Stability Conditions for the Coupled Cluster Equations

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Abstract

The coupled cluster (CC) equations are studied from the point of view of the stability of their solution. The nonlinear nature of these equations may lead to undesired iteration properties including chaotic solutions. Iterations of various types (convergent, oscillatory, chaotic or divergent) are identified by the eigenvalues of the stability (Jacobi) matrix at the fixed points. Explicit (orbital) form of the stability matrix is obtained for the CCSD case, and the various iteration domains are investigated as a function of the control (damping) parameter of the CC iteration. The case of the BeH_2 molecule at various nuclear arrangements is chosen as a numerical example.

INTRODUCTION

Owing to the size and the nonlinear nature of the coupled cluster (CC) equations, one uses, almost exclusively, iterative procedures to locate their solutions representing the fixed points of the iteration scheme. To ensure and accelerate convergence, one often applies control parameters or extrapolation techniques such as DIIS[1]. In case of convergence problems it is also useful to consider rearranged forms of the CC equations that may lead to more suitable iteration pathways. Due to the nonlinear nature of the CC equations, the iterative solution may show oscillatory, chaotic or divergent iteration patterns which have to be avoided in real calculations. In this paper we report an *a posteriori* analysis of CC iterations. Having obtained a solution to the CC equations (at a given truncation level, e.g. singles and doubles, CCSD), the stability matrix of the iteration is constructed at the fixed point. The eigenvalues of this matrix determine the nature of the iteration scheme. The stability matrix is defined as the Jacobi matrix of the iterative form of the CCSD equations, for which explicit orbital-dependent formulae are presented. Since the stability matrix depends on the selected mode of the iteration as well as on the values of any iteration control parameter, iteration patterns of various kinds are determined as functions of these parameters.

As the stability matrices of the CCSD problem have at worst 8 orbital indices, the numerical applications of this study are limited to small systems and small basis sets. Clearly, due to its a posteriori character and the computer-intensive nature, the present approach cannot be used as a practical tool to improve convergence in CC theory. Still we hope that this analysis may lead to a better understanding of the behavior of the iterative CCSD solutions.

One of the authors of an early paper[2] in which the Jacobian of the CC equations appears, is Karol Jankowski, whom the present Volume is dedicated to. The authors of the present paper wish to congratulate him on the occasion of his birthday, and wish him good conditions to continue his outstanding work in many-body theory. The present authors have also realized, not for the first time, that innovative and nontrivial concepts about CC theory, like the Jacobian of the iteration, have been pioneered by Karol Jankowski. His contribution to coupled cluster theory is numerous and significant, we give here only an incomplete list of sample references[3–13].

STABILITY MATRIX OF ITERATIVE SCHEMES

The theory of stability matrices and Ljapunov exponents is well established and can be found in standard mathematical texts[14]. In a previous paper[15] we have applied this theory to study iteration characteristics of the Bloch equation[16, 17] and the idempotency-conserving density matrix iteration scheme[18, 19] which also deal with nonlinear equations. Here we apply it to the CCSD equations.

The theory can be summarized as follows. Consider a general iteration procedure for an m-component vector $\underline{x}$

$$x_i^{(n+1)} \;=\; f_i\left(\underline{x}^{(n)}\right), \qquad i = 1, 2, \ldots m. \tag{1}$$

Let vector $\underline{a}$ be a fixed point of this iteration, that is

$$a_i \;=\; f_i\left(\underline{a}\right), \qquad i = 1, 2, \ldots m, \tag{2}$$

and let us consider small deviations around this fixed point:

$$\underline{x}^{(n)} \;=\; \underline{a} + \underline{\xi}^{(n)}. \tag{3}$$

Substitution of this Ansatz into (1) gives

$$\begin{aligned} a_i + \xi_i^{(n+1)} \;&=\; f_i\left(\underline{a} + \underline{\xi}^{(n)}\right) \\ &=\; f_i(\underline{a}) + \sum_{j=1}^{m} \left.\frac{\partial f_i}{\partial x_j}\right|_{\underline{a}} \xi_j^{(n)} + \mathcal{O}(2) \end{aligned} \tag{4}$$

where we expanded the m-variable function f into Taylor series up to the first order. Using (2) with neglecting terms of $\mathcal{O}(\xi^2)$ leads us to

$$\begin{aligned} \xi_i^{(n+1)} \;&=\; \sum_{j=1}^{m} \left.\frac{\partial f_i}{\partial x_j}\right|_{\underline{a}} \xi_j^{(n)} \\ &=\; \sum_{j=1}^{m} J_{ij}\; \xi_j^{(n)} \end{aligned} \tag{5}$$

with the definition of the Jacobian at point $\underline{a}$

$$J_{ij} = \left.\frac{\partial f_i}{\partial x_j}\right|_{\underline{a}} \tag{6}$$

Matrix $\mathbf{J}$ is also called the stability matrix. Solution of (5) can be looked for in the form

$$\underline{\xi}^{(n)} \;=\; e^{\lambda n} \underline{\xi}^{(0)} \tag{7}$$

which, after substitution into (5) gives us the eigenvalue equation

$$\mathbf{J}\underset{\sim}{\xi}^{(0)} = \mu\underset{\sim}{\xi}^{(0)} \tag{8}$$

with the notation $\mu = e^{\lambda}$. We conclude that the modes $\underset{\sim}{\xi}^{(0)}$ are eigenvectors of the stability matrix while the logarithm of the eigenvalues give parameters λ which are related to the Ljapunov exponents of the problem. (The more common 'dynamical' definition of Ljapunov exponents works with the limit $n \to \infty$; we adopt here a 'static' definition based on the converged solution $\underline{a}$.)

Analysis of convergence properties of the iteration process (1) can be based on the value of the Ljapunov exponents λ, or on their exponentials μ. In the simplest case all μ-s are positive thus all λ-s are real. Then, the procedure converges only if all Ljapunov exponents are negative, that is, if all eigenvalues of the stability matrix satisfy the condition

$$0 < \mu < 1.$$

When at least one of the exponents becomes positive, i.e., $\mu > 1$, the iteration will diverge along the corresponding trajectory.

It may turn out that one or more eigenvalues of the Ljapunov matrix are negative. In this case the corresponding Ljapunov exponents become complex: $\lambda = \lambda_1 + i\lambda_2$. To have a real μ, we require that

$$\text{Im } e^{\lambda} = \sin\lambda_2 \; e^{\lambda_1} = 0,$$

which is satisfied by $\lambda_2 = k\pi$ with any integer k. However, $\mu = \cos\lambda_2 \; e^{\lambda_1}$ is negative only for odd k values, thus we may choose $k = 1$. Therefore, the Ljapunov exponent for real, negative μ can be written as

$$\lambda = \log|\mu| + i\pi$$

leading to the convergence condition

$$\text{Re } \lambda = \log|\mu| < 0,$$

which requires

$$|\mu| < 1. \tag{9}$$

The iterations in this case are not monotonic, but exhibit oscillatory convergence:

$$\underset{\sim}{\xi}^{(n)} \;=\; e^{\lambda n}\underset{\sim}{\xi}^{(0)} \;=\; e^{i\pi n}e^{n\log|\mu|}. \tag{10}$$

As the Jacobian is not symmetric, its eigenvalues μ may also become complex. Let us have $\mu = a + ib$. Then, from $e^{\lambda} = a + ib$ we get

$$\left.\begin{aligned} e^{\lambda_1}\cos\lambda_2 &= a \\ e^{\lambda_1}\sin\lambda_2 &= b \end{aligned}\right\}$$

resulting

$$e^{\lambda_1} = \sqrt{a^2 + b^2} \;=\; |\mu|,$$

which leads again to (9).

In summarizing, the convergence condition $|\mu| < 1$ can be used in all cases. Upon violation of this condition, the procedure usually diverges, but on the borderline of convergence and divergence, nonlinear systems may also exhibit chaotic iterations[20]. This is manifested in irregular and stochastic iteration patterns, as will be illustrated below for the CCSD equations.

THE CC EQUATIONS

Using the CC Ansatz $\Psi = \mathrm{e}^{T}\Phi$, we write the Schrödinger equation as

$$\mathrm{e}^{-T} H\, \mathrm{e}^{T}\Phi \;=\; E\Phi \tag{11}$$

where Φ is the reference state, typically the Hartree-Fock solution. The cluster operator for k-fold excitations T_k is formally written as

$$T_k = \frac{1}{k!}\sum_{\mu} {}^{k}t_{\mu}\hat{E}_{\mu}, \tag{12}$$

where ${}^{k}t_{\mu}$ are the cluster amplitudes to be determined, and $\hat{E}_{\mu}$-s are excitation operators which, for closed shell systems, can be written as

$$\hat{E}_{\mu} = E_u^{\beta} = \sum_{\sigma} a^{\dagger}_{\beta,\sigma} a_{u,\sigma} \tag{13}$$

for single and

$$\hat{E}_{\mu} = E_{uv}^{\beta\gamma} = E_u^{\beta} E_v^{\gamma} \tag{14}$$

for double excitations. From (11), the CC equations for the amplitudes emerge as

$$F_{\nu} \;=\; \langle\Phi|\hat{E}^{\dagger}_{\nu}\, \mathrm{e}^{-T} H\, \mathrm{e}^{T}|\Phi\rangle \;=\; 0. \tag{15}$$

Substituting the Hamiltonian, the above forms of the excitation operators and evaluating the matrix elements, this equation can be reduced to its orbital form ${}^1F_u^\beta = 0$ and ${}^2F_{uv}^{\beta\gamma} = 0$. The resulting formulae are collected in Appendix I. The ${}^1t$ and ${}^2t$ equations detailed there, (22) and (23), are both of the form

$$F(\underline{t}) = 0,$$

and there are several ways to recast them into an iterative form

$$t = f(t).$$

We have considered two possible rearrangements I and II, which differ only in the choice of the denominator:

I.

$$t_u^\beta \;=\; t_u^\beta \;-\; \frac{{}^1F_u^\beta}{f_\beta^\beta - f_u^u - \eta} \tag{16}$$

$$t_{uv}^{\beta\gamma} \;= t_{uv}^{\beta\gamma} \;-\; \frac{{}^2F_{uv}^{\beta\gamma}}{f_\beta^\beta + f_\gamma^\gamma - f_u^u - f_v^v - 2\eta} \tag{17}$$

II.

$$t_u^\beta \;=\; t_u^\beta \;-\; \frac{{}^1F_u^\beta}{h_\beta^\beta - h_u^u - \eta} \tag{18}$$

$$t_{uv}^{\beta\gamma} \;= t_{uv}^{\beta\gamma} \;-\; \frac{{}^2F_{uv}^{\beta\gamma}}{h_\beta^\beta + h_\gamma^\gamma - h_u^u - h_v^v - 2\eta} \tag{19}$$

for the ${}^1t$ and ${}^2t$ amplitudes, respectively. Form I uses Møller-Plesset type denominators, while form II uses the diagonals of intermediates h introduced in (24). Parameter η is introduced merely to control the iteration by damping or accelerating the sequence[1].

THE STABILITY MATRIX OF THE CCSD EQUATION

The stability matrix of the CCSD problem can be obtained by taking the derivatives of the iterative equations with respect to the independent parameters. In our case, the latter

[1] Note that negative(positive) values for η will damp(accelerate) the iteration by increasing(decreasing) the denominators, respectively.

are represented by the cluster amplitudes ${}^1t_\mu$ and ${}^2t_\mu$. Since the CCSD equations for these amplitudes are coupled, the stability matrix will be composed of four blocks which we denote by ${}^{11}\mathbf{J}$, ${}^{12}\mathbf{J}$, ${}^{21}\mathbf{J}$, ${}^{22}\mathbf{J}$, respectively, where ${}^{mn}\mathbf{J}$ stands for the derivatives of the m-equations with respect to the ${}^nt$ amplitudes. The explicit results for these derivatives are listed in Appendix II. They define the four blocks of the stability matrix as

$$\begin{aligned}
\mathbf{J}^{11}_{u\beta,l\lambda} &= \delta_{ul}\delta_{\beta\lambda} - \frac{\frac{\partial\ {}^1F_{u\beta}}{\partial t^\lambda_l}}{f^\beta_\beta - f^u_u - \eta} \\
\mathbf{J}^{12}_{u\beta,lm\lambda\mu} &= -\frac{\frac{\partial\ {}^1F_{u\beta}}{\partial t^{\lambda\mu}_{lm}}}{f^\beta_\beta - f^u_u - \eta} \\
\mathbf{J}^{21}_{uv\beta\gamma,l\lambda} &= -\frac{\frac{\partial\ {}^2F_{uv\beta\gamma}}{\partial t^\lambda_l}}{f^\beta_\beta + f^\gamma_\gamma - f^u_u - f^v_v - 2\eta} \\
\mathbf{J}^{22}_{uv\beta\gamma,lm\lambda\mu} &= \delta_{ul}\delta_{vm}\delta_{\beta\lambda}\delta_{\gamma\mu} - \frac{\frac{\partial\ {}^2F_{uv\beta\gamma}}{\partial t^{\lambda\mu}_{lm}}}{f^\beta_\beta + f^\gamma_\gamma - f^u_u - f^v_v - 2\eta}
\end{aligned} \tag{20}$$

in the iteration scheme I, cf. Eqs.(16) and (17) . If scheme II is used, the denominators have to be changed accordingly. Though in case II the denominators depend on the cluster amplitudes, their derivatives do not enter the stability matrix since they are multiplied by ${}^1F$ or ${}^2F$ which are zero at the CCSD solutions.

Though our numerical experience showed that denominators of type II are often favorable, in the calculations presented below we used the Møller-Plesset type denominators I. This was sufficient to distinguish between convergent and chaotic cases, the transition between which, approximately speaking, appear merely at a different value of control parameter η.

The above equations show that the stability matrix $\mathbf{J}$ is in close connection to the Jacobi matrix $\mathbf{J}^0$ of the CCSD equations (we are grateful to one of our Referees for calling our attention to this). The symbolic structure Eqs. (20) is

$$J_{ab} = \delta_{ab} - \frac{J^0_{ab}}{\Delta_{ab} - \eta} \tag{21}$$

where Δ_{ab} stands for the energy denominator in the iterative equations corresponding to the $a \to b$ excitation. Using Eq.(15), we obtain

$$J^o_{ab} = \frac{\partial F_a}{\partial t_b} = \langle\Phi|\hat{E}^\dagger_a\ \mathrm{e}^{-T}[H, \hat{E}_b]\ \mathrm{e}^T|\Phi\rangle = 0$$

The eigenvalue equation of this matrix is known as the EOM-CC equation for excitation energies[21–25], which, via Eq. (21), reveals an interesting connection between excitation

energies (eigenvalues of $\mathbf{J}^0$) and the Ljapunov exponents (eigenvalues of $\mathbf{J}$). Note however that matrices $\mathbf{J}$ and $\mathbf{J}^0$ do not commute in general.

It is important to emphasize the following two features of the above analysis:

- It is valid only if no more complicated extrapolation techniques like DIIS are used to govern the iteration. While the DIIS method is known to be highly efficient in accelerating convergence, it does not change the *nature* of the fixed point. If, by a wrongly chosen value for η, the fixed point of the iteration is made repellent, neither DIIS nor any other extrapolation technique can be expected to ensure convergence.

- The Ljapunov exponents as defined above characterize the nature of the fixed point, rather than the process of the iteration. We always assume the the initial amplitudes lie in the sufficient proximity of the fixed point.

RESULTS

The system on which some demonstrative calculations are presented is the BeH_2 molecule at various geometrical arrangements (see Fig. 1). The standard split-shell polarized basis set 6-31G** was used.

The first point we investigate is the dependence of the number of iteration steps (to achieve an accuracy of 10^{-7} a.u. in energy) on the denominator shift value. Two examples are shown on Figs. 2a and 2b, for geometry points A and F, respectively. A common feature is that as we increase η from a negative value to a positive one (cf. the footnote 1), a significant reduction of the step number can be observed, up to a certain point where it starts to increase suddenly. This outburst increase is very sharp for case F. The turning point is at $\eta = 0.2$ for case A and $\eta = 0.12$ for case F. Damping factors larger than this value produce a divergent CC iteration. The conclusion from this is twofold: (i) denominator shifts affect the convergence drastically, and a suitable (slightly positive) shift value can be quite effective, even in the absence of any more sophisticated techniques like DIIS; (ii) it is not easy to find the most appropriate value a priori, because of the danger of divergence when approaching the optimal value.

The next question is whether the stability analysis, i.e., eigenvalues of the stability matrix, can explain the situation. The answer is affirmative: in Fig. 3 one may see the most critical

exponents as a variation of the control parameter η. For geometry A, the domain $\eta < 0.3$ is convergent, all exponents being negative. At around $\eta = 0.3$ the largest exponent turns positive spoiling the convergence of the CC iteration. In Figs. 3.b. and 3.c. we plotted the two largest exponents to show their crossings at around 0.15 (geometry F) and 0.2 (geometry I), above which the CC iterations diverge. It is interesting that in these cases not the first, only slightly negative exponent turns positive, but the second one, coming up suddenly from the deep part of the Ljapunov spectrum.

Analyses at other geometries of BeH_2, not presented here, led to conclusions similar to the cases shown in Figs, 2. and 3. It is interesting to note that optimal denominator shift is around 0.2, irrespective of the geometry.

The next issue of investigation is iteration with an inappropriate value for η, i.e. a value at which positive Ljapunov exponents arise. First, in Fig. 4, we present the case of geometry B with $\eta = 0.28$, a value slightly above the convergence limit, where there is just one small positive exponent. In spite of this, the first few iterations give the impression of a convergent, though oscillatory iteration (Fig. 4.a.). An extrapolated value gives a good estimation of the CCSD correlation energy. However, continuing the iterations the amplitude of oscillation increases (Fig. 4.b.), and finally a typical bifurcation pattern is developed (Fig. 4.c.). The zoom into one of the branches shows that after some chaotic steps the bifurcated values get stabilized at a completely unphysical number. Note that this value is not a fixed point, thus does not correspond to one of the unphysical solutions of the CC equations, investigated previously by Karol Jankowski and coworkers[3].

As a final example, we performed a calculation at geometry A, with $\eta = 0.325$, a number which is significantly higher than the optimal value 0.2. With this parameter the CCSD iteration did not converge, but showed a fully chaotic pattern. Plotting these energies does not make any sense, since there is not any structure in this figure. However, one may present two different types of figures which illustrate the chaotic behavior of the iteration. One is to plot the iterated quantities (the CC amplitudes in our case) against each other. This would be analogous to a configuration space trajectory in a dynamical system. The other, in analogy to a phase space trajectory, can be constructed by plotting the variation of an amplitude (e.g., its difference in consecutive iterations) as a function of the value of the amplitude. Such diagrams are presented in Fig. 5. for a calculation when we followed the chaotic iterations up to 186 steps. The 'configuration space' cross section (Fig. 5.a.) was

obtained by plotting the HOMO–LUMO double excitation amplitude with respect to the HOMO–next-LUMO amplitude, while the variation of the HOMO–LUMO amplitude was used to construct Fig. 5.b. Note that in a non-chaotic, convergent situation, after a few transient steps (before the convergence is reached), the configuration space trajectory would be represented by a single point in the diagram corresponding to the converged amplitude values. Similarly, the phase space diagram would show a single point with its y coordinate zero. In contrast, as Fig. 5. shows, the chaotic case is well illustrated with densely populated, widespread trajectories.

The above numerical examples seem to suggest that a sufficiently large damping always ensures convergence. We cannot provide a formal proof for this statement. Even if one finds a large enough value for η so that all Ljapunov exponents are negative, this means only that the fixed point of the iteration is attractive. Starting from a set of amplitudes far from the converged ones, the iteration may diverge or may converge to another fixed point. However, we have not yet treated any cases in which convergence was impossible to achieve. (Note that a convergent iteration does not mean that one had reached the desired state.)

In concluding, the nature of the fixed points of the CCSD equations can be analysed by finding the eigenvalues of the stability matrix which have the largest absolute value. The logarithm of the modulus of the eigenvalue (admitting complex solutions) can be regarded as the Ljapunov exponent of the problem which should be negative to ensure convergence. The nature of the fixed points can be effectively controlled by denominator shifts which may either damp or accelerate the iteration.

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APPENDICES

Appendix I: CC equations and intermediates

We adopt the notation convention and the intermediates as introduced by Scuseria et al.[26], and write

$$\begin{aligned} {}^1F_u^\beta &= f_u^\beta - 2f_a^i t_i^\beta t_u^a + h_a^\beta t_u^a - h_u^i t_i^\beta + h_a^i \left(2t_{iu}^{a\beta} - t_{ui}^{a\beta} + t_u^a t_i^\beta\right) + \\ &+ \left(2v_{au}^{i\beta} - v_{ua}^{i\beta}\right) t_i^a + \left(2v_{ab}^{i\beta} - v_{ba}^{i\beta}\right) \tau_{iu}^{ab} - \left(2v_{au}^{ij} - v_{au}^{ji}\right) \tau_{ij}^{a\beta} = 0, \end{aligned} \tag{22}$$

for the single substitution ${}^1t$ amplitudes, while for the doubles' ${}^2t$ amplitudes one has

$$\begin{aligned} {}^2F_{uv}^{\beta\gamma} &= v_{uv}^{\beta\gamma} + a_{uv}^{ij}\tau_{ij}^{\beta\gamma} + b_{ab}^{\beta\gamma}\tau_{uv}^{ab} + \\ +P_{uv}^{\beta\gamma}\Big[g_a^\beta t_{uv}^{a\gamma} &- g_u^i t_{iv}^{\beta\gamma} + \left(v_{ua}^{\beta\gamma} - v_{ua}^{i\gamma}t_i^\beta\right) t_v^a - \left(v_{uv}^{\beta i} + v_{ua}^{\beta i}t_v^a\right) t_i^\gamma + \\ +\frac{1}{2}\Big(2j_{ua}^{\beta i} &- k_{ua}^{i\beta}\Big)\left(2t_{iv}^{a\gamma} - t_{iv}^{\gamma a}\right) - \frac{1}{2}k_{ua}^{i\beta}t_{iv}^{\gamma a} - k_{ua}^{i\gamma}t_{iv}^{\beta a}\Big] = 0. \end{aligned} \tag{23}$$

The intermediates and other shorthands collected from [26] are listed below for completeness:

$$\begin{aligned} h_u^i &= f_u^i + \left(2v_{ab}^{ij} - v_{ba}^{ij}\right)\tau_{uj}^{ab} \\ h_a^\beta &= f_a^\beta - \left(2v_{ab}^{ij} - v_{ab}^{ji}\right)\tau_{ij}^{\beta b} \\ h_a^i &= f_u^i + \left(2v_{ab}^{ij} - v_{ba}^{ij}\right) t_j^b \\ \tau_{ij}^{ab} &= t_{ij}^{ab} + t_i^a t_j^b \\ g_u^i &= h_u^i + f_a^i t_u^a + \left(2v_{ua}^{ij} - v_{ua}^{ji}\right) t_j^a \\ g_a^\beta &= h_a^\beta - f_a^i t_i^\beta + \left(2v_{ab}^{\beta i} - v_{ba}^{\beta i}\right) t_i^b \\ a_{uv}^{ij} &= v_{uv}^{ij} + v_{ua}^{ij}t_v^a + v_{av}^{ij}t_u^a + v_{ab}^{ij}\tau_{uv}^{ab} \\ b_{ab}^{\beta\gamma} &= v_{ab}^{\beta\gamma} - v_{ab}^{\beta i}t_i^\gamma - v_{ab}^{i\gamma}t_i^\beta \\ j_{ua}^{\beta i} &= v_{ua}^{\beta i} - v_{ua}^{ji}t_j^\beta + v_{ba}^{\beta i}t_u^b - v_{ab}^{ij}T_{uj}^{b\beta} + \frac{1}{2}\left(2v_{ab}^{ij} - v_{ba}^{ij}\right)t_{uj}^{\beta b} \\ k_{ua}^{i\beta} &= v_{ua}^{i\beta} - v_{ua}^{ij}t_j^\beta + v_{ba}^{i\beta}t_u^b - v_{ba}^{ij}T_{uj}^{b\beta} \\ T_{ij}^{ab} &= \frac{1}{2}t_{ij}^{ab} + t_i^a t_j^b \\ P_{uv}^{\beta\gamma}[...]_{uv}^{\beta\gamma} &= [...]_{uv}^{\beta\gamma} + [...]_{vu}^{\gamma\beta}. \end{aligned} \tag{24}$$

Further, $v_{rs}^{pq} = [pq|rs]$ are two-electron integrals in the [12|12] convention and f is the Fockian.

Appendix II: Intermediate derivatives

Taking the derivatives of Eqs. (22) and (23), we obtain:

$$\begin{aligned}\frac{\partial\ {}^1F_{u\beta}}{\partial t_l^\lambda} &= -2\left(f_\lambda^i t_i^\beta \delta_{ul} - t_u^a f_a^l \delta_{\beta\lambda}\right) + \frac{\partial h_a^\beta}{\partial t_l^\lambda} t_u^a + h_\lambda^\beta \delta_{ul} - \frac{\partial h_u^i}{\partial t_l^\lambda} t_i^\beta \\ &- h_u^l \delta_{\beta\lambda} + \frac{\partial h_a^i}{\partial t_l^\lambda}\left(2t_{iu}^{a\beta} - t_{ui}^{a\beta} + t_u^a t_i^\beta\right)\left(+h_a^l t_u^a \delta_{\beta\lambda} + t_i^\beta \delta_{ul} h_\lambda^i\right) \\ &+ \left(2v_{\lambda u}^{l\beta} - v_{u\lambda}^{l\beta}\right) + \left(2v_{ab}^{i\beta} - v_{ba}^{i\beta}\right)\frac{\partial \tau_{iu}^{ab}}{\partial t_l^\lambda} - \left(2v_{au}^{ij} - v_{au}^{ji}\right)\frac{\partial \tau_{ij}^{a\beta}}{t_l^\lambda},\end{aligned} \tag{25}$$

$$\begin{aligned}\frac{\partial\ {}^1F_{u\beta}}{\partial t_{lm}^{\lambda\mu}} &= \frac{\partial h_a^\beta}{\partial t_{lm}^{\lambda\mu}} t_u^a - \frac{\partial h_u^i}{\partial t_{lm}^{\lambda\mu}} t_i^\beta + \left(2h_\lambda^l \delta_{um}\delta_{\beta\mu} - \delta_{ul} h_\lambda^m \delta_{\beta\mu}\right) \\ &+ \left(2v_{ab}^{i\beta} - v_{ba}^{i\beta}\right)\frac{\partial \tau_{iu}^{ab}}{\partial t_{lm}^{\lambda\mu}} - \left(2v_{au}^{ij} - v_{au}^{ji}\right)\frac{\partial \tau_{ij}^{a\beta}}{\partial t_{lm}^{\lambda\mu}}\end{aligned} \tag{26}$$

and

$$\begin{aligned}\frac{\partial\ {}^2F_{uv\beta\gamma}}{\partial t_l^\lambda} &= \frac{\partial a_{uv}^{ij}}{\partial t_l^\lambda}\tau_{ij}^{\beta\gamma} + a_{uv}^{ij}\frac{\partial \tau_{ij}^{\beta\gamma}}{\partial t_l^\lambda} + \frac{\partial b_{ab}^{\beta\gamma}}{\partial t_l^\lambda}\tau_{uv}^{ab} + b_{ab}^{\beta\gamma}\frac{\tau_{uv}^{ab}}{\partial t_l^\lambda} \\ &+ P_{uv}^{\beta\gamma}\left[\frac{\partial g_a^\beta}{\partial t_l^\lambda} t_{uv}^{a\gamma} - \frac{\partial g_u^i}{\partial t_l^\lambda} t_{iv}^{\beta\gamma} + \left(v_{u\lambda}^{\beta\gamma} - v_{u\lambda}^{i\gamma} t_i^\beta\right)\delta_{vl} - v_{ua}^{l\gamma}\delta_{\beta\lambda}\right. \\ &- \left(v_{uv}^{\beta l} + v_{ua}^{\beta l} t_v^a\right)\delta_{\gamma\lambda} - v_{u\lambda}^{\beta i} t_i^\gamma \delta_{vl} \\ &+ \left.\left(\frac{\partial j_{ua}^{\beta i}}{\partial t_l^\lambda} - \frac{1}{2}\frac{\partial k_{ua}^{i\beta}}{\partial t_l^\lambda}\right)(2t_{iv}^{a\gamma} - t_{iv}^{\gamma a}) - \frac{1}{2}\frac{\partial k_{ua}^{i\beta}}{\partial t_l^\lambda} t_{iv}^{\gamma a} - \frac{\partial k_{ua}^{i\gamma}}{\partial t_l^\lambda} t_{iv}^{\beta a}\right]\end{aligned} \tag{27}$$

$$\begin{aligned}\frac{\partial\ {}^2F_{uv\beta\gamma}}{\partial t_{lm}^{\lambda\mu}} &= \frac{\partial a_{uv}^{ij}}{\partial t_{lm}^{\lambda\mu}}\tau_{ij}^{\beta\gamma} + a_{uv}^{ij}\frac{\partial \tau_{ij}^{\beta\gamma}}{\partial t_{lm}^{\lambda\mu}} + b_{ab}^{\beta\gamma}\frac{\partial \tau_{uv}^{ab}}{\partial t_{lm}^{\lambda\mu}} \\ &+ P_{uv}^{\beta\gamma}\left[\frac{\partial g_a^\beta}{\partial t_{lm}^{\lambda\mu}} t_{uv}^{a\gamma} + g_\lambda^\beta \delta_{ul}\delta_{vm}\delta_{\gamma\mu} - \frac{\partial g_u^i}{\partial t_{lm}^{\lambda\mu}} t_{iv}^{\beta\gamma} - g_u^l \delta_{vm}\delta_{\beta\lambda}\delta_{\gamma\mu}\right. \\ &+ \frac{1}{2}\left(2\frac{\partial j_{ua}^{\beta i}}{\partial t_{lm}^{\lambda\mu}} - \frac{\partial k_{ua}^{i\beta}}{\partial t_{lm}^{\lambda\mu}}\right)(2t_{iv}^{a\gamma} - t_{iv}^{\gamma a}) + \frac{1}{2}\left(2j_{ua}^{\beta l} - k_{ua}^{l\beta}\right)\delta_{vm}\left(2\delta_{a\lambda}\delta_{\gamma\mu} - \delta_{\gamma\lambda}\delta_{a\mu}\right) \\ &- \left.\frac{1}{2}\frac{\partial k_{ua}^{i\beta}}{\partial t_{lm}^{\lambda\mu}} t_{iv}^{\gamma a} - \frac{1}{2}k_{u\mu}^{l\beta}\delta_{vm}\delta_{\gamma\lambda} - \frac{\partial k_{ua}^{i\gamma}}{\partial t_{lm}^{\lambda\mu}} t_{iv}^{\beta a} - k_{u\mu}^{l\gamma}\delta_{vm}\delta_{\beta\lambda}\right]\end{aligned} \tag{28}$$

with the intermediate derivatives listed as

$$\frac{\partial h_u^i}{\partial t_l^\lambda} = \left(2v_{ab}^{ij} - v_{ba}^{ij}\right)\frac{\partial \tau_{uj}^{ab}}{\partial t_l^\lambda}$$

$$
\begin{aligned}
\frac{\partial h_u^i}{\partial t_{lm}^{\lambda\mu}} &= (2v_{ab}^{ij} - v_{ba}^{ij})\frac{\partial \tau_{uj}^{ab}}{\partial t_{lm}^{\lambda\mu}} \\
\frac{\partial h_a^\beta}{\partial t_l^\lambda} &= -\left(2v_{ab}^{ij} - v_{ab}^{ji}\right)\frac{\partial \tau_{ij}^{\beta b}}{\partial t_l^\lambda} \\
\frac{\partial h_a^\beta}{\partial t_{lm}^{\lambda\mu}} &= -\left(2v_{ab}^{ij} - v_{ab}^{ji}\right)\frac{\partial \tau_{ij}^{\beta b}}{\partial t_{lm}^{\lambda\mu}} \\
\frac{\partial h_a^i}{\partial t_l^\lambda} &= \left(2v_{a\lambda}^{ij} - v_{\lambda a}^{ij}\right)\delta_{jl} \\
\frac{\partial \tau_{ij}^{ab}}{\partial t_l^\lambda} &= t_i^a\delta_{jl}\delta_{b\lambda} + t_j^b\delta_{il}\delta_{a\lambda} \\
\frac{\partial \tau_{ij}^{ab}}{\partial t_{lm}^{\lambda\mu}} &= \delta_{il}\delta_{jm}\delta_{a\lambda}\delta_{b\mu} \\
\frac{\partial g_u^i}{\partial t_l^\lambda} &= \frac{\partial h_u^i}{\partial t_l^\lambda} + f_a^\lambda\delta_{ul} + \left(2v_{u\lambda}^{il} - v_{u\lambda}^{li}\right) \\
\frac{\partial g_u^i}{\partial t_{lm}^{\lambda\mu}} &= \frac{\partial h_u^i}{\partial t_{lm}^{\lambda\mu}} \\
\frac{\partial g_a^\beta}{\partial t_l^\lambda} &= \frac{\partial h_a^\beta}{\partial t_l^\lambda} - f_a^l\delta_{\beta\lambda} + \left(2v_{a\lambda}^{\beta l} - v_{\lambda a}^{\beta l}\right) \\
\frac{\partial g_a^\beta}{\partial t_{lm}^{\lambda\mu}} &= \frac{\partial h_a^\beta}{\partial t_{lm}^{\lambda\mu}} \\
\frac{\partial a_{uv}^{ij}}{\partial t_l^\lambda} &= v_{u\lambda}^{ij}\delta_{vl} + v_{\lambda v}^{ij}\delta_{ul} + v_{ab}^{ij}\frac{\partial \tau_{uv}^{ab}}{\partial t_l^\lambda} \\
\frac{\partial a_{uv}^{ij}}{\partial t_{lm}^{\lambda\mu}} &= v_{ab}^{ij}\frac{\partial \tau_{uv}^{ab}}{\partial t_{lm}^{\lambda\mu}} \\
\frac{\partial b_{ab}^{\beta\gamma}}{\partial t_l^\lambda} &= -v_{ab}^{\beta l}\delta_{\gamma\lambda} - v_{ab}^{l\gamma}\delta_{\beta\lambda} \\
\frac{\partial j_{ua}^{\beta i}}{\partial t_l^\lambda} &= -v_{ua}^{li}\delta_{\beta\lambda} + v_{\lambda a}^{\beta i}\delta_{ul} - v_{ab}^{ij}\frac{\partial \tau_{uj}^{b\beta}}{\partial t_l^\lambda} \\
\frac{\partial j_{ua}^{\beta i}}{\partial t_{lm}^{\lambda\mu}} &= -v_{ab}^{ij}\frac{\partial T_{uj}^{b\beta}}{\partial t_{lm}^{\lambda\mu}} + \frac{1}{2}\left(2v_{a\mu}^{im} - v_{\mu a}^{im}\right)\delta_{ul}\delta_{\beta\lambda} \\
\frac{\partial k_{ua}^{i\beta}}{\partial t_l^\lambda} &= -v_{ua}^{il}\delta_{\beta\lambda} + v_{\lambda a}^{i\beta}\delta_{ul} - v_{ba}^{ij}\frac{\partial \tau_{uj}^{b\beta}}{\partial t_l^\lambda} \\
\frac{\partial k_{ua}^{i\beta}}{\partial t_{lm}^{\lambda\mu}} &= -v_{ba}^{ij}\frac{\partial T_{uj}^{b\beta}}{\partial t_{lm}^{\lambda\mu}} \\
\frac{\partial T_{ij}^{ab}}{\partial t_{lm}^{\lambda\mu}} &= \frac{1}{2}\delta_{il}\delta_{jm}\delta_{a\lambda}\delta_{b\mu}.
\end{aligned}
$$

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FIGURE LEGENDS

Figure 1. Standardized geometries of the BeH_2 molecule[27]

Figure 2. Dependence of necessary iteration steps on the denominator shift value for (a) geometry A and (b) geometry F

Figure 3. Dependence of the most critical Ljapunov exponents on the denominator shifts
(a) Geometry A, largest exponent
(b) Geometry F, largest two exponents
(c) Geometry I, largest two exponents

Figure 4. Apparent convergence (a), diverging oscillations (b), and bifurcation (c) in course of the CCSD iteration for BeH_2 with $\eta = 0.28$ at geometry B. Part (d) shows a zoom into the lower branch of part (c).

Figure 5. Chaotic patterns of CCSD iterations with an inappropriate denominator shift value ($\eta = 0.325$) for geometry A. The trajectories are sampled by 186 points (iteration steps).
(a) "Configuration space" trajectory (see text)
(b) "Phase space" trajectory

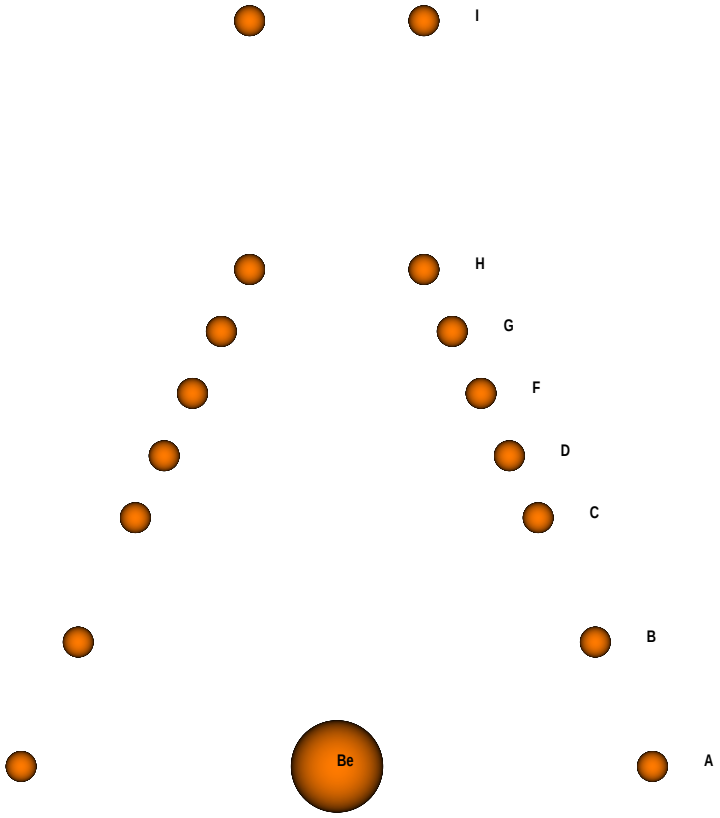
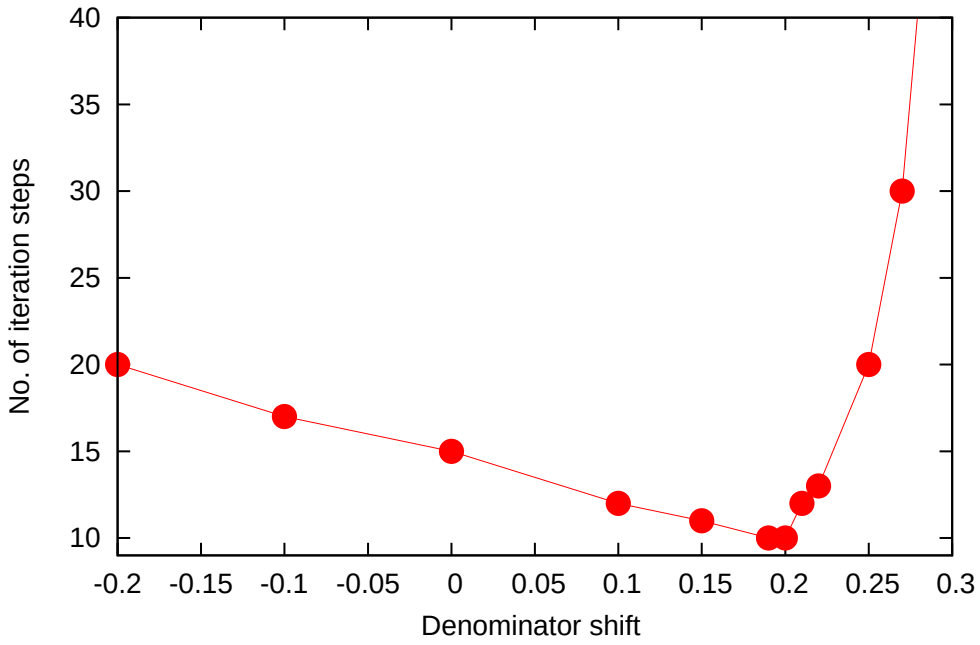


Fig. 1.

(a)


No. of iteration steps
Denominator shift
40
35
30
25
20
15
10
-0.2
-0.15
-0.1
-0.05
0
0.05
0.1
0.15
0.2
0.25
0.3

(b)

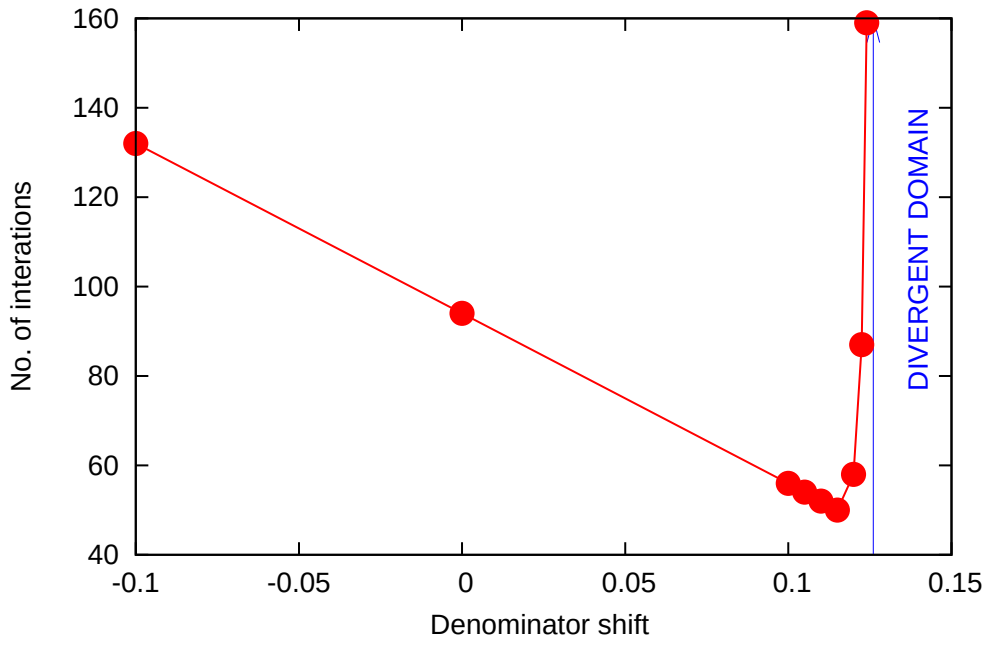
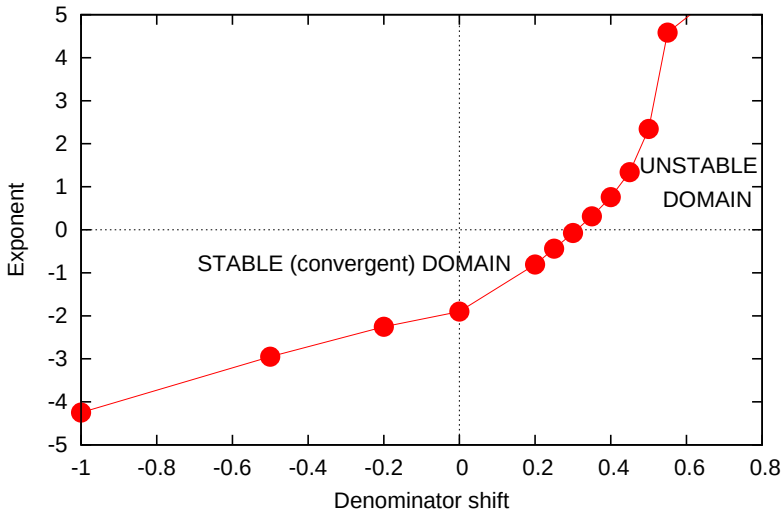
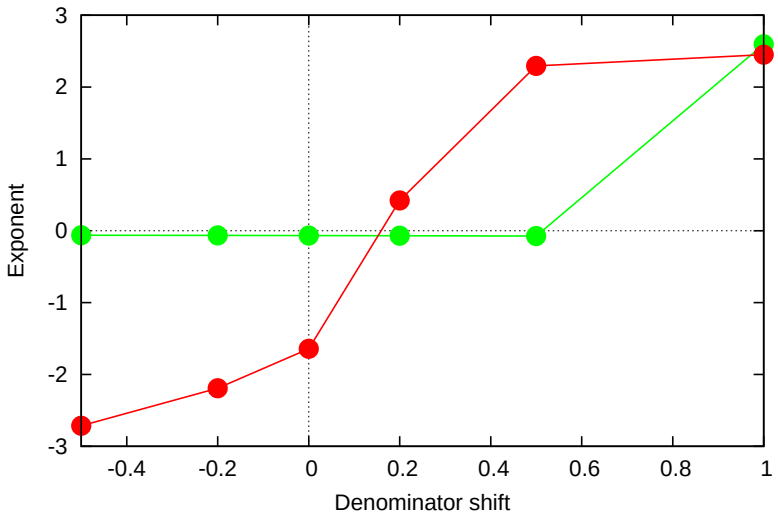

No. of interations
Denominator shift
DIVERGENT DOMAIN
160
140
120
100
80
60
40
-0.1
-0.05
0
0.05
0.1
0.15

Fig. 2.

(a)


Exponent
Denominator shift
UNSTABLE
DOMAIN
STABLE (convergent) DOMAIN

(b)


Exponent
Denominator shift

(c)

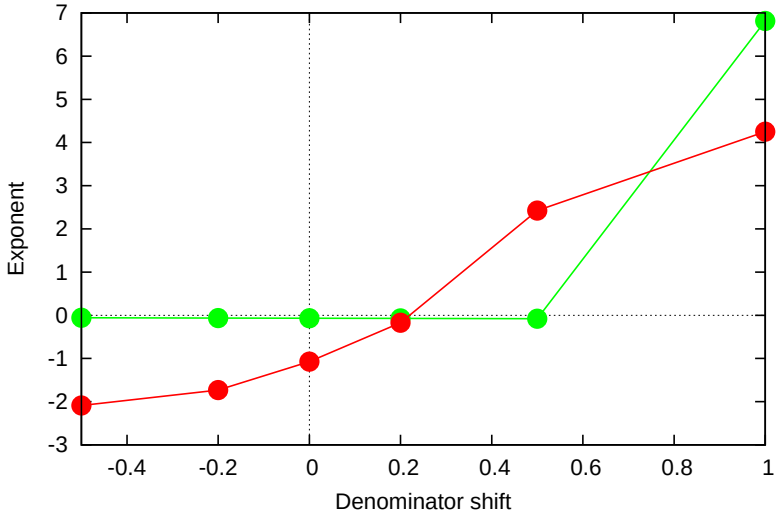
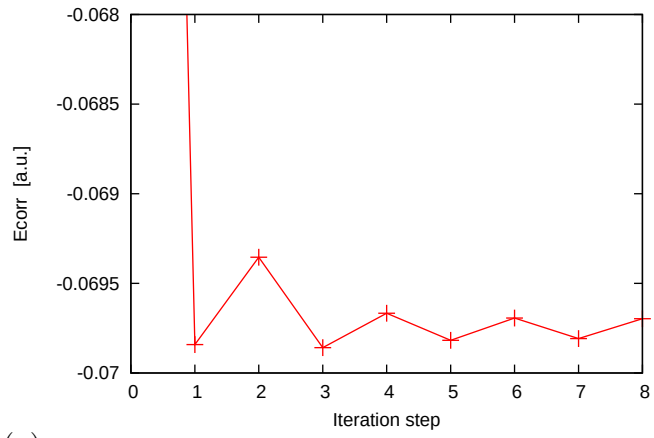
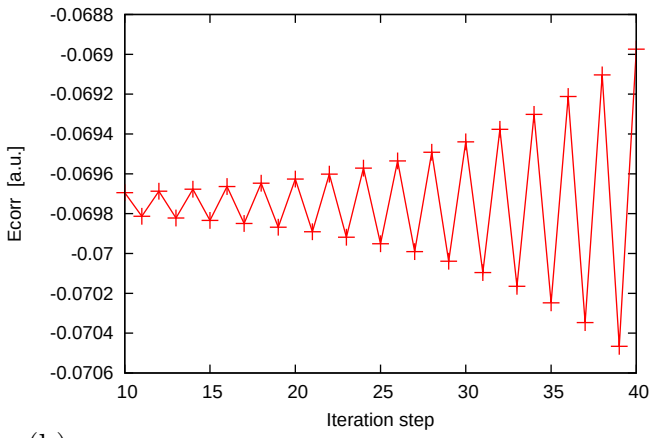

Exponent
Denominator shift

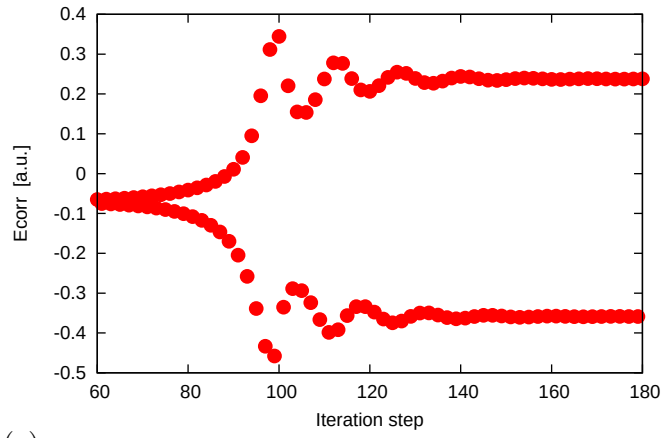
Fig. 3.


-0.068
-0.0685
-0.069
-0.0695
-0.07
Ecorr [a.u.]
0
1
2
3
4
5
6
7
8
Iteration step

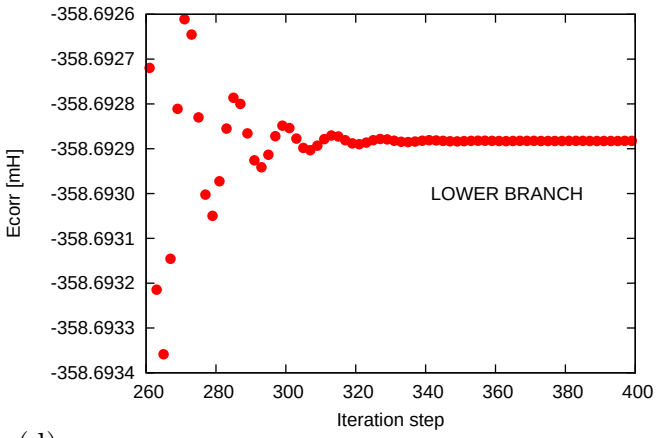
(a)


-0.0688
-0.069
-0.0692
-0.0694
-0.0696
-0.0698
-0.07
-0.0702
-0.0704
-0.0706
Ecorr [a.u.]
10
15
20
25
30
35
40
Iteration step

(b)


0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
Ecorr [a.u.]
60
80
100
120
140
160
180
Iteration step

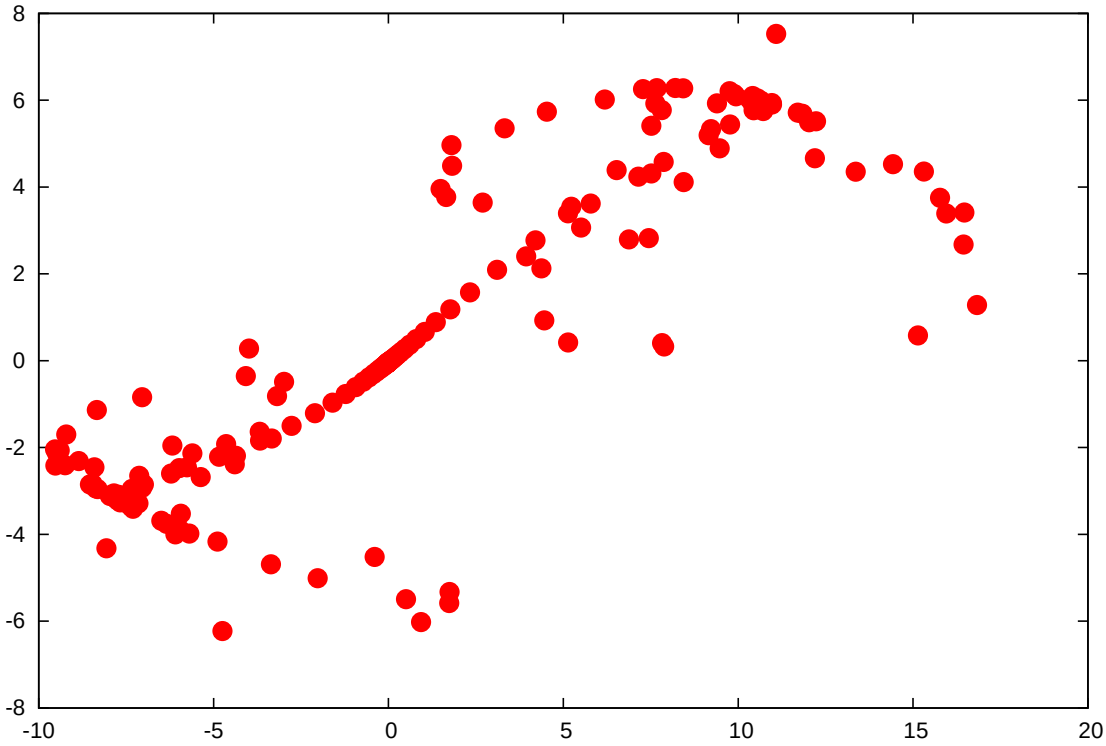
(c)


-358.6926
-358.6927
-358.6928
-358.6929
-358.6930
-358.6931
-358.6932
-358.6933
-358.6934
Ecorr [mH]
LOWER BRANCH
260
280
300
320
340
360
380
400
Iteration step

(d)

Fig. 4.

(a)



(b)

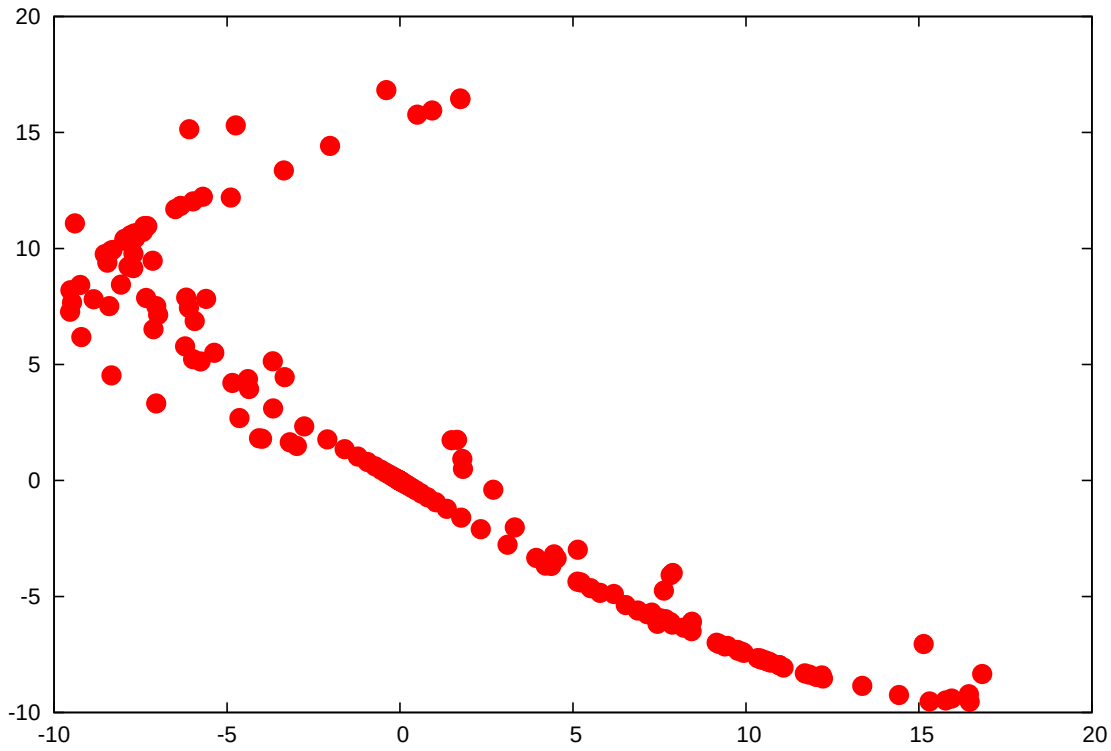


Fig. 5.