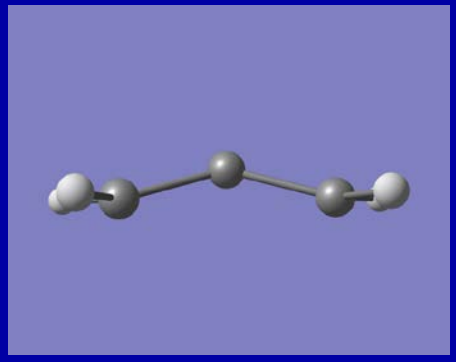
On the non-invariance of QD-NEVPT2 theory

Alexander A. Granovsky

Firefly Project

September 29th , 2011



Introduction

- **Most commonly used Multi-State Multi-Reference Perturbation Theories**
  - MCQDPT2
  - MS-CASPT2
    - SS-SR-CASPT2
    - MS-MR-CASPT2
  - QD-NEVPT2 (relatively recent development)
  - ***And now the XMCQDPT2 and XMS-CASPT2***
- All of these theories are of the diagonalize-perturb-diagonalize (D-P-D) type (note XMCQDPT2 limit is the P-D theory)
- Internally contracted vs. non-contracted
  - Internally contracted
    - MS-CASPT2, XMS-CASPT2
    - QD-NEVPT2
  - Non-contracted
    - MCQDPT2, XMCQDPT2

Model-space invariance

- According to XMCQDPT paper (A. A. Granovsky, J. Chem. Phys. 134, 214113 (2011), model-space invariance is the important mathematical and physical property of any correctly formulated MS-MR-PT
  - Invariant theories
    - Eigenvalues of effective Hamiltonian are functions of the subspace spanned by the selected CI vectors rather than functions of any particular choice of basis in this subspace (model space).
      - Uniquely and non-ambiguously defined PT
      - Computed energies are uniquely defined, continuous and smooth functions of the molecular geometry and any other external parameters
        - Continuous and artifact-free Potential Energy Surfaces (PES)

Model-space invariance

- Non-invariant theories
  - Eigenvalues of effective Hamiltonian are functions of the specific basis set in the model space rather than the entire subspace.
    - Non-uniquely defined PT
    - Computed energies are not uniquely defined, continuous and smooth functions of the molecular geometry and any other external parameters
    - Non-continuous PES with artifacts near Conical Intersection (CI) points and avoided crossings.

Possible reasons of non-invariance

- As stated in XMCQDPT paper, there are at least three sources of non-invariance
  - The most important is the non-invariance of H^0 on a model space ("Type I" non-invariance)
    - Examples: MCQDPT2, all MS-CASPT2 versions
  - The second is the use of state-specific, non-universal "perturbers" (i.e. states allowed to perturb a model space) in the formulation of theory ("Type II" non-invariance)
    - Examples: SS-SR-CASPT2, QD-NEVPT2
  - Finally, the incorrect use of multi-partitioning (MP) scheme by Zaitsevskii and Malrieu resulting in non-uniformly defined H^0 ("Type III" non-invariance)
    - Examples: SS-SR-CASPT2, QD-NEVPT2
- The last two sources of non-invariance are closely related but not necessary identical,
  - For example, non-invariant MP-based version of MCQDPT2 with state-universal secondary space (the space spanned by "perturbers") exists and is rather straightforward.

Model-space invariance

- Invariant theories
  - XMCQDPT2
  - XMS-CASPT2
- Non-invariant theories
  - MCQDPT2
  - MS-CASPT2
- What can be said about the QD-NEVPT2?

What can be expected of QD-NEVPT2?

- QD-NEVPT2
  - Is formulated in the basis of CASCI eigenvectors
  - Is based on the use of Dyall's Hamiltonian as the model operator
    - H^0 is invariant on the model space. More precisely, the non-diagonal block of PH^0P is not explicitly considered within QD-NEVPT2, however it is vanished in the basis of CASCI eigenvectors
  - Is based on the use of state-specific "perturbers"
  - Is based on the use of Multi-partitioning scheme
- We can *a priori* expect some non-invariance although most likely to a lesser extent than that of MCQDPT2 and MS-CASPT2
- There exist two forms of QD-NEVPT2 theory namely Strongly Contracted (SC) and Partially Contracted (PC)
  - As SC implies some averaging, we can expect it to be more invariant as compared with PC version which is typically considered to be superior to SC
  - More precisely:
    - QD-SC-NEVPT2 is expected to be Type III non-invariant
    - QD-PC-NEVPT2 is expected to be Type II and Type III non-invariant

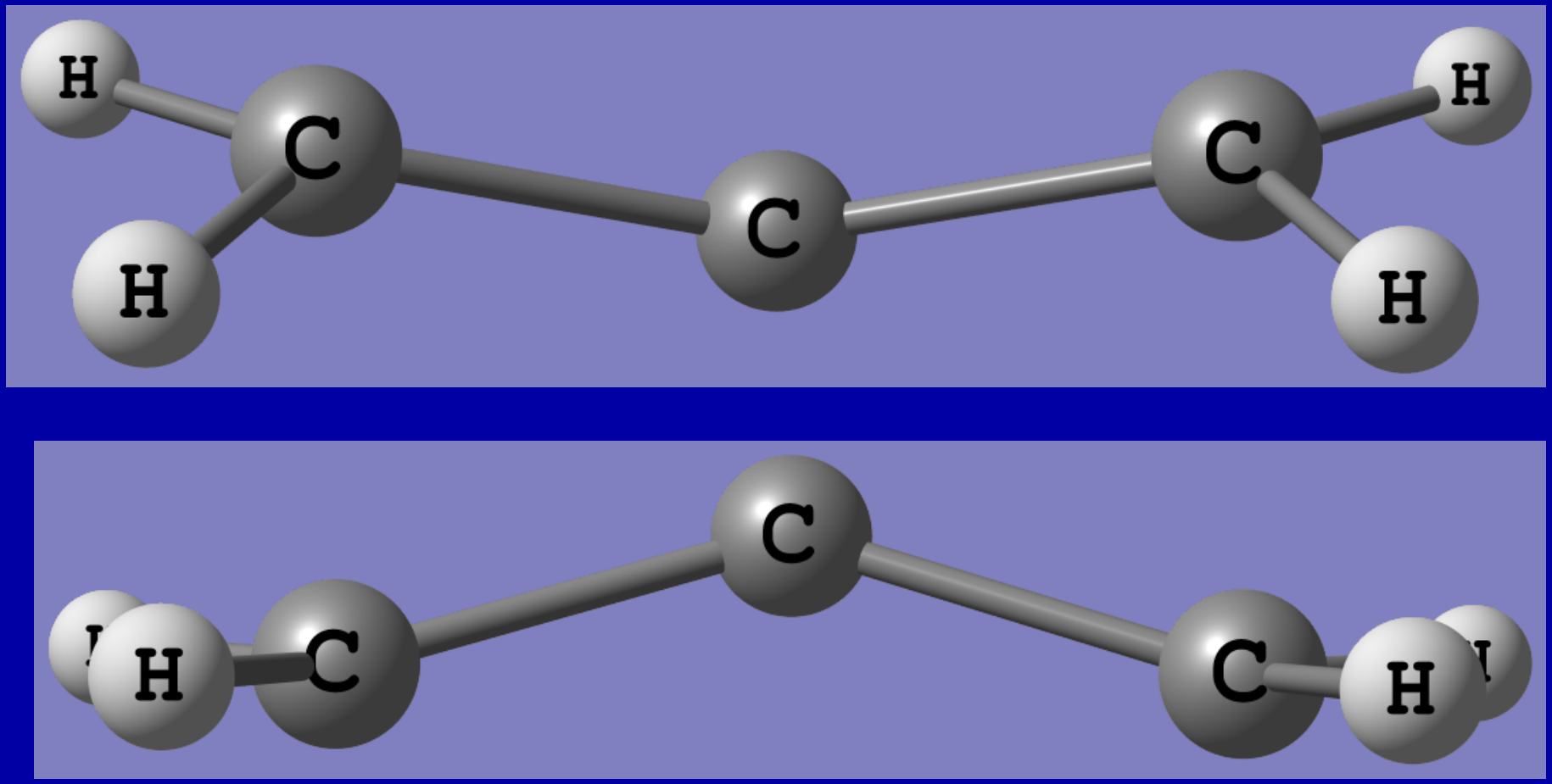
Numerical experiment

- Search for singularities and other artifacts on computed PES segments as the manifestation of the non-invariance

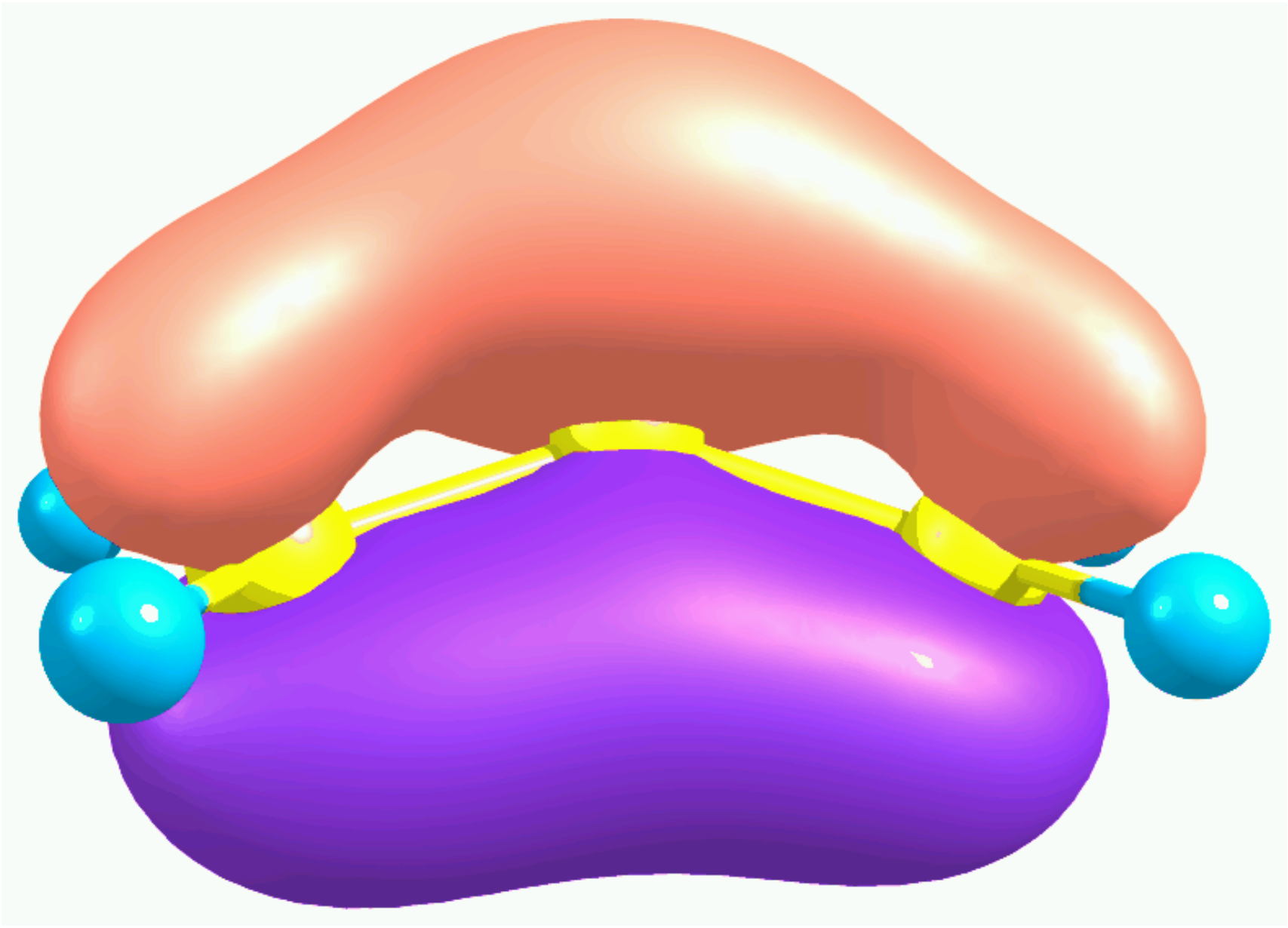
Benchmark I. Vicinity of the A'_1 - A'_2 SA-CASSCF minimum energy conical intersection (MECI) in the allene molecule

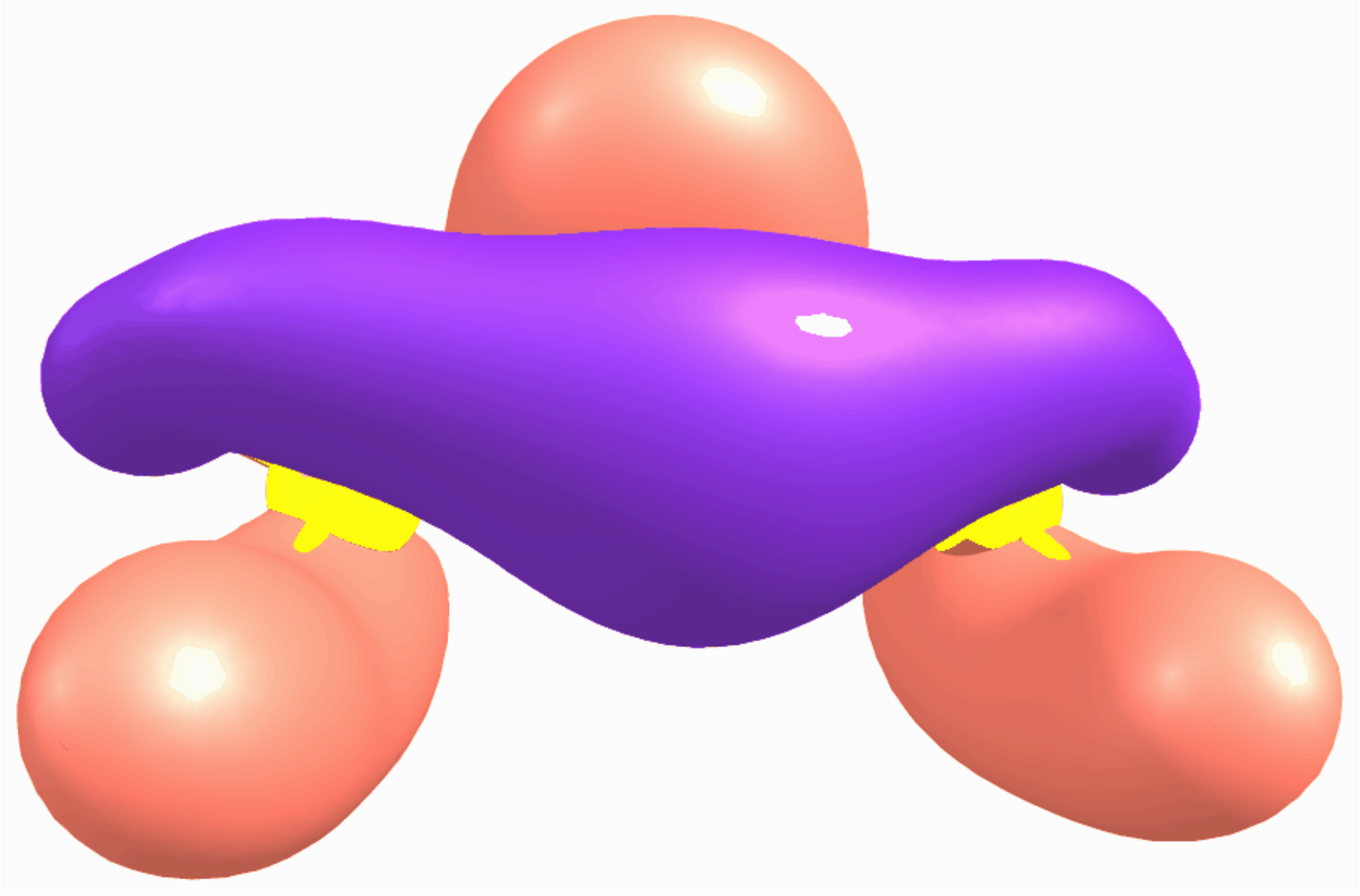
- Exactly the same methodology as in the XMCQDPT paper
  - C_s point group
  - SA-CASSCF(4,4), 12 CSFs in A′ subspace
    - 3 A′ + 1 A″ orbitals
  - GAMESS (US) style DH basis set (using pure spherical harmonics)

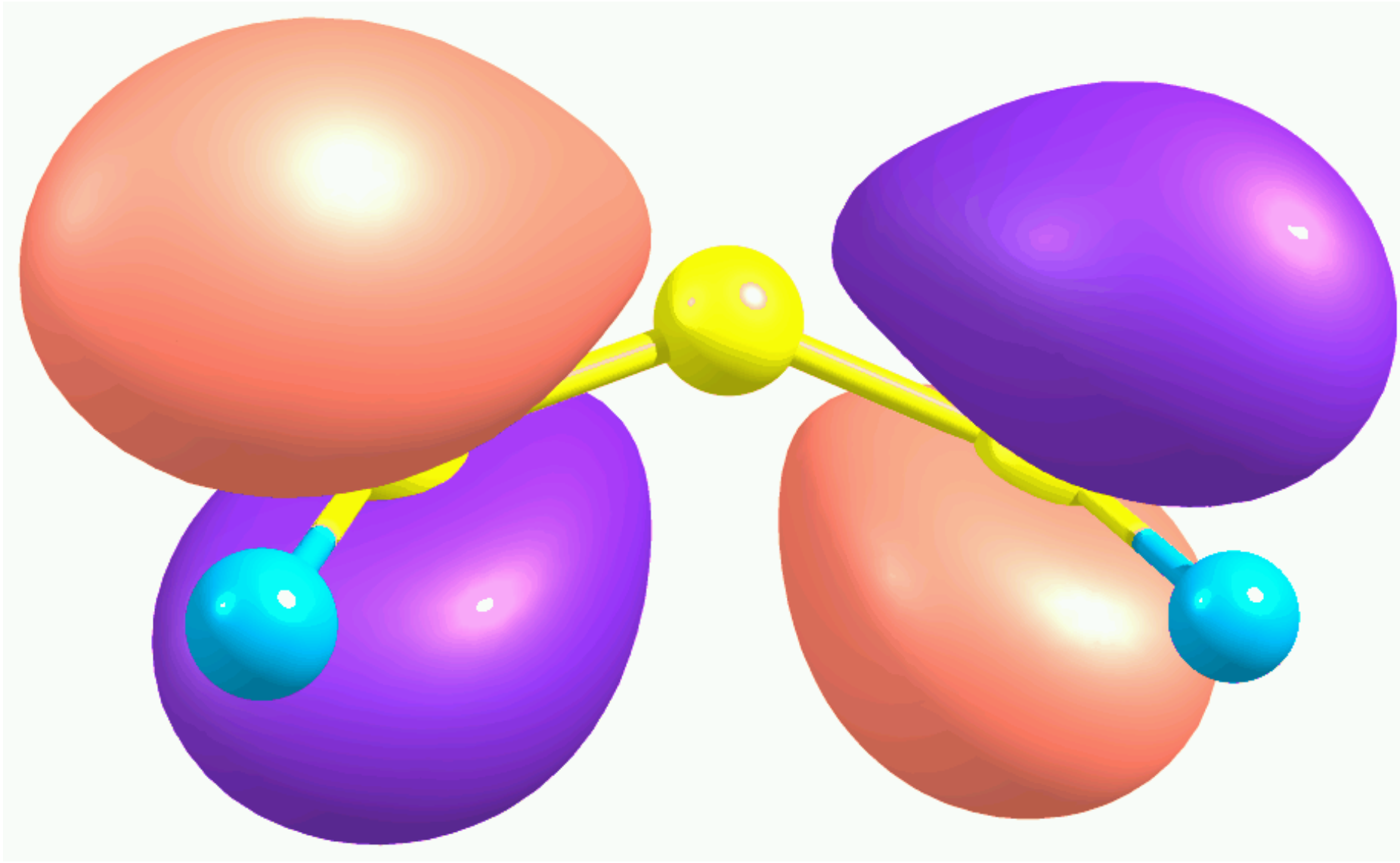
A'_1 - A'_2 MECI in allene:

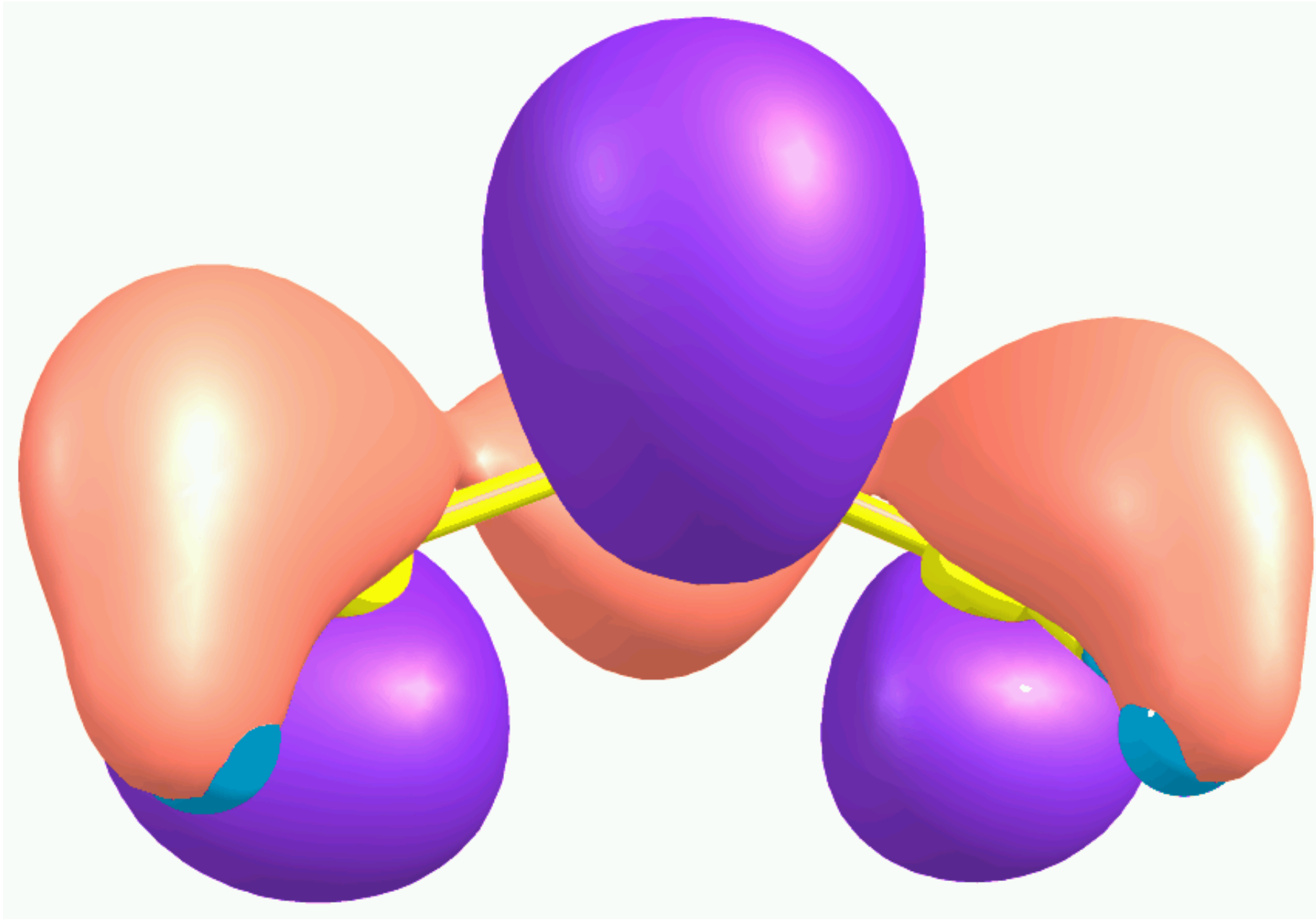


Active space



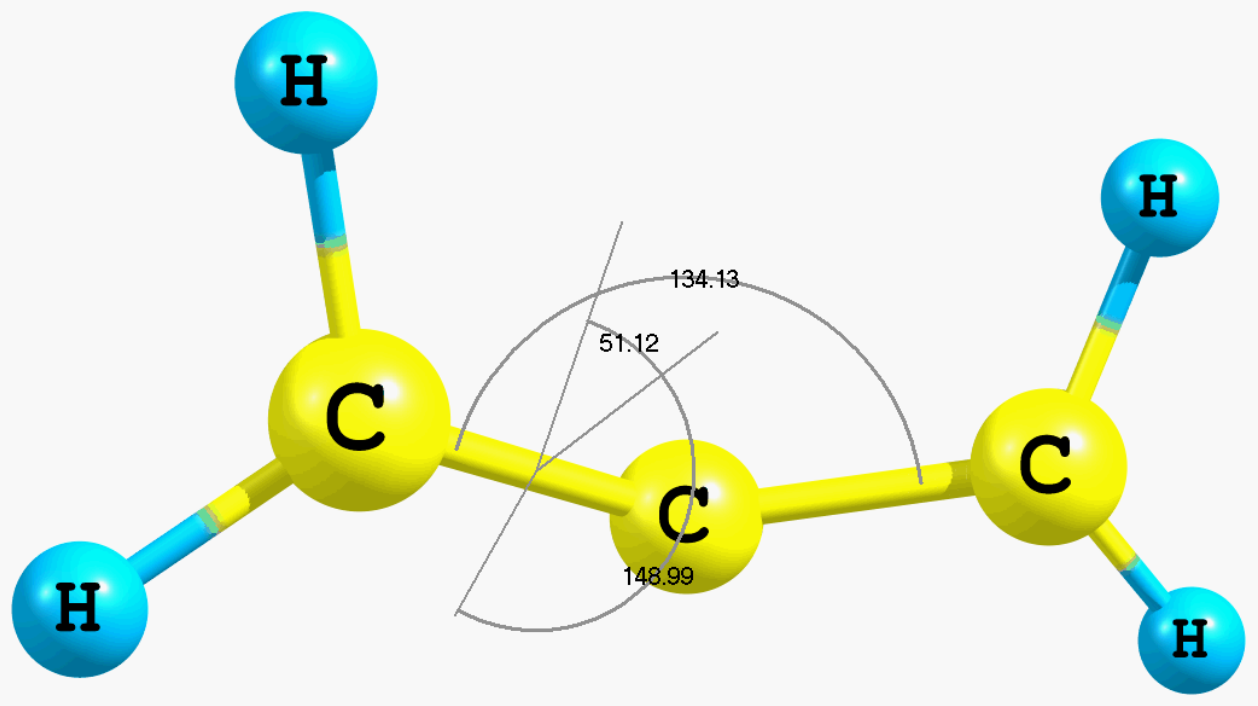




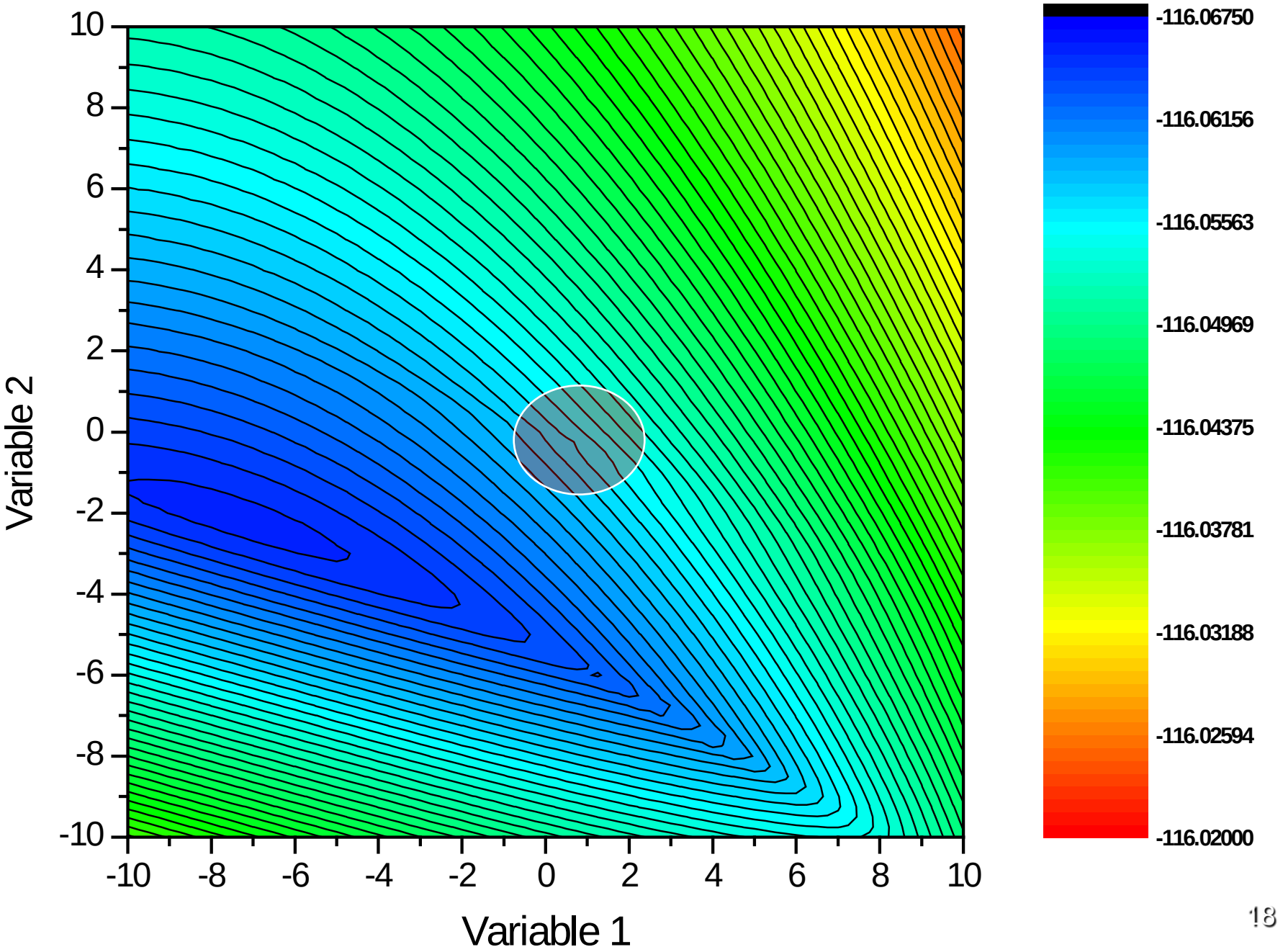


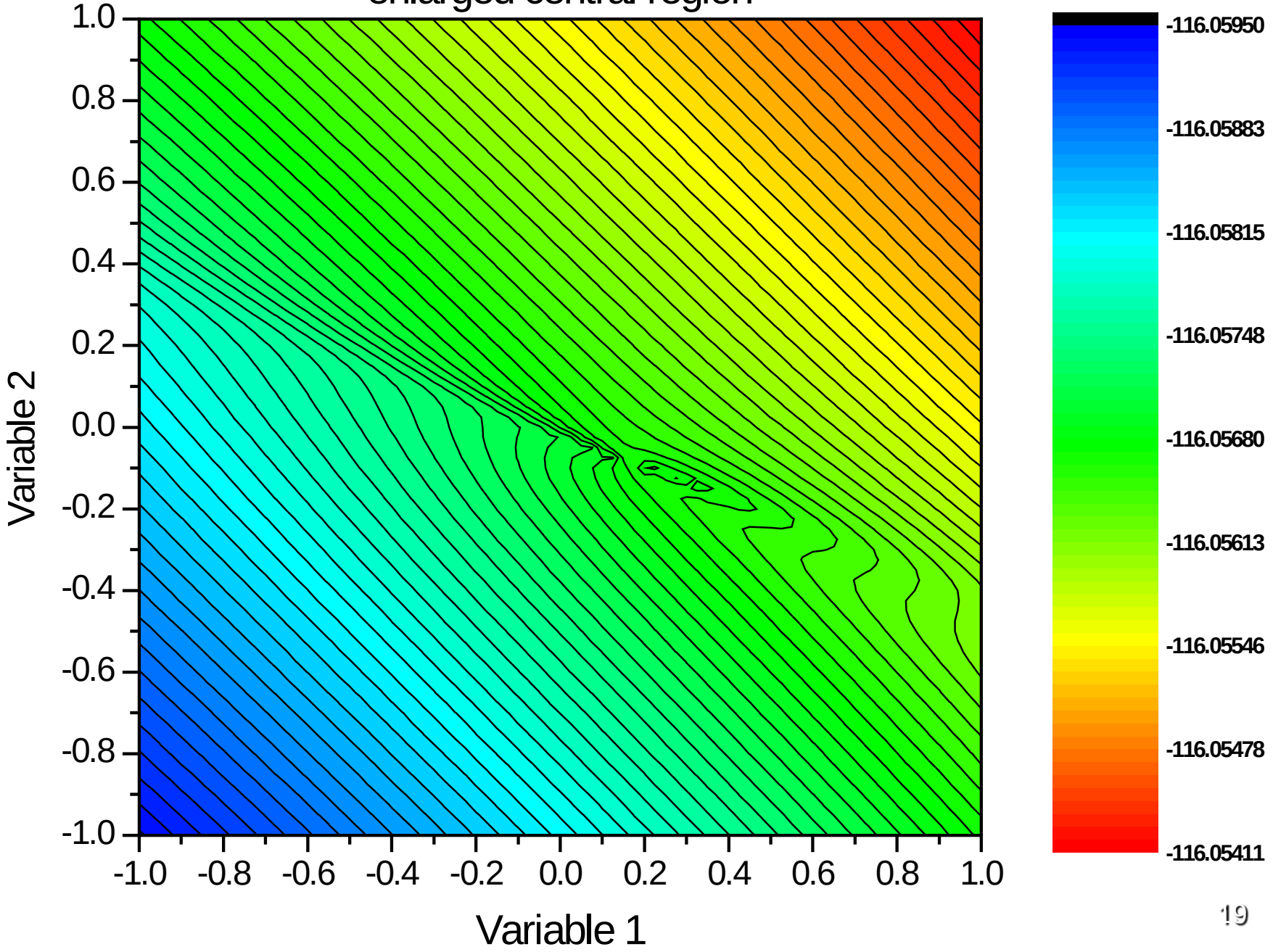
A'_1 - A'_2 MECI in allene: scan variables

Variable 1 is the CCC bending (in degrees), variable 2 is the simultaneous change of two CCCH torsions (in degrees) for H atoms located on the same carbon atom. Exact C_s symmetry is enforced. Coordinate origin is at the CASSCF's MECI geometry.

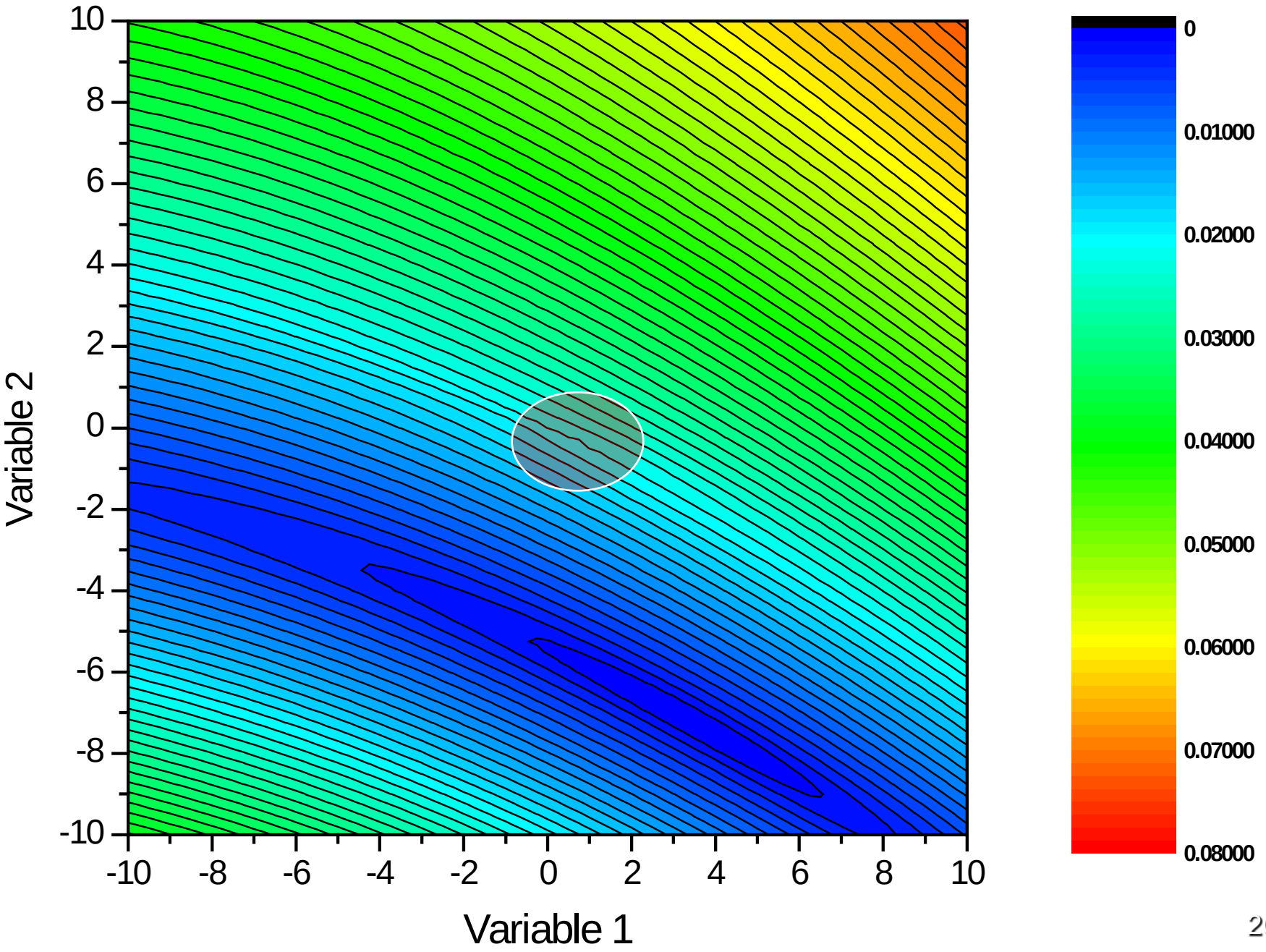


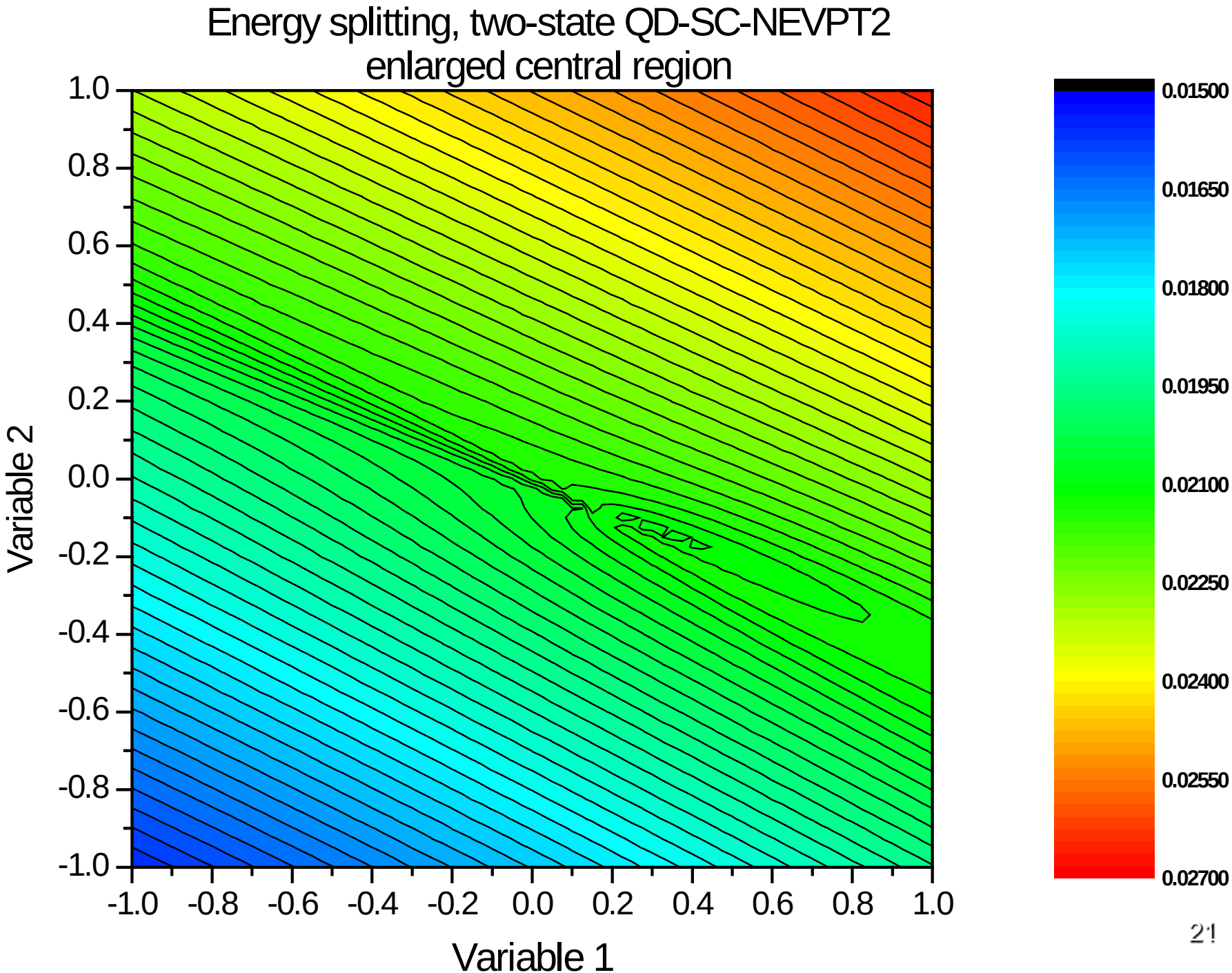
Scans (scan technique is identical to that of XMCQDPT paper)

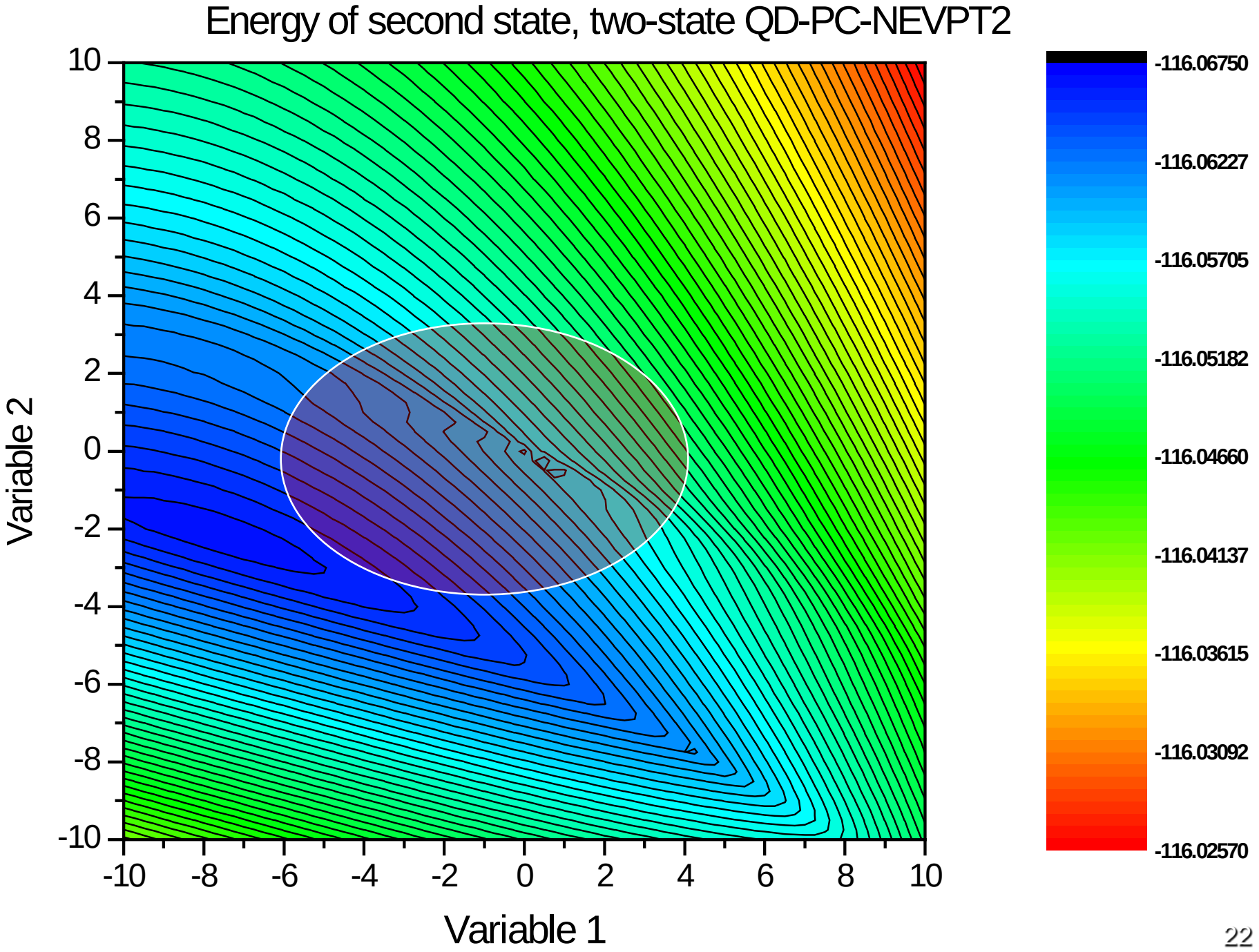

Energy of second state, two-state QD-SC-NEVPT2
Variable 2
Variable 1
10
8
6
4
2
0
-2
-4
-6
-8
-10
-10
-8
-6
-4
-2
0
2
4
6
8
10
-116.06750
-116.06156
-116.05563
-116.04969
-116.04375
-116.03781
-116.03188
-116.02594
-116.02000

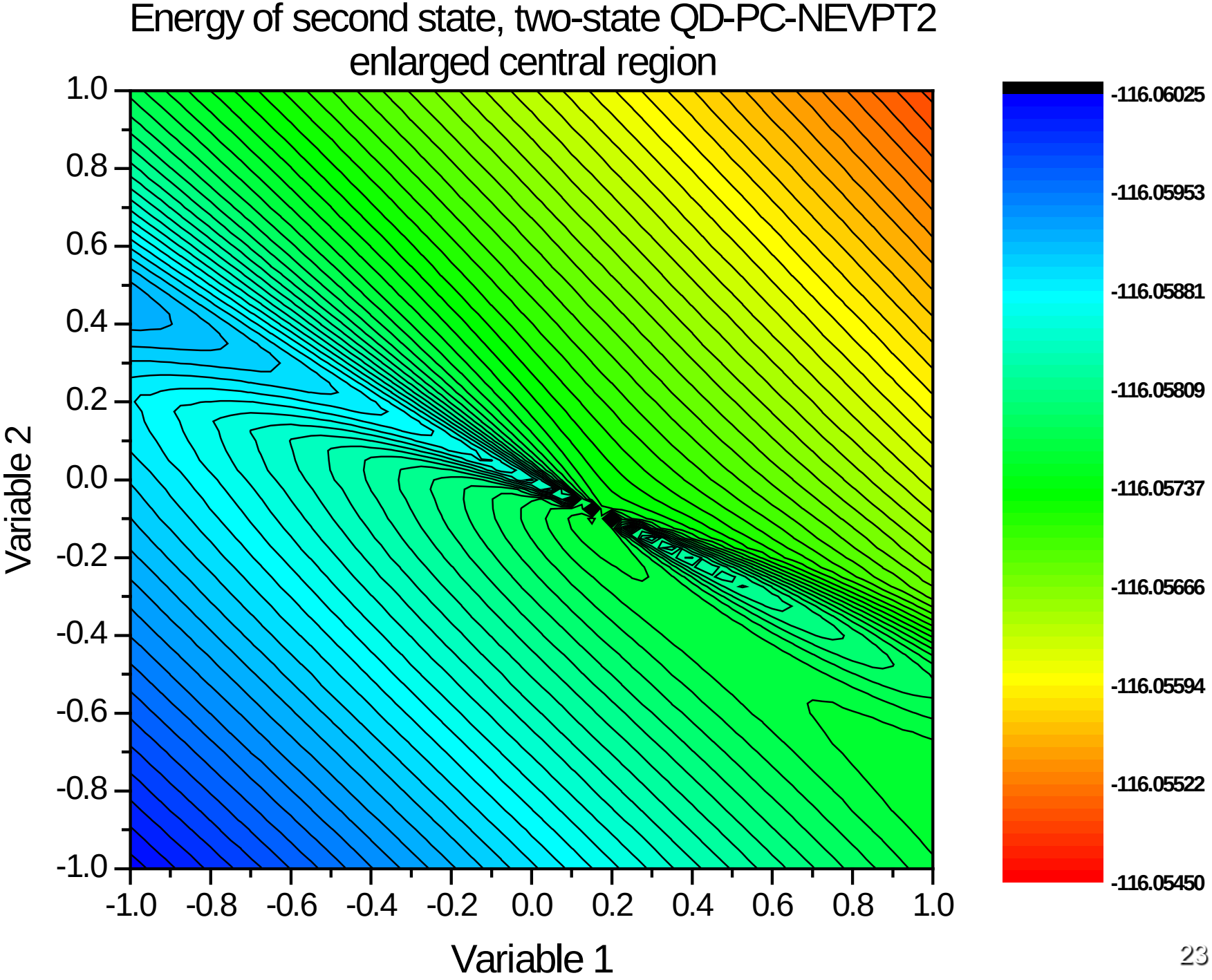

Energy of second state, two-state QD-SC-NEVPT2
enlarged central region
Variable 2
Variable 1
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
-116.05950
-116.05883
-116.05815
-116.05748
-116.05680
-116.05613
-116.05546
-116.05478
-116.05411

Energy splitting, two-state QD-SC-NEVPT2

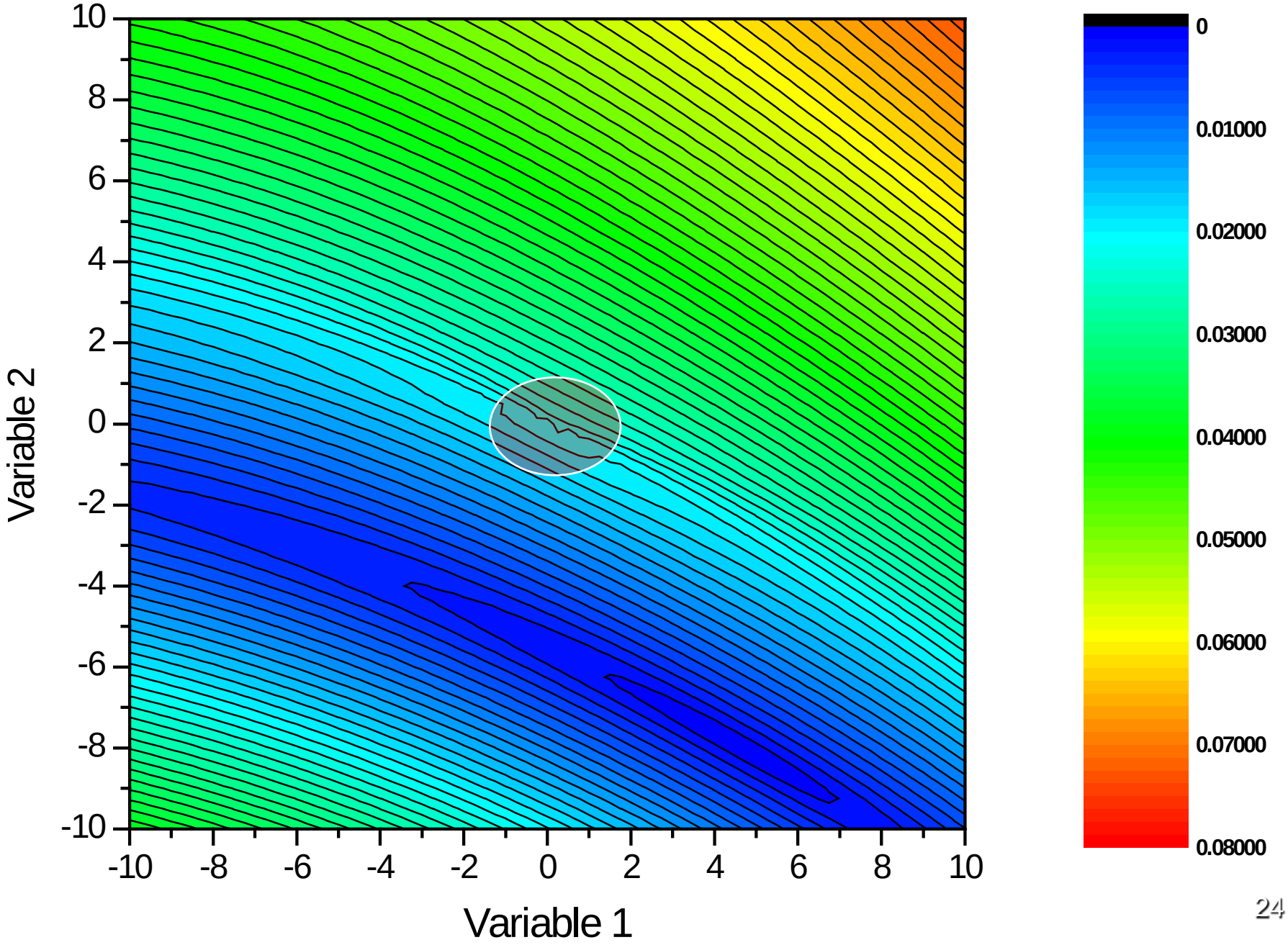


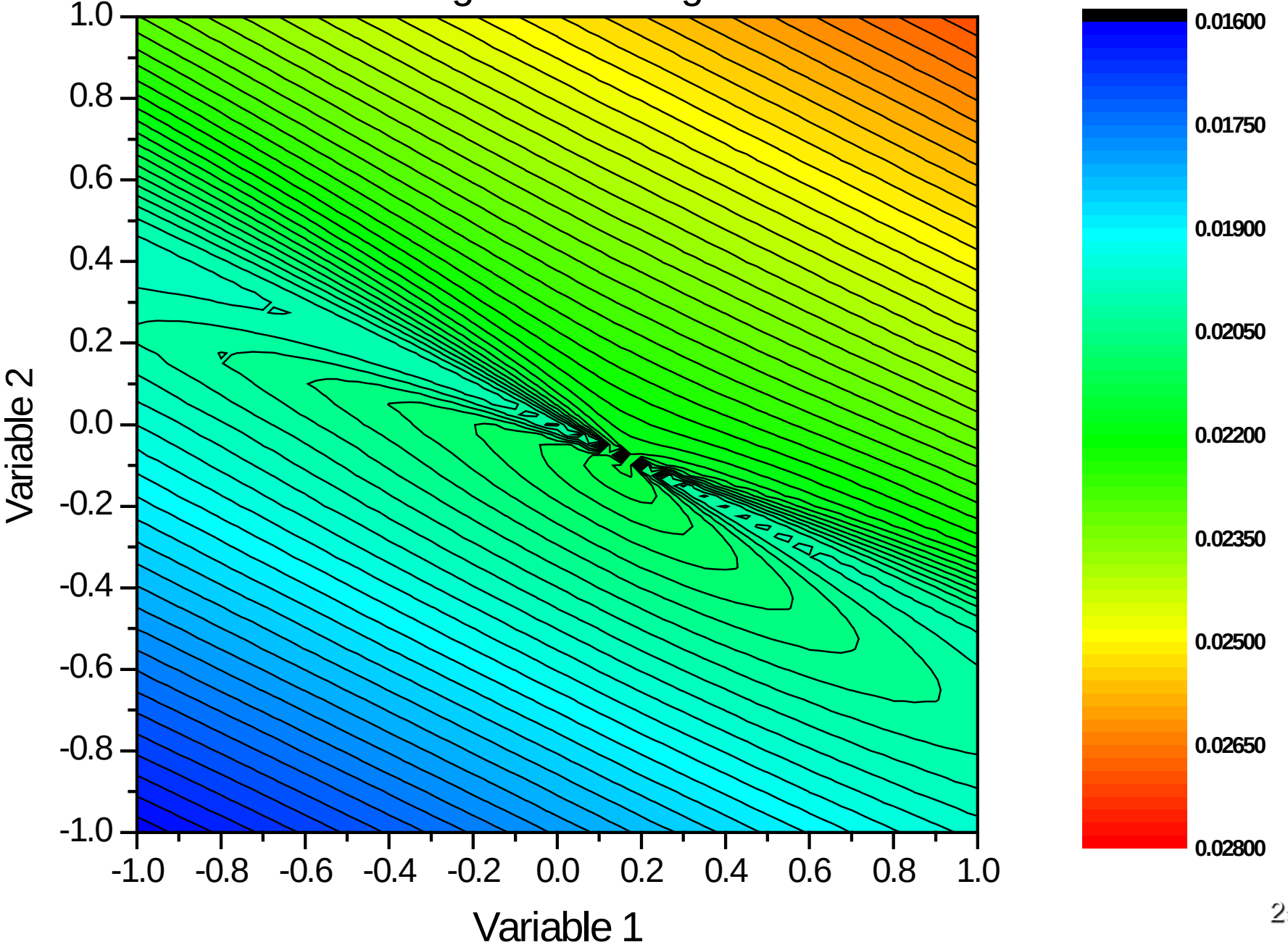

Energy splitting, two-state QD-SC-NEVPT2
enlarged central region
Variable 2
Variable 1
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
0.01500
0.01650
0.01800
0.01950
0.02100
0.02250
0.02400
0.02550
0.02700

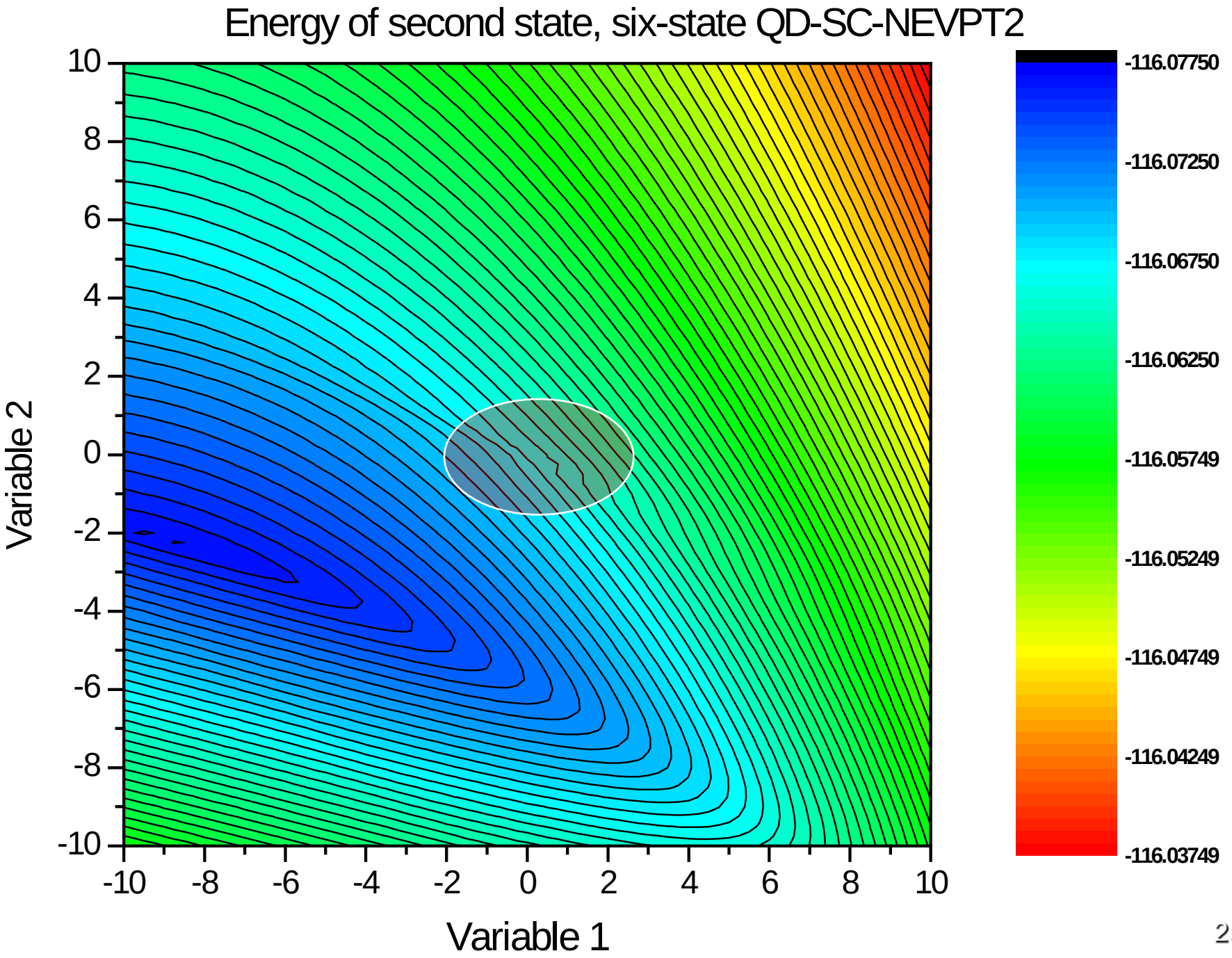

Energy of second state, two-state QD-PC-NEVPT2
Variable 2
Variable 1
10
8
6
4
2
0
-2
-4
-6
-8
-10
-10
-8
-6
-4
-2
0
2
4
6
8
10
-116.06750
-116.06227
-116.05705
-116.05182
-116.04660
-116.04137
-116.03615
-116.03092
-116.02570

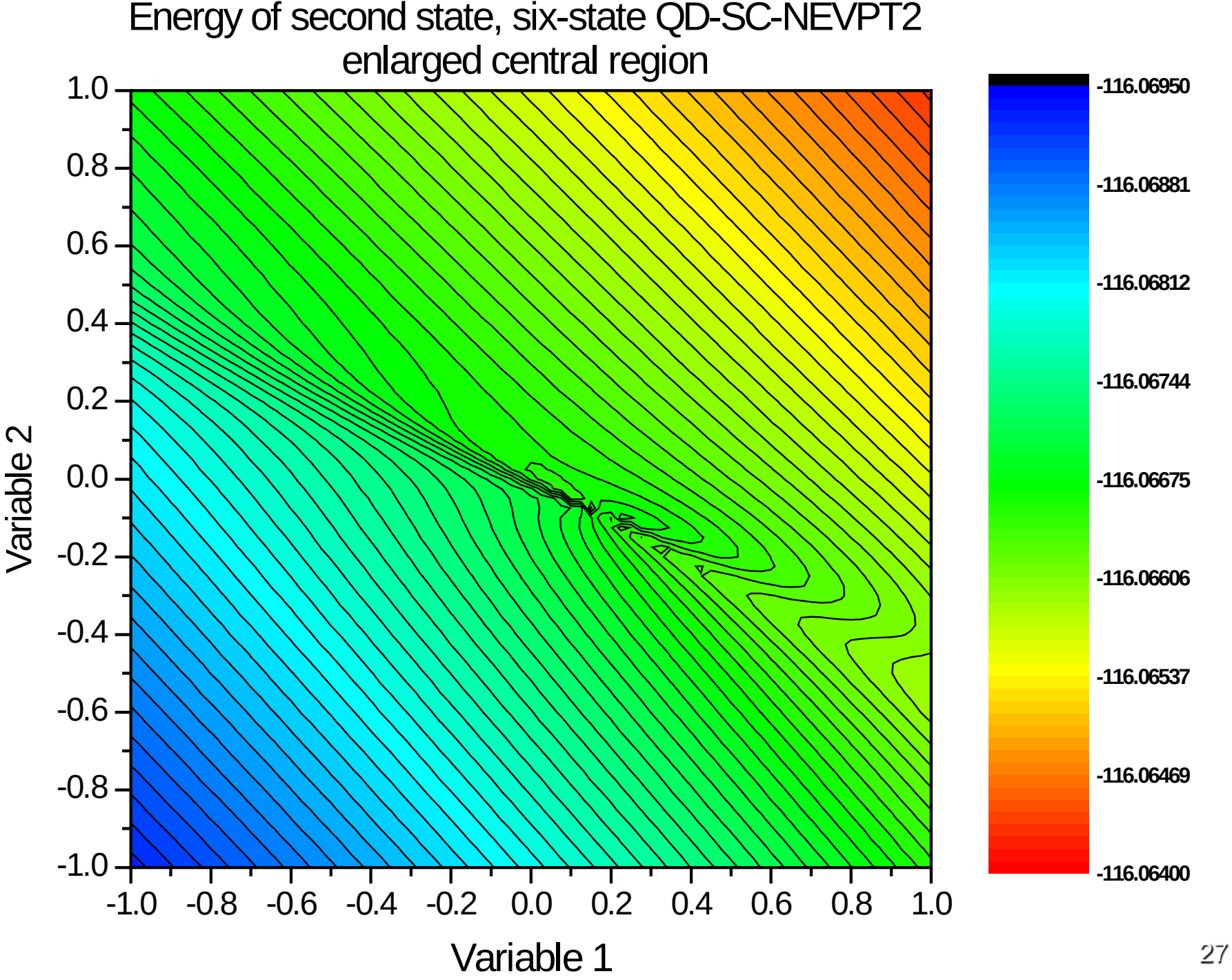

Energy of second state, two-state QD-PC-NEVPT2
enlarged central region
Variable 2
Variable 1
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
-116.06025
-116.05953
-116.05881
-116.05809
-116.05737
-116.05666
-116.05594
-116.05522
-116.05450

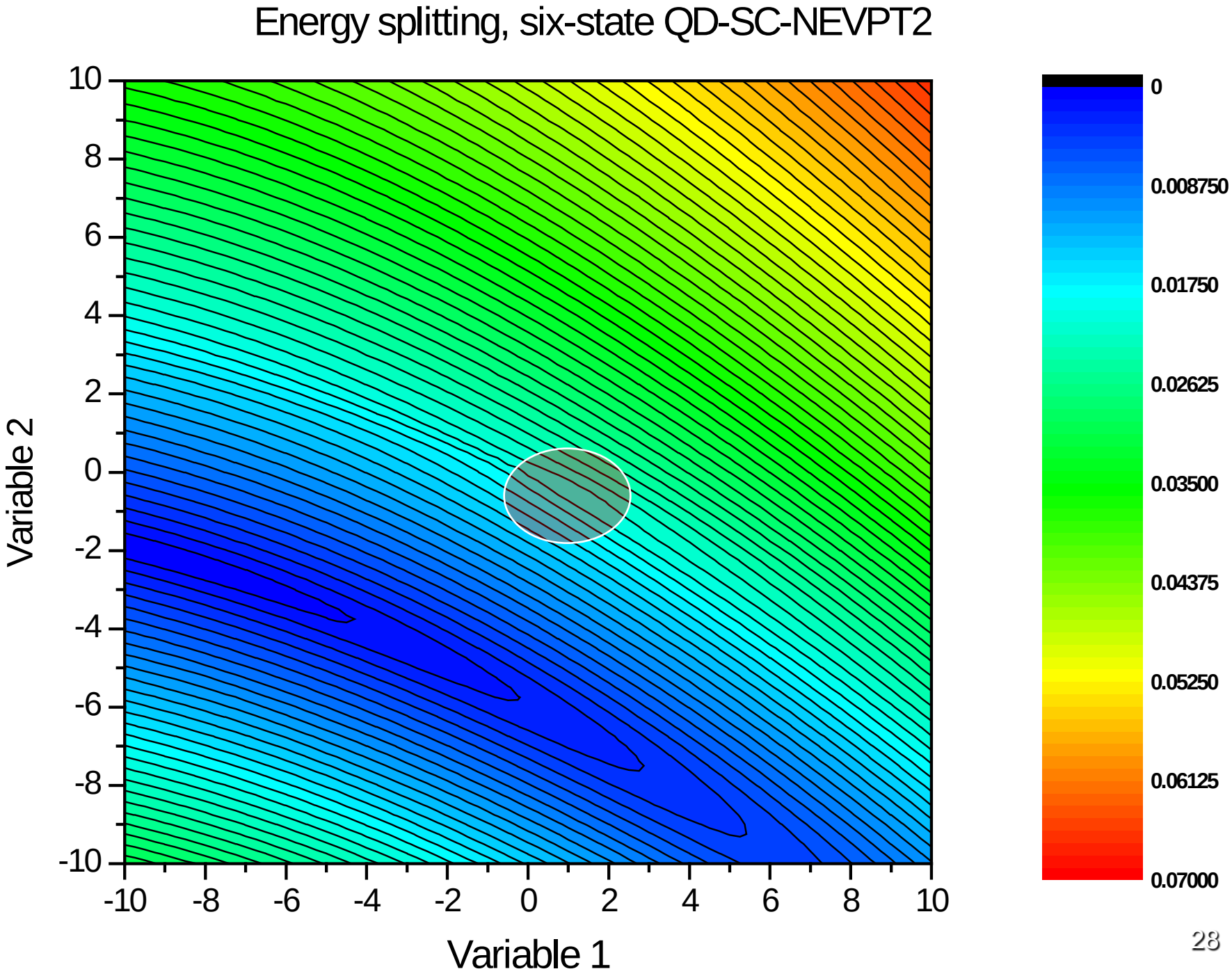
Energy splitting, two-state QD-PC-NEVPT2

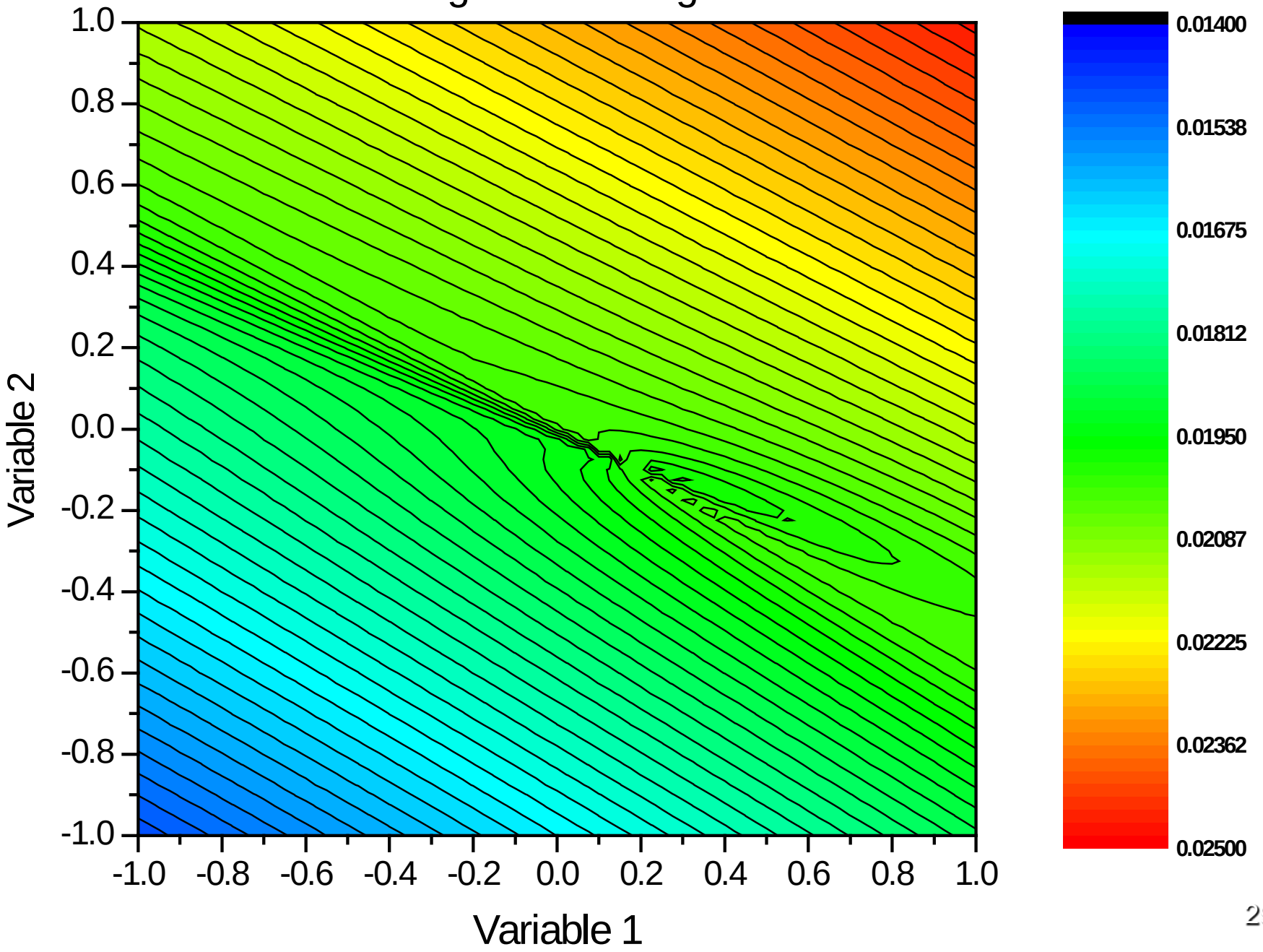


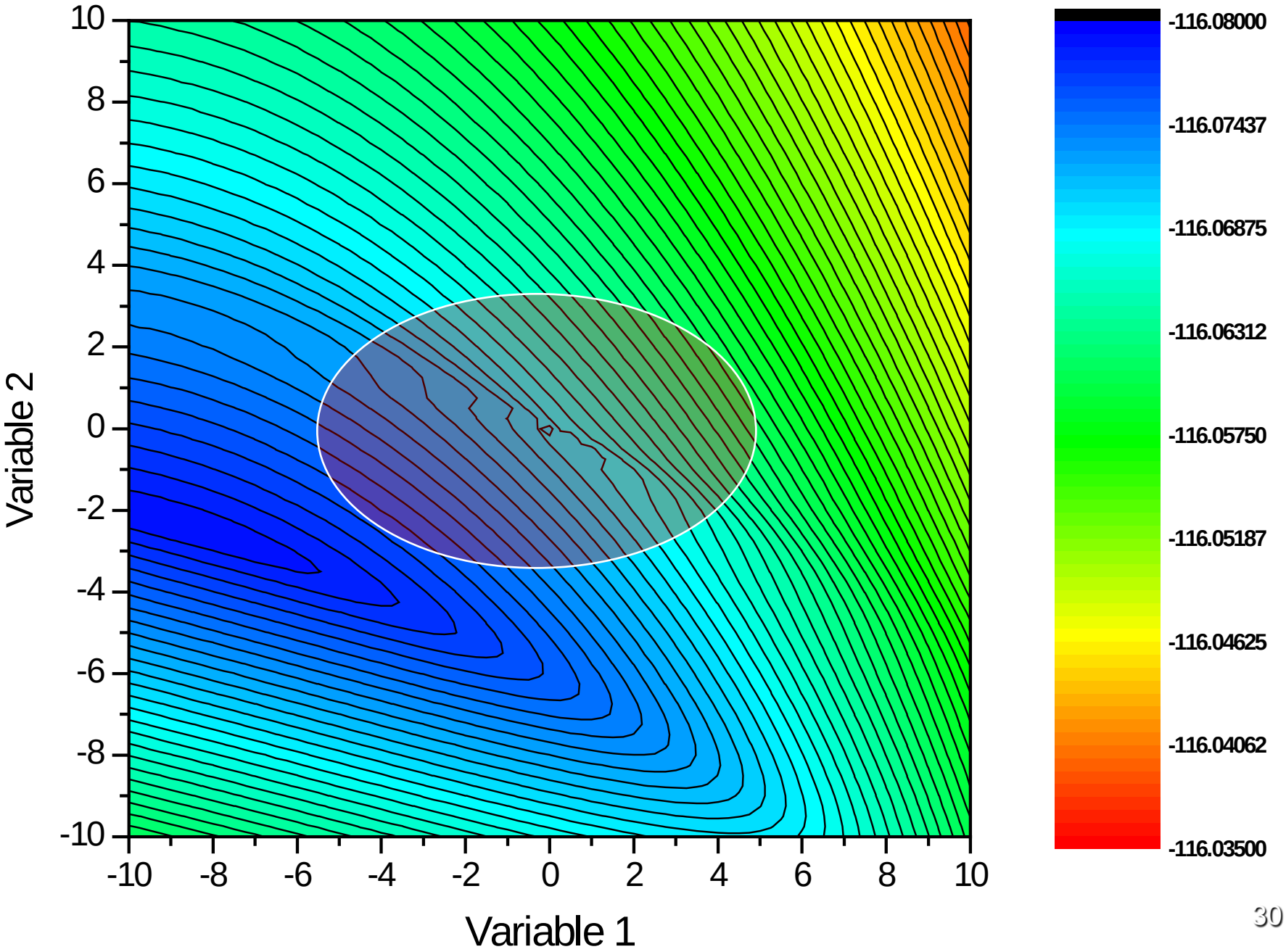

Energy splitting, two-state QD-PC-NEVPT2
enlarged central region
Variable 2
Variable 1
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
0.01600
0.01750
0.01900
0.02050
0.02200
0.02350
0.02500
0.02650
0.02800

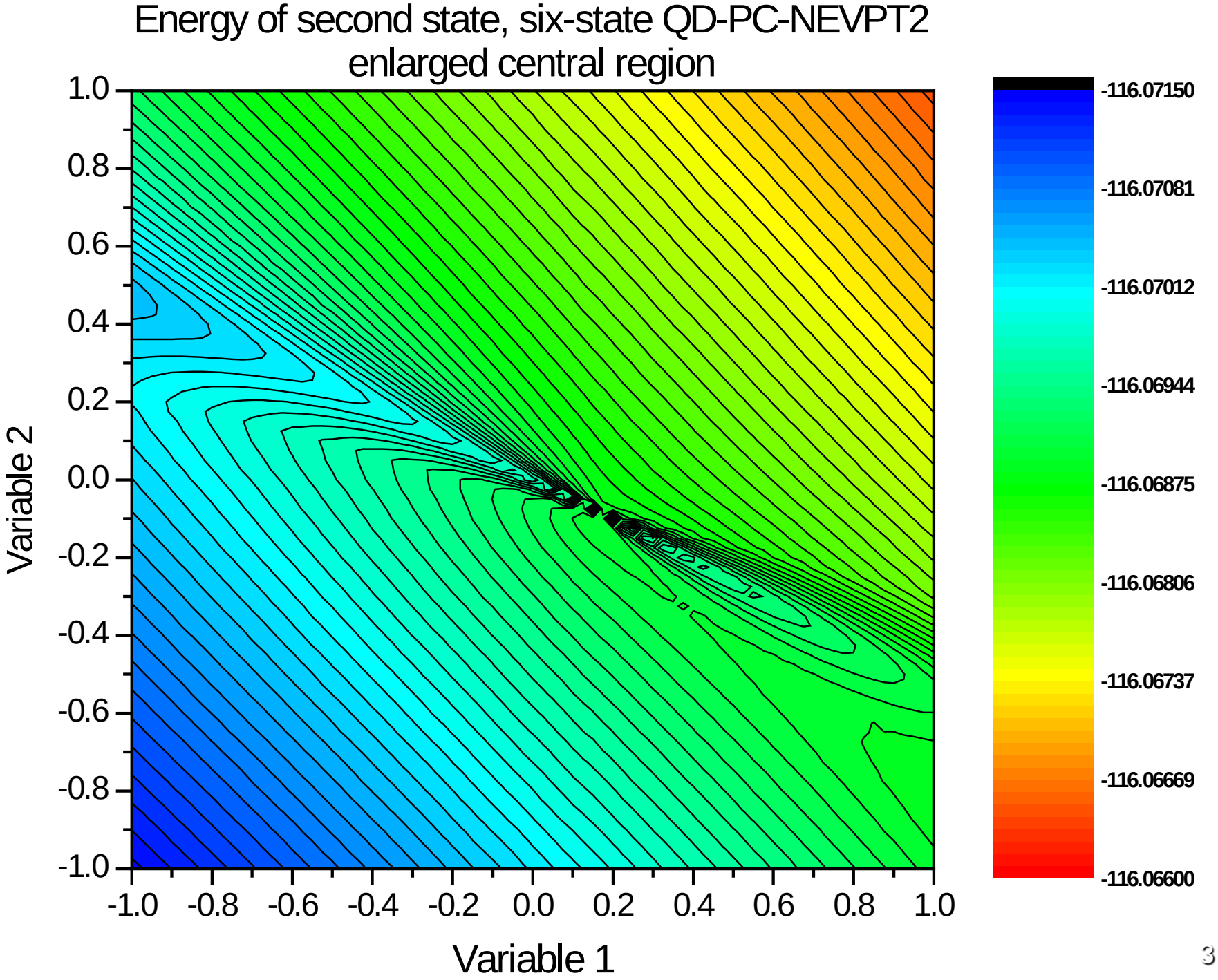

Energy of second state, six-state QD-SC-NEVPT2
Variable 2
Variable 1
10
8
6
4
2
0
-2
-4
-6
-8
-10
-10
-8
-6
-4
-2
0
2
4
6
8
10
-116.07750
-116.07250
-116.06750
-116.06250
-116.05749
-116.05249
-116.04749
-116.04249
-116.03749

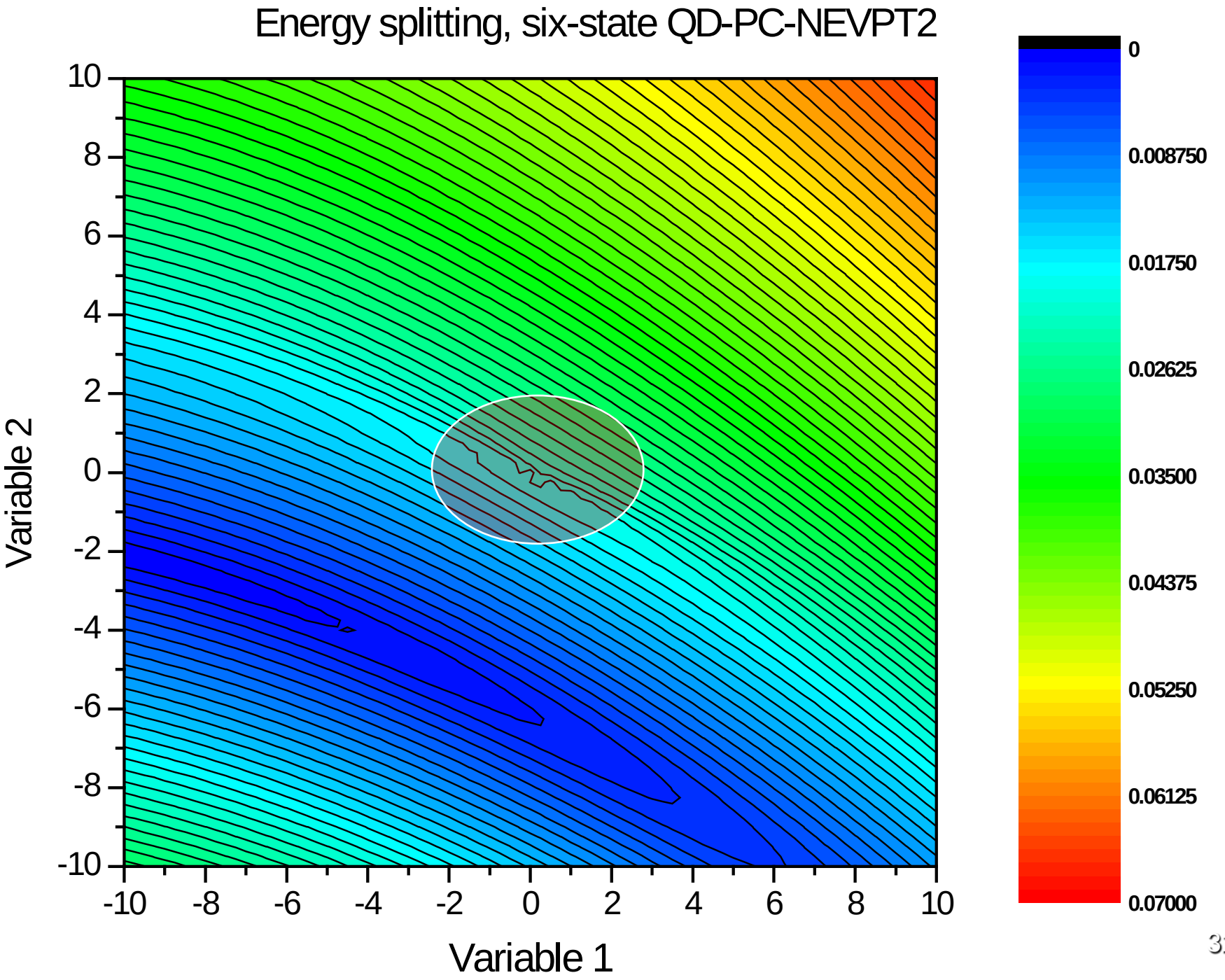

Energy of second state, six-state QD-SC-NEVPT2
enlarged central region
Variable 2
Variable 1
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
-116.06950
-116.06881
-116.06812
-116.06744
-116.06675
-116.06606
-116.06537
-116.06469
-116.06400

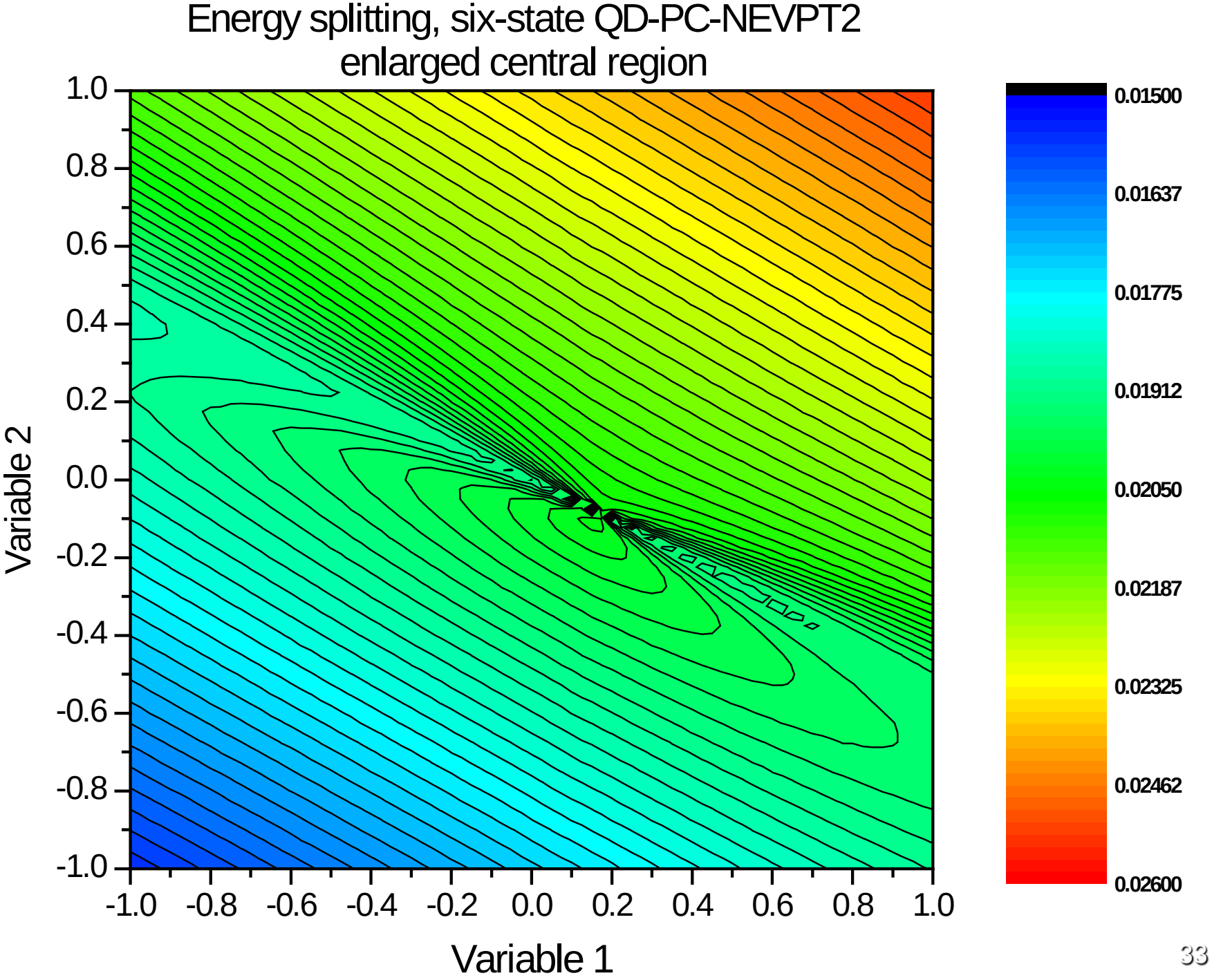

Energy splitting, six-state QD-SC-NEVPT2
Variable 2
Variable 1
10
8
6
4
2
0
-2
-4
-6
-8
-10
-10
-8
-6
-4
-2
0
2
4
6
8
10
0
0.008750
0.01750
0.02625
0.03500
0.04375
0.05250
0.06125
0.07000


Energy splitting, six-state QD-SC-NEVPT2
enlarged central region
Variable 2
Variable 1
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.0 -0.8 -0.6 -0.4 -0.2 0.0 0.2 0.4 0.6 0.8 1.0
0.01400
0.01538
0.01675
0.01812
0.01950
0.02087
0.02225
0.02362
0.02500


Energy of second state, six-state QD-PC-NEVPT2
Variable 2
Variable 1
10
8
6
4
2
0
-2
-4
-6
-8
-10
-10
-8
-6
-4
-2
0
2
4
6
8
10
-116.08000
-116.07437
-116.06875
-116.06312
-116.05750
-116.05187
-116.04625
-116.04062
-116.03500

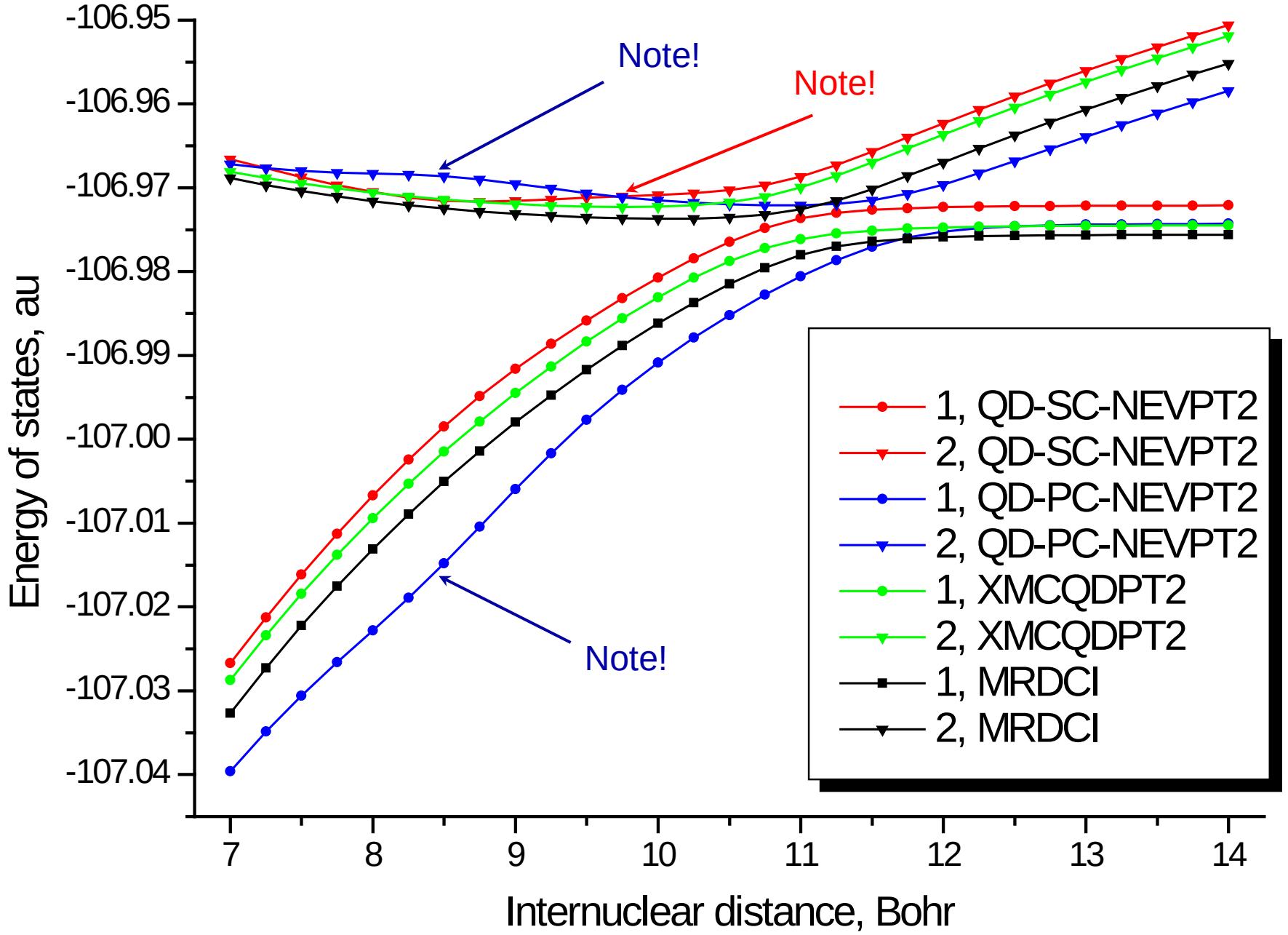

Energy of second state, six-state QD-PC-NEVPT2
enlarged central region
Variable 2
Variable 1
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
-116.07150
-116.07081
-116.07012
-116.06944
-116.06875
-116.06806
-116.06737
-116.06669
-116.06600

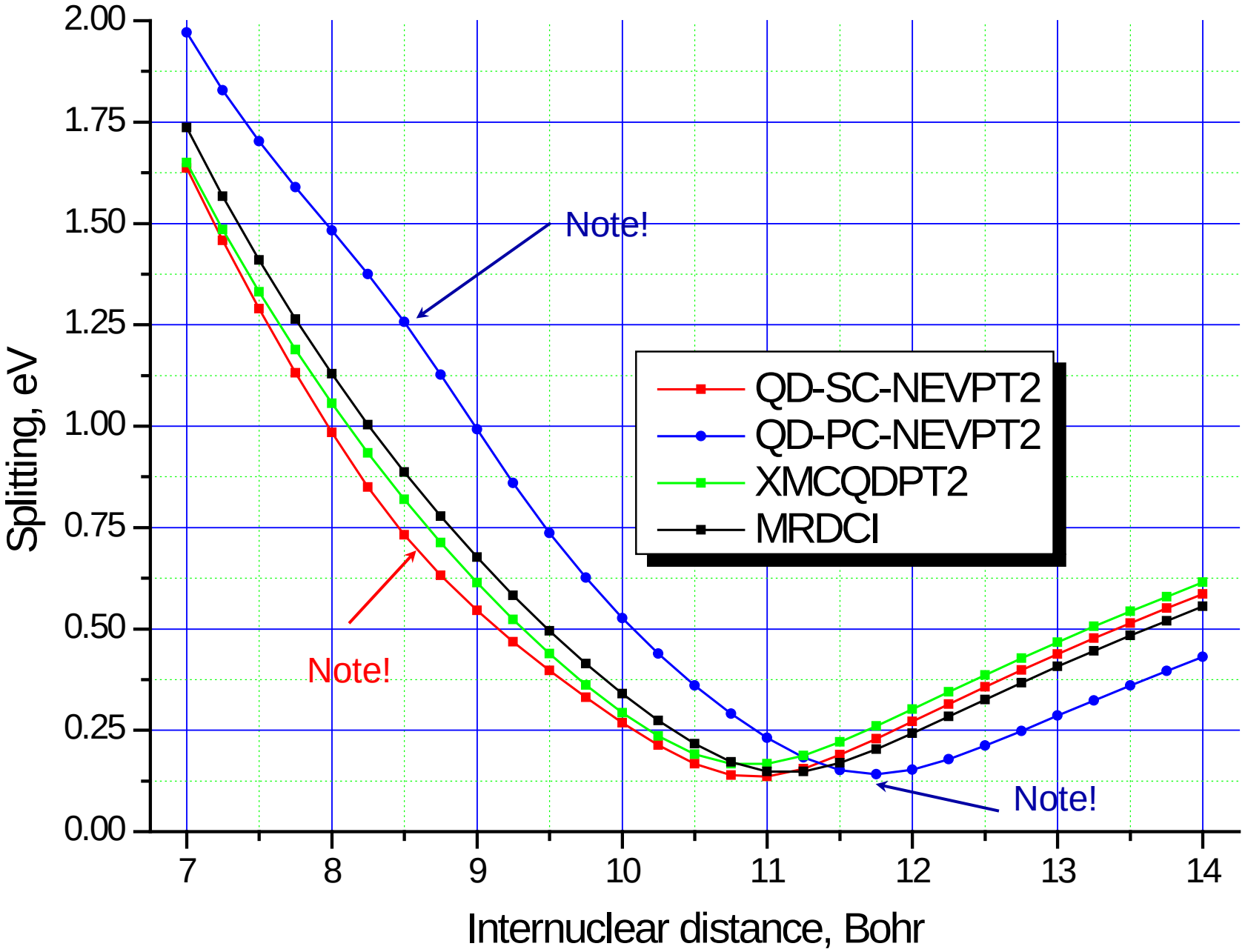

Energy splitting, six-state QD-PC-NEVPT2
Variable 2
Variable 1
10
8
6
4
2
0
-2
-4
-6
-8
-10
-10
-8
-6
-4
-2
0
2
4
6
8
10
0
0.008750
0.01750
0.02625
0.03500
0.04375
0.05250
0.06125
0.07000


Energy splitting, six-state QD-PC-NEVPT2
enlarged central region
Variable 2
Variable 1
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.0 -0.8 -0.6 -0.4 -0.2 0.0 0.2 0.4 0.6 0.8 1.0
0.01500
0.01637
0.01775
0.01912
0.02050
0.02187
0.02325
0.02462
0.02600

Benchmark II. The neutral to ionic avoided crossing in the LiF molecule

- Exactly the same methodology as in the XMCQDPT paper
  - Li(9s5p)/[4s2p], F(9s6p1d)/[4s3p1d] basis set employed by Bauschlicher and Langhoff in their FCI study on LiF
  - Model space generated by SA-2-CASSCF(6,6)
  - Two chemical core orbitals are frozen in PT2 treatment
  - MRDCI *without Davidson correction* as the reference to compare with


-106.95
-106.96
-106.97
-106.98
-106.99
-107.00
-107.01
-107.02
-107.03
-107.04
Energy of states, au
7
8
9
10
11
12
13
14
Internuclear distance, Bohr
Note!
Note!
Note!
1, QD-SC-NEVPT2
2, QD-SC-NEVPT2
1, QD-PC-NEVPT2
2, QD-PC-NEVPT2
1, XMCQDPT2
2, XMCQDPT2
1, MRDCI
2, MRDCI


2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
Splitting, eV
7
8
9
10
11
12
13
14
Internuclear distance, Bohr
QD-SC-NEVPT2
QD-PC-NEVPT2
XMCQDPT2
MRDCI
Note!
Note!
Note!

Conclusions

- Both SC and PC variants of QD-NEVPT2 are non-invariant
  - In both benchmarks, non-invariance results in distorted and/or singular PES segments
  - The non-invariance of QD-NEVPT2 is less prominent as compared with the “Type I” non-invariant theories (MCQDPT2, MS-CASPT2)
  - The SC variant of theory seems to be almost invariant and thus could be the preferred version of QD-NEVPT2 in many applications e.g., in computing terms of diatomics or mixed states
  - Similar to “Type I” non-invariant theories, artifacts caused by the non-invariance of QD-NEVPT2 increase with the dimension of the model space
  - It seems that both variants of QD-NEVPT2 result in more prominent artifacts in the energies of quasi-degenerated states as compared with the transition energies between these states

Credits

- Celestino Angeli & Renzo Cimiraglia
- Andrei V. Zaitsevskii

Thank you for your attention!