

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

the canonical Fock basis so that

$$\langle\langle [a_s, H], a_{s'}^\dagger \rangle\rangle_+ = \varepsilon_s \delta_{ss'}, [a_s, a_{s'}^\dagger]_+ = \delta_{ss'}, \quad (1)$$

with the Hamiltonian [2]

$$H = \sum_{ss'} h_{ss'} a_s^\dagger a_{s'} + \frac{1}{2} \sum_{rr' ss'} (rr' | ss') a_s^\dagger a_r^\dagger a_{r'} a_{s'}. \quad (2)$$

The electron propagator is defined as the form

$$G_{rs}(E) = \langle\langle a_r; a_s^\dagger \rangle\rangle_E, \quad (3)$$

with the equation of motion

$$(E - \varepsilon_r) G_{rs}(E) = \delta_{rs} + \langle\langle b_r; a_s^\dagger \rangle\rangle_E; \quad b_r \equiv [a_r, H] - \varepsilon_r a_r. \quad (4)$$

The residual operators b_r must not be neglected in situations where electronic correlation is significant. Extensions beyond conventional self-consistent field theory involves a suitable extension of the operator manifold [6]. Presently we include the set of tensor products of elementary operators with three factors,

$$\{a_r^\dagger a_s a_{s'} | r \neq s, r \neq s'\} \quad (5)$$

which opens to the possibility that the scattered electron couples to electronically excited modes of the target molecule. As a result of this extension one obtains a propagator equation with an energy dependent self-energy M :

$$(E - \varepsilon_r) G_{rs}(E) = \delta_{rs} + \sum_{s'} M_{rs'}(E) G_{s's}(E). \quad (6)$$

The self-energy is derived, in this algebraic formulation, from the equation of motion and the detailed formalism has been described well in the review by Öhrn and Born [7].

Electron correlation effects are contained in the self-energy. There will be energy values where bound states are degenerate with states with a free electron and these will give rise to poles in the self-energy $M(E)$. An illustration of this feature comes about by considering an operator in the manifold (5),

$$\tilde{b} = \sum_{rss'} a_r^\dagger a_s a_{s'} c_{rss'}; \langle\langle [\tilde{b}, a_r^\dagger] \rangle\rangle_+ = 0; \quad \forall r, \quad (7)$$

with the stationary property that

$$\frac{\partial}{\partial c_{rss'}} \{E_b \langle\langle [\tilde{b}, \tilde{b}^\dagger] \rangle\rangle_+ - \langle\langle [[\tilde{b}, H], \tilde{b}^\dagger] \rangle\rangle_+\} = 0; \quad \forall rss'. \quad (8)$$

The stationary energy value E_b represents an approximation to a bound state which is orthogonal to the normal state plus one free electron in the fashion discussed by Fano [9]. The method follows closely the development by Rice [10] and used for discussions of predissociation, a related problem to the present one. We define the coefficients c_r through the relation

$$\langle\langle [b, \tilde{b}^\dagger] \rangle\rangle_+ = 1; \langle\langle [a_r, H], \tilde{b}^\dagger \rangle\rangle_+ = c_r \quad (9)$$

and obtain a simple self-energy form as

$$M_{rs}(E) = \frac{c_r c_s^\dagger}{E - E_b}. \quad (10)$$

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This separable form admits the direct solution of the Green function as

$$G_{rs}(E) = \frac{\delta_{rs}}{E - \varepsilon_r} + \frac{1}{E - \varepsilon_r} T_{rs}(E) \frac{1}{E - \varepsilon_s}; \quad T_{rs}(E) = \frac{c_r c_s^\dagger}{E - \alpha(E) - i\beta(E)}, \quad (11)$$

where the auxiliary quantities

$$\alpha(E) = E_b + \Re \sum_{s'} \frac{|c_{s'}|^2}{E - \varepsilon_{s'}}; \quad \beta(E) = \Im \sum_{s'} \frac{|c_{s'}|^2}{E - \varepsilon_{s'}}. \quad (12)$$

appear. This analysis requires a formulation admitting a continuous spectrum. Numerical calculations are conveniently performed in a finite basis by invoking the dilatation analytical properties of the electronic hamiltonian [8]. Amplitudes from the definition (9) allow us to assign symmetry and energy for the continuum states which couple effectively to the bound state.

The amplitude c_r has the explicit form

$$c_r = \sum_{r'ss'} \{ (rs'|r's) - (rs|r's') \} c_{r'ss'} \equiv \int dx u_r^*(x) f(x), \quad (13)$$

and we are concerned with the case that the spin orbital $u_r(x)$ is a continuum one while the three other spin orbitals in any one integral are bound. It follows that appreciable amplitudes are obtained for low energy states with modest oscillatory behaviour in the molecular region of space. An estimate of the quantities $\alpha(E)$ and $\beta(E)$ of eq. (12) can be obtained from the Coulomb Green function [2] in the Wentzel–Kramers–Brillouin approximation. The most significant contribution comes from the p -wave, which can penetrate the molecular electron distribution to a certain extent. Thus it can be argued that the function $\beta(E)$ should be similar to the differential oscillator strength distribution and that $\alpha(E)$ should be related thereto through a dispersion relation. Such forms were calculated some time ago [11] and exhibit the kind of behavior given by Fano [9].

Cross sections for recombination are found from the imaginary part of the diagonal elements of the T -matrix, according to the optical theorem. Thus they are proportional to $\beta(E)$ and exhibit the approximate E^{-1} form as indicated by Bardsley and Biondi [12].

3. Fragmentation of carbonium

Transition from a free electron state to a bound, electronically excited one will generally not be accompanied by a rapid nuclear adjustment. The system is 'born' in a conformation where forces are acting on the nuclei and a motion is induced. Diatomic systems will then often dissociate [12]. A polyatomic system has the possibility of several channels and the observation of substantial propensities for the creation of more than two fragments [1] requires a detailed investigation of the nature of the excited electronic states that are accessible in the process.

Results for the carbonium cation, CH_3^+ , are as follows [1, 13]:

$$e^- + \text{CH}_3^+ \rightarrow \begin{cases} \text{CH}_2 + \text{H} & \Delta E = 5.0 \text{ eV} & 40\% \pm 10\% \\ \text{CH} + \text{H}_2 & \Delta E = 5.2 \text{ eV} & 14\% \pm 10\% \\ \text{CH} + \text{H} + \text{H} & \Delta E = 0.7 \text{ eV} & 16\% \pm 15\% \\ \text{C} + \text{H}_2 + \text{H} & \Delta E = 1.6 \text{ eV} & 30\% \pm 8\% \end{cases}$$

and show that nearly one half of the cases ends with three fragments, even though the energy release is much smaller than in the other channels. It will be argued here that the crucial element of the electronic structure in this system is that the highest occupied molecular orbital energy level, in a standard description, is twofold degenerate and that low lying electronically excited states of the neutral system are thus degenerate. Accordingly we expect that the neutral system, after having incorporated the free electron, finds itself in an electronically degenerate state and is subjected to Jahn–Teller distortions.

The equilibrium ground state conformation of the carbonium ion has the point group D_{3h} and the electronic configuration $(1a'_1)^2(2a'_1)^2(1e')^4$. Normal modes of vibration are the uniform stretch A'_1 , the umbrella mode A''_2 , and four E' -modes which are combinations of stretch and bend. Only the latter ones will be effective in splitting the degeneracy of the e' -type molecular orbital. The maximal splitting between the electronically degenerate states occurs for a particular linear combination of nuclear stretch and bend distortions and to first order the splitting is equally large for a directly opposite displacement of the atoms. There is a further three-fold equivalence arising from the permutational symmetry of the protons.

A series of calculations, of varying sophistication, have been performed in order to search for the intramolecular displacements which generate the largest energy splitting between the relevant excited states of the carbonium ion and its neutral radical. Qualitative molecular orbital theory shows, in the energy weighted maximum overlap form [14] that E -type bending modes give a larger splitting than the corresponding magnitude stretch, in figure 1. It appears that the nearly pure bend is the more effective distortion in raising the energy of the highest occupied molecular orbital and thus decrease the excitation energy to an unoccupied orbital with little dependence on the distortion such as the empty a''_2 -orbital on the carbon atom.

Accurate calculations of the triplet excitation energy from the closed shell ground state give a similar picture of the effect of atomic displacements. Such investigations have been performed with the program system DALTON [15]. A set of energy surfaces have been constructed, based on a series of small displacements with different mixture of bend and

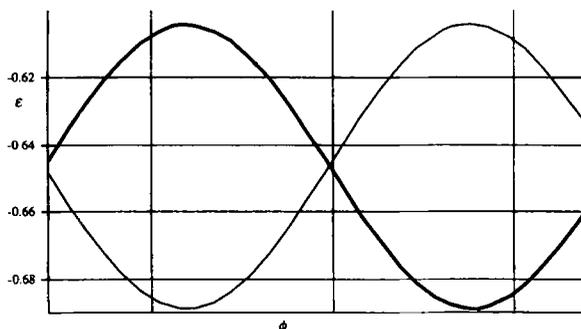


Figure 1. Molecular orbital energies for the two highest occupied levels as functions of the mixing angle ϕ when the distortion from the regular conformation is composed of a linear superposition of a stretch, with amplitude $\cos \phi$ and a bend with amplitude $\sin \phi$. The energy scale is in Hartrees.

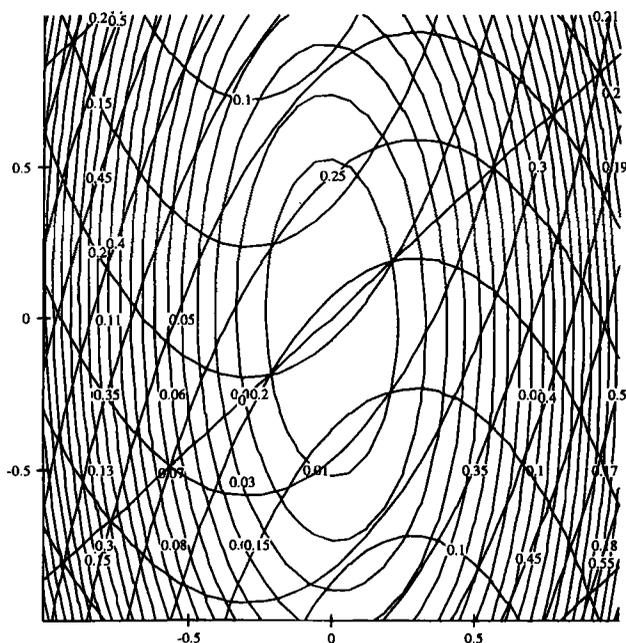


Figure 2. Contour diagrams of the energy surfaces of the carbonium ion ground state and its first two excited states in the two-dimensional subspace spanned by the bending and stretching modes leading to the descent in symmetry from D_{3h} to C_{2v} . The ground state equipotential curves are centered in the middle of the graph. The two triplet states have, in the present second degree polynomial fitting, their minima towards the upper left and the lower right. The straight line through the center indicates a combination of stretch and bend which results in no splitting of the 3E -states in first order. The horizontal axis represents stretching displacement while the vertical refers to bending.

stretch mode, for the ground state singlet and the first two triplet states of the carbonium ion. The ground state is a self-consistent multiconfigurational state and the excitation energies are derived from response calculation, all within a moderately large basis set with 115 contracted functions and including f -orbitals on carbon and d -orbitals on hydrogen. Figure 2 gives an impression of the energy surfaces. The most effective splitting between the 3E -states is here a stretch-bend combination where the mixing angle ϕ (defined in the legend to figure 1) is about -1 or $\pi - 1$. These analyses indicate that electronic configurations with a hole in the highest occupied molecular orbital of the ground state of the carbonium ion will be accompanied by atomic displacements of the E -type.

There are four dimensions to the space of E type displacements, each of the two bends and the two stretches may be labeled as A_1 or B_2 in a reduced C_{2v} symmetry. An A_1 distortion reduces D_{3h} to C_{2v} while a finite B_2 bend or stretch leaves only a plane of reflection as a symmetry element. The ground state symmetry ensures that the first order energy changes are equivalent for the two varieties. It turns out that the accurate calculations of the triplet excitation energies show maximal splitting for atomic displacements that can be interpreted as having a fixed configuration of the three protons in an

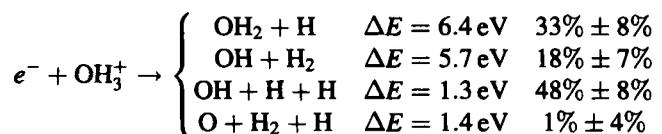
equilateral triangle where the central carbon can oscillate in a practically circular potential well.

A neutral, excited state of the methyl radical CH_3 couples well to free electron states at near zero kinetic energy. It will be characterized by a hole in the e' -type orbitals of the D_{3h} ionic equilibrium structure and two electrons in the $(1a_2'', 3a_1')$ -manifold. The instability of the degenerate E -type states at the equilibrium geometry opens distortion channels where the bonding between the carbon and the hydrogens is reduced. Either the carbon gets closer to one of the hydrogens and the bond weakens to the other two indicating a dissociation which involves a CH-fragment or it moves away from one of the hydrogens which may leave the rest. The fate of the two remaining hydrogens in the former case will depend on the electron distribution, if the electron configuration initially is $(1a_2'')^2$ there will be little bonding between the hydrogens and we expect the result $\text{CH}+\text{H}+\text{H}$, while a configuration $(1a_2''3a_1')$ provides for the exit channel $\text{CH}+\text{H}_2$. A corresponding situation occurs in the case that the carbon moves away from one hydrogen. Then the configuration $(1a_2'')^2$ will tend to keep the CH_2 as a unit while $(1a_2''3a_1')$ favors dissociation to fragments C and H_2 due to the antibonding character of the $3a_1'$ relating to the carbon-hydrogen bonds. The nuclear motions of the system are not restricted to planar ones and the coupling between E' - and E'' -states mixes the electronic symmetry labels.

Detailed calculations of the possibilities for fragmentation of the carbonium ion are required in order to ascertain the relative propensities for the various channels. The previous arguments demonstrate the opportunities which are available through the mechanisms of Jahn–Teller instabilities of degenerate electronic states.

4. Fragmentation of oxonium

Experiments on the dissociative recombination of oxonium or hydronium ions provide the propensities [1, 13]



and it is seen that nearly half of the events give three fragments. Free oxygen atoms appear only rarely while free carbon occurred in about a third of the events in the carbonium investigations. The closed shell electronic ground state of oxonium does not provide low lying electronic states, a 3A_1 is the first accessible one at some 11.5 eV in the ground state geometry [16]. This cannot be compensated for by binding an additional electron, the first empty orbital being located at a binding energy of some 4.7 eV.

There are no electronically excited states that can provide a sizeable coupling through the self energy in the propagator formulation above and it is then necessary to look for a description beyond the Born–Oppenheimer formulation such as is provided in the work by Cederbaum [17]. Considerations of the coupling to the nuclear motions are possibly more critical to include in the oxonium case, where no major electronic channel is available as in carbonium, but the detailed treatment is beyond the scope of this presentation.

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Three fragment results are also available for the water cation, OH_2^+ , where no less than 70% of the events show total break-up [1, 13]. Since the ion ground state is a doublet it seems likely that the recombination to a triplet state could be favored and that this will reduce the binding considerably.

5. Remarks

Discussions in this paper have concentrated on the possible electronic features of the dissociative recombination in carbonium ions. A Green function formulation was used in order to put forth the basic many-particle nature of the process. The available, low energy triplet state provides a channel for the acceptance of an electron into a spatially degenerate state which admits two principal and distinct distortions originating from the Jahn–Teller theorem. Initial nuclear motions have been determined but a full dynamic treatment of the process remains to be seen. It is necessary to invoke detailed descriptions of the interactions between electronic states and the nuclear motions in order to obtain a satisfactory appreciation of the propensities for different dissociation products. This is even more imperative for the oxonium and water cation cases.

A conclusion from the present effort is that inelastic electron scattering from molecular species is quite a complex problem which requires a substantial theoretical effort to master.

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