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Towards a theory of dissociative recombination

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Abstract. Current experiments in storage rings at Aarhus and Stockholm reveal that ions such as CH_3^+, OH_3^+, OH_2^+ and CH_5^+ recombine and fragment into three parts more often than into just two. Analysis of the possible resonances between free electron and bound electron states for the ions require a detailed examination of the correlation effects as well as the coupling to nuclear degrees of freedom. The problem is well suited for the propagator approach. An analysis of the structure of the self-energy kernel shows the presence of possible resonances with degenerate electronic states which are unstable according to the Jahn–Teller theorem and provides channels for multiple fragmentation.

Keywords. Dissociative recombination; Green function; Jahn–Teller splitting.

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1. Introduction

ASTRID, the Aarhus STorage Ring In Denmark, has been used to study electron collisions with molecular ions at very low energy. The ions are running around in the ring and electrons are injected parallel to the beam of ions at the same velocity. Recombination to neutral molecules or radicals takes place and results in dissociation when the surplus energy is disposed of. It was found that carbonium and oxonium ions [1] fragmented into three parts equally often as into two. This rather unexpected result requires a somewhat detailed study of the electronic process and it is interpreted here as a correlation effect.

Electron propagator calculations are a convenient means to examine the scattering of electrons by molecular targets [2]. Efforts by Reinhardt and collaborators [3] have demonstrated the possibilities and applications to stable negative ions by Simons [4] have been successful in establishing the techniques relevant for the study of weakly bound systems.

The next section of this paper presents notations and forms to be used in the analysis, thereupon a section is devoted to examples of numerical calculations based on regular *ab initio* calculations. The paper concludes with a part on the possibilities of more detailed examinations.

2. Forms and notations

Second quantization [2, 5] will be used as a vehicle. Creation $\{a_s^\dagger\}$ and annihilation $\{a_s\}$ operators are defined with respect to an orthonormal basis of spin orbitals for a fixed geometry nuclear framework of the molecular species. It may be assumed that the basis is