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The short-range reaction matrix in MQDT treatment of dissociative recombination and related processes

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Abstract. We discuss the Lippmann-Schwinger equation which governs the short-range reaction matrix (**K**-matrix) in the two-step multichannel quantum defect theory (MQDT) of dissociative recombination and related processes. We show that, if the energy dependence of the electronic coupling between the dissociative state and the ionization continua can be neglected, the convergence of the Born expansion of the Lippmann-Schwinger equation is achieved at second order. For the case of energy-dependent interaction, higher order effects are tested using a non-perturbative method for solving the Lippmann-Schwinger equation. Numerical examples are given for the dissociative recombination and vibrational de-excitation of the H_2^+ molecular ion.

PACS. 34.80.Gs Molecular excitation and ionization by electron impact – 34.80.Ht Dissociation and dissociative attachment by electron impact – 34.80.Lx Electron-ion recombination and electron attachment

1 Introduction

Collisions between slow electrons and molecular ions induce various processes (ro-vibrational excitation and de-excitation, dissociative recombination) which may influence the ro-vibrational temperature and the ionization degree of cold molecular plasmas, as those occurring in the interstellar medium, or at the wall of the fusion devices. The experimental determination of the rate coefficients for these processes, and for specific ion initial states, is difficult, especially for the case of homonuclear diatomic ions. Indeed, the absence of permanent dipole prevents homonuclear diatomic from relaxing radiatively, even when stored for several seconds in ion storage rings [1]. It is therefore important that theoretical evaluation of these rate coefficients may support or complement their experimental determination, both to assess their absolute values for a given ion initial state, and to analyze the reaction mechanism which may radically affect the order of magnitude of the cross-sections and rates.

The theoretical study of such processes involves two equally important aspects, which may be treated in a single step or in sequence, depending on the approach. One first needs a good knowledge of the electronic structure of the system, both of the ion AB^+ and of the neutral molecule AB formed by electron recombination: potential energy curves, electronic or non-adiabatic interactions, Rydberg states and their quantum defects. The second aspect is the treatment of the dynamics, which involves both electronic and nuclear dynamics, and their mutual interactions. Indeed, especially when dissociation occurs as in dissociative recombination, we have to deal with a "reactive" collision event with electron scattering in the entrance channel, and heavy particles as products. Besides global approaches such as the R-matrix, mostly used for calculating vibrational [2] and rotational [3] transitions, a 2-step method [4], adapted from the multichannel quantum defect theory [5] (MQDT), has been widely used and improved along the past 20 years. This approach rests on a quasi-diabatic description of molecular states [6], in which only part of the electronic Hamiltonian is diagonalized, within subspaces of electronic states of similar nature: Rydberg states with ground state ion core (*i.e.* mono-excited states), Rydberg states with excited ion core and various kinds of valence states (*i.e.* di-excited or more).

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These molecular states serve as a basis for defining a first set of scattering channels (electron-ion or atom-atom), which are then coupled by the remaining electronic couplings, not included in the basis molecular states. These couplings should not be too strong (or else, an adiabatic representation is certainly more appropriate), but play the main role in the dynamics of the reactive process, by mixing the various types of channels which leads to various types of fragmentation.

Starting from the electronic couplings left out in the basis set definition, encompassed in an operator $\mathbf{V}$, a short-range reaction matrix $\mathbf{K}$ is built, by solving the Lippmann-Schwinger integro-differential equation [7]

$$\mathbf{K} = \mathbf{V} + \mathbf{V}\frac{1}{\mathbf{E} - \mathbf{H}_0}\mathbf{K} \tag{1}$$

where $\mathbf{H}_0$ is the Hamiltonian operator excluding the electronic interaction $\mathbf{V}$.

The method for solving the Lippmann-Schwinger equation depends both on the strength of the interaction $\mathbf{V}$, and on its variations with the electron energy. In the case of a weak Rydberg-valence interaction, a perturbative solution, based on a Born expansion in terms of the interaction matrix elements, can be used. In the original application of MQDT to DR and related processes [4], only the first term of the series was retained, *i.e.* $\mathbf{K} = \mathbf{V}$. Later, Gubermann and Giusti-Suzor [8] extended the range of validity of the method by including the second order of perturbation.

Takagi [9] was the first to investigate the possibility of solving the Lippmann-Schwinger equation beyond perturbation theory. Using an iterative grid method, he obtained a fixed-mesh numerical solution which, in case of strongly energy-dependent channel interactions, was quite different from the approximate one. Some years later, Pichl and his co-workers [11] re-visited the subject and treated the singular kernel analytically.

The purpose of this paper is mainly to assess the range of validity of the so-called perturbative treatment of the $\mathbf{K}$-matrix, at first and second order, and to evaluate when and how much higher-order effects may change the magnitude or the shape of the cross-sections. In the following we show that:

(i) if the energy-dependence of the electronic interaction $\mathcal{V}(R)$ between the dissociative states and the ionization continua can be neglected, convergence of the Born expansion of the Lippmann-Schwinger equation is actually achieved at second order, which means that the second order perturbation formula

$$\mathbf{K} = \mathbf{V} + \mathbf{V}\frac{1}{\mathbf{E} - \mathbf{H}_0}\mathbf{V} \tag{2}$$

is, in fact, *exact.* This approximation is often valid since the electronic coupling is mainly built at short distance where the external electron is strongly accelerated by the Coulomb attraction and thus insensitive to small differences in kinetic energy;

(ii) if the energy-dependence of the electronic coupling cannot be neglected, but can be factorized with respect to its R-dependence, *i.e.*

$$\mathcal{V}_\varepsilon(R) = p(\varepsilon)\mathcal{V}(R) \tag{3}$$

Pichl *et al.* have shown that a tractable solution of the Lippmann-Schwinger may be obtained by solving a system of algebraic equations [11]. Using this efficient numerical method we present some model calculations showing the effects of higher orders of the $\mathbf{K}$-matrix induced *via* the energy-dependence of the electronic interaction.

2 The short-range reaction matrix

The elements of the short-range reaction matrix K are subject to the Lippmann-Schwinger equation (1) which gives rise to a system of coupled integro-differential equations in coordinate representation. In the energy representation, this system of equations may be written:

$$K_{ji}(E', E) = V_{ji}(E', E) + \sum_k P \int \mathrm{d}E'' \frac{V_{jk}(E', E'')K_{ki}(E'', E)}{E - E''} \cdot \tag{4}$$

Here, we note by $V_{ji}(E', E)$ the matrix elements obtained from the coupling operator linking two *electronic* states, $\mathcal{V}_\varepsilon(R)$ in coordinate representation, by integration over the nuclear coordinate R. Actually, our choice of quasi-diabatic representation for the molecular states implies that the interaction operator $\mathbf{V}$ has no matrix elements between two ionization channels, nor between two dissociation channels:

$$V_{v_1 v_2}(E'_1, E'_2) = 0 \tag{5}$$

$$V_{d_1 d_2}(E_1, E_2) = 0. \tag{6}$$

As for the interaction between an ionization channel and a dissociative one, it is built on the coupling between the corresponding electronic states, $\mathcal{V}_\varepsilon(R)$, which may depend on the energy ε of the outer electron in the ionization channel:

$$V_{vd}(E', E) = V_{dv}(E, E') = \int \chi_v(R)\mathcal{V}\varepsilon(R)F_{d\epsilon}(R)\mathrm{d}R$$
$$\varepsilon = E' - E_v \qquad \epsilon = E - E_d \tag{7}$$

where $F_{d\epsilon}$ is the energy-normalized regular eigenfunction in the dissociative channel, E_d the asymptotic energy of the electronic dissociative state, ϵ the kinetic energy release of the atomic products, and χ_v the ion vibrational wave-function with energy E_v.

2.1 Case of energy-independent interchannel coupling

We first evaluate the reaction matrix element corresponding to the interaction between two dissociative channels, $K_{d_1d_2}(E_1,E_2)$,

$$\begin{aligned}K_{d_1d_2}(E_1,E_2) &= V_{d_1d_2}(E_1,E_2)\\ &+\sum_d P\int \mathrm{d}E\frac{V_{d_1d}(E_1,E)K_{dd_2}(E,E_2)}{E_2-E}\\ &+\sum_v P\int \frac{V_{d_1v}(E_1,E')K_{vd_2}(E',E_2)}{E_2-E'}\mathrm{d}E'.\end{aligned} \tag{8}$$

The first two terms in the right hand side are zero in our quasi-diabatic approach (Eq. (6)). We now assume that the electronic couplings are independent on the energy of the external electron (Rydberg or in the continuum), which implies, according to equation (7), that the interaction matrix elements, after integration over the nuclear coordinate, depend exclusively on the kinetic energy release of the dissociating molecule:

$$V_{d_1v}(E_1,E') \equiv V_{d_1v}(E_1) \tag{9}$$

$$V_{vd_1}(E',E_1) \equiv V_{vd_1}(E_1). \tag{10}$$

The expression (8) for the valence-valence **K**-matrix element thus reduces to:

$$K_{d_1d_2}(E_1,E_2)=\sum_v V_{d_1v}(E_1)P\int\frac{K_{vd_2}(E',E_2)}{E_2-E'}\mathrm{d}E' \tag{11}$$

which is decoupled with respect to the two energy variables E_1 and E_2. To go one step further, we need to express the Rydberg-valence reaction matrix elements $K_{vd_2}(E',E_2)$. Following equation (4), we obtain:

$$\begin{aligned}K_{vd_2}\,(E',E_2) &= V_{vd_2}(E',E_2)\\ &+\sum_{d_3}P\int\frac{V_{vd_3}(E',E_3)K_{d_3d_2}(E_3,E_2)}{E_2-E_3}\mathrm{d}E_3\\ &+\sum_v P\int \mathrm{d}E_1'\frac{V_{vv_1}(E',E_1')K_{v_1d_2}(E_1',E_2)}{E_2-E_1'}\end{aligned} \tag{12}$$

which, owing to equations (10, 5), reduces to:

$$K_{vd_2}(E_2)=V_{vd_2}(E_2)+\sum_{d_3}P\int\frac{V_{vd_3}(E_3)K_{d_3d_2}(E_3,E_2)}{E_2-E_3}\mathrm{d}E_3. \tag{13}$$

These **K**-matrix elements do not depend on E'. The expression (11) thus becomes

$$K_{d_1d_2}(E_1,E_2)=\sum_v V_{d_1v}(E_1)K_{vd_2}(E_2)I(E_2)=0 \tag{14}$$

since the principal part integral $I(E_2)$

$$I(E_2)=P\int_{-\infty}^{\infty}\frac{\mathrm{d}E'}{E_2-E'}=0 \tag{15}$$

is obviously zero. The formula (14) was used in reference [8] *on*-the-energy-shell ($E_1=E_2$), but we show here that (i) this equation is *exact* and (ii) it also applies *off*-the-energy-shell.

Coming back to $K_{vd_2}(E',E_2)$, equation (13) now reduces to:

$$K_{vd_2}(E',E_2)=V_{vd_2}(E',E_2)=V_{vd_2}(E_2) \tag{16}$$

since $K_{d_3d_2}(E_3,E_2)=0$ from equation (14). This is the second order formula for the $K_{vd_2}(E',E_2)$ matrix element (12), which is in fact *exact* and depends on E_2 (the right-hand-side argument) only.

For the Rydberg-Rydberg matrix elements $K_{v_1v_2}(E_1',E_2')$, we have, according to equation (4):

$$\begin{aligned}K_{v_1v_2}\,(E_1',E_2') &= V_{v_1v_2}(E_1',E_2')\\ &+\sum_v P\int \mathrm{d}E'\frac{V_{v_1v}(E_1',E')K_{vv_2}(E',E_2')}{E_2'-E'}\\ &+\sum_d P\int \mathrm{d}E\frac{V_{v_1d}(E_1',E)K_{dv_2}(E,E_2')}{E_2'-E}\end{aligned} \tag{17}$$

which, following equations (5, 10), reads:

$$K_{v_1v_2}(E_1',E_2')=\sum_d P\int \mathrm{d}E\frac{V_{v_1d}(E)K_{dv_2}(E,E_2')}{E_2'-E}. \tag{18}$$

We already see that $K_{v_1v_2}(E_1',E_2')$ is independent of E_1', the left-hand-side energy argument. To go further, we need to express explicitly the matrix elements $K_{dv_2}(E,E_2')$ which may not be directly written as in equation (16), since E and E_2' do not appear symmetrically in equation (4). We start from

$$\begin{aligned}K_{dv_2}(E,E_2') &= V_{dv_2}\,(E,E_2')\\ &+\sum_v V_{dv}(E)P\int\frac{K_{vv_2}(E',E_2')}{E-E'}\mathrm{d}E',\end{aligned} \tag{19}$$

and, since $K_{vv_2}(E',E_2')$ is independent of the left-hand-side argument E', the integral term vanishes as in equation (15), and we get:

$$K_{dv_2}(E,E_2')=V_{dv_2}(E,E_2')=V_{dv_2}(E) \tag{20}$$

which is similar to equation (16). Finally, using equations (20, 18), we obtain:

$$\begin{aligned}K_{v_1v_2}(E_1',E_2') &= \sum_d P\int \mathrm{d}E\frac{V_{v_1d}(E)V_{dv_2}(E)}{E_2'-E}\\ &= K_{v_1v_2}(E_2'),\end{aligned} \tag{21}$$

which is the previously used second order $K_{v_1v_2}(E_1',E_2')$ matrix element [8], being in fact *exact* and dependent on E_2' only. This completes the proof that for energy-independent coupling, the second order perturbative solution coincides with the exact one, *both on*-shell and *off*-shell.

Coming to computational aspects, the $K_{v_1v_2}$ terms in (21), written more explicitly as:

$$K_{v_1v_2}(E) = P\int \mathrm{d}\epsilon \frac{\langle\chi_{v_1}|\mathcal{V}(R)|F_\mathrm{d}(\epsilon)\rangle\langle F_\mathrm{d}(\epsilon)|\mathcal{V}(R)|\chi_{v_2}\rangle}{E-(E_d+\epsilon)} \tag{22}$$

may be evaluated directly by calculating the principal part (or Cauchy) integral in this energy representation, *e.g.* with a Chebyshev integration method. Alternatively we may use, as in reference [8], the *on*-shell ($E = E_d + \epsilon$) expression in the R representation:

$$K_{v_1v_2}(E) = \frac{1}{w}\iint \chi_{v_1}(R)\mathcal{V}(R)F_{d\epsilon}(R_<) \times G_{d\epsilon}(R_>)\mathcal{V}(R')\chi_{v_2}(R')\mathrm{d}R\mathrm{d}R' \tag{23}$$

where $G_{d\epsilon}$ is the irregular solution of the dissociative state nuclear Schrödinger equation, lagging in phase by $\pi/2$ with respect to the regular solution $F_{d\epsilon}$, and w is the Wronskian of the two functions $F_{d\epsilon}$ and $G_{d\epsilon}$.

We have checked numerically the excellent agreement between these two methods, provided the integral in (21) is carried out on the whole energy spectrum (bound and continuum) of the dissociative wave functions $F_{d\epsilon}$ involved.

2.2 Case of energy-dependent interchannel coupling

In general, the electronic coupling also depends on the electron energy ε to a certain extent, and therefore, according to (7), the integral matrix element $V_{dv}(E, E')$ depends on the two energy variables, E' and E. However, if the coupling $\mathcal{V}_\varepsilon(R)$ can be factorized as in equation (3), the matrix element $V_{dv}(E, E')$ decouples in E and E'. Pichl *et al.* [11] recently discussed this case in detail, under the name of quasi-separable coupling. Let us briefly summarize their results since we compare below the **K**-matrix solutions for constant and general electron energy profiles. Due to equation (3), the energy kernel (7) in Lippmann Schwinger equation (4) ($E' = E_v + \varepsilon$ and $E = E_d + \epsilon$) separates in the form

$$V_{dv}(E, E') = p(E' - E_v)V_{dv}(E), \tag{24}$$

where $V_{dv}(E)$ is given by equation (7), and the on-shell **K**-matrix solution, from which the cross-sections will be obtained, are given explicitly as

$$K_{dd}(E) = \sum_v \pi_v\beta_v V_{dv}(E), \quad K_{vd}(E) = \beta_v p(E - E_v) \tag{25}$$

and

$$\begin{aligned} K_{v_1v_2}(E) &= \gamma_{v_1v_2}p(E - E_{v_1}), \\ K_{dv}(E) &= \sum_{v'}\left[p\left(E - E_v\right)\delta_{vv'} + \pi_{v'}\gamma_{v'v}\right]V_{dv'}(E), \end{aligned} \tag{26}$$

where $K_{ij}(E)$ stands for $K_{ij}(E, E)$ for simplicity. The reduced matrix elements β and γ in the above equations are solutions of the linear systems

$$\begin{aligned} &\sum_{v'}[\delta_{vv'} - \pi_{vv'}\pi_{v'}]\beta_{v'} = V_{dv}(E), \\ &\sum_{v'}[\delta_{v_1v'} - \pi_{v_1v'}\pi_{v'}]\gamma_{v'v_2} = p(E - E_{v_2})\pi_{v_1v_2}, \end{aligned} \tag{27}$$

and π_v, $\pi_{vv'}$ are principal value integrals respectively given by

$$\pi_v(E) \equiv P\int_{-\infty}^{\infty} \frac{p^2(E' - E_v)}{E - E'}\,\mathrm{d}E'$$

and

$$\pi_{vv'}(E) \equiv P\int_{E_d}^{\infty} \frac{V_{dv}(E')V_{dv'}(E')}{E - E'}\,\mathrm{d}E'. \tag{28}$$

This **K**-matrix solution is more general than the previous one, restricted to energy-independent interchannel couplings. For the still more general case of *non-separable* interaction, an exact **K**-matrix can also be obtained by solving a larger system of coupled equations resulting from an expansion of the interaction- and reaction-matrix elements in Chebyshev polynomials [11].

3 Calculations

We have used the tools presented in Section 2 to compute cross-sections for dissociative recombination (DR) and super-elastic collisions (transitions $v \to v', v' < v$) (SEC) of H_2^+ ions with slow electrons, using a non-perturbative resolution of the Lippmann-Schwinger equation. By comparing the results obtained at second order of the **K**-matrix for energy-independent electronic coupling, with the results of the resolution of linear coupled equations for an energy-dependent coupling, we can check the off-shell effects, since the perturbation series of the **K**-matrix was found to converge at second order in the case of energy-independent electronic interaction. In addition, in the case of constant coupling we will compare the results obtained at first and second order of the **K**-matrix.

These test calculations are performed for the 2 lowest vibrational states ($v = 0, 1$) of H_2^+, and only the lowest $(2p\sigma_u)^2\ {}^1\Sigma_g^+$ dissociative state of H_2 was considered. The short-range **K**-matrix is built from the electronic coupling between this doubly excited state and the mono-excited manifold with ${}^1\Sigma_g^+$ symmetry (either electron-ion continuum or Rydberg states, which are treated in an unified way in the MQDT approach). For the tests with an energy-dependent electronic coupling, we have used a coupling function for which the energy- and R-dependence may be factorized as in equation (3). The R-dependent part $\mathcal{V}(\mathrm{R})$ of the coupling is the same function as in our previous calculations [12,13] while the energy profile $p(\varepsilon)$ is extracted from calculations performed by Hara and Sato [10] in the static exchange approximation, with a linear extrapolation below the threshold. To be more specific, their calculations, performed only for the dσ partial wave of the continuum electron, lead to a coupling function — plotted

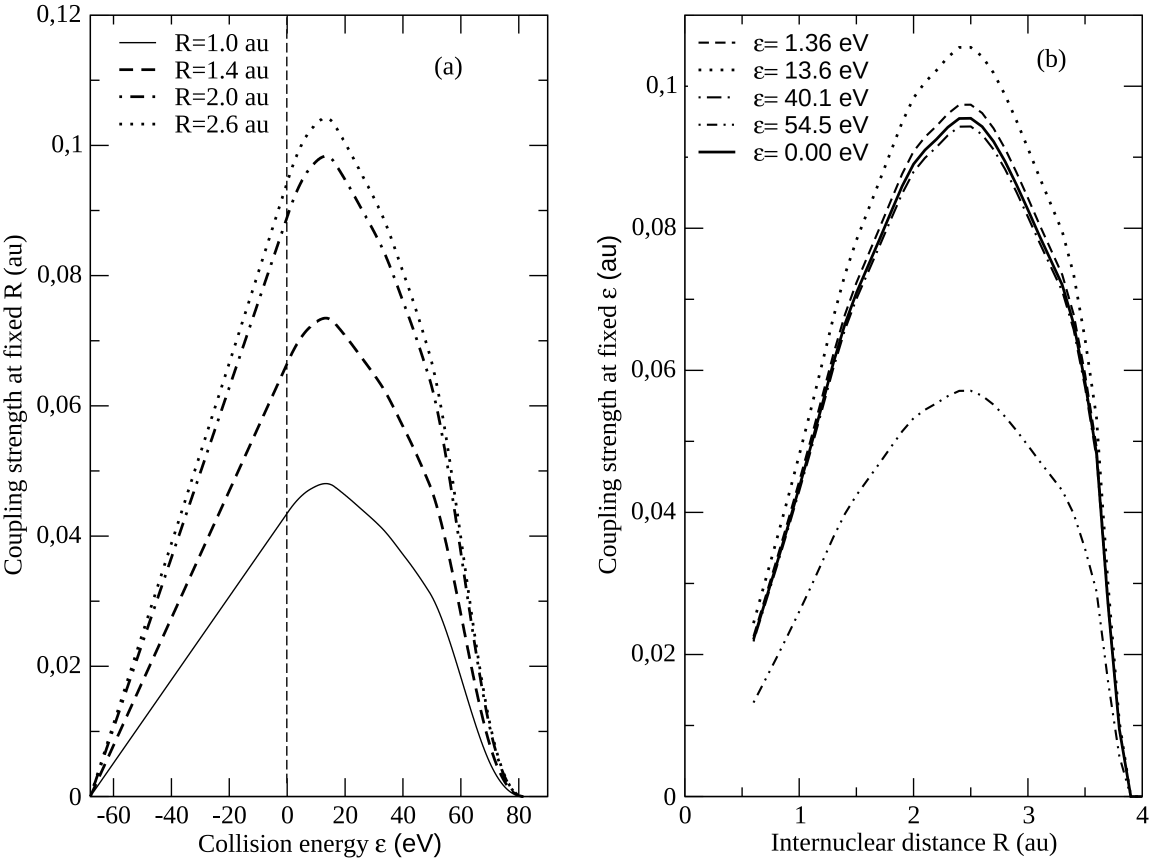

Fig. 1. Coupling strength of the dσ partial wave of the continuum electron with the ${}^1\Sigma_g^+(2p\sigma_u)^2$ dissociative state for H$_2$. The couplings $\mathcal{V}_\varepsilon(\mathcal{R})$ is represented in (a) as a function of collision energy for some internuclear distances and in (b) as a function of internuclear distance for some values of the collision energy (adapted from Ref. [10]).

in Figure 1 — which has been shown by Pichl *et al.* [11] to be nearly separable. The energy factor $p(\varepsilon)$ in equation (3) has been adjusted such that the resulting coupling $\mathcal{V}_\varepsilon(R)$ coincides for $\varepsilon = 0$ with our R-dependent constant coupling *i.e.* $p(0) = 1$. Our calculations also involve the $s\sigma$ electron partial wave for which the electronic coupling [12,13] is assumed here to have the same energy-dependence as for the dσ partial wave.

Figure 2 shows the DR (for $v = 0$ initial ion level, left-hand side) and the SEC ($v = 1 \rightarrow \ v = 0$, rigth-hand side) cross-sections obtained in three calculations where the Lippmann-Schwinger equation is solved with different methods *i.e.* first order perturbative method (a), second order (b) and non-perturbative method (c). The couplings used in calculations (a) and (b) are energy-independent while those of calculation (c) depend on the electron energy. For each case, we show the cross-sections obtained for the so-called direct process, in which only the direct transition from the electron continuum to the dissociative state is considered, and for the total one (direct + indirect) in which temporary capture into Rydberg states is included. The magnitudes of the direct cross-sections are very close in the three calculations, proving that the differences found in the total cross-sections can be attributed to the change in both positions and shapes of the Rydberg resonances due to the indirect process. The resonance pattern of cross-sections (a) is very different from that of calculations (b) and (c). In the first order cross-sections (a) the resonances are pure windows while in (b) and (c) they are either windows or peaks, which proves that part of the indirect mechanism is not taken into account in the first order calculations. This is clearly displayed in SEC cross-sections (right-hand side of Fig. 2). This process has been shown [13] to be dominated by electronic interactions which indirectly couple the vibrational levels of Rydberg states *via* the doubly excited state, and the **K**-matrix elements linked to these interactions are neglected in first order calculations.

In order to evaluate the averaged effect of the higher order **K**-matrix, we have convoluted the cross-sections of Figure 2 over an anisotropic Maxwellian distribution of electron velocity, with two temperatures ($kT_{e\perp} = 12$ meV and $kT_{e\parallel} = 0.1$ meV) typical of recent storage ring experiments [1]. The convoluted cross-sections are shown in Figure 3. Except for very low energy ($\varepsilon < 10^{-2}$ eV), the differences between the energy-independent calculations (dashed lines) and the energy-dependent ones (full lines) are generally small. The larger differences near threshold (about a factor of 2) are due to the low-lying resonances and are restricted to a small energy range (note the logarithmic energy scale of the figures).

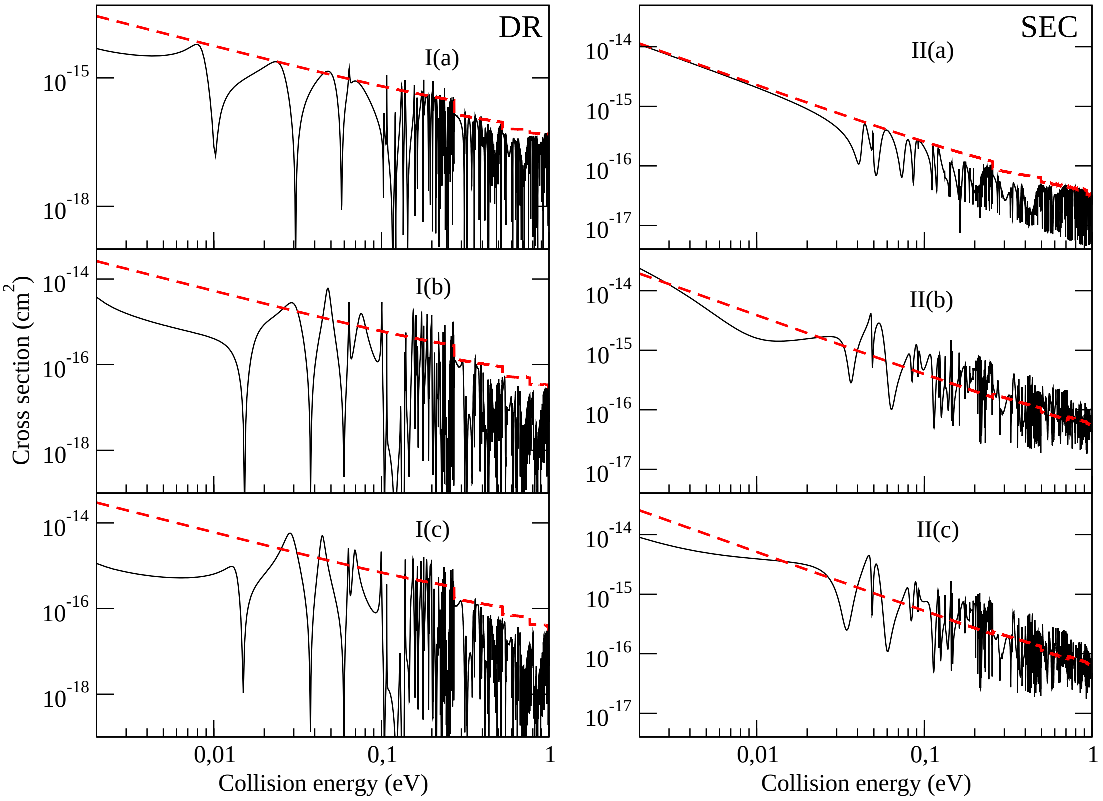

Fig. 2. Cross-sections for (I) dissociative recombination ($v = 0$) and (II) super-elastic collisions ($v = 1 \rightarrow v = 0$) of H_2^+; (a) and (b) are obtained respectively from first and second order calculations with energy-independent couplings, while (c) is obtained from a non perturbative calculation with energy-dependent couplings. (Full lines: total; dashed lines: direct.)

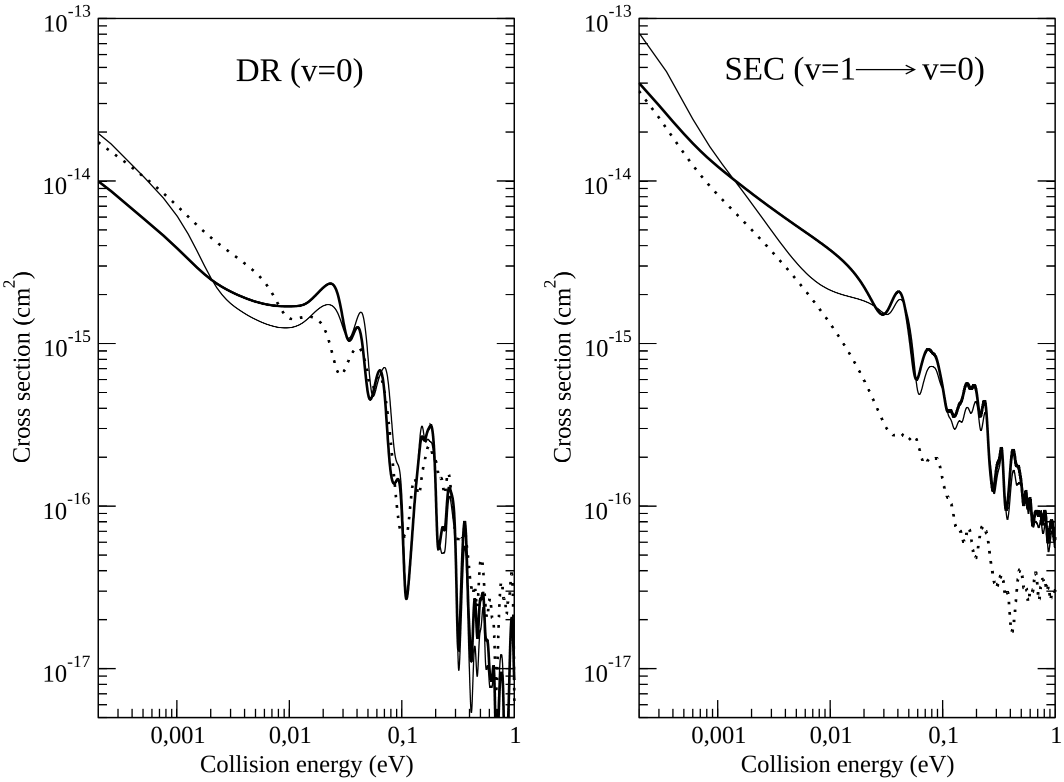

Fig. 3. Cross-sections for H_2^+ DR ($v = 0$) and SEC ($v = 1 \rightarrow v = 0$), convoluted with an anisotropic Maxwellian distribution of electron velocity (dotted lines: first order; dashed lines: second order; full lines: non-pertubative).

4 Conclusion

In this paper, we have investigated the dominant contributions for the calculation of the short range **K**-matrix which is part of the two-step MQDT treatment of DR and related processes. We obtained two sets of results.

(i) For an energy-independent interchannel coupling, the perturbation expansion of the **K**-matrix associated with this coupling converges at second order, whatever the size of the coupling matrix elements. On the other hand, the second order **K**-matrix clearly encompasses physical mechanisms which are not accounted for at first order. It is especially true for collision-induced vibrational transitions when they are mostly driven by indirect electronic couplings. Second order calculations are therefore recommended, and are reliable provided there is no indication for a violent energy-dependence of the short-range interactions. Most of the recent MQDT studies of dissociative recombination (for He_2^+ [14], CH^+ [15], NO^+ [16], H_2^+ [13]), HeH^+ [17]...) have been performed with a second-order **K**-matrix calculation.

(ii) Higher order effects may be induced by off-shell terms in the **K**-matrix when the short-range coupling depends on the electron energy ε. In this case, rather than evaluating higher orders of the **K**-matrix perturbation series, it is more suitable to perform the exact calculation by solving a system of coupled algebraic equations. The effect on cross-section values for the direct processes, involving open channels only, is very small. It is more substantial, especially at very low energy, for the resonance pattern due to closed channels, *i.e.* to temporary capture into bound Rydberg states. Nevertheless, the convolution over experimental velocity distribution results in very close cross-sections for constant and energy-dependent short range couplings.

These tests have been performed for a case where the initial set of ionization and dissociation channels are coupled by an electronic coupling and for electron colliding with a single electron target. The formalism also applies to more complex cases (many electron target, closely lying dissociative resonances) as much as a coupling matrix **V** can be defined with the set of ionization channels. The dimension of the coupling matrix may be larger and the calculation of the **K**-matrix heavier, but the steps of the calculations will be identical. On the other hand the two-step method has also been used when non-adiabatic interchannel couplings drive the DR process, in systems without crossing between a doubly excited states and the ionic ground state [17,18]. Although these couplings might depend more strongly on the electron energy than the electronic couplings which are built at very short range, in the inner core of the electronic cloud, there are generally much weaker so that the second-order perturbative treatment is still usually justified.

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