



# Non adiabatic theory of collisions in a radiative field. Semi-classical limit

N. Feautrier, E. Roueff, A. Spielfiedel

## ► To cite this version:

N. Feautrier, E. Roueff, A. Spielfiedel. Non adiabatic theory of collisions in a radiative field. Semi-classical limit. Journal de Physique, 1988, 49 (11), pp.1911-1923. 10.1051/jphys:0198800490110191100 . jpa-00210871

**HAL Id: jpa-00210871**

**<https://hal.science/jpa-00210871>**

Submitted on 4 Feb 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification  
Physics Abstracts  
34.50

## Non adiabatic theory of collisions in a radiative field. Semi-classical limit

N. Feautrier, E. Roueff and A. Spielfiedel

Département Atomes et Molécules en Astrophysique, Observatoire de Paris, Section de Meudon, 5 Place Jules Janssen, 92195 Meudon Principal Cedex, France

(Reçu le 7 juin 1988, accepté le 19 juillet 1988)

**Résumé.** — La théorie quantique des collisions en présence d'un champ de rayonnement est maintenant bien établie, notamment dans le cas des champs faibles qui nous intéressent ici. Certains résultats concernant les sections efficaces radiatives et la redistribution de polarisation se comparent très bien aux résultats expérimentaux. Les approches semi-classiques permettent souvent une meilleure interprétation physique, par contre les résultats montrent que les effets de trajectoire ou de réorientation de l'axe internucléaire au cours de la collision sont très importants, ce qui nécessite le développement de méthodes semi-classiques très élaborées. Dans cet article (article 1), les équations couplées semi-classiques ainsi que les sections efficaces radiatives sont obtenues comme limite aux grands moments angulaires des expressions quantiques correspondantes ce qui permet de s'affranchir d'une hypothèse de trajectoire rectiligne. Un choix adéquat des systèmes d'axes permet d'établir une correspondance exacte avec l'approche semi-classique directe. Ceci nous a conduit à interpréter physiquement les branches spectroscopiques  $P$ ,  $Q$ ,  $R$  en termes de rotation de l'axe internucléaire durant la collision.

**Abstract.** — The quantal theory of atomic collisions in a radiative field is now well established for weak fields which we consider here. Several calculations of radiative cross sections and redistribution of polarization compare extremely well with experimental results. Semi-classical approaches often allow a better physical interpretation. However, the above mentioned results show that trajectory and internuclear reorientation effects during the collision play an essential role so that sophisticated methods have to be developed. In this paper (paper 1), we derive the semi-classical close coupled equations in the limit of large quantum numbers of the quantal equations thereby avoiding the rectilinear trajectory assumption. An adequate choice of the axis frame of reference allows us to show the exact correspondence between this approach and the direct semi-classical derivation of the close coupled equations. This leads us to interpret physically the  $P$ ,  $Q$ ,  $R$  spectroscopic branches in terms of the rotation of the internuclear axis during the collision.

### 1. Introduction.

The physical interpretation of collision theory is easier when the relative motion is described in a semi-classical approach. Many results have been obtained in a rectilinear trajectory approximation concerning various total cross sections which compare well with experimental results. At low energies, however, and in the presence of inelastic processes, small angular momenta play an important role so that trajectory effects should be considered. Then, the application of semi-classical methods may appear somewhat arbitrary since it is impossible to define a single trajectory. In the Hund's case a (or c) collisional molecular picture, one may consider that

the relative motion of the nuclei is determined in each channel by the channel electronic energy, but this description is not valid for all internuclear distances  $R$  and, it is known that the Hund's case (e) representation is well adapted at large  $R$  values corresponding to a mixing of the molecular channels.

So, it would appear quite unreasonable to try to define a trajectory and to develop semi-classical methods since each considered reaction channel has a different potential energy curve. However, since the transition region is well localized, the potential curves are similar around the curve crossing (or pseudo curve crossing).

Inelastic contributions arising from other regions located far from the curve crossing are expected to

be very small so that the actual choice of one common potential to describe the collision dynamics is far from critical. Thus, in a semi-classical picture, we can define one common trajectory.

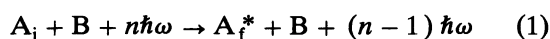
In this paper, we start from the quantal equations and we derive their limit at large values of the relative orbital angular momentum which yields the semi-classical formulation. This process allows us to interpret physically the different branches  $P$ ,  $Q$ ,  $R$  in terms of the rotation of the internuclear axis.

The method used is based on the original work of Berson [1] and is related in some aspects to the work developed by Gaussorgues *et al.* [2] for atomic collisions without radiative field. Our purpose here is to emphasize the radiative coupling treatment owing to the difficulty of the unspherical symmetry after the collisional orientation average.

Section 2 gives a rapid summary of the close coupled quantal theory of atomic collisions in the presence of a radiative field, section 2 describes the main aspects of the method leading to the semi-classical limit of the quantum theory. We focus our attention on the radiative contribution and we establish the expression of the relevant radiative cross-sections.

## 2. Quantum mechanical description : summary of the theory.

We consider the collision of two atoms A and B and we assume that B is a structureless  $^1S_0$  atom whereas A is characterized by angular momentum quantum numbers  $j m_j$ . The collision in the presence of light is described by the reaction :



where  $n$  is the number of photons of energy  $\hbar\omega$  in the incident field.

**2.1 HAMILTONIAN.** — Since the details of the theory have been described by several authors [3-6], we will only present a summary of the theory. The total Hamiltonian  $H$  is given by :

$$H = H^{\text{mol}} + H^{\text{rad}} + V^{\text{rad}} \quad (2)$$

where  $H^{\text{mol}}$  is the total molecular Hamiltonian (in barycentric coordinates) :

$$H^{\text{mol}} = T + H^e + B(R) \ell^2 + H^{\text{SO}} \quad (3)$$

where  $T$  is the kinetic energy operator,  $H^e$  is the electronic Hamiltonian whose eigenvalues are the Born Oppenheimer molecular potentials  $W_{|A|}(R)$

$$H^e |\alpha L \Lambda\rangle = W_{|A|}(R) |\alpha L \Lambda\rangle \quad (4)$$

$B(R) \ell^2$  is the rotational operator with  $\ell = \mathbf{J} - \mathbf{L} - \mathbf{S}$ .  $\mathbf{L}$  and  $\mathbf{S}$  are the electronic orbital and

spin angular momenta with the corresponding approximate quantum numbers for the molecular Hamiltonian.  $H^{\text{SO}}$  is the spin orbit operator.  $H^{\text{rad}}$  is the free radiative field, and  $V^{\text{rad}}$  is the dipole interaction operator given by :

$$V^{\text{rad}} = E_0 \cdot \hat{\varepsilon}_0 \cdot \mathbf{d} \quad (5)$$

with  $E_0 = (2 \pi \hbar \omega \phi / c)^{1/2}$ .  $\phi$  is the photon flux, and the polarization vector  $\hat{\varepsilon}_0$  is taken along the space fixed Oz direction. We will consider here sufficiently weak incident radiative field so that  $V^{\text{rad}}$  will be treated as a perturbation. Typical magnitudes are  $\hbar \omega \phi < 10^6 \text{ W cm}^{-2}$  for absorption in the wings of an optical collision, and  $\hbar \omega \phi < 10^9 \text{ W cm}^{-2}$  for a radiative collision [4].

**2.2 BASIS STATES.** — At low kinetic energies, the total wave function of the system is expanded on a molecular basis. At large interatomic distances  $R$ , the molecular Hamiltonian is diagonal in a Hund's case (e) basis  $|\alpha j \ell, J M p\rangle$ . Here  $J$  and  $M$  are the total angular momentum and its space fixed projection,  $p$  is the parity.  $j$  is the electronic angular momentum of A, well defined for  $R \rightarrow \infty$ . At small  $R$  values, it is convenient to introduce a case (a) or case (c) molecular basis to represent the electronic rotational states. Since these two basis are connected by a unitary transformation involving the approximate electronic quantum numbers only, both are equivalent from the point of view of semi-classical limit. For simplicity, we have chosen here to expand the wave function on the Hund's case (c) molecular basis dressed by the radiation field with energy  $\hbar\omega$  :

$$|i\rangle = |\alpha_i j_i \bar{\Omega}_i, J_i M_i p_i\rangle \otimes |n \hbar \omega \hat{\varepsilon}_0\rangle \quad (6)$$

where  $\bar{\Omega}_i = |\Omega_i|$ .

In this basis, the molecular wave functions are quantized with respect to the internuclear axis OZ in the rotating frame OXYZ. The parity  $p_i$  corresponds to the operation  $E^*$  of inversion of space fixed Cartesian coordinates of all particles. Larsson [7] has clearly established that the symmetry operation  $E^*$  operating on the Hund's case (a) molecular basis is given by :

$$E^* |\alpha \Lambda S \Sigma, J M \Omega\rangle = (-1)^{J-S+s} |\alpha - \Lambda S - \Sigma, J M - \Omega\rangle \quad (7)$$

where  $s = 1$  for  $\Sigma^-$  states and zero otherwise. This relation leads to the following definition for the Hund's case (a) basis of definite parity  $p$  :

$$\begin{aligned} |\alpha \bar{\Lambda} S \bar{\Sigma}, J M p\rangle &= \frac{1}{\sqrt{2 - \delta_{\bar{\Lambda},0} \delta_{\bar{\Sigma},0}}} \{ |\alpha \bar{\Lambda} S \bar{\Sigma}, J M \bar{\Omega}\rangle \\ &\quad + (1 - \delta_{\bar{\Lambda},0} \delta_{\bar{\Sigma},0}) (-1)^{J-S+s} \\ &\quad \times p |\alpha - \bar{\Lambda} S - \bar{\Sigma}, J M - \bar{\Omega}\rangle \} \quad (8) \end{aligned}$$

From the active point of view (Brink and Satchler [8]), the rotational wave functions  $|JM\Omega\rangle$  are given by :

$$|JM\Omega\rangle = \left( \frac{2J+1}{8\pi^2} \right)^{1/2} \mathcal{D}_{M\Omega}^{J*}(\alpha\beta\gamma). \quad (9)$$

Following the usual conventions in the scattering theory, the Euler angle  $\gamma$  is taken equal to zero which corresponds to the symmetry operation  $C_2(x)$  applied to the rotational variables. With this particular choice ( $\gamma = 0$ ), one has to consider the reflexion operator  $\sigma_v(yz)$  for the electronic wave function [7]. This point will be important in the semi-classical limit.

The usual transformation between Hund's case (a) and case (c) basis states may be written :

$$|\alpha\bar{L}S\bar{\Sigma}\rangle = \sum_j \langle L\bar{L}S\bar{\Sigma}|j\bar{\Omega}\rangle |\alpha j\bar{\Omega}\rangle \quad (10)$$

where  $\langle L\bar{L}S\bar{\Sigma}|j\bar{\Omega}\rangle$  is a Clebsch Gordan coefficient. Using relations (8) and (10), we may now define the Hund's case (c) basis states of parity  $p$  :

$$|\alpha j\bar{\Omega}, JMp\rangle = \frac{1}{\sqrt{2 - \varepsilon p \delta_{\bar{\Omega},0}}} \sqrt{\frac{2J+1}{4\pi}} \times$$

$$\times \left\{ \mathcal{D}_{M\bar{\Omega}}^{J*}(\theta, \phi, 0) |\alpha j\bar{\Omega}\rangle + (1 - \delta_{\bar{\Omega},0}) \times \varepsilon p \mathcal{D}_{M-\bar{\Omega}}^{J*}(\theta, \phi, 0) |\alpha j - \bar{\Omega}\rangle \right\}. \quad (11)$$

where  $\varepsilon = (-1)^{J-j+L}$ .

The rotation of Euler angles  $(\theta, \phi, 0)$  brings the space fixed (Oxyz) frame onto the body fixed (OXYZ) frame. The relation between the case (c) and the case (e) basis states is given by [9] :

$$|\alpha j\ell, JMp\rangle = \sum_{\bar{n}} \sqrt{\frac{2}{1 + \varepsilon p \delta_{\bar{n},0}}} \sqrt{\frac{2\ell+1}{2J+1}} \times \langle j\bar{\Omega}\ell 0 | J\bar{\Omega}\rangle |\alpha j\bar{\Omega}, JMp\rangle. \quad (12)$$

**2.3 CLOSE COUPLED EQUATIONS.** — For each initial channel  $i$  and total energy  $E$ , the total wave function is expanded as following :

$$\psi_i(R) = \frac{1}{R} \left[ \sum_{i'} F_{i'}(R) |i'\rangle + \sum_f F_f(R) |f\rangle \right]. \quad (13)$$

The sums  $\sum_{i'}$  and  $\sum_f$  include all channels that can be reached by collisional or radiative coupling. The radial wave functions  $F$  satisfy the coupled equations :

$$\begin{aligned} \left[ \frac{d^2}{dR^2} + k_i^2 - \frac{\langle i | \ell^2 | i \rangle}{R^2} - \frac{2\mu}{\hbar^2} U_i(R) \right] F_i &= \frac{2\mu}{\hbar^2} \left[ \sum_{i' \neq i} V_{ii'} F_{i'} + \sum_f V_{if}^{\text{rad}} F_f \right] \\ \left[ \frac{d^2}{dR^2} + k_f^2 - \frac{\langle f | \ell^2 | f \rangle}{R^2} - \frac{2\mu}{\hbar^2} U_f(R) \right] F_f &= \frac{2\mu}{\hbar^2} \left[ \sum_{f' \neq f} V_{ff'} F_{f'} + \sum_i V_{fi}^{\text{rad}} F_i \right] \end{aligned} \quad (14)$$

where  $U_i$  and  $U_f$  represent the diagonal parts of the  $H^e$  matrix.  $V_{ii'}$  and  $V_{ff'}$  are the electronic coupling terms given from (4) together with the unitary transformation (10), or the rotational matrix elements. They are diagonal in  $J$ ,  $M$ , and  $p$ .

It can be shown that the rotational matrix elements are given by :

$$\begin{aligned} \langle \alpha_i j_i \bar{\Omega}_i, J_i M_i p_i | \ell^2 | \alpha_i j_i \bar{\Omega}_i \pm 1, J_i M_i p_i \rangle &= \\ &= - (1 + \varepsilon_i p_i \delta_{\bar{\Omega}_i,0})^{1/2} [j_i(j_i+1) - \bar{\Omega}_i(\bar{\Omega}_i \pm 1)]^{1/2} [J_i(J_i+1) - \bar{\Omega}_i(\bar{\Omega}_i \pm 1)]^{1/2} \end{aligned} \quad (15)$$

and :

$$\begin{aligned} \langle \alpha_i j_i \bar{\Omega}_i, J_i M_i p_i | \ell^2 | \alpha_i j_i \bar{\Omega}_i, J_i M_i p_i \rangle &= \\ &= j_i(j_i+1) + J_i(J_i+1) - 2\bar{\Omega}_i^2 - \varepsilon_i p_i \delta_{\bar{\Omega}_i,1/2} \sqrt{j_i(j_i+1) - \bar{\Omega}_i(\bar{\Omega}_i-1)} \sqrt{J_i(J_i+1) - \bar{\Omega}_i(\bar{\Omega}_i-1)}. \end{aligned} \quad (16)$$

The derivation of the radiative coupling terms is detailed in appendix 1.

In absorption, we find :

$$\begin{aligned} V_{fi}^{\text{rad}} &= \frac{E_0(1 - p_i p_f)}{2 \sqrt{1 + \varepsilon_i p_i \delta_{\bar{\Omega}_i,0}} \sqrt{1 + \varepsilon_f p_f \delta_{\bar{\Omega}_f,0}}} \sqrt{\frac{2J_i+1}{2J_f+1}} \langle J_i M_i 1 q | J_f M_f \rangle \times \\ &\times (1 - p_i p_f) [\langle J_i \bar{\Omega}_i 1 \bar{\Omega}_f - \bar{\Omega}_i | J_f \bar{\Omega}_f \rangle \mu_{\bar{\Omega}_f - \bar{\Omega}_i} + \varepsilon_i p_i \langle J_i - \bar{\Omega}_i 1 \bar{\Omega}_f + \bar{\Omega}_i | J_f \bar{\Omega}_f \rangle \mu_{\bar{\Omega}_f + \bar{\Omega}_i}] \end{aligned} \quad (17)$$

$k_i^2$  and  $k_f^2$  satisfy the relation of conservation of the total energy  $E$  :

$$E = E_i + \frac{\hbar^2 k_i^2}{2\mu} + n\hbar\omega = E_f + \frac{\hbar^2 k_f^2}{2\mu} + (n-1)\hbar\omega \quad (18)$$

where  $E_i$  and  $E_f$  are the total internal energies of atoms A and B at large  $R$  internuclear distances.

In the limit of large angular momenta ( $J$  or  $\ell$ ), the diagonal rotational terms are :

$$\begin{aligned} \langle i | \ell^2 | i \rangle &\simeq J_i(J_i + 1) \\ \langle f | \ell^2 | f \rangle &\simeq J_f(J_f + 1). \end{aligned} \quad (19)$$

These terms are identical among the initial states  $i, i'$  or the final states  $f, f'$  and they may differ for radiatively coupled states according to the  $P, Q, R$  spectroscopic branches.

### 3. Semi-classical limit.

Many studies have been devoted to this problem, and we avoid here all difficulties connected to the existence of the different turning points. We assume further that the turning points relevant to different channels are the same :  $R_i \simeq R_0$ .

**3.1 EQUATIONS.** — We introduce an average potential  $U_0$  and an average momentum  $J_0$ , so that the system (14) can be written as :

$$\begin{aligned} \left[ \frac{d^2}{dR^2} + \kappa_i^2 \right] F_i(R) &= \left[ \frac{2\mu}{\hbar^2} (U_i - U_0) + \frac{J_i(J_i + 1) - J_0(J_0 + 1)}{R^2} \right] F_i(R) \\ &+ \frac{2\mu}{\hbar^2} \sum_{j \neq i} V_{ij} F_j(R) \end{aligned} \quad (20)$$

with

$$\kappa_i^2 = k_i^2 \left[ 1 - \frac{J_0(J_0 + 1)}{k_i^2 R^2} - \frac{2\mu}{\hbar^2 k_i^2} U_0(R) \right].$$

Following Berson [1], we write :

$$F_i(R) = \frac{a_i^+(R)}{\sqrt{\kappa_i}} e^{i\mathcal{S}_i(R)} - \frac{a_i^-(R)}{\sqrt{\kappa_i}} e^{-i\mathcal{S}_i(R)} \quad (21)$$

where  $\mathcal{S}_i(R)$  is the reduced radial action :

$$\mathcal{S}_i(R) = \int_{R_0}^R \kappa_i(R') dR'.$$

The unknown functions  $a_i^+(R)$  and  $a_i^-(R)$  are obtained through the method of variation of par-

ameters. We assume that the usual semi-classical condition :

$$\frac{1}{\sqrt{\kappa_i^3}} \frac{d^2}{dR^2} \left( \frac{1}{\sqrt{\kappa_i}} \right) \ll 1 \quad (22)$$

is satisfied and that the relation

$$|\mathcal{S}_i - \mathcal{S}_j| \ll |\mathcal{S}_i + \mathcal{S}_j| \quad (23)$$

holds between two coupled channels.

We further choose the relation which simplifies the equations without any further constraint :

$$e^{i\mathcal{S}_i(R)} \frac{da_i^+}{dR} = e^{i\mathcal{S}_i(R)} \frac{da_i^-}{dR} \quad (24)$$

leading to the following equations :

$$\begin{aligned} i \frac{da_i^+}{dR} &= \frac{1}{2\kappa_i} \left[ \frac{2\mu}{\hbar^2} (U_i - U_0) + \frac{J_i(J_i + 1) - J_0(J_0 + 1)}{R^2} \right] a_i^+ \\ &+ \frac{2\mu}{\hbar^2} \sum_j \frac{1}{\sqrt{\kappa_i \kappa_j}} V_{ij} a_j^+ e^{i(\mathcal{S}_j - \mathcal{S}_i)} \\ -i \frac{da_i^-}{dR} &= \frac{1}{2\kappa_i} \left[ \frac{2\mu}{\hbar^2} (U_i - U_0) + \frac{J_i(J_i + 1) - J_0(J_0 + 1)}{R^2} \right] a_i^- \\ &+ \frac{2\mu}{\hbar^2} \sum_j \frac{1}{\sqrt{\kappa_i \kappa_j}} V_{ij} a_j^- e^{-i(\mathcal{S}_j - \mathcal{S}_i)}. \end{aligned} \quad (25)$$

At this point, it is convenient to introduce a new set of coefficients  $b_i^\pm$  :

$$b_i^\pm = a_i^\pm \exp \pm i \int_{R_0}^R h_i(R') dR' \quad (26)$$

with :

$$h_i(R) = \frac{\mu}{\hbar^2 \kappa_i} (U_i - U_0) + \frac{J_i(J_i + 1) - J_0(J_0 + 1)}{2\kappa_i R^2}.$$

Finally, we assume that the kinetic energy is large enough to write  $\kappa_i \simeq \kappa_j \simeq \kappa_0$  except for the differences  $\kappa_i - \kappa_j$ , so that we can write the relation between the internuclear distance  $R$  and the time  $t$  associated to a trajectory of a particle of mass  $\mu$  moving in a potential  $U_0$  with an angular momentum  $J_0 + \frac{1}{2}$  :

$$t = \pm \int_{R_0}^R \frac{\mu}{\hbar \kappa_0} dR'. \quad (27)$$

The  $b_i$  coefficients satisfy the equations :

$$i\hbar \frac{db_i}{dt} = \sum_j V_{ij} b_j \exp i \int' \left\{ \frac{\hbar \kappa_0}{\mu} (\kappa_j - \kappa_i) + \frac{1}{\hbar} (U_i - U_j) + \frac{\hbar^2}{2\mu R^2(t')} [J_i(J_i + 1) - J_j(J_j + 1)] \right\} dt' \quad (28)$$

where  $b_i(t) = b_i^-(R)$  for  $t \leq 0$   
and  $b_i(t) = b_i^+(R)$  for  $t \geq 0$ .

These semi-classical equations are valid provided that :

- the turning point is approximately the same for all coupled channels,
- the JWKB condition (22) is satisfied,
- high frequency oscillations are negligible,
- $\kappa$  is approximately the same  $\kappa_0$  in all channels.

It is interesting to examine particularly the semi-classical limit of the rotational and the radiative coupling terms, since they involve the relative orbital quantum number.

**3.2 ROTATIONAL COUPLING TERMS.** — In this case, the total angular momentum is the same for the two coupled channels  $i, i'$  or  $f, f'$ . So, the argument of the exponential factor is :

$$-\frac{i}{\hbar} \int' (U_{i'} - U_i) dt'.$$

For large values of  $J_i$ ,  $V_{ii'}$  (Eq. (15)) becomes :

$$V_{ii'} = -\frac{\hbar^2}{2\mu R^2} J_i (1 + \varepsilon_i p_i \delta_{\bar{n}_i, 0})^{1/2} \times [j_i(j_i + 1) - \bar{n}_i(\bar{n}_i \pm 1)]^{1/2}. \quad (29)$$

The factor  $J_i/\mu R^2$  is related to the time derivative  $\dot{\theta} = d\theta/dt$  of the rotation angle  $\theta$  of the internuclear axis :

$$\frac{J_i}{\mu R^2} = \frac{\dot{\theta}}{\hbar} \quad (30)$$

so that the semi-classical rotational coupling term in (28) is equal to :

$$W_{ii'} = -\hbar \dot{\theta} \exp \left[ -\frac{i}{\hbar} \int' (U_{i'} - U_i) dt' \right] \times \frac{1}{2} (1 + \varepsilon_i p_i \delta_{\bar{n}_i, 0})^{1/2} [j_i(j_i + 1) - \bar{n}_i(\bar{n}_i \pm 1)]^{1/2} \quad (31)$$

in agreement with the direct semi-classical result (see appendix 2).

**3.3 RADIATIVE COUPLING TERM.** — For two channels  $i$  and  $f$  coupled by the radiative field at frequency  $\omega$ , the conservation of the total energy leads to the relation :

$$\pm \hbar \Delta\omega = \frac{\hbar^2}{2\mu} (k_f^2 - k_i^2) \approx \frac{\hbar \kappa_0}{\mu} (\kappa_f - \kappa_i) \quad (32)$$

where  $\Delta\omega = \omega - \omega_0$  represents the detuning of the incident radiation related to the asymptotic difference  $\hbar\omega_0$  of molecular potential curves. The + sign corresponds to absorption and - sign to emission.

According to the branch  $B = J_f - J_i$ , the total angular momentum is different for the channels  $i$  and  $f$  and we can write :

$$\hbar \left[ \frac{J_i(J_i + 1) - J_f(J_f + 1)}{2\mu R^2} \right] = -B\dot{\theta} \quad (33)$$

so that the exponential factor in (28) becomes :

$$\exp -\frac{i}{\hbar} (\phi_f - \phi_i) \cdot \exp -iB(\theta - \theta_0) \quad (34)$$

with :

$$\phi_f - \phi_i = \int' (-\hbar \Delta\omega + U_f - U_i) dt' \quad (35)$$

$\theta_0$  is the initial value of  $\theta$ .

For the low intensities of the radiative field considered here, the Wigner Eckart theorem may be used to remove the explicit  $M$  dependence from the coupled equations. The full formalism first introduced by De Vries and George [3] and then discussed by Mies [4] will not be detailed here. The complete radiative coupling term (17) is expressed in the following form :

$$V_{fi}^{\text{rad}} = \langle J_f M_f 1 - q | J_i M_i \rangle \times (-1)^{M_f - M_i} \langle f || V^{\text{rad}} || i \rangle \quad (36)$$

and the coupled equations are solved with the reduced radiative coupling  $\langle f || V^{\text{rad}} || i \rangle$ .

We now use the asymptotic form of the Clebsch Gordan coefficients (8) :

$$\langle J_1 M_1 J_2 M_2 | J_3 M_3 \rangle \approx (-1)^{J_1 - J_2 + J_3} d_{J_3 - J_2, M_1}^{J_1} (-\beta) \quad (37)$$

with  $J_2, J_3 \gg J_1$  and  $\cos(-\beta) = \frac{M_3}{J_3}$  to evaluate

$$\langle J_i \bar{n}_i 1 \bar{n}_f - \bar{n}_i | J_f \bar{n}_f \rangle \quad \text{and} \quad \langle J_i - \bar{n}_i 1 \bar{n}_f + \bar{n}_i | J_f \bar{n}_f \rangle.$$

$J_i$  and  $J_f$  are large, and  $\bar{n}_i$  and  $\bar{n}_f$  are small so that  $\beta \approx \frac{\pi}{2}$ .

So, the reduced radiative coupling term  $W_{fi}$  is :

$$W_{fi} = E_0 \frac{1 - p_i p_f}{2 \sqrt{1 + \varepsilon_i p_i \delta_{\bar{n}_i,0}} \sqrt{1 + \varepsilon_f p_f \delta_{\bar{n}_f,0}}} e^{-\frac{i}{\hbar}(\phi_f - \phi_i)} \times \\ \times \left\{ \mathcal{D}_{B, \bar{n}_f - \bar{n}_i}^{1*} \left( \theta - \theta_0 - \pi, -\frac{\pi}{2}, 0 \right) \cdot \mu_{\bar{n}_f - \bar{n}_i} + \varepsilon_i p_i \mathcal{D}_{B, \bar{n}_f + \bar{n}_i}^{1*} \left( \theta - \theta_0 - \pi, -\frac{\pi}{2}, 0 \right) \mu_{\bar{n}_f + \bar{n}_i} \right\}. \quad (38)$$

The particular choice  $\theta_0 = -\frac{\pi}{2}$  leads to the semi-classical result obtained directly in appendix II, if we use the relations :

$$B = J_f - J_i \leftrightarrow p \\ -p_i p_f \leftrightarrow -\pi_i \pi_f (-1)^p. \quad (39)$$

The method presented here gives the exact correspondence between the quantal and semi-classical equations. It is particularly interesting to note that the  $P$ ,  $Q$ , and  $R$  branches can be physically interpreted in terms of the rotation of the molecular dipole during the collision. This result was not obvious *a priori* since the total angular momentum is not preserved in the semi-classical methods.

#### 4. Radiative cross-sections.

As mentioned by Gaussorgues *et al.* [2],  $a_j^-$  has the meaning of a probability amplitude of excitation to the state  $j$  when the incident particles move in a convergent wave from infinity and  $a_j^+$  has the same meaning for a divergent wave, so that  $a_j^-(\infty) \simeq \delta_{ji}$  where  $i$  denotes the initial channel.  $a_j^-$  and  $a_j^+$  are connected through the continuity relation :

$$a_j^+(R_0) = a_j^-(R_0). \quad (40)$$

The asymptotic form of the radial wave function (21) gives the relation between the  $S$ -matrix in the Hund's case (c) representation and the amplitudes

$a^+$  or  $b^+$ . For large values of  $R$ ,  $F_f(R)$  can be written as :

$$F_f(R) \simeq -\frac{1}{\sqrt{\kappa_f}} \times \\ \times \left[ \delta_{fi} \exp -i \left( k_f \cdot R - J_f \cdot \frac{\pi}{2} \right) \cdot \exp(-i\sigma_f) \right. \\ \left. - a_f^+(+\infty) \cdot \exp i \left( k_f R - J_f \cdot \frac{\pi}{2} \right) \cdot \exp(i\sigma_f) \right] \quad (41)$$

$$\text{where } \sigma_f = \lim_{R \rightarrow \infty} \left( S_f - k_f \cdot R + J_f \cdot \frac{\pi}{2} \right).$$

In the limit of large angular momenta  $J_i$  or  $J_f$ , one can immediately deduce :

$$\langle \alpha_f j_f \bar{\Omega}_f p_f | S_\omega | \alpha_i j_i \bar{\Omega}_i J_i p_i \rangle = \\ = \exp(-i\alpha_i) \cdot \exp -iB \left( \Theta - \frac{\pi}{2} \right) \cdot S_{fi}^{\infty} \quad (42)$$

with :

$$S_{fi}^{\infty} = b_f(+\infty) \exp -\frac{i}{\hbar} \int^\infty (-\hbar \Delta \omega + U_f - U_i) dt'$$

$\Theta$  represents the rotation of the internuclear axis at the end of the collision.  $\alpha_i$  is a constant phase shift which disappears in the expression of the radiative cross-section after we sum the contribution of the initial states.

Using the notations of Julienne and Mies [12], we now introduce the linear transformation (12) to obtain the reduced  $S$ -matrix elements in the case (e) basis :

$$S_\omega^B(j_f \ell_f \leftarrow j_i \ell_i J_i p_i) = \sum_{\bar{n}_i \bar{n}_f} \frac{1}{\sqrt{2 - \varepsilon_i p_i \delta_{\bar{n}_i,0}}} \cdot \frac{1}{\sqrt{2 - \varepsilon_f p_f \delta_{\bar{n}_f,0}}} \times \\ \times \langle \ell_i 0 j_i \bar{\Omega}_i | J_i \bar{\Omega}_i \rangle \langle \ell_f 0 j_f \bar{\Omega}_f | J_f \bar{\Omega}_f \rangle \exp -iB \left( \Theta - \frac{\pi}{2} \right) \langle \alpha_f j_f \bar{\Omega}_f J_f p_f | S_\omega | \alpha_i j_i \bar{\Omega}_i J_i p_i \rangle. \quad (43)$$

Further use of the asymptotic form of the Clebsch Gordan coefficients leads to :

$$\langle \ell_i 0 j_i \bar{\Omega}_i | J_i \bar{\Omega}_i \rangle \langle \ell_f 0 j_f \bar{\Omega}_f | J_f \bar{\Omega}_f \rangle \exp -iB \left( \Theta - \frac{\pi}{2} \right) = \\ = \mathcal{D}_{j_i - \ell_i, \bar{n}_i}^{j_i*} \left( \Theta - \frac{\pi}{2}, -\frac{\pi}{2}, 0 \right) \mathcal{D}_{j_f - \ell_f, \bar{n}_f}^{j_f} \left( \Theta - \frac{\pi}{2}, -\frac{\pi}{2}, 0 \right) \exp -i \left[ (\ell_f - \ell_i) \left( \Theta - \frac{\pi}{2} \right) \right]. \quad (44)$$

It follows that :

$$S_{\omega}^B(j_f \ell_f \leftarrow j_i \ell_i J_i p_i) = \exp(-i\alpha_i) \cdot \exp - \left[ i(\ell_f - \ell_i) \left( \Theta - \frac{\pi}{2} \right) \right] \times \langle \alpha_f j_f M_{j_f} | S_{sc}^B | \alpha_i j_i M_{j_i} \rangle \quad (45)$$

with  $M_{j_f} = J_f - \ell_f$  and  $M_{j_i} = J_i - \ell_i$ .

The states  $|\alpha_j M_j\rangle$  are related to  $|\alpha_j \bar{\Omega} J p\rangle$  through the transformation :

$$|\alpha_j M_j\rangle = \sum_{\bar{n}} \sqrt{2 - \varepsilon p \delta_{\bar{n},0}} \cdot \mathcal{D}_{M_j, \bar{n}}^{j*} \left( \Theta - \frac{\pi}{2}, -\frac{\pi}{2}, 0 \right) |\alpha_j \bar{\Omega} J p\rangle \quad (46)$$

$\langle \alpha_f j_f M_{j_f} | S_{sc}^B | \alpha_i j_i M_{j_i} \rangle$  represents the S-matrix relative to a space fixed frame which can be deduced from the OXYZ axis (at the end of the collision) by the rotation  $R^{-1} \left( \Theta - \frac{\pi}{2}, -\frac{\pi}{2}, 0 \right)$ . This corresponds to the usual « collisional axis » (see appendix 2). Consequently,  $M_{j_i}$  and  $M_{j_f}$  denote the projection of  $j_i$  and  $j_f$  in the space fixed collision frame.

Standard scattering theory techniques (Julienne and Mies [12]) lead to the expression of the radiative cross-sections in terms of the  $S^B$  matrix elements for each branch B :

$$\sigma_{\omega}(j_f m_f \leftarrow j_i \varepsilon_i q) = \frac{\pi}{(2j_i + 1) k_i^2} \sum_{\substack{t_i \ell_f \\ J_i J_f J_f'}} A \cdot S_{\omega}^B(j_f \ell_f \leftarrow j_i \ell_i J_i p_i) S_{\omega}^{B'*}(j_f \ell_f \leftarrow j_i \ell_i J_i p_i) \quad (47)$$

where :

$$A = \sum_{M_f} \langle \ell_f(M_f - m_f) j_f m_f | J_f M_f \rangle \langle J_i M_i 1 q | J_f M_f \rangle \langle \ell_f(M_f - m_f) j_f m_f | J_f' M_f \rangle \times \\ \times \langle J_i M_i 1 q | J_f' M_f \rangle \quad (48)$$

$J_i, J_f, J_f'$  and  $\ell_f$  are large.

In the large angular momenta limit (8) :

$$A \approx \sum_{M_f} d_{J_f - \ell_f, m_f}^{j_f}(-\beta) \cdot d_{J_i - J_f, -q}^1(-\beta) \cdot d_{J_f' - \ell_f, m_f}^{j_f}(-\beta) \cdot d_{J_i - J_f', -q}^1(-\beta) \\ = \sum_{M_f} d_{M_{j_f}, m_f}^{j_f}(-\beta) \cdot d_{-B, -q}^1(-\beta) \cdot d_{M_{j_f'}, m_f}^{j_f}(-\beta) \cdot d_{-B', -q}^1(-\beta) \quad (49)$$

with  $\cos(-\beta) \approx \frac{M_f}{J_f}$ .

The relation of contraction of rotation matrices gives :

$$A = \sum_{t'} (2t + 1)(2t' + 1) \begin{pmatrix} j_f & 1 & t \\ m_f & -q & \nu \end{pmatrix} \begin{pmatrix} j_f & 1 & t' \\ m_f & -q & \nu \end{pmatrix} \begin{pmatrix} j_f & 1 & t \\ M_{j_f} & -B & \mu \end{pmatrix} \begin{pmatrix} j_f & 1 & t' \\ M_{j_f'} & -B' & \mu' \end{pmatrix} \times \\ \times \sum_{M_f} d_{\mu\nu}^t(-\beta) d_{\mu'\nu}^{t'}(-\beta) \quad (50)$$

For large values of  $J_f$ , the sum  $\sum_{M_f}$  can be replaced by an integral :

$$\sum_{M_f} d_{\mu\nu}^t(-\beta) \cdot d_{\mu'\nu}^{t'}(-\beta) \approx \int_0^\pi d[J_f \cdot \cos(-\beta)] \cdot d_{\mu\nu}^t(-\beta) d_{\mu'\nu}^{t'}(-\beta) = \frac{2J_f}{2t + 1} \delta_{tt'} \delta_{\mu\mu'} \quad (51)$$

This relation is equivalent to the angular average in the direct semi-classical approach.

If we introduce the impact parameter  $b \approx \frac{J_i}{k_i} \approx \frac{J_f}{k_i}$ , we find that the cross-sections (47) are :

$$\sigma_{\omega}(j_f m_f \leftarrow j_i \varepsilon_i q) = \frac{2\pi}{2j_i + 1} \sum_{\substack{M_{j_f} M_{j_f'} \\ BB' t M_{j_i} \mu}} (-1)^{-(B+B')} (2t + 1) \begin{pmatrix} j_f & 1 & t \\ m_f & -q & \nu \end{pmatrix}^2 \begin{pmatrix} j_f & 1 & t \\ M_{j_f} & -B & \mu \end{pmatrix} \times \\ \times \begin{pmatrix} j_f & 1 & t \\ M_{j_f'} & -B' & \mu \end{pmatrix} \int b db \langle \alpha_f j_f M_{j_f} | S_{sc}^B | \alpha_i j_i M_{j_i} \rangle \langle \alpha_f j_f M_{j_f'} | S_{sc}^{B'} | \alpha_i j_i M_{j_i} \rangle^* \quad (52)$$



$\mu$  is related to  $M_{j_f}$  and  $M'_{j_f}$  through :

$$\mu = M_{j_f} - B = M'_{j_f} - B'. \quad (53)$$

Similarly to the quantum expression [12] we may rewrite (47) as :

$$\sigma_\omega(j_f m_f \leftarrow j_i \varepsilon_i q) = \sum_t 3 \frac{\langle j_f m_f 1 - q | t(m_f - q) \rangle^2}{2t + 1} \sigma_\omega^t(j_f) \quad (54)$$

where :

$$\sigma_\omega^t(j_f) = \frac{2\pi}{2j_i + 1} \int b db \frac{1}{3} \sum_{\substack{M_{j_i} \\ \mu}} \left| \sum_{M_{j_f} B} (-1)^B \langle \alpha_f j_f M_{j_f} | S_{sc}^B | \alpha_i j_i M_{j_i} \rangle \times \sqrt{2t + 1} \begin{pmatrix} j_f & 1 & t \\ M_{j_f} & -B & \mu \end{pmatrix} \right|^2. \quad (55)$$

This expression is exactly the same as the semi-classical expression obtained directly in appendix 2.

If we are only interested in the total rate of absorption (or emission) resulting from single collisions, we need the cross-sections defined by :

$$\sigma_\omega(j_f) = \sum_{m_f} \sigma_\omega(j_f m_f \leftarrow j_i \varepsilon_i q). \quad (56)$$

The sum over  $m_f$  in (52) is easily performed since  $m_f$  occurs only in a  $3j$  coefficient :

$$\sigma_\omega(j_f) = \sum_t \sigma_\omega^t(j_f) \quad (57)$$

with  $\sigma_\omega^t(j_f)$  given by (55). Furthermore, we may now sum over  $t$ . Thus :

$$\sigma_\omega(j_f) = \frac{2\pi}{2j_i + 1} \int b db \cdot \frac{1}{3} \times \sum_{\substack{M_{j_f} M_{j_i} \\ B}} \left| \langle \alpha_f j_f M_{j_f} | S_{sc}^B | \alpha_i j_i M_{j_i} \rangle \right|^2. \quad (58)$$

When the  $S$ -matrix is obtained in the Hund's case (c) basis (particularly in the case of asymptotically forbidden transitions), we may transform expression (58) according to (A.11) relating the (e) and (c) basis states. The total cross-section is :

$$\sigma_\omega(j_f) = \frac{2\pi}{2j_i + 1} \int b db \frac{1}{3} \times \sum_{B \bar{n}_f \bar{n}_i} \sqrt{2 - \delta_{\bar{n}_i, 0}} \sqrt{2 - \delta_{\bar{n}_f, 0}} \times \left| \langle \alpha_f j_f \bar{\Omega}_f \pi_f | S_{sc}^B | \alpha_i j_i \bar{\Omega}_i \pi_i \rangle \right|^2. \quad (59)$$

## 5. Conclusion.

A systematic treatment of the semi-classical limit of the quantum scattering theory allows us to obtain the usual set of coupled time dependent differential equations. The calculation of the radiatively assisted

cross-section for production of the final state  $j_f m_f$  presents no particular difficulty. These cross-sections may be used to determine the absorption coefficient of the incident radiation and to calculate the orientation or alignment of the excited atom. One of the main results of this study is to interpret the spectroscopic  $P$ ,  $Q$ ,  $R$  branches of the quantum approach in terms of the rotation of the molecular dipole during the collision. This rotation is essential for polarization studies. We have also established the equivalence between the sum over  $M$  and the angular average of the semi-classical theory. It is important to notice that the step by step quantal-semi-classical correspondence (in particular for coupled equations) involves the choice of the *same* body fixed frame (with the  $Ox$  axis perpendicular to the collision plane). This non standard choice for the collision frame is the only one which enables to directly connect the quantal to the semi-classical channels.

## Appendix 1 : radiative coupling between molecular channel states.

The radiative coupling between the molecular field channel states is induced by the operator  $V^{\text{rad}}$  [4]

$$V^{\text{rad}} = \sqrt{2\pi\hbar\omega/\mathcal{V}} \cdot \mathbf{d} \cdot [\hat{\varepsilon}_q^* \cdot a^+ + \hat{\varepsilon}_q \cdot a] \quad (\text{A.1})$$

where  $\mathbf{d}$  represents the dipole moment of the system ( $A - B$ ),  $a$  and  $a^+$  are respectively the annihilation and creation operator of a photon with pulsation  $\omega$  and unit polarization vector  $\hat{\varepsilon}_q$ . The matrix elements of  $a$  and  $a^+$  between radiation field eigenstates  $|n\omega q\rangle$  and  $|n'\omega q\rangle$  vanish unless  $n' = n \pm 1$  :

$$\langle n\omega q | V^{\text{rad}} | n + 1 \omega q \rangle = \sqrt{2\pi\hbar\omega(n+1)/\mathcal{V}} \cdot \hat{\varepsilon}_q \cdot \mathbf{d}. \quad (\text{A.2})$$

The quantity  $\sqrt{2\pi\hbar\omega(n+1)/\mathcal{V}}$  represents the amplitude  $E_0$  of the incident field.

The vector  $\hat{\varepsilon}_q$  is defined in the space fixed frame whereas the dipole interaction operator  $\mathbf{d}$  is most easily known in the molecule fixed frame. So we use the rotation matrix  $\mathcal{D}_{m\sigma}^{1*}(\theta, \phi, 0)$  to obtain :

$$\begin{aligned}\hat{\varepsilon}_q \cdot \mathbf{d} &= \hat{\varepsilon}_q \cdot \sum_m d_m \cdot \hat{e}_m^* \\ &= \sum_{m\sigma} d_\sigma \cdot \mathcal{D}_{m\sigma}^{1*}(\theta, \phi, 0) \cdot \hat{e}_m^* \cdot \hat{\varepsilon}_q\end{aligned}\quad (\text{A.3})$$

where  $d_\sigma$  represents the dipole moment in the body fixed frame. If Oz is chosen along the direction

$\hat{\varepsilon}_q$  for a linearly polarized radiation or along the direction of propagation for a circular polarization, the space fixed unit vectors  $\hat{e}_m^*$  verify the following relation :

$$\hat{e}_m^* \cdot \hat{\varepsilon}_q = \delta_{mq} \quad (\text{A.4})$$

Then the radiative coupling operator is given by :

$$V^{\text{rad}} = E_0 \cdot \sum_{\sigma} d_\sigma \cdot \mathcal{D}_{q\sigma}^{1*}(\theta, \phi, 0) \quad (\text{A.5})$$

which leads to :

$$\begin{aligned}V_{fi}^{\text{rad}} &= \langle n\omega q | \langle \alpha_f j_f \bar{\Omega}_f, J_f M_f p_f | V^{\text{rad}} | \alpha_i j_i \bar{\Omega}_i, J_i M_i p_i \rangle | (n+1) \omega q \rangle \\ &= E_0 \cdot \sum_{\sigma} \langle \alpha_f j_f \bar{\Omega}_f, J_f M_f p_f | d_\sigma \cdot \mathcal{D}_{q\sigma}^{1*}(\theta, \phi, 0) | \alpha_i j_i \bar{\Omega}_i, J_i M_i p_i \rangle.\end{aligned}\quad (\text{A.6})$$

For each  $R$  value, we define the molecular transition moments as follows :

$$\mu_{\bar{n}_f - \bar{n}_i}(R) = \langle \alpha_f j_f \bar{\Omega}_f | d_\sigma | \alpha_i j_i \bar{\Omega}_i \rangle \cdot \delta_{\sigma, \bar{n}_f - \bar{n}_i} \quad (\text{A.7})$$

and

$$\mu_{\bar{n}_f + \bar{n}_i}(R) = \langle \alpha_f j_f \bar{\Omega}_f | d_\sigma | \alpha_i j_i - \bar{\Omega}_i \rangle \cdot \delta_{\sigma, \bar{n}_f + \bar{n}_i}.$$

When we contract the rotation matrices as in [8] and after some algebra, we finally obtain :

$$\begin{aligned}V_{fi}^{\text{rad}} &= \frac{E_0}{2 \sqrt{1 + \varepsilon_i p_i \cdot \delta_{\bar{n}_i, 0}} \sqrt{1 + \varepsilon_f p_f \cdot \delta_{\bar{n}_f, 0}}} \cdot \sqrt{\frac{2J_i + 1}{2J_f + 1}} \cdot \langle J_i M_i 1 q | J_f M_f \rangle \cdot (1 - p_i p_f) \times \\ &\times [ \langle J_i \bar{\Omega}_i 1 \bar{\Omega}_f - \bar{\Omega}_i | J_f \bar{\Omega}_f \rangle \cdot \mu_{\bar{n}_f - \bar{n}_i}(R) + \varepsilon_i p_i \langle J_i - \bar{\Omega}_i 1 \bar{\Omega}_f + \bar{\Omega}_i | J_f \bar{\Omega}_f \rangle \cdot \mu_{\bar{n}_f + \bar{n}_i}(R) ].\end{aligned}\quad (\text{A.8})$$

The second term exists for  $\bar{\Omega}_i = \bar{\Omega}_f = \frac{1}{2}$  only.

## Appendix 2 : semi-classical calculation of radiative cross-sections.

We consider collisions in the presence of a radiative field and our goal is to derive an expression for the relevant cross-sections. We adopt a molecular description of the collision.

1. BASIS SETS. — Let us define (Fig. 1) :

— the laboratory frame  $Ox_L y_L z_L$  with  $Oz_L$  as the quantization axis,  $\hat{\varepsilon}_q$  is the radiation field polarization in this frame ;

— the collisional frame  $Oxyz$  such that  $Oz$  is perpendicular to the collision plane. The  $Oxyz$  frame can be deduced from the  $Ox_L y_L z_L$  frame by the rotation of Euler angles  $(\alpha \beta \gamma) = \Omega$  ;

— the body fixed frame  $OXYZ$  such that  $OZ$  is along the internuclear axis. Contrarily to the usual conventions, we choose the  $OX$  axis perpendicular to the collision plane in order to define molecular

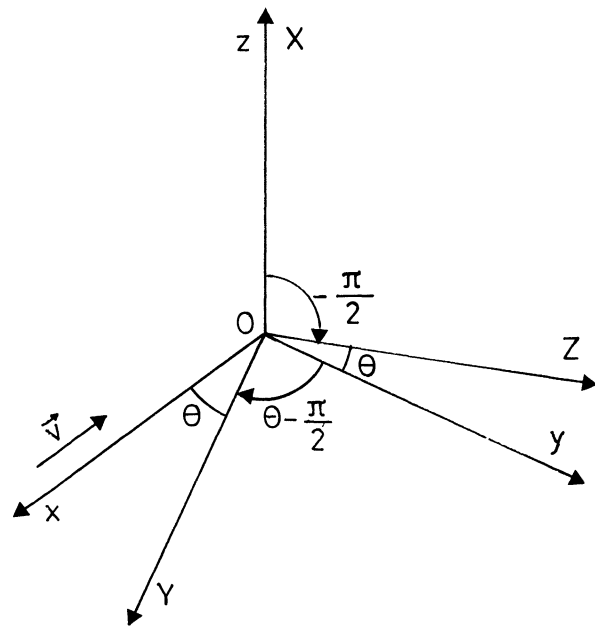


FIGURE 1. — Frames of reference and Euler angles.

states with symmetry  $\sigma_v(YZ)$  according to our conventions for the Hund's case (c) molecular basis in the quantum approach. This last point is very important for the comparison between the two methods. The OXYZ frame can be deduced from the Oxyz frame by the rotation of Euler angles  $\left(\theta - \frac{\pi}{2}, -\frac{\pi}{2}, 0\right)$  where  $\theta$  represents the rotation angle at time  $t$  of the molecular axis,  $\theta = 0$  at the beginning of the collision.

We note :

$$\begin{aligned} |\alpha j \Omega\rangle & \text{ the kets in the rotating frame} \\ |\alpha j M_j\rangle & \text{ the kets in the collisional frame} \\ |\alpha j m_j\rangle & \text{ the kets in the laboratory frame.} \end{aligned}$$

From the active point of view [8], we can write :

$$|\alpha j m_j\rangle = \sum_{M_j} |\alpha j M_j\rangle \cdot \mathcal{D}_{M_j M_j}^{j*}(\alpha \beta \gamma) \quad (\text{A.9})$$

$$|\alpha j M_j\rangle = \sum_{\Omega} |\alpha j \Omega\rangle \cdot \mathcal{D}_{M_j \Omega}^{j*}\left(\theta - \frac{\pi}{2}, -\frac{\pi}{2}, 0\right).$$

On the analogy of the quantum approach, we may introduce the Hund's case (c) basis states of parity  $\pi$  relative to  $\sigma_v(YZ)$  symmetry :

$$\begin{aligned} |\alpha j \bar{\Omega} \pi\rangle &= \frac{1}{\sqrt{2 - \delta_{\Omega, 0}}} \cdot [|\alpha j \bar{\Omega}\rangle + \pi \times \\ &\times (1 - \delta_{\Omega, 0}) \cdot |\alpha j - \bar{\Omega}\rangle] \quad (\text{A.10}) \end{aligned}$$

where  $\bar{\Omega} = |\Omega|$ .

The relation between these  $|\alpha j \bar{\Omega} \pi\rangle$  states and the  $|\alpha j M_j\rangle$  states is :

$$\begin{aligned} |\alpha j M_j\rangle &= \sum_{\Omega} \mathcal{D}_{M_j \Omega}^{j*}\left(\theta - \frac{\pi}{2}, -\frac{\pi}{2}, 0\right) \times \\ &\times \sqrt{2 - \delta_{\Omega, 0}} \cdot |\alpha j \bar{\Omega} \pi\rangle \quad (\text{A.11}) \end{aligned}$$

with  $\pi = (-1)^{j - M_j}$ .

2. SEMI-CLASSICAL COUPLED EQUATIONS. — Using the same method as in the quantum approach, we expand the total wave function on the Hund's case (c) molecular basis dressed by the radiation field [13]

$$\begin{aligned} \psi(t) &= \sum_{i'} a_{i'}(t) \cdot |\alpha_{i'} j_{i'} \bar{\Omega}_{i'} \pi_{i'}\rangle \cdot |n \omega q\rangle + \\ &+ \sum_{f'} a_{f'}(t) \cdot |\alpha_{f'} j_{f'} \bar{\Omega}_{f'} \pi_{f'}\rangle \cdot |n - 1 \omega q\rangle. \end{aligned} \quad (\text{A.12})$$

The

$$i' = |\alpha_{i'} j_{i'} \bar{\Omega}_{i'} \pi_{i'}\rangle \cdot |n \omega q\rangle$$

and

$$f' = |\alpha_{f'} j_{f'} \bar{\Omega}_{f'} \pi_{f'}\rangle \cdot |n - 1 \omega q\rangle$$

states are coupled by the dipole radiative field.

The  $a(t)$  coefficients are solutions of the time dependent Schrödinger equation :

$$i \hbar \frac{\partial \psi}{\partial t} = (H_e + H_\omega + V^{\text{rad}}) \cdot \psi. \quad (\text{A.13})$$

The internuclear distance  $R$  is a function of  $t$  so that the time derivative  $\frac{\partial \psi}{\partial t}$  includes terms  $\dot{a} = \frac{da}{dt}$  together with terms  $\frac{d}{dt} |\alpha j \bar{\Omega} \pi\rangle$ . The « time  $t$  » state  $|\alpha j \bar{\Omega} \pi\rangle_t$  can be deduced from the « time  $t = 0$  » state  $|\alpha j \bar{\Omega} \pi\rangle_0$  by a rotation of angle  $\theta$  around the OX axis.

Thus :

$$i \hbar \frac{d}{dt} |\alpha j \bar{\Omega} \pi\rangle_t = \dot{\theta} \cdot j_X \cdot |\alpha j \bar{\Omega} \pi\rangle_0 \quad (\text{A.14})$$

where  $j_X$  is the OX projection of the angular momentum  $j$  and  $\dot{\theta}$  is the time derivative of  $\theta$ . This derivative term leads to the rotational coupling.

The  $a(t)$  coefficients are solutions of the following coupled equations :

$$\begin{aligned} i \hbar \dot{a}_i &= [E_i + n \hbar \omega + U_i(R)] \cdot a_i + \sum_{i' \neq i} [\langle i | H_e | i' \rangle - \dot{\theta} \cdot \langle i | j_X | i' \rangle] \cdot a_{i'} + \sum_f \langle i | V^{\text{rad}} | f \rangle \cdot a_f \\ i \hbar \dot{a}_f &= [E_f + (n - 1) \hbar \omega + U_f(R)] \cdot a_f + \sum_{f' \neq f} [\langle f | H_e | f' \rangle - \dot{\theta} \cdot \langle f | j_X | f' \rangle] \cdot a_{f'} \\ &+ \sum_i \langle f | V^{\text{rad}} | i \rangle \cdot a_i. \end{aligned} \quad (\text{A.15})$$

Let us introduce a new set of coefficients  $b_{i(f)}(t)$  :

$$b_{i(f)}(t) = a_{i(f)}(t) \cdot \exp\left(\frac{i}{\hbar} \cdot \phi_{i(f)}(t)\right) \quad (\text{A.16})$$

with

$$\phi_{i(f)}(t) = \exp\left(\frac{i}{\hbar} \cdot \int^t [E_{i(f)} + n_{(n-1)} \cdot \hbar \omega + V_{i(f)}] \cdot dt'\right).$$

The  $b_{i(f)}$  coefficients satisfy the equations

$$i\hbar \cdot \dot{b}_i = \sum_{i' \neq i} [\langle i | H_e | i' \rangle - \dot{\theta} \cdot \langle i | j_X | i' \rangle] \cdot b_{i'} \cdot \exp\left(-\frac{i}{\hbar} \cdot (\phi_{i'} - \phi_i)\right) + \sum_f \langle i | V^{\text{rad}} | f \rangle \cdot b_f \cdot \exp\left(-\frac{i}{\hbar} \cdot (\phi_f - \phi_i)\right) \quad (\text{A.17})$$

$$i\hbar \cdot \dot{b}_f = \sum_{f' \neq f} [\langle f | H_e | f' \rangle - \dot{\theta} \cdot \langle f | j_X | f' \rangle] \cdot b_{f'} \cdot \exp\left(-\frac{i}{\hbar} \cdot (\phi_{f'} - \phi_f)\right) + \sum_i \langle f | V^{\text{rad}} | i \rangle \cdot b_i \cdot \exp\left(-\frac{i}{\hbar} \cdot (\phi_i - \phi_f)\right)$$

where

$$\phi_{i'} - \phi_i = \int^t (U_{i'} - U_i) \cdot dt' \quad \text{and} \quad \phi_f - \phi_i = \int^t (U_f - U_i - \hbar \cdot \Delta\omega) \cdot dt'.$$

Using expression (A.10) for the basis states, the rotational coupling term is obtained as :

$$\begin{aligned} & -\hbar \dot{\theta} \cdot \langle \alpha j(\bar{\Omega} + 1) \pi | j_X | \alpha j \bar{\Omega} \pi \rangle = \\ & = -\hbar \dot{\theta} \cdot \langle \alpha j \bar{\Omega} \pi | j_X | \alpha j(\bar{\Omega} + 1) \pi \rangle \\ & = -\frac{\hbar \dot{\theta}}{2} \cdot (1 + \pi \cdot \delta_{\bar{n},0}) \cdot \sqrt{j(j+1)} - \bar{\Omega}(\bar{\Omega} + 1). \end{aligned} \quad (\text{A.18})$$

The polarization vector  $\hat{\varepsilon}_q$  of the incident radiative field may be expressed in terms of the unit vectors  $\hat{E}_\sigma$  of the rotating frame as :

$$\begin{aligned} \hat{\varepsilon}_q &= \sum_{p\sigma} \mathcal{D}_{qp}^{1*}(\alpha\beta\gamma) \times \\ & \times \mathcal{D}_{p\sigma}^{1*}\left(\theta - \frac{\pi}{2}, -\frac{\pi}{2}, 0\right) \cdot \hat{E}_\sigma \end{aligned} \quad (\text{A.19})$$

so that the radiative coupling operator is equal to :

$$\begin{aligned} V^{\text{rad}} &= E_0 \cdot \hat{\varepsilon}_q \cdot \mathbf{d} = E_0 \cdot \sum_{p\sigma} \mathcal{D}_{qp}^{1*}(\alpha\beta\gamma) \times \\ & \times \mathcal{D}_{p\sigma}^{1*}\left(\theta - \frac{\pi}{2}, -\frac{\pi}{2}, 0\right) \cdot d_\sigma. \end{aligned} \quad (\text{A.20})$$

Similarly to the quantum approach, we may introduce a reduced radiative coupling in the collisional frame :

$$V^p = E_0 \cdot \sum_{p\sigma} \mathcal{D}_{p\sigma}^{1*}\left(\theta - \frac{\pi}{2}, -\frac{\pi}{2}, 0\right) \cdot d_\sigma. \quad (\text{A.21})$$

Then the radiative coupling terms in equation (A.17) are given by :

$$\begin{aligned} \langle f | V^p | i \rangle &= \frac{E_0}{\sqrt{(2 - \delta_{\bar{n}_i,0})(2 - \delta_{\bar{n}_f,0})}} \cdot \{ [1 - (-1)^p \cdot \pi_i \pi_f (1 - \delta_{\bar{n}_i,0})(1 - \delta_{\bar{n}_f,0})] \times \\ & \times \mathcal{D}_{p, \bar{n}_f - \bar{n}_i}^{1*}\left(\theta - \frac{\pi}{2}, -\frac{\pi}{2}, 0\right) \langle \alpha_f j_f \bar{\Omega}_f | d_{\bar{n}_f - \bar{n}_i} | \alpha_i j_i \bar{\Omega}_i \rangle + [(1 - \delta_{\bar{n}_i,0}) - (-1)^p \cdot \pi_i \pi_f (1 - \delta_{\bar{n}_f,0})] \\ & \times \pi_i \cdot \mathcal{D}_{p, \bar{n}_f + \bar{n}_i}^{1*}\left(\theta - \frac{\pi}{2}, -\frac{\pi}{2}, 0\right) \cdot \langle \alpha_f j_f \bar{\Omega}_f | d_{\bar{n}_f + \bar{n}_i} | \alpha_i j_i - \bar{\Omega}_i \rangle \}. \end{aligned} \quad (\text{A.22})$$

3. RADIATIVE CROSS SECTIONS. — In equation (A.17) we expand the reduced  $S$ -matrix elements  $\langle \alpha_f j_f \bar{\Omega}_f \pi_f | S_\omega^p | \alpha_i j_i \bar{\Omega}_i \pi_i \rangle$  in the Hund's case (c) basis and relations (A.9) may be used to derive the  $\langle \alpha_f j_f M_{j_f} | S_\omega^p | \alpha_i j_i M_{j_i} \rangle$  elements in the collisional frame. A perturbative treatment of the radiative coupling gives the  $S$ -matrix in the laboratory frame :

$$\begin{aligned} \langle \alpha_f j_f m_f | S_\omega^q | \alpha_i j_i m_i \rangle &= \sum_{p M_{j_i} M_{j_f}} \langle \alpha_f j_f M_{j_f} | S_\omega^p | \alpha_i j_i M_{j_i} \rangle \times \\ & \times \mathcal{D}_{m_f M_{j_f}}^{j_f}(\alpha\beta\gamma) \cdot \mathcal{D}_{m_i M_{j_i}}^{j_i}(\alpha\beta\gamma) \cdot \mathcal{D}_{qp}^{1*}(\alpha\beta\gamma). \end{aligned} \quad (\text{A.23})$$

When we average the transition amplitudes over the initial states, we find :

$$\begin{aligned} \sigma_{\omega}(j_f m_f \leftarrow j_i \varepsilon_i q) &= \frac{2\pi}{(2j_i + 1)} \cdot \int_0^{\infty} b \, db \cdot \sum_{m_i} \frac{1}{8\pi^2} \cdot \int d\Omega \\ &\times \sum_{pM_{j_f}M_{j_i}} \langle \alpha_f j_f M_{j_f} | S_{\omega}^p | \alpha_i j_i M_{j_i} \rangle \cdot \mathcal{D}_{m_f M_{j_f}}^{j_f}(\alpha\beta\gamma) \cdot \mathcal{D}_{m_i M_{j_i}}^{j_i*}(\alpha\beta\gamma) \cdot \mathcal{D}_{qp}^{1*}(\alpha\beta\gamma) \\ &\times \sum_{p'M_{j_f}M_{j_i}'} \langle \alpha_f j_f M_{j_f}' | S_{\omega}^{p'} | \alpha_i j_i M_{j_i}' \rangle^* \cdot \mathcal{D}_{m_f M_{j_f}'}^{j_f}(\alpha\beta\gamma) \cdot \mathcal{D}_{m_i M_{j_i}'}^{j_i}(\alpha\beta\gamma) \cdot \mathcal{D}_{qp'}^1(\alpha\beta\gamma). \end{aligned} \quad (\text{A.24})$$

The closure relation of the rotation matrices yields :

$$\sum_{m_i} \mathcal{D}_{m_i M_{j_i}}^{j_i*}(\alpha\beta\gamma) \cdot \mathcal{D}_{m_i M_{j_i}}^{j_i}(\alpha\beta\gamma) = \delta_{M_{j_i} M_{j_i}}. \quad (\text{A.25})$$

Using the contraction relation of two rotation matrices

$$\begin{aligned} \mathcal{D}_{m_f M_{j_f}}^{j_f}(\alpha\beta\gamma) \cdot \mathcal{D}_{qp}^{1*}(\alpha\beta\gamma) &= (-1)^{q-p} \cdot \sum_t (2t+1) \cdot \begin{pmatrix} j_f & 1 & t \\ m_f & -q & q-m_f \end{pmatrix} \\ &\times \begin{pmatrix} j_f & 1 & t \\ M_{j_f} & -p & p-M_{j_f} \end{pmatrix} \cdot \mathcal{D}_{q-m_f, p-M_{j_f}}^{t*}(\alpha\beta\gamma). \end{aligned} \quad (\text{A.26})$$

We obtain :

$$\begin{aligned} \sigma_{\omega}(j_f m_f \leftarrow j_i \varepsilon_i q) &= \frac{2\pi}{(2j_i + 1)} \cdot \int_0^{\infty} b \, db \cdot \frac{1}{8\pi^2} \int d\Omega \times \\ &\times \sum_{\substack{pM_{j_f}M_{j_i} \\ p'M_{j_f}M_{j_i}'}} \langle \alpha_f j_f M_{j_f} | S_{\omega}^p | \alpha_i j_i M_{j_i} \rangle \cdot \langle \alpha_f j_f M_{j_f}' | S_{\omega}^{p'} | \alpha_i j_i M_{j_i}' \rangle^* \\ &\times (-1)^{-p-p'} \cdot \sum_{t'} (2t+1)(2t'+1) \begin{pmatrix} j_f & 1 & t \\ m_f & -q & q-m_f \end{pmatrix} \begin{pmatrix} j_f & 1 & t \\ M_{j_f} & -p & p-M_{j_f} \end{pmatrix} \cdot \mathcal{D}_{q-m_f, p-M_{j_f}}^{t*}(\alpha\beta\gamma) \\ &\times \begin{pmatrix} j_f & 1 & t' \\ m_f & -q & q-m_f \end{pmatrix} \begin{pmatrix} j_f & 1 & t' \\ M_{j_f}' & -p' & p'-M_{j_f}' \end{pmatrix} \cdot \mathcal{D}_{q-m_f, p'-M_{j_f}'}^{t'}(\alpha\beta\gamma). \end{aligned} \quad (\text{A.27})$$

When we integrate over final scattering angles, we find that the radiative cross-sections are :

$$\begin{aligned} \sigma_{\omega}(j_f m_f \leftarrow j_i \varepsilon_i q) &= \frac{2\pi}{(2j_i + 1)} \int_0^{\infty} b \, db \cdot \sum_{\substack{pM_{j_f}M_{j_i} \\ p'M_{j_f}M_{j_i}'}} \langle \alpha_f j_f M_{j_f} | S_{\omega}^p | \alpha_i j_i M_{j_i} \rangle \cdot \langle \alpha_f j_f M_{j_f}' | S_{\omega}^{p'} | \alpha_i j_i M_{j_i}' \rangle^* \\ &\times (2t+1) \cdot (-1)^{-p-p'} \cdot \begin{pmatrix} j_f & 1 & t \\ m_f & -q & q-m_f \end{pmatrix}^2 \cdot \begin{pmatrix} j_f & 1 & t \\ M_{j_f} & -p & p-M_{j_f} \end{pmatrix} \cdot \begin{pmatrix} j_f & 1 & t \\ M_{j_f}' & -p' & p'-M_{j_f}' \end{pmatrix}. \end{aligned} \quad (\text{A.28})$$

We may rewrite (A.28) as follows :

$$\sigma_{\omega}(j_f m_f \leftarrow j_i \varepsilon_i q) = \sum_t 3 \cdot \frac{\langle j_f m_f 1 - q | t(m_f - q) \rangle^2}{(2t+1)} \cdot \sigma_{\omega}^t(j_f) \quad (\text{A.29})$$

with

$$\begin{aligned} \sigma_{\omega}^t(j_f) &= \frac{2\pi}{(2j_i + 1)} \cdot \frac{1}{3} \cdot \int_0^{\infty} b \, db \sum_{\substack{M_{j_i} \\ \mu}} \left| \sum_{M_{j_f} p} \langle \alpha_f j_f M_{j_f} | S_{\omega}^p | \alpha_i j_i M_{j_i} \rangle \cdot (-1)^{-p} \times \right. \\ &\quad \left. \times \begin{pmatrix} j_f & 1 & t \\ M_{j_f} & -p & \mu \end{pmatrix} \cdot \sqrt{2t+1} \times \delta(\mu, p - M_{j_f}) \right|^2. \end{aligned} \quad (\text{A.30})$$

The total cross-section  $\sigma_{\omega}(j_f \leftarrow j_i \varepsilon_i q)$  is given by :

$$\sigma_{\omega}(j_f \leftarrow j_i \varepsilon_i q) = \sum_{m_f} \sigma_{\omega}(j_f m_f \leftarrow j_i \varepsilon_i q). \quad (\text{A.31})$$

It is easy to sum  $\sigma_{\omega}(j_f m_f \leftarrow j_i \varepsilon_i q)$  in (A.24) over the final states  $m_f$ , so that after some angular algebra we find the total cross-section is :

$$\sigma_{\omega}(j_f \leftarrow j_i \varepsilon_i q) = \frac{2\pi}{(2j_i + 1)} \cdot \frac{1}{3} \cdot \int_0^{\infty} b \, db \cdot \sum_{\substack{M_{j_f}^p \\ M_{j_i}}} \left| \langle \alpha_f j_f M_{j_f} | S_{\omega}^p | \alpha_i j_i M_{j_i} \rangle \right|^2. \quad (\text{A.32})$$

### References

- [1] BERSON, I. Ja., *Latv PSR Zin. Akad. Vestis. Fiz. Tech.* **4** (1968) 47.
- [2] GAUSSORGUES, C., LE SECH, C., MASNOU-SEEUWS, F., MC CARROLL, R. and RIERA, A., *J. Phys. B: Atom. Molec. Phys.* **8** (1975) 239.
- [3] DE VRIES, P. L. and GEORGE, T. F., *Mol. Phys.* **36** (1978) 151.
- DE VRIES, P. L. and GEORGE, T. F., *Mol. Phys.* **38** (1979) 56.
- [4] MIES, F. H., *Theoretical Chemistry: Advances and Perspectives*, V6B (Academic Press, 1981).
- [5] KULANDER, K. C. and REBENTROST, F., *J. Chem. Phys.* **80** (1984) 5623.
- [6] VAHALA, L. L., JULIENNE, P. S. and HAVEY, M. D., *Phys. Rev. A* **34** (1986) 1856.
- [7] LARSSON, M., *Physica Scripta* **23** (1981) 835.
- [8] BRINK, D. M. and SATCHLER, G. R., « *Angular Momentum* » (Clarendon Press Oxford, Oxford University Press) 1968.
- [9] LAUNAY, J. M., *J. Phys. B: Atom. Molec. Phys.* **9** (1976) 1823.
- [10] BATES, D. R. and CROTHERS, D. S. F., *Proc. Roy. Soc. A* **315** (1970) 465.
- [11] LE SECH, C., Thesis, Orsay, Paris XI, France, 1976.
- [12] JULIENNE, P. S. and MIES, F. H., *Phys. Rev. A* **30** (1984) 831.
- [13] YAKOVLENKO, S. I., *Sov. J. Quant. Electron.* **8** (1978) 151.