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## **MQDT operatorial formalism analysis of molecular Rydberg states in weak electric fields : application to Na<sub>2</sub>**

P. F. Brevet, Ch. Bordas, M. Broyer, G. Jalbert and P. Labastie

Laboratoire de Spectrométrie Ionique et Moléculaire, Université Lyon I, Bât 205, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

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**Résumé.** — Nous présentons la théorie du défaut quantique à plusieurs voies dans son formalisme opératoriel ainsi que son application au problème des états de Rydberg d'une molécule diatomique en champ électrique. L'analyse théorique consiste principalement à décrire le rapport étroit qui existe entre l'opérateur résolvante et la matrice densité d'états qui définit entièrement les propriétés du spectre. Dans le cas particulier du spectre discret en champ électrique faible, les propriétés des états liés sont déduites des pôles de cette matrice. Nous donnons un exemple de l'utilisation de cette théorie dans le cas de Na<sub>2</sub> mais elle pourrait être appliquée aussi bien à tout autre système non hydrogénoïde. Des spectres calculés d'états de Rydberg de Na<sub>2</sub> en champs faibles sont comparés aux données expérimentales. La présence d'extra-raies et l'apparition des multiplets hydrogénoïdes sont discutées. Nous démontrons l'influence des séries  $n\ell A$  pénétrantes sur la forme des multiplets et en déduisons l'ordre de grandeur de leurs défauts quantiques.

**Abstract.** — We present the Multichannel Quantum Defect Theory in its operatorial form and its application to the problem of Rydberg states of a diatomic molecule in external electric fields. The theoretical analysis consists in the description of the close connection between the resolvent operator and the Density-Of-State matrix which defines the whole spectrum. In the particular case of the discrete spectrum in weak electric fields, bound states are deduced from the poles of this matrix. We give an example of the use of this theory in the case of Na<sub>2</sub> but it could be applied to any other non hydrogenic system as well. Calculated spectra of Rydberg states of Na<sub>2</sub> in weak fields are compared to experimental data. The presence of extra-lines and the emergence of hydrogenic multiplets is emphasized. We also show the influence of the penetrating  $n\ell A$  series on the shape of the multiplets and estimate orders of magnitude for their quantum defects.

### **1. Introduction.**

For a long time [1, 2], electric fields have been known to act on atoms and molecules, both on the structure (Stark effect) and on the dynamics [3] of the excited states (electric field ionization and field induced predissociation). The Stark effect and field ionization of atoms has been widely studied, particularly in the case of simple atoms such as hydrogen or alkali-

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metals. Although molecules have been poorly studied in comparison, the dominant features of the molecular Stark effect and electric field ionization are expected to be of the same nature. However, over the last two decades, a lot of new effects have been observed in non-hydrogenic systems. These are related to the conjugated action of the field and of the ionic core on highly excited electronic states. The most foreseeable of these effects is a decrease of the lifetime of states by core coupling [4]. On the contrary, interference effects can instead lead to the stabilization of some states which acquire a very long lifetime [5]. Another kind of interference effect responsible for a dramatic variation of the distribution of the oscillator strength is shown in reference [6]. All these studies involve states which are bound when the field is zero. Another kind of experiment is concerned with states which are autoionizing in zero-field. In this case, the lifetime of these states generally increases when the field is applied because the mixing induced by the electric field may reduce the coupling between the quasi-discrete states and the continuum [7]. This effect has been also discussed in the context of dielectronic recombination.

When one goes to molecules, all the above effects can be observed, especially the increase in lifetime of autoionizing states as for example in the field-hindered vibrational autoionization [8]. A new effect has been observed which is specific to molecules. It is the rotational autoionization induced by the field [9], also named forced rotational autoionization [10, 11]. However, quantitative treatments of molecular field effects are often lacking and the purpose of this article is to present a particular approach of this problem. We present here a theoretical calculation of the electric field effects on molecular Rydberg states which takes advantage of the close connection between the resolvent operator and the Density-Of-States (DOS) matrix. As an example, we apply our formalism to the case of the Stark effect of  $\text{Na}_2$  which has been described in an earlier publication [12].

The s and d Rydberg states of the  $\text{Na}_2$  molecule have been extensively studied in our group [13]. Because of the large size of the ionic core  $\text{Na}_2^+$ , the rotation and Rydberg frequencies may be of the same order of magnitude. This leads to the observability of a resonance between the nuclear and electronic motions: the « stroboscopic effect » [14]. Further, these states can be accurately calculated by a zero-field MQDT theory [15-18], and a classical analog can be derived [19], showing that the coupling between the core rotation and the Rydberg electron orbit leads under certain conditions to a chaotic motion. Some interesting effects are expected if one adds an electric field. First, the electron motion contains two frequencies instead of one, each of which can be resonant with the core rotation frequency. Further, by coupling the low and high angular momentum values, the field decreases the average couplings to the core which is maximum in the low  $\ell$  states. The motion could thus be globally less chaotic at high than at low field.

Without any external electric field, the hydrogen atom problem can be solved in either spherical or parabolic coordinates because of the high symmetry of the Coulombic potential. When an electric field is applied, the spherical symmetry is broken but the parabolic symmetry still survives. Hence we have to deal with the parabolic quantum numbers  $n_1$  and  $n_2$  instead of the principal quantum number  $n$  and the orbital angular momentum  $\ell$  which is no longer conserved. The projection  $m$  of the electronic angular momentum onto the field axis is the only common good quantum number. The parabolic and spherical quantum numbers are connected by the relation

$$n_1 + n_2 = n - |m| - 1 \quad (1a)$$

$$n_1 - n_2 = -n + |m| + 1, \quad -n + |m| + 3, \dots, n - |m| - 1 \quad (1b)$$

In the pure Coulomb + Stark potential, i.e. in atomic hydrogen, the principal quantum number  $n$  is still a good quantum number even in the strong field regime. On the contrary, in a

non hydrogenic system,  $n$  is not conserved. The spherical set of quantum numbers  $(n\ell m)$  is replaced by the parabolic set  $(n_1 n_2 m)$ , although it is sometimes more convenient to use the set  $(n\beta m)$  where  $\beta$  is the separation constant defined in zero-field by [20]

$$n_1 = n\beta - \frac{1}{2} (|m| + 1). \quad (2)$$

As long as the applied electric field is weak as compared to the atomic or molecular field experienced by the electron, perturbation methods hold true and it is easy to get, for example, the first-order energy correction in a weak field

$$E = E_0 + \frac{3}{2} n(n_1 - n_2) F \quad (3)$$

where  $E_0$  is the unperturbed energy [20]. However the influence of the field on highly excited states of atoms or molecules can no longer be treated exactly by perturbation theory. The perturbation parameter is determined by the ratio between the width of the Stark multiplet ( $3n^2F$  in atomic units, value deduced from Eq. (3)) and the energy gap between two successive hydrogenic levels ( $n^{-3}$  in atomic units) [21]. This quantity is thus  $3n^5F$ . The value  $F_c$  of the field corresponding to the relation  $3n^5F_c = 1$  is called the Inglis-Teller limit. Well below  $F_c$  is the weak field regime. The strong field regime,  $F \geq F_c$ , also called  $n$ -mixing regime, is characterized by the overlap of the successive  $n$  manifolds which are completely mixed in any non hydrogenic system. The Inglis-Teller limit is about 1200 V/cm for  $n = 17$ , but in the vicinity of  $n = 50$ , it is only 5 V/cm. Thus, in case of highly excited states and even with modest fields, as soon as  $3n^5F > 1$ , the perturbation basis must include many different  $n$  values. This causes rapidly an explosion of the perturbation basis, aggravating the numerical treatment. Further, the Coulomb + Stark potential is not bound and all the Stark states, even below the classical saddle point energy ( $-2\sqrt{F}$  in a.u.) are coupled to the continuum *via* tunnel ionization. This is the origin of the divergence of the perturbation development at high order or near the saddle point. This divergence is the major limitation of perturbation theory in strong fields. In addition, the diagonalization of the total hamiltonian in the spherical basis (matrix elements are not generally computable in the parabolic basis) does not take any advantage of the separability of the hydrogen Stark hamiltonian. Therefore, the perturbation methods fail rapidly, even at low values of the field, for high lying states. Hence, the problem of Rydberg states in external electric fields requires another theoretical approach. We use the Multichannel Quantum Defect Theory, thereafter noted MQDT, which has proved to be of great efficiency to treat electron-core interactions in zero-field problems in the discrete as well as in the continuous spectra.

MQDT was first introduced in atomic physics by Seaton [15] and extended to non-Coulombic potentials by Fano [16]. Either for atomic or molecular problems in zero-field, this powerful tool gave important results. In molecular physics, for example, MQDT can treat predissociation and autoionization on an equal footing [17]. General features of molecular applications of MQDT have been reviewed by Greene and Jungen [18]. The extension of MQDT to external fields was first worked out by Fano [22]. This allowed Harmin [23] to extend the theory and to interpret the spectra of alkaline atoms in electric fields. This latter work introduced the fundamental, Density-Of-States matrix, referred to as the DOS matrix, gathering all the spectral informations. We have recently placed this matrix in a wider context known as the operatorial form of MQDT [24]. Using the results of Harmin, Sakimoto [25] has presented a formulation of MQDT for studying the effects of an electric field on molecules in highly excited states which differs appreciably from the present work. He applied his model to the case of  $H_2$ . Unfortunately, no experimental results could be compared to the calculated spectra.

We believe that the present operatorial formalism is more general, although the application to  $\text{Na}_2$  in section 5 is restricted to the weak field regime.

We will first deal with this operatorial formalism and recall the main steps of the connection between the resolvent operator and the DOS matrix. The section ends with the general formula for this matrix and its relation with the familiar form of MQDT in the particular case of the discrete spectrum of the Coulombic potential. We come to the molecular + electric field problem in section 3 where we discuss the frame transformation and the related matrix  $U^{FM_J}$  (the superscripts  $F$  and  $M_J$  stand respectively for the electric field and the projection along the field axis of the total angular momentum of the molecule, namely  $\mathbf{J}$ ). The restriction of our theory to the quasi-discrete spectrum in weak fields is described in section 4. Examples of calculated spectra of  $\text{Na}_2$  are shown and discussed in section 5 in comparison with experimental spectra. We then discuss briefly the question of extra-lines, hydrogenic multiplets and especially the problem of penetrating  $nfA$  Rydberg series whose influence on the shape of the multiplet is determining enough to evaluate orders of magnitude for the unknown quantum defects.

## 2. Operatorial formalism of MQDT.

The operatorial formulation of MQDT is based on the close connection between the resolvent operator and the DOS matrix. Let us recall the main steps of such a connection.

The problem to be solved is represented by a perturbed hamiltonian  $H$  related to an unperturbed hamiltonian  $H_0$  through

$$H = H_0 + V \quad (4)$$

where  $V$  is a perturbation that contains only the non-Coulombic part of the interaction between the atomic (or molecular) core and the Rydberg electron. In other words, the potential part of  $H_0$  is (in atomic units) the sum of the Coulombic potential  $-1/r$  plus the Stark potential  $-\mathbf{F} \cdot \mathbf{r}$ , i.e. the hamiltonian of atomic hydrogen in an external field  $\mathbf{F}$ . From the general scattering theory [26], one can introduce two resolvent operators, functions of the complex energy  $z$

$$G_0(z) = (z - H_0)^{-1} \quad (5)$$

$$G(z) = (z - H)^{-1}. \quad (6)$$

These latter functions can be expanded with the help of the spectral densities of states,  $P_E^0$  and  $P_E$  respectively, related to the hamiltonians  $H_0$  and  $H$ . The spectral theorem [26] leads to

$$G_0(z) = \int_{-\infty}^{+\infty} \frac{P_E^0 dE}{z - E} \quad (7)$$

$$G(z) = \int_{-\infty}^{+\infty} \frac{P_E dE}{z - E} \quad (8)$$

These two functions  $G_0(z)$  and  $G(z)$  may have poles from the discrete part of the spectrum and a branch cut from the continuous part. The spectral density can be deduced back from the  $G$  operators by

$$P_E = \frac{1}{2i\pi} [G^{(-)}(E) - G^{(+)}(E)] \quad (9)$$

which is to be interpreted as follows. If  $E$  is on the branch cut of  $G$ , we have

$$G^{(\pm)}(E) = \lim_{\varepsilon \rightarrow 0^+} G(E \pm i\varepsilon) \tag{10}$$

If  $E = E_n$  corresponds to a pole of  $G(z)$  situated on the real axis, we take

$$P_E = \delta(E - E_n) \text{Res}(G(z), E_n) \tag{11a}$$

where

$$\text{Res}(G(z), E_n) = \lim_{z \rightarrow E_n} (z - E_n) G(z) \tag{11b}$$

Actually, in the sense of distributions, equation (9) is always valid.

We then split  $G_0$  into two parts, one analytic and the other not. The latter part contains the spectral information. We proceed as follows

We write  $P_E^0$  as

$$P_E^0 = \sum_i |E, i\rangle \rho(E, i) \langle E, i| \tag{12}$$

Here,  $i$  stands for a set of indices, collectively referred to as a *channel*, which, together with the energy, form a complete set of commuting observables. The quantity (actually a distribution)  $\rho(E, i)$  is the density of states.

By a suitable renormalization, the wavefunctions  $|E, i\rangle$  can be chosen analytic in energy in most cases. The analytic continuation to complex energies is also analytic (at least in a strip containing the real axis) and we write the corresponding function  $|z, i\rangle$ .

The analyticity of the wavefunctions allows to state that the two integrals

$$G_0(z) = \sum_i \int_{-\infty}^{+\infty} dE |E, i\rangle \frac{\rho(E, i)}{z - E} \langle E, i| \tag{13a}$$

and

$$G_0^{(1)}(z) = \sum_i |z, i\rangle \left( \int_{-\infty}^{+\infty} dE \frac{\rho(E, i)}{z - E} \right) \langle z, i| \tag{13b}$$

differ but by an analytic operator  $G_0^{(a)}(z)$ . That is

$$G_0(z) = \sum_i |z, i\rangle C(z, i) \langle z, i| + G_0^{(a)}(z) \tag{14a}$$

with

$$C(z, i) = \int_{-\infty}^{+\infty} dE \frac{\rho(E, i)}{z - E}. \tag{14b}$$

All the spectral information contained in  $G_0(z)$  comes from the singularities of the coefficients  $C(z, i)$ , which are now functions rather than operators and thus much easier to handle.  $G_0^{(a)}(z)$  is the smooth Green function introduced by Greene *et al.* [27]. We now turn to the total resolvent  $G(z)$ .

From equations (5), (6) and (7), and skipping the  $z$ -dependence, we can write  $G(z)$  as

$$G = G_0 + G_0 V G \tag{15}$$

This relation could be the starting point of a perturbation treatment. Here, we introduce the smooth reaction operator

$$K = V + VG_0^{(a)}K \quad (16)$$

and the smooth wave operators

$$\Omega = 1 + G_0^{(a)}K \quad (17a)$$

$$\Omega' = 1 + KG_0^{(a)} \quad (17b)$$

we then get (inserting Eq. (14a) into Eq. (15) and rearranging)

$$G = G_0^{(a)} + G_0^{(a)}KG_0^{(a)} + \sum_J \Omega |z, J\rangle C(z, J) (\langle z, J | + \langle z, J | VG). \quad (18)$$

Projecting on the left on  $\langle z, i | V$  and adding  $\langle z, i |$ , we get, owing to equations (13) and (14)

$$\sum_J (\delta_{ij} - \langle z, i | K | z, J \rangle C(z, J)) (\langle z, J | + \langle z, J | VG) = \langle z, i | \Omega' \quad (19)$$

The next step is to realize that equation (19) is a linear system of equations with unknown  $\langle z, J | + \langle z, J | VG$ . Defining

$$(\mathbf{K})_{ij} = \langle z, i | K | z, J \rangle \quad (20a)$$

and

$$(\mathbf{C})_{ij} = C(z, i) \delta_{ij}$$

we get

$$\langle z, J | + \langle z, j | VG = \sum_i (\mathbf{1} - \mathbf{KC})_{ji}^{-1} \langle z, i | \Omega' \quad (21)$$

which we insert into equation (19) to obtain

$$G = G_0^{(a)} + G_0^{(a)}KG_0^{(a)} + \sum_{i,j} \Omega |z, i\rangle (\mathbf{C}^{-1} - \mathbf{K})_{ij}^{-1} \langle z, j | \Omega'. \quad (22)$$

Equation (22) requires a few comments. First, the functions  $|z, i\rangle$  are generally unbounded when  $r$  tends towards infinity. On the other hand,  $V$  is supposed to be zero for  $r > r_0$ . This ensures the existence of products such as  $V|z, i\rangle$  and  $VG_0^{(a)}$ . Second,  $K$  is an analytic operator, provided equation (13) behaves well. Unfortunately, this latter point is difficult to prove and is the mathematical weakness of our theory. From now on, we assume that  $K(z)$  is analytic. Then, the only singularities of  $G$  come from those of  $(\mathbf{C}^{-1} - \mathbf{K})^{-1}$ . Further, the branch cut is only due to that of  $\mathbf{C}$ .

Now, using equation (9), we get

$$P_E = \sum_{i,j} \Omega |E, i\rangle \mathbf{D}_{ij} \langle E, j | \Omega^+. \quad (23)$$

Note that  $\Omega' = \Omega^+$  on the real axis. The  $\mathbf{D}$  matrix is the Density-Of-State (DOS) matrix introduced by Harmin [23], and defined more generally here as

$$2i\pi\mathbf{D} = \left( \frac{1}{\mathbf{C}^{(-)}} - \mathbf{K} \right)^{-1} - \left( \frac{1}{\mathbf{C}^{(+)}} - \mathbf{K} \right)^{-1} \quad (24)$$

with the same conventions as in equations (9)-(11)

Equation (24) is the starting point for any MQDT treatment

In the particular case where  $H_0$  does not contain any long-range potential except the Coulomb potential (zero-field limit), equation (24) may be developed further. Dealing with a pure Coulomb potential at long distance allows to introduce some simplifications [27]. Without going deeply into details, it consists in taking a suitable redefinition of  $|z, i\rangle$ , the so-called functions normalized by energy unit, and consequently modify the definition of  $G_0^{(a)}$ , in such a way that it is no longer analytic, but nevertheless continuous and smooth.

With the above assumptions, we can define the **C** and **K** matrices for the Coulomb potential. As usual for MQDT, we define the channels by the state of the ionic core and the angular quantum numbers  $\ell, m$  of the Rydberg electron. The effective quantum number

$$\nu_i = \frac{1}{\sqrt{2(E_i - z)}} \tag{25}$$

is associated to each channel  $E_i$  is the energy of the ionic core in channel  $i$ . Then **C** is given by

$$(\mathbf{C})_i = \begin{cases} \pi \cot(\pi \nu_i) & (\text{Re}(z - E_i) < 0) & \text{(discrete spectrum)} \\ \pm i & (\text{Re}(z - E_i) > 0, z = E \pm i\varepsilon) & \text{(continuum)} \end{cases} \tag{26}$$

and **K** is related to the familiar **R** matrix by

$$\pi \mathbf{K} = -\mathbf{R}.$$

In the discrete region of the spectrum, the poles of **D** are the values of  $z$  for which the matrix

$$\tan(\pi \nu) + \mathbf{R}$$

is singular, that is

$$\det(\tan(\pi \nu) + \mathbf{R}) = 0 \tag{27}$$

Equation (27) is the original equation of Seaton [15]. The resolution of this equation gives the entire discrete spectrum in the absence of any external field.

### 3. Frame transformation and matrix transformation in an electric field.

3.1 INTRODUCTION — It is customary in MQDT to use another basis in channel space, where the **R** matrix is diagonal, instead of the **C** matrix. One usually imposes the basis transformation to be unitary. Thus the problem amounts to find the (unique within phase factors) transformation **U** such that  $\mathbf{U}^{-1} \mathbf{R} \mathbf{U}$  is diagonal. However, **R**, **C** and **D** behave like scalar product matrices, not like operators. That is, for any transformation

$$|z, \alpha\rangle = \sum_i a_{i\alpha} |z, i\rangle, \tag{28}$$

the  $\rho$  [Eq. (12)], **C** [Eq. (20b)] and **D** matrices transform as

$$(\mathbf{C})_{\alpha\beta} = (\mathbf{a}^{-1})_{i\alpha} (\mathbf{C})_{ij} (\mathbf{a}^{-1})_{j\beta}^*$$

That is

$$\mathbf{C}^{(\alpha)} = \mathbf{a}^{-1} \mathbf{C}^{(i)} (\mathbf{a}^{-1})^+ \tag{29a}$$



while  $\mathbf{K}$  and  $\mathbf{R}$  transform contragrediently

$$\mathbf{R}^{(\alpha)} = \mathbf{a}^+ \mathbf{R}^{(1)} \mathbf{a} . \quad (29b)$$

The basis transformations which diagonalize  $R$  are therefore not unique and not necessary unitary. The purpose of this section is to describe such a basis change in the non-zero-field case, which allows to use the zero-field quantities. Detailed calculations may be found in the papers by Harmin [23], and Sakimoto [25]

### 3.2 RELATION BETWEEN THE $K$ MATRICES WITH AND WITHOUT FIELD.

**3.2.1 Solutions of  $H_0$**  — First, we have to specify the set of indices, appropriate to the description of the eigenfunctions of  $H_0$ . Since  $H_0$  is the sum of a core hamiltonian and of the outer electron Coulomb-Stark hamiltonian, the wavefunctions are the product of a core wavefunction and an electron wavefunction solution of the hydrogenic Stark problem. The core is specified by its rotational quantum numbers  $N^+$  and  $M_{N^+}$ . Here and in the following, we do not consider the core vibration. The electron is specified by the first parabolic quantum number  $n_1$ , and the projection of the angular momentum onto the field axis  $m$ . The whole molecule is characterized by the total angular momentum  $J$  ( $J = N^+ + \ell$ ) and its projection  $M$  onto the field axis.  $M$  is the only quantum number strictly conserved in the field. This decomposition of the total wavefunction is typical of the Hund's case (d). The total energy is

$$z = E_{N^+} + \varepsilon = E_{N^+} - \frac{1}{2 \nu_{N^+}^2} \quad (30)$$

where  $E_{N^+}$  is the rotational energy of the core and  $\varepsilon$  the binding energy of the electron relative to the channel  $N^+$ . Hence, the wavefunction  $|z, i\rangle$  may be written as the following product :

$$|z, i\rangle = |N^+ M_{N^+}\rangle | \nu_{N^+} n_1 m \rangle \quad (31)$$

The ket  $|N^+ M_{N^+}\rangle$  is the rotational wavefunction of the core and the ket  $| \nu_{N^+} n_1 m \rangle$  is the product of the parabolic eigenfunctions [23]

$$\langle \xi \eta \varphi | \nu_{N^+} n_1 m \rangle = \Xi_{n_1}(\xi) Y_{n_1}(\eta) \frac{e^{im\varphi}}{\sqrt{2\pi}} \quad (32)$$

where

$$\xi = r + z \quad (33a)$$

$$\eta = r - z \quad (33b)$$

$$\varphi = \text{Arctan}(y/x) \quad (33c)$$

are parabolic coordinates (here  $z$  stands for the third coordinate, not the complex energy)

The function  $\Xi_{n_1}$  is a solution of

$$\left( -\frac{d}{d\xi} \xi \frac{d}{d\xi} + \frac{m^2}{4\xi} - \frac{\xi\varepsilon}{2} + \frac{F\xi^2}{4} \right) \Xi_{n_1}(\xi) = \beta \Xi_{n_1}(\xi) \quad (34a)$$

where  $\varepsilon$  may be replaced by  $-1/2 \nu_{N^+}^2$ .

The effective potential along the  $\xi$  axis is

$$V_1(\xi) = \frac{m^2}{8\xi^2} - \frac{\beta}{2\xi} + \frac{1}{8}\xi F \quad (34b)$$

$V_1(\xi)$  is always bound

Equation (34) possesses solutions only for a discrete set of  $\beta$  (the separation constant introduced in Eq (2)), which we label by the integer  $n_1$  in increasing order of  $\beta$ . For definiteness, we specify that  $\Xi_{n_1}(\xi)$  behaves as

$$\Xi_{n_1}(\xi) \approx \xi^{|m| + 1/2} \tag{35}$$

when  $\xi \rightarrow 0$

The function  $Y_{n_1}(\eta)$  is a solution of

$$\left( -\frac{d}{d\eta} \eta \frac{d}{d\eta} + \frac{m^2}{4\eta} - \frac{\eta\varepsilon}{2} - \frac{F\eta^2}{4} \right) Y_{n_1}(\eta) = (1 - \beta) Y_{n_1}(\eta) \tag{36a}$$

The effective potential along the  $\eta$  axis is

$$V_2(\eta) = \frac{m^2}{8\eta^2} - \frac{1 - \beta}{2\eta} - \frac{1}{8} \eta F \tag{36b}$$

This potential is not strictly bound and tends towards  $-\infty$  as  $\eta$  increases. Under certain conditions, this potential supports discrete states that are affected by tunnel ionization.

When  $\eta \rightarrow 0$ , the function  $Y_{n_1}(\eta)$  behaves as

$$Y_{n_1}(\eta) \approx \eta^{|m| + 1/2} \tag{37}$$

**3.2.2 Connection between parabolic and spherical coordinates** — Similar to all MQDT treatment, the key idea is to partition the space into several regions corresponding to different dominating potentials.

The ability to relate the  $\mathbf{K}$  matrices with and without field relies on the presence of a region in space where one can neglect both the external field and the detailed structure of the core. This region lies at distances  $r$  from the core comprised between  $r_c$ , the range of the non-Coulombic  $V$  interaction ( $r_c \approx 10$  a.u.), and  $r_F$ , the distance at which the external field becomes non negligible as compared to the nuclei field,  $r_F \ll F^{-1/2}$  ( $\approx 2\,000$  a.u. for  $F \approx 1\,000$  V/cm). In this region, one can choose

(i) the Hund's case (d) parabolic functions  $|z, \iota\rangle$  to be linear combinations of the Hund's case (d) functions in spherical coordinates at zero-field  $|z, \mu\rangle$ , because these functions are solution of the same partial differential equation. Here,  $\mu$  stands for the set of indices  $\{N^+, M_{N^+}, \ell, m\}$ , and by expanding  $|z, \iota\rangle$  onto the spherical harmonics [22, 23], we have

$$|z, \iota\rangle = \sum_{\mu} \alpha_{i\mu} |z, \mu\rangle \tag{38}$$

(ii) the analytic operator  $G_0^{(a)}$  to be the same with and without field, by a suitable choice of the coefficient  $C(z, \iota)$  [23, 25].

The  $K$  operator is thus independent of the field, and the  $(\mathbf{R})_{\mu\mu'}$  matrix in spherical coordinates is the same as in zero-field. In parabolic coordinates

$$(\mathbf{R})_{i i'} = \sum_{\mu, \mu'} b_{i\mu}^* (\mathbf{R})_{\mu\mu'} b_{i'\mu'} \tag{39}$$

The  $b$  coefficients are related to the  $\alpha$ 's by

$$b_{i\mu} = \frac{N_i}{N_{\mu}} \alpha_{i\mu} \tag{40}$$

where  $N_i$  and  $N_\mu$  are the normalization coefficients which normalize the wavefunctions per unit of energy [20]. At low field, and in the vicinity of  $\nu = n$ ,  $b_{i,\mu}$  can be satisfactorily approximated by the Clebsch-Gordan coefficient [20]

$$b_{i,\mu} = \left\langle \frac{n-1}{2}, \frac{m-k}{2}, \frac{n-1}{2}, \frac{m+k}{2} \mid \ell m \right\rangle \quad (41)$$

where

$$k = n_1 - n_2 = 2n_1 + |m| + 1 - n \quad (42)$$

is the electric quantum number and  $n_1$  varies from 0 to  $n - |m| - 1$  by steps of unity.

**3.3 THE TRANSFORMATION MATRIX.** — We have now to perform the transformation from the spherical uncoupled  $|z, \mu\rangle$  basis to the close coupling  $|z, \alpha\rangle$  basis where  $\mathbf{R}$  is diagonal. However the set of indices  $\alpha$  is already known [18]. It stands for the Born-Oppenheimer quantum numbers

- $\ell$ , the total angular momentum of the electron
- $\Lambda$ , the projection of the electronic angular momentum onto the molecular axis
- $J$ , the total angular momentum
- $M$ , the  $J_z$  component ( $M = M_{N^+} + m$ ).

The function  $|z, \alpha\rangle$  is then

$$|z, \alpha\rangle = |\ell \Lambda\rangle_{\text{electronic}} |JM - \Lambda\rangle_{\text{rotation}} \quad (43)$$

and is a Hund's case (a) coupling wavefunction.

The transformation from  $|z, \mu\rangle$  to  $|z, \alpha\rangle$  is thus performed in two stages

(i) coupling of  $\ell$  and  $N^+$  to give  $J$  The transformation coefficient is simply the Clebsch-Gordan  $\langle N^+ M_{N^+}; \ell m \mid JM \rangle$

(ii) coupling of  $\ell$  onto the molecular axis The transformation coefficient is  $U_{N^+ \Lambda}^{\ell} = \langle \ell \Lambda J - \Lambda \mid N^+ 0 \rangle$ .

Actually,  $\ell$  is not strictly a good quantum number in a molecule, even at zero-field. However in most of the molecular Rydberg series and particularly in  $\text{Na}_2$ , it has been shown to be conserved in the core interaction [28]

The total parity of the core is  $(-1)^{N^+}$ . The total parity of the molecule is the product of the parity of the electron and that of the core,  $(-1)^{N^+ + \ell}$ . Since the total parity and  $\ell$  are not affected by the electron-core interaction, so is the core parity. Hence, the core parity is a good quantum number for all the interactions, because the core itself is not supposed to be affected by the field. For example the field by itself does not mix the various  $N^+$  components because the matrix element of the dipolar electric hamiltonian between states having different  $N^+$  is zero. Nevertheless, electron-core interactions ( $\ell$ -uncoupling) mixes the states with different values of  $N^+$ . The conservation of the parity decreases by roughly a factor of two the number of channels to be considered. To take advantage of this fact, we use  $|\Lambda|$  and the  $A'/A''$  parity  $p$  [29] instead of  $\Lambda$  as a close-coupling quantum number. The core parity can also be expressed as  $(-1)^{J + \ell + p}$ . The transformation coefficient  $U_{N^+ \Lambda}^{\ell p}$  in point (ii) above becomes now

$$U_{N^+ 0}^{\ell} = \langle \ell 0 J 0 \mid N^+ 0 \rangle \quad \text{if } \Lambda = 0$$

$$U_{N^+ \Lambda}^{\ell p} = \frac{1}{\sqrt{2}} [\langle \ell \Lambda J - \Lambda \mid N^+ 0 \rangle + (-1)^p \langle \ell - \Lambda J \Lambda \mid N^+ 0 \rangle] \quad \text{if } \Lambda \neq 0 \quad (44)$$

The total transformation coefficient  $a_{i\alpha}$  (see Eq (28)) is then the product of the three coefficients above

$$a_{i\alpha} = b_{i\mu} \langle N^+ M_{N^+}, \ell m | JM \rangle U_{N^+}^{\ell p} \quad (45)$$

where  $i, \mu, \alpha$  stands for the set of indices

$$\begin{aligned} i &= \{N^+ M_{N^+} n_1 m\} : \text{Hund's case (d) parabolic basis} \\ \mu &= \{N^+ M_{N^+} \ell m\} : \text{Hund's case (d) spherical basis} \\ \alpha &= \{\ell J \Lambda M\} : \text{Hund's case (a) basis} \end{aligned}$$

and we have  $M = M_{N^+} + m$  as a conserved quantum number. The transformation matrix  $a_{i\alpha}$  is in principle of infinite dimension, because the values of  $J$  and  $N^+$  are not restricted by any strict selection rule. However, this matrix can be drastically truncated as described in section 5. Whatever it is before, the  $a_{i\alpha}$  matrix is not unitary after truncation. As shown before, this is not a problem since all the matrices considered transform as in equation (29).

#### 4. Quasi-discrete spectrum in weak electric fields.

4.1 GENERAL FORM OF THE  $D$  MATRIX — Since  $\mathbf{K}$  is analytic, it is defined on the real axis, and there, it is hermitian. The non-analytic matrix  $\mathbf{C}$  is discontinuous on the real axis, and we write

$$\begin{aligned} \mathbf{C} &= \mathbf{h} - i\mathbf{H} \quad \text{above the real axis} \\ \mathbf{C} &= \mathbf{h} + i\mathbf{H} \quad \text{below the real axis} \end{aligned}$$

where both  $\mathbf{h}$  and  $\mathbf{H}$  are defined and hermitian on the axis. Then we have the DOS matrix

$$\mathbf{D} = \frac{1}{2i\pi} \left[ \frac{1}{\frac{1}{\mathbf{h} + i\mathbf{H}} - \mathbf{K}} - \frac{1}{\frac{1}{\mathbf{h} - i\mathbf{H}} - \mathbf{K}} \right] \quad (46)$$

A few algebraic manipulations would lead to the expression of  $\mathbf{D}$  given by Harmin [23]. Here, we take advantage of the numerous zero diagonal elements of the  $\mathbf{K}$  matrix in the  $|\alpha\rangle$  basis. These diagonal elements are zero if the corresponding quantum defect is zero. This is the case for  $\ell > 3$  if one consider  $\text{Na}_2$  for example. Taking  $\mathbf{P}$  as the projector onto the non-zero space of  $\mathbf{K}$ , and  $\mathbf{Q} = 1 - \mathbf{P}$ , we have

$$\mathbf{P} \left( \frac{1}{\frac{1}{\mathbf{C}} - \mathbf{K}} \right) \mathbf{P} = \mathbf{P} \frac{1}{1 - \mathbf{CK}} \mathbf{CP} = \frac{\mathbf{P}}{\mathbf{P} - \mathbf{PCPK}} \mathbf{CP} \quad (47)$$

because  $\mathbf{QK} = \mathbf{KQ} = 0$

Then the  $\mathbf{D}$  matrix is given on the space of non-zero quantum defects by

$$\pi \mathbf{PDP} = \frac{\mathbf{P}}{(\mathbf{P} - \mathbf{KPh}) \frac{\mathbf{P}}{\mathbf{PHP}} (\mathbf{P} - \mathbf{hPK}) + \mathbf{KPHPK}} \quad (48)$$

We thus need only the  $\mathbf{PhP}$  and  $\mathbf{PHP}$  matrices. In its general form, equation (48) is a new result.

In the particular case of  $\text{Na}_2$ ,  $\mathbf{P}$  projects on the s, p, d, f channels only. It is the major advantage of this theory with respect to a perturbation theory to exploit the particular symmetry of the Stark hamiltonian in order to reduce the size of the calculation.

**4.2 CASE OF THE QUASI-DISCRETE LEVELS.** — Harmin [23] gave general expressions for the matrices  $\mathbf{h}$  and  $\mathbf{H}$  in a WKB approximation. Here we consider only states situated well below the potential barrier in the  $\eta$  coordinate (see Fig. 1). In other words, we limit our analysis to the case where the electric field may be considered as weak, i.e. a small fraction of the Inglis-Teller limit  $F_c = 1/3 n^5$ . Note however that, at this point, the present theory is not limited to the weak field regime but may be used in any case provided that the matrix  $\mathbf{h}$  and  $\mathbf{H}$  are calculated without any approximation. The departure from the general case arises when we limit the discussion to the states well below the classical saddle point energy  $(-2\sqrt{F})$ . In fact, this condition is less restrictive than  $F \ll F_c$ . One need only to have  $F \ll 1/16 n^4$  in order to be well below the saddle point. The stronger restriction relative to  $F_c$  will arise later. In this case, the resonances in the spectrum are so narrow that they can be considered as discrete which is equivalent to neglect the matrix  $\mathbf{H}$ . Thus we assume now that  $\mathbf{H} = 0$ . In that case, equation (48) cannot be used as is. The calculation of the Stark spectrum is therefore completely different. Instead of having a  $\mathbf{D}$  matrix without poles on the real axis that gives a continuous spectrum consisting of many lines with finite widths and complex profiles, we get a discrete spectrum corresponding to the poles of the  $\mathbf{D}$  matrix like in the zero-field problem. A discrete state is at an energy  $E_n$  such that  $\mathbf{h}^{-1} - \mathbf{K}$  is singular, and the projector onto this state is

$$P_n = \sum_{\alpha, \beta} \Omega |z, \alpha\rangle \text{Res}_{E=E_n} \left( \frac{1}{\mathbf{h}^{-1} - \mathbf{K}} \right)_{\alpha\beta} \langle z, \beta | \Omega' \quad (49)$$

If one chooses to start from functions normalized per energy unit, the matrix  $\mathbf{h}$ , which is diagonal in the  $\iota = \{N^+, M_{N^+}, n_1, m\}$  basis is [23]

$$\mathbf{h} = \pi \cot \Delta$$

or

$$h_{ij} = \pi \cot \Delta (\nu_{N^+}, n_1, m) \delta_{ij} \quad (50)$$

where  $\Delta$  is the WKB phase shift accumulated in the potential well  $V_2(\eta)$  of figure 1

$$\Delta + \frac{\pi}{2} = \int_{\eta_{\min}}^{\eta_{\max}} k(\eta) d\eta \quad (51a)$$

with

$$k(\eta) = \left( -\frac{m^2}{4\eta^2} + \frac{1 - \beta(n_1)}{\eta} - \frac{1}{4\nu_{N^+}^2} + \frac{1}{4}F(\eta) \right)^{1/2} = \sqrt{\frac{\varepsilon}{2} - 2V_2(\eta)} \quad (51b)$$

when the field is low, one can expand  $\Delta$  to first order in  $F$ , which gives, if  $\nu_{N^+}$  is in the vicinity of  $n$

$$\Delta(\nu_{N^+}, \beta, m) = \pi(\nu_{N^+} - n) - \frac{3}{2}\pi k \nu_{N^+}^4 F \quad (52)$$

where the electric quantum number  $k$  is given by equation (42). This second approximation limits the present discussion to the regime  $F \ll F_c = (3n^5)^{-1}$  where one can neglect the

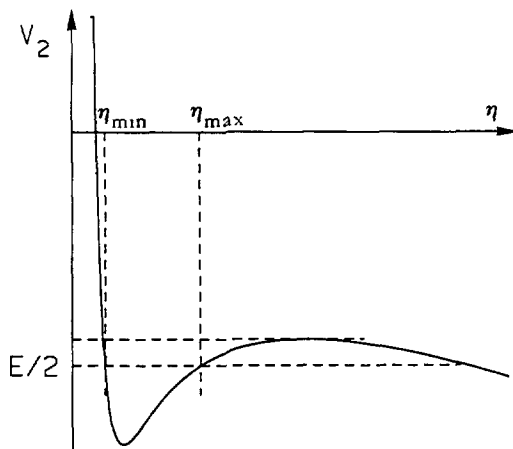


Fig 1 — Effective potential along the  $\eta$  axis For a state at a given energy  $E$ ,  $\eta_{min}$  and  $\eta_{max}$  are the boundaries of the elliptic integral  $\Delta$  [Eq (51)]

overlap between different  $n$  manifolds. Once again, there is no formal impediment to a complete calculation of  $\mathbf{H}$  and of the elliptic integral  $\Delta$  which would extend the validity of our theory to the strong field regime at the expense of an inflation of the numerical calculation.

Equation (52) is fundamental in the sense that if the matrix  $H$  is neglected, the integral  $\Delta$  is the only quantity where the field strength is introduced.

It is customary to use the  $\mathbf{R}$  matrix instead of the  $\mathbf{K}$  matrix with the relation

$$\mathbf{R} = -\pi\mathbf{K}$$

The  $\mathbf{R}$  matrix is diagonal in the  $\alpha = \{\ell\Lambda JM\}$  basis. The diagonal matrix elements are related to the eigenquantum defects  $\mu_{\ell\Lambda}$  by

$$R_{\alpha\beta} = \tan[\pi\mu_{\ell\Lambda}] \delta_{\alpha\beta} \tag{53}$$

**4.3 QUANTIZATION OF THE ENERGY AND TRANSITION INTENSITIES IN THE QUASI-DISCRETE SPECTRUM.** — The transition intensity from an initial state  $|0\rangle$  towards the state of energy  $E_n$  is proportional to

$$I = \langle 0 | TP_n T | 0 \rangle \tag{54}$$

where  $P_n$  is given by equation (49) and  $T$  is the dipole operator. The quantities  $\langle 0 | T\Omega | z, \alpha \rangle = T_\alpha$  are difficult to calculate exactly and are assumed to be constant over the whole spectrum. The set of non-zero  $T_\alpha$  is generally extremely restricted. For example, in the case of  $\text{Na}_2$  discussed in the next section, the initial state  $|0\rangle$  is a  $p\Sigma$  state. Then,  $T_\alpha$  differs from zero only for  $\ell = 0$  and  $2$  and  $\Lambda = 0$  and  $1$ . Only three parameters ( $T_{s\Sigma}$ ,  $T_{d\Sigma}$  and  $T_{d\Pi}$ ) are required. They have been determined experimentally [13, 28]. The transition intensity is then

$$I = \sum_{\alpha, \beta} T_\alpha T_\beta^* \text{Res}_{E=E_n} \left( \frac{1}{\mathbf{h}^{-1} - \mathbf{K}} \right)_{\alpha\beta} \tag{55}$$

If the  $T_\alpha$ 's are zero for zero quantum defects such as in the application discussed below, one

can use equation (47) to restrict the calculation to the projected matrix, which can also be written as

$$\mathbf{P} \frac{1}{\mathbf{h}^{-1} - \mathbf{K}} \mathbf{P} = \pi \cos(\pi \boldsymbol{\mu}) \mathbf{P} \mathbf{q}^{-1} \mathbf{P} \mathbf{h} \mathbf{P} \quad (56)$$

for computational ease, with  $\mathbf{q}$  given by

$$\mathbf{q} = \mathbf{P} \cos(\pi \boldsymbol{\mu}) \mathbf{P} + \mathbf{P} \mathbf{a}^+ \cot(\Delta) \mathbf{a} \sin(\pi \boldsymbol{\mu}) . \quad (57)$$

The energies  $E_n$  are solutions of the equation

$$\det \mathbf{q} = 0 . \quad (58)$$

Equation (58) is the weak field analogue of the fundamental equation of MQDT in zero-field (see Eq (27)).

If we introduce a non-zero vector  $|A\rangle$  solution of

$$\mathbf{q} |A\rangle = 0 \quad (E = E_n) \quad (59)$$

then the intensity of the transition towards the state  $|A\rangle$  is given by

$$I = \sum_{\alpha \beta} T_{\alpha} T_{\beta}^* A_{\alpha} A_{\beta}^* \frac{1}{\mathcal{N}} \cos(\pi \mu_{\alpha}) \cos(\pi \mu_{\beta}) \quad (60)$$

with a normalization factor  $\mathcal{N}$  given by (assuming  $d\mathbf{R}/dE = 0$ )

$$\mathcal{N} = \langle A | \sin(\pi \boldsymbol{\mu}) \mathbf{a}^+ \frac{\mathbf{v}^3}{\sin^2 \Delta} \mathbf{a} \sin(\pi \boldsymbol{\mu}) |A\rangle + 0(F) \quad (61)$$

The  $\mathbf{v}$  matrix is diagonal in the  $i = \{N^+, M_{N^+}, n_1, m\}$  basis

$$\mathbf{v}_{ij} = \nu_{N^+} \delta_{ij} . \quad (62)$$

Equations (55) to (62) allows the complete determination of the Stark spectrum in the weak field approximation

**4.4 EXPANSION ON THE PARABOLIC BASIS.** — Once the intensities have been obtained, it is often desirable to get the parabolic content of a given state. Up to now, we have managed to calculate and use only the expansion coefficients on the non-zero quantum defects eigenchannels. However, it is easy to obtain the other coefficients from  $\mathbf{P}|A\rangle$  since  $|A\rangle$  must satisfy also

$$[\cos(\pi \boldsymbol{\mu}) + \mathbf{a}^+ \cot(\Delta) \mathbf{a} \sin(\pi \boldsymbol{\mu})] |A\rangle = 0 \quad (63)$$

and we obtain the components  $\mathbf{Q}|A\rangle$  by

$$\mathbf{Q}|A\rangle = -\mathbf{Q} \mathbf{a}^+ \cot(\Delta) \mathbf{a} \sin(\pi \boldsymbol{\mu}) |A\rangle , \quad (64)$$

using the fact that  $\sin(\pi \boldsymbol{\mu})$  is non-zero only on the space spanned by  $\mathbf{P}$ , and  $\cos(\pi \boldsymbol{\mu}) = 1$  on the space spanned by  $\mathbf{Q}$ . Then the parabolic basis coefficients  $|B\rangle$  are given by

$$|B\rangle = \mathbf{a} \cos(\pi \boldsymbol{\mu}) |A\rangle \quad (65)$$

## 5. Calculated spectra of Na<sub>2</sub> Rydberg states.

Because of the various approximations made in the previous section, we will restrict the application of our theory to the quasi-discrete spectrum of Na<sub>2</sub> Rydberg states in weak electric fields. Working in the weak field limit allows us to perform drastic truncations on the different basis which include in principle an infinity of channels  $N^+$  or  $J$ . The frame transformation described in section 3 as well as the equations derived in section 4 will be used in straight way.

First of all, let us recall briefly the experimental techniques used to record the Stark spectra of Rydberg states of Na<sub>2</sub>.

**5.1 EXPERIMENTAL SPECTRA OF Na<sub>2</sub> RYDBERG STATES** — A detailed description of our experimental set-up is available in references [12], [28] and [30]. The Na<sub>2</sub> molecules are produced in a free expansion molecular beam which interacts at right angle with two counter-propagating laser beams. The spectral width of the two pulsed tunable dye lasers is about  $0.2 \text{ cm}^{-1}$ . The Rydberg states are populated by a two step resonant excitation. The first laser is tuned to a selected  $v', J'$  rovibrational level of the intermediate A  $^1\Sigma_u^+$  state. This state has a strong 3p character. The second laser is scanned to explore the ionization region. Owing to the 3p character of the A state, the Rydberg states excited in zero-field are almost pure nd states with  $J = J'$  or  $J' \pm 1$  and  $v = v'$  (off-diagonal vibrational transitions are negligible). The rovibrational interactions among these series have been analyzed in the framework of MQDT [13, 28].

In the interaction region, a DC electric field is applied between two circular plates 1 cm apart perpendicularly to the molecular and laser beams. Photoelectrons produced by auto- or field-ionization are extracted through a grid at the center of the positive plate and detected by a secondary electron multiplier. The electron signal is averaged by a boxcar integrator before being stored in a microcomputer as a function of the second laser photon energy. In the presence of an electric field,  $\ell$  is no longer defined but the intensity of the transitions depends essentially on the nd component, and to a negligible extent on the ns component, of the Stark states.

The  $v' = 4, J' = 6$  level of the A state has been selected to record the two experimental spectra displayed in figure 2. Both spectra are taken in the vicinity of the  $n = 17, v = 4$  Rydberg states. The bottom spectrum was recorded with a field of 400 V/cm and the top spectrum with a field of 600 V/cm. The ratio  $F/F_c (= 3n^5F)$  is respectively 0.11 and 0.17, compatible with the weak field regime described above ( $F \ll F_c$ ). In both spectra, the width of the observed line exceeds the laser bandwidth, indicating that an unresolved structure is underlying. However the characteristic  $3nF$  spacing [12] is clearly visible in the spectrum recorded with  $F = 600 \text{ V/cm}$  ( $3nF \approx 1.3 \text{ cm}^{-1}$ ). The unresolved and complex internal structure of each individual line is due to the electron-core rotation coupling. The comparison between experimental and calculated spectra is thus reduced to

- (i) the splitting between the observed lines
- (ii) the relative intensities of these lines and especially the envelop of the  $n = 17$  manifold
- (iii) the appearance of extra-lines

As far as the envelope of the  $n = 17$  manifold is concerned, its effective width is symptomatic of the non hydrogenic behaviour of Na<sub>2</sub> in weak fields. In the top spectrum ( $F = 600 \text{ V/cm}$ ) of figure 2 for example, only 4 lines of the multiplet are intense. In the quasi-hydrogenic approximation, one would expect a fully developed Stark manifold with  $(n - 1)$  components and a smooth variation of the relative intensities as a function of  $n_1$ . The weakness of the lines corresponding to the extreme values of  $n_1$  ( $n_1 \approx 0$  and  $n_1 \approx n$ ) is revealing of the incomplete  $\ell$ -mixing at moderate fields. The numerical application described below, shows that this effect



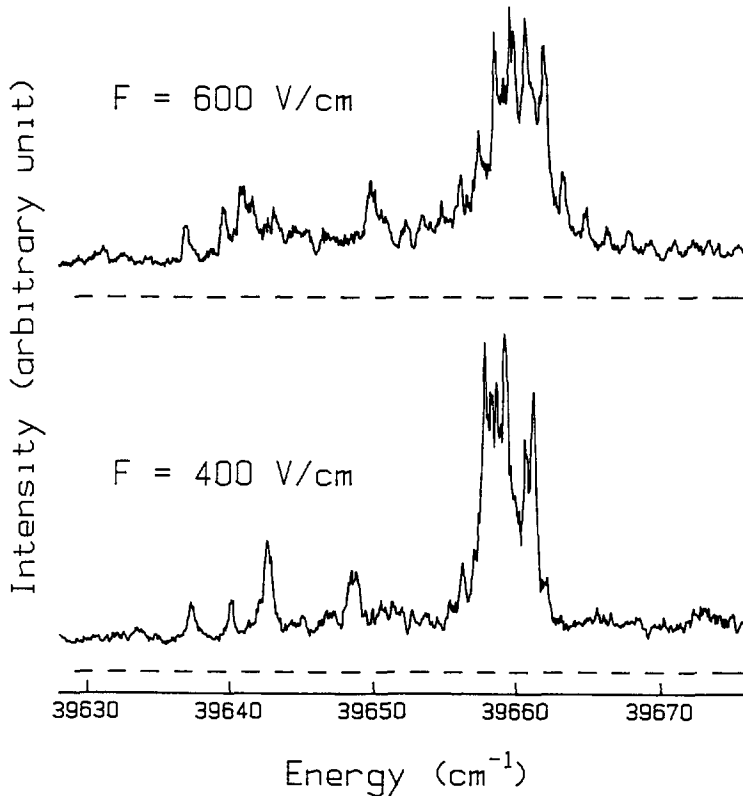


Fig. 2. — Experimental spectra of  $\text{Na}_2$  Rydberg states recorded in the vicinity of  $n = 17$  ( $v = 4$ ) with the intermediate level  $v' = 4$ ,  $J' = 6$  at  $F = 400$  V/cm (bottom) and  $600$  V/cm (top). The total width of the hydrogenic multiplet ( $3n^2F$ ) is respectively  $15$  and  $22$   $\text{cm}^{-1}$  while the observed width is only about  $5$   $\text{cm}^{-1}$ . All energies are relative to the bottom of the ground state potential well.

arises from the relatively large value of the  $nf$  series quantum defects which precludes the complete  $\ell$ -mixing at moderate field where  $nf$  states are still separated from the hydrogenic multiplet.

**5.2 BASES AND TRUNCATIONS** — We have to deal with two infinite basis sets: the spherical Hund's case (a) one, represented with the notation  $\{\alpha\}$  and the parabolic Hund's case (d) one represented with the notation  $\{i\}$ . The complete quantum description of both basis has already been given in section 3. We have now to perform truncations in order to achieve computations.

As seen above, the  $\{\alpha\}$  set can be reduced to the few states with non-zero quantum defect. Thus, according to previous results [13, 31], we have to consider states with  $\ell \leq 3$  and so  $|A| \leq 3$  as well. To ensure the presence of the rotational structure in spectra, we have to keep at least the three  $J$  values  $J' - 1$ ,  $J'$ ,  $J' + 1$  where  $J'$  is the total angular momentum of the initial state which is well described with a single spherical Hund's case (a) wavefunction [28]. This is obviously a minimal set since these three  $J$  values are those present in the zero-field spectrum. Because the  $\{\alpha\}$  basis is mostly relevant to short-range electron-core interactions where the Stark field is of minor importance, the zero-field set  $\{J' - 1, J', J' + 1\}$  is a reliable first order truncation. Moreover, the introduction of additional  $J$  values in some selected cases has shown that it does not introduce significant effects. This is a major difference with

respect to a perturbative treatment [32] where one has to introduce explicitly all the  $J$  values compatible with the relation  $\ell + N^+ = J$ . The extension of the range of  $J$  values to include high order phenomena is of course possible but the number of channels would increase proportionally and strongly slow down computations. These phenomena are also too weak for our purpose. In order to compare our model with the experimental spectra of figure 2, we have chosen the  $J' = 6$  level of the  $A^1\Sigma_u^+$  state as initial state. Hence the set of 48 wavefunctions is finally reduced to 24 if we take into account the core parity which is odd because the initial state has a strong  $p\Sigma^+$  character [28] and an even  $J'$  value.

The channels we have used are

$$\begin{aligned} J = 5, 7 & \quad ns\Sigma^+ \quad np\Pi^- \quad nd\Sigma^+ \quad nd\Pi^+ \quad nd\Delta^+ \quad nf\Pi^- \quad nf\Delta^- \quad nf\phi^- \\ J = 6 & \quad np\Sigma^+ \quad np\Pi^+ \quad nd\Pi^- \quad nd\Delta^- \quad nf\Sigma^+ \quad nf\Pi^+ \quad nf\Delta^+ \quad nf\phi^+ \end{aligned}$$

The truncation of the  $i$  set is performed on the three quantum numbers  $m$ ,  $k$  and  $N^+$ . We use the electric quantum number  $k$ , difference between  $n_1$  and  $n_2$  for commodity. The  $m$  and  $k$  quantum numbers are related through equation (42),  $k$  ranging from  $-n + |m| + 1$  to  $n - |m| - 1$  by step of two. We have to note that  $m$ , as projection along the field axis of the electronic momentum  $\ell$ , is confined (though not conserved) to the few values  $|m| \leq 3$  because only s, p, d and f levels have non-zero quantum defect. But for each  $(m, k)$  set we may have an infinity of  $N^+$  values. With respect to the accessible  $J$  and  $\ell$  values, and the odd core parity of the initial state, we can assume that  $N^+$  ranges from  $J' - \ell - 1$  to  $J' + \ell + 1$  and is odd. For  $J' = 6$  it yields

$$N^+ = 3, 5, 7, 9.$$

This set is exactly the set of  $N^+$  values present in the zero-field  $J' = 6$  spectra. However, the justification of this truncation is quite different from the  $J'$ 's truncation. Indeed, the electric field is not responsible for any direct coupling between different  $N^+$  values (see Sect. 3.3) and thus the truncation to the zero-field  $\{i\}$  basis is not so restrictive. Once again, adding other  $N^+$  values does not change significantly the calculated spectra.

Finally, as noted in section 3,  $M$  is the only good quantum number. However, since it is not selected in the initial state, one has to add several calculated spectra to get the equivalent of an experimental spectrum. The splitting of the Stark states as a function of  $M$  is the main origin of the unresolved sub-structure of the observed lines.

The set  $\{i\} = \{N^+ = 3, 5, 7, 9, m = 0, \pm 1, \pm 2, \pm 3; k = -n + |m| + 1, -n + |m| + 3, \dots, n - |m| - 1\}$  still holds 428 wavefunctions. Finding the poles of the DOS matrix (Eq. (58)) consists in finding the zeros of a  $24 \times 24$  determinant and dealing with a  $24 \times 428$  transformation matrix.

**5.3 QUANTUM DEFECTS** — Once settled with the various bases and the frame transformation, the question of the zero-field energy levels arises. Rotational interactions are automatically taken into account owing to the suitable choice of the frame transformation. We have then to approach the problem of quantum defects. These quantities may be reasonably considered as constants over the whole spectra and independent on the  $J$  value and on the parity. Assuming all the series with  $\ell > 3$  as hydrogenic ( $\mu = 0$ ), we have to input in our computations 10 parameters among which only 4 are known [13, 28]. There are

$$\begin{aligned} \mu_{s\Sigma} &= -0.40 & \mu_{d\Sigma} &= 0.21 \\ \mu_{d\Pi} &= -0.01 \\ \mu_{d\Delta} &= 0.42 \end{aligned}$$

As opposed to many atoms and small molecules, the quantum defects of the  $nf$  series of  $\text{Na}_2$  are far from being negligible. This is mainly a consequence of the large spatial extension of the  $\text{Na}_2^+$  core which renders these series penetrating. Thereby, these parameters cannot be set to zero and cannot be estimated by a multipolar expansion relevant to the non-penetrating case. The magnitude of the  $f$  series quantum defects is crucial because the mixing between the  $nd$  states that bear all the oscillator strength and the hydrogenic complex ( $\ell > 3$ ) occurs *via* the  $nf$  states. The  $\mu_{fA}$ 's determine the aspect of the  $\text{Na}_2$  Stark manifold at weak field. On the other hand, the  $p$  series quantum defects are also unknown. Finally, the quantum defects of the high  $\ell$  series ( $\ell > 3$ ) can be neglected because they are probably less than 0.05 and they do not have any important effect as soon as the  $nfA$  quantum defects are larger.

Let us now discuss the  $np$  series quantum defects. In a small molecule like  $\text{H}_2$ , it is possible to deduce the quantum defects of the high  $n$  states from those of the lowest members of the same series. In  $\text{Na}_2$ , the A and B states form the first pair of  $p\Sigma$  and  $p\Pi$  states. Their quantum defects are 0.90 and 0.61. However, nothing can be deduced from these values. Indeed, if we examine the results of Schawlow *et al.* about the low  $nd$  Rydberg states of  $\text{Na}_2$  [33], we find that the quantum defects of the  $4d\Sigma_g$  and  $3d\Pi_g$  states are respectively 0.02 and  $-0.51$ , which have nothing to do with the high  $n$  values of 0.21 and  $-0.01$  respectively. Hence, it is clear that in  $\text{Na}_2$ , it is irrelevant to extrapolate quantum defects of the lowest states to the high Rydberg states. Similarly, *ab initio* calculations are only available for low  $n$  states, mostly of gerade symmetry [34], and no acceptable values are known for the high Rydberg states, even for the  $ns$  and  $nd$  series. Nevertheless, few experimental results give some indications about the  $np$  series. We have reported a previous work where microwave transitions between  $\text{Na}_2$  Rydberg states were performed [31]. Several lines were recorded and a Rydberg series,  $np\Sigma$  or  $nf\Sigma$ , was found to have a quantum defect of 0.14. We have decided, after many calculations, to affect this quantum defect to the  $nf\Sigma$  Rydberg series because the  $np\Sigma$  should have a much stronger quantum defect. Anyhow, this is only an assumption that is convenient to fit correctly the experimental spectra. We could obviously try the other choice but this would lead to theoretical spectra generally more different from the experimental ones. The second quantum defect we already know comes from a detailed assignation of the lines of Stark spectra. Figure 3 shows an ensemble of spectra recorded with  $v' = 2$ ,  $J' = 6$  as intermediate level near  $n = 21$  and for various field values ranging from 0 to 120 V/cm. The appearance of extra-lines arranged in a Rydberg series (when compared with other  $n$  values) with a quantum defect of 0.23 is clearly visible. The quasi quadratic Stark effect of this state at low field is also visible in figure 3. Considering the intensities of these extra-lines and their evolution with the field, we have assumed that it was a  $nf\Pi$  Rydberg series. For the other series included in the calculations we have taken empirically fitted values. A set of quantum defects that gives acceptable agreement with the experiments is

$$\begin{aligned} \mu_{p\Sigma} &= 0.35 & \mu_{f\Sigma} &= 0.14 \\ \mu_{p\Pi} &= 0.20 & \mu_{f\Pi} &= 0.23 \\ & & \mu_{f\Delta} &= 0.18 \\ & & \mu_{f\phi} &= -0.06. \end{aligned}$$

Obviously this choice is not unique because many sets of coefficients may produce acceptable theoretical spectra.

**5.4 COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED SPECTRA.** — Assuming the bases truncations and the quantum defects described above, we have calculated the two spectra of figure 4. These spectra correspond to the experimental data presented in figure 2 (i.e.  $v' = 4$ ,  $J' = 6$ ,  $n = 17$ ,  $F = 400$  and  $600$  V/cm). One spectrum is calculated for each

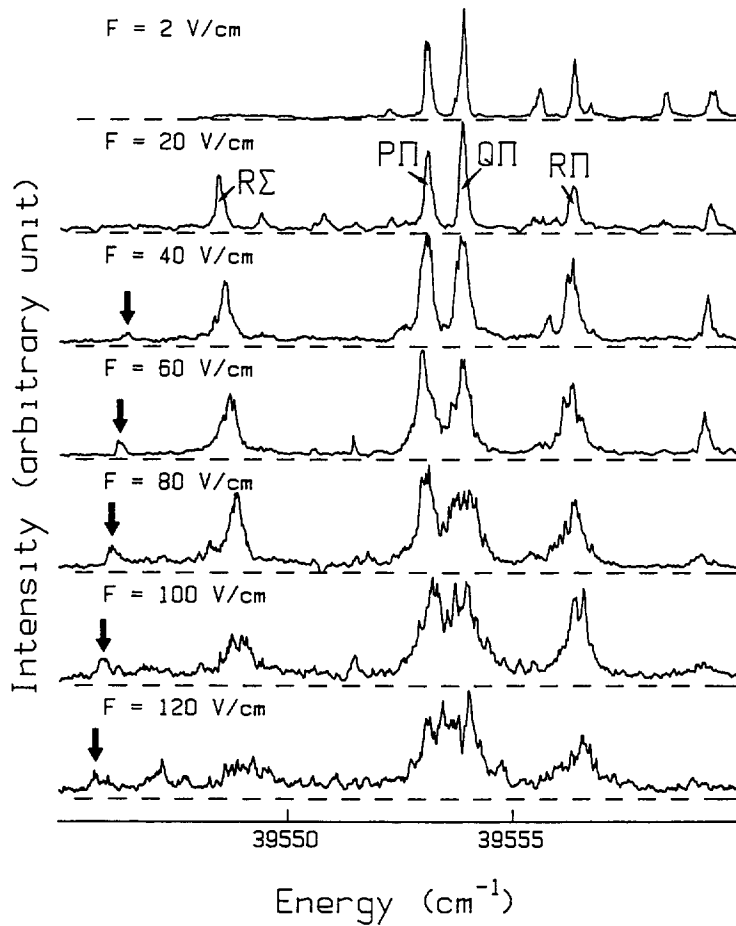


Fig 3 — Experimental spectra of  $\text{Na}_2$  around  $n = 21$  ( $v = 2$ ) recorded using the intermediate level  $v' = 2, J' = 6$ . Field strength ranges from 0 to 120 V/cm. The extra line near  $39\,546\text{ cm}^{-1}$  (quantum defect  $\approx 0.23$ ) is indicated by an arrow. This state is located below the ionization threshold at  $F = 2\text{ V/cm}$  ( $v^+ = 0, N^+ = 3$  level of the ion, lowered by  $-2\sqrt{F}$ , see Ref [9]) but almost  $15\text{ cm}^{-1}$  above this threshold at  $F = 20\text{ V/cm}$  at which it is not yet visible. The intensity of this extra line increases with the field and it is repelled quadratically towards low energy.

possible  $M$  value, the summation over  $M$  and the convolution with a  $0.2\text{ cm}^{-1}$  width are done afterwards. The overall features of the experimental spectra are correctly reproduced by the calculation, namely

- (i) the appearance of extra-lines on the red side of the manifold,
- (ii) the  $3nF$  splitting between the observed intense lines, and
- (iii) the relatively low number of intense lines that gives the apparent small width of the manifold.

However, the exact energies and intensities of the observed transitions is very sensitive to the  $npA$  and  $nfA$  unknown quantum defects but the precise determination of these quantities is nonetheless impossible and the agreement is only qualitative. The relatively large number of varying parameters (the 10 quantum defects of which only 4 are known undoubtedly) combined with the heaviness of the calculation preclude the optimum fitting of such

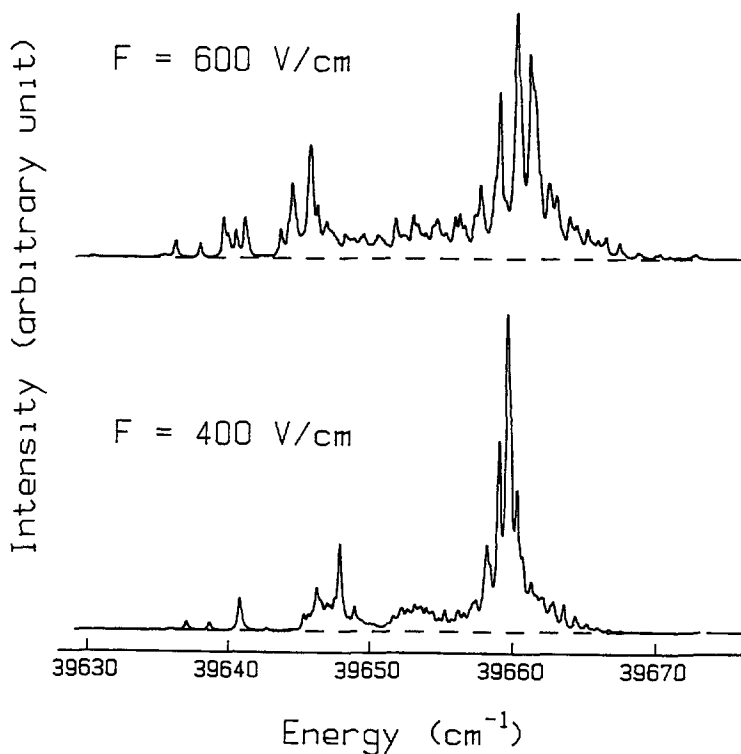


Fig 4 — Calculated spectra corresponding to the experimental parameters used to record experimental spectra of figure 2 (i.e.  $v' = 4$ ,  $J' = 6$ ,  $n = 17$ ,  $F = 400$  V/cm (bottom) and  $600$  V/cm (top)) Calculated spectra are convoluted with an experimental width of  $0.2$   $\text{cm}^{-1}$ . Agreement with experimental data is only qualitative owing to the many unknown quantum defects. However, the general aspects of the spectra of figure 2 are correctly reproduced.

parameters. Nevertheless, the correct description of the most prominent aspects of the  $\text{Na}_2$  Stark spectra demonstrates the high capability of our theory to analyze molecular Stark effect, especially in a case where a perturbative treatment would require a prohibitively large number of rotational ( $N^+$  and  $J$ ) and electronic ( $\ell$  and even  $n$ ) channels.

For example, the general shape of the experimental spectra, without any strong extra-line on the blue side of the multiplet, indicates that the unknown quantum defects should be positive, and their relative distance from the multiplet accounts for a rather high absolute value of the  $np$  defects as discussed in the preceding chapter. A detailed assignment of the extra-lines cannot be performed because the wavefunction, though completely known numerically, is spread over the whole basis whatever it is, the spherical Hund's case (a) or the parabolic Hund's case (d) basis set. In other words, the Stark states are neither well described by a dominant  $\ell$ ,  $n_1$  or  $N^+$  quantum number.

The second point to discuss is the hydrogenic multiplet. The parabolic Hund's case (d) wavefunction is a product of an electronic part, the subset  $\{m, k\}$  and an ionic core part. We are then expecting as many hydrogenic multiplets as there are  $N^+$  values. Because of the truncations, only four are explicitly present, two being more intense,  $N^+ = 5$  and  $N^+ = 7$ , because the rotational level of the initial state is  $J' = 6$ . These sublevels of the multiplets are interpenetrating themselves, forming only one pattern with a regular  $3nF$  structure already observed in atomic spectra [35]. Since the initial A state has a strong  $3p$

character, only the low  $m$  components are involved in our spectra. Although  $m$  is not a good quantum number, the non degeneracy of the  $\ell \leq 3$  states gives rise to the (quasi-) degeneracy of the various  $m$  components (in fact of their various combination) as noted before in non hydrogenic atomic systems [35]. This degeneracy induces the  $3nF$  structure instead of the hydrogenic  $3/2nF$  structure present when odd and even  $m$  levels are populated. Such a pattern is superimposed to the zero-field rotational structure of the  $17dII$  state. Although rotational structure gradually fades away as the electric field is increased [12], its reminiscence for the field values of 400 V/cm and 600 V/cm is the signature of penetrating  $nfA$  Rydberg series with relatively high quantum defects. Nevertheless, the one corresponding to the  $nf\phi$  series is allowed to be much weaker because this Rydberg series is not coupled to the  $nd$  states by any electric dipolar coupling. The numerical parameters used in the present calculations are in complete agreement with these assumptions.

### Conclusion.

The operational formalism of the Multichannel Quantum Defect Theory is shown to be a well suited formalism to recast in a wider context the Density-Of-State matrix. It is shown how closely related this DOS matrix and the resolvent operator are and how the whole spectrum arises from its singularities. We emphasize that, at this stage of the work, the problem is not reduced to the Stark problem but could take into account other long range potential.

This formalism has been applied to the  $\text{Na}_2$  molecular Rydberg states in weak electric fields.

Although we have considerably shortened the basis sets involved in the calculations, simulated spectra in good agreement with experimental data have been obtained.

The truncation of the various bases has been proved to be of minor consequence, at least in the weak field regime, and allows numerical calculations of reasonable size.

Provided the  $H$  matrix and the elliptic integral  $\Delta$  are explicitly calculated, the high field regime may be efficiently treated with the same formalism. The  $n$ -mixing as well as the line profiles could be simulated with a high accuracy at the cost of a slightly larger computation.

As compared to a perturbative treatment, our MQDT operatorial formalism possesses the following advantages :

- (i) it reduces the size of the computation by eliminating the zero quantum defect channels,
- (ii) reasonable truncations allow the reduction of the number of the  $N^+$  and  $J$  values to be taken into account, in order to describe correctly electron/core coupling,
- (iii) if  $H$  and  $\Delta$  are explicitly calculated, this formalism is not limited to the quasi-discrete spectrum as the perturbative approach is, and line positions, line profiles and ionization rates may be predicted even above the classical saddle point energy.

However, one has to recognize at least two advantages in favor of the perturbation theory :

- (i) its simple and familiar formalism,
- (ii) only one large matrix has to be diagonalized to calculate one region (one or several  $n$  manifold) of the spectrum instead of the step by step search of the successive poles of the DOS matrix in the quasi-discrete spectrum ( $H = 0$ ) or of the calculation of the photoionization cross section as a continuous function of the energy in the general case ( $H \neq 0$ ).

In the specific case of  $\text{Na}_2$ , the MQDT operatorial formalism has proved to be the best suited to analyze and simulate Stark spectra because of the large number of  $N^+/J$  values needed in a perturbative treatment. On the contrary, in the case of the  $\text{H}_3$  molecule, other results [32] show that, owing to the fact that the zero-field states are almost pure case (d) states (with  $N^+ = 1$ , which limits drastically the size of the perturbation basis), the perturbative treatment is more appropriate.

However, triatomic hydrogen is certainly not a typical example and the formalism presented in this paper is certainly more general and more adapted to complex situations than any perturbative model

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One atomic unit of energy (1 Hartree) =  $\frac{\mu_0^2 m_e e^4 c^3}{8 h^3} \approx 21\,947\,4631 \text{ cm}^{-1}$
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