Radiative transitions under resonance charge exchange.  
\( H + H^- \) collisions

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Abstract. The \( H + H^- \rightarrow H + H + h\omega, H + H^- + h\omega \rightarrow H + H + e \) reactions give examples of bound-bound and bound-free electron transitions in the \( H + H^- \) quasimolecules temporally formed during collisions. The present work is aimed at the calculations of spectral profiles produced in the reactions.

1. Introduction
We present our theoretical study of radiating transitions produced in slow collisions of stable negative ions with neutral parent atoms, \( A + A^- \rightarrow A^- + A + h\omega, A + A^- + h\omega \rightarrow A + A + e \).

In atomic collision physics the process of resonant charge exchange \( A + A^- \rightarrow A^- + A \) is well studied. It can be regarded either in terms of transitions of an electron between two identical atoms – diabatic approach – or in terms of the evolution of an atomic system along \( gerade \) and \( ungerade \) potential energy curves of the adiabatic states of a quasimolecule formed during collisions – adiabatic approach. Accordingly, the radiative transitions produced during collisions can also be regarded in the frames of two approaches. In the diabatic approach the jumps of the electron from one atom to another produce emission of photons. The starting point for the calculation of spectral profiles is the well-known formula of classical electrodynamics for dipole radiation, see Ref. [1]. In the adiabatic approach emission is treated as a consequence of the dipole transition between two quasi-molecular states involved [2].

The radiating transitions have been supposed to take place between two discrete quasi-molecular states. However, another type of transitions can also be treated, namely \( A + A^- + h\omega \rightarrow A + A + e \). The process can be attributed to bound-free electron transitions in quasimolecules or to photo detachment of quasimolecules. The main characteristics of the process are dipole moments of bound-free transitions, which have been calculated in the frame of the LCAO approximation.

2. Bound-bound transitions
We study the specific example of \( H + H^- \) collisions in the frame of the adiabatic approach in order to clarify the main features of spectral profiles produced in the collision processes of charge exchange.
2.1. Potential energy terms

As the first step in accordance with the approach one needs to provide quantum-chemical information on potential energy curves and a dipole transition moment [2]. It is well known that a negative ion of hydrogen can be described with reasonable accuracy by the Zero Range Potential Model [3]. Thus we use the three-dimensional model to calculate the energy terms and the dipole moment [4,5] that depend on the interatomic distance.

It is interesting to note that the one-dimensional zero range potential model (ZRPM) was also used to clarify questions about the calculation of the exchange energy of a homonuclear positive molecular ion \( H_2^+ \) [6]. It was noted that the exchange energy in this model problem can be expressed via the Lambert function. In our problem the potential energy functions can also be expressed in the closed forms through the Lambert function \( W(z) \) which has recently attracted much attention [7] and is a solution of the equation

\[
z = W(z) \exp W(z) .
\]

For example, the potential energies are

\[
U_{g,u}(R) = -\frac{1}{2} \chi_{g,u}^2
\]

where \( \chi_{g,u} \) are connected with the Lambert function through

\[
\chi_{g,u}(R) = \alpha + \frac{W[\pm \exp(-\alpha R)]}{R} ,
\]

and \(-\alpha^2/2\) is the bound energy of an additional electron in the atomic negative ion.

Below the difference potential energy \( \Delta U(R) = U_u - U_g \) is used. Applying Taylor series to the Lambert function leads to

\[
\Delta U = \frac{2\alpha}{R} e^{-\alpha R} - \frac{2}{R^2} e^{-3\alpha R}
\]

at \( \alpha R \geq 1 \). Interestingly, that the Lambert function was recently used in the theory of blackbody radiation functions [8].

2.2. Dipole transition moment

For the first time the dipole transition moment for radiating transitions between gerade-ungerade states produced in charge exchange has been calculated by Mulliken [9] in the linear combination of atomic orbitals (LCAO) approximation

\[
D(R) \approx \frac{R}{2} .
\]

It is the approximation that has been used in [4,5] to calculate the Einstein coefficient for spontaneous emission of the quasimolecule

\[
A(R) = \frac{4}{3g} \left( \frac{\omega}{137} \right)^3 D(R)^2 .
\]

In the present work, in contrast [4, 5] the dipole moment has been calculated directly in the frame of the ZRPM without any further simplifications.
2.3. Spectral profiles

The spectral profile in the quasi-static approximation is

\[ I(\omega) = 4\pi R_c^2 \left[ \frac{A(R_c)}{\partial \Delta U / \partial R_c} \right] \exp \left[ -\frac{U_\omega(R_c)}{kT} \right], \tag{7} \]

where \( R_c \) is the position of the Condon point that is the root of the equation

\[ \Delta U(R_c) = \omega, \tag{8} \]

which has the solution at \( aR \geq 1 \) as

\[ R_c = \frac{1}{a} W \left( \frac{2 \frac{a^2}{\omega} \right). \tag{9} \]

The results of the profile calculations are shown in figures 1 and 2 for two temperatures versus frequency of the radiation and the interatomic distance, respectively.

![Figure 1](image1.png)

**Figure 1.** Spectral profile produced in the \( H + H^- \) collisions versus frequency of the radiation for two temperatures.

![Figure 2](image2.png)

**Figure 2.** Spectral profile produced in the \( H + H^- \) collisions versus the interatomic distance for two temperatures.

The main part of the transitions are concentrated in the region of comparatively large interatomic distances 8-10 a.u. or \( 10^3 \text{ cm}^{-1} \). It should be noted the temperature values on similar graphs in [4] based on LCAO should be changed, that is 1000 ↔ 1500.

3. Free-bound transitions

In the previous Section the radiating processes produced by charge exchange have been considered as an example of bound-bound transitions in quasimolecules. Here, we consider the reaction \( A + A^- + \hbar \omega \rightarrow A + A + e \) as an example of bound-free transitions in quasimolecules or, in other words, photo detachment of quasimolecules.
The cross-section of photo detachment is proportional to the density of oscillator strengths which is the main characteristic of the dipole transitions

\[ \frac{df_{bc}}{d\omega} = 2\omega_{bc}|x_{bc}|^2, \]  

where the matrix element is

\[ x_{bc} = \int_{-\infty}^{\infty} \langle \Psi_b | x | \Psi_c \rangle d\alpha. \]

For simplicity, we discuss the one-dimensional case. Equation (9) indicates that continuous wave functions \( \psi_c \) of the quasimolecule are normalized in accordance with \( \langle \Psi_c(E) | \Psi_c(E') \rangle = \delta(E - E') \). In the frame of the LCAO approximation

\[ \sqrt{\sqrt{\cdots}} \]

where \( \varphi_{b,c}^{\pm} \) mean one-electron wave functions for bound and continuous states centered at the atoms that is at \( \mp \frac{R}{2} \). The symmetry of the quasi-molecular functions in equation (11) accounts for the symmetry of ionic functions \( \varphi_b(-x) = \varphi_b(x), \varphi_c(-x) = -\varphi_c(x) \).

Substitution of Eq. (12) into Eq. (11) leads to the following formulae for the matrix elements of bound-free transitions between \( g \) and \( u \) quasi-molecular states

\[ x_{b=g,c=u} = \frac{1}{2} \langle \varphi_b | x | \varphi_c \rangle + \frac{1}{2} \langle \varphi_b^\dagger | x | \varphi_c^- \rangle, \]

\[ x_{b=u,c=g} = \frac{1}{2} \langle \varphi_b | x | \varphi_c \rangle - \frac{1}{2} \langle \varphi_b^\dagger | x | \varphi_c^- \rangle. \]

The functions \( \varphi_{b,c} \) are centered at the origin, and the factor \( \frac{1}{2} \) is due to the existence of two initial and two final states.

Let us take the one-dimensional ZRPM to describe the negative ion of hydrogen quasimolecule, then

\[ \varphi_b^\pm = \sqrt{a} \exp \left( -\alpha \left[ x \pm \frac{R}{2} \right] \right), \quad \varphi_c^\pm = \frac{1}{\sqrt{\pi k}} \sin k \left[ x \pm \frac{R}{2} \right], \quad E = \frac{k^2}{2}, \]

and

\[ x_{b=g,c=u} = x_{bc}^0 \cos^2 \frac{kR}{2} + \frac{1}{4} \sqrt{\frac{aR}{\pi k \omega}} \sin kR, \]

\[ x_{b=u,c=g} = x_{bc}^0 \sin^2 \frac{kR}{2} - \frac{1}{4} \sqrt{\frac{aR}{\pi k \omega}} \sin kR, \]

where \( x_{bc}^0 = \alpha \sqrt{\frac{aR}{\pi k \omega}} \) is the matrix element for a single ion and \( \omega = \frac{a^2 + k^2}{2} \). Although the quasi-molecular matrix elements increase with increasing \( R \) it does not lead to difficulties at large \( R \). In this case \( U_u = U_g \), and it is obligatory to use the sum of amplitudes of two different ways of detachment, which leads to \( x_{b=g,c=u} + x_{b=u,c=g} = x_{bc}^0. \)
4. Conclusions
Bound-bound and bound-free transitions in quasimolecules formed by colliding atoms and stable ions have been considered in the frame of the ZRPM which is suitable to describe the negative ion of hydrogen. The model used is one-electron, thus one-electron states involved must be brought in line with the real $H_2^-$ states. It can be shown qualitatively that $g$ and $u$ states discussed above are connected with the $\Sigma_{1g,2u}^2$ states of the quasi-molecular ion, but the boundary of the continuum is related with the $\Sigma_{1g}^2$ state of the hydrogen molecule.

Three main results should be emphasized. First, it is the collision $A + A^-$ that produces emission in the absence of any initial electronic excitation in colliding particles. Second, quasi-molecular radiative transitions lead to the formation of ro-vibrational states of the $H_2^-$ molecules at comparatively large interatomic distances about 8-10 a.u. Third, collisions result in a lowering of the threshold of the electron detachment compared with the single ion because $u$ bound quasi-molecular term is repulsive. To calculate the cross-section of the detachment near the threshold, only the square of the matrix element, $x_{g=2u, \Sigma^2}^2$, equation (16), is necessary without any contributions from the $g \rightarrow u$ transitions which are forbidden.

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