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GREEN FUNCTIONS METHOD FOR COLLINEAR ATOM-DIATOM INELASTIC SCATTERING

By A. Raczyński

Institute of Physics, N. Copernicus University, Toruń*

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The Green functions method of Csanak et al. has been applied to calculate vibrational transition probabilities for collinear atom-harmonic oscillator inelastic scattering. A finite basis expansion has been used to express Green's functions appearing in the formulas for the optical potential and the transition potential which have been calculated with all terms of first and second order included. Integral Dyson equations with a non-local potential have been solved. Transition probabilities are compared with those of Ficocelli Varracchio et al.

1. *Introduction*

The aim of our work was to test numerically a certain approximation within the scope of the Green functions method applied to the calculation of transition probabilities in the process of collinear atom-diatom scattering.

The method which is based on the hierarchy of equations for field-theoretical Green's functions and on the decoupling technique of Martin and Schwinger has been proposed and discussed in detail in the series of papers [1-4]. It was originally formulated for electron-atom scattering. Numerical tests for elastic [5] and inelastic [6, 7] electron-atom scattering yielded quite good results though in the latter case the method was applied in the lowest order. Later the method has been generalized to be applied to the case of atom-diatom scattering [8] where there is a need to consider two different fields of atoms and diatoms in the formalism of second quantization.

Numerical tests for a one-dimensional model have been carried out by Ficocelli Varracchio et al. [9] giving satisfactory results. Our work which concerns the same model has been performed independently of theirs and differs from it in one significant point: we use the same approximation from the point of view of the Green functions hierarchy and the decoupling scheme but we made a finite basis expansion of some of the Green functions which the

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* Address: Instytut Fizyki, Uniwersytet M. Kopernika, Grudziądzka 5, 87-100 Toruń, Poland.

authors of [9] calculated exactly. Our version could be convenient for more complicated models for which no exact calculations are possible and also for some models with many open channels so it seems interesting to compare our results with those of [9].

2. *Theory*

In this section we will present the most important features of the theory and the basic equations. A more detailed presentation can be found in paper [8] and a full exposition of the theory in [1]. Let us consider a model of an atom of mass m scattered by a diatomic molecule, $V(\boldsymbol{x}, \boldsymbol{y})$ being the interaction; $\boldsymbol{x}$ denotes the coordinate of the relative motion and $\boldsymbol{y}$ the set of internal coordinates of the molecule.

Our aim is to calculate the elements of the T-matrix which have the following form

$$T_{fi} = \int dx dx' \varphi^{*}_{k_f}(x) \sum (x, x', \varepsilon_{k_i}) f^{(+)}_{k_i}(x') \tag{1}$$

for elastic collisions and

$$T_{fi} = \int dx dx' f^{(-)*}_{k_f}(x) V_{f\leftarrow i}(x, x', \tfrac{1}{2}(\varepsilon_{k_i}+\varepsilon_{k_f})) f_{k_i}(x') \tag{2}$$

for inelastic collisions.

$\boldsymbol{k}_i, \varepsilon_{k_i}, \boldsymbol{k}_f, \varepsilon_{k_f}$ denote momenta and kinetic energies in the initial and final state, respectively. $\sum$ is a complex, non-local, energy-dependent optical potential which allows one to treat the elastic process as a potential scattering, all effects like absorption of the incoming flux, target polarization etc. being included in $\sum$. $V_{f\leftarrow i}$ is a transition potential discussed in detail in [9]. φ is a plane wave and $f^{(\pm)}_k$ are solutions of the following equation with incoming-wave (outgoing-wave) boundary conditions

$$\left(\varepsilon_k + \frac{1}{2m}\nabla^2_x\right) f_k(x) - \int dx' \sum (x, x', \varepsilon_k) f_k(x') = 0, \tag{3}$$

$$\boldsymbol{k} = \boldsymbol{k}_i, \boldsymbol{k}_f, \qquad \varepsilon_k = \frac{k^2}{2m}$$

or in the integral form

$$f_k(x) = \varphi_k(x) + \int dx' dx'' G_0(x, x', \varepsilon_k) \sum (x', x'', \varepsilon_k) f_k(x''). \tag{4}$$

G_0 is a free-particle Green function with appropriate boundary conditions.

Exact expressions for $\sum$ and $V_{f\leftarrow i}$ are very complicated (Eqs. (17″) and (27) of [8]). $\sum$ contains a local first-order part which is the atom-diatom interaction potential averaged in the non-perturbed initial (ground) state of the target. Further components of $\sum$ are of higher orders and can be expressed by means of the functional derivative of $\sum$ with respect to an auxiliary potential and the one-particle Green function which satisfies the following equation

$$\left(\varepsilon_k + \frac{1}{2m}\nabla^2_x\right) G(x, x', \varepsilon_k) - \int dx'' \sum (x, x'', \varepsilon_k) G(x'', x', \varepsilon_k) = \delta(x - x'). \tag{3'}$$

$\boldsymbol{V}_{if\,t}$ can also be expressed by means of the derivative of $\sum$.

A natural approximation is to include only the first-order component of $\sum$ in the functional derivatives. If we do that we obtain the following expressions for $\sum$ and $V_{f\leftarrow i}$

$$\sum(x, x', \varepsilon) = \delta(x-x')V_{ii}(x)+\sum_{n\neq i} V_{in}(x)G(x, x', \varepsilon-\omega_{ni})V_{ni}(x'), \tag{5}$$

$$V_{f\leftarrow i}(x, x', \varepsilon) = -\delta(x-x')V_{fi}(x), \tag{6}$$

where $V_{ni}(x)$ is a matrix element of $V(x, y)$ between the initial and n-th excited state of the target. We have set $\omega_{ni} = E_n-E_i$. Eq. (5) turns out to be a good approximation for the optical potential $\sum$. To get $\sum$ ready for calculations it is necessary to solve Eqs. (3′) and (5) together so that self-cosistency is achieved. Eq. (6) is a crude approximation for the transition potential. We can get a far better one if we use $\sum$ from Eq. (5) and not only the first term of it to be variationally differentiated. We get then

$$V_{f\leftarrow i}(x, x', \varepsilon) = -\delta(x-x')V_{fi}(x)-\sum_{n\neq i,f} V_{fn}(x)G(x, x', \varepsilon+\tfrac{1}{2}(\omega_{fn}-\omega_{ni}))V_{ni}(x')$$

$$-[V_{ff}(x)-V_{ii}(x)]G(x, x', \varepsilon-\tfrac{1}{2}\,\omega_{fi})V_{fi}(x')+W_3. \tag{7}$$

W_3 contains terms of third and higher orders which we will neglect in our computations. In fact it turned out to worsen rather than to improve the results in [9]. One cause of it could be that W_3 did not contain all terms of the third order.

The discussion of different terms of Eq. (7) has been presented elsewhere [4, 9].

To get the transition probabilities we have to solve self-consistently Eqs. (3′) and (5) and then Eq. (4) for the incoming and outgoing wave. Finally we must calculate appropriate matrix elements (Eqs. (1), (2)).

It is convenient to represent the Green's function in its spectral form ([1, 8])

$$G(x, x', \omega) = \lim_{\eta\to 0+} \sum_k \frac{g_k(x)g_k^*(x')}{\omega-\varepsilon_k+i\eta}, \tag{8}$$

where the functions g_k satisfy the equation

$$\left(\varepsilon_k+\frac{1}{2m}\nabla_x^2\right)g_k(x)-\int dx' \sum(x, x', \varepsilon_k)g_k(x') = 0. \tag{9}$$

In the present calculation we made only one step in the procedure of solving (3′) and (5): we neglected the second-order term of $\sum$ in Eq. (9) and got

$$\left(\varepsilon_k+\frac{1}{2m}\nabla_x^2\right)g_k(x)-V_{ii}(x)g_k(x) = 0. \tag{9′}$$

Through (8) we constructed the Green function in the static approximation and after inserting it into (5) we obtained the optical potential.

The main difference between our work and [9] is that we have solved Eq. (9′) in a finite basis set while the authors of [9] used the exact solutions of (9′) and were able to perform the summation over k in (8) in an exact way.

We are aware that in making our approximation we missed the imaginary part of $\sum$ which was responsible for the absorption of the incoming flux and thus for inelastic scattering. In fact the authors of [6] and [7] made a similar approximation for electron-atom collisions and in spite of that they obtained good results.

3. *The model and numerical calculations*

The model to which we will apply the theory is a collinear atom-harmonic oscillator collision with an exponential repulsive potential. The model has often been used to test approximate methods in collision theory [10–12]. By a suitable coordinate transformation [11] the hamiltonian of our problem

$$H = -\frac{1}{2m_A}\frac{\partial^2}{\partial x_A^2} - \frac{1}{2m_B}\frac{\partial^2}{\partial x_B^2} - \frac{1}{2m_C}\frac{\partial^2}{\partial x_C^2} + \tfrac{1}{2}k(x_B - x_C - r_0)^2 + C_1 \exp\left[-\alpha_1(x_A - x_B)\right] \tag{10}$$

can be reduced to the form

$$H = -\frac{1}{2m}\frac{\partial^2}{\partial x^2} + Ce^{-\alpha(x-y)} - \tfrac{1}{2}\frac{\partial^2}{\partial y^2} + \tfrac{1}{2}y^2, \tag{11}$$

which is the hamiltonian of a structureless particle with appropriately reduced mass m colliding with the harmonic oscillator of unit mass and frequency. C is a constant on which the exact transition probabilities do not depend and α describes the steepness of the interaction.

The unit of energy is chosen to be the energy interval between the oscillatory states of the molecule. The potential matrix elements are $V_{mn}(x) = V_{mn}e^{-\alpha x}$, the elements V_{mn} can be found in the paper of Rapp and Sharp [23].

The free-particle Green function $\left(\text{i.e. Green's function for the operator } \varepsilon_k + \frac{1}{2m}\frac{d^2}{dx^2}\right)$ is

$$G_0(x, x', \varepsilon_k) = -\frac{im}{k}e^{ik|x-x'|},$$

$k = \mp\sqrt{2m\varepsilon_k}$ for incoming (outgoing) particle, respectively. As we have mentioned above, Eq. (9′) was solved in a finite basis; we applied the Jacobi diagonalization procedure.

For our model for which there are no atom-diatom bound states the simplest basis one could think of consisted of trigonometric functions. With C taken large enough so that our functions should vanish practically for $x < 0$ they had the following form

$$u_n(x) = \begin{cases} \sqrt{\dfrac{2}{l}}\sin\dfrac{n\pi x}{l} & \text{for } x \in (0, l) \\ 0 & \text{for } x \leqslant 0 \text{ and } x \geqslant l, \end{cases}$$

where l was a parameter which we could change. It seemed reasonable to take l smaller than the whole range of integration of Eq. (3) which meant neglecting the polarization effect outside the interval $(0, l)$ though the static potential was still non-negligible there.

Once the solutions of Eq. (9′) had been obtained we were able to construct the optical potential and the main numerical problem was to solve the integral equation

$$f_k(x) = e^{-ikx} - \frac{im}{k}\int dx'dx''e^{ik|x-x'|}\Big[V_{ii}(x')\delta(x'-x'') + \sum_{n\neq i}\sum_{q}\sum_{sp}\frac{V_{in}(x')a_{qs}u_s(x')a_{qp}u_p(x'')V_{ni}(x'')}{\varepsilon_k-\varepsilon_q-\omega_{ni}}\Big]f_k(x''), \tag{12}$$

where $g_q = \sum_s a_{qs}u_s(x)$ are finite-basis solutions of Eq. (9′).

The integration of (12) for $f_{k_i}^{(+)}$ and $f_{k_f}^{(-)}$ was performed by means of the Sams and Kouri technique [14] suitably adapted for kernels of finite order.

We performed our calculations for the case of "steep interaction" $\alpha = 0.3$, $m = \frac{2}{3}$ (which are the parameters for He—H_2 collision). It seemed that namely in this case our approximation should give the best results because the interval on which the polarization effect was taken into account could be made smaller and our finite-basis expansion should be more accurate. On the other hand our approximation can be used also for "adiabatic interactions" (smaller α) in the cases in which the solutions do not oscillate too quickly (small k_i, k_f).

In our calculations it sufficed to set C equal to 25, the range of integration was taken as 50. The summation over n contained for all energies at least one closed channel which was more than necessary, as verified by Ficocelli Varracchio et al. The number of basic functions was taken equal to 15 which seemed enough for relatively small values of l. Reducing this number to 14 and 13 did not affect the results for $l = 15$ (except for the largest energies for which we got a small quantitative difference).

As only the real part of the optical potential was taken into account, the probabilities of elastic scattering calculated with the T-matrix from Eq. (1) should be equal to unity. In our procedure of solving the integral equation there appeared waves distorted only by the static potential, so we were able to reproduce the DW results of Jackson and Mott [10] without special effort. An examination of the asymptotic form of the functions-solutions of Eq. (12) was also performed. The three tests mentioned above allowed us to check our program and to choose parameters like the range and the step of integration.

The computational effort in our case was proportional to the number of basic functions while in [9] it was proportional to the number of channels included in the summation over n.

4. *Results*

We got relatively the best results for small l ($l = 15$). The $0-1$ transition probabilities are shown in Fig. 1 compared with those yielded by other methods. Our results are better than those of Jackson and Mott who totally neglected the polarization effects. The probabilities calculated in our work are in fairly good agreement with those of [9] both for the cases when $V_{f\leftarrow i}$ contained terms of first and of first and second order. Our points in Fig. 1 show how the probabilities were changing when second-order terms in $V_{f\leftarrow i}$ were being gradually taken into account.

We have also performed some tests for other values of the parameter l and we present some of the results (Fig. 2). For $l = 16\ 2/3$ the results were generally in good qualitative but not quantitative agreement with those for $l = 15$. For larger values of $l (l = 26\ 2/3)$ the results were worse and so were those for $l = 30$ (which we do not present here). There was no even qualitative agreement between the latter two series of transition probabilities as well as between either of them and the results of [9]. It seems due to the fact that our expansion was too short for larger values of l (which was confirmed by a test). Calculations with the basis significantly enriched would not be economical.

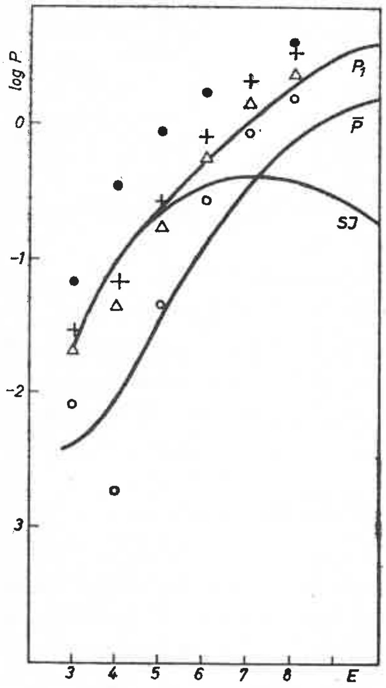

Fig. 1

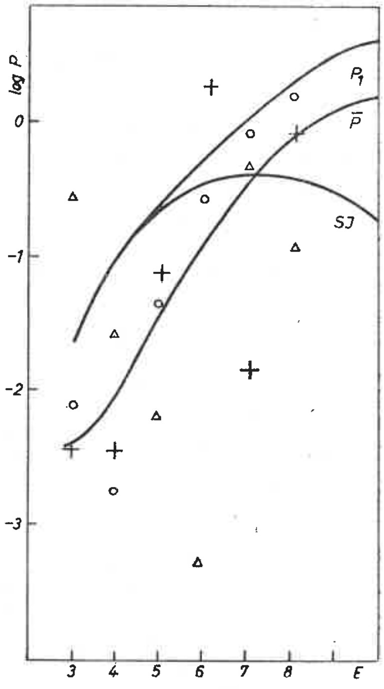

Fig. 2

Fig. 1. 0—1 transition probabilities as functions of energy. SJ — accurate results of Secrest and Johnson, P_1 — results of Ficocelli Varracchio et al. with only the first-order term included in $V_{f\leftarrow i}$, $\bar{P}$ — with terms of first and second order in $V_{f\leftarrow i}$, ● — results of Jackson and Mott, + — present calculations with only the first-order term in $V_{f\leftarrow i}$, ○ — with terms of first and second order in $V_{f\leftarrow i}$, ▵ — without the contribution of the final state correction

Fig. 2. 0—1 transition probabilities as functions of energy. Curves SJ, P_1, $\bar{P}$ as in Fig. 1, ○ — present calculations with terms of first and second order in $V_{f\leftarrow i}$ for $l = 15$, + — the same for $l = 16\ 2/3$, ▵ — the same for $l = 26\ 2/3$

Our results for $0-2$ transitions were much better than those of Jackson and Mott (which were much too small) and do not differ more than by a unit (on a logarithmic scale) from those of [9]. Here the contribution of second-order terms was essential as including only the first-order term yielded the results comparable with those of Jackson and Mott. In Fig. 3 we show our 0 – 2 probabilities for different values of l. For all three cases the qualitative behaviour is satisfactory.

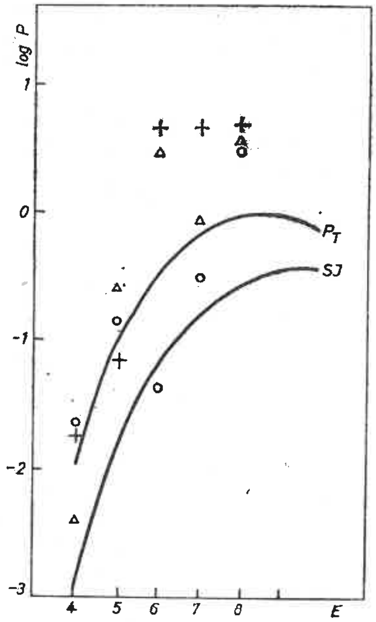

Fig. 3. 0—2 transition probabilities as functions of energy. SJ — accurate results of Secrest and Johnson, P_T — results of Ficocelli Varracchio et al. with terms of first, second and partially third order included in $V_{f\leftarrow i}$, ○ — present calculations with terms of first and second order in $V_{f\leftarrow i}$ for $l = 15$, + — the same for $l = 16\,2/3$, △ — the same for $l = 26\,2/3$

As mentioned above, the exact results do not depend on the constant C. Our calculations for $l = 15$ and a larger C were also performed and the results were in good qualitative but not quantitative agreement with the previous ones. This suggests that it would be more appropriate to use more sophisticated basic functions depending on C as a parameter.

5. *Conclusions*

The Green functions method has been tested on a simple collision model. The approximation based on neglecting the imaginary parts of the second-order optical and transition potentials and on expanding their real parts in a finite basis has been examined. The quantitative results turned out to depend on the length of the interval on which the polarization effects were taken into account. In the case when the basis seemed to be rich enough our probabilities appeared to be better than those of Jackson and Mott and to be, in general, in good qualitative agreement with those of Ficocelli Verracchio et al., however, for some particular energies and transitions there were larger differences.

Though our approximation can cause spurious fluctuations of some transition probabilities it allows one to improve the DWA results and to take into account, however in an imperfect way, some non-adiabatic polarization effects neglected by the latter method. It seems that finite-basis approximations within the Green functions method can be used in the future and should be examined in more detail. In particular one may employ more sophisticated basic functions, try to achieve self-consistence of the Green functions and optical potentials and include in some way non-Hermitian parts of optical and transition potentials. Finite-basis expansions can replace more exact expressions for example when exact DWA solutions are not available, when the self-consistency procedure mentioned above is difficult to perform in another way or, for economical reasons, when the number of open channels to be included is larger than the necessary number of basic functions.

On the other hand the approximation would fail in the cases in which there is a need to expand rapidly oscillating functions on a large interval (i.e. when the mass and kinetic energy of the projectile are large and the interaction potential is slowly decreasing).

We think that an atom-rigid rotator collision would be another even more interesting model to continue testing approximations of the type presented here.

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