

The XY_4-A_2 system : Potential, Line Broadening Theory, Resonance Functions, Symbolic Computation and Source Code Generation

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Abstract

This document contains mathematical developments, as well as some technical details regarding symbolic computation and source code generation, that are complements to a paper entitled “Line broadening coefficients calculations for methane perturbed by nitrogen”, by T. GABARD and V. BOUDON, to be submitted to the Journal of Quantitative Spectroscopy and Radiative Transfer.

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Units

I used the International System of Units [1, 2]. For practical reasons, I did not find it convenient to fully normalize the calculations, using for example atomic units, apart from measuring distances in Å ($\equiv 10^{-10}$ m).

Acronyms, abbreviations

IR : Irreducible Representation.

ME, RME : Matrix Element, Reduced Matrix Element.

MFF, LFF : Molecule Fixed Frame, Laboratory Fixed Frame.

IMF : InterMolecular Frame. For a couple of molecule, this is the frame which z axis is along the line joining the centers of mass of the molecules.

Notations, definitions

l, J : Symmetry labels for IRs of $SO(3)$ or $O(3)$; m, M, k, K : Associated projection numbers; $[l(\text{ or } J)] = 2l(\text{ or } J) + 1$: Dimension of the IR l .

C, Γ : Symmetry labels for IRs of T_d ; σ : Component index of an IR; $[C]$: Dimension of the IR C , 1, 1, 2, 3 and 3 for the IRs A_1, A_2, E, F_1 and F_2 , respectively.

$\mathcal{D}; Y$: WIGNER functions, rotation matrix elements, spherical harmonics.

1; 2 : Index for the optically active molecule, XY_4 ; Index for perturber, A_2 .

f, F : Factors related to the long range interaction between the molecules.

d, D and e, E : Factors related to the short range interaction between the molecules, repulsive and attractive parts, respectively.

A^* : Complex conjugate of quantity A .

$\Omega; \Lambda$: Set of EULER angles; Set of polar coordinates (arguments of spherical harmonics).

$n!! = n(n-2)(n-4) \dots 2$ or 1 .

Note on references

I have used the `natbib` and `hyperref` packages of L^AT_EX [3] for this document but found no convenient way to cite URLs in all cases. Moreover, citations do not properly break across lines, if a URL is present. This should be corrected.

1 Introduction

I describe, in this report, the development of the various computer codes needed for the calculations of line broadening coefficients for the absorption lines of a generic XY_4 molecule (tetrahedral symmetry) perturbed by an homonuclear diatomic molecule. This document is supplementary to a paper that describes the results of such calculations in the case of methane perturbed by nitrogen [4, and references therein]. For the analytical calculations, I used an object oriented symbolic computation software, MuPAD [5]. I did almost all of the programming tasks through automated source code generation. For this, I used the Perl scripting language, the standard library [6, 7] as well as additional packages available from the CPAN [8]. I chose to write a program generator, described below, that handles the hundreds of functions and procedures that appear in the theory.

2 The interaction potential

2.1 Note on rotation operators

I have used two notations for the matrix elements of these operators, either the classical notation, i.e. “WIGNER matrices”, or the double tensor notation. The latter one is defined by

$$\mathcal{D}_{m m'}^{(l_g, l_g)} = [l]^{1/2} \mathcal{D}_{m' m}^{(l)}(\Omega) \quad (1)$$

This definition allows to use the WIGNER-ECKART theorem to derive the ME of rotation operators. In the case of the XY_4 molecule, I will use symmetrized operators (in the T_d group). The expressions of the tensors involved in the potentials of sections 2.2 and 2.3 are [9, Eqs. (5.9) through (5.14), p. 74]

$$\mathcal{D}_0^{(0_g, 0_g 0A_1)} = 1, \quad (2)$$

$$\mathcal{D}_m^{(3_g, 3_g 0A_2)} = -\frac{i}{\sqrt{2}} \left[\mathcal{D}_{m -2}^{(3_g, 3_g)} - \mathcal{D}_{m 2}^{(3_g, 3_g)} \right], \quad (3)$$

$$\mathcal{D}_m^{(4_g, 4_g 0A_1)} = \frac{\sqrt{5}}{2\sqrt{6}} \left[\mathcal{D}_{m -4}^{(4_g, 4_g)} + \mathcal{D}_{m 4}^{(4_g, 4_g)} \right] + \frac{\sqrt{7}}{2\sqrt{3}} \mathcal{D}_{m 0}^{(4_g, 4_g)}, \quad (4)$$

$$\mathcal{D}_m^{(6_g, 6_g 0A_1)} = \frac{\sqrt{7}}{4} \left[\mathcal{D}_{m -4}^{(6_g, 6_g)} + \mathcal{D}_{m 4}^{(6_g, 6_g)} \right] - \frac{1}{2\sqrt{2}} \mathcal{D}_{m 0}^{(6_g, 6_g)}, \quad (5)$$

$$\mathcal{D}_m^{(7_g, 7_g 0A_2)} = i \frac{\sqrt{13}}{4\sqrt{3}} \left[\mathcal{D}_{m 2}^{(7_g, 7_g)} - \mathcal{D}_{m -2}^{(7_g, 7_g)} \right] + i \frac{\sqrt{11}}{4\sqrt{3}} \left[\mathcal{D}_{m 6}^{(7_g, 7_g)} - \mathcal{D}_{m -6}^{(7_g, 7_g)} \right], \quad (6)$$

$$\begin{aligned} \mathcal{D}_m^{(8_g, 8_g 0A_1)} &= \frac{\sqrt{390}}{48} \left[\mathcal{D}_{m -8}^{(8_g, 8_g)} + \mathcal{D}_{m 8}^{(8_g, 8_g)} \right] + \frac{\sqrt{42}}{24} \left[\mathcal{D}_{m -4}^{(8_g, 8_g)} + \mathcal{D}_{m 4}^{(8_g, 8_g)} \right] + \\ &+ \frac{\sqrt{33}}{8} \mathcal{D}_{m 0}^{(8_g, 8_g)}. \end{aligned} \quad (7)$$

The expressions (6) and (7) are given for completeness since, in practical calculations, the potential will not contain angular operators with so high tensorial ranks.

2.2 The electrostatic interaction

For any molecular couple, the long range interaction is represented by a classical multipolar development [10, 11]. In this one, a perturbative development over the electronic states of the molecules allows to extract three contributions, at the second order of the theory: the electrostatic, induction and dispersion interactions. I chose to keep only the electrostatic terms. Higher order terms will be in part taken into account in the short range interaction described in section 2.3. If the reference frame is the IMF, the

electrostatic interaction writes, in terms of spherical tensors,

$$V_{\text{elec}}(r, \Omega_1, \Omega_2) = \sum_{\substack{l_1=0 \\ l_2=0}}^{\infty} V_{l_1, l_2}(r, \Omega_1, \Omega_2), \text{ with} \quad (8)$$

$$V_{l_1, l_2}(r, \Omega_1, \Omega_2) = \frac{1}{4\pi\epsilon_0} \cdot \frac{4\pi(-1)^{l_2}}{[l_1 + l_2]} \left(\frac{(2l + 1)!}{(2l_1 + 1)!(2l_2 + 1)!} \right)^{1/2} \frac{1}{r^{l_1 + l_2 + 1}} \sum_{m_1, m_2} Q_{m_1}^{(l_1)} Q_{m_2}^{(l_2)} \times$$

$$\times \sum_m C(l_1 \ l_2 \ l; m \ -m \ 0) \mathcal{D}_{m_1 \ m}^{(l_1)}(\Omega_1) \mathcal{D}_{m_2 \ -m}^{(l_2)}(\Omega_2)$$

In this equation, r is the distance between the centers of mass of the two molecules, the Ω_k , ($k = 1, 2$) are the sets of angles that defines the rotations from the IMF to the frames tied to molecules 1 and 2. $l = l_1 + l_2$ because the interaction energy must be a spherical invariant, that is a tensor of rank zero. The non-symmetric phase factor comes from the fact that the z axis of the IMF is oriented from molecule 1 to molecule 2. The $Q_{m_k}^{(l_k)}$, ($k = 1, 2$) are the spherical components of the multipolar moments for each molecule, relative to the MFFs. The last sum involves CLEBSCH-GORDAN symbols as well as WIGNER matrix elements $\mathcal{D}_{m_k \ \pm m}^{(l_k)}$, ($k = 1, 2$). Moreover, $|m_k| \leq l_k$, ($k = 1, 2$) and $|m| \leq \inf(l_1, l_2)$. One may thus write a formal expression for this interaction energy,

$$V_{\text{elec}}(r, \Omega_1, \Omega_2) = \frac{1}{4\pi\epsilon_0} \sum_{\substack{l_1=0 \\ l_2=0}}^{\infty} \sum_{m_1, m_2} \sum_m^{m_1, m_2} f^{l_1, l_2} \frac{m_1, m_2 F^{l_1, l_2}}{r^{l_1 + l_2 + 1}} \mathcal{D}_{m_1 \ m}^{(l_1)}(\Omega_1) \mathcal{D}_{m_2 \ -m}^{(l_2)}(\Omega_2) \quad (9)$$

where the f are purely numerical factors, and the F depend on the components of the multipolar moments of the molecules.

For the molecular couple of concern, due to symmetry and at usual orders of development¹, one has

- $l_1 = 3$ and $m_1 = \pm 2$ (octopole); $l_1 = 4$ and $m_1 = 0, \pm 4$ (hexadecapole); $l_1 = 6$ and $m_1 = 0, \pm 4$ (no name ?),
- l_2 even and $m_2 = 0$ (quadrupole, hexadecapole, ...).

The symmetrized version of the potential is obtained the same manner as that of the short range interaction. For that, one introduces double tensors related to molecule 1 using Eq. (1). With the same orders of development than those of the atom-atom potential, there are only two terms,

$$V_{\text{elec}}(r, \Omega_1, \Omega_2) = V_{3,2}(r, \Omega_1, \Omega_2) + V_{4,2}(r, \Omega_1, \Omega_2) \equiv V_{\Omega_{(1)}, \Theta_{(2)}}(r, \Omega_1, \Omega_2) + V_{\Phi_{(1)}, \Theta_{(2)}}(r, \Omega_1, \Omega_2) \quad (10)$$

where the $\Omega_{(1)}$, $\Phi_{(1)}$ and $\Theta_{(2)}$ are the components of the multipolar moments of the molecules. In the case of molecule 1, with tetrahedral symmetry, one has [11–14]

$$\begin{cases} Q_2^{(3)} = -Q_{-2}^{(3)} = i \left(\frac{7}{4\pi} \right)^{1/2} \left(\frac{6}{5} \right)^{1/2} \Omega \\ \Omega = \Omega_{xyz} = \Omega_{\alpha\beta\gamma} \end{cases} \quad (11)$$

where $\alpha\beta\gamma$ is any circular permutation of x , y and z .

$$\begin{cases} Q_4^{(4)} = Q_{-4}^{(4)} = \left(\frac{5}{14} \right)^{1/2} Q_0^{(4)} = \left(\frac{9}{4\pi} \right)^{1/2} \left(\frac{5}{14} \right)^{1/2} \Phi \\ \Phi = \Phi_{\alpha\alpha\alpha\alpha} \end{cases} \quad (12)$$

where $\alpha = x, y$ or z . For molecule 2, diatomic and homonuclear, one has

$$\begin{cases} Q_0^{(l)} = \left(\frac{2l + 1}{4\pi} \right)^{1/2} Q_l, \ \forall l \text{ even,} \\ Q_2 = Q = Q_{zz} \equiv \Theta = \Theta_{zz} \end{cases} \quad (13)$$

¹As far as I know, “usual” means limited to the hexadecapolar moment for the electrostatic interaction.

With these definitions, the octopolar-quadrupolar and hexadecapolar-quadrupolar interaction terms are

$$\bar{V}_{\Omega(1),\Theta(2)}(r, \Omega_1, \Omega_2) = \frac{6\sqrt{2}}{4\pi\epsilon_0} \frac{\Omega(1)\Theta(2)}{r^6} \sum_m C(3\ 2\ 5; m\ -m\ 0) \mathcal{D}_m^{(3g, 3g^0A_2)} \mathcal{D}_{0-m}^{(2)}(\Omega_2) \quad (14)$$

and

$$V_{\Phi(1),\Theta(2)}(r, \Omega_1, \Omega_2) = \frac{2\sqrt{165}}{4\pi\epsilon_0\sqrt{7}} \frac{\Phi(1)\Theta(2)}{r^7} \sum_m C(4\ 2\ 6; m\ -m\ 0) \mathcal{D}_m^{(4g, 4g^0A_1)} \mathcal{D}_{0-m}^{(2)}(\Omega_2) \quad (15)$$

2.3 The short range interaction

For practical line broadening calculations, the short range interaction potential must be developed in terms of radial functions and angular operators. Since no more accurate model was yet available, to my knowledge², I choosed to write that interaction as an atom-atom potential. It is expanded in terms of symmetrized angular operators, as was done in the case of the XY₄-atom system ([9], Eq. (5.15) and table 5.2, p. 76). For that purpose, the symbolic computation procedures used during my thesis were adapted to the MuPAD software [5]. These procedures are modular: any molecular couple may be considered. It requires the definitions for the equilibrium configurations of the molecules. Some simple generic molecules are implemented: XY₄, XY₆, XY₃Z, XY₃, XY₂, X₂, XY and X (atom). Supplementary definitions, for example for the electrostatic terms, must also be set. This way, potentials may be developed up to any orders. To obtain symmetrized expressions, it is also needed to define the coefficients of the linear combinations of angular operators that form quantities of symmetries A₁ or A₂ in the relevant molecular point groups. Only tetrahedral symmetry [Eqs. (2) through (7)] is implemented, for the moment.

For the XY₄-A₂ system, the formal expression of the short range potential is

$$V_{\text{at-at}}(r, \Omega_1, \Omega_2) = \sum_{\substack{l_1=0, \\ l_2=0}}^{l_{\max}} \sum_q \sum_m \left[|m| d_q^{l_1, l_2} \frac{D_q^{l_1, l_2}}{r^{12+q}} - |m| e_q^{l_1, l_2} \frac{E_q^{l_1, l_2}}{r^{6+q}} \right] \mathcal{D}_m^{(l_{1g}, l_{1g}, 0\Gamma_1)} \mathcal{D}_{0-m}^{(l_2)}(\Omega_2) \quad (16)$$

Notations are similar to those of Eq. (9). The d and e are numerical factors, and the D and E are factors depending on the equilibrium configurations of the molecules and on the interaction parameters between pairs of atoms (section 2.5). It would be more consistent to define the potential using

$$\mathcal{D}_{-m}^{(l_{2g}, l_{2g})} = [l_2]^{1/2} \mathcal{D}_{0-m}^{(l_2)}(\Omega_2) \quad (17)$$

but it doesn't change anything to the derivation. The factor $[l_2]^{1/2}$ is in fact accounted for in the calculations of the matrix elements of this operator, for which I used the double tensor notation.

2.4 Formal interaction potential

It is obtained by gathering the expressions of the above sections,

$$\begin{aligned} V_{XY_4, A_2}(r, \Omega_1, \Omega_2) &= \sum_{\substack{l_1=0, \\ l_2=0}}^{l_{\max}} \sum_m V_{|m|}^{l_1, \Gamma_1, l_2}(r) \mathcal{D}_m^{(l_{1g}, l_{1g}, 0\Gamma_1)} \mathcal{D}_{0-m}^{(l_2)}(\Omega_2) = \\ &= \sum_{\substack{l_1=0, \\ l_2=0}}^{l_{\max}} \left(\sum_m \left(|m| f^{l_1, l_2} \frac{F^{l_1, l_2}}{r^{l_1+l_2+1}} + \sum_q \left[|m| d_q^{l_1, l_2} \frac{D_q^{l_1, l_2}}{r^{12+q}} - |m| e_q^{l_1, l_2} \frac{E_q^{l_1, l_2}}{r^{6+q}} \right] \right) \right) \mathcal{D}_m^{(l_{1g}, l_{1g}, 0\Gamma_1)} \mathcal{D}_{0-m}^{(l_2)}(\Omega_2) \end{aligned} \quad (18)$$

Obviously, for the electrostatic interaction, I set

$$|m| f^{l_1, l_2} = C(l_1\ l_2\ l_1 + l_2; m\ -m\ 0) \quad (19)$$

² ... at the time when I begun to work on the subject ...

and the proportionality factors between terms with $m \neq 0$ and the ones with the same labels, but with $m = 0$ are given by analytic formulae. For the short range interaction, there are also such proportionality factors for which I did not try to derive analytic expressions.

2.5 Numerical data

2.5.1 Coefficients of the electrostatic potential

The only “unknown” quantities in Eqs. (14) and (15) are the numerical values of the multipolar moments of the molecules. Following [11]³ (table D.3, p. 577),

$$\begin{aligned}\Omega_{(1),\text{CH}_4} &\approx 2.3 \times 10^{-34} \text{ esu.cm}^3, \Phi_{(1),\text{CH}_4} \approx 4.65 \times 10^{-42} \text{ esu.cm}^4, \\ \Theta_{(2),\text{N}_2} &\approx -1.45 \times 10^{-26} \text{ esu.cm}^2.\end{aligned}\quad (20)$$

I did not check if these values are the best available ones, since the electrostatic terms were found to have minor contributions in line broadening calculations. For example, Ref. [15] gives values that are somewhat different.

Electrostatic units (esu) Whatever the system of units, the AMPÈRE (magnetic) and COULOMB (electric) forces are given by

$$F_m = k_m I_1 I_2 \frac{L}{r} \quad \text{and} \quad F_e = k_e \frac{q_1 q_2}{r^2} \quad (21)$$

where the k are proportionality factors, the I are electric intensities, the q are electric charges, the L and r are lengths. Since, in terms of dimensions, one has $[Q] = [I].T$, in any case, $k_e = k_m c^2/2$ where c is the speed of light in vacuum. $c = 2.99792458 \times 10^8 \text{ m.s}^{-1}$ in the international system of units (MKSA). The electrostatic system of units (esu) was built from the CGS system (**C**entimetre-**G**ram-**S**econd). It is sometimes (rarely ?) called CGSe. In esu, forces [Eq. (21)] are in dyn ($\equiv 10^{-5} \text{ N} = 10 \mu\text{N}$) and lengths are in cm. Moreover,

$$k_{e,\text{CGSe}} = k_{e,\text{esu}} = 1 \quad \text{and} \quad k_{m,\text{CGSe}} = k_{m,\text{esu}} = 2/c_{\text{CGS}}^2 \quad (22)$$

and the charges are equal to one “esu of charge”. Given that in SI units,

$$k_{e,\text{SI}} = 1/4\pi\epsilon_0 \quad \text{and} \quad k_{m,\text{SI}} = \mu_0/2\pi, \quad (23)$$

with $\epsilon_0 \mu_0 c^2 = 1$, that forces are in N and that distances are in m, one can find the unit charge in esu, expressed in SI units,

$$\begin{aligned}q_{\text{SI}} &\equiv (F_{\text{SI}} r_{\text{SI}}^2 / k_{e,\text{SI}})^{1/2} = [F_{\text{SI}} r_{\text{SI}}^2 / (k_{m,\text{SI}} c_{\text{SI}}^2 / 2)]^{1/2} \\ &= 10^{-1} / c_{\text{SI}} = 10^{-1} / 2.99792458 \times 10^8 \approx 3.335641 \times 10^{-10} \text{ C}\end{aligned}\quad (24)$$

One finds $1 \text{ C} = 2.99792458 \times 10^9 \text{ esu}$ (of charge). One may establish the following correspondences between esu and SI units (as well as for au, atomic units⁴)

$$\begin{aligned}\rightarrow \mu (l = 1) [\text{au} : ea_0], \text{ SI} : 1 \text{ C.m} &= 0.299792458 \times 10^{12} \text{ esu.cm}, \text{ Debye} : 1 \text{ D} = 10^{-18} \text{ esu.cm}, \\ \rightarrow Q \equiv \Theta (l = 2) [\text{au} : ea_0^2], \text{ SI} : 1 \text{ C.m}^2 &= 0.299792458 \times 10^{14} \text{ esu.cm}^2, \\ \text{Buckingham} : 1 \text{ B} = 1 \text{ D.}\text{Å} &= 10^{-26} \text{ esu.cm}^2, \\ \rightarrow \Omega (l = 3) [\text{au} : ea_0^3], \text{ SI} : 1 \text{ C.m}^3 &= 0.299792458 \times 10^{16} \text{ esu.cm}^3, \\ \rightarrow \Phi (l = 4) [\text{au} : ea_0^4], \text{ SI} : 1 \text{ C.m}^4 &= 0.299792458 \times 10^{18} \text{ esu.cm}^4.\end{aligned}\quad (25)$$

One Debye has the same order of magnitude as ea_0 . Thus, I found it convenient to define the parameter(s) of a multipolar moment of order l in units of $\text{D.}\text{Å}^{l-1}$.

³This reference gives the units of multipolar moments as esu, which is very confusing. I preferred to use esu.cm^l for an order l moment.

⁴For these ones, the unit of charge is that of the proton, $e = 1.602176487 \times 10^{-19} \text{ C}$, and the unit of length is the radius of the first BOHR orbit, $a_0 = 0.52917720859 \times 10^{-10} \text{ m}$.

2.5.2 Coefficients of the atom-atom potential

The potential was developed with $l_1 \leq l_{\max}$, $l_2 \leq l_{\max}$ and $l_1 + l_2 \leq l_{\max}$, with $l_{\max} = 6$, as well as $q \leq q_{\max} = 14$ (at most). The coefficients are given hereafter as a list of sets of labels associated to expressions for the E terms of Eq. (16)⁵. The sets of labels appear in combined brackets. For example,

$$[[3, g, 0, A_2], [2, 0], 0, 7, 745, 21, 7238, 5] \quad (26)$$

corresponds to the notations

$$[[l_{1\tau}, \tau, 0, \Gamma_1], [l_2, |m_2|], |m|, q, |m|e_{q, n}^{l_1, l_2}, |m|e_{q, d}^{l_1, l_2}, |m|d_{q, n}^{l_1, l_2}, |m|d_{q, d}^{l_1, l_2}] \quad (27)$$

where τ is the parity index associated to l_1 . The four last indications are the numerators and the denominators of the rational numbers e and d in Eq. (16). Following the labels, one finds the polynom corresponding to the attractive E term. The code that calculates this potential uses the `gcd` and `igcd` functions of MuPAD to perform the relevant simplifications and checks that the e and d are effectively rational numbers, not transcendental ones. The D terms associated to the repulsive part of the potential have the same expressions as the ones of the E terms (this is checked by the code), except that one has to make the substitution

$$e_{xa} \rightarrow d_{xa} \text{ and } e_{ya} \rightarrow d_{ya} \quad (28)$$

Note that the D , E and F are what I call the *potential numerical factors* and that the e_{xa} , d_{xa} , e_{ya} , d_{ya} , r_{ga} , r_{xy} , $\Omega_{(1)}$, $\Theta_{(2)}$ and $\Phi_{(1)}$ are the *potential parameters*. In the cases where $l_1 \neq 0$ and $l_2 \neq 0$, the expressions for the different values of $|m|$ are the same, up to numerical factors (checked by the code). This is the indication which is reported after a given term in the list below. It means that the term with $|m| = 0$ has to be multiplied by the given factor to obtain the term with the same labels but $|m| \neq 0$.

$l_1 = 0, l_2 = 0$, isotropic potential

$$q = 0, [[0, g, 0, A_1], [0, 0], 0, 0, 1, 1, 1, 1] : 2(e_{xa} + 4e_{ya}).$$

$$q = 2, [[0, g, 0, A_1], [0, 0], 0, 2, 5, 1, 22, 1] : 2((e_{xa} + 4e_{ya})r_{ga}^2 + 4e_{ya}r_{xy}^2).$$

$$q = 4, [[0, g, 0, A_1], [0, 0], 0, 4, 2, 1, 143, 5] : 14((e_{xa} + 4e_{ya})r_{ga}^4 + 4e_{ya}r_{xy}^2(r_{xy}^2 + 10/3r_{ga}^2)).$$

$$q = 6, [[0, g, 0, A_1], [0, 0], 0, 6, 15, 1, 572, 1] : 4((e_{xa} + 4e_{ya})r_{ga}^6 + 4e_{ya}r_{xy}^2(r_{xy}^4 + 7r_{ga}^2r_{xy}^2 + 7r_{ga}^4)).$$

$$q = 8, [[0, g, 0, A_1], [0, 0], 0, 8, 1, 1, 442, 5] : \\ 22(5(e_{xa} + 4e_{ya})r_{ga}^8 + 4e_{ya}r_{xy}^2(5r_{xy}^6 + 60r_{ga}^2r_{xy}^4 + 126r_{ga}^4r_{xy}^2 + 60r_{ga}^6)).$$

$$q = 10, [[0, g, 0, A_1], [0, 0], 0, 10, 7, 1, 1292, 1] : \\ 26((e_{xa} + 4e_{ya})r_{ga}^{10} + 4e_{ya}r_{xy}^2(r_{xy}^8 + 55/3r_{ga}^2r_{xy}^6 + 66r_{ga}^4r_{xy}^4 + 66r_{ga}^6r_{xy}^2 + 55/3r_{ga}^8)).$$

$$q = 12, [[0, g, 0, A_1], [0, 0], 0, 12, 10, 1, 3553, 1] : \\ 4(7(e_{xa} + 4e_{ya})r_{ga}^{12} + 4e_{ya}r_{xy}^2(7r_{xy}^{10} + 182r_{ga}^2r_{xy}^8 + 1001r_{ga}^4r_{xy}^6 + 1716r_{ga}^6r_{xy}^4 + 1001r_{ga}^8r_{xy}^2 + 182r_{ga}^{10})).$$

$$q = 14, [[0, g, 0, A_1], [0, 0], 0, 14, 3, 1, 9614, 5] : \\ 136((e_{xa} + 4e_{ya})r_{ga}^{14} + 4e_{ya}r_{xy}^2(r_{xy}^{12} + 35r_{ga}^2r_{xy}^{10} + 273r_{ga}^4r_{xy}^8 + 715r_{ga}^6r_{xy}^6 + 715r_{ga}^8r_{xy}^4 + 273r_{ga}^{10}r_{xy}^2 + 35r_{ga}^{12})).$$

$l_1 = 0, l_2 = 2$

$$q = 2, [[0, g, 0, A_1], [2, 0], 0, 2, 2, 1, 7, 1] : 16(e_{xa} + 4e_{ya})r_{ga}^2.$$

$$q = 4, [[0, g, 0, A_1], [2, 0], 0, 4, 25, 7, 44, 1] : 32((e_{xa} + 4e_{ya})r_{ga}^2 + 28/3e_{ya}r_{xy}^2)r_{ga}^2.$$

$$q = 6, [[0, g, 0, A_1], [2, 0], 0, 6, 5, 3, 286, 5] : 32(5(e_{xa} + 4e_{ya})r_{ga}^4 + 12e_{ya}r_{xy}^2(7r_{xy}^2 + 10r_{ga}^2))r_{ga}^2.$$

$$q = 8, [[0, g, 0, A_1], [2, 0], 0, 8, 7, 11, 52, 1] : 160(5(e_{xa} + 4e_{ya})r_{ga}^6 + 44e_{ya}r_{xy}^2(3r_{xy}^4 + 9r_{ga}^2r_{xy}^2 + 5r_{ga}^4))r_{ga}^2.$$

$$q = 10, [[0, g, 0, A_1], [2, 0], 0, 10, 2, 13, 187, 7] : \\ 160/3(105(e_{xa} + 4e_{ya})r_{ga}^8 + 52e_{ya}r_{xy}^2(77r_{xy}^6 + 396r_{ga}^2r_{xy}^4 + 462r_{ga}^4r_{xy}^2 + 140r_{ga}^6))r_{ga}^2.$$

⁵I verified that these expressions are the same as the ones of the potential numerical factors procedure produced by the program generator, obviously.

$$q = 12, [[0, g, 0, A_1], [2, 0], 0, 12, 3, 1, 7106, 7] : \\ 64(7(e_{xa} + 4e_{ya})r_{ga}^{10} + 4e_{ya}r_{xy}^2(91r_{xy}^8 + 715r_{ga}^2r_{xy}^6 + 1430r_{ga}^4r_{xy}^4 + 910r_{ga}^6r_{xy}^2 + 175r_{ga}^8))r_{ga}^2.$$

$$q = 14, [[0, g, 0, A_1], [2, 0], 0, 14, 25, 17, 2717, 3] : \\ 64(21(e_{xa} + 4e_{ya})r_{ga}^{12} + 68e_{ya}r_{xy}^2(21r_{xy}^{10} + 234r_{ga}^2r_{xy}^8 + 715r_{ga}^4r_{xy}^6 + 780r_{ga}^6r_{xy}^4 + 315r_{ga}^8r_{xy}^2 + 42r_{ga}^{10}))r_{ga}^2.$$

$l_1 = 0, l_2 = 4$

$$q = 4, [[0, g, 0, A_1], [4, 0], 0, 4, 1, 7, 6, 5] : 768(e_{xa} + 4e_{ya})r_{ga}^4.$$

$$q = 6, [[0, g, 0, A_1], [4, 0], 0, 6, 5, 11, 12, 1] : 256(3(e_{xa} + 4e_{ya})r_{ga}^2 + 4e_{ya}r_{xy}^2)r_{ga}^4.$$

$$q = 8, [[0, g, 0, A_1], [4, 0], 0, 8, 14, 143, 33, 5] : 512(15(e_{xa} + 4e_{ya})r_{ga}^4 + 52e_{ya}r_{xy}^2(11r_{xy}^2 + 10r_{ga}^2))r_{ga}^4.$$

$$q = 10, [[0, g, 0, A_1], [4, 0], 0, 10, 3, 143, 22, 7] : \\ 9216(7(e_{xa} + 4e_{ya})r_{ga}^6 + 4e_{ya}r_{xy}^2(143r_{xy}^4 + 273r_{ga}^2r_{xy}^2 + 105r_{ga}^4))r_{ga}^4.$$

$$q = 12, [[0, g, 0, A_1], [4, 0], 0, 12, 15, 221, 143, 7] : \\ 512(63(e_{xa} + 4e_{ya})r_{ga}^8 + 68e_{ya}r_{xy}^2(143r_{xy}^6 + 468r_{ga}^2r_{xy}^4 + 378r_{ga}^4r_{xy}^2 + 84r_{ga}^6))r_{ga}^4.$$

$$q = 14, [[0, g, 0, A_1], [4, 0], 0, 14, 3, 323, 26, 5] : \\ 5632(63(e_{xa} + 4e_{ya})r_{ga}^{10} + 76e_{ya}r_{xy}^2(221r_{xy}^8 + 1105r_{ga}^2r_{xy}^6 + 1530r_{ga}^4r_{xy}^4 + 714r_{ga}^6r_{xy}^2 + 105r_{ga}^8))r_{ga}^4.$$

$l_1 = 0, l_2 = 6$

$$q = 6, [[0, g, 0, A_1], [6, 0], 0, 6, 2, 33, 1, 1] : 4096(e_{xa} + 4e_{ya})r_{ga}^6.$$

$$q = 8, [[0, g, 0, A_1], [6, 0], 0, 8, 1, 11, 22, 5] : 8192((e_{xa} + 4e_{ya})r_{ga}^2 + 20e_{ya}r_{xy}^2)r_{ga}^6.$$

$$q = 10, [[0, g, 0, A_1], [6, 0], 0, 10, 35, 11, 1859, 5] : 8192/51(3(e_{xa} + 4e_{ya})r_{ga}^4 + 68e_{ya}r_{xy}^2(3r_{xy}^2 + 2r_{ga}^2))r_{ga}^6.$$

$$q = 12, [[0, g, 0, A_1], [6, 0], 0, 12, 3, 1, 3718, 5] : \\ 8192/323(35(e_{xa} + 4e_{ya})r_{ga}^6 + 76e_{ya}r_{xy}^2(85r_{xy}^4 + 119r_{ga}^2r_{xy}^2 + 35r_{ga}^4))r_{ga}^6.$$

$$q = 14, [[0, g, 0, A_1], [6, 0], 0, 14, 2, 17, 169, 3] : \\ 45056/19(15(e_{xa} + 4e_{ya})r_{ga}^8 + 4e_{ya}r_{xy}^2(1615r_{xy}^6 + 3876r_{ga}^2r_{xy}^4 + 2594r_{ga}^4r_{xy}^2 + 420r_{ga}^6))r_{ga}^6.$$

$l_1 = 3, l_2 = 0$

$$q = 3, [[3, g, 0, A_2], [0, 0], 0, 3, 1, 1, 28, 5] : 256\sqrt{35}/21e_{ya}r_{xy}^3.$$

$$q = 5, [[3, g, 0, A_2], [0, 0], 0, 5, 5, 3, 154, 5] : 512\sqrt{35}/21e_{ya}(r_{xy}^2 + 3r_{ga}^2)r_{xy}^3.$$

$$q = 7, [[3, g, 0, A_2], [0, 0], 0, 7, 7, 33, 52, 5] : 256\sqrt{35}/9e_{ya}(15r_{xy}^4 + 110r_{ga}^2r_{xy}^2 + 99r_{ga}^4)r_{xy}^3.$$

$$q = 9, [[3, g, 0, A_2], [0, 0], 0, 9, 14, 143, 11, 1] : 5120\sqrt{35}/3e_{ya}(r_{xy}^6 + 13r_{ga}^2r_{xy}^4 + 143/5r_{ga}^4r_{xy}^2 + 429/35r_{ga}^6)r_{xy}^3.$$

$$q = 11, [[3, g, 0, A_2], [0, 0], 0, 11, 7, 13, 374, 3] : \\ 512\sqrt{35}e_{ya}(r_{xy}^8 + 20r_{ga}^2r_{xy}^6 + 78r_{ga}^4r_{xy}^4 + 572/7r_{ga}^6r_{xy}^2 + 143/7r_{ga}^8)r_{xy}^3.$$

$$q = 13, [[3, g, 0, A_2], [0, 0], 0, 13, 7, 17, 2717, 15] : \\ 1024\sqrt{35}/3e_{ya}(3r_{xy}^{10} + 85r_{ga}^2r_{xy}^8 + 510r_{ga}^4r_{xy}^6 + 6630/7r_{ga}^6r_{xy}^4 + 12155/21r_{ga}^8r_{xy}^2 + 663/7r_{ga}^{10})r_{xy}^3.$$

$l_1 = 3, l_2 = 2$

$$q = 5, |m| = 0, [[3, g, 0, A_2], [2, 0], 0, 5, 5, 3, 116, 5] : 256\sqrt{35}e_{ya}r_{ga}^2r_{xy}^3, \times 1.$$

$$q = 5, |m| = 1, [[3, g, 0, A_2], [2, 0], 1, 5, 5, 1, 224, 5] : 512\sqrt{70}/21e_{ya}r_{ga}^2r_{xy}^3, \times 2\sqrt{2}/21.$$

$$q = 5, |m| = 2, [[3, g, 0, A_2], [2, 0], 2, 5, 5, 1, 28, 1] : 256\sqrt{7}/21e_{ya}r_{ga}^2r_{xy}^3, \times \sqrt{5}/105.$$

$$q = 7, |m| = 0, [[3, g, 0, A_2], [2, 0], 0, 7, 745, 21, 7238, 5] : 512\sqrt{35}/63e_{ya}(7r_{xy}^2 + 9r_{ga}^2)r_{ga}^2r_{xy}^3, \times 1.$$

$$q = 7, |m| = 1, [[3, g, 0, A_2], [2, 0], 1, 7, 5, 21, 33, 5] : 2048\sqrt{70}/7e_{ya}(7r_{xy}^2 + 9r_{ga}^2)r_{ga}^2r_{xy}^3, \times 36\sqrt{2}.$$

$$q = 7, |m| = 2, [[3, g, 0, A_2], [2, 0], 2, 7, 25, 21, 22, 1] : 512\sqrt{7}/21e_{ya}(7r_{xy}^2 + 9r_{ga}^2)r_{ga}^2r_{xy}^3, \times 3\sqrt{5}/5.$$

$$q = 9, |m| = 0, [[3, g, 0, A_2], [2, 0], 0, 9, 469, 99, 468, 1] : \\ 1280\sqrt{35}/7e_{ya}(7r_{xy}^4 + 22r_{ga}^2r_{xy}^2 + 11r_{ga}^4)r_{ga}^2r_{xy}^3, \times 1.$$

$$q = 9, |m| = 1, [[3, g, 0, A_2], [2, 0], 1, 9, 49, 33, 104, 1] : \\ 2560\sqrt{70}/21e_{ya}(7r_{xy}^4 + 22r_{ga}^2r_{xy}^2 + 11r_{ga}^4)r_{ga}^2r_{xy}^3, \times 2\sqrt{2}/3.$$

$$q = 9, |m| = 2, [[3, g, 0, A_2], [2, 0], 2, 9, 35, 33, 52, 1] : \\ 1280\sqrt{7}/21e_{ya}(7r_{xy}^4 + 22r_{ga}^2r_{xy}^2 + 11r_{ga}^4)r_{ga}^2r_{xy}^3, \times \sqrt{5}/15.$$

$$q = 11, |m| = 0, [[3, g, 0, A_2], [2, 0], 0, 11, 406, 143, 1793, 3] : \\ 5120\sqrt{35}/21e_{ya}(21r_{xy}^6 + 117r_{ga}^2r_{xy}^4 + 143r_{ga}^4r_{xy}^2 + 39r_{ga}^6)r_{ga}^2r_{xy}^3, \times 1.$$

$$q = 11, |m| = 1, [[3, g, 0, A_2], [2, 0], 1, 11, 112, 143, 121, 1] : \\ 10240\sqrt{70}/63e_{ya}(21r_{xy}^6 + 117r_{ga}^2r_{xy}^4 + 143r_{ga}^4r_{xy}^2 + 39r_{ga}^6)r_{ga}^2r_{xy}^3, \times 2\sqrt{2}/3.$$

$$q = 11, |m| = 2, [[3, g, 0, A_2], [2, 0], 2, 11, 14, 143, 11, 1] : \\ 25600\sqrt{7}/63e_{ya}(21r_{xy}^6 + 117r_{ga}^2r_{xy}^4 + 143r_{ga}^4r_{xy}^2 + 39r_{ga}^6)r_{ga}^2r_{xy}^3, \times \sqrt{5}/3.$$

$$q = 13, |m| = 0, [[3, g, 0, A_2], [2, 0], 0, 13, 329, 13, 31042, 3] : \\ 512\sqrt{35}/9e_{ya}(21r_{xy}^8 + 180r_{ga}^2r_{xy}^6 + 390r_{ga}^4r_{xy}^4 + 260r_{ga}^6r_{xy}^2 + 45r_{ga}^8)r_{ga}^2r_{xy}^3, \times 1.$$

$$q = 13, |m| = 1, [[3, g, 0, A_2], [2, 0], 1, 13, 21, 13, 1496, 3] : \\ 1024\sqrt{70}/7e_{ya}(21r_{xy}^8 + 180r_{ga}^2r_{xy}^6 + 390r_{ga}^4r_{xy}^4 + 260r_{ga}^6r_{xy}^2 + 45r_{ga}^8)r_{ga}^2r_{xy}^3, \times 18\sqrt{2}/7.$$

$$q = 13, |m| = 2, [[3, g, 0, A_2], [2, 0], 2, 13, 7, 13, 374, 3] : \\ 2560\sqrt{7}/21e_{ya}(21r_{xy}^8 + 180r_{ga}^2r_{xy}^6 + 390r_{ga}^4r_{xy}^4 + 260r_{ga}^6r_{xy}^2 + 45r_{ga}^8)r_{ga}^2r_{xy}^3, \times 3\sqrt{5}/7.$$

$l_1 = 4, l_2 = 0$

$$q = 4, [[4, g, 0, A_1], [0, 0], 0, 4, 1, 3, 14, 5] : -1024\sqrt{21}/21e_{ya}r_{xy}^4.$$

$$q = 6, [[4, g, 0, A_1], [0, 0], 0, 6, 5, 33, 4, 1] : -1024\sqrt{21}/9e_{ya}(3r_{xy}^2 + 11r_{ga}^2)r_{xy}^4.$$

$$q = 8, [[4, g, 0, A_1], [0, 0], 0, 8, 14, 429, 11, 5] : -2048\sqrt{21}/9e_{ya}(15r_{xy}^4 + 130r_{ga}^2r_{xy}^2 + 143r_{ga}^4)r_{xy}^4.$$

$$q = 10, [[4, g, 0, A_1], [0, 0], 0, 10, 3, 143, 22, 7] : -4096\sqrt{21}/3e_{ya}(7r_{xy}^6 + 105r_{ga}^2r_{xy}^4 + 273r_{ga}^4r_{xy}^2 + 143r_{ga}^6)r_{xy}^4.$$

$$q = 12, [[4, g, 0, A_1], [0, 0], 0, 12, 5, 221, 143, 21] : \\ -2048\sqrt{21}/9e_{ya}(63r_{xy}^8 + 1428r_{ga}^2r_{xy}^6 + 6426r_{ga}^4r_{xy}^4 + 7956r_{ga}^6r_{xy}^2 + 2431r_{ga}^8)r_{xy}^4.$$

$$q = 14, [[4, g, 0, A_1], [0, 0], 0, 14, 1, 323, 26, 15] : \\ -22528\sqrt{21}/9e_{ya}(63r_{xy}^{10} + 1995r_{ga}^2r_{xy}^8 + 13566r_{ga}^4r_{xy}^6 + 29070r_{ga}^6r_{xy}^4 + 20995r_{ga}^8r_{xy}^2 + 4199r_{ga}^{10})r_{xy}^4.$$

$l_1 = 4, l_2 = 2$

$$q = 6, |m| = 0, [[4, g, 0, A_1], [2, 0], 0, 6, 65, 21, 298, 5] : -2048\sqrt{21}/9e_{ya}r_{ga}^2r_{xy}^4, \times 1.$$

$$q = 6, |m| = 1, [[4, g, 0, A_1], [2, 0], 1, 6, 55, 21, 34, 1] : -1024\sqrt{70}/15e_{ya}r_{ga}^2r_{xy}^4, \times \sqrt{30}/10.$$

$$q = 6, |m| = 2, [[4, g, 0, A_1], [2, 0], 2, 6, 1, 3, 14, 5] : -1024\sqrt{35}/7e_{ya}r_{ga}^2r_{xy}^4, \times 3\sqrt{15}/14.$$

$$q = 8, |m| = 0, [[4, g, 0, A_1], [2, 0], 0, 8, 89, 33, 148, 1] : -10240\sqrt{21}/63e_{ya}(7r_{xy}^2 + 11r_{ga}^2)r_{ga}^2r_{xy}^4, \times 1.$$

$$q = 8, |m| = 1, [[4, g, 0, A_1], [2, 0], 1, 8, 65, 33, 76, 1] : -1024\sqrt{70}/21e_{ya}(7r_{xy}^2 + 11r_{ga}^2)r_{ga}^2r_{xy}^4, \times \sqrt{30}/10.$$

$$q = 8, |m| = 2, [[4, g, 0, A_1], [2, 0], 2, 8, 5, 33, 4, 1] : -1024\sqrt{35}/7e_{ya}(7r_{xy}^2 + 11r_{ga}^2)r_{ga}^2r_{xy}^4, \times 3\sqrt{15}/10.$$

$$q = 10, |m| = 0, [[4, g, 0, A_1], [2, 0], 0, 10, 2, 33, 55, 7] : \\ -20480\sqrt{21}/9e_{ya}(63r_{xy}^4 + 234r_{ga}^2r_{xy}^2 + 143r_{ga}^4)r_{ga}^2r_{xy}^4, \times 1.$$

$$q = 10, |m| = 1, [[4, g, 0, A_1], [2, 0], 1, 10, 50, 429, 11, 1] : \\ -2048\sqrt{70}/9e_{ya}(63r_{xy}^4 + 234r_{ga}^2r_{xy}^2 + 143r_{ga}^4)r_{ga}^2r_{xy}^4, \times \sqrt{30}/30.$$

$$q = 10, |m| = 2, [[4, g, 0, A_1], [2, 0], 2, 10, 10, 429, 11, 7] : \\ -2048\sqrt{35}/9e_{ya}(63r_{xy}^4 + 234r_{ga}^2r_{xy}^2 + 143r_{ga}^4)r_{ga}^2r_{xy}^4, \times \sqrt{15}/30.$$

$$q = 12, |m| = 0, [[4, g, 0, A_1], [2, 0], 0, 12, 1043, 143, 5918, 3] : \\ -8192\sqrt{21}/63e_{ya}(21r_{xy}^6 + 135r_{ga}^2r_{xy}^4 + 195r_{ga}^4r_{xy}^2 + 65r_{ga}^6)r_{ga}^2r_{xy}^4, \times 1.$$

$$q = 12, |m| = 1, [[4, g, 0, A_1], [2, 0], 1, 12, 17, 143, 506, 21] : \\ -4096\sqrt{70}/3e_{ya}(21r_{xy}^6 + 135r_{ga}^2r_{xy}^4 + 195r_{ga}^4r_{xy}^2 + 65r_{ga}^6)r_{ga}^2r_{xy}^4, \times 7\sqrt{30}/2.$$

$$q = 12, |m| = 2, [[4, g, 0, A_1], [2, 0], 2, 12, 7, 143, 22, 3] : \\ -4096\sqrt{35}/7e_{ya}(21r_{xy}^6 + 135r_{ga}^2r_{xy}^4 + 195r_{ga}^4r_{xy}^2 + 65r_{ga}^6)r_{ga}^2r_{xy}^4, \times 3\sqrt{15}/2.$$

$$q = 14, |m| = 0, [[4, g, 0, A_1], [2, 0], 0, 14, 925, 2431, 4121, 21] : \\ -4096\sqrt{21}/9e_{ya}(231r_{xy}^8 + 2244r_{ga}^2r_{xy}^6 + 5610r_{ga}^4r_{xy}^4 + 4420r_{ga}^6r_{xy}^2 + 935r_{ga}^8)r_{ga}^2r_{xy}^4, \times 1.$$

$$q = 14, |m| = 1, [[4, g, 0, A_1], [2, 0], 1, 14, 19, 2431, 65, 21] : \\ -10240\sqrt{70}/3e_{ya}(231r_{xy}^8 + 2244r_{ga}^2r_{xy}^6 + 5610r_{ga}^4r_{xy}^4 + 4420r_{ga}^6r_{xy}^2 + 935r_{ga}^8)r_{ga}^2r_{xy}^4, \times 5\sqrt{30}/2.$$

$$q = 14, |m| = 2, [[4, g, 0, A_1], [2, 0], 2, 14, 5, 2431, 13, 21] : \\ -2048\sqrt{35}e_{ya}(231r_{xy}^8 + 2244r_{ga}^2r_{xy}^6 + 5610r_{ga}^4r_{xy}^4 + 4420r_{ga}^6r_{xy}^2 + 935r_{ga}^8)r_{ga}^2r_{xy}^4, \times 3\sqrt{15}/2.$$

$$l_1 = 6, l_2 = 0$$

$$q = 6, [[6, g, 0, A_1], [0, 0], 0, 6, 2, 33, 1, 1] : -65536\sqrt{26}/117e_{ya}r_{xy}^6.$$

$$q = 8, [[6, g, 0, A_1], [0, 0], 0, 8, 1, 11, 22, 5] : -131072\sqrt{26}/117e_{ya}(r_{xy}^2 + 5r_{ga}^2)r_{xy}^6.$$

$$q = 10, [[6, g, 0, A_1], [0, 0], 0, 10, 35, 11, 1859, 5] : -131072\sqrt{26}/5967e_{ya}(3r_{xy}^4 + 34r_{ga}^2r_{xy}^2 + 51r_{ga}^4)r_{xy}^6.$$

$$q = 12, [[6, g, 0, A_1], [0, 0], 0, 12, 1, 1, 3718, 15] : \\ -131072\sqrt{26}/12597e_{ya}(35r_{xy}^6 + 665r_{ga}^2r_{xy}^4 + 2261r_{ga}^4r_{xy}^2 + 1615r_{ga}^6)r_{xy}^6.$$

$$q = 14, [[6, g, 0, A_1], [0, 0], 0, 14, 2, 17, 169, 3] : \\ -720896\sqrt{26}/2223e_{ya}(15r_{xy}^8 + 420r_{ga}^2r_{xy}^6 + 2394r_{ga}^4r_{xy}^4 + 3876r_{ga}^6r_{xy}^2 + 1615r_{ga}^8)r_{xy}^6.$$

3 Line broadening theory

I describe here some complementary points of the theory that was outlined in Ref. [4].

3.1 Energies, eigenfunctions and matrix elements of the potential for methane

The associated symmetry adapted tensorial formalism is described elsewhere, e.g. in Refs. [16, 17], and in references cited therein. Energies and eigenfunctions are obtained through the diagonalization of an effective Hamiltonian. For a given polyad, this Hamiltonian is block diagonal with respect to J , the total angular momentum and C , the T_d symmetry label of the wavefunctions. Eigenfunctions are expressed in terms of basis functions through a unitary transformation,

$$|J_g C \alpha \sigma\rangle = \sum_{n_r, C_r, \{v_s\}, C_v} U_{n_r, C_r, \{v_s\}, C_v}^{(J, C, \alpha)} |J_g n_r C_r; \{v_s\} C_v; C \sigma\rangle \quad (29)$$

Eigenstates are thus labeled by an implicit polyad number, J (g parity), the symmetry C and α , an order index that numbers energies in increasing order at fixed polyad, J and C . σ is a component index (for degenerate symmetries). Basis functions are obtained through the coupling of functions describing the rotation and the vibration of the molecule.

Rotational functions : $|J_g n_r C_r \sigma_r\rangle$. The C_r symmetry labels in T_d are obtained by decomposing the J_g IR of $O(3)$ into IRs of the subgroup. n_r is a multiplicity index in case a given C_r appears more than once. σ_r is the component index of C_r .

Vibrational functions : $|\{v_s\} C_v \sigma_v\rangle$. $\{v_s\}$ is the set of quantum numbers that identify a vibrational sublevel inside a given polyad. C_v is the final symmetry label resulting from the coupling of the basis functions related to each normal mode that form the $\{v_s\}$ vibrational sublevel. σ_v is the associated component index.

The C symmetry label results from the coupling of C_r and C_v . The Hamiltonian models, the sets of labels for basis functions, the energies and the eigenfunctions in the lower and upper polyads, relevant for a given set of experimental lines, are calculated using the STDS package [18, 19].

The symmetrized angular operators of the potential of Eq. (18), and related ones, are particular cases of a more general rovibrational operator written as

$$\left[\mathcal{D}^{(l_g, l_g, n_c \Gamma_c)} \times \left(R^{\Omega(K_g, N\Gamma_r)} \times \epsilon V_{\{n\}\{n'\}}^{\Gamma_n \Gamma_{n'}(\Gamma_v)} \right)_{(\Gamma_o)} \right]^{(\Gamma)} \quad (30)$$

where \mathcal{D} is a symmetrized multipole direction cosine, R is a rotational operator and V is a vibrational operator. For R , Ω is the degree in elementary rotational operators (components of the rigid rotor angular momentum). K_g is the tensorial rank of the resulting operator in $O(3)$. N and Γ_r are the multiplicity and symmetry indices of the operator in T_d . For V , $\{n\}$ and $\{n'\}$ are the sets of labels that specify the elementary creation and annihilation operators used to build the transition moment. Γ_n and $\Gamma_{n'}$ are the symmetry labels resulting from the coupling of these operators. Γ_v is the vibrational symmetry label obtained by coupling Γ_n and $\Gamma_{n'}$. ϵ is the parity index of the operator. The surrounding $[\dots]$ stands for a symmetrized tensorial product, since the direction cosine and the rovibrational operator do not commute in general. The connection between the operator of Eq. (30) and an angular operator related to methane in the interaction potential is made with

$$\mathcal{D}^{(l_{1g}, l_{1g}, 0\Gamma_1)} \equiv \left[\mathcal{D}^{(l_{1g}, l_{1g}, 0\Gamma_1)} \times (\text{Id}_r^{(A_1)} \times \text{Id}_v^{(A_1)})_{(A_1)} \right]^{(\Gamma_1)} \quad (31)$$

that involves two identity operators related to rotation and vibration of the molecule. A first program calculates all the symmetry allowed operators (at fixed orders of development) separately for the lower and upper polyads of the considered lines. Using, in addition, the labels for the basis functions, determined by an other program, the matrix elements of the operators of Eq. (30) are calculated. The RMEs of these generic operators, between basis functions, are given by

$$\begin{aligned} & \langle J_g, J_g n_r C_r; \{v_s\} C_v; C \| \left[\mathcal{D}^{(l_g, l_g, n_c \Gamma_c)} \times \left(R^{\Omega(K_g, N\Gamma_r)} \times \epsilon V_{\{n\}\{n'\}}^{\Gamma_n \Gamma_{n'}(\Gamma_v)} \right)_{(\Gamma_o)} \right]^{(\Gamma)} \| J'_g, J'_g n'_r C'_r; \{v'_s\} C'_v; C' \rangle = \\ & = \frac{1}{2} (-1)^l ([\Gamma][\Gamma_o][C][C'] [J][l][J'])^{1/2} \langle \{v_s\} C_v \| \epsilon V_{\{n\}\{n'\}}^{\Gamma_n \Gamma_{n'}(\Gamma_v)} \| \{v'_s\} C'_v \rangle \times \left\{ \langle J' \| R^{\Omega(K)} \| J' \rangle \times \right. \\ & \times \sum_{C''_r} \left[\left\{ \begin{array}{cccc} \Gamma_r & \Gamma_v & \Gamma_o & \Gamma \\ C'_r & C'_v & C' & C_r \\ C''_r & C_v & \Gamma_c & C \end{array} \right\} \sum_{n''_r} K \begin{pmatrix} J_g & l_g & J'_g \\ n_r C_r & n_c \Gamma_c & n''_r C''_r \end{pmatrix} K \begin{pmatrix} J'_g & K_g & J'_g \\ n''_r C''_r & N\Gamma_r & n'_r C'_r \end{pmatrix} \right] + \\ & \quad + (-1)^{C_r + C'_r + C_v + C'_v + C + C' + \Gamma_c + \Gamma_r + \Gamma_v + \Gamma + J + J'} \langle J \| R^{\Omega(K)} \| J \rangle \times \\ & \times \sum_{C''_r} \left[\left\{ \begin{array}{cccc} \Gamma_r & \Gamma_v & \Gamma_o & \Gamma \\ C_r & C_v & C & C'_r \\ C''_r & C'_v & \Gamma_c & C' \end{array} \right\} \sum_{n''_r} K \begin{pmatrix} J_g & K_g & J_g \\ n_r C_r & N\Gamma_r & n''_r C''_r \end{pmatrix} K \begin{pmatrix} J_g & l_g & J'_g \\ n''_r C''_r & n_c \Gamma_c & n'_r C'_r \end{pmatrix} \right] \left. \right\} \quad (32) \end{aligned}$$

In the right hand side of this equation, the $\langle \dots \| \dots \| \dots \rangle$ are RME of vibrational or rotational operators [16]. The $\{ \dots \}$ are $12C$ recoupling symbols and the K are isoscalar factors for the chain of group $O(3) \supset T_d$. Note that in the basis functions of Eq. (32) I have used a double tensor notation. These calculations are done by a second program.

Finally, a third program reads the results of the above computations and takes additional arguments such as some numerical parameters for the multipolar operators and the name of the file containing the quantum assignments of the considered lines. With these data and the Hamiltonian model computed from the STDS package, only the relevant RME and energy spacings between eigenfunctions involved in transitions are calculated.

3.2 Line broadening coefficients

As stated in Ref. [4], I still rely on the classical expression for the calculations of these coefficients,

$$\begin{aligned} \gamma_{fi} = & \frac{1}{2\pi c} L \frac{T_0}{TP_0} \int_0^\infty dv v \times 4\pi \left(\frac{\mu}{2\pi K_B T} \right)^{3/2} v^2 \exp(-\mu v^2 / 2K_B T) \times \\ & \times \sum_{\{2\}} \rho_{\{2\}} \int_{r_{c0}}^\infty 2\pi r_c dr_c \left(\frac{v'_c}{v} \right)^2 [1 - \exp(-S_{2,fi,\{2\}})] \end{aligned} \quad (33)$$

In practice, I replaced the average over velocities by calculations at the mean thermal velocity.

3.2.1 Modification of the theory

According to Refs. [20, 21], two aspects of the original theory developed by ROBERT and BONAMY [22] might need to be revised. The first point deals with the application of the Linked Cluster Theorem [23] for the cumulant expansion [24, 25] regarding the states of the perturbers. An equivalent form of Eq. (33) is given by

$$\gamma_{fi, \text{RB}} = \frac{n_b}{2\pi c} \int_0^\infty dv v f(v) \times \int_0^\infty 2\pi b db \langle [1 - \exp(-S_2)] \rangle_{\{2\}} \quad (34)$$

The new expression might be [21]

$$\gamma_{fi, \text{New}} = \frac{n_b}{2\pi c} \int_0^\infty dv v f(v) \times \int_0^\infty 2\pi b db [1 - \exp(-\langle S_2 \rangle_{\{2\}})] \quad (35)$$

where n_b is the number of perturbers per unit volume. This modification results from the fact that diagonal matrix elements in the LIOUVILLE space (relative to perturber quantum states) are in fact non-diagonal when they are expressed back in the HILBERT space. I note that no mention is made of the tensorial ranks of the quantities involved (in the LIOUVILLE space) in Ref. [21]. This is important in discussing the diagonality of operators. In fact, noone has never examined what the tensorial rank of a vector or operator in the LIOUVILLE space, and its relation to transformation properties, really means. As stated by MA et al., one assumes that the computation techniques relevant for the ordinary HILBERT space may directly be used in the line space. An other implicit assumption in Refs. [20, 21], as well as in the more general theoretical elements developed in Ref. [26], is that the molecules involved are linear. Anyway, this point needs to be examined further. Although this does not constitute any rigorous proof, extensive numerical tests should be able to show the relevance of that modification. Up to now, I am not able to draw any definitive conclusion about that.

The second point concerns the various levels of approximation used in the calculations of the relative molecular trajectories. The internal rovibrational states of the molecules do influence the trajectories, which may have important effects, for example, in the computations of vibrational shifts [27]. I will need to address this point too.

3.2.2 Liouville space vectors

These vectors are in fact operators in the HILBERT space.

Active molecule, XY_4 : The eigenfunctions for the lower and upper states of a given transition have to be coupled in the IMF and in the MFF,

$$\begin{aligned} |J_f, J_f C_f \alpha_f; J_i, J_i C_i \alpha_i; LM_L, A_2\rangle = & (-1)^{L-M_L} [L]^{1/2} \sum_{M_i, M_f} \sum_{\sigma_i, \sigma_f} (-1)^{J_i - M_i} \begin{pmatrix} J_f & J_i & L \\ M_f & -M_i & -M_L \end{pmatrix} \times \\ & \times F \begin{pmatrix} C_f & C_i & A_2 \\ \sigma_f & \sigma_i & \end{pmatrix} |J_f M_f, J_f C_f \alpha_f \sigma_f\rangle \langle J_i M_i, J_i C_i \alpha_i \sigma_i| \end{aligned} \quad (36)$$

For infrared transitions, $L = 1$, which corresponds to the A_2 tetrahedral label in the MFF (as results from the coupling of the dipole moment with the direction cosine). For simplicity, I also omitted the implicit $O(3)$ groups parity labels.

Perturber, \mathbf{A}_2 : These vectors form quantities of zero tensorial rank, since the perturbers are not involved in optical transitions,

$$|\{\gamma_2\}J_2; \{\gamma_2\}J_2; 0\ 0\rangle = \frac{(-1)^{J_2-M_2}}{[J_2]^{1/2}} |\{\gamma_2\}J_2M_2\rangle \langle\{\gamma_2\}J_2M_2| \quad (37)$$

$\{\gamma_2\}$ stands for all the supplementary quantum labels not involved in the coupling.

3.2.3 Outer and middle terms

The second order term in the exponential of Eq. (33) is splitted into three parts,

$$S_{2,f,i,\{2\}} = S_{2,i,\{2\}} + S_{2,f,\{2\}} + S_{2,f,i,\{2\},\text{mid}} \quad (38)$$

Schematically, the first two ones describe the effects of inelastic collisions on the lower or upper state of the transition. The third one accounts for elastic collisions that change the orientation of the angular momentum in both states of the transition.

The expressions for practical calculations are obtained by expressing the angular operators of the interaction potential in the LFF (see below), by decoupling the LIOUVILLE space vectors of section 3.2.2 and by accounting for appropriate properties and orthogonality rules for the coupling symbols that appear in matrix elements calculations [9, Chapter 3].

The second term of Eq. (38) is given by

$$\begin{aligned} S_{2,f,\{2\}} &= \frac{\hbar^{-2}}{2[J_f, C_f, J_2]} \sum_{J_{f'}, C_{f'}, \alpha_{f'}} \sum_{J_2'} \sum_{l_1, l_2} [l_1, l_2]^{-1} \times \\ &\times \sum_{m_1, m_2} \left| \int_{-\infty}^{\infty} dt e^{i(\omega_{f,f'} + \omega_{2,2'})t} \sum_m V_{|m|}^{l_1, \Gamma_1, l_2}(R(t)) \mathcal{D}_{m_1 m}^{(l_1)}(\Omega(t)) \mathcal{D}_{m_2 -m}^{(l_2)}(\Omega(t)) \right|^2 \times \\ &\times \left| \langle J_f; J_f C_f \alpha_f || \mathcal{D}^{(l_1 g, l_1 g, 0 \Gamma_1)} || J_{f'}; J_{f'} C_{f'} \alpha_{f'} \rangle \right|^2 \times \\ &\times V \left(\begin{array}{ccc} J_2 & l_2 & J_2' \\ 0 & 0 & 0 \end{array} \right)^2 \frac{\left| \langle J_2; J_2 || \mathcal{D}^{(l_2, l_2)} || J_2'; J_2' \rangle \right|^2}{[J_2][J_2']} \end{aligned} \quad (39)$$

The first term is exactly the same except that all f labels are replaced by i ones. The third term is given by

$$\begin{aligned} S_{2,f,i,\{2\},\text{mid}} &= -\frac{\hbar^{-2}}{2[J_2]} (-1)^{J_i + J_f + L} \sum_{J_2'} \sum_{l_1, l_2} \frac{(-1)^{l_1}}{[l_1, l_2]} \left\{ \begin{array}{ccc} l_1 & J_f & J_f \\ L & J_i & J_i \end{array} \right\} \times \\ &\times \sum_{m_1, m_2} \left| \int_{-\infty}^{\infty} dt e^{i\omega_{2,2'}t} \sum_m V_{|m|}^{l_1, \Gamma_1, l_2}(R(t)) \mathcal{D}_{m_1 m}^{(l_1)}(\Omega(t)) \mathcal{D}_{m_2 -m}^{(l_2)}(\Omega(t)) \right|^2 \times \\ &\times \langle J_f; J_f C_f \alpha_f || \mathcal{D}^{(l_1 g, l_1 g, 0 \Gamma_1)} || J_f; J_f C_f \alpha_f \rangle^* \langle J_i; J_i C_i \alpha_i || \mathcal{D}^{(l_1 g, l_1 g, 0 \Gamma_1)} || J_i; J_i C_i \alpha_i \rangle \times \\ &\times V \left(\begin{array}{ccc} J_2 & l_2 & J_2' \\ 0 & 0 & 0 \end{array} \right)^2 \frac{\left| \langle J_2; J_2 || \mathcal{D}^{(l_2, l_2)} || J_2'; J_2' \rangle \right|^2}{[J_2][J_2']} \end{aligned} \quad (40)$$

This expression simplifies a bit further since $L = 1$.

3.2.4 Important note

I found that while implementing Eqs. (39) and (40), it was necessary to take great care of the correctness of the various numerical coefficients and phase factors involved. To handle this, I used hash tables in the program generator (section 5) to properly distinguish the cases $\{l_1 \neq 0, l_2 = 0\}$, $\{l_1 = 0, l_2 \neq 0\}$ and $\{l_1 \neq 0, l_2 \neq 0\}$, for example.

3.3 Resonance functions

I choosed to implement the parabolic model for the relative trajectories of the centers of mass of the two molecule. This allows to give analytical forms to the FOURIER transforms in Eqs. (39) and (40).

3.3.1 Principle

The formal potential of Eq. (18) is expressed in the IMF. The resonance functions, that result from FOURIER transforms of the potential along the collisionel trajectories, are calculated by first switching from the IMF to the LFF. These transformations involve supplementary WIGNER matrix elements for the two molecules⁶,

$$\mathcal{D}_{m}^{(l_1g, l_1g, 0\Gamma_1)} \mathcal{D}_{0-m}^{(l_2)}(\Omega_2) \longrightarrow \sum_{m_1=-l_1}^{l_1} \mathcal{D}_{m_1 m}^{(l_1)}(\Omega(t)) \mathcal{D}_{m_1}^{(l_1g, l_1g, 0\Gamma_1)} \times \sum_{m_2=-l_2}^{l_2} \mathcal{D}_{m_2 -m}^{(l_2)}(\Omega(t)) \mathcal{D}_{0 m_2}^{(l_2)}(\Omega_2) \quad (41)$$

where $\Omega(t)$ is the angle between the two z axis of the frames. The time dependence of the relative trajectories of the centers of mass of the molecules is contained in this angle and in $R(t)$, the distance between these points.

3.3.2 Wigner functions

Matrix elements of a rotation operation are given by [11]⁷

$$\begin{aligned} \mathcal{D}_{m m'}^{(l)}(\phi, \theta, \chi) &= e^{-i(m\phi+m'\chi)} [(l+m)!(l-m)!(l+m')!(l-m')!]^{1/2} \times \\ &\times \sum_q (-1)^q [(l+m-q)!(l-m'-q)!q!(q-m+m')!]^{-1} \times \\ &\times \left(\cos \frac{\theta}{2}\right)^{2l+m-m'-2q} \left(\sin \frac{\theta}{2}\right)^{2q-m+m'} \end{aligned} \quad (42)$$

I found that Eq. (42) did not allow to implement easily the parabolic trajectory model because the trigonometric functions involve the angle $\theta/2$ and not θ directly. As a consequence, the functions do not properly simplify during symbolic computation. There is an alternative way to calculate these matrix elements that solves this problem [28],

$$\mathcal{D}_{m m'}^{(l)}(\phi, \theta, \chi) = e^{-im\phi} d_{m m'}^{(l)}(\theta) e^{-im'\chi} \quad (43)$$

with

$$d_{m m'}^{(l)}(\theta) = \zeta_{m m'} \left[\frac{s!(s+\mu+\nu)!}{(s+\mu)!(s+\nu)!} \right]^{1/2} \left(\sin \frac{\theta}{2}\right)^\mu \left(\cos \frac{\theta}{2}\right)^\nu P_s^{(\mu, \nu)}(\cos \theta) \quad (44)$$

⁶For convenience, I used the same notations, m_1 and m_2 , as in Eq. (8), for example, although these numbers do not refer to the same frames.

⁷In this equation, this is the passive point of view that is adopted. One can obtain an equivalent expression using the active mode through the property

$$\mathcal{D}_{m m'}^{(l)}(\Omega) = (-1)^{m+m'} \mathcal{D}_{-m' -m}^{(l)}(\Omega^{-1})$$

In fact, which point of view is adopted is not really essential since only squared modula of these matrix elements are involved in the theory. But, in general, it is absolutly necessary to choose between the active or passive point of view once and for all to avoid, for example, problems with phase factors.

In this relation,

$$\mu = |m - m'|, \nu = |m + m'|, s = l - \frac{\mu + \nu}{2} \text{ and } \zeta_{m m'} = \begin{cases} 1, & \text{if } m' \geq m \\ (-1)^{m' - m}, & \text{if } m' < m \end{cases} \quad (45)$$

The $P_s^{(\mu, \nu)}$ are JACOBI polynomials [5]. These polynomials are calculated, for s integer, through a recursion relation,

$$2s c_s c_{2s-2} P_s^{(\mu, \nu)}(x) = c_{2s-1} (c_{2s-2} c_{2s} x + \mu^2 - \nu^2) P_{s-1}^{(\mu, \nu)}(x) - 2(s-1+\mu)(s-1+\nu) c_{2s} P_{s-2}^{(\mu, \nu)}(x) \quad (46)$$

with

$$c_t = t + \mu + \nu, \quad P_0^{(\mu, \nu)}(x) = 1 \quad \text{and} \quad P_1^{(\mu, \nu)}(x) = \frac{\mu - \nu}{2} + \left(1 + \frac{\mu + \nu}{2}\right) x \quad (47)$$

For μ and ν real numbers such that $\mu > -1$ and $\nu > -1$, these polynomials are orthogonal in the interval $[-1, +1]$ with the weighting function $(1-x)^\mu (1+x)^\nu$.

3.3.3 Parabolic trajectory model

The following elements are taken in part from my thesis [9]. Eq. (53) was wrong in my thesis and was corrected. In the model that I use, the relative molecular trajectories are treated classically and are approximated by parabola. These trajectories are governed by the isotropic part of the interaction potential.

$$\overrightarrow{R}(t) = \overrightarrow{r}_c + \overrightarrow{v}_c t + \frac{\overrightarrow{F}_{\text{iso}}(R = r_c)}{2\mu} t^2, \quad (48)$$

where r_c is the distance (between the centers of mass of the molecules) at the time of closest approach and v_c is the corresponding velocity. $\overrightarrow{F}_{\text{iso}}(R = r_c) = \overrightarrow{F}_c$ is the force that derives from the isotropic interaction at the same time. One also sets

$$R^2(t) = \left(\overrightarrow{r}_c + \frac{\overrightarrow{F}_c}{2\mu} t^2 \right)^2 + v_c^2 t^2 \approx r_c^2 + \left(v_c^2 + \frac{\overrightarrow{r}_c \cdot \overrightarrow{F}_c}{\mu} \right) t^2 = r_c^2 + v_c'^2 t^2, \quad (49)$$

which allows to define v_c' , the velocity at the time of closest approach on the straight line trajectory equivalent to the parabolic trajectory. It is also called the apparent velocity. The quantities involved in the time dependence of the relative trajectories are thus

$$x = v_c' t / r_c, \quad (50)$$

$$R(t) = r_c \sqrt{1 + x^2}, \quad (51)$$

$$\sin \psi(t) = \frac{v_c}{v_c' (1 + x^2)^{1/2}}, \quad (52)$$

$$\cos \psi(t) = \frac{1}{(1 + x^2)^{1/2}} \left[1 + \frac{1}{2} \left(1 - \left(\frac{v_c}{v_c'} \right)^2 \right) x^2 \right] \quad (53)$$

To derive the expressions for v_c and v_c' , the isotropic potential of section 2.5.2 is written as

$$V_{\text{iso}}(R) = \sum_i \frac{C_i}{R^{p_i}} \quad (54)$$

For a collision with impact parameter b , occurring with a relative velocity v at infinite separation, the conservation laws for the energy and for the orbital momentum are

$$\frac{1}{2} \mu v^2 = \frac{1}{2} \mu v_c^2 + V_{\text{iso}}(r_c) \quad \text{and} \quad \mu v b = \mu v_c r_c \quad (55)$$

where μ is the reduced mass of the molecular couple. This implies that

$$v_c = v \left[1 - \frac{2}{\mu v^2} \sum_i \frac{c_i}{r_c^{p_i}} \right]^{1/2} \quad (56)$$

and

$$v'_c = v \left[1 + \frac{1}{\mu v^2} \sum_i \frac{c_i(p_i - 2)}{r_c^{p_i}} \right]^{1/2} \quad (57)$$

Also, the smallest distance of closest approach, r_{c0} , is found by solving

$$\frac{1}{2} \mu v^2 = V_{\text{iso}}(r_{c0}) = \sum_i \frac{c_i}{r_{c0}^{p_i}} \quad (58)$$

This is done numerically using standard techniques [29, 30]. All the calculations described in Ref. [4] were in fact done at the mean thermal velocity,

$$v = \bar{v} = \left(\frac{8K_B T}{\pi \mu} \right)^{1/2} \quad (59)$$

Using Eq. (41), the angular operators of the anisotropic part of the potential are expressed in the LFF. The angles involved are given by

$$\Omega(t) = (\phi(t), \theta(t), \chi(t)) = (\pi/2, \psi(t), 0), \quad (60)$$

the sine and cosine of $\psi(t)$ being given by Eqs. (52) and (53), respectively.

With the elements of section 3.3.2, it was possible to implement this parabolic model, using symbolic computation, in a fully automated manner. This allows, for example, to properly extract and calculate, starting from the FOURIER transforms of Eq. (39)⁸, the integrals

$$I_{p+q}^{(l_1, l_2) m_1, m_2, m}(r_c, v_c, v'_c, \omega) = \frac{1}{v'_c r_c^{p+q-1}} \int_{-\infty}^{+\infty} dx e^{ikx} \frac{1}{(1+x^2)^{(p+q)/2}} \mathcal{D}_{m_1 m}^{(l_1)}(\Omega(t)) \mathcal{D}_{m_2 -m}^{(l_2)}(\Omega(t)) \quad (61)$$

where x is given by Eq. (50), and where

$$k = \omega r_c / v'_c \quad (62)$$

ω is the pulsation associated to the energy spacings between two couples of quantum states,

$$\omega = \omega_{1,1'} + \omega_{2,2'}, \text{ with } \omega_{1,1'} = \omega_{i,i'} \text{ or } \omega_{f,f'} \quad (63)$$

Accounting for the definition of $\Omega(t)$ and for the expressions of the WIGNER functions, the integrals in Eq. (61) involve simpler ones given by

$$I(k, m, n) = \int_{-\infty}^{+\infty} dx e^{ikx} \frac{x^m}{(1+x^2)^n} \quad (64)$$

General expressions for these integrals are derived by first writing

$$I(k, m, n) = i^{-m} \frac{d^m}{dk^m} \left[\int_{-\infty}^{+\infty} dx e^{ikx} \frac{1}{(1+x^2)^n} \right] = i^{-m} \frac{d^m}{dk^m} [I(k, 0, n)]. \quad (65)$$

Then, one sets $n = r/2$ and two cases arise.

⁸The ones in Eq. (40) are the same.

– If $r = 2\nu + 1$ (n is half-integer), then⁹

$$I(k, 0, r/2) = \frac{2^{1-\nu} \Gamma(1/2)}{\Gamma(\nu + 1/2)} k^\nu K_\nu(k) = \frac{2}{(2\nu - 1)!!} k^\nu K_\nu(k), \quad (66)$$

where K is a modified BESSEL function. These functions have an analytical expression¹⁰. The $I(k, m, n)$ functions are then calculated using

$$\frac{d}{dk} K_\nu(k) = -K_{\nu-1}(k) - \frac{\nu}{k} K_\nu(k). \quad (67)$$

– If $r = 2\nu$ (n is integer), then contour integration gives, for any $p \equiv n \equiv \nu$,

$$I(k, 0, p) = 2i\pi \lim_{z \rightarrow i} \frac{1}{(p-1)!} \frac{d^{p-1}}{dz^{p-1}} \left[\frac{e^{ikz}}{(z+i)^p} \right] \quad (68)$$

If one sets

$$f_p(z) = \frac{e^{ikz}}{(z+i)^p} \text{ and } f_p^{(t)}(z) = \frac{d^t}{dz^t} f_p(z), \quad (69)$$

one can show that

$$f_p^{(t)}(z) = \sum_{s=0}^t (-1)^s \frac{t!}{s!(t-s)!} (ik)^{t-s} \frac{(p+s-1)!}{(p-1)!} f_{p+s}(z), \quad (70)$$

thus that

$$I(k, 0, p) = \frac{\pi e^{-k}}{2^{2p-2}(p-1)!} \sum_{s=0}^{p-1} \left[\frac{(2p-s-2)!(2k)^s}{s!(p-s-1)!} \right] \quad (71)$$

4 Modular symbolic computation procedures

They are sorted in alphabetical order and I added comments and/or explanations where I found it appropriate. Some auxiliary procedures are not listed.

Appell.mu : The APPELL function,

$$F(\alpha, \beta; \gamma, \delta; x, y) = \sum_{u,v=0}^{\infty} \frac{(\alpha)_{u+v} (\beta)_{u+v}}{(\gamma)_u (\delta)_v} \frac{x^u y^v}{u! v!}. \quad (72)$$

See the description of **VLJ_InvRnS.mu**, below.

BVSymb.mu : The V coupling symbols, as defined by FANO and RACAH [31]¹¹,

$$\begin{aligned} V \begin{pmatrix} l_1 & l_2 & l_3 \\ k_1 & k_2 & k_3 \end{pmatrix} &= \delta_{k_1+k_2+k_3,0} (-1)^{l_3+k_3} \Delta(l_1, l_2, l_3) \times \\ &\times [(l_1+k_1)!(l_1-k_1)!(l_2+k_2)!(l_2-k_2)!(l_3+k_3)!(l_3-k_3)!]^{1/2} \times \\ &\times \sum_p (-1)^p [p!(l_1+l_2-l_3-p)!(l_1-k_1-p)!(l_3-l_2+k_1+p)!(l_2+k_2-p)!(l_3-l_1-k_2+p)!]^{-1} \end{aligned} \quad (73)$$

CGCoeff.mu : The CLEBSCH-GORDAN symbols. They are proportional to the V or $3J$ symbols,

$$V \begin{pmatrix} l_1 & l_2 & l_3 \\ k_1 & k_2 & k_3 \end{pmatrix} = (-1)^{l_1+l_2+l_3} \begin{pmatrix} l_1 & l_2 & l_3 \\ k_1 & k_2 & k_3 \end{pmatrix} = (-1)^{l_3-k_3} [l_3]^{-1/2} C(l_1 \ l_2 \ l_3; k_1 \ k_2 \ -k_3) \quad (74)$$

⁹ <http://functions.wolfram.com/03.04.07.0006.01>

¹⁰ <http://functions.wolfram.com/03.04.03.0004.01>

¹¹ These are in fact the \bar{V} symbols of that reference.

`DeltaFunc.mu` : The Δ function,

$$\Delta(l_1, l_2, l_3) = \left[\frac{(l_1 + l_2 - l_3)!(l_2 + l_3 - l_1)!(l_3 + l_1 - l_2)!}{(l_1 + l_2 + l_3 + 1)!} \right]^{1/2} \quad (75)$$

`IKMFunc.mu` : The $I(k, m, n)$ functions of Eq. (64). I first used the `transform::fourier` library function of MuPAD, but found that the results returned by the version of the software that I had were wrong. I notified the authors of the software and they corrected the mistake. The bug is still there in release 3.2. However, it is fixed in release 4.0, and higher ones, obviously¹². I thus derived and/or checked Eqs. (65) through (71) and implemented them using the `remember` procedure option to speed up calculations.

`PRFunc_Generator.mu` : Potential and Resonance Functions Generator. The calling sequence for this top level procedure is

```
PRFunc_Generator := proc( MCKeyWord : DOM_IDENT,
  p_r : Type::PosInt, p_a : Type::PosInt,
  l1Max : Type::PosInt, l2Max : Type::PosInt, qMax : Type::PosInt,
  StrGrp1 = "None" : DOM_STRING, StrGrp2 = "None" : DOM_STRING,
  StrTmdl = "Default" : DOM_STRING )
```

The meanings of the arguments is more or less clear and is also described in Ref. [4]. All these ones must have appropriate `Types` or `DOMains`. Some arguments have default values. What this procedure does is also described in Ref. [4]. In addition, it may optionally compute formal expressions for the angular operators of the potential¹³. This last functionality is intended to be used to compare our potential to other models, such as the one reported in Ref. [15].

`VLJ_Dispterm.mu` : Makes the relevant simplifications, calculates and checks the numerical factors for the radial functions of the interaction potential given by Eq. (18). For example, it allowed to put in proper forms the e and d numbers and the polynomials of section 2.5.2.

`VLJ_GetParams.mu` : Data for the calculations of potentials. For example, it contains the definitions for the equilibrium configurations of molecules as a table (indexed by keywords for molecules names) of arrays of sets of equations for the coordinates of atoms¹⁴. As already stated, some simple generic molecular types are implemented: XY_4 , XY_6 , XY_3Z , XY_3 , XY_2 , X_2 , XY and X (atom).

`VLJ_InvRnS.mu` : Computes the two centers expansions of the inverse n -th powers of the distance between atom $1i$ of a first molecule and atom $2j$ of a second one [32–34],

$$\frac{1}{r_{1i,2j}^n} = \sum_{\substack{l_1=0 \\ l_2=0}}^{\infty} \sum_{m=-l_1}^{l_1} \sum_{m_1=-l_1}^{l_1} \sum_{m_2=-l_2}^{l_2} G_n(l_1, l_2; m_1, m_2, m; r_{1i}, r_{2j}, \Lambda_{1i}^{Mol}, \Lambda_{2j}^{Mol}; R) \times \\ \times \mathcal{D}_{m_1 m}^{(l_1)}(\Omega_1) \mathcal{D}_{m_2 -m}^{(l_2)}(\Omega_2), \quad (76)$$

where $r_{1i}, r_{2j}, \Lambda_{1i}^{Mol}$ and Λ_{2j}^{Mol} are the radial and angular coordinates of the atoms in the MFF of each molecule. $l_< = \inf(l_1, l_2)$. R is the distance between the centers of mass of the molecules.

$$G_n(l_1, l_2; m_1, m_2, m; r_{1i}, r_{2j}, \Lambda_{1i}^{Mol}, \Lambda_{2j}^{Mol}; R) = \frac{(-1)^{l_1+l_2}}{\sqrt{4\pi}} Y_{m_1}^{(l_1)}(\Lambda_{1i}^{Mol}) Y_{m_2}^{(l_2)}(\Lambda_{2j}^{Mol}) \times \\ \times \sum_{l=|l_1-l_2|}^{l_1+l_2} [l] \begin{pmatrix} l_1 & l_2 & l \\ m & -m & 0 \end{pmatrix} f_n(l_1, l_2, l; r_{1i}, r_{2j}; R), \quad (77)$$

¹² Matlab, version 7.7.0.471 (R2008b), has version 5.1 of the Symbolic Math Toolbox. I suppose that it corresponds to the MuPAD version.

¹³For this, the WIGNER functions procedure has a special option that adds an index, for example 1 or 2, to the names of the angular arguments of the functions.

¹⁴ ... as well as some other such funny objects (!)

with

$$f_n(l_1, l_2, l; r_{1i}, r_{2j}; R) = (-1)^{l_1} \left[\frac{(4\pi)^3}{[l_1][l_2]} \right]^{1/2} \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} \times \quad (78)$$

$$\times \frac{(n/2)_\Lambda ([n-1]/2)_\lambda}{(1/2)_{l_1} (1/2)_{l_2}} \frac{r_{1i}^{l_1} r_{2j}^{l_2}}{R^{n+l_1+l_2}} F \left(\Lambda + \frac{n}{2}, \lambda + \frac{n-1}{2}; l_1 + \frac{3}{2}, l_2 + \frac{3}{2}; \frac{r_{1i}^2}{R^2}, \frac{r_{2j}^2}{R^2} \right).$$

In the above equation, $(a)_b$ is an incomplete factorial,

$$(a)_b = a(a+1) \cdots (a+b-1) = \Gamma(a+b)/\Gamma(a) \quad (\text{NB: } (a)_0 = 1, (1)_b = b!). \quad (79)$$

$\Lambda = (l_1 + l_2 + l)/2$, $\lambda = \Lambda - l = (l_1 + l_2 - l)/2$ and F is an APPELL function.

VLJ_Main.mu : Self explanatory, i.e. it calls the other VLJ_mu procedures. It computes the short range interaction for any molecular couple, provided that the corresponding data are defined in the VLJ_GetParams.mu procedure. It determines what terms are proportional and, if so, keeps only the relevant terms and the proportionality factors. It does symmetrization if applicable, i.e. if a keyword for a molecular point group is specified and the corresponding data are defined in VLJ_GetParams.mu.

WDFunc.mu : The WIGNER functions, Eqs. (43) and (44)¹⁵. An optional argument to this procedure allows to make the appropriate variable substitutions to implement the parabolic trajectory model (section 3.3.3).

5 Source code generation

This is done with a Perl script called **WS_MkSrc.pl**. It uses some packages from the standard library [6, 7] such as **Getopt::Long** for extended processing of options, **Pod::Usage** that prints usage from the embedded pod [35], and **IO::File** that supplies object methods for filehandles. It also uses some packages from the CPAN [8] such as **Text::Template** that expands template text with embedded Perl code. The template files are briefly described in section 5.3.

5.1 Description and synopsis

The following list of options is extracted from the pod section of the script. I added comments and explanations where appropriate.

¹⁵ Nevertheless, Eq. (44) was not coded as is, because in the function

$$f(\theta) = \left(\sin \frac{\theta}{2} \right)^\mu \left(\cos \frac{\theta}{2} \right)^\nu,$$

μ and ν have the same parity. Thus, $|\mu - \nu|$ is always an even integer. So, if $\mu = \nu$,

$$f(\theta) = \left(\sin \frac{\theta}{2} \cos \frac{\theta}{2} \right)^\mu = \left(\frac{1}{2} \sin \theta \right)^\mu$$

If $\mu > \nu$,

$$f(\theta) = \left(\sin \frac{\theta}{2} \right)^{\mu-\nu} \left(\sin \frac{\theta}{2} \cos \frac{\theta}{2} \right)^\nu = \left(\sin^2 \frac{\theta}{2} \right)^{(\mu-\nu)/2} \left(\frac{1}{2} \sin \theta \right)^\nu = \left(\frac{1 - \cos \theta}{2} \right)^{(\mu-\nu)/2} \left(\frac{1}{2} \sin \theta \right)^\nu$$

If $\mu < \nu$,

$$f(\theta) = \left(\sin \frac{\theta}{2} \cos \frac{\theta}{2} \right)^\mu \left(\cos \frac{\theta}{2} \right)^{\nu-\mu} = \left(\frac{1}{2} \sin \theta \right)^\mu \left(\cos^2 \frac{\theta}{2} \right)^{(\nu-\mu)/2} = \left(\frac{1}{2} \sin \theta \right)^\mu \left(\frac{1 + \cos \theta}{2} \right)^{(\nu-\mu)/2}$$

With these modifications, only trigonometric functions of θ are involved.

Obviously, I verified that if one of the projection numbers is equal to 0, the procedure computes the ordinary spherical harmonics. For example,

$$Y_m^{(l)}(\theta, \phi) = \sqrt{\frac{[l]}{4\pi}} \mathcal{D}_{m0}^{(l)*}(\phi, \theta, \chi)$$

-
- AddMM : Adds all possible functions (FOURIER transforms) without restriction. But, if two functions have the same labels except changes in signs for all projection quantum numbers, the squared modulus of them should be equal and only one function need to be included. In that case, a factor of 2 will be accounted for where relevant (see the template files). This affects only functions for which l_1 and l_2 are non zero. When only l_1 or l_2 is non zero, this was already accounted for in the symbolic computation code.
- debug : Prints db info to a file in `~/exec/spg_*` which name is constructed using the molecular couple keyword. Also, status informations are issued at various db points depending on the `%DBPoints` hash.
- help|H : Prints a short help and exits.
- Lang=f9x : Specifies the output language for the procedures. The `f9x` option is the default output format, and is the only language implemented up to now.
- Limit=L1Max:L2Max:QMax : Specifies the limits for the potential expansion. Files base names will be selected according to these specifications.
- MC=Keyword : Specifies the molecular couple to be considered. It has the form `KW1:KW2`, because some generated procedures and/or pieces of code may be specific to the first or second molecule. THIS OPTION IS MANDATORY. Available keyword(s): `XY4:A2`.
- Only=file : Implements the calculations for the source files for which the labels are specified in the file. Application: Keep only the electrostatic contributions in the potential, while keep on using the isotropic potential calculated from short range contributions. The file must have lines giving sets of values of l_1 , l_2 , p and q (comma separated). Spaces are irrelevant for these lines. Any line (or part of) beginning with `#` are comments and will be ignored. WARNING: the file must be placed in `~/exec`. See this directory for example files. A special line defining `ExtraParams`: with a comma separated list of parameters names may be given, if these basic parameters have to be read in the relevant file. The generated program will display the labels read in `file` at startup.
- OpenMP : Adds OpenMP directives. EXPERIMENTAL.
- Ptl=file : Name of the file containing the potential labels and coefficients and the associated source code. This file must reside in the symbolic computation directory. THIS OPTION IS MANDATORY.
- RAExps=RepExp:AttExp : Specify the leading exponents for the repulsive and attractive parts of the short range interaction. Default is LJ 12-6. Note that this option is irrelevant if these informations can be read in the name of the potential file.
- Scheme=Keyword : Defines the rule on how to group procedures. An example for an input file name is `SRC.XY4A2.03.02.06.05.01.02.00.txt`, where `XY4A2` is the molecular couple keyword (the one given to the `--MC` option, without the `:` separator). The two digits integers correspond to l_1 , l_2 , p , q , m_1 , m_2 and m , in that order. The `--Scheme` options specifies how to build the procedure files base names, and may take the following values.
- A : In this scheme, mentions of m_1 and m_2 are suppressed. Thus, each generated procedure contains all the resonance functions at fixed values of l_1 , l_2 , p , q and m . This scheme is not consistent with the theory. It was the originally implemented one, only to test that procedures were grouped properly. It is kept for backward compatibility.
 - B : In this scheme, mentions of p , q and m are suppressed. Thus, each generated procedure contains all the resonance functions at fixed values of l_1 , l_2 , m_1 and m_2 . THIS IS THE DEFAULT SCHEME.
- verb=Integer : Sets the verbosity level. Defaults to 0. NOT YET IMPLEMENTED.
-

In addition to these options, the behaviour of the script may be modified by setting the entries of some hash tables to true or false.

%AltAlg : It allows to implement **Alternate Algorithms**. For example, one entry, if set to true, will make the main program reorganize its loops so that to implement the modification of the theory described in section 3.2.1.

%DBPoints : Setting entries to true in this hash will display various processing steps of the data. This is to ensure that the codes are properly generated at various stages.

%SCDBPoints : This hash allows to add various writing instructions directly in the source codes to check the consistency of the calculations.

Since the majority of the entries in these tables default to false, the above features are not handled by options.

5.2 Procedures

FindL1L2Scheme : From the current file name or file pattern, it identifies if it corresponds to one of the three cases, $\{l_1 \neq 0, l_2 = 0\}$, $\{l_1 = 0, l_2 \neq 0\}$ and $\{l_1 \neq 0, l_2 \neq 0\}$. Each of these cases needs a specific treatment, as explained in section 3.2.4.

GetFBaseNames : It gets the relevant file basenames as defined from the current scheme, and accounting for the options **--Limit** and **--Only**, if applicable.

GetFileNames : It simply gets all the names of the files generated during symbolic computation, according to the molecular couple keyword.

GetPt1Hash : It reads the labels, the numerical factors and the associated source codes of the various radial functions of the potential and stores these informations in a hash table. It formats the source code according to the source type. It expands the hash table by adding the repulsive part of the short range potential and doing the appropriate mappings for the parameters. It scans the labels of the radial functions in the table to search for the isotropic ones and build the part of the corresponding code to be put in the potential numerical factors procedure. While doing this, it searches for the names of the variables in the numerical factors (e. g., atom-atom parameters). Before calling this procedure, if the **--Only** option was given and a **ExtraParams**: line was present in the specified file, the associated names were accounted for and not searched again.

MkPt1NFacts : For a given set of file names, it builds the corresponding potential numerical factors for the anisotropic interaction. It loops over the file names and does this only once according to the file names pattern. Numerical factors and radial functions are numbered on the fly and these informations are stored in specific tables. While doing this, it keeps on searching for the names of the variables in the numerical factors. This is because some variables names may be present in the isotropic potential and not in the anisotropic potential, and inversely.

PadInt : It makes a string from an integer and adds a leading 0 if the integer is less than 10. These integers (labels) are used to build the file names. This way, files are properly sorted automatically according to these names.

SplitSrcLine : It conveniently splits and cuts source code lines by prepending and adding appropriate character strings. It uses a regular expression as argument to find where to cut lines. I found that the **Text::Wrap** package method did not appropriate things. Thus, I wrote my own function.

TransformCode : Self-explanatory. For example, it transforms function calls to table assignments, since in real calculations functions need to be calculated only once and used several times. Also, it determines the maximum functions arguments that depend on the current file labels. This way, strictly necessary calls will be done in the final code.

`WriteCode` : Self-explanatory, too. This is a container for a call to `SplitSrcLine`, that depends on the source type.

5.3 Templates

A total of 17 template files are used to generate programs. Each template file defines its own name space, which avoids conflicts between variables names and types. These templates contain the instructions to write the source code of a portion of the final program. I only describe them shortly here since the conventions for file names, as well as their contents, is always subject to change. I found it handy to store the references to these templates in a specific hash table upon construction.

`Generic-Head.tpl` : This is used to create comments on top of a given procedure. In particular, it adds the relevant description for its purpose as read from a dedicated hash table, `%StringCat` (string catalog).

`Pt1-Par-Box.tpl`, `Pt1-Par-Sub.tpl` : These ones allow to build the procedure with the potential numerical factors. This is done once all the files with the resonance functions have been processed. Since, at this stage, the names of all the potential parameters are known, instructions for reading and checking them, in alphabetical order, are built and added at the beginning of the procedure.

`RF-IFBlk-Mod.tpl`, `RF-1112-IFBlk.tpl`, `RF-1112-m1m2-IFBlk.tpl` : The interface blocks for the various functions, as well as the modules that contains them, are constructed with these templates.

`RF-1112-Call.tpl`, `RF-1112.tpl` : These ones build the calling sequences and the bodies for the functions with the generic names `XY4A2_11_12.f90`.

`RF-1112-m1m2-Call.tpl`, `RF-1112-m1m2-mq.tpl`, `RF-1112-m1m2.tpl` : For the functions with the generic names `XY4A2_11_12_m1_m2.f90`, these ones produce the calling sequences, the subfunctions and functions bodies.

`XY4-GetEMS.tpl`, `XY4-I02Files.tpl` : These ones generate a procedure that reads the multipolar matrix elements and an other one that does generic file input/output operations.

`XY4A2-Ignition.tpl`, `XY4A2-Main.tpl`, `XY4A2-RelSpeed.tpl`, `XY4A2-S2Fcn.tpl` : These templates create procedures for doing initializations, for the main program, for calculating relative velocities and for building a general interface that calls the various `XY4A2_11_12.f90` functions, as parts of Eqs. (39) and (40).

As seen from the last two items of the description above, some templates are in fact specific to a given molecule or molecular couple. For real modularity, these templates will need some rewriting. The other templates are modular, since the keyword for the molecular couple is used to generate the names of files, functions or interface blocks and modules, for example.

To have an idea of the generated source codes, see the file `MkSrc-Log-14.txt` (if provided with the present document). It contains the processing informations of the script invoked with

```
WS_MkSrc.pl --MC=XY4:A2 --Pt1=IntPt1_XY4A2_12_06_06_16.txt --Limit=6:6:14
```

In this call, one sees that the analytical calculations were done up to $q_{\max} = 16$, whereas the code generation was limited to l_1 and l_2 less than $l_{\max} = 6$ and $q_{\max} = 14$. With these limits, 845 basic FOURIER transforms are included. 76 procedures of the type `XY4A2_11_12_m1_m2.f90` are generated. Also, 8 procedures of the type `XY4A2_11_12.f90` are created. Apart of the main program, 8 complementary procedures and interface blocks modules are produced. It represents about 50,000 lines of code. But, this information is irrelevant, since all this is auto-generated.

5.4 Technical improvements

The source code generator will need to be made fully compliant to the standard syntax for Perl modules [36]. For the moment, different procedures can share the same name space, for example. This is not a convenient practice, since the code is not modular.

The code for actual calculations is generated as simple sources that are compiled in a separate process. It would be more adapted to produce shared object libraries on the fly. For this, appropriate `Makefiles` may possibly be generated using the `ExtUtils::MakeMaker` package of Perl.

As stated in section 5.1, the code generator has an option that adds OpenMP directives [37]. This attempt was not really successful up to now. For example, in one attempt, I added too much parallel region. The code happened to spend most of its time in copying data from one memory location to another, and thus was slower than the sequential version (!). With another tentative implementation, different threads accessed the same memory location, which produced (fatal !) segmentation violations. It seems thus appropriate to parallelize the top most loop(s), and to closely look on what objects and data need to be shared or private to avoid memory faults. Also, how OpenMP is built into the compiler may play a role in performance. I had to unmask `gcc`, version 4.2.3, on my operating system [38, 39] to be able to start using OpenMP. At the time of this report, this is not the latest `gcc` version available. Obviously, profiling techniques should be used together with these developments. As said in the synopsis above, this aspect needs deep experimentation. Finally, I will need to use a versioning system (`subversion` ? `CVS` ? ...), to avoid handling this by hand.

6 And now ?

For what concerns the line broadening theory and the comparisons with the experimental data, I do not repeat here the discussion and the conclusion made in Ref. [4].

The technical details that I briefly described above are only partly representative of the various tools that could be suitable for the practical implementation of the theories in the area of molecular collisional processes. The use of automated program generation happened to be particularly adapted, owing to the complexity of the theory for such physical problems. In fact, all these technical aspects are constantly evolving and being improved. Certainly, there is much more to explore, in conjunction with doing so in the development of the theory itself.

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