Schwinger-Lanczos algorithm for calculation of off-shell T-matrix elements and Wynn's epsilon algorithm

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Abstract

A generalization of the Schwinger-Lanczos algorithm for the calculation of the off-shell T-matrix elements is presented and shown to be equivalent to the Wynn's epsilon algorithm for acceleration of the Born series. Both methods are applied to the calculation of cross section for the dissociative attachment of electrons to hydrogen molecule, $e^- + \mathrm{H}_2 \to \mathrm{H} + \mathrm{H}^-$. Although formally fully equivalent both methods behave very differently numerically. It is shown that the Schwinger-Lanczos algorithm is more stable and generally superior to all other methods discussed in this paper.

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1 Introduction

A very efficient method for computing the T-matrix elements in the presence of non-local interactions, the Schwinger-Lanczos algorithm, was proposed recently [1]. This method has been successfully used in several realistic applications [2]-[4] to calculate cross sections for vibrational excitation, associative detachment and dissociative attachment based on the use of the non-local resonance model (NRM), where the non-locality of the nuclear dynamics stems from coupling of a discrete resonance state to the continuum. Originally, the method was designed for calculation of the diagonal T-matrix elements. In principle, it can be used also for calculation of non-diagonal T-matrix elements resulting from multichannel collisions, but the calculation is rather cumbersome and the incoming and outgoing states are not treated symmetrically. It is the purpose of this work to present a generalization of the Schwinger-Lanczos algorithm for the multichannel case and to establish its relation to other methods.

As is well known the T-matrix can be represented in the form of the Born series, which however often converges very slowly or does not converge at all [5]. Several methods have been developed to sum such a divergent series. In Section 4 one of these methods, the Wynn's epsilon algorithm, is discussed and proved to be equivalent to our generalization of the Schwinger-Lanczos algorithm. This formal equivalence does not imply equivalence of numerical properties. To show this we compare the numerical performance of all three methods applied to the dissociative attachment of an electron to the H_2 molecule. The model system studied represents a typical example of a resonance process in which a strong non-local interaction affects the nuclear dynamics. The development of very efficient procedures for the calculation of the T-matrix elements is important for case such as associative detachment calculations, where many partial waves contribute to cross section (see [6] for a $H+H^-$ associative detachment calculation including non-local effects).

We review briefly the Schwinger-Lanczos method in Section 2 and generalize it in Section 3. In section 4, a relation between the Wynn's epsilon algorithm and the generalized Schwinger-Lanczos method is established. A description of the dissociative attachment is shortly outlined in Section 5 and applications of the studied algorithms to this problem are discussed in more details. The numerical performance of all methods as applied to the problem of dissociative attachment is discussed in Section 6.

2 Short review of the Schwinger-Lanczos approach

According to the Schwinger variational principle [7] the T-matrix element

$$T_{\rm fi} \equiv \langle\phi_{\rm f}|T|\phi_{\rm i}\rangle = \langle\phi_{\rm f}|V(V - VG_0V)^{-1}V|\phi_{\rm i}\rangle \tag{1}$$

is given by the stationary value of the functional

$$T[\psi_-, \psi_+] = \langle\phi_{\rm f}|V|\psi_+\rangle + \langle\psi_-|V|\phi_{\rm i}\rangle - \langle\psi_-|V - VG_0V|\psi_+\rangle, \tag{2}$$

where V is an interaction potential and G_0 the free particle Green's function. This stationary value is achieved for $|\psi_\pm\rangle$ being solutions of the corresponding Lippmann-Schwinger equations. Considering $|\psi_\pm\rangle$ in the form

$$|\psi_\pm\rangle = \sum_{k=1}^{N} c_k^{(\pm)}|g_k\rangle, \tag{3}$$

with variational parameters $c_k^{(\pm)}$ we obtain an approximation to the T-matrix

$$T_{\rm fi}^N = \sum_{k,l=1}^{N} \langle\phi_{\rm f}|V|g_k\rangle(M^{-1})_{kl}\langle g_l|V|\phi_{\rm i}\rangle, \tag{4}$$

where the matrix M is given by $M_{kl} = \langle g_k|V - VG_0V|g_l\rangle$. The set of vectors $\{|g_k\rangle\}_{k=1}^N$ can be chosen arbitrarily (not necessarily orthogonal) provided that M_{kl} is a regular matrix. The Schwinger-Lanczos method (SLM) was proposed for calculation of the diagonal T-matrix elements [1], e.g. $|\phi_{\rm f}\rangle = |\phi_{\rm i}\rangle = |\phi\rangle$. In this method $T_{\rm fi}^N$ is calculated according to (4), with $|g_1\rangle = |\phi\rangle\langle\phi|V|\phi\rangle^{-1/2}$ and the set $\{|g_k\rangle\}_{k=1}^N$ is taken as V-orthogonal

$$\langle g_k|V|g_l\rangle = \delta_{kl} \tag{5}$$

and such that matrix VG_0V is tridiagonal

$$\begin{aligned} \langle g_{k-1}|VG_0V|g_k\rangle = \langle g_k|VG_0V|g_{k-1}\rangle &= \beta_{k-1}, & (6)\\ \langle g_k|VG_0V|g_k\rangle &= \alpha_k, & (7)\\ \langle g_k|VG_0V|g_l\rangle &= 0 \qquad \text{for} \quad |k-l| \geq 2. & (8)\end{aligned}$$

Let us note that the complex-symmetric scalar product (i.e. without complex conjugation) is used throughout this paper and not the usual (hermitian) one, since G_0 is a symmetric but non-hermitian operator. Only the matrix element $(M^{-1})_{11}$ is needed in (4) and this element is for a tridiagonal matrix M easily expressible in the form of a continued fraction. The T-matrix then reads

$$T^N = \langle\phi|V|g_1\rangle(M^{-1})_{11}\langle g_1|V|\phi\rangle = \frac{\langle\phi|V|\phi\rangle}{1-\alpha_1-\frac{\beta_1^2}{1-\alpha_2-\frac{\beta_2^2}{1-\alpha_3-\ldots-\frac{\beta_{N-1}^2}{1-\alpha_N}}}}. \qquad (9)$$

The numbers α_k, β_k and the vectors $|g_k\rangle$ with properties (5)-(8) are constructed according to the recurrence (see [1] and the refs. therein for more details about the Lanczos algorithm)

$$\begin{aligned} |r_k\rangle &= G_0V|g_k\rangle - \beta_{k-1}|g_{k-1}\rangle, & (10)\\ \alpha_k &= \langle g_k|V|r_k\rangle, & (11)\\ |s_k\rangle &= |r_k\rangle - \alpha_k|g_k\rangle, & (12)\\ \beta_k &= \langle s_k|V|s_k\rangle^{1/2}, & (13)\\ |g_{k+1}\rangle &= \beta_k^{-1}|s_k\rangle, & (14)\end{aligned}$$

with $|g_1\rangle = |\phi\rangle\langle\phi|V|\phi\rangle^{-\frac{1}{2}}$ and $\beta_0 = 0$.

The off-diagonal matrix elements of the $T-$matrix are also often needed in the applications. The same Lanczos basis with the properties (5)-(8) generated by the algorithm (10)-(14) and with the starting vector $|g_1\rangle = |\phi_\mathrm{i}\rangle\langle\phi_\mathrm{i}|V|\phi_\mathrm{i}\rangle^{-1/2}$ can be used in such a case. The formula for the T-matrix element resulting from (4) will be slightly more complicated than in the previous case

$$T_\mathrm{fi}^N = \sum_{k=1}^{N}\langle\phi_\mathrm{f}|V|g_k\rangle(M^{-1})_{k1}\langle g_1|V|\phi_\mathrm{i}\rangle. \qquad (15)$$

Note that now the first column of M^{-1} is needed instead of the single element M^{-1}_{11}. Using elementary algebra it turns out that

$$(M^{-1})_{k1} = \frac{\beta_1}{f_1}\frac{\beta_2}{f_2}\cdots\frac{\beta_{k-1}}{f_{k-1}}\frac{1}{f_k}, \tag{16}$$

where the quantities

$$f_k = 1 - \alpha_k - \beta_k^2/f_{k+1}, \qquad f_N = 1 - \alpha_N \tag{17}$$

are involved also in the calculation of the continued fraction (9). As pointed out in the reference [1] this approach does not treat in and out states in a symmetrical manner. For this reason the band Lanczos algorithm [8] was proposed [1] which leads to a banded instead of a tridiagonal matrix. Another approach preserving the tridiagonality of the matrix, but using different basis sets for in- and outgoing states will be presented in the next section. This approach represents a generalization of the standard SLM. We will refer to it as GSLM.

3 Generalization of SLM for off-diagonal T-matrix elements

A generalization of the SLM is obtained by expressing the functions $|\psi_\pm\rangle$ in the Schwinger variational principle (2) in the form

$$|\psi_\pm\rangle = \sum_{k=1}^{N} c_k^{(\pm)}|g_k^{(\pm)}\rangle, \tag{18}$$

introducing two different basis sets $\{|g_k^{(+)}\rangle\}_{k=1}^N$ and $\{|g_k^{(-)}\rangle\}_{k=1}^N$. The value of the functional (2) stationary with respect to variations of the coefficients $c_k^{(\pm)}$ is

$$T_{\rm fi}^N = \sum_{k,l=1}^{N} \langle\phi_{\rm f}|V|g_k^{(+)}\rangle(M^{-1})_{kl}\langle g_l^{(-)}|V|\phi_{\rm i}\rangle, \tag{19}$$

with

$$M_{kl} = \langle g_k^{(-)}|V - VG_0V|g_l^{(+)}\rangle.$$

If we define $|g_k^{(\pm)}\rangle$ in such a way, that

$$\begin{aligned}
\langle g_k^{(-)}|V|g_l^{(+)}\rangle &= \delta_{kl}, & (20)\\
\langle g_{k-1}^{(-)}|VG_0V|g_k^{(+)}\rangle = \langle g_k^{(-)}|VG_0V|g_{k-1}^{(+)}\rangle &= \beta_{k-1}, & (21)\\
\langle g_k^{(-)}|VG_0V|g_k^{(+)}\rangle &= \alpha_k, & (22)\\
\langle g_k^{(-)}|VG_0V|g_l^{(+)}\rangle &= 0 \qquad \text{for} \quad |k-l| \geq 2 & (23)
\end{aligned}$$

and $|g_1^{(+)}\rangle = |\phi_{\rm i}\rangle\langle\phi_{\rm f}|V|\phi_{\rm i}\rangle^{-1/2}$, $\langle g_1^{(-)}| = \langle\phi_{\rm f}|V|\phi_{\rm i}\rangle^{-1/2}\langle\phi_{\rm f}|$ then in analogy with (9)

$$T_{\rm fi}^N = \langle\phi_{\rm f}|V|g_1^{(+)}\rangle(M^{-1})_{11}\langle g_1^{(-)}|V|\phi_{\rm i}\rangle = \frac{\langle\phi_{\rm f}|V|\phi_{\rm i}\rangle}{1-\alpha_1-\frac{\beta_1^2}{1-\alpha_2-\frac{\beta_2^2}{1-\alpha_3-\ldots-\frac{\beta_{N-1}^2}{1-\alpha_N}}}}. \qquad (24)$$

It is simple to show by mathematical induction that vectors $|g_i^{(\pm)}\rangle$ with the properties (20)-(23) can be constructed from $|g_1^{(\pm)}\rangle$ according to the recurrence relations

$$\begin{aligned}
\langle r_k^{(-)}| &= \langle g_k^{(-)}|VG_0 - \beta_{k-1}\langle g_{k-1}^{(-)}|, & (25)\\
|r_k^{(+)}\rangle &= G_0V|g_k^{(+)}\rangle - \beta_{k-1}|g_{k-1}^{(+)}\rangle, & (26)\\
\alpha_k &= \langle g_k^{(-)}|V|r_k^{(+)}\rangle = \langle r_k^{(-)}|V|g_k^{(+)}\rangle, & (27)\\
\langle s_k^{(-)}| &= \langle r_k^{(-)}| - \alpha_k\langle g_k^{(-)}|, & (28)\\
|s_k^{(+)}\rangle &= |r_k^{(+)}\rangle - \alpha_k|g_k^{(+)}\rangle, & (29)\\
\beta_k &= \langle s_k^{(-)}|V|s_k^{(+)}\rangle^{1/2}, & (30)\\
\langle g_{k+1}^{(-)}| &= \beta_k^{-1}\langle s_k^{(-)}|, & (31)\\
|g_{k+1}^{(+)}\rangle &= \beta_k^{-1}|s_k^{(+)}\rangle. & (32)
\end{aligned}$$

4 GSLM and the Wynn's epsilon algorithm

In this Section we prove that our generalization of the Schwinger-Lanczos method is mathematically equivalent to the Wynn s epsilon algorithm. This equivalence does not mean, however, that both methods are equally efficient when used as tools for numerical calculations.

From Eqs. (25) - (32) it is obvious that the numbers α_j, β_j needed for calculation of $T_{\rm fi}^N$ can be expressed in terms of the quantities $\langle\phi_{\rm f}|V(G_0V)^k|\phi_{\rm i}\rangle$, which constitute the Born series for $T_{\rm fi}$ (for the determination of the $T_{\rm fi}^N$ only the quantities with $k < 2N$ are needed). The algorithm (25) - (32) together with the equation (24) can thus be understood as means of re-summation of the Born series. In light of this it therefore appears important to compare this algorithm with other algorithms for the acceleration of convergence of power series.

Let us write the T-matrix in terms of the Born series

$$T_{\rm fi} = \langle\phi_{\rm f}|V|\phi_{\rm i}\rangle + \langle\phi_{\rm f}|VG_0V|\phi_{\rm i}\rangle + \langle\phi_{\rm f}|VG_0VG_0V|\phi_{\rm i}\rangle + \dots \tag{33}$$

Introducing a coupling constant $V \to \lambda V$ this becomes a power series

$$T(\lambda) = \sum_{k=0}^{\infty} a_k\lambda^k = \lim_{n\to\infty} s_n, \tag{34}$$

with $a_0 = 0$ and $a_k = \langle\phi_{\rm f}|V(G_0V)^{k-1}|\phi_{\rm i}\rangle$ for $k > 0$. Formally, the sum of this series is defined as the limit of the sequence $s_0, s_1, s_2, \dots$ $\left(s_n = \sum_{k=1}^{n} a_k\lambda^k\right)$. In reality, however, this limit often does not exist or the series converges very slowly. Several methods how to accelerate the convergence can be found in the literature (Padé approximation, the MCF approach of Horacek and Sasakawa [9], [10], the Shanks transformation [11], etc.). The Shanks transformation of the sequence $\{s_n\}_{n=0}^{\infty}$ of an order k is the sequence $\{e_k(s_n)\}_{n=0}^{\infty}$ defined by the following ratio of determinants

$$e_k(s_n) = \begin{vmatrix} s_n & \dots & s_{n+k} \\ b_{n+1} & \dots & b_{n+k+1} \\ \vdots & \ddots & \vdots \\ b_{n+k} & \dots & b_{n+2k} \end{vmatrix} \Bigg/ \begin{vmatrix} 1 & \dots & 1 \\ b_{n+1} & \dots & b_{n+k+1} \\ \vdots & \ddots & \vdots \\ b_{n+k} & \dots & b_{n+2k} \end{vmatrix}, \tag{35}$$

where the abbreviation $b_j = s_j - s_{j-1} = a_j\lambda^j$ was used. Shanks showed that this transformation is equivalent to the Padé approximant $[n+k, k]_T(\lambda)$. The expression (35) is not convenient for numerical calculations due to occurrence of determinants. However, as shown by Wynn, the quantities $e_k(s_n)$ can be expressed in terms of other quantities, $\epsilon_i^{(j)}$, obtained from the following nonlinear recurrence scheme (Wynn's epsilon algorithm - see [12])

$$\epsilon_{-1}^{(n)} = 0 \qquad \epsilon_0^{(n)} = s_n \tag{36}$$

$$\epsilon_{k+1}^{(n)} = \epsilon_{k-1}^{(n+1)} + 1/[\epsilon_k^{(n+1)} - \epsilon_k^{(n)}]. \tag{37}$$

Both quantities are related as follows

$$\epsilon_{2k}^{(n)} = e_k(s_n) \text{ and } \epsilon_{2k+1}^{(n)} = 1/e_k(a_n\lambda^n). \tag{38}$$

To accelerate the convergence of the sequence $\{s_n\}_{n=0}^{\infty}$ by means of the Shanks transformation means to replace the sequence $\{s_n\}_{n=0}^{\infty}$ by $\{e_n(s_0)\}_{n=0}^{\infty}$. In what follows we prove that the quantities $T_{\text{fi}}^{(N)}$ obtained from GSLM coincide with $e_N(s_0)$.

According to the recurrence relations (25) - (32), the vectors $\{|g_k^{(+)}\rangle\}_{k=1}^{N}$ span the same space (the Krylov space) as the vectors

$$\{|p_k\rangle\}_{k=1}^{N} = \{|\phi_{\text{i}}\rangle, G_0V|\phi_{\text{i}}\rangle, ..., (G_0V)^{N-1}|\phi_{\text{i}}\rangle\} \tag{39}$$

and vectors $\{\langle g_k^{(-)}|\}_{k=1}^{N}$ the same as

$$\{\langle q_k|\}_{k=1}^{N} = \{\langle\phi_{\text{f}}|, \langle\phi_{\text{f}}VG_0, ..., \langle\phi_{\text{f}}|(VG_0)^{N-1}\}. \tag{40}$$

Thus from the equation (19), $T_{\text{fi}}^{(N)}$ can be written as

$$T_{\text{fi}}^{N} = \sum_{k,l=1}^{N} \langle\phi_{\text{f}}|V|p_k\rangle(M^{-1})_{kl}\langle q_l|V|\phi_{\text{i}}\rangle = \sum_{k,l=1}^{N} b_k(M^{-1})_{kl}b_l, \tag{41}$$

where

$$M_{kl} = \langle q_k|V - VG_0V|p_l\rangle = b_{k+l-1} - b_{k+l}. \tag{42}$$

With the use of the Cramer's rule $(M^{-1})_{kl} = (-1)^{k+l}m_{kl}/|M|$ (where m_{kl} are minors of the matrix M), the T-matrix, equation (41), can be expressed in the form $T_{\text{fi}}^{(N)} = t/|M|$ with

$$t = \sum_{k,l} b_k b_l m_{kl}(-1)^{k+l} = \sum_k b_k B_k. \tag{43}$$

Here, B_k are obtained from the matrix M by replacing the k^{th} column of M by the vector $(b_1, b_2, ..., b_N)$

$$B_k \equiv \begin{vmatrix} b_1 - b_2 & b_2 - b_3 & \dots & b_1 & \dots & b_N - b_{N+1} \\ b_2 - b_3 & b_3 - b_4 & \dots & b_2 & \dots & b_{N+1} - b_{N+2} \\ \vdots & \vdots & & \vdots & & \vdots \\ b_N - b_{N+1} & b_{N+1} - b_{N+2} & \dots & b_N & \dots & b_{2N-1} - b_{2N} \end{vmatrix}. \tag{44}$$

If we interchange the first and the k-th column and subsequently subtract the new first column from the second, then second from the third, ..., $(k-1)$-th from the k-th we obtain

$$B_k = \begin{vmatrix} b_1 & \dots & b_k & b_{k+1} - b_{k+2} & \dots & b_N - b_{N+1} \\ b_2 & \dots & b_{k+1} & b_{k+2} - b_{k+3} & \dots & b_{N+1} - b_{N+2} \\ \vdots & & \vdots & \vdots & & \vdots \\ b_N & \dots & b_{N+k-1} & b_{N+k} - b_{N+k+1} & \dots & b_{2N-1} - b_{2N} \end{vmatrix}. \tag{45}$$

Repeated use of the formula

$$\begin{vmatrix} a_1 + b_1 & A_{12} & \dots & A_{1N} \\ \vdots & \vdots & & \vdots \\ a_N + b_N & A_{N2} & \dots & A_{NN} \end{vmatrix} = \begin{vmatrix} a_1 & A_{12} & \dots & A_{1N} \\ \vdots & \vdots & & \vdots \\ a_N & A_{N2} & \dots & A_{NN} \end{vmatrix} + \begin{vmatrix} b_1 & A_{12} & \dots & A_{1N} \\ \vdots & \vdots & & \vdots \\ b_N & A_{N2} & \dots & A_{NN} \end{vmatrix} \tag{46}$$

yields

$$t = \sum_{k=1}^{N} b_k \sum_{l=k}^{N} (-1)^{N+l} C_{l+1} \tag{47}$$

with

$$C_{l+1} = \begin{vmatrix} b_1 & \dots & b_l & b_{l+2} & \dots & b_{N+1} \\ b_2 & \dots & b_{l+1} & b_{l+3} & \dots & b_{N+2} \\ \vdots & & \vdots & \vdots & & \vdots \\ b_N & \dots & b_{N+l-1} & b_{N+l+1} & \dots & b_{2N} \end{vmatrix}. \tag{48}$$

Changing the order of the sums we obtain

$$t = \sum_{l=1}^{N} \sum_{k=1}^{l} (-1)^{N+l} b_k C_{l+1} = \sum_{l=1}^{N} (-1)^{N+l} s_l C_{l+1}, \tag{49}$$

which is the first row expansion of

$$t = (-1)^N \begin{vmatrix} s_0 & s_1 & \dots & s_N \\ b_1 & b_2 & \dots & b_{N+1} \\ \vdots & \vdots & \ddots & \vdots \\ b_N & b_{N+1} & \dots & b_{2N} \end{vmatrix}. \tag{50}$$

Furthermore

$$|M| = \begin{vmatrix} b_1 - b_2 & \dots & b_N - b_{N+1} \\ \vdots & \ddots & \vdots \\ b_N - b_{N+1} & \dots & b_{2N-1} - b_{2N} \end{vmatrix} = \sum_k (-1)^{N+k+1} C_k, \tag{51}$$

which is the first row expansion of the determinant

$$(-1)^N \begin{vmatrix} 1 & 1 & \dots & 1 \\ b_1 & b_2 & \dots & b_{N+1} \\ \vdots & \vdots & \ddots & \vdots \\ b_N & b_{N+1} & \dots & b_{2N} \end{vmatrix}. \tag{52}$$

Comparing $t/|M|$ with the definition (35) we clearly see that $T_{\mathrm{fi}}^{(N)} = e_N(s_0) = [N/N]_T(\lambda)$. This completes the proof.

5 Dissociative electron attachment on H_2

As it was shown in the previous section the GSLM and WEA are fully equivalent and should therefore yield same results. In fact the two methods are quite different from the numerical point of view. Especially in the case of strongly divergent Born series we expect the performance of WEA to be rather poor, because relevant information about the dynamic is lost by storing large terms of the divergent series in computer memory with a limited accuracy.

In the derivation of GSLM we have seen that a more flexible basis was used in GSLM than that for SLM and therefore GSLM is expected to converge more rapidly. On the other hand more calculations are needed for one iteration of GSLM.

To compare the performance of SLM, GSLM and WEA on the physically relevant system we have chosen the non-local resonance model of Gertitschke and Domcke [13] for the dissociative attachment (DA) of an electron to $\mathrm{H_2}$ molecule. The importance of the non-local effects for this system has been emphasised [13, 14] and usual methods for solving the Schrödinger equation can not be applied. The model is described in detail elsewhere [13]. Here we discuss only the aspects of the model relevant for the application of the tested method.

The model is based on the projection operator description of the diabatic discrete state (describing the unstable $\mathrm{H_2^-}$ scattering complex) interaction with the continuum ($\mathrm{H_2}$+$\mathrm{e^-}$). Motion of nuclei in the discrete state is described with the potential $V_{\mathrm{d}}(R)$ (R is the internuclear distance). Coupling with the continuum adds the non-local effective potential F to this local term.

The scattering state $\langle K^{(-)}|$ with the outgoing asymptotic condition and with $E = \frac{1}{2\mu}K^2$ being the kinetic energy of the dissociative motion H+H$^-$ is the unique solution of the Lippmann-Schwinger equation (see [15])

$$\langle K^{(-)}| = \langle K_{\mathrm{d}}^{(-)}| + \langle K^{(-)}|FG_{\mathrm{d}}, \tag{53}$$

where $\langle K_{\mathrm{d}}^{(-)}|$ is the scattering solution for the local potential $V_{\mathrm{d}}(R)$ and G_{d} is the Green function

$$G_{\mathrm{d}} = (E - T_{\mathrm{N}} - V_{\mathrm{d}} + i\varepsilon)^{-1}, \qquad T_{\mathrm{N}} = -\frac{1}{2\mu}\frac{d^2}{dR^2} \tag{54}$$

for this potential. Cross section σ_{DA} for the dissociative attachment of an electron with energy $\frac{1}{2}k_i^2$ (atomic units) to the molecule H_2 in the vibrational state $|\nu_i\rangle$ reads

$$\sigma_{\mathrm{DA}} = \frac{4\pi^3}{k_i^2}\nu|T_{\mathrm{DA}}|^2, \tag{55}$$

where

$$T_{\mathrm{DA}} = \langle K^{(-)}|V_{\mathrm{d}k_i}|\nu_i\rangle \tag{56}$$

is the T-matrix element and $V_{\mathrm{d}k}(R)$ the discrete-state-continuum coupling. The functions $V_{\mathrm{d}k}(R)$, $V_{\mathrm{d}}(R)$ and the operator F for the model of Gertitschke and Domcke are given in [13].

Equation (56) together with (53) gives

$$T_{\mathrm{DA}} = \langle K_{\mathrm{d}}^{(-)}|F(F - FG_{\mathrm{d}}F)^{-1}F \cdot F^{-1}V_{\mathrm{d}k_i}|\nu_i\rangle, \tag{57}$$

which is of the form (1) and variational approach (18) - (24) can be applied with $\langle\phi_f| \to \langle K_{\mathrm{d}}^{(-)}|$, $V \to F$, $G_0 \to G_{\mathrm{d}}$ and $|\phi_i\rangle \to F^{-1}V_{\mathrm{d}k_i}|\nu_i\rangle$ and with the vectors $|g_k^{(\pm)}\rangle$ and the numbers α_k, β_k given by the recurrence (25) - (32). There are two ways how to avoid the occurrence of F^{-1}. First is to write T_{DA} as

$$T_{\mathrm{DA}} = \langle K_{\mathrm{d}}^{(-)}|V_{\mathrm{d}k_i}|\nu_i\rangle + \langle K_{\mathrm{d}}^{(-)}|F(F - FG_{\mathrm{d}}F)^{-1}F \cdot G_{\mathrm{d}}V_{\mathrm{d}k_i}|\nu_i\rangle, \tag{58}$$

and to calculate $\langle K_{\mathrm{d}}^{(-)}|F(F - FG_{\mathrm{d}}F)^{-1}F \cdot G_{\mathrm{d}}V_{\mathrm{d}k_i}|\nu_i\rangle$ with the starting vector $|\phi_i\rangle = G_{\mathrm{d}}V_{\mathrm{d}k_i}|\nu_i\rangle$. We did our calculations in the second way, starting directly from (57), but rewriting the algorithm (25)-(32) for vectors

$|g_k^{;(+)}\rangle = V|g_k^{(+)}\rangle$. This only changes the order of operators V and G_0 in (26) and V is not present in (27) and (30). The starting vector is $|g_1^{;(+)}\rangle = V_{\mathrm{d}k_i}|\nu_i\rangle\langle K_{\mathrm{d}}^{(-)}|V_{\mathrm{d}k_i}|\nu_i\rangle^{-1/2}$.

The accurate calculation of the DA cross section in the threshold region is known to be a difficult task. It turns out that GSLM for DA converges rather slowly for energies near the threshold. As was shown in [3] the convergence can be accelerated if a certain local approximation V_{L} is subtracted from F and included in V_{d}. The local approximation proposed in [3] is

$$V_{\mathrm{L}}(R) = \int_0^\infty F(R,R')dR'. \tag{59}$$

Subtraction of this local potential is done so that in all the results F is replaced by $F_{\mathrm{L}} = F - V_{\mathrm{L}}$ and V_{d} with $V_{\mathrm{d}} + V_{\mathrm{L}}$. Especially the T-matrix element reads

$$T_{\mathrm{DA}} = \langle K_{\mathrm{L}}^{(-)}|F_{\mathrm{L}}(F_{\mathrm{L}} - F_{\mathrm{L}}G_{\mathrm{L}}F_{\mathrm{L}})^{-1}F_{\mathrm{L}} \cdot F_{\mathrm{L}}^{-1}V_{\mathrm{d}k_i}|\nu_i\rangle \tag{60}$$

where $\langle K_{\mathrm{L}}^{(-)}|$ is the scattering solution in the potential $V_{\mathrm{d}} + V_{\mathrm{L}}$ and $G_{\mathrm{L}} = (E - T_{\mathrm{N}} - V_{\mathrm{d}} - V_{\mathrm{L}} - i\varepsilon)^{-1}$.

The Green's function G_{L} or G_d needed for evaluation of the T_{DA} can be expressed in terms of the regular and the irregular solution of the Schrödinger equation with the potential $V_{\mathrm{d}}(R)$ and $V_{\mathrm{d}}(R)+V_{\mathrm{L}}(R)$ respectively, using usual formula

$$G(E,R,R') = -\frac{1}{W}\psi_{\mathrm{r}}(E,R_<)\psi_{\mathrm{irr}}(E,R_>), \tag{61}$$

where $\psi_{\mathrm{r}}(E,R)$ and $\psi_{\mathrm{irr}}(E,R_>)$ are the regular and the irregular solutions, W is their Wronskian and $R_<$, $R_>$ is the smaller and the larger of the values R, R' respectively.

6 Test of numerical performance

In this Section we apply all three methods, SLM, GSLM and WEA to the calculation of the dissociative attachment cross section for attachment of low-energy electrons to H_2 molecule as described in the previous Section. All calculations were done in REAL*8 Fortran77 arithmetics. The wave functions were calculated for internuclear distances $R < 8$ a.u. on a grid using 1000 mesh points. To calculate the non-local potential F methods described in detail in [3] were used; *i.e.* F was expanded in eigenstates of the adiabatic Hamiltonian for the electronic ground state of H_2. In the case of H_2, 24 expansion functions guarantee convergence for all the calculations discussed in this paper.

Let us first discuss the original SL method. To calculate the T-matrix, T_{DA}^N, for N iterations of the method N basis functions $\{|g_i\rangle\}_{i=1}^N$ are needed. We denote as σ_N the cross section obtained from (55) with $T_{\mathrm{DA}} = T_{\mathrm{DA}}^N$.

To evaluate the T-matrix using GSLM to the same order N, however, $2N$ basis functions $\{|g_i^\pm\rangle\}_{i=1}^N$ are required. To account for this we denote as σ_{2N} the cross section derived from T_{DA}^N in this case. The most time-consuming step in the calculation is the application of the non-local potential F to a wave function $|\psi\rangle$ (calculation of an element $\langle\psi'|F|\psi\rangle$ is much faster). In the SLM and GSLM this needs to be done N and $2N$ times, respectively. The calculation of $e_N(S_0)$ in WEA requires knowledge of the matrix elements

$$\langle\phi_{\mathrm{f}}|V|\phi_{\mathrm{i}}\rangle, \langle\phi_{\mathrm{f}}|VG_0V|\phi_{\mathrm{i}}\rangle, ..., \langle\phi_{\mathrm{f}}|V(G_0V)^{2N-1}|\phi_{\mathrm{i}}\rangle,$$

which means $2N$ applications of F. For the same reason we denote as σ_{2N} the cross section obtained from $T_{\mathrm{DA}}^N = e_N(s_0)$ in this case. Thus N measures time of the calculation of σ_N in all three methods.

As is well known the DA cross section changes dramatically when energy of the incident electron approaches the threshold. For this reason we found it necessary to test all methods for two energies; one just above the threshold and one sufficiently high above the threshold.

Numerical performance of all the methods is shown in Figures 1-4. Logarithm (base 10) of the relative error $|\sigma_N - \sigma_\infty|/\sigma_\infty$ is plotted against the number of iterations N. The value σ_N with N sufficiently large (so that σ_N does not change with increasing N) is taken as σ_∞. Since WEA did not always fully converge it was necessary to take σ_∞ from other methods. The full line represents GSLM, dashed line SLM with T_{DA} computed according to (15)-(17) and diamonds represent the results of WEA.

Figure 1 shows the rate of convergence of the calculation of the dissociative attachment cross section for all three methods at the energy of the incoming electron $E_{\mathrm{el}} = 8$ eV; i.e. at an energy far from the DA threshold, $E_{th} = 3.71$ eV. At this energy we observe that both SLM and GSLM methods fully converged after 25-30 steps with SLM showing slightly faster convergence. The WEA behaves differently. As expected the first few iterations of WEA yielded almost the same values as that of GSLM. Then after giving roughly four significant figures of σ, WEA failed to converge due to the accumulation of numerical errors.

As shown in Section 4 both methods, GSLM and WEA, are formally equivalent. WEA may be interpreted as a Schwinger approach using the Krylov vectors $|p_k\rangle = (G_0V)^{(k-1)}|\phi_i\rangle$. Since the $|p_k\rangle$ and the Lanczos vectors $|g_1^{(+)}\rangle$ used in GSLM span the same space, the results of WEA and GLSM must be identical when the calculation is performed with infinite precision. Using finite precision, however, $|p_k\rangle$ and $|p_{k+1}\rangle$ become indistinguishable for sufficient large k because $|p_k\rangle$ converges for $k \to \infty$ towards the eigenvector of G_0V with the absolute largest eigenvalue. Additional iterations can then no longer improve the WEA results.

The performance of the WEA can be improved by subtracting the local approximation mentioned above (60) because this reduces the absolute values of the eigenvalues of G_0V. The results obtained in this way are plotted in Figure 2. Now all methods yield fully converged results.

As mentioned above the calculation at an energy close to the threshold is much more difficult. In Figure 3 we show results obtained at the energy $E_{\mathrm{el}} = 3.72$eV. At this energy the Born series diverges strongly and also the WEA fails to yield convergent results. Both methods are completely useless in this energy range. On the other hand, GSLM and SLM converge even in this case (though slowly). Subtraction of the local potential, see Figure 4, improves the convergence and WEA and GSLM give practically identical results. Again the original SLM method provides fastest convergence.

7 Conclusions

The SLM has been generalized for the calculation of the non-diagonal matrix elements of the T-matrix resulting from the multichannel collisions. This generalization is shown to be mathematically equivalent to the Wynn's epsilon algorithm for the acceleration of the Born series. This however does not imply that both methods are equally efficient numerically. All methods, SLM, GSLM and WEA were tested on the example of dissociative attachment process treated in the resonance model with strongly non-local dynamics (dissociative attachment of an electron to H_2 molecule) which represents a very typical example of molecular resonance processes. It was shown that despite its formal equivalence with GSLM, WEA breaks down for energies near the DA threshold where the Born series strongly diverges. GSLM and SLM converge (though slowly) even in this case. It is possible to improve the convergence rate of all methods by extracting a part of the non-local interaction redefining the local potential. If this is done the WEA and GSLM yield results of comparable quality. Concluding we may say that the original SLM method which proved so successful in all previous calculations represents the most reliable methods from that discussed in this paper. It is numerically stable, converges even without modifications of the non-local potential for all energies. The generalized method GSLM yields results very similar to that of SLM. The WEA as well as the Born series cannot be generally used without significant modifications of the underlying interactions.

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Figure 1: Convergence rates for the calculation of the e^-+H_2 dissociative attachment cross section at the electron energy $E_{\rm el} = 8$ eV. Logarithm (base 10) of the relative error is plotted against the number of calculation steps (see the text). Solid line: - the results of GSLM, dashed line: - the results obtained by the original SLM method; diamonds: - the results of WEA.

Figure 2: Convergence rates for the calculation of the e^-+H_2 dissociative attachment cross section at the same electron energy $E_{\rm el} = 8$ eV as in Figure 1. The rate of convergence was accelerated by subtracting a local approximation V_L, Eq. (60), from the non-local potential F.

Figure 3: The same as in Figure 1 but for the energy $E_{\rm el} = 3.72$ eV (just above the threshold).

Figure 4: The same as in Figure 3 but the local approximation was subtracted from the non-local potential F.

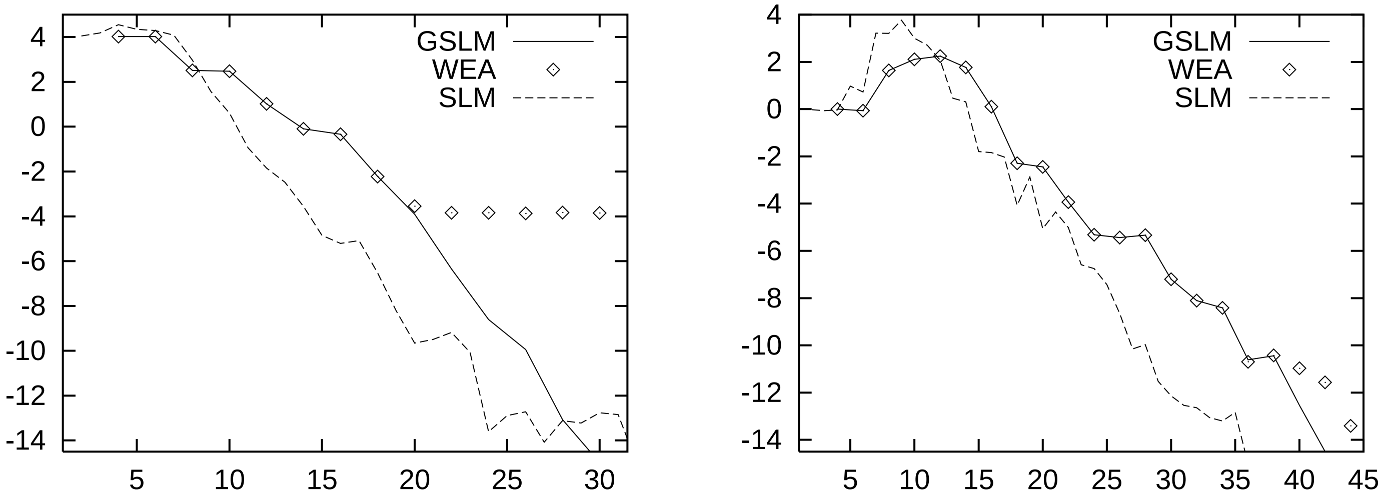

Figure 1,2

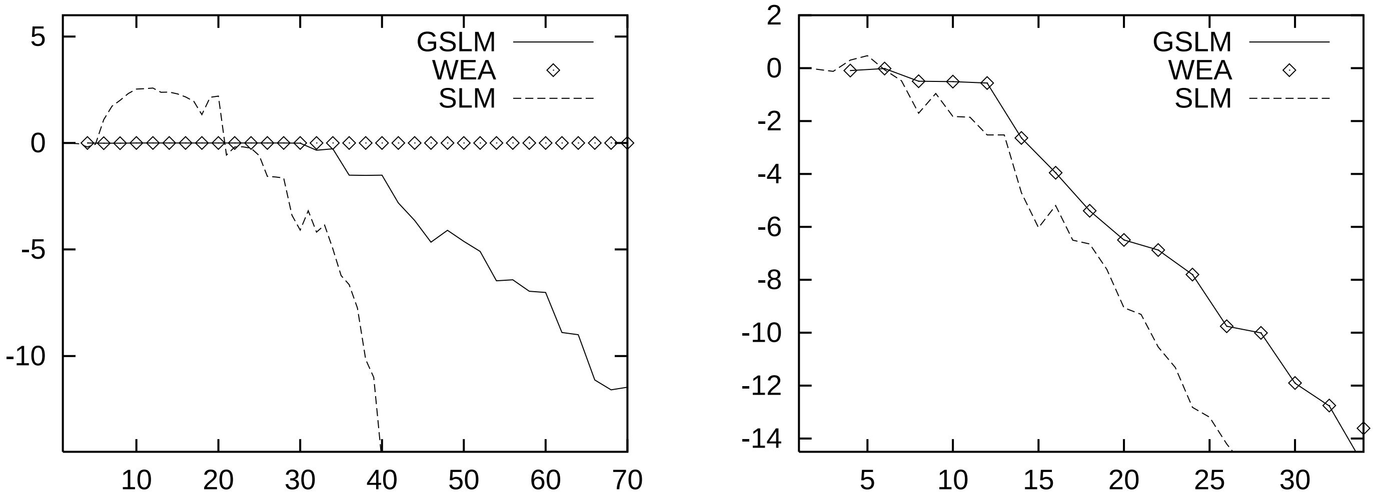

Figure 3,4