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Iterative solution of Bloch-type equations: stability conditions and chaotic behavior

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Two different form of nonperturbative Bloch-type equations are studied: one for the wave operator of the N-electron Schrödinger equation, another one for obtaining first-order density matrix P in one-electron theories (Hartree–Fock or Kohn–Sham). In both cases, we investigate the possibility of an iterative solution of the nonlinear Bloch equation. To have a closer view on convergence features, we determine the stability matrix of the iterative procedures and determine the Ljapunov exponents from its eigenvalues. For some of the cases when not every exponents are negative, chaotic solutions can be identified, which should of course be carefully avoided in practical iterations.

KEY WORDS: Bloch equation, density matrix, stability, chaos

1. Introduction

An equation which determines the wave operator can be called a Bloch equation in a general sense. The wave operator in a many-electron theory, often denoted by Ω, projects the exact wave function form a reference function. In a one-electron theory, the wave operator can be substituted to the first-order density matrix P which projects to the subspace of occupied orbitals. In what follows we first briefly review a derivation of Bloch-type equations for both Ω and P.

1.1. A Bloch-type equation in N-electron space

The Bloch equation [1], in the form presented by Lindgren [2–4] and Kvasnička [5–7] is a nonlinear equation for the wave operator Ω. It is mostly written in a perturbative form which assumes a splitting of the Hamiltonian

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into a zero-order part and a perturbation. Here we present a simplified, non-perturbative form of this equation, which was called the nonlinear Schrödinger equation by Löwdin [8], and which has the same mathematical form as the Bloch-type equation for the density matrix discussed in the forthcoming section.

We consider a normalized reference state Φ which is assumed to be a meaningful approximation to the exact wave function Ψ. The wave operator Ω maps Φ into Ψ:

$$\Psi = \Omega\Phi.$$

The formal representation of this wave operator is clearly:

$$\Omega = |\Psi\rangle\langle\Phi|. \tag{1}$$

Using intermediate normalization, i.e. $\langle\Psi|\Phi\rangle = 1$, it is easy to find that the wave operator is idempotent, $\Omega^2 = \Omega$, although it is not Hermitian.[1] To get an equation for Ω, we start from the Schrödinger equation

$$H|\Psi\rangle = E|\Psi\rangle \tag{2}$$

from which, upon multiplying by $\langle\Phi|$, we get the transition formula for the energy

$$E = \langle\Phi|H|\Psi\rangle. \tag{3}$$

Let us now study the expression

$$\begin{aligned} H\Omega &= H|\Psi\rangle\langle\Phi| \\ &= |\Psi\rangle E\langle\Phi| \\ &= |\Psi\rangle\langle\Phi|H|\Psi\rangle\langle\Phi|, \end{aligned}$$

where we have utilized the Schrödinger equation (2) and the energy formula (3). Identifying the formal definition of the wave operator (1), we finally get

$$H\Omega = \Omega H\Omega, \tag{4}$$

which is a nonlinear equation for the wave operator. It can also be written as

$$(1 - \Omega)H\Omega = 0. \tag{5}$$

[1] Idempotent but non-Hermitian operators are sometimes termed as *skew projectors* (see, e.g. [8]).

1.2. Bloch-type equation for the density matrix

An equation of the very same mathematical structure applies also for the one-electron density matrix P in Hartree–Fock theory. To get this, we recall that the Fockian F and P are simultaneously diagonal in the basis of canonical MOs, thus their matrices in an orthogonal basis commute.[2]

$$FP = PF. \tag{6}$$

We recall also that P is Hermitian

$$P^{\dagger} = P,$$

its trace is equal to the number of electrons:

$$TrP = N,$$

and it is idempotent

$$P^2 = P.$$

By virtue of the latter property, multiplying equation(6) by P from the right, we get

$$FP = PFP, \tag{7}$$

which can also be written as

$$(1 - P)FP = 0, \tag{8}$$

or, by introducing the hole-density matrix $Q = 1 - P$, as

$$QFP = 0.$$

This result is rather trivial: it expresses that the Fockian does not have matrix elements between virtual and occupied MOs, which is a direct consequence of the Brillouin theorem. As noted by Mazziotti [9], the very same result can easily be obtained also from the first-order contracted Schrödinger equation[10].

The form of equation (8) is analogous to equation(5), indicating the similar mathematical structure of the two, otherwise quite different, problems.

[2]If the underlying basis set is not orthogonal, this equation has to be modified appropriately. In the present paper, to simplify the formulae, we write the expressions in orthogonal basis. Generalization to the nonorthogonal case is a trivial exercise.

2. Iterative solution of the Bloch equation

2.1. Iterative solution of the N-electron Bloch-equation

Equation (5) suggest the iteration scheme

$$\Omega' = \Omega + \eta(1 - \Omega)H\Omega, \tag{9}$$

which has fixed point when equation (5) holds. Here η is a free parameter which can be used to tune convergence.

An important feature of this iteration scheme is that it preserves the idempotency of an initially idempotent approximation:

$$\begin{aligned}\Omega'^2 &= (\Omega + \eta(1 - \Omega)H\Omega)^2 \\ &= \Omega^2 + \eta(1 - \Omega)H\Omega\Omega \\ &= \Omega + \eta(1 - \Omega)H\Omega = \Omega'.\end{aligned}$$

Therefore, starting with a physically correct idempotent guess to Ω, this iteration sequence, if converges, leads to an exact wave operator of the system. It is to be emphasized that the converged wave operator can belong to any states, and the careful choice of the initial guess as well as that of the iteration parameter η is important to ensure that one reaches the desired target state.

2.2. Iterative solution of Bloch-type equation for the density matrix

An essential difference between the equations determining Ω and P is in the auxiliary conditions: while Ω need not be Hermitian, the final density matrix P should. It is easy to prove [11] that the iteration formula (9) cannot yield a Hermitian solution. Therefore, for obtaining P we devised the following double iteration procedure:

$$\begin{aligned}P' &= P + \eta(QFP), \\ P'' &= P' + \eta(P'FQ')\end{aligned} \tag{10}$$

with $Q' = 1 - P'$. The second iteration step has fixed point when $PFQ = 0$. When this iteration converges, that is $P = P' = P''$, we have therefore

$$QFP = PFQ = 0$$

with an idempotent and Hermitian P and Q, which both commute with the Fockian [12].

Instead of this double iteration, Mazziotti [9] suggested to Hermitize QHP by iterating via

$$P' = P + \eta(QHP + PHQ).$$

This way, Hermiticity of P is exactly ensured at each iteration step, but its idempotency is violated. This can be corrected for by inserting a purification step [13–18] at each iteration.[3]

The convergence properties of this iteration sequence, similarly to the single iteration procedure (9), are not excellent: neither form facilitates quadratic convergence. However, according to our numerical practice [11, 12], scheme (10) converges within a reasonable number of steps if parameter η is appropriate. To gain a more thorough insight into the convergence features, it is worth looking at the problem of stability analysis of these equations.

3. Stability matrices and Ljapunov exponents for Bloch-type equations

3.1. General formulation

The theory of stability matrices and Ljapunov exponents is well established and can be found in standard mathematical texts [20]. Here we summarize an essence of this theory to apply it for Bloch type equations.

Consider an general iteration procedure for an N-component vector $\underline{\mathrm{x}}$

$$x^{(n+1)} = f_i(\underline{\mathrm{x}}^{(n)}), \quad i = 1, 2, \ldots N. \tag{11}$$

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

$$\mathrm{a}_i = f_i(\underline{\mathrm{a}}), \quad i = 1, 2, \ldots N \tag{12}$$

and let us consider small deviations around this fixed point:

$$\underline{\mathrm{x}}^{(n)} = \underline{\mathrm{a}} + \underline{\xi}^{(n)}.$$

Substitution of this Ansatz into (11) gives

$$\begin{aligned} \mathrm{a}_i + \xi^{(n+1)} &= f_i\left(\underline{\mathrm{a}} + \underline{\xi}^{(n)}\right) \\ &= f_i\left(\underline{\mathrm{a}}\right) + \sum_{j=1}^{N} \left.\frac{\partial f_i}{\partial x_j}\right|_{\underline{\mathrm{a}}} \xi_j^{(n)} + \mathcal{O}(2), \end{aligned} \tag{13}$$

[3]Note that the "Diophantine solution" to the purification problem used by Szekeres and Mezey [19] cannot be applied here, since we aim to avoid any explicit diagonalization steps.

where we expanded the N-variable function f into Taylor series up to the first-order. Using (12) with neglecting terms of $\mathcal{O}(\xi^2)$ leads us to

$$\begin{aligned}\xi_i^{(n+1)} &= \sum_{j=1}^{N} \left.\frac{\partial f_i}{\partial x_j}\right|_{\underline{a}} \xi_j^{(n)} \\ &= \sum_{j=1}^{N} A_{ij}\xi_j^{(n)}\end{aligned} \tag{14}$$

with the definition of the first-order Ljapunov (Jacobi) matrix

$$A_{ij} = \left.\frac{\partial f_i}{\partial x_j}\right|_{\underline{a}}. \tag{15}$$

Solution of (14) can be searched in the form

$$\underline{\xi}^{(n)} = e^{\lambda n}\underline{\xi}^{(0)},$$

which, after substitution into (14) gives us the eigenvalue equation

$$A\underline{\xi}^{(0)} = \mu\underline{\xi}^{(0)}$$

with the notation $\mu = e^{\lambda}$. We conclude that the modes $\xi^{(0)}$ are eigenvectors of the Ljapunov matrix while the eigenvalues correspond to the logarithms of parameters λ which are called the Ljapunov exponents of the problem.

Analysis of converge properties of the iteration process (11) can be based on the value of the Ljapunov exponents λ, or on their exponentials μ. In the simplest cases 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 Ljapunov matrix satisfy the condition

$$0 > m > 1.$$

When at least one of the exponents becomes positive, the iteration will diverge along the corresponding trajectory.

It may turn out that one or more eigenvalues of the Ljapunov matrix become negative. In this case the corresponding Ljapunov exponents can be written as

$$\lambda = \log|m| + i\pi,$$

leading to the convergence condition

$$Re\lambda = \log|m| < 0,$$

which requires

$$|m| < 1.$$

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

$$\underline{\xi}^{(n)} = e^{\lambda n}\underline{\xi}^{(0)} = e^{i\pi n}e^{\log|m|}.$$

On the borderline of convergence and divergence, nonlinear systems may also exhibit chaotic iterations [21]. Examples for this case will be shown in the numerical section.

3.2. *Stability matrix for the wave operator* Ω

The Ljapunov matrix for Ω-iteration (9) can be obtained by the matrix representation of the wave operator and considering matrix elements $\Omega_{\mu\nu}$ as iteration parameters $\underline{x}_i$. Here the hyperindex i is identified to the composite label $(\mu\nu)$. Using definition (15), we formally write

$$\begin{aligned} A_{ij} &= \frac{\partial f_i}{\partial \Omega_j} \\ &= \delta_{ij} + \eta \frac{\partial}{\partial \Omega_j}\left[\left(1-\Omega^{(n)}\right) H\Omega^{(n)}\right]_i, \end{aligned}$$

where the form (9) was taken into account for f. Resolving the hyperindices to composite ones and evaluating matrix multiplications, with the notations $i = (\mu\nu)$, $j = (\lambda\sigma)$ we finally get

$$\begin{aligned} A_{\mu\nu,\lambda\sigma} = {} & \delta_{\mu\lambda}\delta_{\nu\sigma} + \eta\delta_{\nu\sigma}H_{\mu\lambda} \\ & -\eta\delta_{\mu\lambda}(H\Omega)_{\sigma\nu} \\ & -\eta\delta_{\nu\sigma}(\Omega H)_{\mu\lambda}. \end{aligned} \tag{16}$$

Eigenvalues of matrix A_{ij} will be related to the Ljapunov exponents of Ω-iteration. This matrix is not Hermitean, but in the numerical calculations reported below we have never noticed any complex eigenvalues. The eigenproblem of nonsymmetric matrices are easily solvable by standard procedures [22].

3.3. *Stability matrix for the density matrix* P

The Ljapunov matrix for the P-iteration (10) can be obtained in an analogous way. Here the independent elements of matrix P are used as iteration

parameters. The result

$$A_{\mu\nu,\lambda\sigma} = -\delta_{\mu\lambda}\delta_{\nu\sigma} - \eta(HP)_{\sigma\nu}\delta_{\mu\lambda} - \eta(PH)_{\mu\lambda}\delta_{\nu\sigma} + \eta(QH)_{\mu\lambda}\delta_{\nu\sigma} + \eta(HQ)_{\sigma\nu}\delta_{\mu\lambda} \\ \eta^2(QH)_{\mu\lambda}(HQ)_{\sigma\nu} + \eta^2(PH)_{\mu\lambda}(HP)_{\sigma\nu}$$

appears to be a bit more complicated than (16) due to the double iteration used in (10) to ensure the Hermiticity of converged P.

In the following section, we present a few examples to the significance of the eigenvalues of these matrices and show some representative iteration patterns.

4. Numerical analysis

4.1. The Bloch-equation in N-electron space

We emphasize that examples for using (9) are included here merely to study the iteration properties of these equations, and definitely not to propose any effective computational methods to determine the wave operator. Therefore, we have chosen simple two-electron systems, the H_2 molecule in the double-zeta-sized 6-31G basis [23] and the He atom in a triple-zeta-sized 6-311G basis. For both of these sample cases the full-CI Hamiltonian, the matrix of the exact wave operator, as well as the Ljapunov matrices fit into the operative memory of a small PC.

Let us see first the case of the H_2 molecule. In table 1 the largest Ljapunov exponents are shown as a function of the control parameter of the iteration (η). The table clearly shows that until the largest exponent is negative, convergence can be achieved, but the number of iteration steps needed for this depend heavily on η. As the largest exponent exceeds the zero threshold, the iteration starts to oscillate between two points. For even larger exponents, the number of bifurcations starts to increase and suddenly one finds a completely chaotic iteration.

Similar findings are reported for the He atom in Table 2. Dependence of the largest Ljapunov exponent on parameter η is shown in figure 1 for this case. In

Table 1
Iteration features for the Bloch equation of wave operator in the case of the H_2 molecule. The value of 10^{-8} was used as the criterion of convergence in total energy.

η	Largest Ljapunov exponent (λ)	effect
−0.100	−0.370	converges in 158 steps
−0.500	−0.423	converges in 44 steps
−0.605	0.002	oscillates between 2 states
between −0.770 and −0.776	> 0	several bifurcations
below −0.777	> 0	chaos

Table 2
Iteration features for the Bloch equation of wave operator in the case of the He atom.

η	Largest Ljapunov exponent (λ)	effect
−0.100	−1.2600	converges in 119 steps
−0.155	−0.0104	converges in 260 steps
−0.156	+0.0026	oscillates
−0.198	+0.4329	bifurcations (4 branches)
−0.200	+0.4494	chaos
−0.240	+0.7328	diverges to ∞

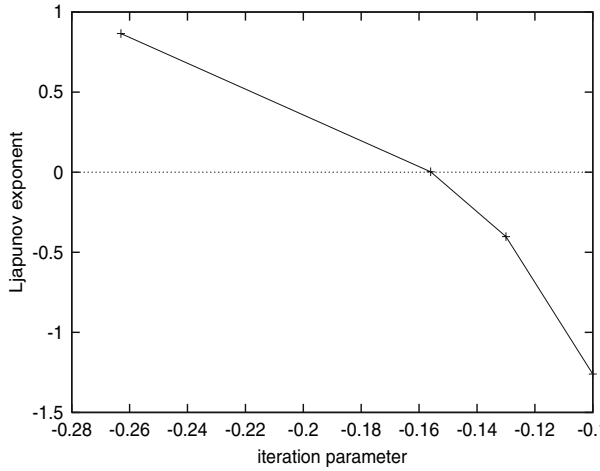

Figure 1. Dependence of the largest Ljapunov exponent for the iterative solution of the Bloch equation in the case of the He atom.

agreement with table 2, the figure shows that convergence can only be expected for $\eta \gtrsim -0.155$. Appearance of branching (the first bifurcation) at $\eta = -0.157$ is illustrated in figure 2., while an example for chaotic iteration is shown in figure 3. As typical for chaotic systems [21], as the iteration parameter deviates from its optimal value (around −0.5 in this case), more and more bifurcations occur, suddenly ending in a completely chaotic iteration.

The fact that chaotic iterations appear upon iterative solution of Bloch type equations is not surprising since at the so called *logistic map*

$$x' = \eta x(1 - x),$$

which can be viewed as a one-dimensional Bloch-type equation with fixed points 0 or 1, represents a prototype for simple chaotic systems [21].

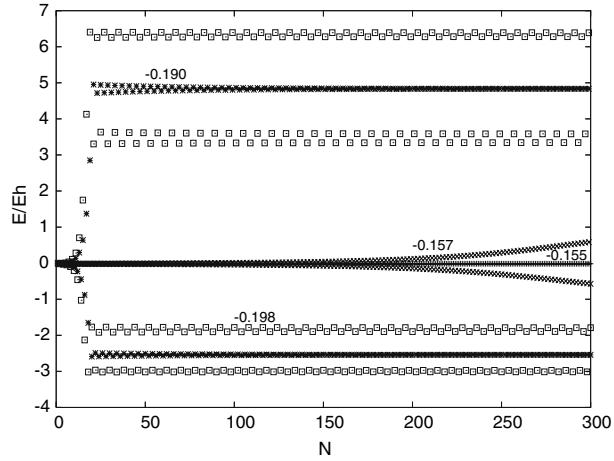

Figure 2. Convergent iterations versus branchings for the iterative solution of the Bloch equation in the case of the He atom.

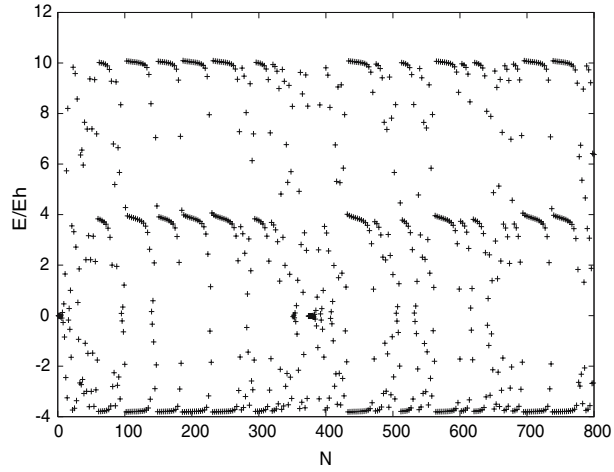

Figure 3. Chaotic iteration for the Bloch equation in the case of the He atom. The value of the iteration parameter was $\eta = -0.22$. The corresponding largest Ljapunov exponent was 0.6011.

4.2. *Bloch-type equation for the density matrix*

We have performed a somewhat more detailed analysis on the iteration properties of equation (10). First, we have performed an *ab inito* Hartree–Fock calculation for 60 water molecules arranged into a H-bonded chain in a split-shell basis set. The results are not reported here, since we found the rather trivial effect that as one deviates from the optimal value of η the number of

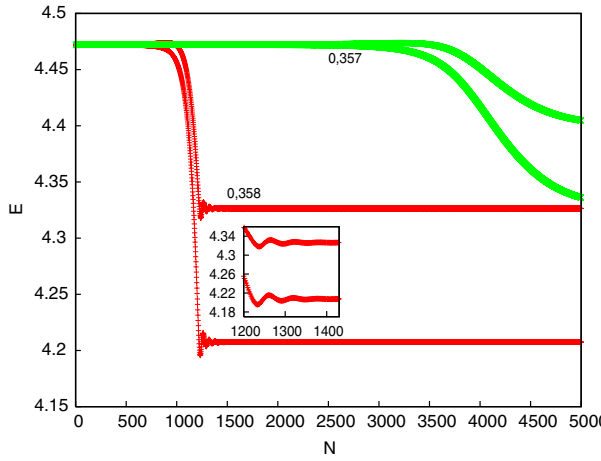

Figure 4. Bifurcations during iterations for the density matrix P in the case of the Hückel treatment of butadiene. The energy is plotted in units of β. The numbers at the curves indicate the value of parameter η.

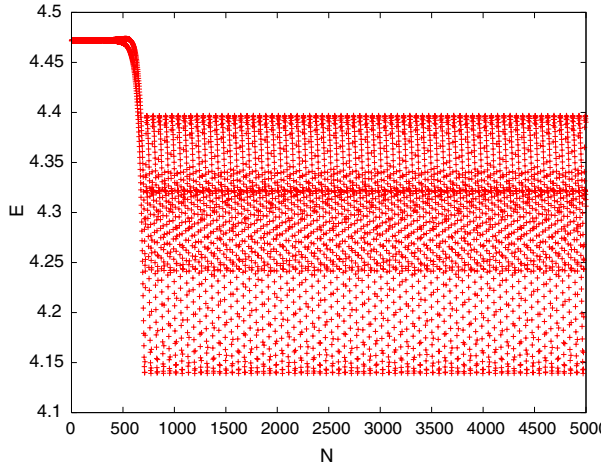

Figure 5. The same as in figure 4, at $\eta = 0.39$ with $\lambda = 0.021$, producing already a chaotic pattern.

necessary iteration steps first increase, then the iteration diverges; however, no sign of chaos was found in this case.

Next, we turned to the simple problem of determining the Hückel density matrix for butadiene by equation (10). We found that the iteration converges up to $\eta < 0.355$, after which bifurcations (figure. 4.) and chaotic behavior were found. The latter is shown in figures 5–8. Figure 5. shows the seemingly structure-less pattern of a chaotic iteration, while plotting density matrix elements against each other (in analogy to the configuration space of dynamical systems)

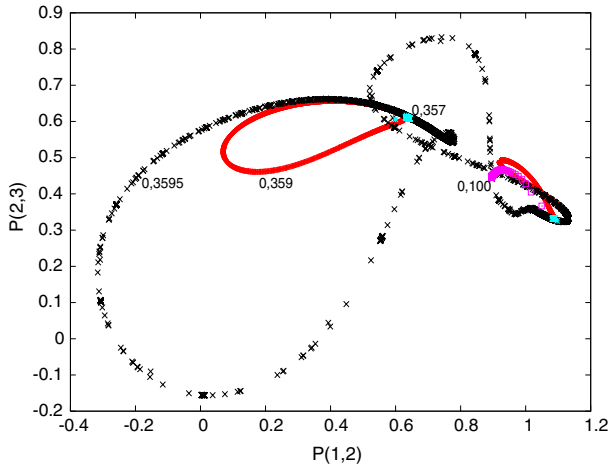

Figure 6. Plots of chaotic iterations for density matrix elements in the 'configuration space' of parameters. The numbers at the curves indicate the value of parameter η.

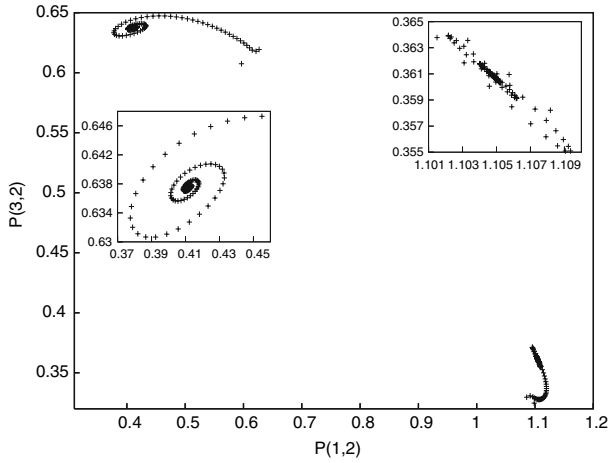

Figure 7. The same as in figure 6. for $\eta = 0.358$.

leads to the characteristic orbital patterns shown in figures 6 and 7. The difference between the trajectory corresponding to $\eta = 0.357$ in figure 6. and $\eta = 0.358$ (figure 7.) is remarkable. In the latter case, as illustrated in the enlarged insets, two spiral attractors are shown, thus the iteration procedure fails to converge to a unique solution. The direct iteration energy sequences for these two cases are shown in figure 4, where the oscillatory pattern of the latter case is also exhibited in the inset.

Another interesting way to visualize chaotic iterations is shown in figure 8, where the change (the "derivative")of a density matrix element between

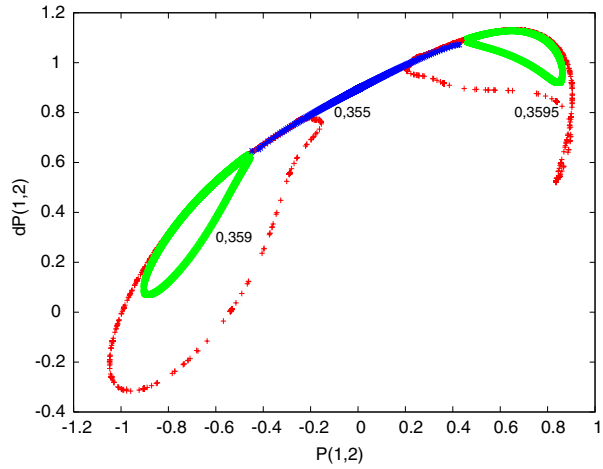

Figure 8. Plots of chaotic iterations for density matrix element P_{12} in the 'phase space'. The numbers at the curves indicate the value of parameter η.

subsequent iterations is shown as a function of the matrix element value. This is analogous to plots in phase space of dynamical systems. A characteristic feature of the plot is the orbitals consist of disconnected loops (note that trajectories can never cross themselves in phase space).

5. Closing remarks

A practical conclusion from the above studies is that one has to select carefully the appropriate value of the iteration control parameter in order to find convergent pathways in course of the iterative solution of Bloch type systems. As the presented numerical examples indicate, there is a clear relation between the control parameter η and the largest Ljapunov exponent of the problem, λ. Fortunately, our numerical practice indicates [11, 12] that the optimal value of parameter η is, although quite sensitive to the quality of the basis set, is highly transferable between chemically similar systems of different size. Therefore, an appropriate value for η can be established for small systems, and there is no need to perform the Ljapunov analysis in each case, which would be computationally prohibitive for larger molecules due to the size of the stability matrices.

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