Conical Intersections and Multiconfiguration Quasi-Degenerate Perturbation Theories

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Firefly Project

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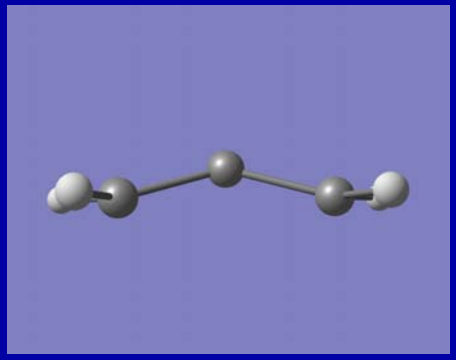

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Introduction

Multiconfiguration Quasi-Degenerate Perturbation Theories

- Most widely used
  - MS-CASPT2
    - SS-SR-CASPT2
    - MS-MR-CASPT2
  - MCQDPT2
  - Recent development - QD-NEVPT2
  - And now the XMCQDPT2!
- All of the D-P-D type (note XMCQDPT2 limit is the P-D theory).
- Internally Contracted
  - MS-CASPT2
  - QD-NEVPT2
- Non-contracted
  - MCQDPT2, XMCQDPT2

Similarities

Selection of H_0

- MCQDPT, MS-CASPT, QD-NEVPT2
  - In the model space, H_0 is explicitly defined using projectors to CI vectors and is not invariant with respect to unitary transformation of the model space. This results to the non-invariant perturbation theories and (artificial) many-particle nature of perturbation
- XMCQDPT
  - In contrast, XMCQDPT uses definition of H_0 that is invariant with respect to unitary transformation of the model space. This results to the theory that is invariant as well; with perturbation being the true two-particle operator

MCQDPT: primary paper

J. Chem. Phys., Vol. 99, No. 10, 15 November 1993

Quasidegenerate perturbation theory with multiconfigurational self-consistent-field reference functions

Haruyuki Nakano[a)]
Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan

(Received 22 December 1992; accepted 13 August 1993)

A quasidegenerate perturbation theory based on multiconfigurational self-consistent-field (MCSCF) reference functions is derived. The perturbation theory derived here is for multistate, where several MCSCF functions obtained by the state-averaged MCSCF method are used as the reference and an effective Hamiltonian is constructed by perturbation calculation. The energies of states interested in are obtained simultaneously by diagonalization of the effective Hamiltonian. An explicit formula of the effective Hamiltonian through second order is derived as well as general formalism, and is applied to calculate potential curves of the system H_2, Be–H_2, CO, NO, BN, and LiF. The results agree well with those of full configuration interaction or multireference single and double excitation configuration interaction methods for both the ground and the excited states.

Comment on MCQDPT

- As we have shown previously, the paper above has several crude mistakes
  - What is especially important is that the declared form of the H_0 is not actually the form used in the MCQDPT approach

MCQDPT2: true H^0

- Let's denote true H^0 of MCQDPT2 as H^0_{true}, as opposed to H^0 given in Nakano paper
- P-P block: H^0_{true} is diagonal and is:

$$H^{0}_{pp^{true}} = \sum_{\alpha} |\alpha\rangle\langle\alpha|H^{0}|\alpha\rangle\langle\alpha|$$

  – where summation runs over CI vectors $|\alpha\rangle$ in the model space

MCQDPT2: true H^0 drawbacks

- H^0_{true} is absolutely non-invariant
- It is evident that by this definition H^0_{true} is many-particle operator for any non-trivial model space
  - Hence, the perturbation is many-particle operator as well
- The main sources of various problems!

Similar formulations

- Both MS-CASPT2 and QD-NEVPT2 has the same drawback as can be easily seen from the equations given in the corresponding papers. Below, the important relevant statements will be marked in red.

MS-CASPT2

ELSEVIER

22 May 1998

Chemical Physics Letters 288 (1998) 299–306

CHEMICAL PHYSICS LETTERS

The multi-state CASPT2 method

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Received 3 October 1997; in final form 20 February 1998

Abstract

An extension of the multiconfigurational second-order perturbation approach CASPT2 is suggested, where several electronic states are coupled at second order via an effective-Hamiltonian approach. The method has been implemented into the MOLCAS-4 program system, where it will replace the single-state CASPT2 program. The accuracy of the method is illustrated through calculations of the ionic-neutral avoided crossing in the potential curves for LiF and of the valence-Rydberg mixing in the V-state of the ethylene molecule.

3. The multi-state CASPT2 method

Multi-state CASPT2 (MS-CASPT2) chooses a multidimensional reference space, or P space, spanned by two or more state average CASSCF (SA-CASSCF), or CASCI states

$$P = \sum_{\alpha=1}^{d} |\alpha\rangle\langle\alpha|, \qquad (16)$$

where d is the dimension of the reference space and where, for MS-CASPT2, the reference states $|\alpha\rangle$ are eigenfunction of H_0^α,

$$H_0^\alpha|\alpha\rangle = E_0^\alpha|\alpha\rangle \quad (\alpha = 1, 2, \cdots, d). \qquad (17)$$

The remainder of the Hilbert space is spanned by the secondary space Q.

The model states $|\Psi_p{}^0\rangle$ are the projections on the exact states of interest $|\Psi_p\rangle$ into the P space,

$$P|\psi_p\rangle = |\psi_p^0\rangle \quad (p = 1, 2, \cdots, d). \qquad (18)$$

In Eq. (20), there is a separate partitioning for each reference space ket $|\alpha\rangle$

$$H = H_0^\alpha + V^\alpha \quad (\alpha = 1, 2, \cdots, d). \qquad (21)$$

An order-by-order expansion exists for Ω^P,

$$\Omega^P = 1 + \Omega_1^P + \Omega_2^P + \cdots, \qquad (22)$$

where Ω_n^P has n perturbative factors V. The zeroth-order Hamiltonians is chosen to be identical to the ones used for SS-CASPT2,

$$H_0^\alpha = \sum_\beta |\beta\rangle\langle\beta|\hat{F}^\alpha|\beta\rangle\langle\beta| + \sum_k |k\rangle\langle k|\hat{F}^\alpha|k\rangle\langle k| + Q_{sd}^\alpha \hat{F}^\alpha Q_{sd}^\alpha + Q_{tq}^\alpha \ldots \hat{F}^\alpha Q_{tq}^\alpha \ldots + \cdots$$

$$(\alpha = 1, 2, \cdots, d), \qquad (23)$$

where the sum over β includes all reference space states, also $|\alpha\rangle$. By substituting Eq. (22) into Eq. (20) and identifying the terms for the first order ($n = 1$), we get

$$\left(E_0^\alpha - \hat{F}^\alpha\right)\Omega_1^P|\alpha\rangle = Q_{sd}^\alpha H|\alpha\rangle$$

$$(\alpha = 1, 2, \cdots, d), \qquad (24)$$

where Eq. (23) and similar identities as in SS-CASPT2 have been used (see Eqs. (11)–(13)).

Comparing Eqs. (14) and (24) we see that

$$\Omega_1^P|\alpha\rangle = \Omega_1^\alpha|\alpha\rangle \quad (\alpha = 1, 2, \cdots, d). \qquad (25)$$

Hence, the multireference wave-operator Ω_1^P is just a linear combination of SS wave-operators

$$\Omega_1^P = \sum \Omega_1^\alpha|\alpha\rangle\langle\alpha|. \qquad (26)$$

QD-NEVPT2

JOURNAL OF CHEMICAL PHYSICS VOLUME 121, NUMBER 9 1 SEPTEMBER 2004

A quasidegenerate formulation of the second order *n*-electron valence state perturbation theory approach

Celestino Angeli, Stefano Borini, Mirko Cestari, and Renzo Cimiraglia[a)]
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(Received 29 April 2004; accepted 11 June 2004)

The *n*-electron valence state perturbation theory (NEVPT) is reformulated in a quasidegenerate (QD) approach. The new theory allows the treatment of cases where the proximity of the energies causes artifacts in the zero order description. Problems of quasidegeneration are relevant in the dynamics involving regions at avoided crossings (or conical intersections) and in spectroscopy where the energies and oscillator strengths can be strongly influenced by the mixing of states of different nature. Two test cases are analyzed concerning (a) the ionic-neutral avoided crossing in LiF and (b) the valence/Rydberg mixing in the excited states of ethene. The QD-NEVPT2 is shown to be a useful tool for such systems.
[DOI: 10.1063/1.1778711]

Adopting a partition of the Hamiltonian, $H=H_0+V$, with $H_0\Psi_m^{(0)}=E_m^{(0)}\Psi_m^{(0)}$ and resorting to a perturbation expansion of Ω and H_{eff},

$$\Omega=P+\Omega^{(1)}+\Omega^{(2)}+\cdots, \tag{9}$$

$$H_{\text{eff}}=H_{\text{eff}}^{(0)}+H_{\text{eff}}^{(1)}+H_{\text{eff}}^{(2)}+\cdots, \tag{10}$$

one promptly arrives at order-by-order working formulas, of which we report the first order term for Ω,

$$[\Omega^{(1)},H_0]=QVP \tag{11}$$

and the terms up to the second order for H_{eff},

$$H_{\text{eff}}^{(0)}=PH_0P, \tag{12}$$

$$H_{\text{eff}}^{(1)}=PVP=0, \tag{13}$$

$$H_{\text{eff}}^{(2)}=PV\Omega^{(1)}. \tag{14}$$

In order to obtain a manageable formulation of the $H_{\text{eff}}^{(2)}$ operator, the multipartitioning technique of Zaitsevskii and Malrieu[16] is adopted, consisting in the use of different partitions of the Hamiltonian according to the various $\Psi_m^{(0)}$ functions of the model space,

$$H=H_0(m)+V(m), \tag{15}$$

$$H_0(m)=|\Psi_m^{(0)}\rangle E_m^{(0)}\langle\Psi_m^{(0)}|+\sum_{m'\neq m}^{CAS}|\Psi_{m'}^{(0)}\rangle E_{m'}^{(0)}\langle\Psi_{m'}^{(0)}|$$

$$+\sum_{k,l,\mu}|\Psi_{l,\mu}^{(k)}(m)\rangle E_{l,\mu}^{(k)}(m)\langle\Psi_{l,\mu}^{(k)}(m)|, \tag{16}$$

where the perturbers $\Psi_{l,\mu}^{(k)}(m)$ are the ones generated by $\Psi_m^{(0)}$ via the application of the excitation operators. This leads to the following expression for the application of $\Omega^{(1)}$ to a model function $\Psi_m^{(0)}$:

$$\Omega^{(1)}\Psi_m^{(0)}=\sum_{k,l,\mu}\frac{|\Psi_{l,\mu}^{(k)}(m)\rangle\langle\Psi_{l,\mu}^{(k)}(m)|H|\Psi_m^{(0)}\rangle}{E_m^{(0)}-E_{l,\mu}^{(k)}(m)}. \tag{17}$$

The expression for the H_{eff} matrix elements up to second order are accordingly

$$\langle\Psi_n^{(0)}|H_{\text{eff}}|\Psi_m^{(0)}\rangle$$

$$=\delta_{mn}E_m^{(0)}+\sum_{k,l,\mu}\frac{\langle\Psi_n^{(0)}|H|\Psi_{l,\mu}^{(k)}(m)\rangle\langle\Psi_{l,\mu}^{(k)}(m)|H|\Psi_m^{(0)}\rangle}{E_m^{(0)}-E_{l,\mu}^{(k)}(m)}. \tag{18}$$

Diagonalization of the H_{eff} matrix produces the approximate projections $\tilde{\Psi}_m$ and eigenvalues E_m.

Where the Differences appear: XMCQDPT2!

XMCQDPT2 in Firefly – the clever approach

- **If**

$$H = \begin{bmatrix} H^0_{pp} + V_{pp} & H_{ps} \\ H_{sp} & H^0_{ss} + V_{ss} \end{bmatrix}$$

- **Then, using Van Vleck-type PT expansion one gets:**

$$h_0 = H^0_{pp}, \qquad h_1 = V_{pp},$$

$$h_2 = \frac{1}{2}[H_{ps}v_1 + v_1^{+}H_{sp}], \text{ where } v_1 \text{ is defined}$$

by the following linear equation :

$$H_{sp} + H^0_{ss}v_1 = v_1 H^0_{pp}$$

After some simple math

If $H_{sp} + H^0_{ss} v_1 = v_1 H^0_{pp}$ is held, then :

$$H_{sp} O + H^0_{ss} (v_1 O) = (v_1 O)(O^+ H^0_{pp} O)$$

Using $h_2 = \frac{1}{2}[H_{ps} v_1 + v_1^+ H_{sp}]$, one gets :

$$O^+ h_2 O = \frac{1}{2}[(O^+ H_{ps})(v_1 O) + (O^+ v_1^+)(H_{sp} O)]$$

What this mean is:

- *h_2 has trivial (and very nice) transformation properties with respect to rotations of basis in model space*
- *We just need to diagonalize H^0_{pp} and transform reference CI vectors accordingly:*
  - *H^0 is now fully diagonal in S+P*
  - *The working equations of MCQDPT2 do not assume the reference vectors are CI eigenvectors*
- ***Thus, we can easily apply the existing state-of-the-art Firefly's MCQDPT2 code to perform XMCQDPT2 calculations by using rotated CI vectors (intermediate basis)***

Some nice XMCQDPT2 properties

- ***True 1-particle MP2-like H^0***
- ***Nice invariance properties***
- ***Completely equivalent to MR-MP2 for single-reference case***
- ***Unlike MCQDPT2 it is stable with respect to model space extension***
  - ***The limit is just the fully uncontracted theory***
- ***Does not result in artificially large off-diagonal elements***
  - ***Note – large off-diagonal element of H^0_{pp} typically corresponds to large off-diagonal in MCQDPT2 calculations***
    - ***We can predict MCQDPT2 failures by just examining H^0_{pp}***

Preliminary conclusions

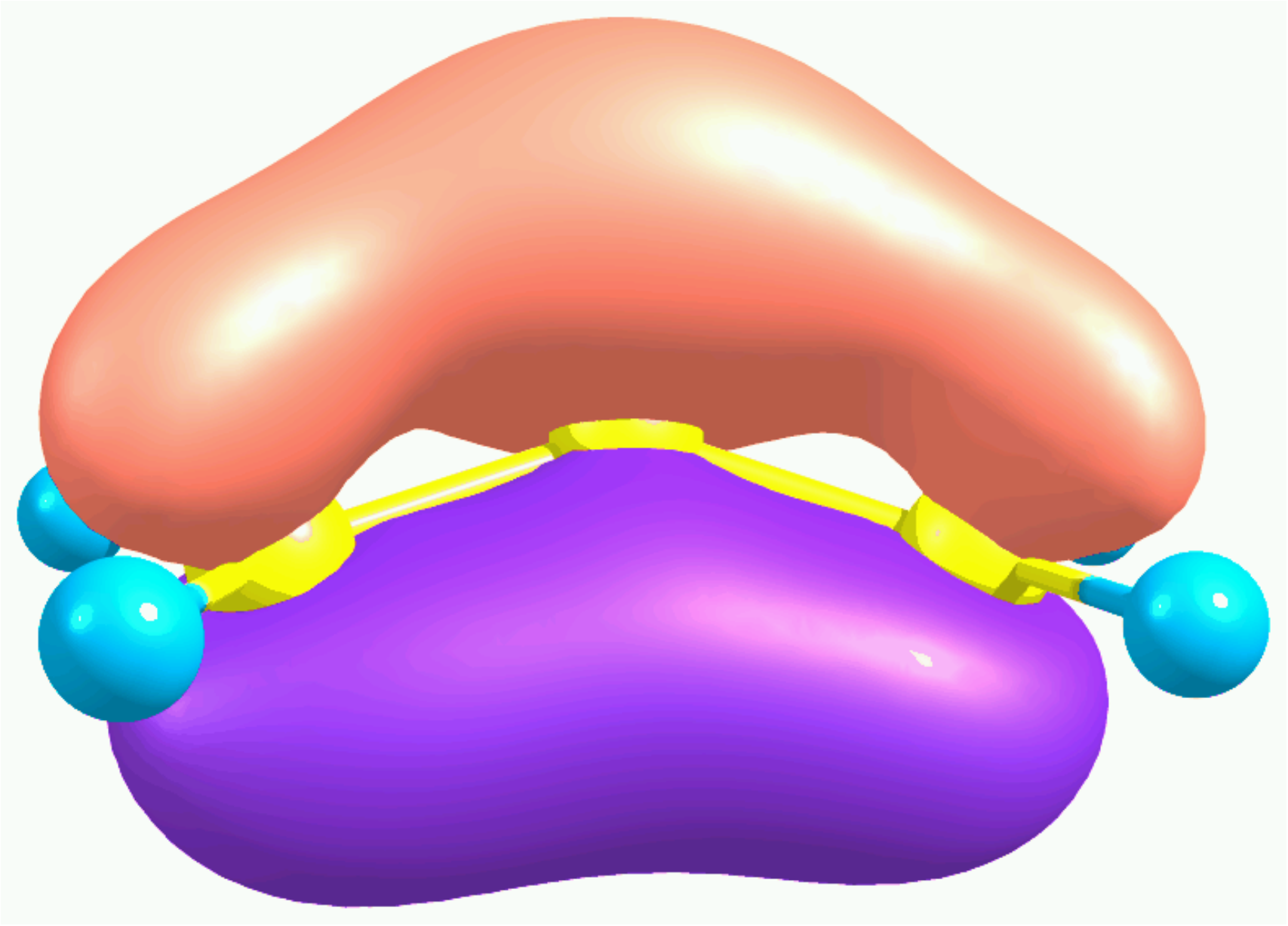
- What we can expect for non-invariant QDPT theories is:
  - **Weird behavior near geometries of CASSCF's conical intersections**
    - **Sequence of non-invariance with respect to mixing of CI vectors**
  - **Will be examined in this presentation**
  - **The complete loss of size-extensivity if any**
    - Esp., random and artificially large off-diagonal elements of H_{eff} for large molecular systems
  - **Will not be addressed in this presentation**
    - Already was checked multiple times with MCQDPT2
    - Would need Petaflop Computer to model large systems with MS-CASPT2 or QD-NEVPT2
      - No need actually… the results are quite predictable

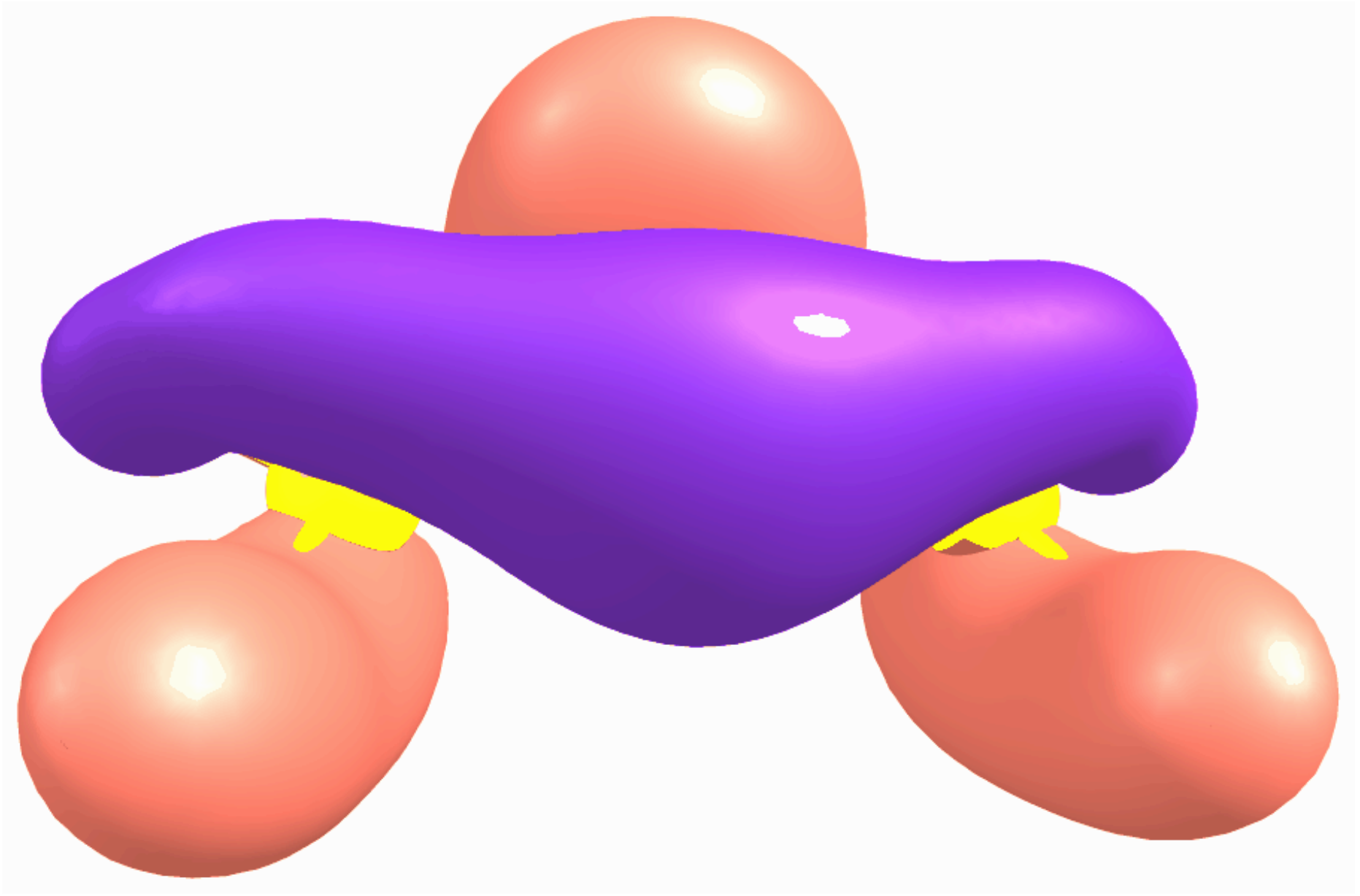
Experiment

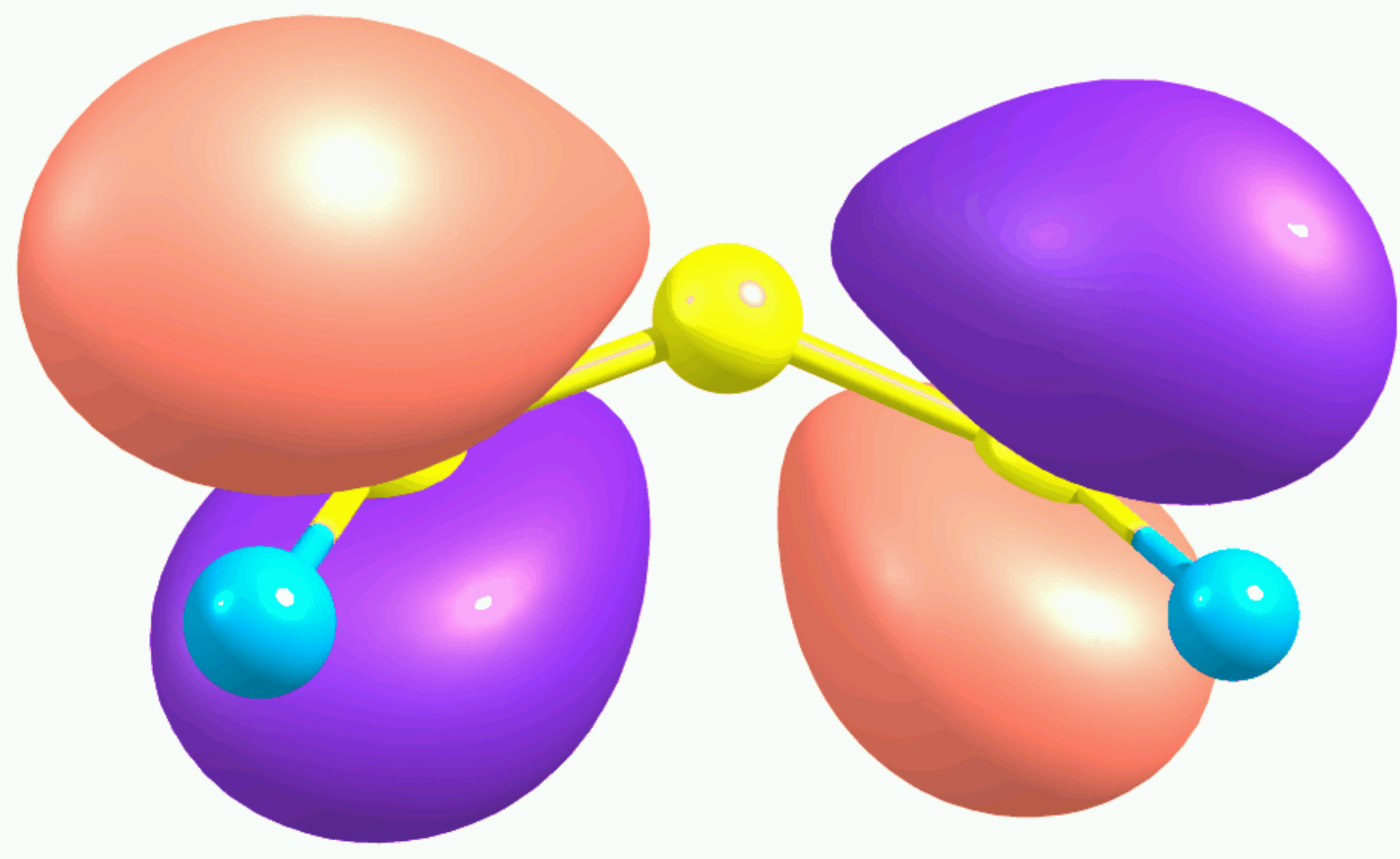
Model system

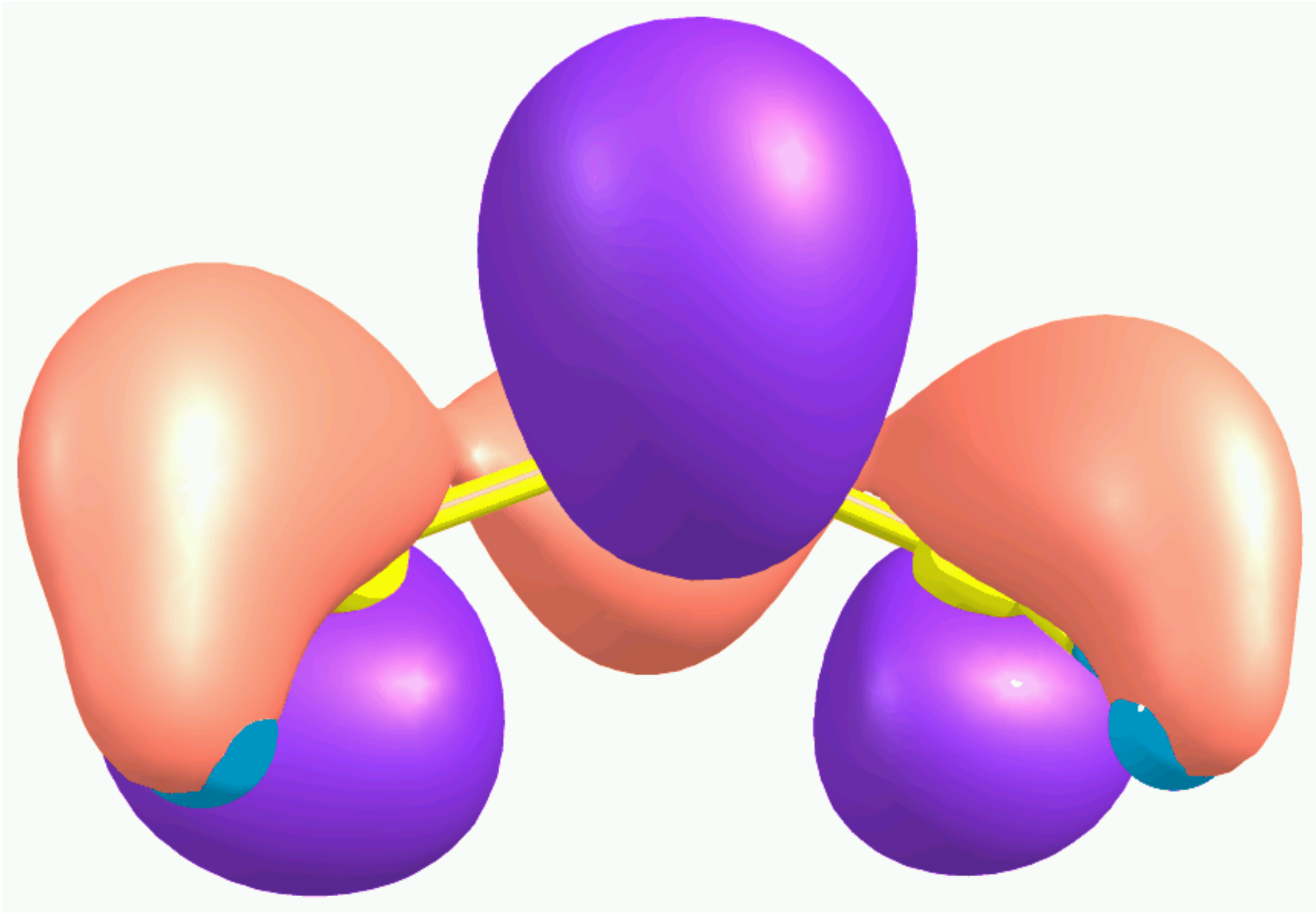
- A'_1 - A'_2 conical intersection (CI) optimization in allene molecule
- C_s point group
- SA-CASSCF(4,4), 12 CSFs in A′ subspace
  - 3 A′ + 1 A″ orbitals
- GAMESS (US) style DH basis set (using pure spherical harmonics)
  - **$BASIS GBASIS=DH NDFUNC=1 POLAR=DUNNING $END**
- **Exact geometry and basis set are available from author upon request**

Active space

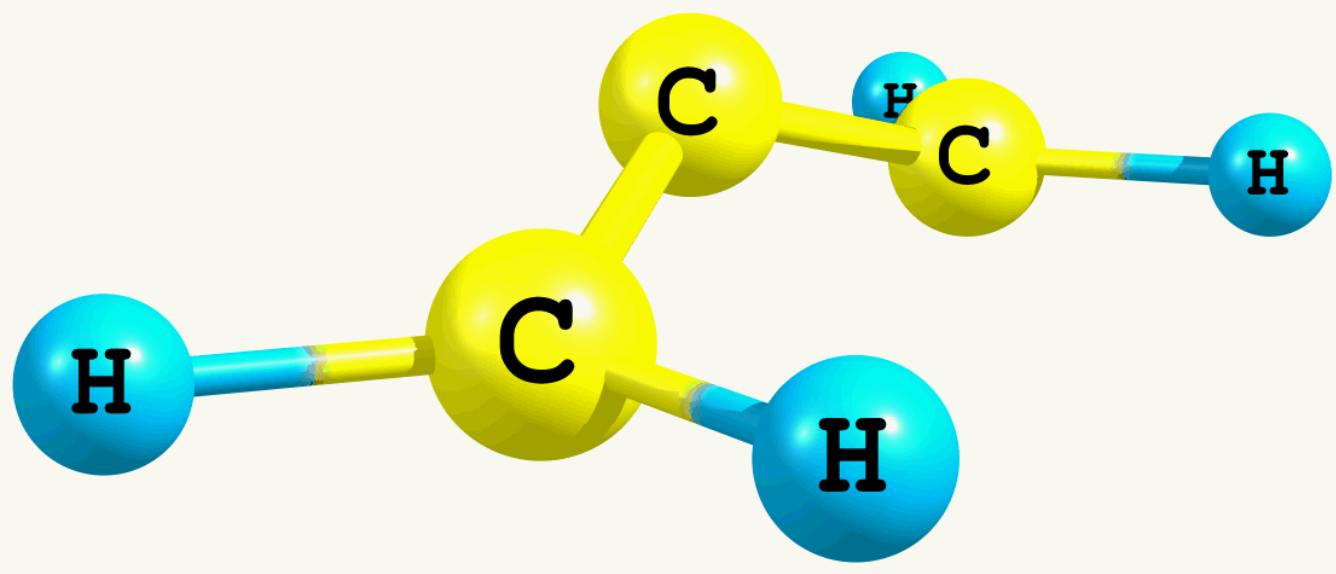


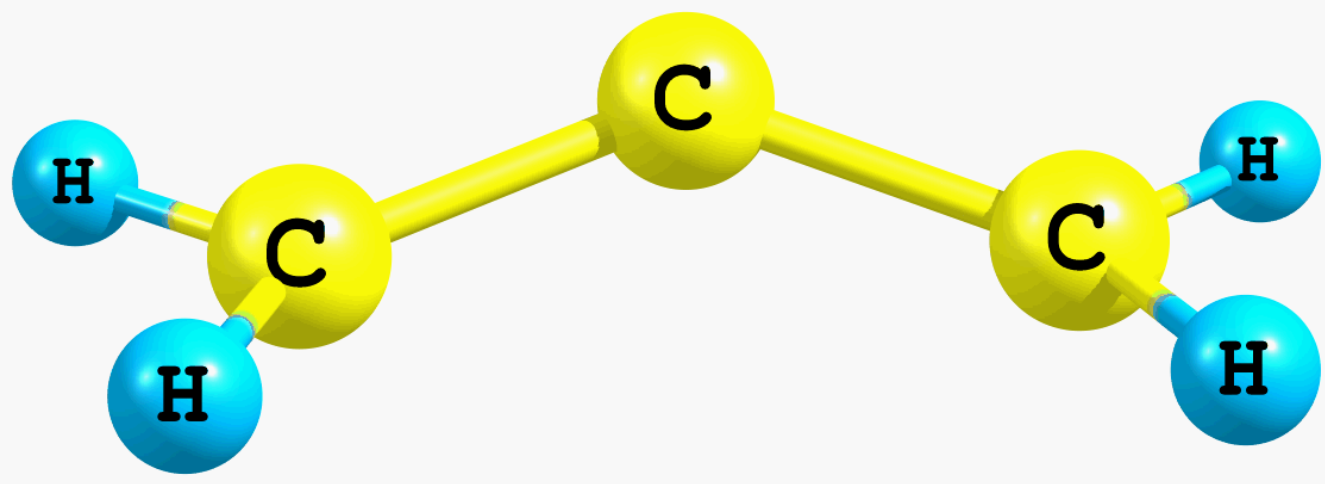




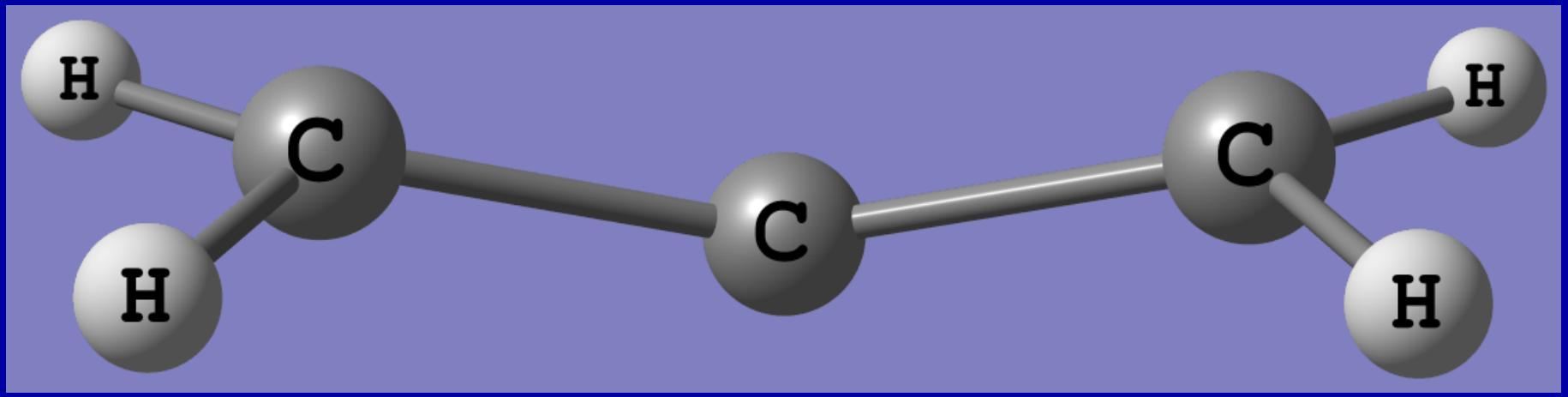


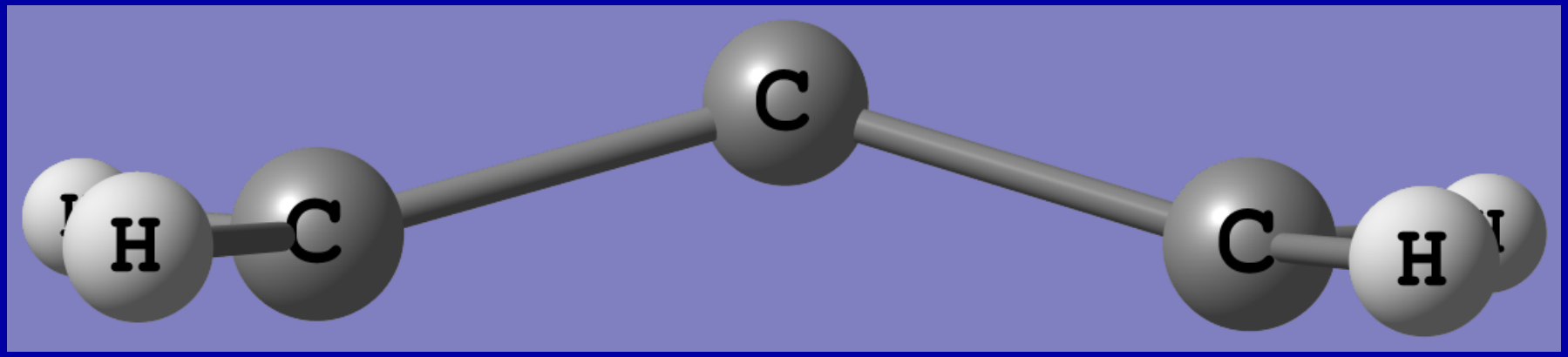
A'_1 - A'_2 CI in allene:



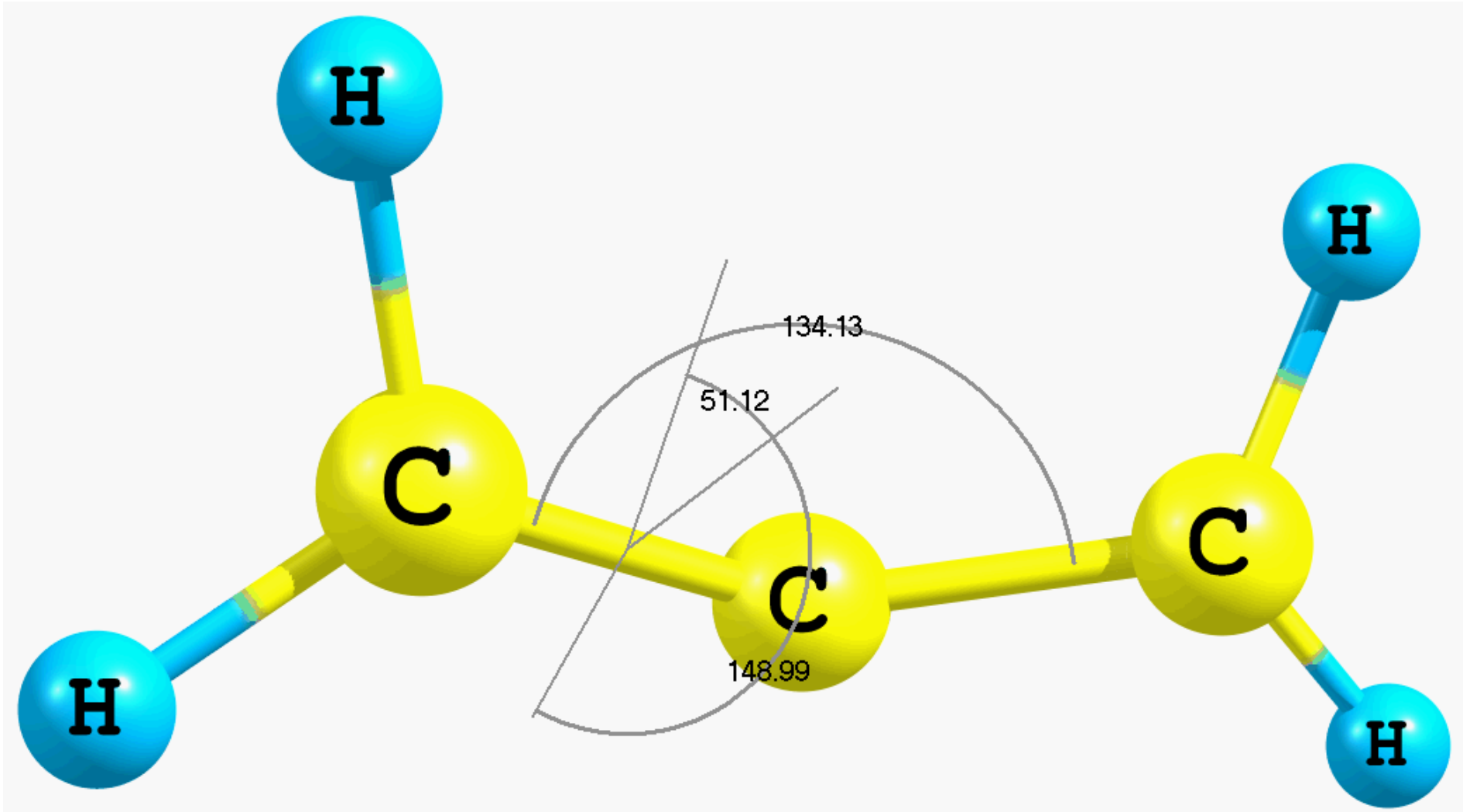


A'_1 - A'_2 CI in allene – just another view:





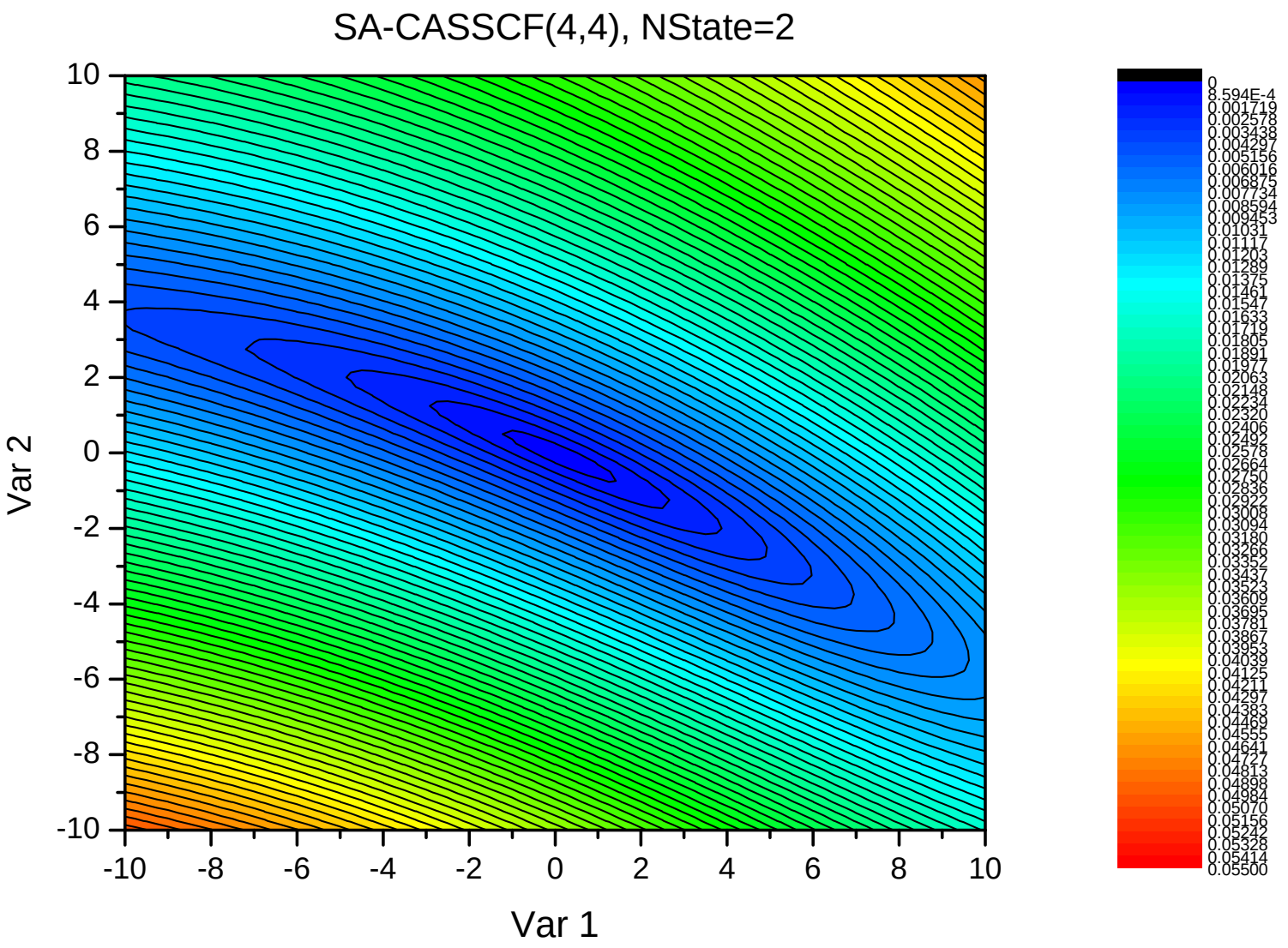
A'_1 - A'_2 CI in allene: scan variables



Var1 is CCC angle, Var2 is the simultaneous change of CCCH torsions (degrees) for H atoms on the same carbon to vary degree of pyramidalization. Exact Cs symmetry is enforced. Zero corresponds to CASSCF's CI geometry.

Scans

(Note, shown on all plots is the energy delta between two states.
Scan grid: 81 by 81 points.
Surface plots: 64 iso-surfaces)


SA-CASSCF(4,4), NState=2
Var 2
Var 1
10
8
6
4
2
0
-2
-4
-6
-8
-10
-10
-8
-6
-4
-2
0
2
4
6
8
10
0
8.594E-4
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0.002578
0.003438
0.004297
0.005156
0.006016
0.006875
0.007734
0.008594
0.009453
0.01031
0.01117
0.01203
0.01289
0.01375
0.01461
0.01547
0.01633
0.01719
0.01805
0.01891
0.01977
0.02063
0.02148
0.02234
0.02320
0.02406
0.02492
0.02578
0.02664
0.02750
0.02836
0.02922
0.03008
0.03094
0.03180
0.03266
0.03352
0.03437
0.03523
0.03609
0.03695
0.03781
0.03867
0.03953
0.04039
0.04125
0.04211
0.04297
0.04383
0.04469
0.04555
0.04641
0.04727
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0.04898
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0.05070
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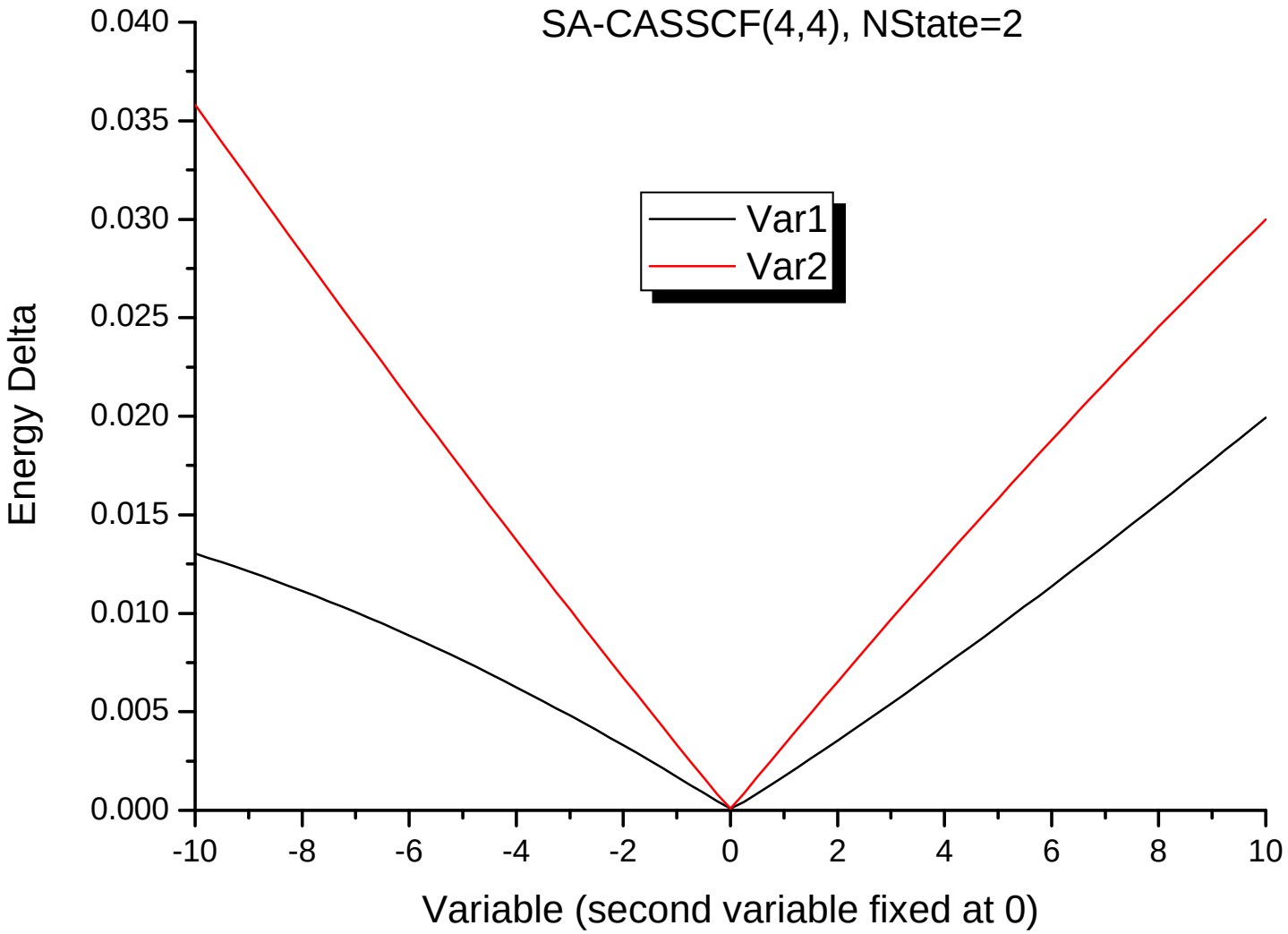
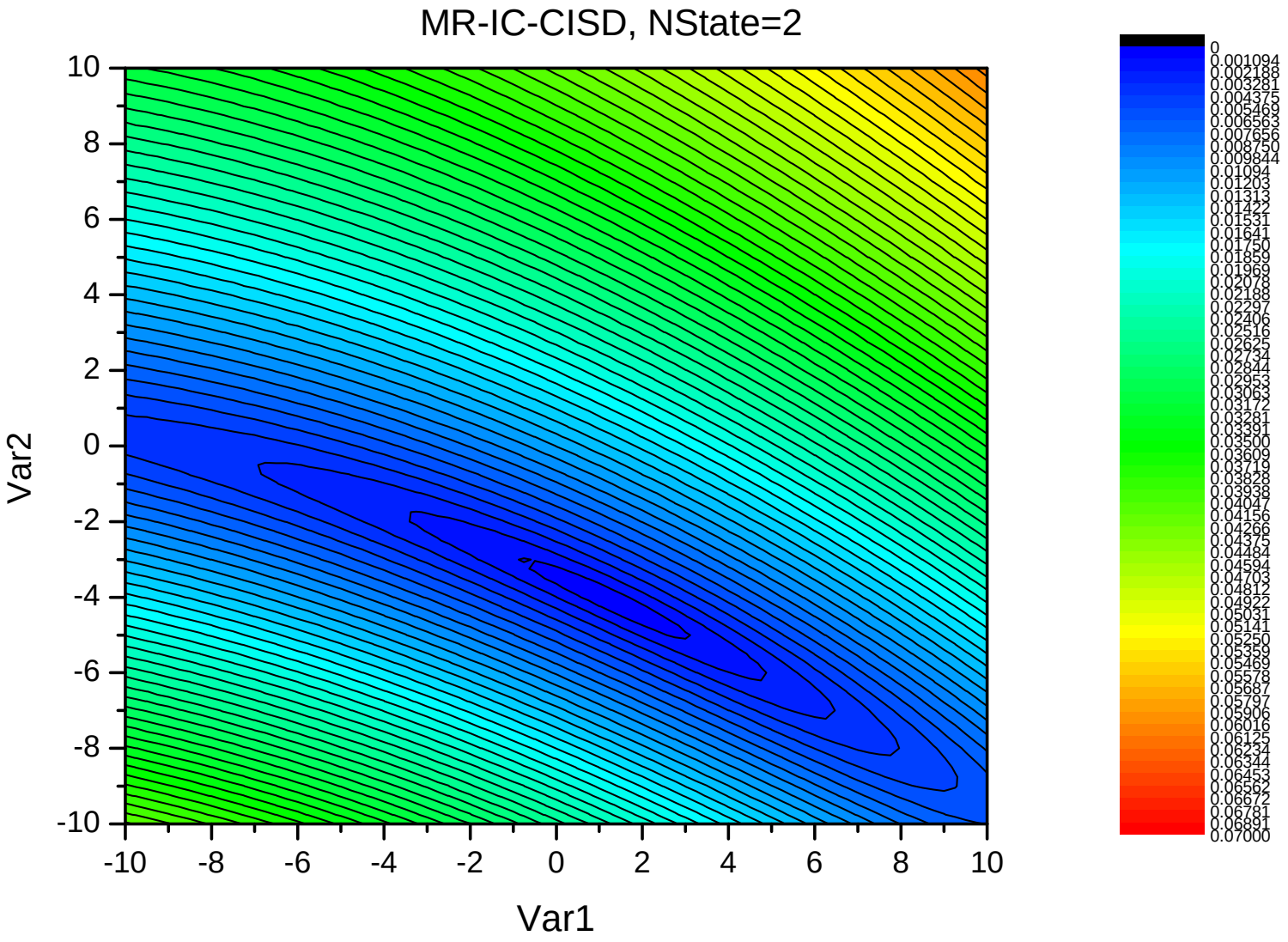
0.05242
0.05328
0.05414
0.05500


SA-CASSCF(4,4), NState=2
Var1
Var2
Energy Delta
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-10
-8
-6
-4
-2
0
2
4
6
8
10
Variable (second variable fixed at 0)


MR-IC-CISD, NState=2
Var2
Var1
10
8
6
4
2
0
-2
-4
-6
-8
-10
-10
-8
-6
-4
-2
0
2
4
6
8
10
0
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0.002188
0.003281
0.004375
0.005469
0.006563
0.007656
0.008750
0.009844
0.01094
0.01203
0.01313
0.01422
0.01531
0.01641
0.01750
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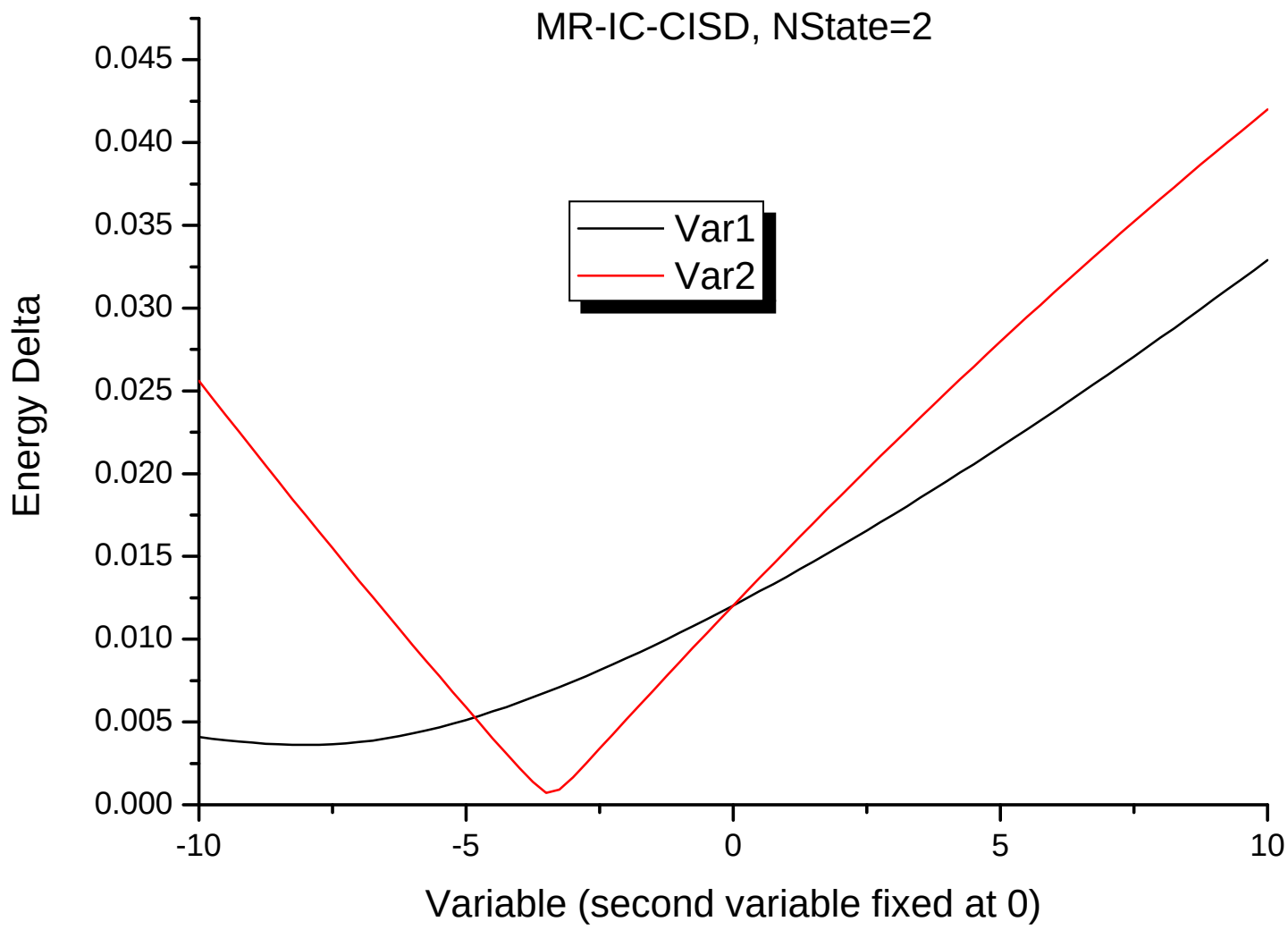
MR-IC-CISD, NState=2
Energy Delta
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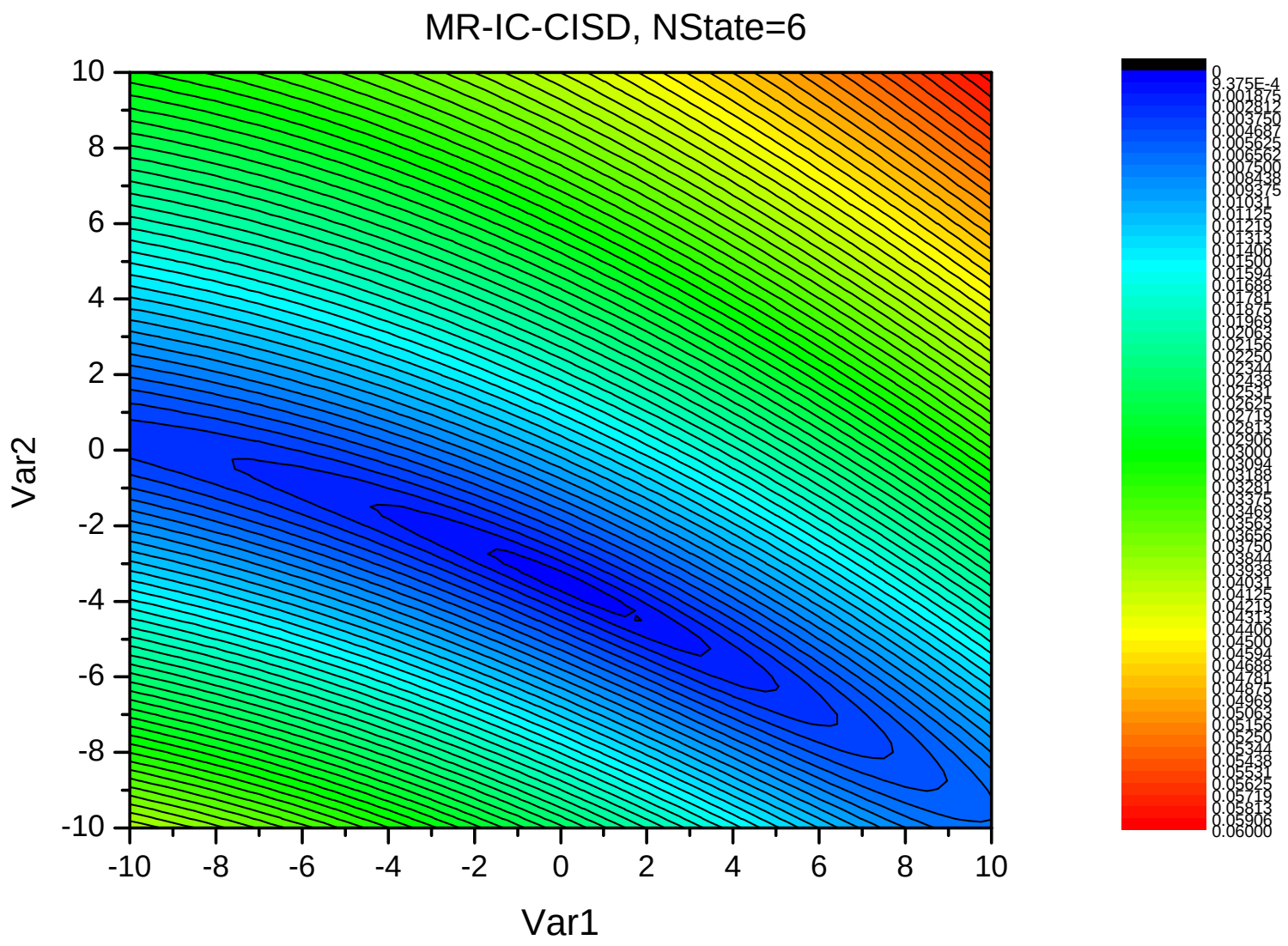
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-10
-5
0
5
10
Variable (second variable fixed at 0)
Var1
Var2


MR-IC-CISD, NState=6
Var2
Var1
10
8
6
4
2
0
-2
-4
-6
-8
-10
-10
-8
-6
-4
-2
0
2
4
6
8
10
0
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0.007500
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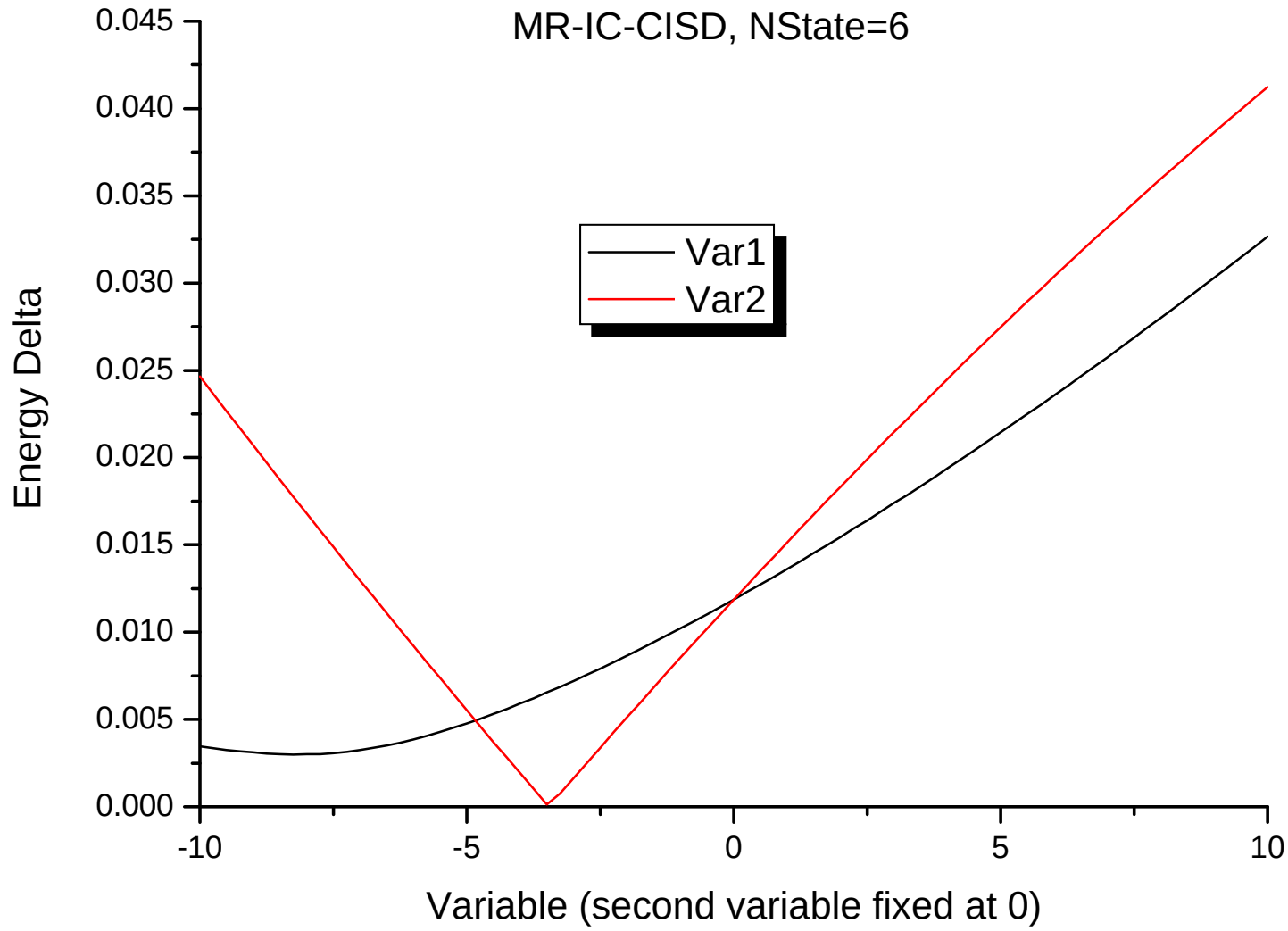
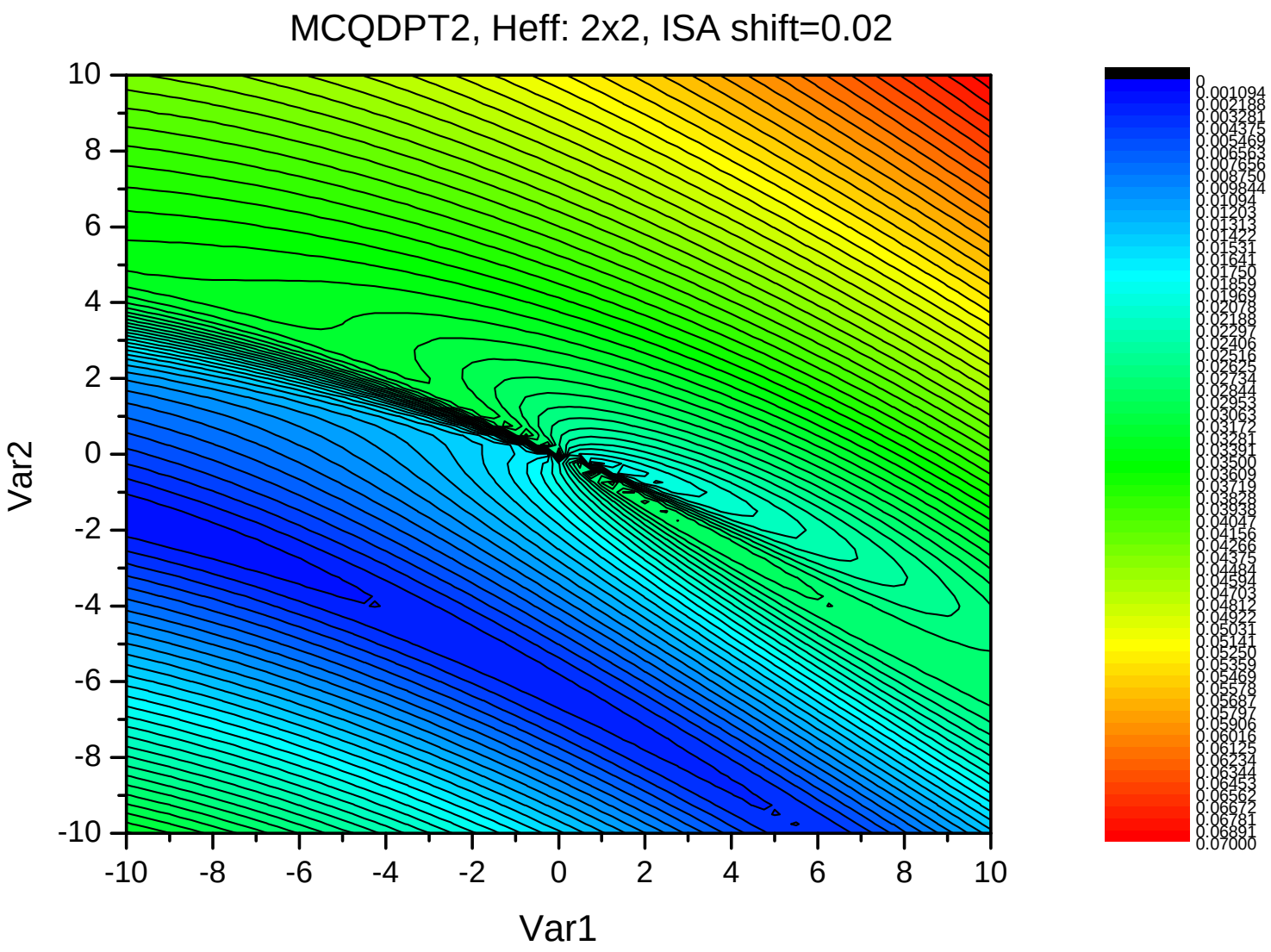
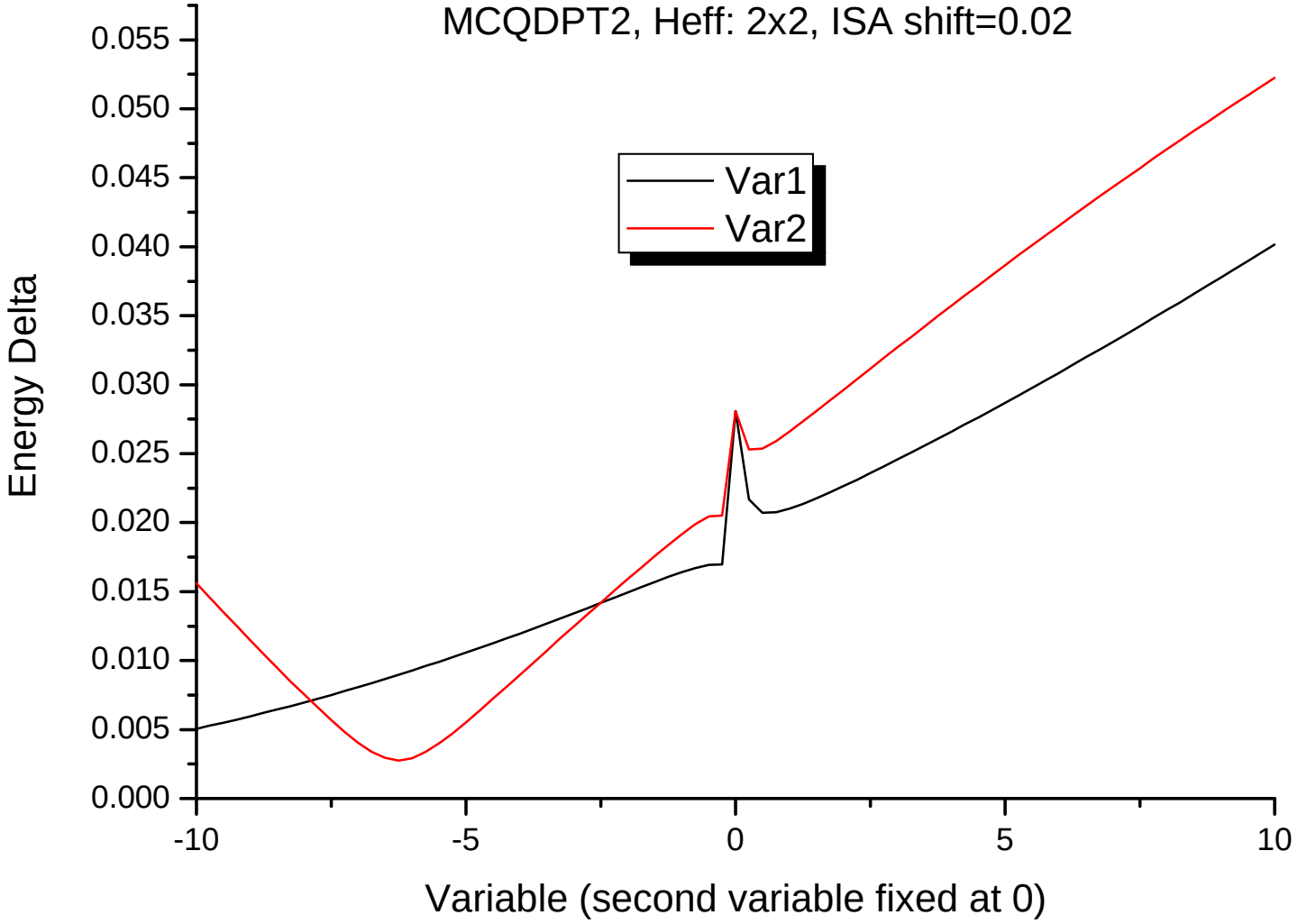
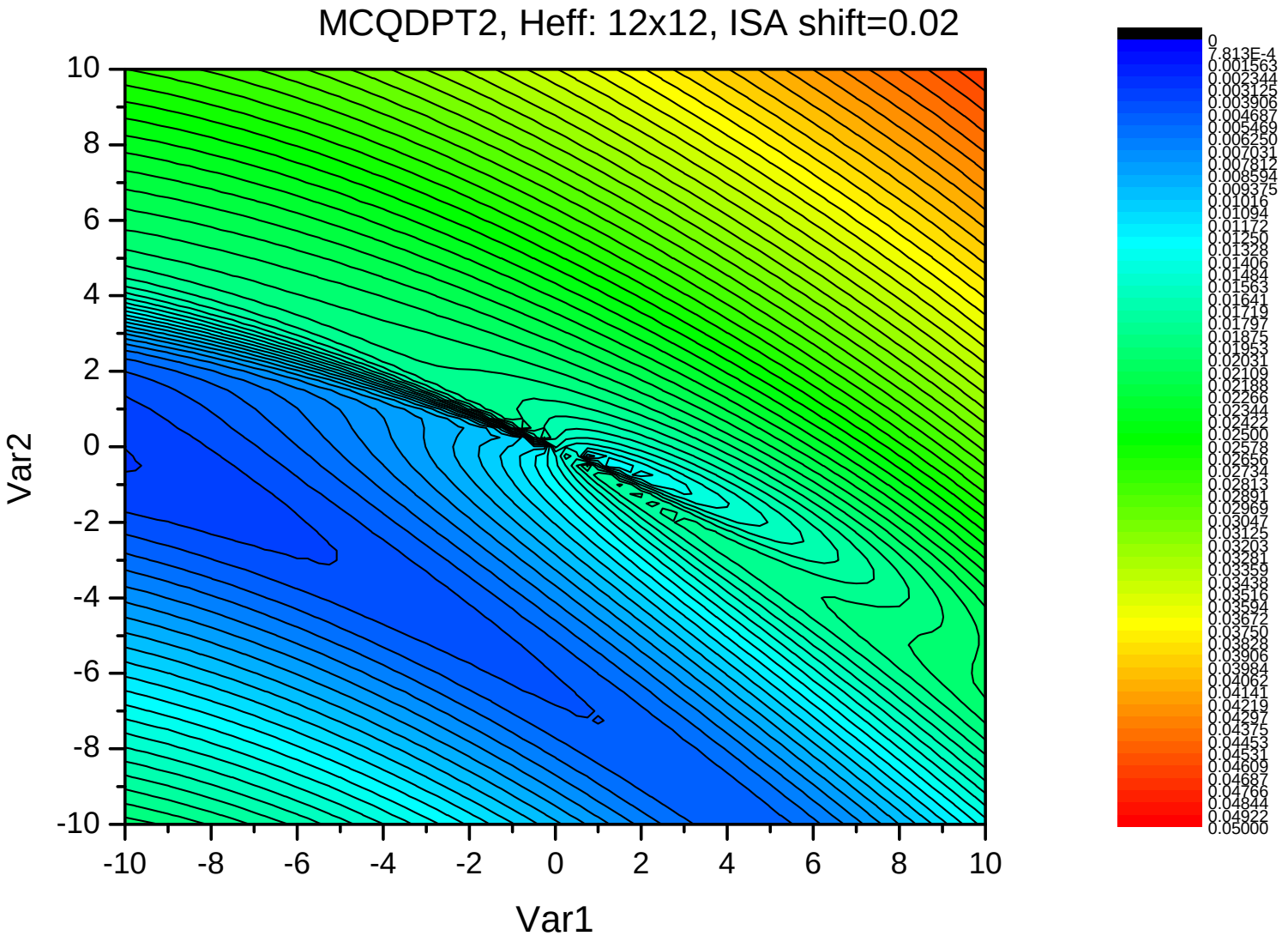
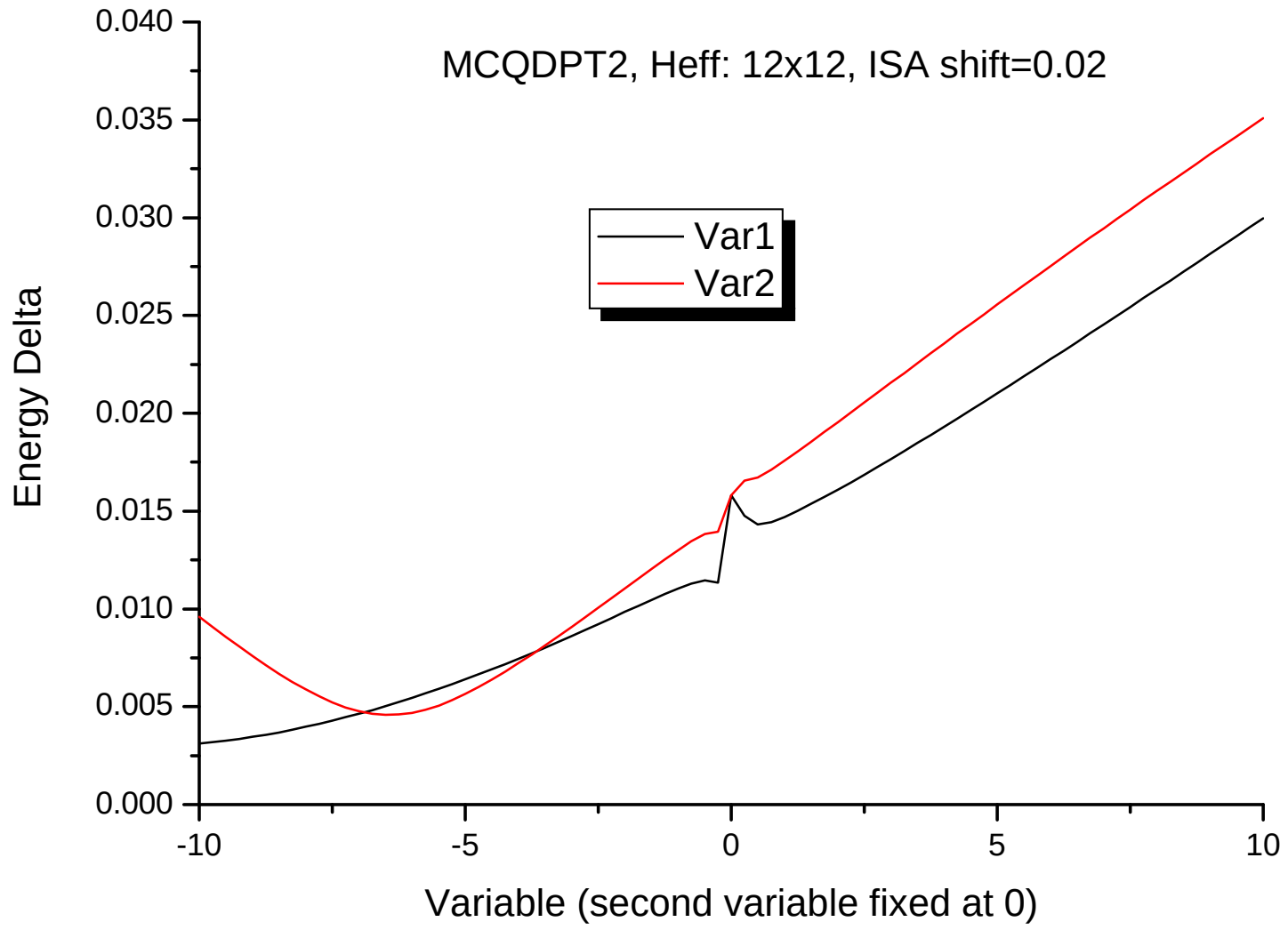
0.06000

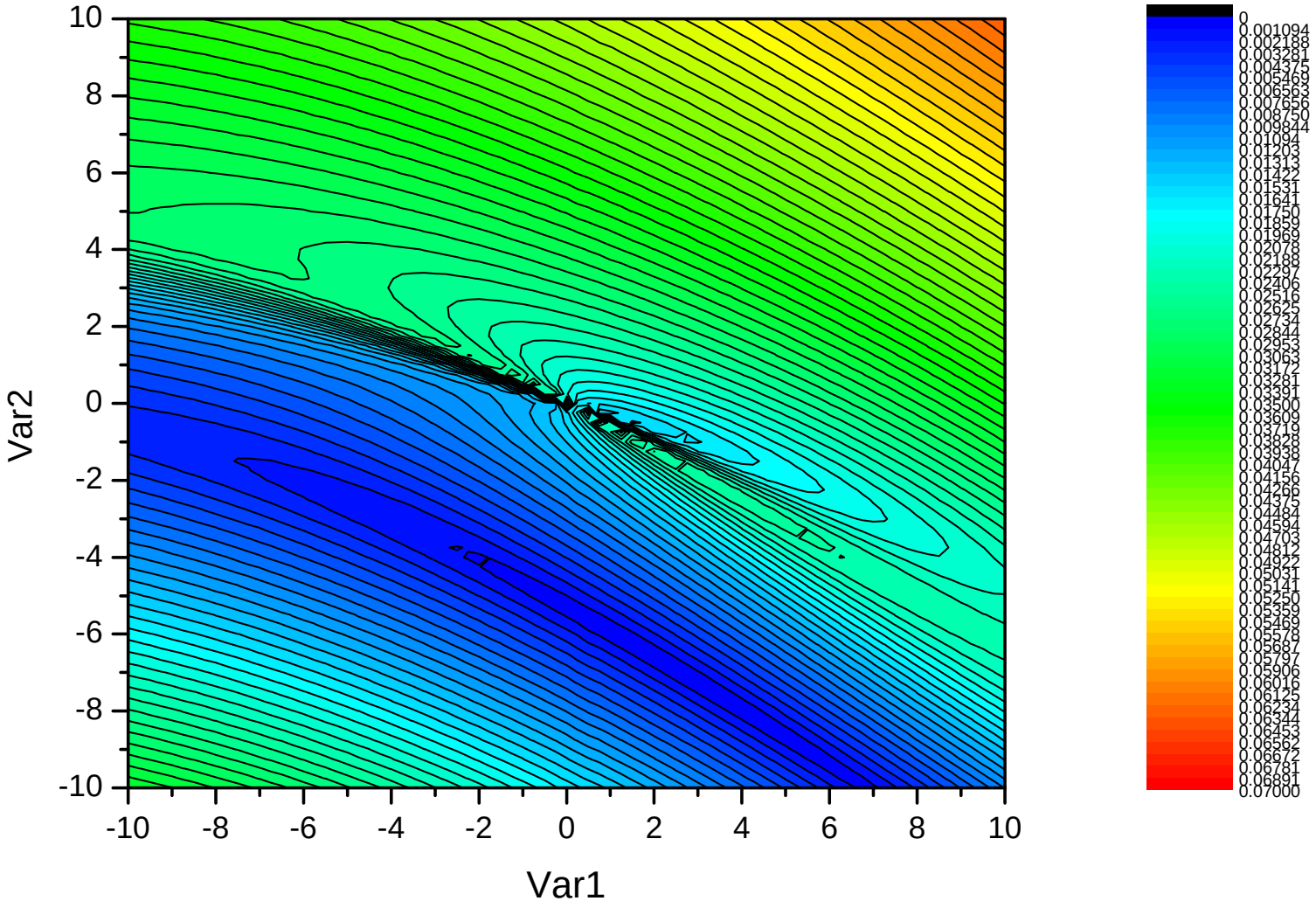

MR-IC-CISD, NState=6
Energy Delta
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-10
-5
0
5
10
Variable (second variable fixed at 0)
Var1
Var2

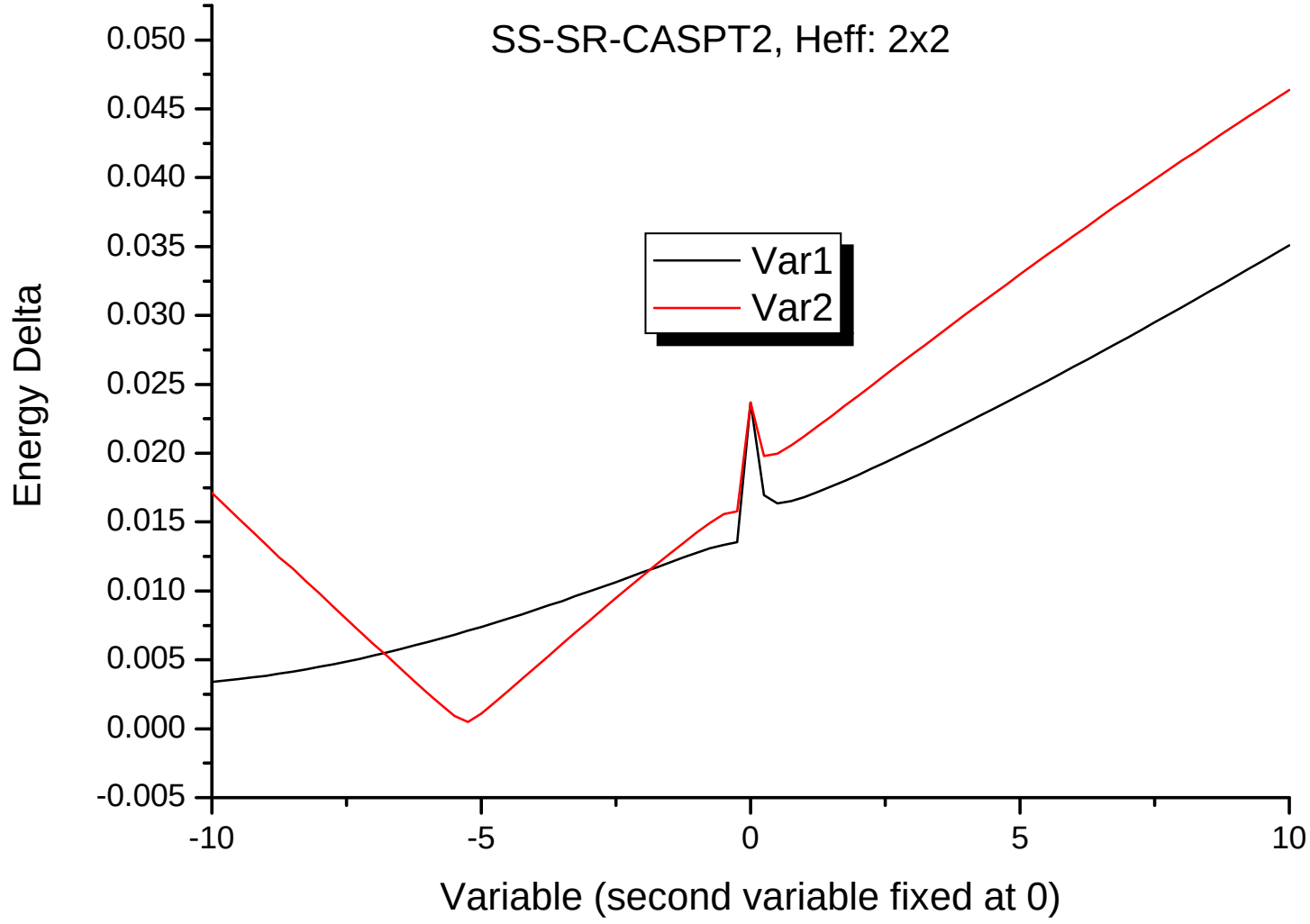

MCQDPT2, Heff: 2x2, ISA shift=0.02
Var2
Var1
10
8
6
4
2
0
-2
-4
-6
-8
-10
-10
-8
-6
-4
-2
0
2
4
6
8
10
0
0.001094
0.002188
0.003291
0.004375
0.005469
0.006563
0.007656
0.008750
0.009844
0.01094
0.01203
0.01313
0.01422
0.01531
0.01641
0.01750
0.01859
0.01969
0.02078
0.02188
0.02297
0.02406
0.02516
0.02625
0.02734
0.02844
0.02953
0.03063
0.03172
0.03281
0.03391
0.03500
0.03609
0.03719
0.03828
0.03938
0.04047
0.04156
0.04266
0.04375
0.04484
0.04594
0.04703
0.04812
0.04922
0.05031
0.05141
0.05250
0.05359
0.05469
0.05578
0.05687
0.05797
0.05906
0.06016
0.06125
0.06234
0.06344
0.06453
0.06562
0.06672
0.06781
0.06891
0.07000

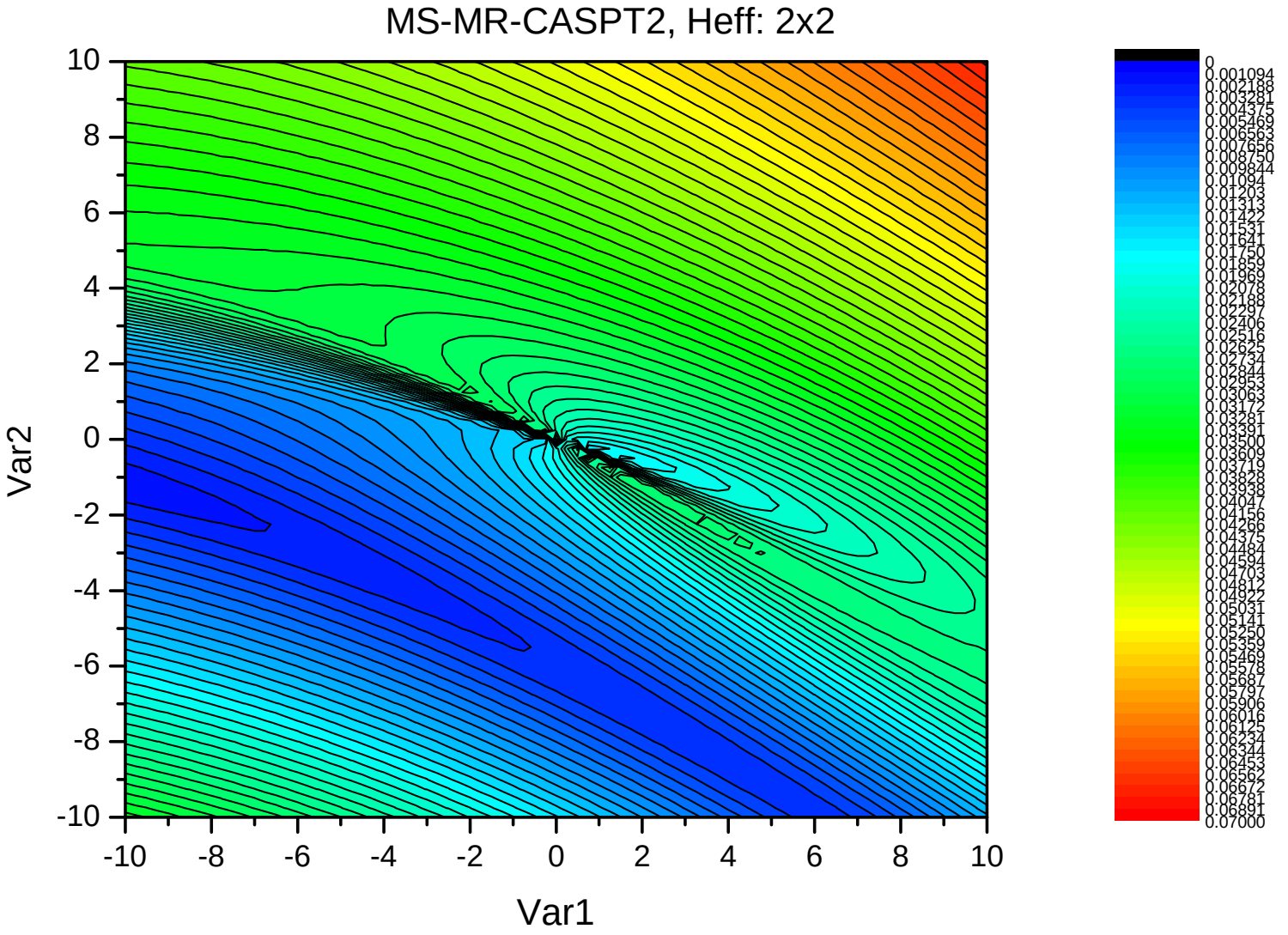

MCQDPT2, Heff: 2x2, ISA shift=0.02
Energy Delta
0.055
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-10
-5
0
5
10
Variable (second variable fixed at 0)
Var1
Var2

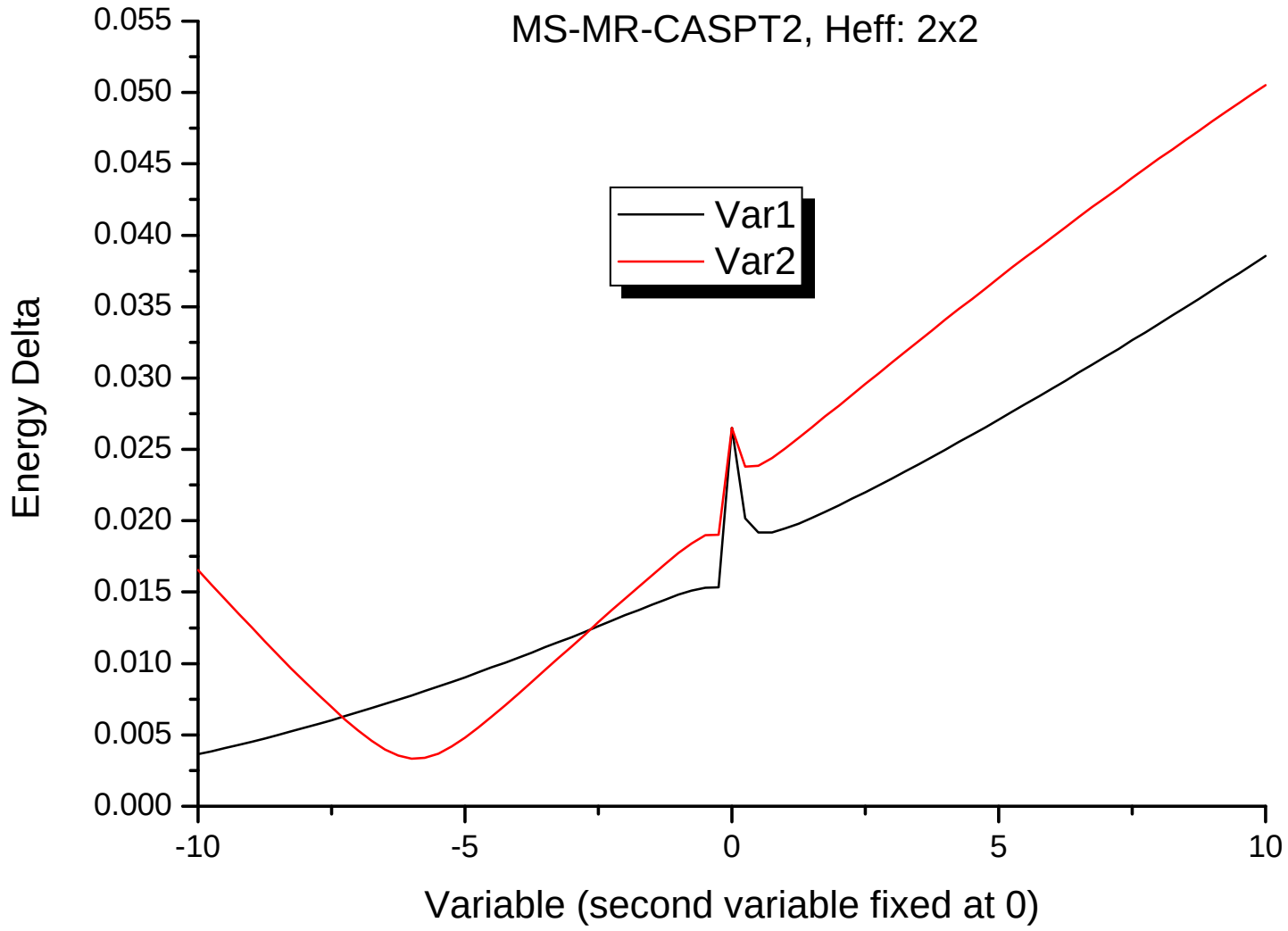

MCQDPT2, Heff: 12x12, ISA shift=0.02
Var1
Var2
10
8
6
4
2
0
-2
-4
-6
-8
-10
-10
-8
-6
-4
-2
0
2
4
6
8
10
0
7.813E-4
0.001563
0.002344
0.003125
0.003906
0.004687
0.005469
0.006250
0.007031
0.007812
0.008594
0.009375
0.01016
0.01094
0.01172
0.01250
0.01328
0.01406
0.01484
0.01563
0.01641
0.01719
0.01797
0.01875
0.01953
0.02031
0.02109
0.02188
0.02266
0.02344
0.02422
0.02500
0.02578
0.02656
0.02734
0.02813
0.02891
0.02969
0.03047
0.03125
0.03203
0.03281
0.03359
0.03438
0.03516
0.03594
0.03672
0.03750
0.03828
0.03906
0.03984
0.04062
0.04141
0.04219
0.04297
0.04375
0.04453
0.04531
0.04609
0.04687
0.04766
0.04844
0.04922
0.05000

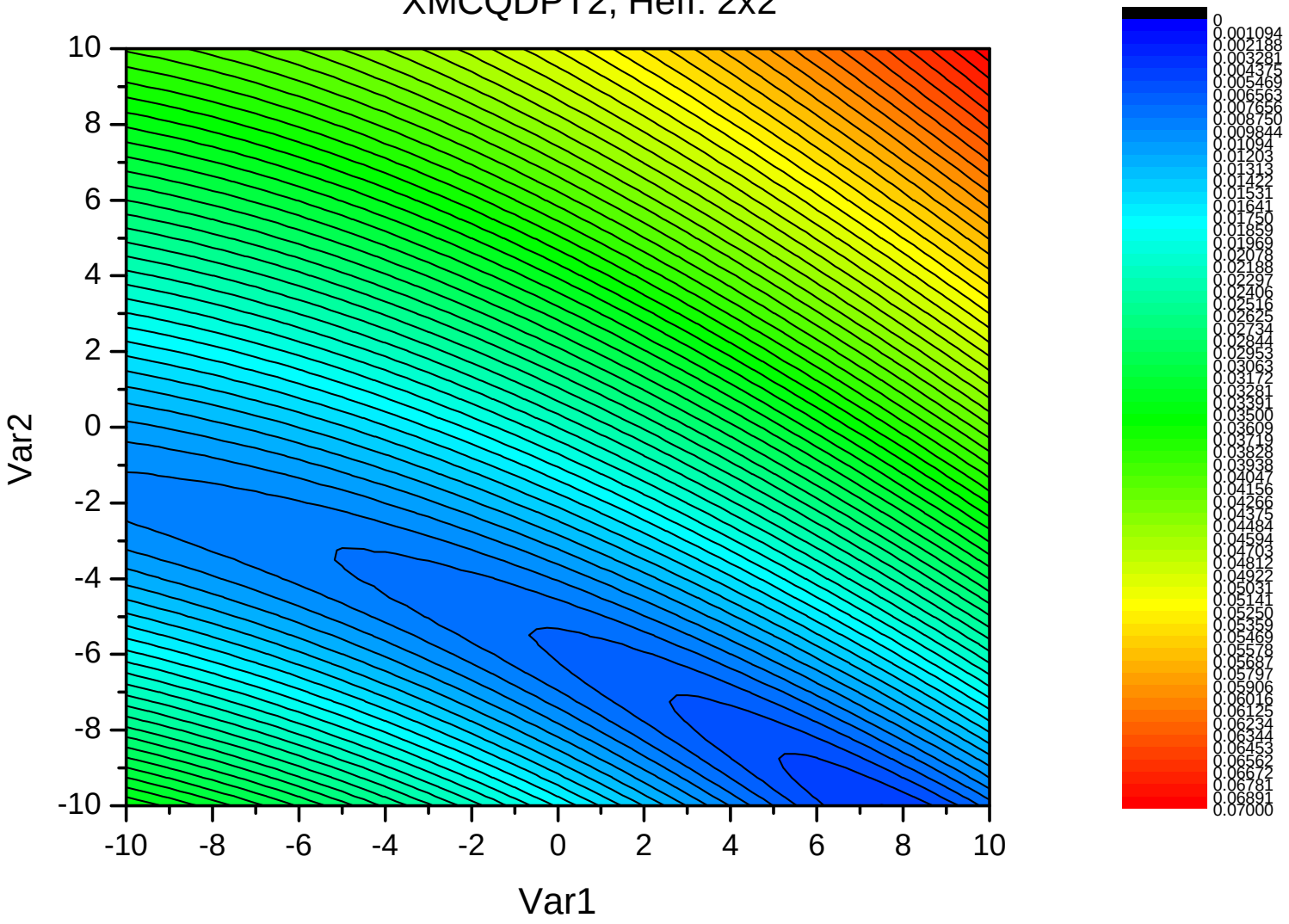

MCQDPT2, Heff: 12x12, ISA shift=0.02
Energy Delta
Variable (second variable fixed at 0)
Var1
Var2
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-10
-5
0
5
10

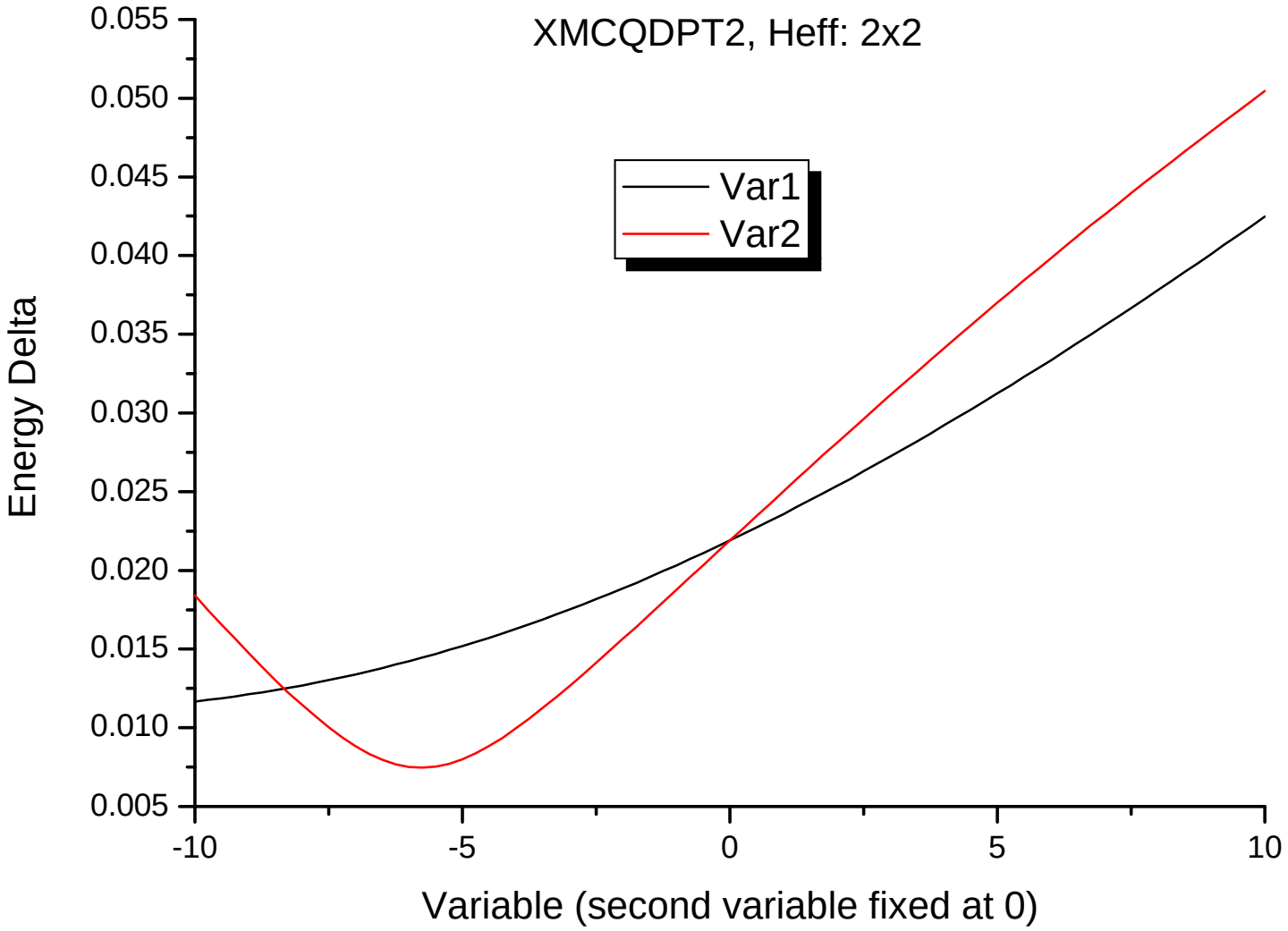

SS-SR-CASPT2, Heff: 2x2
Var2
Var1
10
8
6
4
2
0
-2
-4
-6
-8
-10
-10
-8
-6
-4
-2
0
2
4
6
8
10
0
0.001094
0.002188
0.003281
0.004375
0.005469
0.006563
0.007656
0.008750
0.009844
0.01094
0.01203
0.01313
0.01422
0.01531
0.01641
0.01750
0.01859
0.01969
0.02078
0.02188
0.02297
0.02406
0.02516
0.02625
0.02734
0.02844
0.02953
0.03063
0.03172
0.03281
0.03391
0.03500
0.03609
0.03719
0.03828
0.03938
0.04047
0.04156
0.04266
0.04375
0.04484
0.04594
0.04703
0.04812
0.04922
0.05031
0.05141
0.05250
0.05359
0.05469
0.05578
0.05687
0.05797
0.05906
0.06016
0.06125
0.06234
0.06344
0.06453
0.06562
0.06672
0.06781
0.06891
0.07000

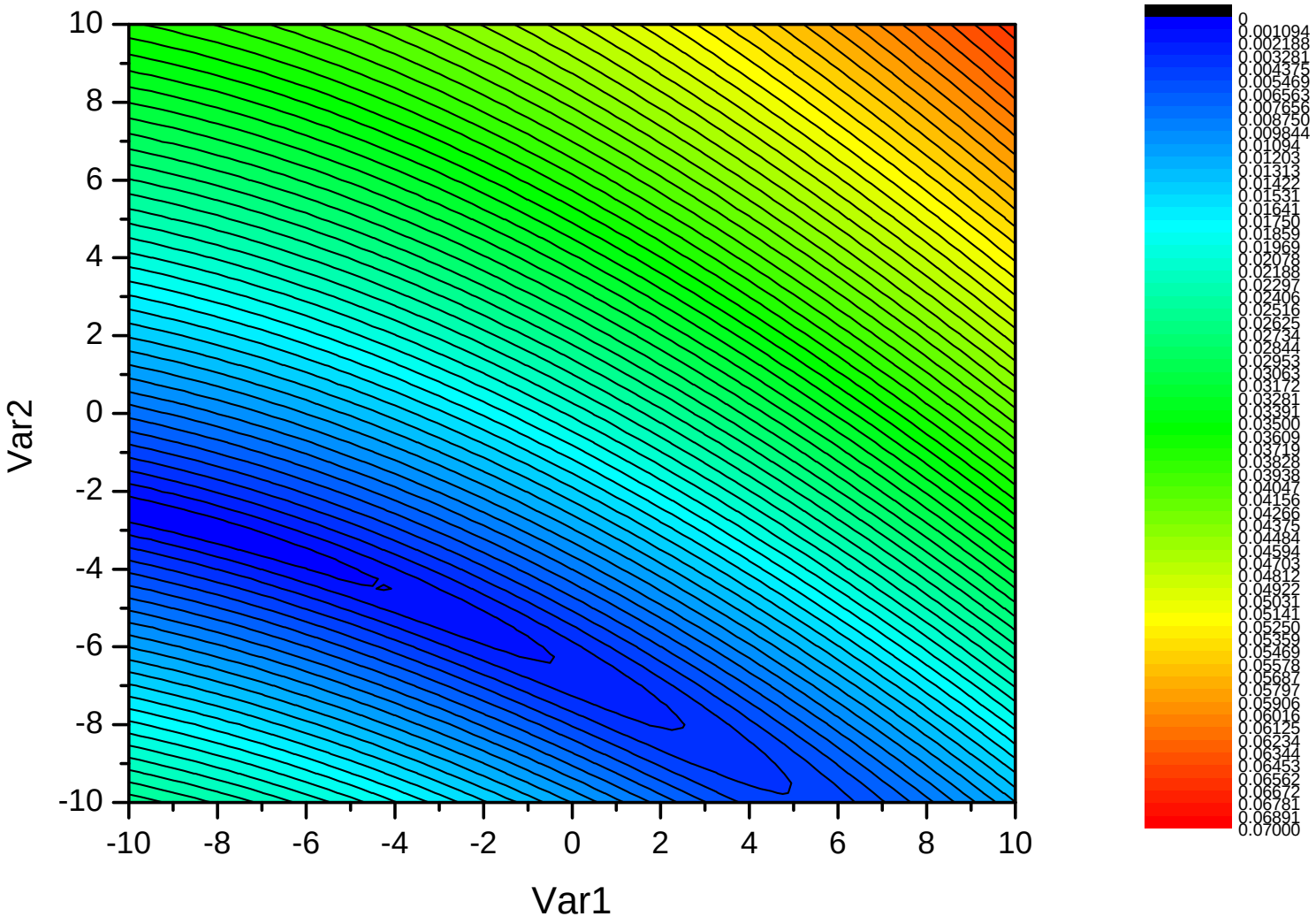

SS-SR-CASPT2, Heff: 2x2
Energy Delta
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-0.005
-10
-5
0
5
10
Variable (second variable fixed at 0)
Var1
Var2

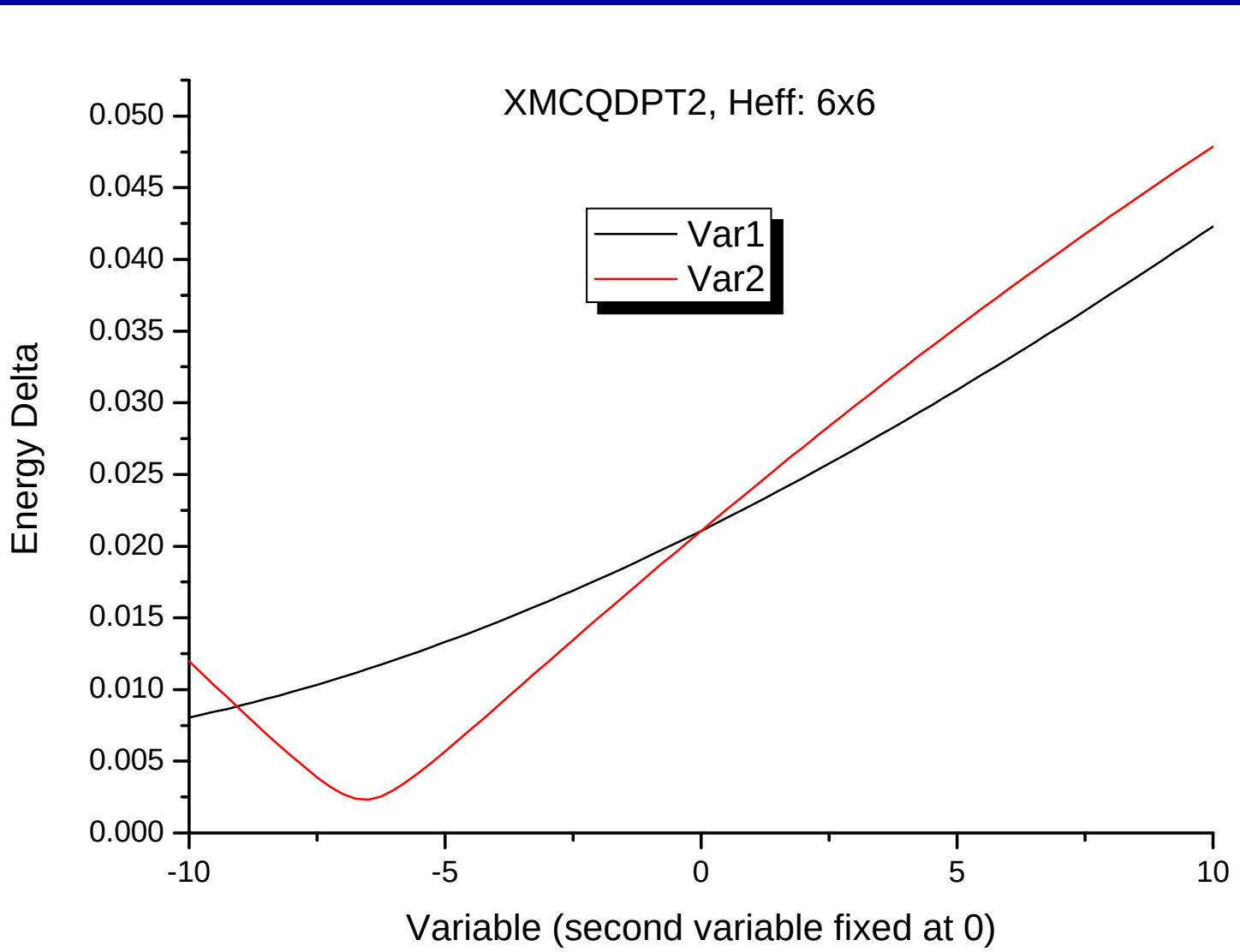

MS-MR-CASPT2, Heff: 2x2
Var2
Var1
10
8
6
4
2
0
-2
-4
-6
-8
-10
-10
-8
-6
-4
-2
0
2
4
6
8
10
0
0.001094
0.002188
0.003281
0.004375
0.005469
0.006563
0.007656
0.008750
0.009844
0.01094
0.01203
0.01313
0.01422
0.01531
0.01641
0.01750
0.01859
0.01969
0.02078
0.02188
0.02297
0.02406
0.02516
0.02625
0.02734
0.02844
0.02953
0.03063
0.03172
0.03281
0.03391
0.03500
0.03609
0.03719
0.03828
0.03938
0.04047
0.04156
0.04266
0.04375
0.04484
0.04594
0.04703
0.04812
0.04922
0.05031
0.05141
0.05250
0.05359
0.05469
0.05578
0.05687
0.05797
0.05906
0.06016
0.06125
0.06234
0.06344
0.06453
0.06562
0.06672
0.06781
0.06891
0.07000

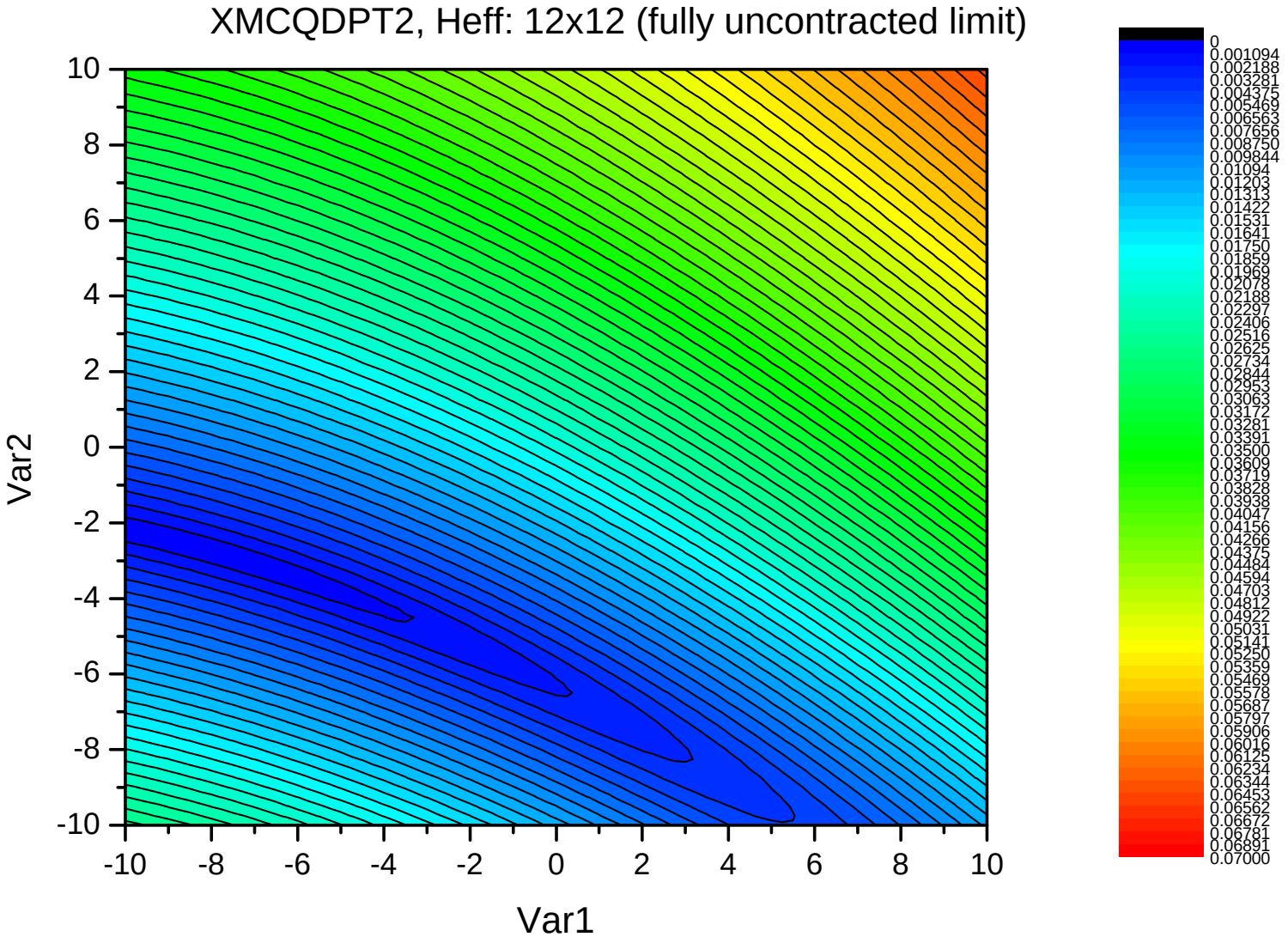

MS-MR-CASPT2, Heff: 2x2
Var1
Var2
Energy Delta
0.055
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-10
-5
0
5
10
Variable (second variable fixed at 0)

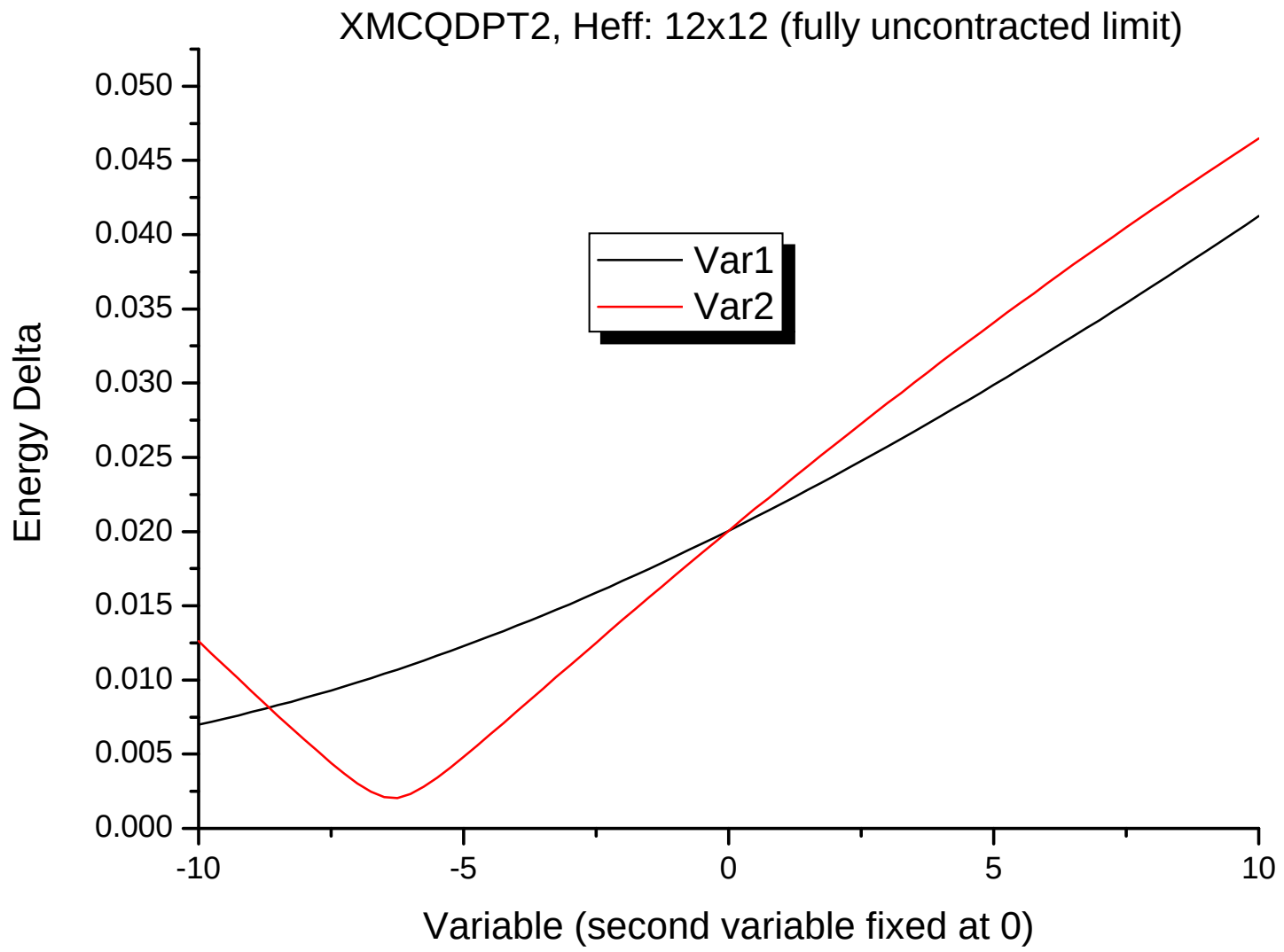

XMCQDPT2, Heff: 2x2
Var2
Var1
10
8
6
4
2
0
-2
-4
-6
-8
-10
-10
-8
-6
-4
-2
0
2
4
6
8
10
0
0.001094
0.002188
0.003281
0.004375
0.005469
0.006563
0.007656
0.008750
0.009844
0.01094
0.01203
0.01313
0.01422
0.01531
0.01641
0.01750
0.01859
0.01969
0.02078
0.02188
0.02297
0.02406
0.02516
0.02625
0.02734
0.02844
0.02953
0.03063
0.03172
0.03281
0.03391
0.03500
0.03609
0.03719
0.03828
0.03938
0.04047
0.04156
0.04266
0.04375
0.04484
0.04594
0.04703
0.04812
0.04922
0.05031
0.05141
0.05250
0.05359
0.05469
0.05578
0.05687
0.05797
0.05906
0.06016
0.06125
0.06234
0.06344
0.06453
0.06562
0.06672
0.06781
0.06891
0.07000


XMCQDPT2, Heff: 2x2
Var1
Var2
Energy Delta
0.055
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
-10
-5
0
5
10
Variable (second variable fixed at 0)


XMCQDPT2, Heff: 6x6
Var2
Var1
10
8
6
4
2
0
-2
-4
-6
-8
-10
-10
-8
-6
-4
-2
0
2
4
6
8
10
0
0.001094
0.002188
0.003281
0.004375
0.005469
0.006563
0.007656
0.008750
0.009844
0.01094
0.01203
0.01313
0.01422
0.01531
0.01641
0.01750
0.01859
0.01969
0.02078
0.02188
0.02297
0.02406
0.02516
0.02625
0.02734
0.02844
0.02953
0.03063
0.03172
0.03281
0.03391
0.03500
0.03609
0.03719
0.03828
0.03938
0.04047
0.04156
0.04266
0.04375
0.04484
0.04594
0.04703
0.04812
0.04922
0.05031
0.05141
0.05250
0.05359
0.05469
0.05578
0.05687
0.05797
0.05906
0.06016
0.06125
0.06234
0.06344
0.06453
0.06562
0.06672
0.06781
0.06891
0.07000


XMCQDPT2, Heff: 6x6
Var1
Var2
Energy Delta
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-10
-5
0
5
10
Variable (second variable fixed at 0)


XMCQDPT2, Heff: 12x12 (fully uncontracted limit)
Var2
Var1
10
8
6
4
2
0
-2
-4
-6
-8
-10
-10
-8
-6
-4
-2
0
2
4
6
8
10
0
0.001094
0.002188
0.003281
0.004375
0.005469
0.006563
0.007656
0.008750
0.009844
0.01094
0.01203
0.01313
0.01422
0.01531
0.01641
0.01750
0.01859
0.01969
0.02078
0.02188
0.02297
0.02406
0.02516
0.02625
0.02734
0.02844
0.02953
0.03063
0.03172
0.03281
0.03391
0.03500
0.03609
0.03719
0.03828
0.03938
0.04047
0.04156
0.04266
0.04375
0.04484
0.04594
0.04703
0.04812
0.04922
0.05031
0.05141
0.05250
0.05359
0.05469
0.05578
0.05687
0.05797
0.05906
0.06016
0.06125
0.06234
0.06344
0.06453
0.06562
0.06672
0.06781
0.06891
0.07000


XMCQDPT2, Heff: 12x12 (fully uncontracted limit)
Energy Delta
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-10
-5
0
5
10
Variable (second variable fixed at 0)
Var1
Var2

Conclusions

- The scan pictures are exactly as expected
  - Note problems exist not only in CI vicinity but near the entire avoided crossing manifold
- It is just not enough to formulate arbitrary multi-reference perturbation theory and then trivially extend it to multidimensional model space
- The real problem is the proper initial formulation that allows correct reformulation or extension for the case of multidimensional model space

Credits

- Sergei O. Adamson
- Vladimir I. Pupyshev
- Andrei V. Zaitsevskii

Thank you for your attention!