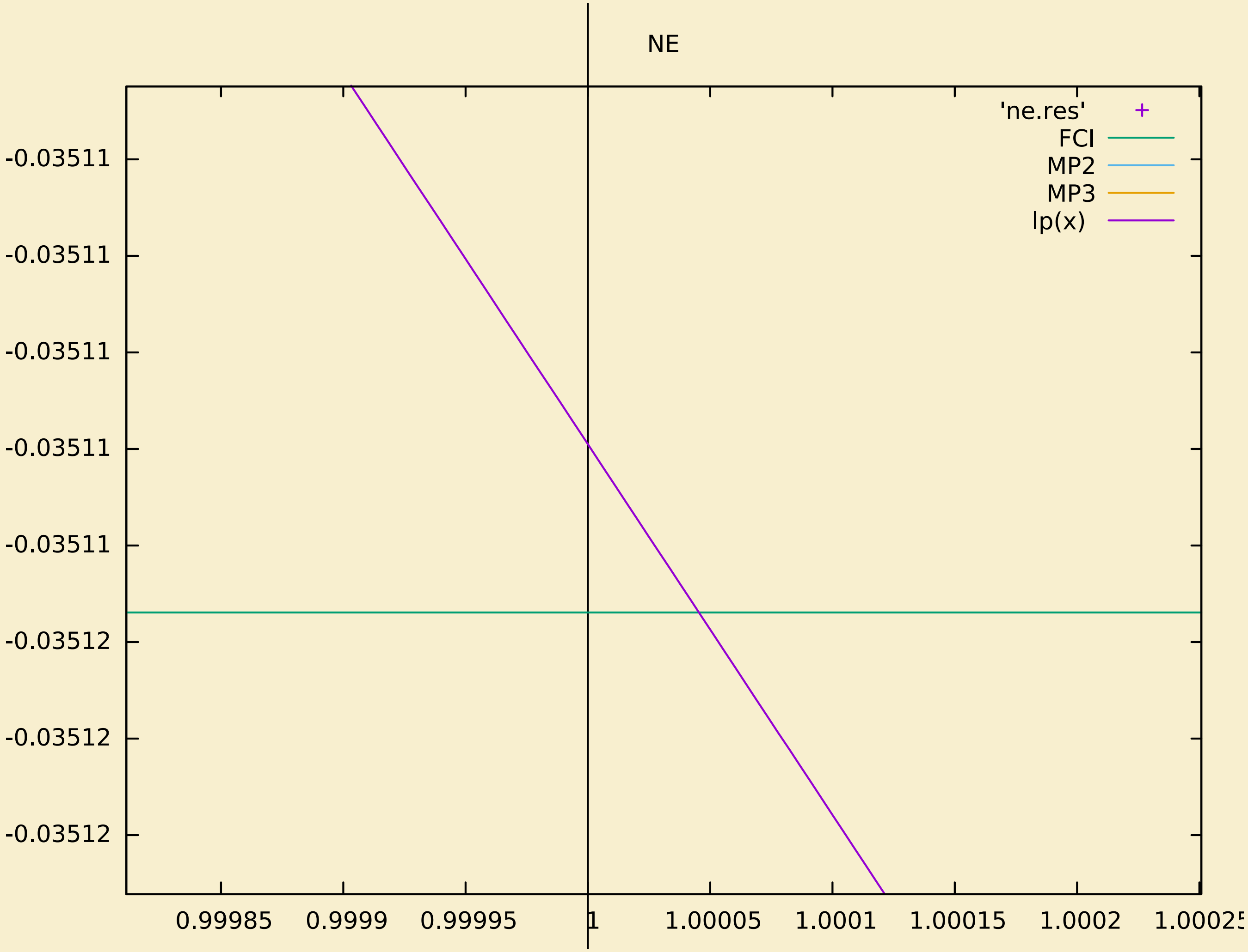



'ne.res'
FCI
MP2
MP3
p(x)
-0.031
-0.032
-0.033
-0.034
-0.035
-0.036
0.94
0.95
0.96
0.97
0.98
0.99
1
1.01

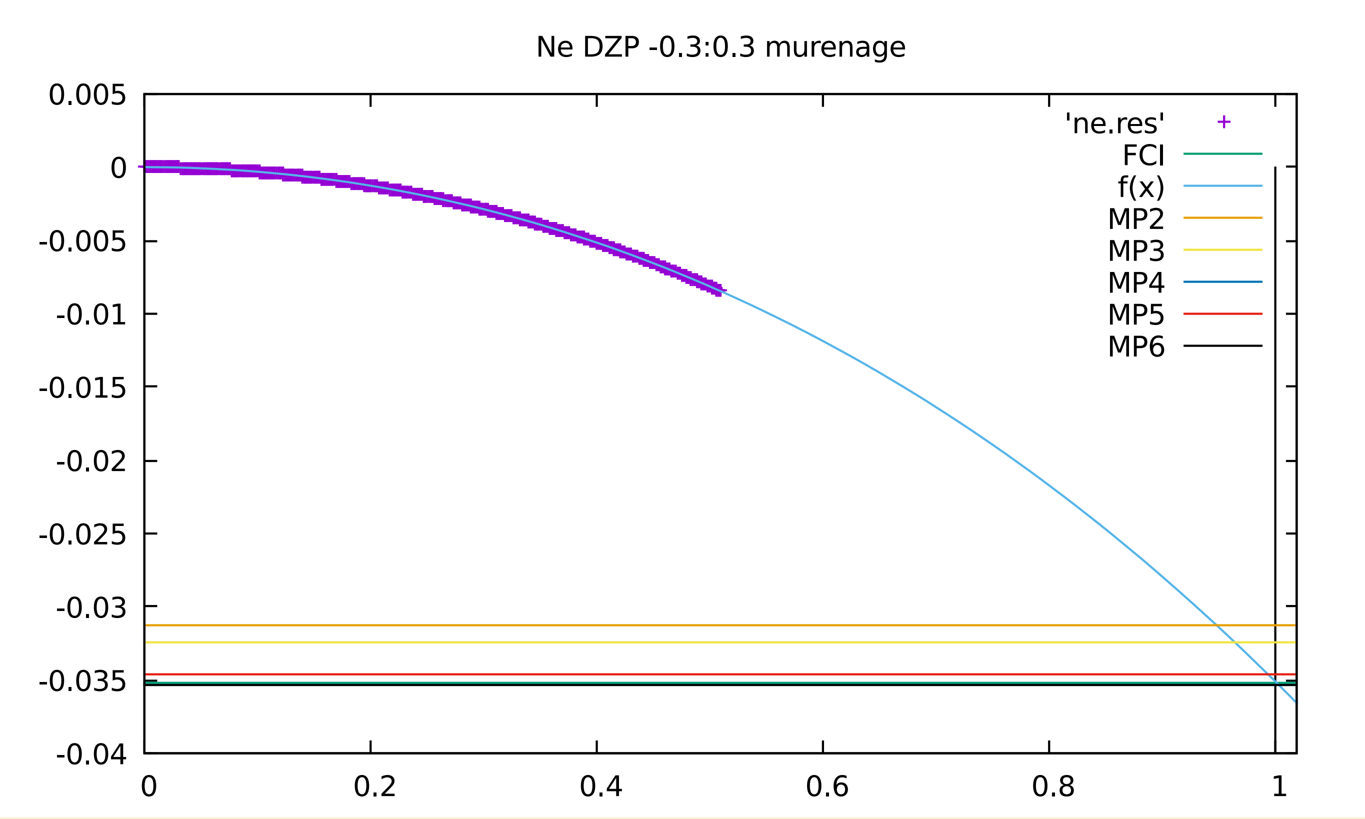
Neon atom:
Analitic continuation with linear Padé approximant

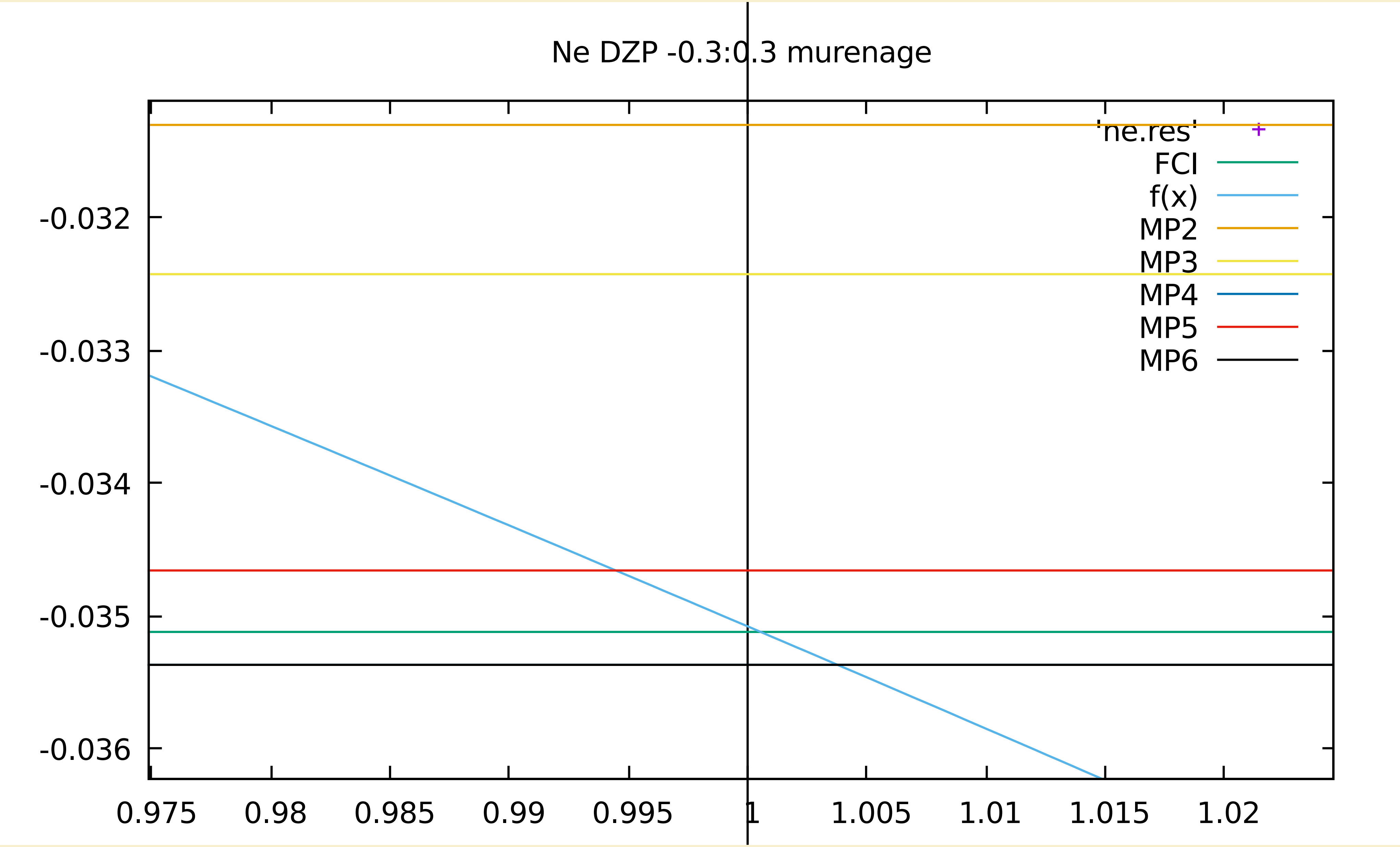



NE
'ne.res'
FCI
MP2
MP3
lp(x)
-0.031
-0.032
-0.033
-0.034
-0.035
-0.036
0.92
0.94
0.96
0.98
1
1.02
1.04


NE
'ne.res'
FCI
MP2
MP3
lp(x)
-0.03511
-0.03511
-0.03511
-0.03511
-0.03511
-0.03512
-0.03512
-0.03512
0.99985
0.9999
0.99995
1
1.00005
1.0001
1.00015
1.0002
1.00025

Neon atom:
Analitic continuation with quadratic Padé approximant




Ne DZP -0.3:0.3 murenage
'ne.res'
FCI
f(x)
MP2
MP3
MP4
MP5
MP6
-0.032
-0.033
-0.034
-0.035
-0.036
0.975
0.98
0.985
0.99
0.995
1
1.005
1.01
1.015
1.02

Singularity Analysis

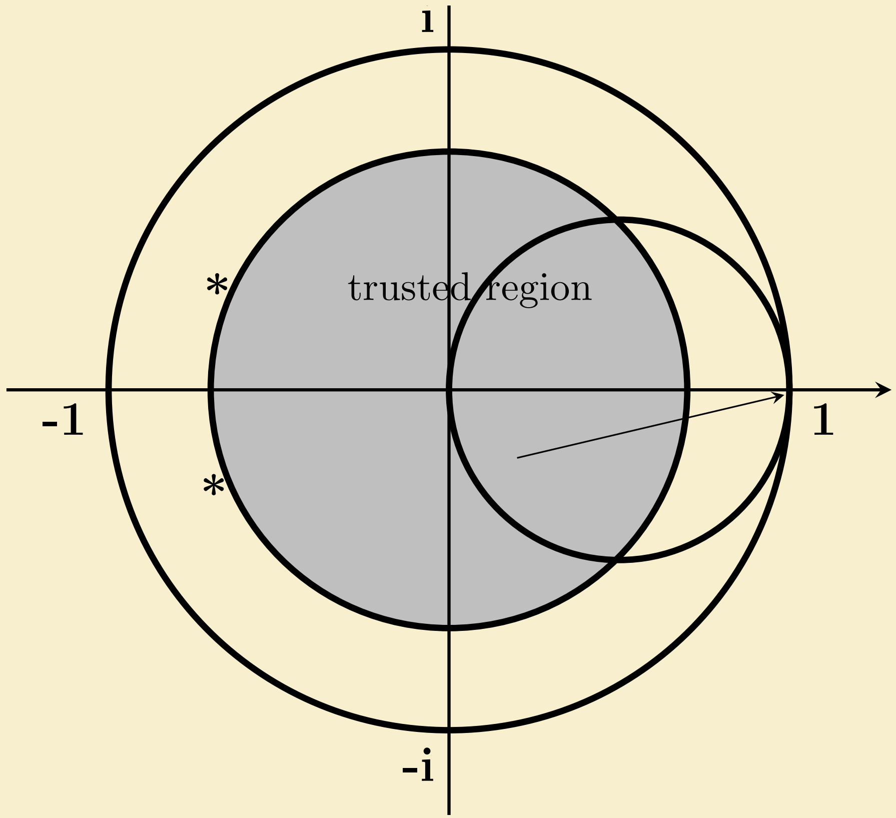
$$H(z) = H^0 + z\,W \qquad\qquad z \in \mathbb{C}$$

$$H(z)\,\Psi(z) = E(z)\,\Psi(z)$$

PT : $$E(z) = \sum_{\mu}^{\infty} z^{\mu} E^{\mu}$$

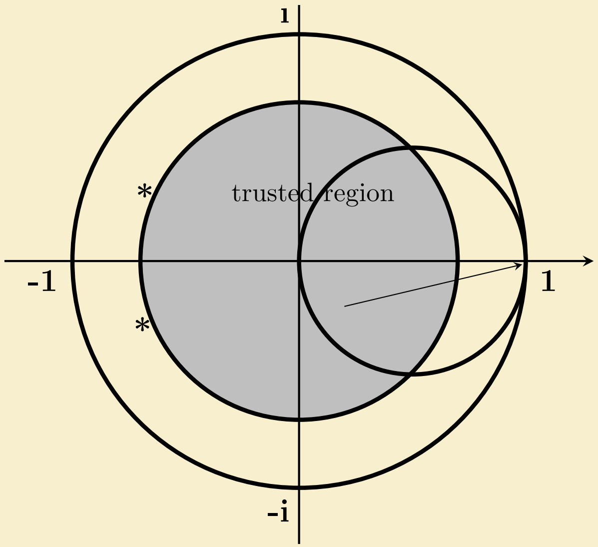
convergent if $E(z)$ is analytic.

Assuming singularities in the complex plane (branch-points)



Prediction of singularity locations: quadratic Padé approximants?

The inverse boundary problem

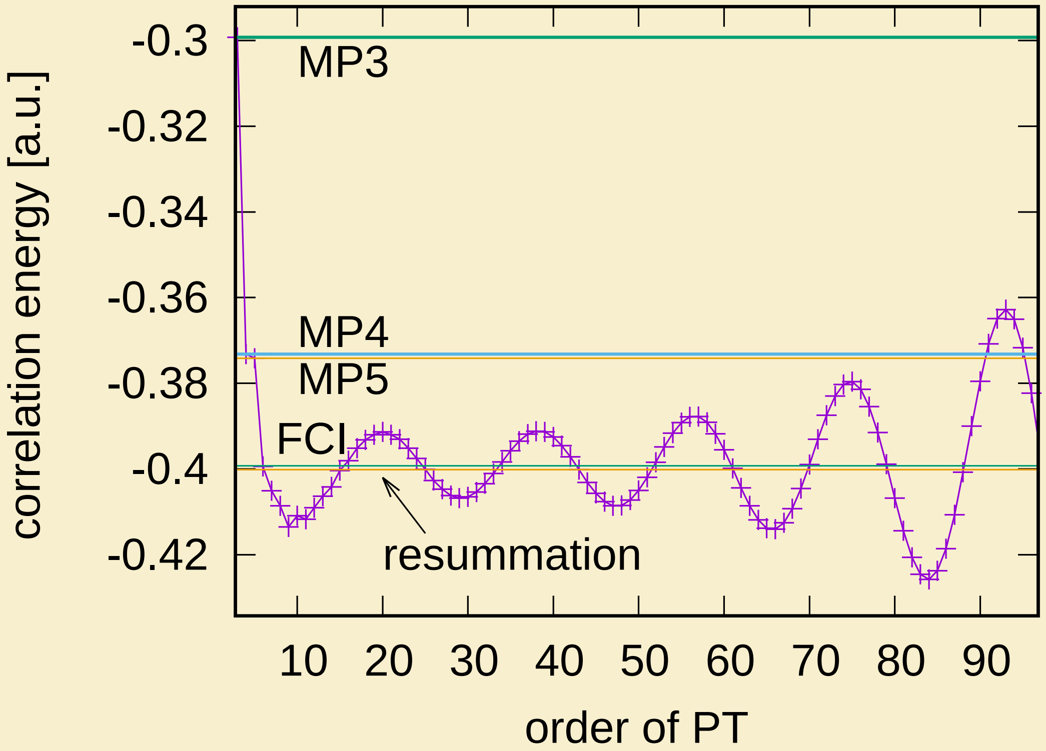


$$E(z) = u(x, y) + i\,v(x, y)$$

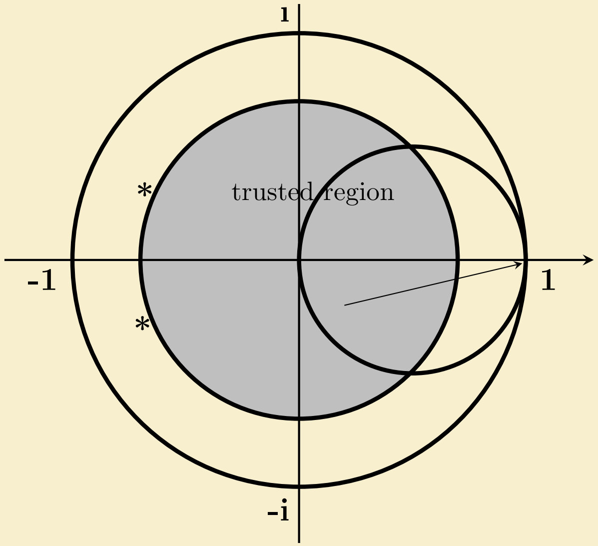
$$\Delta u(x, y) = 0$$

What are the boundary values on the small, displaced circle, by which the Laplace equation reproduces the exact values within the trusted region?

Water, prolongated OH bonds



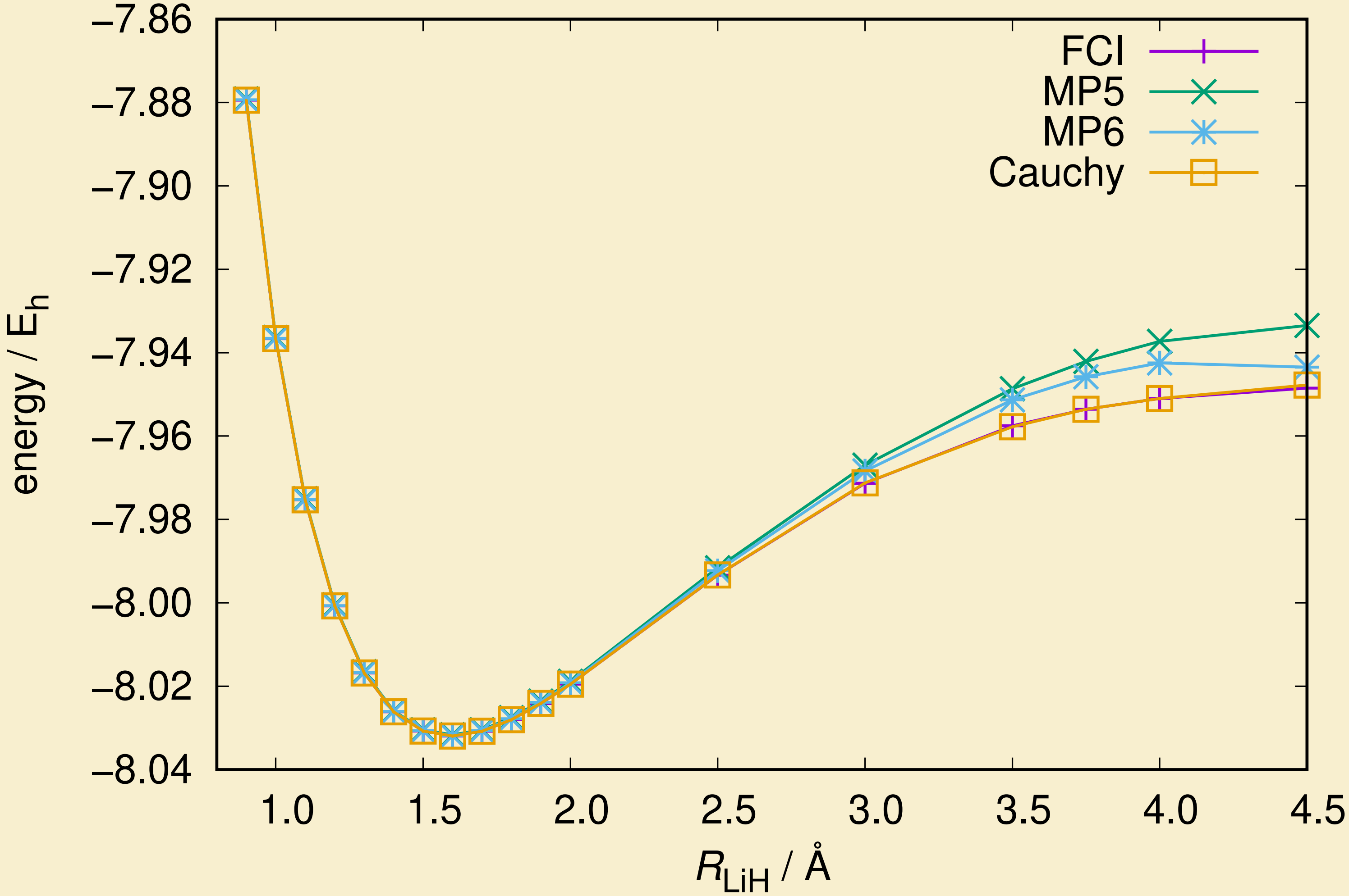
Analytic continuation with the Cauchy integral formula



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

- compute the integral numerically
- adjust boundary values to reproduce "gray" values z_0
- much cheaper than to solve $\Delta u = 0$

LiH potential curve



Open problems

- **Find a more roboust extrapolation or analytic continuation method**
- **Find a method which works with a few low orders only**
- **Avoid finding "trivial" analytic functions (e.g., a finite polynom)**

  An idea: apply penalty functions?
- **Machine learning????**

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