Quantum mechanical and uniform quasi-classical approaches for total cross-sections: the radiative collisions

$He(1^1S) + Ne + h\omega \rightarrow He(2^1S) + Ne$ at low energies

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Abstract. The total cross sections of the radiative collisional process $He(1^1S) + Ne + h\omega \rightarrow He(2^1S) + Ne$ have been calculated in the framework of the exact quantum mechanical and uniform quasi-classical approaches for the row of energies $1 - 220 \text{ cm}^{-1}$. The dependence of the total cross sections on the frequency and polarization of light has been investigated. Although the process involves only atoms in the symmetric S-states the results demonstrate the azimuthal scattering asymmetry. The disagreement between the quantum and quasi-classical approaches does not exceed 10 per cent for collision energies $50 - 220 \text{ cm}^{-1}$, but increases up to 25-40 per cent with collision energy decreasing to $1 - 10 \text{ cm}^{-1}$ on retention of a functional dependence on angle. The reason of the disagreement is mainly due to the loss of accuracy of the WKB approximation for the ground state wave function at low energies.

1. Introduction

The present work has been motivated by two reasons. Firstly, in recent years, considerable interest has been shown in analysing the cross sections of the radiative-collisional processes that lead to the collisionally induced radiative excitation of metastable states for one of the colliding atoms. The first crossed beam experiment devoted to the investigation of the angular and spectral distributions produced in collisionally induced radiative excitation of metastable Ca($4s3d\ 1D$) state have been reported in [1]. The total and differential cross sections for the process

$He(1^1S) + Ne + h\omega \rightarrow He(2^1S) + Ne$ (1)

have been calculated in [2-4] starting from the uniform quasiclassical approximation [2,5].

Secondly, it has been shown recently [6] that different radiative characteristics of quasimolecules formed by colliding atoms are determined by different regions of interatomic distances. But the best
way to check the input quantum chemical data set that is potential energy surfaces and optical transition moments seems to be to compare the results of experiments with calculations of the scattering cross sections for the reactions like (1). As for the theoretical part of the work it seems that the analytical approaches would be favourable for two reasons at least. The influence of input data variations on radiative characteristics is immediately evident from analytical results and such approaches are best suited for fitting the results of calculations.

This work is devoted to the calculation of the total cross sections of the collision process (1) as the functions of the frequency and polarization of light at low collision energies 1-200 cm$^{-1}$. The present results have been obtained in the frame of a uniform quasi-classical approach. As a rule quasi-classical approaches produce analytical results but although the general criteria of the approaches are quite clear they do not lead to precise boundaries and limitations in specific cases in the domain low collision energies which we are especially interested in. Thus, the present work includes the exact quantum mechanical calculations too, and the comparison of the exact quantum mechanical, and the uniform quasi-classical approaches is aimed at a conclusion about the applicability limit of the uniform quasi-classical approximation utilized in the work. We should stress that the reaction (1) gives a unique example of the reaction that involves atoms in the symmetric S-states both for the initial and final states. Until recently the polarization effects in scattering have been studied for aligned and oriented atoms in non-symmetrical states, e.g. [7].

2. Quantum mechanical and uniform quasi-classical approaches
The mechanism of the collisional process (1) was described in detail in [8,9]. At low radiation intensities ($I \leq 10 \text{ GW/cm}^2$) the total and the differential cross sections of process (1) can be determined using the distorted-wave method [10]. In this case the dependence of the cross section on the intensity is linear. In our calculations we used a scale factor corresponding to an intensity $I = MW/cm^2$. The total cross sections for the polarizations parallel and perpendicular to the initial relative interatomic momentum are expressed via the $S$-matrix elements by the formulas [4]

$$\sigma_\parallel = (\pi / k_f^2) \cdot \sum_{l,l'} 1/(2l + 1) \cdot \left| S_{l \to l',l} - (l + 1) \cdot S_{l \to l',l'} \right|^2,$$

$$\sigma_\perp = (\pi / 2k_f^2) \cdot \sum_{l,l'} l(l + 1)/(2l + 1) \cdot \left| S_{l \to l',l} + S_{l \to l',l'} \right|^2.$$  

For the case of an in-collision plane linear polarization of the light the differential cross sections have the form

$$\frac{d\sigma(\theta_p)}{d\Omega} = \frac{k_f}{k_i} \left( \cos^2 \theta_p \cdot |f_0(\theta)|^2 + \sin^2 \theta_p \cdot |f_{(\parallel)}(\theta)|^2 \pm \sin(2\theta_p) \Re \left[ f_0(\theta)f_{(\parallel)}^*(\theta) \right] \right).$$

and for the right-hand and the left-hand circular polarizations we obtain

$$\frac{d\sigma_{r/l}}{d\Omega} = (k_f / k_i) \left( |f_0(\theta)|^2 + 1/2 \cdot |f_{(\parallel)}(\theta)|^2 \pm \Im \left[ f_0(\theta)f_{(\parallel)}^*(\theta) \right] \right).$$

Here
\[ f_{(1)}(\theta) = (4k, k_{f})^{1/2} \sum_{l=0}^{\infty} \left[ S_{l-1-l} + S_{l+1-l} \right] P_{l}(\cos \theta), \]

where \( S_{l-1-l} \) are the spherical components of the scattering amplitude [4], and \( \theta_{p} \) is the polarization angle (angle between the initial relative interatomic momentum and the light polarization vector). The upper and lower signs in Eq. (3) correspond to the leftward (the final relative interatomic momentum and the polarization vector are in the same half-plane) and rightward scatterings, respectively. The upper and lower signs in Eq. (4) correspond to the leftward and the rightward scatterings for a right-hand circular polarization and vice versa for a left-hand case.

In the framework of the distorted wave method the \( S \)-matrix elements have the form

\[ S_{l-1-l} = -\text{i}2\pi \exp[i(\Delta l_{l} + \Delta l_{f})] \int_{0}^{\infty} \Psi_{E_{l}}(R) \cdot V(R) \cdot \Psi_{E_{f}}^{\dagger}(R) dR, \]

where \( \Psi_{E_{l}}(R) \) are the radial, regular (at zero) real wave functions normalized to the \( \delta \)-function of energy, \( V(R) = E_{0} d(R)/2 \) is the interaction matrix element, and \( \Delta l_{l} \) are the elastic scattering phase shifts.

The exact quantum mechanical approach consists in a numeral evaluation of the \( S \)-matrix elements starting from the wave functions \( \Psi_{E_{l}}(R) \) for the initial and the excited quasimolecular states obtained by numerical integration of the radial Schrödinger equations

\[ d^{2}\Psi_{E_{l}} / dR^{2} + k^{2}(R)\Psi_{E_{l}} = 0, \]

where \( k(R) = \sqrt{2\mu(E - U(R)) - J^{2}/R^{2}} \) is the momentum function, \( \mu = 6089 \) is the reduced mass of the colliding atoms, and \( J = \sqrt{l(l+1)}. \)

On the other hand, the uniform quasi-classical approach deals with the uniform Langer’s (Airy’s) approximations [10] for the radial wave functions

\[ \Psi_{E_{l}}(R) = (2\mu)^{1/2} \left( \xi(R)/k^{2}(R) \right)^{1/4} Ai(-\xi(R)), \]

and the overlap integral (6) is calculated analytically using the uniform saddle points method [5,11]. Moreover, as has been emphasized in [9], it is necessary for asymptotically forbidden processes like (1) to take into account the steep (exponential) dependence of the interaction matrix element on the interatomic distance, \( V(R) = V_{0}(R) \exp(-\gamma R) \) \( (V_{0} \) is a smooth function of \( R \), in accordance with [9] \( V_{0} = 2.78 \cdot 10^{-3}, \gamma = 0.92 \) ) that leads to the following correction of the well-known Franck-Condon approximation. Instead the condition

\[ \Delta U = \Delta \omega, \]
where $\Delta U = U_f - U_i$ is the difference potential, $\Delta \omega$ is the detuning of the radiation frequency $\omega$ from the frequency of the forbidden atomic line $\omega_0 = 166278 \text{ cm}^{-1}$, the saddle points are determined by the equations

$$ (k_f - k_i)(R_z) = \pm i\gamma . \quad (9) $$

The final formula for the $S$-matrix element then has the form [5]

$$ S_{i \to f} = (F^+ [+] + F^- [-])\exp(iA), \quad (10) $$

where

$$ [\pm] = B^{1/4} Ai(-B) \pm iB^{-1/4} Ai^*(-B), $$

$$ F^+ = -2^{1/2} \pi \mu V_0(R_z)[k_jk_i(k'_j - k'_i)(R_z)]^{-1/2}, $$

$$ 2A = i\gamma(R_+ + R_+) + S_i(R_+) - S_j(R_-) - S_j(R_+) + S_j(R_-) + 2(\delta^{ji} + \delta^{j'i}), $$

$$ (4/3)B^{3/2} = i\gamma(R_+ - R_-) + S_i(R_-) + S_i(R_-) - S_j(R_-) - S_j(R_-), $$

and

$$ \delta^J = \lim_{R \to \infty} [S(R) - kR] + J\pi / 2 \text{ is the quasi-classical limit for the phase shift.} $$

### 3. Total cross-sections

Starting from the $S$-matrix elements we have calculated the total and differential cross sections of the process (1) by exact numeral summation over the partial waves (see Eqs. (2-5)). The data have been obtained for the range of the collision energies $E = 1-200 \text{ cm}^{-1}$ and for the different detunings (including both wings and the center of the forbidden atomic line) and polarizations of light. The number of partial waves which must be included in summation never exceeds 40 for the energies considered. To specify the application limit of the uniform quasi-classical approximation both the exact quantum mechanical and the uniform quasi-classical calculations have been performed in all cases. Figure 1 shows the total cross section averaged over the polarizations of light

$$ \sigma = (\sigma_\parallel + 2\sigma_\perp) / 3 $$

together with the polarization coefficient

$$ P = \frac{\sigma_\perp - \sigma_\parallel}{\sigma_\perp + \sigma_\parallel} $$

as the functions of the detuning $\Delta \omega$. 
Figure 1. Total cross sections $\sigma, 10^{-22} \text{ cm}^2$ (a,c) of the process (1) and the polarization coefficients $P$ (b,d) versus detuning $\Delta \omega = \omega - \omega_0, \text{ cm}^{-1}$; (a,b) $E = 100 \text{ cm}^{-1}$ and (c,d) $E = 10 \text{ cm}^{-1}$; (black line) exact quantum mechanical calculation, (red line) uniform quasi-classical result. The scale factor corresponds to $I = MW/\text{cm}^2$.

Let us note that disagreement between the exact quantum mechanical and the uniform quasi-classical approximations never exceeds 10 per cent in the case of the collision energy $E = 100 \text{ cm}^{-1}$ but increase up to 25 per cent when the collision energy decreases to $E = 10 \text{ cm}^{-1}$. In the first case disagreement is mainly due to the use of the uniform saddle points method in the quasi-classical calculations instead of the exact numeral evaluation of the overlapping integrals (6). With decreasing energy the difference in the ground state wave functions obtained in the frame of the two different approaches becomes more essential and for an energy of $E = 10 \text{ cm}^{-1}$ makes the main contribution to the observed disagreement. Note also that for specific detunings ($\Delta \omega = 0$ for $E = 100 \text{ cm}^{-1}$ and $\Delta \omega = -4 \text{ cm}^{-1}, 123 \text{ cm}^{-1}$ for $E = 10 \text{ cm}^{-1}$) the total cross sections does not depend on the polarization of light ($P = 0$).

4. Conclusion
The radiative-collisional process (1) with atoms in the symmetric S-states have been analyzed in large detail for collision energies $1 - 220 \text{ cm}^{-1}$. For all collision energies considered total cross sections depend on the frequency and the polarization of light. It has been shown that there are some specific frequencies at which the total cross section does not depend on the polarization of light. The dependencies of cross sections on collision energy and absorbed photon frequency open up fresh opportunities for tests of the potential energies and dipole moments.

The comparison of the exact quantum mechanical calculations with the uniform quasi-classical calculations results in the conclusion that the exactness of the uniform quasi-classical approach
depends mainly on the exactness of the WKB approximation for the elastic radial wave functions corresponding to the different collision channels. For the collisions considered the low limit of the collision energies for the validity of the uniform quasi-classical approximation is $E \sim 10\text{ cm}^{-1}$. It should be stressed that this conclusion has been obtained starting from the exponential approximations for the ground state and the excited state quasi-molecular potentials [9].

**References**

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