ARTICLE TEMPLATE

Stability Analysis of the Lippmann-Schwinger equation

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ABSTRACT
The Lippmann-Schwinger type equation for Bruckner's reaction operator is analysed with respect to its convergence properties for the case of small deviations from the fixed point. It is found that the eigenvalues of the Jacobian of the iterative equation predict the convergence to a good approximation.

KEYWORDS
Iterations, Jacobian, Stability analysis, Lippmann-Schwinger equation, Convergence properties

1. Introduction

The basic equation of molecular physics, the time-independent Schrödinger equation, being an eigenproblem of a linear Hamiltonian $\hat{H}$, $\hat{H}\Psi = E\Psi$, is a linear equation. Linear equations are often easy to solve. However, due to the complexity of molecular Hamiltonians, and, in matrix representations, the extreme size of Hamiltonian matrices, the solution requires iterative techniques in most cases. This holds both for huge eigenproblems and for perturbative considerations. Moreover, approximate methods or models are often nonlinear, necessitating iterative solutions, self-consistent problems or coupled cluster techniques providing good examples. For this reason, analysis of iterative techniques are of principal importance. The necessary mathematical tools are well elaborated.

One important operator in molecular physics, connected to a generalized formalism of perturbation theory, is Bruckner's reaction operator $\hat{t}$, having the property

$$E = E^0 + \langle \varphi | \hat{t} | \varphi \rangle \tag{1}$$

where E^0 is the zero order energy in some

$$\hat{H} = \hat{H}^0 + \hat{W} \tag{2}$$

partitioning of the Hamiltonian, φ is the corresponding zero order wave function,

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Dedicated to the 60th birthday of Péter Szalay

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i.e., $H^0\varphi = E^0\varphi$ and $E^0 = \langle\varphi|H^0|\varphi\rangle$. Reaction operator $\hat{t}$ is known to satisfy the Lippmann-Schwinger equation

$$\hat{t} = \hat{W} + \hat{W}\hat{Q}\hat{t}, \tag{3}$$

where operator $\hat{Q}$ is the reduced resolvent of $\hat{H}^0$:

$$\hat{Q} = \frac{\hat{P}}{E - \hat{H}^0} \tag{4}$$

with

$$\hat{P} = 1 - |\varphi\rangle\langle\varphi| \tag{5}$$

Eq. (4) is written in a somewhat symbolic notation. For mathematically correct definition of reduced resolvents (inverse in subspaces) see the works by Löwdin[1, 2].

Eq. (3), through operators $\hat{Q}$ and $\hat{t}$, depend on the energy E. As shown in Sect.2, Eq. (3) should be taken at an exact energy E, i.e., at one of the eigenvalues of $\hat{H}$.

Eq. (3) suggests a formal iteration sequence

$$\hat{t}^{(n+1)} = \hat{W} + \hat{W}\hat{Q}\hat{t}^{(n)}. \tag{6}$$

with superscript n enumerating iteration steps.

Starting the iteration with $\hat{t}^{(0)} = 0$, one recovers the Brillouin-Wigner perturbation series[3, 4]

$$\hat{t} = \hat{W} + \hat{W}\hat{Q}\hat{W} + \hat{W}\hat{Q}\hat{W}Q\hat{W} + \cdots \tag{7}$$

the convergence issues of which are *eo ipso* interesting to analyse.

In this short paper we shall use the iterative scheme exhibited in Eq.(6) to determine $\hat{t}$ for model Hamiltonians, and analyse the mathematical characteristics of these iterations assuming $\hat{t}^{(n)}$ being close to a fixed point of (6).

By means of this analysis one can distinguish between convergence and divergence, and, as we shall see, one may introduce techniques to ensure convergence in originally divergent cases. Before reporting the results, we review the derivation of (3) and the theory of stability analysis of iteration schemes for completeness.

It is apparent from Eqs.(6) and (7) that the operator product $\hat{Q}\hat{W}$ plays an important role in this theory. We remark in this connection that the minimization of the norm of this operator was proposed in Refs[5, 6] to improve convergence properties of Rayleigh-Schrödinger perturbation theory. The same operator product was utilized also by Mazziotti[7].

2. Compact derivation of the Lippmann-Schwinger equation

While the Lippmann-Schwinger equation appeared in the physical literature in form of an integral equation topical in quantum scattering theory[8], a distilled formulation for general use was presented by Löwdin in his "Studies in Perturbation Theory" series[1].

The essence, relevant to the present formulation begins with the Dyson equation

$$\hat{R} = \hat{Q} + \hat{Q}\hat{W}\hat{R}, \tag{8}$$

connecting the reduced resolvent of the Hamiltonian $\hat{H}$,

$$\hat{R} = \frac{\hat{P}}{E - \hat{H}}. \tag{9}$$

and the reduced resolvent $\hat{Q}$ of the zero-order Hamiltonian $\hat{H}^0$, Eq. (4). Equation (8) is a direct consequence of the partitioning introcuded in (2), and is valid at any value of parameter E. At this point we make use of the expression for E, as an exact eigenvalue of $\hat{H}$, stemming from the partitioning technique

$$\begin{aligned} E &= \langle\varphi|\hat{H} + \hat{H}\hat{R}\hat{H}|\varphi\rangle \\ &= E^0 + \langle\varphi|\hat{W} + \hat{W}\hat{R}\hat{W}|\varphi\rangle. \end{aligned} \tag{10}$$

Comparing this result to definition (1), one recovers the reaction operator in the form

$$\hat{t} = \hat{W} + \hat{W}\hat{R}\hat{W}. \tag{11}$$

The most explicit definition of the reaction operator is provided by Eq.(11) above. Its implicit definition in Eq.(1) reflects that in the present context only its action on the zero order wavefunction, φ is relevant.

The resolvent $\hat{R}$ satisfies Eq. (8), which, upon substituting in Eq. (11), results

$$\hat{t} = \hat{W} + \hat{W}\hat{Q}\hat{t},$$

the Lippmann-Schwinger equation.

Note the more recent works by Hubač and coworkers[9–12] on quantum chemical applications of the Lippmann-Schwinger equation.

It is interesting to observe that the Dyson equation (8) and the Lippmann-Schwinger equation (3) exhibit similar mathematical structures. This analogy is deceptive, however. Eq. (8) is valid at any values E. For our present purpose, $\hat{t}$ is to be evaluated at an exact eigenvalue for Eq.(1) to be satisfied. A further difference is that Eq. (8) is reduced to the $\hat{P}$-space, while operator $\hat{t}$ in (3) acts on the reference function φ (cf. Eq. 5). This is reflected by the fact that operator $\hat{Q}\hat{W}$ stands in the second term of the right hand side of (8), while $\hat{W}\hat{Q}$ is seen in (3).

3. Stability analysis of the Lippmann-Schwinger equation

Let us denote a fixed point of Eq. (3) for some state by $\hat{t}^*$. That is, it satisfies

$$\hat{t}^* = \hat{W} + \hat{W}\hat{Q}\hat{t}^*. \tag{12}$$

With the aim of studying the properties of this fixed point, the reaction operator is written in the form

$$\hat{t} = \hat{t}^* + \hat{\tau}, \tag{13}$$

where operator $\hat{\tau}$ is assumed to be small in some sense. Substituting this form into Eq. (6) and using (12), one gets

$$\hat{\tau}^{(n+1)} = \hat{W}\hat{Q}\hat{\tau}^{(n)}. \tag{14}$$

Here superscript n enumerates iteration steps.

Eq. (14) is seemingly linear in $\hat{\tau}$, but in fact, the reduced resolvent $\hat{Q}$ also depends on $\hat{\tau}$ implicitly through its energy-dependence. To form the Jacobian of the mapping, we intend to linearise this equation wrt $\hat{\tau}$. This is equivalent to neglecting the $\hat{\tau}$-dependence of $\hat{Q}$, so that operator

$$\hat{J} = \hat{W}\hat{Q}. \tag{15}$$

serves as the Jacobian. Assuming exponential convergence feature to an attractive fixed point represented by $\hat{\tau}^{(n)} \to 0$ for $n \to \infty$, and similarly, exponential divergence if the fixed point is repulsive, we may try to substitute the Ansatz

$$\hat{\tau}^{(n)} = e^{\lambda n}\ \hat{\tau}_0 \tag{16}$$

into Eq.(14) to get

$$\hat{J}\hat{\tau}_0 = e^{\lambda}\hat{\tau}_0. \tag{17}$$

This result tells us that mode $\hat{\tau}_0$ appears as an eigenoperator of the Jacobian $\hat{J}$ corresponding to the eigenvalue $j = e^{\lambda}$, thus λ plays the role of a Ljapunov-type exponent[13]. The sign of the latter will decide between convergence (for $\lambda < 0$) of divergence (for $\lambda > 0$) of the iteration. Alternatively, separation between convergent and divergent cases can be done by checking whether $j \gtrless 1$.

Since the Jacobian is not hermitian, it may possess complex eigenvalues. In that case the iteration pattern will not be monotonic (cf. the discussion in ref.[14]).

Similar studies of stability conditions have been carried out on the coupled cluster equations formerly in our laboratory[14–16] and by other authors[17–20].

4. Numerical illustration

The method outlined above is a tool of understanding and analysis. Considering that the eigenvalue problem of the nonsymmetric Jacobian $\hat{J}$ is more costly than that of $\hat{H}$, the stability analysis does not provide a practical computational scheme. This section illustrates the connection between the absolutely maximal eigenvalue of the Jacobian and the convergence features of the Lippmann-Schwinger equation for two simple quantum chemical systems, for which the exact solutions are also easily available. The model molecules are LiH and HF diatomics, treated in a polarized triple-zeta (TZP) type basis set[21] at the configuration interaction with singles and doubles (CISD) level. The Lippmann-Schwinger equation is solved, and the Jacobian is constructed, in

Table 1. Correlation energies (Ecorr) in a.u., number of iterations (Nit) to achieve 10^{-8} a.u. energy accuracy of the Lippmann Schwinger equation, and maximal absolute value of the eigenvalue $|j|$ of the Jacobian for the LiH molecule at various inter-atomic distances R [Å]. *: 10^{-5} accuracy

R	Nit	Ecorr	max $\lvert j\rvert$
1.0	21	-0.0501842	0.593
2.0	25	-0.0456292	0.633
3.0	44	-0.0540327	0.771
4.0	55	-0.0742359	0.852
5.0	56	-0.0979742	0.862
7.0	80*	-0.1284498	0.878

matrix representation using the Hartree-Fock determinant and excited spin-adapted configurations built up by canonical molecular orbitals.

4.1. The LiH molecule

The closed-shell singlet ground state of LiH treated at the CISD level generates a spin adapted CI Hamiltonian ($\hat{H}$) of dimension 1035. This Hamiltonian was diagonalized at various Li−H bond distances. Diagonals of $\hat{H}$ define the zero-order Hamiltonian (Epstein–Nesbet partitioning[22, 23]).

Table 1. presents the correlation energies and the maxima of the converged Jacobian eigenvalues (absolute values) for some selected bond lengths. The number of iterations necessary to get the Lippmann-Schwinger equation for the reaction operator t are also indicated.

It is well illustrated by Table 1. that the number of iterations grow with increasing bond length, which is a consequence of the gradually deteriorating character of the single determinant Hartree-Fock reference state. This is also illustrated by the increasing value of the correlation energies. The Lippmann-Schwinger iterations for the reaction operator remain convergent for all R. This is well reflected by the fact that all eigenvalues of J are smaller than 1 in absolute values. Though the values max $|j|$ increase with increasing R, they tend to saturate and remain below 1.0 even for large distances.

Since the Jacobian in Eq.(15) depends on the iterations through the energy-dependence of the resolvent Q, it is interesting to check how max $|j|$ values evolve during the iteration. This is depicted in Fig.1. for R=4.0 Å.

The figure shows that initial estimations of the max $|j|$ value is quite bad: the first estimate is above the critical value of 1, thus it would predict divergence. However, the maximal eigenvalue decreases below 1.0 at n=2, and soon approximates its converged value around 0.85.

Even if all converged max $|j|$ values are below 1.0 according to Table 1, their actual values carry a message. This is illustrated by Fig. 2. comparing the energy convergence patterns at $R = 1.0$, 5.0 and 7.0 Å. The convergence is fast at equilibrium and becomes slower with increasing R, in parallel with the increase of the maximum eigenvalue exhibited in Table 1.

We finally note that, just for the sake of analysis, one may eliminate the energy-dependence of the Jacobian by inserting the exact converged energy from the very beginning. Without plotting these results, we mention that this leads to significantly faster convergence.

Figure 1. Convergence of the energy and the maximal absolute eigenvalue of the Jacobian during the iteration of the Lippmann-Schwinger equation for the LiH molecule at R_{LiH}=4.0 Å.

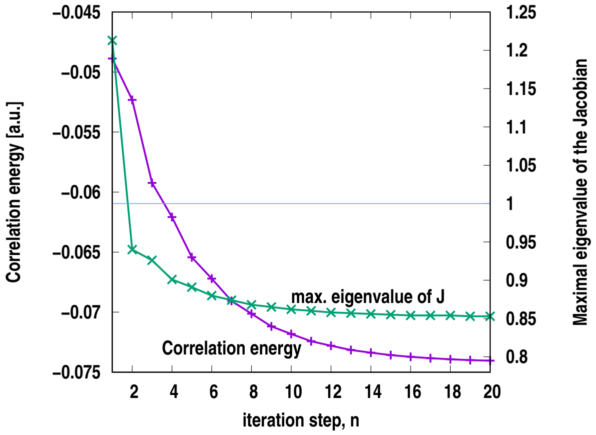


Figure 2. Convergence of the relative correlation energies $E_n - E$ (0 being the converged value) during the iteration of the Lippmann-Schwinger equation for the LiH molecule at various bond distances.

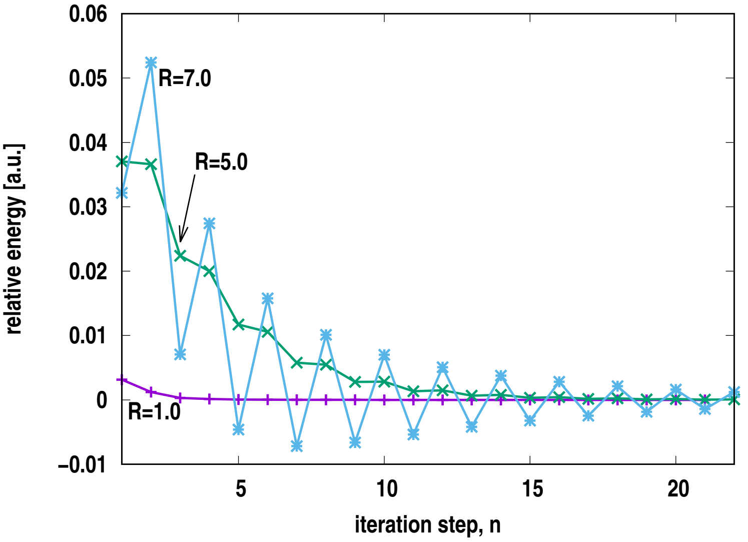


Table 2. The number of iterations (Nit) to achieve 10^{-8} a.u. energy accuracy of the Lippmann Schwinger equation, and maximal absolute value of the eigenvalue $|j|$ of the Jacobian for the HF molecule at various inter-atomic distances R [Å]. Symbol ∞ indicates divergence.

R [Å]	No. of iterations	max $\|j\|$
1.0	21	0.64
1.5	39	0.84
2.0	88	1.01
2.5	326	1.10
3.0	∞	1.42

4.2. The HF molecule

The case of the HF molecule is different because at larger distances the Lippmann-Schwinger equation becomes divergent. The CISD model calculations were obtained with frozen F core and using 19 virtual orbitals (the top four was left frozen), resulting a CI Hamiltonian of dimension 1891.

Our conclusions are collected in Table 2. showing that the rapidly convergent cases (R=1.0 and 1.5) are characterized by Jacobian exponent well below 1.0, and the clear divergence (R=3.0) is indicated by max $|j|$=1.42. However, at the borderline of convergence and divergence we see two, seemingly convergent cases corresponding to max $|j|$ values slightly above 1.00. This could be either a consequence of the approximations of the stability analysis, or a divergence occurring after an apparent convergence to the prescribed numerical accuracy.

Once divergence appears, one may wonder how the iteration could be converted to a convergent one. The calculation for R =3.0 Å was repeated by the *a posteriori* analysis with fixed reduced resolvent, in which the precomputed exact energy was inserted. This resulted a convergent iteration where the 10^{-8} a.u. energy accuracy was achieved in 198 steps. This emphasizes that the simple Brillouin-Wigner type iteration, where the energy denominators are updated, could perhaps be improved by appropriate level shifts. Such ideas were found to be successful in previous studies in connection with Rayleigh-Schrödinger perturbation theory[5, 6].

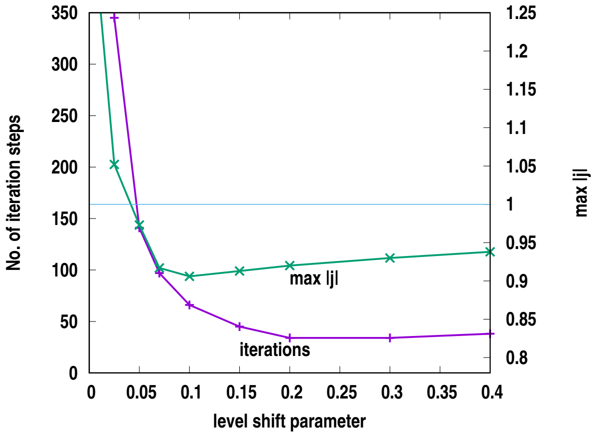
To study the effect of level shifts, we modify the partitioniong (2) to write

$$\hat{H} = \underbrace{\hat{H}^0 + \eta\hat{P}}_{\hat{H}^{0\prime}} + \underbrace{\hat{W} - \eta\hat{P}}_{\hat{W}^{\prime}}, \tag{18}$$

where P is the projector defined in Eq. (5).

Fig. 3. depicts the dependence of the number of required iterations and that of the maximal absolute Jacobian eigenvalue on parameter η for the divergent case of the HF molecule at 3.0 Å. It shows that using level shifts $\eta \geq 0.05$ results in a convergent iteration and pushes max $|j|$ below one. The number of iterations reaches its minimum at around $\eta = 0.2$. From this point, max $|j|$ values start to grow again, and the no. of iterations increases, too. However, the minimal value of max $|j|$ at $\eta = 0.1$ does not coincide exactly with the minimal no. of iterations. The points when iterations converge generally correspond to those where max $|j| < 1.0$ with the exception of $\eta = 0.025$ where the iteration is quite slow but converges within 345 steps, while $j = 1.05$.

Figure 3. The number of iteration steps to achieve 10^{-7} a.u. accuracy in energy when iterating the Lippmann-Schwinger equation for the HF molecule at $R = 3.0A$, as a function of the level shift parameter η. The maximal absolute valjue of Jacobian eigenvalues are also shown.



5. Conclusions

The stability analysis of the quasi-linear Lippman Schwinger equation for the energy-dependent reaction operator was performed on simplified models representd by electronic Hamiltonian matrices having a few thousands dimensions. Some of the Hamiltonians (those which correspond to much prolongated bond lengths in diatomics) described strongly correlated systems. The convergence of the iterations was set in parallel with the absolutely largest eigenvalue of the Jacobian of the iteration formula. It was found that the the criterion max $|j| < 1.0$ matches the convergence with a few exceptional points at the borderline. Appropriate level shift parameters may cure occurring divergences effectively, and parallels their influence on max $|j|$ values.

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