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Radiative transitions in few-electron quasi-molecules

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Abstract

The review is aimed at the discussion of recent results on spectral profiles produced in collisions of few-electron atoms/ions. Calculations of spectral profiles produced by atom/ion collisions need some preliminary quantum-chemical information such as potential energy surfaces, dipole transition moments, etc. The main advantage of few-electron systems is that all input data can be obtained ab initio or analytically, thus the profiles calculated do not include any fit parameters. Two specific examples have been discussed. The first one deals with radiative transitions accompanying charge-exchange in collisions of one-electron ions with bare nuclei. The second example concerns radiative transitions produced by $H^- + H$ collisions.

Keywords: Collision induced radiative transitions; Energy terms; Dipole moments; Few-electron ions; Negative ion of hydrogen; The Lambert function

1. Introduction. Quasi-molecular approach

1.1. Quasi-static approximation

By radiative transitions in quasi-molecules are meant optical transitions between states that are formed in collisions of atoms or ions. Probably, for the first time, the concept of radiative transitions between such states, or quasi-molecular states, was formulated in the modern form by Jablonski (1945), and since then it is widely used for describing spectral profiles and especially for describing the so-called satellites of spectral lines of atoms and ions.

From classical point of view the spectrum $K(\omega, T)$ of optical transitions with frequency ω from a state with a quasi-molecular potential U_i to another state with a potential U_f is proportional to the statistical weight of the initial quasi-molecular configuration with the interatomic separation R_c that satisfies the Franck–Condon principle and is called a Condon point. Thus, in the case of the Maxwell distribution of velocities of colliding atoms, the spectrum, for example in the case of emission, can be described by the formulae of the quasi-static approximation (in au), e.g., Devdariani (1999):

$$K(\omega, T) = 4\pi R_c^2 \frac{A(R_c)}{\left|\frac{d\Delta U}{dR}\right|_{R_c}} \exp\left(-\frac{U_i(R_c)}{kT}\right), \tag{1}$$

with R_c from the following equation

$$\omega = \Delta U(R_c), \tag{2}$$

where $\Delta U = U_i - U_f$ is the difference of the energies of the initial and final states and

$$A(R_c) = \frac{4}{3g}(\alpha\omega)^3 |D(R_c)|^2, \tag{3}$$

is the probability of radiation or the Einstein coefficient for spontaneous emission, D is the electric dipole moment for transitions between the two states involved. According to Eqs. (1)–(3), to calculate the intensity it enough to solve only the quantum-chemical part of the problem, i.e., to calculate the potentials and the Einstein coefficient of the proper transition in dependence on the interatomic distance.

The simplicity and physical clearness of the quasi-static approximation made it very popular, especially in reconstructing the potentials from the experimental data on temperature dependencies of intensities. However, the

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disadvantages of the quasi-static approximation are rather apparent (Devdariani, 1999). Some of them are related to the form of Eq. (1), which does not describe the spectra produced by transitions in the vicinity of extrema of the difference potential or in the vicinity of the turning points of classical trajectories. Other disadvantages are more fundamental in nature and related to the limit applicability of one of the main assumptions of the quasi-static approach that the transitions only between two isolated states are to be considered. During the collision the terms can approach and even cross the terms of other states, which gives rise to non-adiabatic transitions between quasi-molecular states. The influence of such interactions on the spectra requires special consideration. The last circumstance is especially important in describing some transitions that are forbidden in the limit of separated atoms, because the prohibition of optical transition is removed only due to an interatomic interaction with at least one additional state.

1.2. Semi-classical approach

Some disadvantages of quasi-static approximation mentioned above in Section 1.1 can be overcome in the frame of semi-classical approach. In this approach it supposed that the atoms move on classical trajectories $R(t)$ but transitions between states are described in terms of quantum-mechanical amplitudes. If the wave function of the initial discrete state under atomic movement is

$$\Psi(t) = a(t)\exp\left(-i\int U_i(t')dt'\right), \tag{4}$$

then the amplitude of the transition to a final continuum state, corresponding to a photon energy ω, in the first order of perturbation theory is

$$b(\omega) = -i\int\sqrt{\frac{A(t)}{2\pi}}a(t)\exp\left[-i\int(\Delta U-\omega)dt'\right]dt, \tag{5}$$

and can be considered as the Fourier transform of the dipole moment, which has been calculated with time-dependent quasi-molecular wave functions. Eq. (5) generalizes the approach accepted in the classical theory of spectral line broadening (for e.g., Sobel'man, 1968). To obtain the spectrum $K(\omega, T)$ averaged over angular momenta and the Maxwell distribution of velocities of colliding atoms, it is sufficient to carry out the corresponding double averaging of the square of the modulus of $b(\omega)$, Eq. (5). The further studies starting from Eq. (5) have shown that the approach based on the Fourier transform allows one to describe a number of specific features of the quasi-molecular radiative transitions (Devdariani, 1999).

1.3. Why few-electron quasi-molecules

In what follows both quasi-static approach and semi-classical approach are used. But it should be noted that for specific calculations both approaches need quantum chemistry information about adiabatic potential energy curves and dipole moments. And what is more, spectral profiles produced in collisions prove to be rather sensitive to the quality of a quantum chemical input. The last circumstance is especially important for asymptotically forbidden transitions because in contrast to allowed transitions strong dependences of dipole moments on interatomic distances have necessarily to be taken into account (Allard et al., 2004; Devdariani et al., 2006). In particular fit calculations must be preceded by accurate treatment of the interatomic regions in which transitions determining the form of spectral profiles take place.

Quite naturally that the most reliable quantum chemical calculations can be performed for atomic systems with a small number of electrons. Thus few-electron quasi-molecules are of importance to test different approaches in profile calculations in the light of the following applications of spectral profiles for purposes of diagnostic. Moreover, light elements are the most abundant in the Universe, and spectral features related to their interactions are of interest for astrophysics. It is interesting to note that processes in high-Z few-electron systems are intensively studied in modern atomic physics, see, e.g., Fritzsche et al. (2005).

2. One-electron-two-center problem

2.1. Motivations

The following Section 2 is dedicated to the simplest quasi-molecules formed by two bare nuclei with charges $Z_{1,2}$ and one bound electron e. The reason for this choice is threefold. First, the Z_1eZ_2 problem is of fundamental importance. It seems that Pauli (1922) was the first who recognized the problem in the case $Z_{1,2} = 1$ as the key problem in molecular physics similar to the hydrogen atom problem in atomic physics. The energy terms and the dipole moments for quasi-molecules Z_1eZ_2 can be obtained straightforwardly in nonrelativistic case with any desired precision and without any approximations, which are typical for neutrals quasi-molecules, see Section 2.2. Second, most if not all of the features in the spectral profiles produced in collisions can be found and analyzed using the Z_1eZ_2 problem as an example (Devdariani et al., 2010). Third, there are numerous applications in physics including laboratory plasma and astrophysics. Of the new applications which have appeared recently, the optical spectroscopy of collisions, in particular, charge-exchange processes which are basic for the interaction of high-temperature plasma with cold gases (Greenwood et al. 2001) should be mentioned.

2.2. Energy terms and dipole optical transition moments

The most comprehensive review of the energy term calculations in the Z_1eZ_2 problem can be found in Komarov et al. (1976). Among new results the scaling relation for