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Ab initio effective rotational Hamiltonians - A comparative study

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Abstract

Two independent methods to obtain *ab initio* effective rotational Hamiltonians have been implemented recently. The first one is based on a generalization of perturbation theory to non-commutative rings, the other one on contact transformation techniques. In principle, both methods are able to give rotational Hamiltonian including centrifugal distortion effects of arbitrary high orders. These methods are compared for the first time in this article on calculations of the rotational levels of methane vibrational ground state.

1 Introduction

The resolution of the molecular Schrödinger equation gives in principle the energy levels commonly associated with the rotational spectrum of a polyatomic molecule. The term “rotational” is coined because the corresponding levels are mainly related to the quantization of molecular rotational motion. However, for their accurate characterisation an account of the coupling with other types of nuclear motion is mandatory, and it becomes rapidly prohibitive to deal with all molecular degrees of freedom (dof) as the number of atoms increases. So, it is often desirable to separate electronic from nuclear dof, and also within nuclear dof, to separate “vibrational” dof from the “rotational” ones. Then, to obtain the rotational energy levels of a polyatomic molecule, one has only to solve an effective rotational Hamiltonian eigenvalue problem for a given vibrational state.

A formal derivation of effective models in quantum mechanics using a separation of a Hamiltonian into a zeroth-order approximation and a perturbation has been the subject of many studies. The well-known Rayleigh-Schrödinger perturbation theory has been extended for a derivation of effective Hamiltonians defined on a degenerate zeroth-order eigenspace by Bogolyubov and Tiablikov [1], Bloch [2], Des Cloizeaux [3], Soliveres [4], and other investigators using projector and resolvent operators. Another approach using unitary Contact Transformations (CT), originally suggested by Van Vleck [5] gave rise to a series of successful applications, particularly in molecular physics. A comparison of various general methods for effective Hamiltonian derivation have been discussed in detail by Klein [6], Tyuterev et al. [7–9] and Jorgensen [10]. In these works it has been shown that different perturbative methods resulted in formally different effective Hamiltonians which however, could be related by suitably chosen transformations. More recently Watson [11] has given a supplementary insight on formal relations between several general approaches, including those implemented in the present work, and Bloch expansion [2]. These studies are very useful to understand the fundamental ambiguities inherent to the fitting of empirical Hamiltonian parameters to experimental energy levels. They have paved the path to the development in molecular spectroscopy of reduction theory [12–

15], which aims at the derivation of empirical effective Hamiltonians containing uniquely defined parameters, by means of transformations within the subspace spanned by the corresponding effective wave functions.

However, very few studies are yet available concerning the numerical accuracy and convergence properties of *ab initio* derived effective Hamiltonians. In this paper we focus on accurate calculations close to spectroscopic accuracy, based on two types of perturbation approaches, using computer codes developed by the authors. The first one, obtained from a formalism called the Rayleigh-Schrödinger perturbation theory generalized to the ring spanned by angular momentum operators [16–19] is equivalent to the “standard unitary solution” of section 8 of [11]. The second one, is a generalized formulation of the CT method using super-operator techniques [7,9]. Both methods, implemented by the authors, are applied in this work to the calculation of methane rotational levels in the vibrational ground state, starting from the complete vibration-rotational Hamiltonian in the Eckart-Watson form [20–22].

Methane is a very important molecule for various applications in particular for planetary physics and chemistry. Rotational spectra of methane have been observed through transparency windows in Saturn and Titan atmospheres [23–25]. Many new experimental measurements are currently in progress [26–29]. Furthermore, recent improvements in *ab initio* calculations of methane potential energy surfaces (PES) [30–33], make this molecule a good candidate for advanced, benchmark, ro-vibrational calculations. All calculations in this study were performed by using the same accurate PES recently constructed by Nikitin et al. [33], which will be referred to as the NRT PES in what follows. To apply our perturbation calculations, this PES has been re-expressed in rectilinear normal coordinates up to the 10th order.

Throughout this article, “methane” will designate the main isotopologue, ¹²CH₄, of this molecular species. Note that a modeling of methane experimental spectra requires a sophisticated effective Hamiltonian formalism because of its high symmetry [34]. On another hand, in theoretical investigations, high symmetry is very useful to diagnose

bugs in computer codes. The purpose of the present article is to focus on numerical and convergence issues on a concrete example. As for the formal comparison of the methods and techniques of calculations, we refer the reader to the above mentioned bibliography, in particular [9,11].

The article is organized as follows: In Part 2, the generalized Rayleigh-Schrödinger perturbation theory is briefly reviewed. In part 3, the contact transformation technique as implemented in this work is outlined. In Part 4, we proceed to a comparison of the effective rotational Hamiltonians given by the two methods for different orders up to eight in angular momentum operators. We conclude on the reliability and the effectiveness of both approaches.

2 Effective separation of variables and perturbation theory

Let us first introduce a key notation for an effective separation of variables technique, that is particularly efficient when it is coupled to perturbation theory. It is applicable to Hamiltonians of the form, $H(X, Y)$, depending upon two sets of operators X and Y acting on two distinct subsets of dof \mathbf{x} and \mathbf{y} respectively. We suppose that the Hamiltonian can be decomposed as,

$$H(X, Y) = H_0(X) \otimes Id_{\mathbf{y}} + H_1(X, Y). \quad (1)$$

The traditional Rayleigh-Schrödinger theory would correspond to the case where the sets Y and \mathbf{y} are empty.

The operators in X act on a Hilbert space, $V_{\mathbf{x}}$, of square integrable functions of the \mathbf{x} dof. Similarly, those in Y act on a Hilbert space, $V_{\mathbf{y}}$, of square integrable functions of the \mathbf{y} dof. The Hilbert space of the whole system is the tensor product, $V = V_{\mathbf{x}} \otimes V_{\mathbf{y}}$. The identity on $V_{\mathbf{x}}$ (respectively $V_{\mathbf{y}}$) is written $Id_{\mathbf{x}}$ (respectively $Id_{\mathbf{y}}$).

To generalize the Rayleigh-Schrödinger theory for this Hamiltonian, we recall the derivation procedure by Cassam-Chenai [19]. However, very similar formulation and notation

for the separation of \mathbf{x} and \mathbf{y} dof by CT have been described by Makushkin and Tyuterev [9]. Thus the considerations of the next sub-section equally apply to both methods used in this paper.

2.1 Eigen equation for effective operators

Let $(\psi_n)_n$, (respectively $(\Psi_K)_K$), be a normalized Hilbertian basis set of $V_{\mathbf{x}}$ (respectively $V_{\mathbf{y}}$), we have: $Id_{\mathbf{x}} = \sum_n |\psi_n\rangle\langle\psi_n|$, (respectively $Id_{\mathbf{y}} = \sum_K |\Psi_K\rangle\langle\Psi_K|$). A basis of V is obtained by taking the tensor product of basis functions, $(\psi_n \otimes \Psi_K)_{n,K}$. Since we are free to choose the basis set of $V_{\mathbf{x}}$, we can take for $(\psi_n)_n$ a set of orthonormal eigenvectors of H_0 . We label this set with positive integers and denote the associated eigenvalues by $(\nu_n)_n$. For simplicity, we assume that the eigenstates of $H_0(X)$ are non-degenerate, but the method is general.

To solve perturbationally the eigenvalue equation,

$$H(X, Y)\phi = E\phi, \quad (2)$$

we introduce a real parameter, $\varepsilon \in [0, 1]$, and the Hamiltonian,

$$H(X, Y, \varepsilon) = H_0(X) \otimes Id_{\mathbf{y}} + \varepsilon H_1(X, Y), \quad (3)$$

such that, $H(X, Y, 0) = H_0(X) \otimes Id_{\mathbf{y}}$ and $H(X, Y, 1) = H(X, Y)$.

So, for $\varepsilon = 0$, given our choice for $(\psi_n)_n$,

$$H(X, Y, 0)|\psi_n \otimes \Psi_K\rangle = \nu_n|\psi_n \otimes \Psi_K\rangle \quad \forall K. \quad (4)$$

The eigenspaces are degenerate of dimension, $dim V_{\mathbf{y}}$.

Note that we use the same symbols, $\langle \dots |$ and $|\dots\rangle$, for Dirac bra's and ket's indifferently in V , $V_{\mathbf{x}}$ or $V_{\mathbf{y}}$. Substituting $|\Psi_K\rangle$ by $|\Psi_K\rangle\langle\Psi_K|$ in $|\psi_n \otimes \Psi_K\rangle = |\psi_n\rangle \otimes |\Psi_K\rangle$ of Eq.(4), and summing over K , one obtains,

$$(H_0(X) \otimes Id_{\mathbf{y}})|\psi_n\rangle_{\mathbf{x}} \otimes Id_{\mathbf{y}} = \nu_n|\psi_n\rangle_{\mathbf{x}} \otimes Id_{\mathbf{y}}. \quad (5)$$

We will assume that, for some fixed n , in the interval $\varepsilon \in [0, 1]$, the $\dim V_{\mathbf{y}}$ eigenstates $(\psi_n \otimes \Psi_K)_K$ of $H(X, Y, 0)$ are in one-to-one correspondance with $\dim V_{\mathbf{y}}$ eigenstates of $H(X, Y, \varepsilon)$, denoted by $(\phi_{n,K}(\varepsilon))_K$, the latter inheriting their labels from their $\varepsilon = 0$ partners. The $\phi_{n,K}(\varepsilon)$'s can be expanded on the tensorial product basis set as,

$$\phi_{n,K}(\varepsilon) = \sum_{n',K'} c_{n',K'}^{n,K}(\varepsilon) \psi_{n'} \otimes \Psi_{K'}. \quad (6)$$

Introducing $\dim V_{\mathbf{x}}$ linear operators on $V_{\mathbf{y}}$, $\Psi_{n'}(Y, \varepsilon)$, by

$$\forall n', \forall \Psi_K, \quad \Psi_{n'}(Y, \varepsilon) \Psi_K := \sum_{K'} c_{n',K'}^{n,K}(\varepsilon) \Psi_{K'}, \quad (7)$$

we can define a so-called "effective wave operator" from $V_{\mathbf{y}}$ onto $V_{\mathbf{x}} \otimes V_{\mathbf{y}}$, $\phi_n(Y, \varepsilon)$, by

$$\phi_n(Y, \varepsilon) = \sum_{n'} \psi_{n'} \otimes \Psi_{n'}(Y, \varepsilon). \quad (8)$$

Combining Eqs. (7) and (8), we see from Eq. (6), that the action of the effective wave operator on the basis functions Ψ_K gives the exact eigenfunctions of $H(X, Y, \varepsilon)$,

$$\phi_{n,K}(\varepsilon) = \phi_n(Y, \varepsilon) \Psi_K. \quad (9)$$

We define another operator on $V_{\mathbf{y}}$, called the "effective Hamiltonian", $E_n(Y, \varepsilon)$, by its action on the basis functions Ψ_K ,

$$E_n(Y, \varepsilon) \Psi_K = E_{n,K}(\varepsilon) \Psi_K. \quad (10)$$

Inserting Eqs. (9) and (10) in the eigenvalue equation of $H(X, Y, \varepsilon)$, we have for all Ψ_K ,

$$H(X, Y, \varepsilon) \phi_n(Y, \varepsilon) \Psi_K = \phi_n(Y, \varepsilon) E_n(Y, \varepsilon) \Psi_K. \quad (11)$$

Since the Ψ_K 's form a basis set, we can write the following identity between operators acting on $V_{\mathbf{y}}$,

$$H(X, Y, \varepsilon) \phi_n(Y, \varepsilon) = \phi_n(Y, \varepsilon) E_n(Y, \varepsilon). \quad (12)$$

By conjugation, the Hermitic conjugate of the effective wave operator and Hamiltonian satisfy,

$$\phi_n^\dagger(Y, \varepsilon) H(X, Y, \varepsilon) = E_n^\dagger(Y, \varepsilon) \phi_n^\dagger(Y, \varepsilon), \quad (13)$$

where the operators act on $V_{\mathbf{y}}$ on the left. We will make use of the notation $\langle \dots \rangle_{\mathbf{x}}$ to signify that integration is carried over the \mathbf{x} -variables only, for example,

$$\langle \psi_1 \otimes \Psi_1(Y) | \psi_2 \otimes \Psi_2(Y) \rangle_{\mathbf{x}} = \langle \psi_1 | \psi_2 \rangle \Psi_1(Y) \Psi_2(Y). \quad (14)$$

Note that, if we impose the normalization condition,

$$\langle \phi_n^\dagger(Y, \varepsilon) \phi_n(Y, \varepsilon) \rangle_{\mathbf{x}} = Id_{\mathbf{y}}, \quad (15)$$

we obtain easily from Eqs. (12) and (13) that the effective Hamiltonian, $E_n(Y, \varepsilon)$, is Hermitian,

$$E_n(Y, \varepsilon) = E_n^\dagger(Y, \varepsilon). \quad (16)$$

2.2 Perturbational solution of the eigen equation for effective operators

Following Cassam-Chenai [19], let us consider the problem of finding all pairs of operators $E(Y, \varepsilon)$, $\phi(Y, \varepsilon)$ acting on $V_{\mathbf{y}}$, satisfying

$$H(X, Y, \varepsilon) \phi(Y, \varepsilon) = \phi(Y, \varepsilon) E(Y, \varepsilon). \quad (17)$$

We call the latter equation an eigen equation for effective operators. From the previous section, one can assert that its set of solutions is non empty provided minor hypothesis. If one assumes that the eigenpairs $(E_{n,K}(\varepsilon), \phi_{n,K}(\varepsilon))_K$ of $H(X, Y, \varepsilon)$ of some band indexed by quantum number n , are smooth function of ε , one can solve Eq.(17) in a Rayleigh-Schrödinger fashion. Note that, this smoothness hypothesis is the crucial one: In finite dimension, it is always possible to relate bi-univoquely two arbitrary sets of linearly independent functions, provided their cardinal are the same. However, the requirement that this relation should be smooth as ε varies, is an important constraint implying that the band considered undergoes no "catastrophic" mixing with any other band, in the sense of catastrophe theory. We postpone the treatment of such a case to a forthcoming paper on a quasi degenerate version of the present formalism.

So, we expand the effective rotational Hamiltonian and wave operators as a power series of ε :

$$E(Y, \varepsilon) = \nu_n Id_{\mathbf{y}} + \varepsilon E^{(1)}(Y) + \varepsilon^2 E^{(2)}(Y) + \varepsilon^3 E^{(3)}(Y) + \varepsilon^4 E^{(4)}(Y) + \dots, \quad (18)$$

$$\phi(Y, \varepsilon) = \psi_n \otimes Id_{\mathbf{y}} + \varepsilon \phi^{(1)}(Y) + \varepsilon^2 \phi^{(2)}(Y) + \varepsilon^3 \phi^{(3)}(Y) + \varepsilon^4 \phi^{(4)}(Y) + \dots, \quad (19)$$

Inserting these expressions in Eq. (17) and identifying the terms with the same power of ε , together with the set of "Hermiticity" conditions, $\forall k > 0$,

$$\langle \psi_n \otimes Id_{\mathbf{y}} | \phi^{(i)}(Y) \rangle_{\mathbf{x}} = \langle \phi^{(i)\dagger}(Y) | \psi_n \otimes Id_{\mathbf{y}} \rangle_{\mathbf{x}}. \quad (20)$$

and the set of normalization conditions, $\forall k > 0$,

$$\left\langle \sum_{i=0}^k \varepsilon^i \phi^{(i)\dagger}(Y) \middle| \sum_{i=0}^k \varepsilon^i \phi^{(i)}(Y) \right\rangle_{\mathbf{x}} = Id_{\mathbf{y}} + o(\varepsilon^n, Y). \quad (21)$$

where $\phi^{(0)}(Y) = \psi_n \otimes Id_{\mathbf{y}}$ and the notation $o(\varepsilon^k, Y)$ means that $\lim_{\varepsilon \rightarrow 0} \varepsilon^{-k} o(\varepsilon^k, Y) = 0_{\mathbf{y}}$, the null operator on $V_{\mathbf{y}}$, one can determine unambiguously eigensolutions to any order [19].

That is to say, that the perturbative solution to Eq. (17) is actually unique for a given H . Of course, if H is transformed by a unitary mapping, the effective wave operator and effective Hamiltonian will be transformed accordingly.

Making use of the condensed notation,

$$H_1(Y)_{i,j} := \langle \psi_i \otimes Id_{\mathbf{y}} | H_1(X, Y) | \psi_j \otimes Id_{\mathbf{y}} \rangle_{\mathbf{x}}, \quad (22)$$

the following expressions have been obtained [19] for the effective Hamiltonian corrective terms up to order 4,

$$E^{(1)}(Y) = H_1(Y)_{n,n}, \quad (23)$$

$$E^{(2)}(Y) = \sum_{k_1 \neq n} \frac{H_1(Y)_{n,k_1} H_1(Y)_{k_1,n}}{\nu_n - \nu_{k_1}}, \quad (24)$$

$$\begin{aligned}
E^{(3)}(Y) &= \langle \phi^{(0)\dagger}(Y) | H_1(X, Y) | \phi^{(2)}(Y) \rangle_{\mathbf{x}} - \langle \phi^{(0)\dagger}(Y) | \phi^{(2)}(Y) \rangle_{\mathbf{x}} E^{(1)}(Y) \\
&= \sum_{k_1, k_2 \neq n} \frac{H_1(Y)_{n, k_1} H_1(Y)_{k_1, k_2} H_1(Y)_{k_2, n}}{(\nu_n - \nu_{k_1})(\nu_n - \nu_{k_2})} \\
&\quad - \frac{1}{2} \sum_{k_1 \neq n} \frac{H_1(Y)_{n, k_1} H_1(Y)_{k_1, n} H_1(Y)_{n, n} + H_1(Y)_{n, n} H_1(Y)_{n, k_1} H_1(Y)_{k_1, n}}{(\nu_n - \nu_{k_1})^2},
\end{aligned} \tag{25}$$

$$\begin{aligned}
E^{(4)}(Y) &= \sum_{k_1, k_2, k_3 \neq n} \frac{H_1(Y)_{n, k_1} H_1(Y)_{k_1, k_2} H_1(Y)_{k_2, k_3} H_1(Y)_{k_3, n}}{(\nu_n - \nu_{k_1})(\nu_n - \nu_{k_2})(\nu_n - \nu_{k_3})} \\
&\quad - \frac{1}{2} \sum_{k_1, k_2 \neq n} \frac{H_1(Y)_{n, n} H_1(Y)_{n, k_1} H_1(Y)_{k_1, k_2} H_1(Y)_{k_2, n} + H_1(Y)_{n, k_1} H_1(Y)_{k_1, k_2} H_1(Y)_{k_2, n} H_1(Y)_{n, n}}{(\nu_n - \nu_{k_1})(\nu_n - \nu_{k_2})} \left(\frac{1}{\nu_n - \nu_{k_1}} + \frac{1}{\nu_n - \nu_{k_2}} \right) \\
&\quad - \frac{1}{2} \left(\sum_{k_1 \neq n} \frac{H_1(Y)_{n, k_1} H_1(Y)_{k_1, n}}{(\nu_n - \nu_{k_1})} \right) \left(\sum_{k_1 \neq n} \frac{H_1(Y)_{n, k_1} H_1(Y)_{k_1, n}}{(\nu_n - \nu_{k_1})^2} \right) \\
&\quad - \frac{1}{2} \left(\sum_{k_1 \neq n} \frac{H_1(Y)_{n, k_1} H_1(Y)_{k_1, n}}{(\nu_n - \nu_{k_1})^2} \right) \left(\sum_{k_1 \neq n} \frac{H_1(Y)_{n, k_1} H_1(Y)_{k_1, n}}{(\nu_n - \nu_{k_1})} \right) \\
&\quad + \frac{1}{2} \sum_{k_1 \neq n} \frac{H_1(Y)_{n, n}^2 H_1(Y)_{n, k_1} H_1(Y)_{k_1, n} + H_1(Y)_{n, k_1} H_1(Y)_{k_1, n} H_1(Y)_{n, n}^2}{(\nu_n - \nu_{k_1})^3}.
\end{aligned} \tag{26}$$

Note that some misprints have been corrected in Eq. (26) with respect to [19]. These formulas matches that of section 8 of [11], where the operator T_U can be identified with our normalized effective wave operator. So, order 5 can be found in this reference.

3 The contact transformation method

The method of contact transformations (CT) aims at simplifying solutions of classical or quantum mechanical problems by building some simpler effective Hamiltonian models. The main idea is to transform a full Hamiltonian H to a simpler operator H^{eff} defined in a finite dimensional space, \mathcal{E} , spanned by known eigenfunctions ϕ_k of an exactly solvable zeroth-order approximation. Most often, this is realized by applying a similarity transformation $\widetilde{H} = T^{-1}HT$ followed by a projection \mathcal{P} on the \mathcal{E} subspace i.e. $H^{eff} = \mathcal{P}\widetilde{H}\mathcal{P}$. Once a zeroth-order approximation H_0 is chosen, the perturbation operator $\lambda V = H - H_0$ is commonly expanded as a power series, $\lambda V_1 + \lambda^2 V_2 + \dots$, of a formal parameter

λ considered as being small. In molecular physics, following Van Vleck [5], the operator T is usually chosen in the form of successive unitary CT [5,8,9,11,13,35–38,43,44,47]:

$$\widetilde{H} = \dots e^{i\lambda^2 S_2} e^{i\lambda S_1} H e^{-i\lambda S_1} e^{-i\lambda^2 S_2} \dots = H_0 + \lambda\{V_1 + [iS_1, H_0]\} + \dots \quad (27)$$

In order to preserve the fundamental properties of an Hamiltonian operator in H^{eff} , the generators of the transformations, S_n , are usually chosen to be Hermitian and totally symmetric with respect to the molecular point group. In addition, they should keep the invariance of the Hamiltonian under the time reversal. Furthermore, the CT method is based on the assumption that the CTs, Eq. (27), can be chosen in a way which does not affect the rate of convergence of a Hamiltonian expansion.

An iterative procedure can then be developed by introducing the first transformed Hamiltonian $H^1 = e^{i\lambda S_1} H e^{-i\lambda S_1}$, second transformed Hamiltonian $H^2 = e^{i\lambda S_2} H^1 e^{-i\lambda S_2}$, n -times transformed Hamiltonian $H^n = e^{i\lambda S_n} H^{n-1} e^{-i\lambda S_n}$ and so on, up to $H^\infty \equiv \widetilde{H}$. All these intermediate Hamiltonians are also expanded in powers of the formal parameter $H^k = \sum_n \lambda^n H_n^k$. Using the Hausdorff commutator expansion, recursive formulas have been established [8,9,11,13,37,39] which link the n -th order term of the k -times transformed Hamiltonian, H_n^k , with CT-generators S_1, \dots, S_k and the expansion terms, H_m^{k-1} , of the $(k-1)$ -times transformed Hamiltonian. By ordering considerations, it can be easily shown that the final, transformed Hamiltonian should only contain terms with $n = k$, that is $\widetilde{H} = \sum_n \lambda^n H_n^n$. The explicit expressions for arbitrary n and k can be found in [8,9]. Up to this point these formulae are quite general. Their practical application depends on the meaning of the term "simplification" attached to the transformation (27). In molecular physics and spectroscopy, CTs are usually applied to reduce a complicated problem defined on a complete space of wavefunctions to one defined on a subspace spanned by a limited number of strongly coupled nearby quantum states. Particularly important applications correspond to the case where the subspace can be identified with one component of a tensor product Hilbert space. As we have seen, this occurs in the case of an effective separation of dof. For instance, in the derivation of an effective Hamiltonian for the nuclear motion by separating electronic variables [38] and in the derivation

of effective rotational Hamiltonian by separation of vibrational variables [13,37,39,44].

In a rather wide class of applications, the meaning of "simplification" can be formalized concisely by the constraint, $[\widetilde{H}, \mathcal{A}] = 0$, that the transformed Hamiltonian, \widetilde{H} , should commute with some operator \mathcal{A} called the *modeling operator* [8,9]. Different choices of the modeling operators result in different forms of effective Hamiltonians, H^{eff} . In the case of a zeroth order spectrum having non-degenerate or purely degenerate states [35], $H_0 = \sum_m E_m^{(0)} P_m^{(0)}$, a natural choice is $\mathcal{A} = H_0$. The \widetilde{H} -matrix in the zeroth-order eigenbasis takes then a block-diagonal form $\widetilde{H} = \langle \widetilde{H} \rangle$ where the notation $\langle O \rangle$ stands for the block-diagonal part of an operator, O . The choice $\mathcal{A} = P_m^{(0)}$ where $P_m^{(0)}$ is the projector on the m^{th} eigen-space of the zeroth-order Hamiltonian, associated to the degenerate or non-degenerate eigenvalue, $E_m^{(0)}$, amounts to the Hermitian version of the Bloch projector formulation of perturbation theory [2-4,9]. Extensions of the modeling operator to the quasi-degenerate case has been considered in [8]. In the case of the initial Hamiltonians depending on different types of variable, $H(X, Y)$, discussed in the previous section and given by Eq. (1), the choice $\mathcal{A} = \mathcal{A}(X)$ allows a full or a partial separation of x -variables by CT [7,9].

At n -th order of CT, the conditions applied to the S_n generator and the n -th order effective Hamiltonian term are written as,

$$[iS_n, H_0] + H_n^{n-1} = H_n^n ; \quad [H_n^n, \mathcal{A}] = 0 \quad (28)$$

The general solution of these equations for degenerate or a quasi-degenerate zeroth-order states are given in [8,9] in terms of operations $\langle \dots \rangle$ (taking the block-diagonal part with respect to H_0 eigenstates partitioning) and the inverse of operation, $[H_0, \dots]$, consisting in taking the commutator with H_0 . Some mathematical aspects of these solutions are considered in [9,35,40]. With an appropriate choice of \mathcal{A} the eqs.(28) are invariant under the substitution $S_n \Rightarrow S_n + \langle Z_n \rangle$, where $Z_n \sim \lambda^n$ is an arbitrary Hermitian operator. This gives a variety of effective Hamiltonians in a given \mathcal{E} space and explains how different expressions are obtained with various equivalent formulations of the per-

turbation theory [7–9].

CT can be viewed in terms of the Lie algebra, \mathcal{L} , generated by multiple commutators of iS_n with H_0 and V_n [9,40]. For a given choice of the modeling operator \mathcal{A} , this Lie algebra is decomposed as $\mathcal{L} = \mathcal{L}^{(0)} \oplus \mathcal{L}^{(\perp)}$, where $\mathcal{L}^{(0)}$ denotes the subspace of elements commuting with \mathcal{A} . Consequently the transformed Hamiltonian contains only operators restricted to $\mathcal{L}^{(0)}$, $\widetilde{H} \in \mathcal{L}^{(0)}$, resulting in a full or a partial separation of variables. From the computational point of view two things are essential: programming general solutions of CT equations (28) and calculating structural constants of the Lie algebra. For vibration-rotation Hamiltonian this has been implemented in [41,42].

A separation of variables allows for a drastic reduction of the dimension of Hamiltonian matrices. Consequently, a computational implementation for molecular spectra calculation becomes much easier, and spectroscopic accuracy can be achieved. Moreover, CT provide a mathematical background for intuitively introduced physical models for bound states of semi-rigid molecules near the equilibrium configuration and gives a simple interpretation of effective parameters.

The contact transformation method has been widely used in the literature on high-resolution molecular spectroscopy as reviewed by Amat, Nielsen and co-workers [39,43], Aliev and Watson [13], Camy-Peyret and Flaud [37], Sarka and Demaison [44] and others [9,15,45]. It has been developed for polyatomic molecules by Sibert [46] and applied to methane by Wang and Sibert [47]. This formalism has been reviewed and employed for floppy molecules by Sugny et al. [48]. Most implementations start from an harmonic vibrational approximation in H_0 , with the exception of [49] where the $J = 0$ -Hamiltonian is used. In the notation of the previous section, this method allows for an effective separation of "fast" vibrational variables (X) and "slow" rotational variables (Y) as described in more details in [9]. In this work, CT calculations have been performed with the optimized algorithms and computational techniques developed and implemented in the MOL-CT program suite by Tyuterev, Tashkun and co-workers [41,50].

4 Comparison of *ab initio* effective rotational Hamiltonians

4.1 The Eckart-Watson Hamiltonian

The Hamiltonian of the system considered in this work will be the Eckart-Watson Hamiltonian for non linear molecules [21]. The singularities of the Watson Hamiltonian prevent a proper study of the behaviour of a molecular system in their neighbourhood. However, since their measure is zero in nuclear configuration space, they are not necessarily a problem for the description of the rovibrational energy levels, in the same manner as the cusp of the electronic Hamiltonian do not prevent an accurate determination of the electronic energy levels. Moreover, in this study Hamiltonian singularities are not an issue.

Note that, if one sets, $X = \{(Q_i)_i, (P_k)_k\}$, the set of normal coordinates and conjugate momenta, and $Y = \{\theta, \chi, \phi, P_\theta, P_\chi, P_\phi\}$, the set of Euler angles and momenta, the Eckart-Watson Hamiltonian written as, $H(X, Y)$, can be decomposed as in Eq. (1), as required by the generalized Rayleigh-Schrödinger perturbation theory.

The two approaches for obtaining effective rotational Hamiltonians, recalled in the previous section, will make use of different partitioning of the Eckart-Watson Hamiltonian into a zeroth-order operator and a perturbation. The generalized perturbation theory will take the full ($J = 0$)-vibrational hamiltonian as a zeroth-order approximation written in atomic units as follows,

$$H_0(X) = \frac{1}{2} \sum_k P_k^2 + U + \frac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta} \pi_\alpha \pi_\beta - \frac{1}{8} \sum_\alpha \mu_{\alpha\alpha}. \quad (29)$$

In the equations above, μ is the 3 by 3 effective reciprocal inertia matrix whose series expansion in terms of the normal coordinates is

$$\mu = \sum_{r=0}^{+\infty} \left(\frac{1}{2}\right)^r (r+1) \sum_{k_1, \dots, k_r} I_e^{-1} a_{k_1} I_e^{-1} \dots a_{k_r} I_e^{-1} Q_{k_1} \dots Q_{k_r}, \quad (30)$$

where, I_e^{-1} is the inverse of the inertia tensor $I(Q_1, \dots, Q_n)$ at equilibrium and $(a_k)_k$ the derivatives of the latter with respect to the normal coordinates,

$$a_k = \left(\frac{\partial I}{\partial Q_k} \right)_0. \quad (31)$$

π is the vibrational angular momentum operator determined by the Coriolis coupling constants and only depending upon the operators in the set X . U is the potential energy surface (PES) of electronic origin in the Born-Oppenheimer approximation, expressed as a function of the normal coordinates Q_i .

In this case the perturbation describes the vibration-rotation coupling

$$H_1(X, Y) = \sum_{\alpha\beta} \frac{1}{2} \mu_{\alpha\beta} \otimes \Pi_\alpha \Pi_\beta - \mu_{\alpha\beta} \pi_\alpha \otimes \Pi_\beta. \quad (32)$$

where Π is the total angular momentum, and is the sole quantity depending upon the operators in the set Y .

The current implementation of CT uses the harmonic oscillator Hamiltonian as zeroth-order approximation

$$H_0(X) = \frac{1}{2} \sum_k P_k^2 + U^{(2)} \quad (33)$$

where, $U^{(2)}$ is the PES truncated at second order. In the latter case, anharmonicity, the vibrational Coriolis term and Watson mass-dependent correction are all included in the perturbation operator $H_1(X, Y)$. This results in many more terms to be accounted for in the perturbation expansion. However, the advantage of the simplicity of the zeroth-order approximation is that, it allows one to avoid intermediate summations on virtual vibrational states.

In this comparative study, we have used for U the NRT methane PES [33] expanded as a Taylor series of normal coordinates up to the tenth order. This was done by using analytical formulas, with the help of a symbolic algebra program. A detailed account of this procedure for symmetric molecules has been given by Rey et al. [51].

By construction, an effective Hamiltonians share the same eigenvalues as the original

ones. So, in principle, if the radius of convergence of their expansion series is non zero, both the methods explored in this work should converge towards the same spectra. Whether this convergence hypothesis is met or not is not clear mathematically, since they include non bounded operators. However, it is legitimate to investigate numerically the convergence behaviour of both methods, and to compare one with the other.

4.2 Convergence of the generalized perturbation method

The implementation of the generalized perturbation method depends upon several parameters whose influence on the convergence of the final results will be assessed. These parameters are:

- The order of the Taylor expansion of the NRT PES U in H_0 (see tab. 5)
- The order of the Taylor expansion of the μ -matrix in H_0 (see tab. 6)
- The number of basis functions retained in the last step of the vibrational calculation, which is determined by an energy criterium (see tab. 1)
- The order of the Taylor expansion of the μ -matrix in H_1 (see tab. 2)
- The maximum value of the summation indices k_1, k_2 in the second and third order corrective term of the effective Hamiltonian (see tab. 2)
- The maximum value of the summation indices k_1, k_2, k_3 in the fourth order corrective term of the effective Hamiltonian (see tab. 3)
- The order of the generalized perturbation expansion (see tabs. 2, 3 and 4)

4.2.1 Convergence of the H_0 spectrum

To implement the generalized perturbation method, one need to solve first the eigenvalue problem for the H_0 Hamiltonian. This has been done by performing vibrational mean field configuration interaction (VMFCI) calculations as implemented in the computer code CONVIV developed by Cassam-Chenaï and Liévin [52]. The method will not be described in details, it suffices to say here, that it is a variational method that encom-

passes as particular cases the vibrational self-consistent field (VSCF) method [53–55] and the vibrational configuration interaction (VCI) [56,57]. But it is much more flexible, because it allows one to contract arbitrary groups of dof in a hierarchical manner, while controlling the growth of the basis set size by discarding high energy product basis functions, according to a so-called ”contraction-truncation scheme“. It is different from the traditional contraction method [58–62], because the Hamiltonian of an active group of dof takes into account the effect of the mean field of the spectator groups as proposed by Bowman and Gazdy [63]. However, in contrast with [63], for a given partition of the dof, self-consistency is achieved by iterating VCI calculations for active groups of dof in the mean field of the spectator groups.

The contraction-truncation scheme employed in this work can be written in our notation as MSP-VSCFCI(15,17,15,17)/VSCFCI($\nu_1 - \nu_3$; 48000)/VCI(Z).

MSP-VSCFCI(15,17,15,17) means that, starting from 15 harmonic oscillator (HO) functions for mode 1 (using the conventional spectroscopic ordering), 153 HO product functions such that the sum of quantum numbers is less than 17 for mode 2, 680 HO product functions such that the sum of quantum numbers is less than 15 for mode 3, and 969 HO product functions such that the sum of quantum numbers is less than 17 for mode 4, we have performed a minimal symmetry preserving VMFCI, that is to say, a contracted CI calculation, contracting only degenerate dof together in the mean field of the other dof, and that we have iterated such a VMFCI calculation with the same partitioning up to achieve self-consistency: vibrational self-consistent configuration interaction calculation (VSCFCI). Self-consistency was considered sufficient when after 7 steps the zero point energies (ZPE) of all four modes, mean field Hamiltonians were the same to at least 10 digits. At step 8, the stretching modes 1 and 3 were contracted with truncation of the product basis functions at 48000 cm^{-1} on the sum of the energy of their components. After a single iteration, the ZPE of the three contractions (modes 1-3, mode 2, mode 4) were equal to within $2 \times 10^{-5} \text{ cm}^{-1}$, so we considered that self-consistency was achieved and that step 8 and 9 constitute again a VSCFCI calculation for this new partition. It is denoted by VSCFCI($\nu_1 - \nu_3$; 48000). Finally, all dof were contracted in a vibra-

tional configuration interaction (VCI) step. Different truncation thresholds on the sum of component energies, Z , were considered for constructing the final product basis set.

The convergence of the first vibrational levels that are well-determined experimentally, with the expansion order of the NRT methane PES [33] in terms of normal coordinates along with the effect of the μ -tensor expansion order in the ($J = 0$)-Watson Hamiltonian are displayed in tabs. 5 and 6 of Appendix A. Similar studies have been conducted in the past on different molecules and/or PES [16,52,64–68], and the results obtained in this work essentially confirm previous findings. For the rest of the study, we have chosen a PES re-expansion of 10^{th} order in normal coordinates and a μ -tensor second order expansion in H_0 (see Appendix A for more details).

insert Tab. 1 here.

Having fixed these two parameters, we now discuss the convergence with respect to the threshold Z shown in tab. 1. Tab. 1 shows that for $Z=19318 \text{ cm}^{-1}$, one can expect the ZPE to be converged to within the hundredth of cm^{-1} and the fundamental transitions to the tenth of cm^{-1} . The 24 sublevels of the octad (levels between 3800 cm^{-1} and 4600 cm^{-1}) are expected to be converged to at least the cm^{-1} accuracy. All eigenstates up to 14851 cm^{-1} above ZPE (16864 eigenvalues, counted with their degeneracy, and eigenvectors of a square matrix of dimension 74978) have been obtained for $Z=19318 \text{ cm}^{-1}$ and are available upon request. They are not reported in this article, but of course, convergency deteriorates as the energy increases. However, in the implementation of the generalized Rayleigh-Schrödinger perturbation method, the H_0 eigenstates are used in corrective terms and their contribution to the vibrational ground state effective Hamiltonian decreases as their energy increases. So, we have not found it justified to go beyond $Z=19318 \text{ cm}^{-1}$.

Moreover, preliminary studies of our 10^{th} order polynomial PES shows that it has artefactual barriers. In particular, it is not reliable above 10600 cm^{-1} above the ZPE in the direction of the bending dof. Since the highest initial HO basis functions have already non negligible weight in these pathological regions of the potential, it is not desirable

to increase the size of the initial HO basis set, nor to retain in VMFCI steps high energy contraction basis functions that might have some weight on the highest HO functions. Further work is in progress to overcome these difficulties with the help of other types of initial basis functions.

Despite the limitations of the potential and of our variational calculation, we note that the agreement with the levels derived from experiment by Albert et al. [69], is very satisfactory: most tabulated levels are within the cm^{-1} accuracy, except for bands attributed to harmonics of the ν_4 mode. The quality of the calculated wave numbers for this mode deteriorates with the largest threshold. We anticipate that this has to do with the problem, noticed above, of the Taylor series expansion of the NRT potential. The HO basis set probe already too much of the pathological region of the PES expansion with $Z=19318 \text{ cm}^{-1}$. However, the possible discrepancies in high energy vibrational states used in the perturbation series of the effective Hamiltonians will not be further discussed in the present article since, again, the accuracy of these states is not crucial for our rotational level calculations. We refer the reader interested in the *ab initio* calculation of methane vibrational spectra to the abundant literature on this topics, see refs. [32,33,47,70–75] to quote a few recent works.

4.2.2 Convergence of the rotational calculations

The convergence of the third order of generalized Rayleigh-Schrödinger perturbation has been assessed with respect to the threshold on the number of eigenstates of H_0 used to truncate the series in the expression of second and third order corrective terms. Not surprisingly, the rate of convergence decreases as J increases. However, in Tab. 2, for μ Taylor-expanded to fourth order in H_1 , the calculation with summation over 16863 wave functions (all states up to wave number of about 14851.5 cm^{-1} above ZPE included) shows that summation over 8281 wave functions (all states up to wave number of about 13062.7 cm^{-1} above ZPE included) allows one to converge four decimal places up to $J = 10$.

insert Tab.2 here

For the fifth order μ -expansion, convergence with respect to the maximum value of k_1, k_2 indices seems to follow the same pattern as for the fourth order μ -expansion. So, we have limited ourself to summation over 8281 wave functions. Given the expected oscillatory behaviour of the μ -expansion noticed in [16], we infer that the fourth order μ -expansion allows one to converge the $J = 1$ energy levels to $1.5 \times 10^{-4} \text{ cm}^{-1}$, that is a relative error of about 1.5×10^{-5} . The same order of magnitude for the relative error is observed for the whole range of J -values. Given the accuracy of the electronic calculations, it is probably not justified to aim at a tighter convergence.

The contribution of the fourth order of generalized Rayleigh-Schrödinger perturbation is displayed in Tab. 3. It can be appreciated by comparing, in the central part of Tab.3, the columns "0", which is actually a third order calculation, and the column "4161", which displays essentially converged numbers for a fourth order effective Hamiltonian with truncated sums at $k_i \leq 4161$. At $J = 10$, the relative contribution of the fourth order term is still less than 6×10^{-6} , so fairly small compared to errors probably arising from the electronic calculations.

insert Tab.3 here

The convergence of the spectra with respect to the maximum value of k_1, k_2, k_3 indices in the fourth order corrective term, Eq.(26), is faster than for the lower order terms, as expected: four decimal places of the tabulated numbers are essentially converged when summing over only 2085 vibrational eigenfunctions with respect to the larger calculation, where summation is performed over 4160 eigenfunctions. So, our best converged number would be the last column, reporting a calculation with μ expanded at the fifth order and combining a summation truncation threshold of 8282 up to third order, and a threshold of 4161 at fourth order. However, our best match with empirical energy levels (reported in Tab.4) would occur for a fourth order perturbation calculation with μ expanded at the fourth order.

4.3 Contact Transformations: truncation, ordering and convergence of effective rotational Hamiltonian

After having expanded the PES $U(Q_k)$ and the reciprocal inertia tensor $\mu(Q_k)$ in the Taylor series of normal coordinates Q_k the full vibration-rotation Hamiltonian, Eq. (1), is represented as a sum of elementary terms $H(X, Y) = \sum_{i,j} X_i Y_j$, each term being a product of a vibrational operator of the form $X_i = \{C_{jk\dots rt\dots}^i Q_j Q_k \dots P_r P_t \dots\}$ and of a rotational operator $Y_j \in \{1, \Pi_\alpha, \Pi_\beta \Pi_\gamma, \dots\}$. Following the previously developed CT-algorithm [41] these terms are first converted to a ‘‘canonical representation’’ $H(X, Y) = \sum_i X'_i Y'_i$ based on products of hermitian or anti-hermitian combinations $X'_i = V_{\mathbf{nm}}^{\theta, \Gamma}$ of creation and annihilation operators $(a_1^+)^{n_1} (a_2^+)^{n_2} \dots (a_1)^{m_1} (a_2)^{m_2} \dots$ for vibration normal modes and symmetrized combinations $Y'_j = R_{k_1, k_2, k_3}^{\theta, \Gamma}$ of angular momentum operators. Here Γ stands for a symmetry type and θ for the hermiticity index. The definition and properties of these elementary operators can be found in [41]. The vector indices $\mathbf{n} = (n_1, n_2, \dots)$ and $\mathbf{m} = (m_1, m_2, \dots)$ correspond to powers of vibration operators and indices k_1, k_2, k_3 correspond to powers of body-fixed Eckart frame ladder components Π_+, Π_-, Π_z of the total angular momentum. The transformation from operators expressed in terms of normal coordinates and conjugate momenta to symmetry-adapted vibrational operators, $V_{\mathbf{nm}}^{\theta, \Gamma}$, expressed in terms of creation and annihilation operators, as well as the transformation from operators expressed in terms of angular momentum operators to symmetry-adapted rotational operators, $R_{k_1, k_2, k_3}^{\theta, \Gamma}$, expressed in terms of ladder operators are performed by following the technique described by Rey et al. [51] for symmetric molecules.

In order to perform CT of the full vibration-rotation Hamiltonian to derive an effective rotational one, we use the fast algorithm implemented in the MOL-CT program suite as described by Tyuterev, Tashkun and co-workers [41,50]. In order to be applicable to general systems encountered in molecular spectroscopy, this computer code has been implemented for low-symmetry subgroups of molecular point groups. For instance, it allows for a classification of Hamiltonian terms based on C_s -symmetry (provided the molecu-

lar symmetry group contains a subgroup isomorphic to C_s , such as in methane, where $C_s \subset T_d$) and also it allows for a complete characterisation of the commutator/anti-commutator algebra for vibrational $V_{\mathbf{nm}}^{\theta,\Gamma}$ and rotational $R_{k_1,k_2,k_3}^{\theta,\Gamma}$ operators [41]. The trade-off of such a representation is that, for high-symmetry molecules such as methane, it requires a larger number of Hamiltonian components than a representation which would use the full symmetry. As an example, the Taylor series expansion of the full rotation-vibration Hamiltonian for methane contains more than 60000 terms at fourth order and more than 900000 terms at sixth order according to the Amat-Nielsen ordering scheme [39]. Even though the algorithm of MOL_CT based on the exact analytical formulas for all contributions in commutators and anti-commutators $[V_{\mathbf{nm}}^{\theta,\Gamma}, V_{\mathbf{n}'\mathbf{m}'}^{\theta',\Gamma'}]_{\pm}$ and $[R_{\mathbf{k}}^{\theta,\Gamma}, R_{\mathbf{k}'}^{\theta',\Gamma'}]_{\pm}$ is very fast, the huge number of combination of the terms in the Baker-Campbell-Hausdorff perturbation expansion makes it necessary to choose an optimal selection of the contributions.

There exists many ordering schemes in spectroscopic literature to sort vibration-rotation contributions expressed in terms of normal-mode operators. The most well-known are due to Amat-Nielsen [39], Oka [76], Parker-Watson and collaborators [13], but many other possibilities could be considered to optimize the final accuracy over computational cost ratio. A given ordering-selection scheme, (which will be called ‘‘ansatz’’ in what follows¹) depends on the type of terms which are expected to be important in the effective Hamiltonian.

It is known that, Wigner theorem of perturbation theory can be extended to the CT method [8,9]. Consequently, only one S_1 generator of CT is required to get a second order effective Hamiltonian, and two generators S_1, S_2 are sufficient to compute a fourth order one. It is also well known, that, at a given order of CT, a fewer number of anharmonicity and vibrational Coriolis terms are required for rotational CT calculations than for vibrational ones [9,13,39]. In this paper we present two ansätze, denoted A1 and A2, for CT calculations of methane rotational Hamiltonian in the ground vibrational state.

¹ A similar terminology is often used in electronic structure calculations to denote a set up corresponding to selected contributions

These ordering-selection schemes were found to give optimum accuracy/CPU time ratio for the 2nd order and 4th order CT respectively.

More precisely, denoting by $N(\text{CT})$ for the number of S-generators and by $o(\text{CT})$ the CT order according to the algorithm as explained in refs. [8,9,41], the A1 ansatz corresponds to a standard Amat-Nielsen ordering scheme at second order: $N(\text{CT})=1$, $o(\text{CT})=2$, PES expanded up to cubic terms $\sim K_3Q^3$ and reciprocal inertia tensor up to quadratic terms $\sim \mu_2Q^2$. In the A2 ansatz, higher terms are accounted for: $N(\text{CT})=2$, $o(\text{CT})=4$, the PES is expanded up to quartic terms $\sim K_4Q^4$, the reciprocal inertia tensor up to quartic terms $\sim \langle \mu_4Q^4 \rangle$ in the diagonal part of the centrifugal distortion terms.

The results of our calculations are given in Tab.4. A clear improvement of the agreement with the levels derived from experiment is observed with increasing order of CT.

4.4 Numerical convergence of the two independent approaches

In Tab. 4, the results of CT(1,2) using A1 scheme, are also compared to those of second order generalized perturbation and that of CT(2,4) using A2 scheme with those of third order generalized perturbation. The first pair corresponds to effective Hamiltonians including quartic centrifugal distortion effects, while the second pair corresponds to effective Hamiltonians including up to sextic centrifugal distortion terms. Since the A2 calculation is limited to a quartic μ -tensor expansion, the generalized perturbation results presented in the table, are those also obtained with a quartic μ -tensor expansion. A comparison of sixth order CT with fourth order generalized perturbation has not been included. However, as we have seen, the corrections with respect to A2 and Pert(3) are small, at least up to $J = 10$.

Insert Tab.4 here

Inspecting first the effective quartic rotational Hamiltonian, we see that the one derived from generalized perturbation is clearly closer to empirical wave numbers than that

obtained from A1 compared to the STDS results [77], obtained with the parameters of [78]. This is not surprising, since the orders of the Hamiltonian components included in the two methods are not the same. Pert(2) takes into account many more effects such as the full vibrational anharmonicity, and a quartic μ -expansion in factor of total angular momentum component operators, whereas CT(1,2) is limited to cubic anharmonic terms of the PES and a quadratic μ -expansion. But, in contrast with Pert(2), in the CT(1,2) calculation, the full vibrational eigenvalue problem did not have to be solved prior to the effective Hamiltonian derivation.

However, the results of CT(2,4) using A2 scheme already catch up with those of Pert(3): the differences between the predicted levels are one order of magnitude (or more at low J -values) smaller than the differences between the levels obtained from the quartic Hamiltonians. The relative errors on sextic Hamiltonian eigenvalue differences are actually of the same order of magnitude as fourth order perturbative corrections containing octic centrifugal distortion, or as the relative difference with the empirical results (also obtained from an empirical octic Hamiltonian), and perhaps smaller than the relative errors on the equilibrium geometry or the PES force constants.

5 Conclusion

The construction of effective rotational Hamiltonians and accurate calculations of rotational spectra for polyatomic molecules from *ab initio* potential energy functions is known to be quite a challenging issue. Very few studies are available in this field for molecules having a number of atoms, $N \geq 5$. A recent improvement of *ab initio* electronic calculations for methane has allowed for a precise determination of the molecular equilibrium geometry and of the ground electronic state PES [33]. The latter has been used in this work, in a rectilinear normal coordinates representation for the benchmark calculations of rotational energies up to $J = 10$.

The main objective of the present study was to compare numerically the two different

approaches together. As far as we are aware, beside our previous works [16,33], only one theoretical calculation by Wang and Sibert [72] has predicted methane rotational levels beyond $J = 1$, and none beyond $J = 3$. Hence, the importance of this comparison with the same electronic calculation starting point for the two *a priori* independent ro-vibrational theoretical methods that have proved able to reach high J -values.

The comparison is very satisfactory, because the differences between the predicted rotational spectra are decreasing as the orders of the two methods increase. This important finding should be ascertained in the future by going to higher orders, i.e. beyond the comparison of sextic effective rotational Hamiltonians. However, as a matter of fact, our sextic Hamiltonians give energy levels as close to the empirical levels as they could be expected to lie, at this order of centrifugal distortion. So, this study confirms the effectiveness of both approaches to the prediction of rotational spectra of polyatomic molecules.

Another positive conclusion that can be drawn from this work is that, our two independent methods, which is also different from the one used in [33], confirm the quality of the NRT methane PES for rotational and vibrational spectra predictions.

The computational pitfalls for both methods are completely different, as the result, the two approaches appear to be complementary. The current implementation of the generalized perturbation method starts from the full ($J = 0$)-vibrational Hamiltonian, and therefore, accounts for fine vibrational effects even at low order of perturbation. Its main bottlenecks are arguably the slow convergence of the μ -expansion and the necessity to obtain, and to sum over, a large set of vibrational eigenfunctions. In the CT approach with the harmonic oscillator zeroth-order Hamiltonian, the advantage is that one can handle elementary vibration-rotation terms without truncating their matrix representation, thus, cut-offs for intermediate summations over vibrational quantum numbers are not required. The limitations are related to the efficiency in handling an exponentially growing number of Hamiltonian components that one can achieve.

Work in progress to take advantage of the full molecular symmetry within the tensorial

algebra formalism, that is used in some Hamiltonian transformation steps, should alleviate this limitation for high-symmetry species such as methane. A similar endeavour for the use of non Abelian symmetry in the computer code suite, calculating generalized perturbation effective Hamiltonians, will be undertaken.

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Appendix A: Convergence with respect to the Taylor expansions of U and μ in H_0

insert Tab.5 here.

Table 5 displays the results of three similar VMFCI calculations (same contraction/truncation schemes except for a slight difference for order 8 where the initial HO basis for mode ν_4 was limited to quantum number $n \leq 14$, instead of $n \leq 16$, because high quantum number HO functions probe a pathological domain of the PES polynomial expansion and produce unphysical results). The final VCI calculations, truncated on the sum of the energy of product function components at $Z = 14918 \text{ cm}^{-1}$, have all about 16000 basis functions. This is enough to converge the ZPE to the tenth of cm^{-1} and the fundamental transitions to the cm^{-1} accuracy. The convergence with PES expansion order in normal

coordinates is slow as already demonstrated in previous studies [64–66]. The μ -tensor is expanded at order 0 in the three calculations. It is worth noting that the $\nu_3 + \nu_4$ levels of the octad in italics are not in the experimental order. At order 6 and 10, the A1 level is found before the E and F1 levels, whereas at order 8 the E level is swapped with the A1 level. Note however, that the two highest tabulated levels are found in the right order, in contrast with our previous studies conducted with the Lee, Martin and Taylor PES [30]. We stopped the present study at order 10, which results already in 21884 terms in the polynomial expansion. We believe that the tenth order expansion in rectilinear normal coordinates is a reasonably good approximation to the original PES in curvilinear coordinates, whose variational treatment [33] is shown in the last column. However, care should be exercised in the comparison, since in [33] the exact kinetic operator is used, whereas in the other calculations presented in Tab.5, the μ -tensor is Taylor-expanded to zeroth order. Also, in [33], a fairly small basis set of 131524 HO product basis functions was used, whereas for orders 6 and 10, we started the VMFCI scheme with 1512221400 HO product basis functions. Note that, with the exact kinetic operator and the original NRT PES, Nikitin et al. also found an inversion in the $\nu_3 + \nu_4$ levels.

insert Tab.6 here.

We assume that convergence with respect to PES expansion order is not correlated to convergence with respect to μ -tensor expansion. So, now, we fix the PES expansion order to 10 and study the effect of μ -tensor expansion order on energy levels. From order 1 and onwards, the correct order is found for the $\nu_3 + \nu_4$ E, F1 and A1 energy levels. So although small, Coriolis coupling can determine the ordering of quasi-degenerate levels. Order 2 results are the same as those of order 4 within a few hundredth of cm^{-1} for the tabulated numbers. This accuracy is considered as sufficient for the application of the generalized Rayleigh-Schrödinger method. The number of Coriolis coupling terms in our Eckart-Watson Hamiltonians is 5274 at order 2 and 40223 at order 4 of μ -tensor expansion, so significant computer resources savings can be achieved, with little loss of accuracy.

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Table captions

Table 1

Energies in cm^{-1} of methane vibrational levels for increasing VCI truncation thresholds. In all calculations, the PES is expanded to 10^{th} order in normal coordinates and the μ -tensor to second order. irreps.: irreducible representation label, nb.: number of, ZPE: zero point energy. More digits than significant physically are provided to appreciate numerical convergency.

Table 2

Rotational energy levels in cm^{-1} at order 3 of generalized perturbation theory. The convergence of rotational levels of methane vibrational ground state, (the $J = 0$ level is set to 0 cm^{-1}), is displayed for different μ -matrix Taylor expansion orders in normal coordinates and with respect to different truncation thresholds on the allowed value for the indices k_1, k_2 of vibrational wave functions appearing in Eqs. (24) and (25).

Table 3

Rotational energy levels in cm^{-1} at order 4 of generalized perturbation theory. The convergence of rotational levels of methane vibrational ground state is displayed with respect to different truncation thresholds on the allowed value for the indices k_1, k_2, k_3 of vibrational wave functions appearing in Eqs. (24), (25) and (26). The μ -matrix is expanded at order 5 in normal coordinates in all calculations. The column “max k in $E^{(4)} = 0$ ” corresponds actually to the third order of perturbation theory, since there is no term in the sums of $E^{(4)}$.

Table 4

Comparison of rotational levels (in cm^{-1}) given by generalized perturbation and contact transformation theories. Notation CT(N,M) stands for N contact transformations developed up to order M. The associated ordering schemes ("ansätze") are specified in sect. 4.3. Order two of generalized perturbation theory, Pert(2) and CT(1,2) calculations gives effective rotational Hamiltonians for methane vibrational ground state, H_{rot} , going up to fourth power in components of the total angular momentum, Π . Order three of generalized perturbation theory, Pert(3) and CT(2,4) calculations gives an H_{rot} going up to sixth power in components of Π . Generalized perturbation calculations were performed with μ developed to the fourth power since this is more comparable to CT(2,4) and maximum k -value of 16864, to insure convergency. Empirical values from the STDS code [77], based on the parameters of Roche and Champion [78] are provided for comparison.

Table 5

Energies in cm^{-1} of methane vibrational levels for increasing PES expansion orders in rectilinear normal coordinates. In all VMFCI calculations, the μ -tensor is expanded to zeroth order, and the VCI truncation thresholds of the last step is 14918 cm^{-1} . NRT refers to the variational calculation of ref. [33] for the original PES in curvilinear coordinates. Abréviations as in Tab. 1. Levels not in the experimental order are italicised.

Table 6

Energies in cm^{-1} of methane vibrational levels for increasing μ -expansion orders. In all calculations, the PES is expanded to 10th order, and the VCI truncation thresholds are all equal to 14918 cm^{-1} giving about 16000 basis functions in this last VMFCI step. Abréviations as in Tab. 1. Levels not in the experimental order are italicised.

Table 1

**Energies in cm^{-1} of the vibrational levels of methane
for increasing VCI truncation thresholds**

| Assignment | irreps. | Z= | 14918 | 17955 | 19318 | obs |
|---------------------|---------|----|-------------|-------------|-------------|----------|
| ZPE | A1 | | 9703.183153 | 9703.158167 | 9703.151888 | |
| ν_4 | F2 | | 1310.884071 | 1310.701941 | 1310.683512 | 1310.761 |
| ν_2 | E | | 1533.357656 | 1533.244456 | 1533.215238 | 1533.333 |
| $2\nu_4$ | A1 | | 2586.723627 | 2586.190593 | 2586.023517 | 2587.043 |
| $2\nu_4$ | F2 | | 2614.226307 | 2613.824241 | 2613.706418 | 2614.261 |
| $2\nu_4$ | E | | 2624.801377 | 2624.486356 | 2624.396720 | 2624.618 |
| $\nu_2 + \nu_4$ | F2 | | 2830.167101 | 2829.825414 | 2829.760068 | 2830.316 |
| $\nu_2 + \nu_4$ | F1 | | 2846.040115 | 2845.778627 | 2845.731981 | 2846.074 |
| ν_1 | A1 | | 2916.671492 | 2916.557698 | 2916.540868 | 2916.481 |
| ν_3 | F2 | | 3019.625077 | 3019.495883 | 3019.484118 | 3019.493 |
| $2\nu_2$ | A1 | | 3063.474918 | 3063.265494 | 3063.257150 | 3063.646 |
| $2\nu_2$ | E | | 3065.029711 | 3064.830728 | 3064.822739 | 3065.141 |
| $3\nu_4$ | F2 | | 3870.894713 | 3867.192519 | 3866.772845 | 3870.488 |
| $3\nu_4$ | A1 | | 3909.883837 | 3907.095415 | 3906.729045 | 3909.201 |
| $3\nu_4$ | F1 | | 3922.273060 | 3919.957713 | 3919.724701 | 3920.510 |
| $3\nu_4$ | F2 | | 3932.285535 | 3930.269216 | 3930.061572 | 3930.923 |
| $\nu_2 + 2\nu_4$ | E | | 4101.807398 | 4099.255006 | 4098.520904 | 4101.393 |
| $\nu_2 + 2\nu_4$ | F1 | | 4129.725405 | 4127.634887 | 4127.042967 | 4128.763 |
| $\nu_2 + 2\nu_4$ | A1 | | 4133.601985 | 4131.860209 | 4131.385342 | 4132.861 |
| $\nu_2 + 2\nu_4$ | F2 | | 4143.621528 | 4141.941759 | 4141.443125 | 4142.865 |
| $\nu_2 + 2\nu_4$ | E | | 4152.309114 | 4150.845530 | 4150.422342 | 4151.205 |
| $\nu_2 + 2\nu_4$ | A2 | | 4163.053460 | 4161.727155 | 4161.344455 | 4161.849 |
| $\nu_1 + \nu_4$ | F2 | | 4224.846117 | 4223.912983 | 4223.748102 | 4223.462 |
| $\nu_3 + \nu_4$ | F2 | | 4320.648401 | 4319.634596 | 4319.416652 | 4319.212 |
| $\nu_3 + \nu_4$ | E | | 4323.243001 | 4322.274921 | 4322.094240 | 4322.178 |
| $\nu_3 + \nu_4$ | F1 | | 4323.243001 | 4322.820571 | 4322.635258 | 4322.590 |
| $\nu_3 + \nu_4$ | A1 | | 4323.801743 | 4322.946229 | 4322.742605 | 4322.704 |
| $2\nu_2 + \nu_4$ | F2 | | 4348.714881 | 4347.127873 | 4346.629221 | 4348.716 |
| $2\nu_2 + \nu_4$ | F1 | | 4364.378640 | 4363.022261 | 4362.609191 | 4363.607 |
| $2\nu_2 + \nu_4$ | F2 | | 4379.583223 | 4378.433870 | 4378.093749 | 4378.947 |
| $\nu_1 + \nu_2$ | E | | 4435.983506 | 4435.280907 | 4435.106450 | 4435.120 |
| $\nu_2 + \nu_3$ | F1 | | 4538.366726 | 4537.636977 | 4537.451003 | 4537.548 |
| $\nu_2 + \nu_3$ | F2 | | 4544.486884 | 4543.787163 | 4543.611442 | 4543.757 |
| $3\nu_2$ | E | | 4592.218519 | 4591.193082 | 4590.906703 | 4592.028 |
| $3\nu_2$ | A2 | | 4595.819982 | 4594.857697 | 4594.594324 | 4595.269 |
| $3\nu_2$ | A1 | | 4595.960023 | 4594.981484 | 4594.711558 | 4595.503 |
| nb. basis functions | | | 15803 | 47162 | 74978 | |

Table 2

Rotational energy levels in cm^{-1} at order 3 of generalized perturbation theory

| μ -expansion order max k in sums J | irreps. | 4 | | | | | 5 | | | |
|--|---------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| | | 1052 | 2086 | 4161 | 8282 | 16864 | 1052 | 2086 | 4161 | 8282 |
| 1 | F1 | 10.48171 | 10.48163 | 10.48162 | 10.48161 | 10.48161 | 10.48157 | 10.48148 | 10.48147 | 10.48146 |
| 2 | E | 31.44232 | 31.44208 | 31.44204 | 31.44200 | 31.44200 | 31.44190 | 31.44163 | 31.44159 | 31.44155 |
| 2 | F2 | 31.44259 | 31.44235 | 31.44231 | 31.44227 | 31.44227 | 31.44217 | 31.44189 | 31.44185 | 31.44182 |
| 3 | F1 | 62.87618 | 62.87571 | 62.87563 | 62.87556 | 62.87556 | 62.87534 | 62.87480 | 62.87472 | 62.87465 |
| 3 | F2 | 62.87724 | 62.87678 | 62.87670 | 62.87663 | 62.87663 | 62.87641 | 62.87586 | 62.87579 | 62.87571 |
| 3 | A2 | 62.87857 | 62.87811 | 62.87803 | 62.87796 | 62.87796 | 62.87774 | 62.87720 | 62.87712 | 62.87705 |
| 4 | A1 | 104.77351 | 104.77277 | 104.77264 | 104.77252 | 104.77252 | 104.77212 | 104.77122 | 104.77109 | 104.77098 |
| 4 | F1 | 104.77537 | 104.77463 | 104.77450 | 104.77438 | 104.77438 | 104.77399 | 104.77309 | 104.77296 | 104.77284 |
| 4 | E | 104.77670 | 104.77596 | 104.77583 | 104.77572 | 104.77571 | 104.77532 | 104.77442 | 104.77429 | 104.77417 |
| 4 | F2 | 104.78068 | 104.77996 | 104.77983 | 104.77971 | 104.77971 | 104.77932 | 104.77842 | 104.77829 | 104.77817 |
| 5 | F1 | 157.12534 | 157.12430 | 157.12410 | 157.12393 | 157.12392 | 157.12328 | 157.12195 | 157.12175 | 157.12158 |
| 5 | F2 | 157.12892 | 157.12789 | 157.12769 | 157.12752 | 157.12752 | 157.12687 | 157.12554 | 157.12535 | 157.12517 |
| 5 | E | 157.13819 | 157.13719 | 157.13700 | 157.13683 | 157.13682 | 157.13618 | 157.13485 | 157.13466 | 157.13449 |
| 5 | F1 | 157.13991 | 157.13892 | 157.13873 | 157.13856 | 157.13855 | 157.13791 | 157.13658 | 157.13639 | 157.13622 |
| 6 | E | 219.91487 | 219.91353 | 219.91326 | 219.91302 | 219.91301 | 219.91201 | 219.91018 | 219.90991 | 219.90967 |
| 6 | F2 | 219.91645 | 219.91511 | 219.91484 | 219.91460 | 219.91460 | 219.91360 | 219.91176 | 219.91149 | 219.91126 |
| 6 | A2 | 219.92125 | 219.91991 | 219.91964 | 219.91940 | 219.91939 | 219.91839 | 219.91656 | 219.91629 | 219.91606 |
| 6 | F2 | 219.93816 | 219.93691 | 219.93664 | 219.93640 | 219.93639 | 219.93540 | 219.93358 | 219.93331 | 219.93307 |
| 6 | F1 | 219.94266 | 219.94141 | 219.94114 | 219.94091 | 219.94090 | 219.93991 | 219.93809 | 219.93782 | 219.93758 |
| 6 | A1 | 219.94663 | 219.94540 | 219.94513 | 219.94489 | 219.94488 | 219.94390 | 219.94208 | 219.94181 | 219.94157 |
| 7 | F1 | 293.12486 | 293.12327 | 293.12291 | 293.12259 | 293.12258 | 293.12110 | 293.11871 | 293.11834 | 293.11803 |
| 7 | F2 | 293.12842 | 293.12682 | 293.12646 | 293.12615 | 293.12614 | 293.12465 | 293.12226 | 293.12190 | 293.12159 |
| 7 | A2 | 293.15606 | 293.15464 | 293.15428 | 293.15397 | 293.15396 | 293.15249 | 293.15011 | 293.14975 | 293.14944 |
| 7 | F2 | 293.16643 | 293.16499 | 293.16463 | 293.16433 | 293.16432 | 293.16285 | 293.16047 | 293.16011 | 293.15981 |
| 7 | E | 293.17110 | 293.17056 | 293.17020 | 293.16990 | 293.16989 | 293.16842 | 293.16605 | 293.16569 | 293.16538 |
| 7 | F1 | 293.18054 | 293.17914 | 293.17879 | 293.17848 | 293.17847 | 293.17701 | 293.17464 | 293.17428 | 293.17398 |
| 8 | A1 | 376.73286 | 376.73110 | 376.73063 | 376.73024 | 376.73023 | 376.72810 | 376.72509 | 376.72463 | 376.72424 |
| 8 | F1 | 376.73614 | 376.73436 | 376.73390 | 376.73351 | 376.73349 | 376.73136 | 376.72836 | 376.72790 | 376.72751 |
| 8 | E | 376.73807 | 376.73627 | 376.73581 | 376.73542 | 376.73541 | 376.73327 | 376.73027 | 376.72981 | 376.72942 |
| 8 | F2 | 376.78828 | 376.78683 | 376.78637 | 376.78599 | 376.78598 | 376.78386 | 376.78088 | 376.78043 | 376.78004 |
| 8 | F1 | 376.80718 | 376.80566 | 376.80520 | 376.80482 | 376.80480 | 376.80270 | 376.79973 | 376.79927 | 376.79889 |
| 8 | E | 376.82368 | 376.82227 | 376.82181 | 376.82143 | 376.82141 | 376.81932 | 376.81635 | 376.81590 | 376.81552 |
| 8 | F2 | 376.82866 | 376.82725 | 376.82679 | 376.82641 | 376.82640 | 376.82430 | 376.82134 | 376.82089 | 376.82051 |
| 9 | F1 | 470.72000 | 470.71819 | 470.71762 | 470.71715 | 470.71713 | 470.71415 | 470.71049 | 470.70992 | 470.70945 |
| 9 | F2 | 470.72339 | 470.72154 | 470.72096 | 470.72049 | 470.72047 | 470.71749 | 470.71384 | 470.71326 | 470.71279 |
| 9 | E | 470.80110 | 470.80074 | 470.80017 | 470.79971 | 470.79969 | 470.79674 | 470.79312 | 470.79256 | 470.79209 |
| 9 | F1 | 470.80830 | 470.80703 | 470.80646 | 470.80600 | 470.80598 | 470.80304 | 470.79942 | 470.79885 | 470.79839 |
| 9 | A1 | 470.83396 | 470.83250 | 470.83194 | 470.83147 | 470.83146 | 470.82852 | 470.82492 | 470.82435 | 470.82389 |
| 9 | F1 | 470.85800 | 470.85676 | 470.85620 | 470.85574 | 470.85572 | 470.85279 | 470.84920 | 470.84864 | 470.84818 |
| 9 | F2 | 470.86806 | 470.86685 | 470.86628 | 470.86582 | 470.86581 | 470.86288 | 470.85930 | 470.85873 | 470.85827 |
| 9 | A2 | 470.87591 | 470.87473 | 470.87417 | 470.87371 | 470.87369 | 470.87078 | 470.86719 | 470.86663 | 470.86617 |
| 10 | E | 575.05502 | 575.05337 | 575.05267 | 575.05211 | 575.05209 | 575.04802 | 575.04369 | 575.04299 | 575.04243 |
| 10 | F2 | 575.05641 | 575.05474 | 575.05404 | 575.05348 | 575.05346 | 575.04939 | 575.04506 | 575.04436 | 575.04380 |
| 10 | A2 | 575.05942 | 575.05769 | 575.05699 | 575.05643 | 575.05641 | 575.05234 | 575.04801 | 575.04732 | 575.04676 |
| 10 | F2 | 575.17379 | 575.17305 | 575.17236 | 575.17181 | 575.17179 | 575.16776 | 575.16349 | 575.16280 | 575.16225 |
| 10 | F1 | 575.18801 | 575.18720 | 575.18651 | 575.18596 | 575.18594 | 575.18192 | 575.17766 | 575.17697 | 575.17642 |
| 10 | A1 | 575.22662 | 575.22619 | 575.22551 | 575.22496 | 575.22494 | 575.22094 | 575.21669 | 575.21601 | 575.21546 |
| 10 | F1 | 575.26346 | 575.26271 | 575.26202 | 575.26148 | 575.26146 | 575.25747 | 575.25324 | 575.25256 | 575.25201 |
| 10 | E | 575.27559 | 575.27486 | 575.27418 | 575.27364 | 575.27362 | 575.26964 | 575.26541 | 575.26473 | 575.26419 |
| 10 | F2 | 575.28908 | 575.28846 | 575.28778 | 575.28724 | 575.28722 | 575.28324 | 575.27902 | 575.27834 | 575.27780 |

Table 3

Rotational energy levels in cm^{-1} at order 4 of generalized perturbation theory

| max k in $E^{(2)}$ and $E^{(3)}$ | | 1052 | 4161 | | | | 8282 |
|------------------------------------|---------|-----------|-----------|-----------|-----------|-----------|-----------|
| max k in $E^{(4)}$ | | 1052 | 0 | 1052 | 2086 | 4161 | 4161 |
| J | irreps. | | | | | | |
| 1 | F1 | 10.48157 | 10.48147 | 10.48147 | 10.48147 | 10.48147 | 10.48146 |
| 2 | E | 31.44190 | 31.44159 | 31.44158 | 31.44158 | 31.44158 | 31.44155 |
| 2 | F2 | 31.44216 | 31.44185 | 31.44185 | 31.44185 | 31.44185 | 31.44181 |
| 3 | F1 | 62.87532 | 62.87472 | 62.87470 | 62.87470 | 62.87470 | 62.87462 |
| 3 | F2 | 62.87638 | 62.87579 | 62.87576 | 62.87576 | 62.87576 | 62.87569 |
| 3 | A2 | 62.87771 | 62.87712 | 62.87709 | 62.87709 | 62.87709 | 62.87702 |
| 4 | A1 | 104.77206 | 104.77109 | 104.77103 | 104.77103 | 104.77103 | 104.77091 |
| 4 | F1 | 104.77392 | 104.77296 | 104.77289 | 104.77289 | 104.77289 | 104.77277 |
| 4 | E | 104.77525 | 104.77429 | 104.77422 | 104.77422 | 104.77422 | 104.77410 |
| 4 | F2 | 104.77923 | 104.77829 | 104.77821 | 104.77821 | 104.77820 | 104.77809 |
| 5 | F1 | 157.12313 | 157.12175 | 157.12160 | 157.12160 | 157.12160 | 157.12142 |
| 5 | F2 | 157.12672 | 157.12535 | 157.12520 | 157.12519 | 157.12519 | 157.12502 |
| 5 | E | 157.13600 | 157.13466 | 157.13448 | 157.13447 | 157.13447 | 157.13430 |
| 5 | F1 | 157.13772 | 157.13639 | 157.13620 | 157.13620 | 157.13620 | 157.13602 |
| 6 | E | 219.91171 | 219.90991 | 219.90961 | 219.90960 | 219.90960 | 219.90936 |
| 6 | F2 | 219.91330 | 219.91149 | 219.91120 | 219.91119 | 219.91118 | 219.91094 |
| 6 | A2 | 219.91811 | 219.91629 | 219.91601 | 219.91600 | 219.91599 | 219.91575 |
| 6 | F2 | 219.93503 | 219.93331 | 219.93294 | 219.93293 | 219.93293 | 219.93269 |
| 6 | F1 | 219.93953 | 219.93782 | 219.93744 | 219.93744 | 219.93743 | 219.93719 |
| 6 | A1 | 219.94351 | 219.94181 | 219.94142 | 219.94141 | 219.94141 | 219.94117 |
| 7 | F1 | 293.12056 | 293.11834 | 293.11781 | 293.11779 | 293.11778 | 293.11747 |
| 7 | F2 | 293.12412 | 293.12190 | 293.12137 | 293.12136 | 293.12135 | 293.12103 |
| 7 | A2 | 293.15180 | 293.14975 | 293.14906 | 293.14904 | 293.14903 | 293.14872 |
| 7 | F2 | 293.16217 | 293.16011 | 293.15944 | 293.15943 | 293.15941 | 293.15911 |
| 7 | E | 293.16774 | 293.16569 | 293.16501 | 293.16500 | 293.16499 | 293.16468 |
| 7 | F1 | 293.17630 | 293.17428 | 293.17357 | 293.17355 | 293.17354 | 293.17324 |
| 8 | A1 | 376.72718 | 376.72463 | 376.72372 | 376.72369 | 376.72367 | 376.72328 |
| 8 | F1 | 376.73047 | 376.72790 | 376.72700 | 376.72697 | 376.72695 | 376.72656 |
| 8 | E | 376.73240 | 376.72981 | 376.72893 | 376.72890 | 376.72888 | 376.72849 |
| 8 | F2 | 376.78266 | 376.78043 | 376.77923 | 376.77919 | 376.77917 | 376.77879 |
| 8 | F1 | 376.80158 | 376.79927 | 376.79815 | 376.79812 | 376.79810 | 376.79772 |
| 8 | E | 376.81810 | 376.81590 | 376.81468 | 376.81465 | 376.81463 | 376.81425 |
| 8 | F2 | 376.82309 | 376.82089 | 376.81967 | 376.81964 | 376.81962 | 376.81924 |
| 9 | F1 | 470.71271 | 470.70992 | 470.70848 | 470.70843 | 470.70840 | 470.70792 |
| 9 | F2 | 470.71609 | 470.71326 | 470.71187 | 470.71181 | 470.71178 | 470.71131 |
| 9 | E | 470.79479 | 470.79256 | 470.79060 | 470.79054 | 470.79051 | 470.79004 |
| 9 | F1 | 470.80110 | 470.79885 | 470.79691 | 470.79686 | 470.79683 | 470.79636 |
| 9 | A1 | 470.82679 | 470.82435 | 470.82262 | 470.82257 | 470.82254 | 470.82207 |
| 9 | F1 | 470.85085 | 470.84864 | 470.84669 | 470.84664 | 470.84660 | 470.84614 |
| 9 | F2 | 470.86091 | 470.85873 | 470.85676 | 470.85671 | 470.85667 | 470.85621 |
| 9 | A2 | 470.86878 | 470.86663 | 470.86463 | 470.86458 | 470.86454 | 470.86408 |
| 10 | E | 575.04582 | 575.04299 | 575.04080 | 575.04070 | 575.04066 | 575.04010 |
| 10 | F2 | 575.04721 | 575.04436 | 575.04219 | 575.04210 | 575.04205 | 575.04149 |
| 10 | A2 | 575.05023 | 575.04732 | 575.04520 | 575.04511 | 575.04507 | 575.04451 |
| 10 | F2 | 575.16472 | 575.16280 | 575.15975 | 575.15966 | 575.15961 | 575.15906 |
| 10 | F1 | 575.17895 | 575.17697 | 575.17400 | 575.17390 | 575.17385 | 575.17330 |
| 10 | A1 | 575.21760 | 575.21601 | 575.21267 | 575.21257 | 575.21251 | 575.21197 |
| 10 | F1 | 575.25448 | 575.25256 | 575.24957 | 575.24947 | 575.24942 | 575.24887 |
| 10 | E | 575.26662 | 575.26473 | 575.26171 | 575.26162 | 575.26156 | 575.26102 |
| 10 | F2 | 575.28013 | 575.27834 | 575.27523 | 575.27513 | 575.27508 | 575.27454 |

Table 4

Comparison of rotational levels (in cm^{-1}) given by generalized perturbation and contact transformation theories

| J | irreps. | H_{rot} up to $\Pi^{(4)}$ | | | H_{rot} up to $\Pi^{(6)}$ | | | Empirical |
|-----|---------|-----------------------------|-----------|-----------------|-----------------------------|-----------|-----------------|-----------|
| | | Pert(2) | CT(1,2) | Pert(2)-CT(1,2) | Pert(3) | CT(2,4) | Pert(3)-CT(2,4) | |
| 1 | F1 | 10.48162 | 10.48027 | 0.00135 | 10.48161 | 10.48158 | 0.00003 | 10.48165 |
| 2 | E | 31.44202 | 31.43807 | 0.00395 | 31.44200 | 31.44191 | 0.00009 | 31.44212 |
| 2 | F2 | 31.44228 | 31.43832 | 0.00396 | 31.44227 | 31.44217 | 0.00010 | 31.44239 |
| 3 | F1 | 62.87555 | 62.86793 | 0.00762 | 62.87556 | 62.87537 | 0.00019 | 62.87578 |
| 3 | F2 | 62.87658 | 62.86893 | 0.00765 | 62.87663 | 62.87643 | 0.00020 | 62.87684 |
| 3 | A2 | 62.87786 | 62.87018 | 0.00768 | 62.87796 | 62.87776 | 0.00020 | 62.87817 |
| 4 | A1 | 104.77244 | 104.76035 | 0.01209 | 104.77252 | 104.77220 | 0.00032 | 104.77284 |
| 4 | F1 | 104.77424 | 104.76210 | 0.01214 | 104.77438 | 104.77406 | 0.00032 | 104.77470 |
| 4 | E | 104.77552 | 104.76336 | 0.01216 | 104.77571 | 104.77538 | 0.00033 | 104.77603 |
| 4 | F2 | 104.77937 | 104.76711 | 0.01226 | 104.77971 | 104.77935 | 0.00036 | 104.78001 |
| 5 | F1 | 157.12355 | 157.10652 | 0.01703 | 157.12392 | 157.12344 | 0.00048 | 157.12434 |
| 5 | F2 | 157.12702 | 157.10990 | 0.01712 | 157.12752 | 157.12702 | 0.00050 | 157.12793 |
| 5 | E | 157.13600 | 157.11867 | 0.01733 | 157.13682 | 157.13627 | 0.00055 | 157.13719 |
| 5 | F1 | 157.13767 | 157.12029 | 0.01738 | 157.13855 | 157.13799 | 0.00056 | 157.13892 |
| 6 | E | 219.91204 | 219.89009 | 0.02195 | 219.91301 | 219.91231 | 0.00070 | 219.91346 |
| 6 | F2 | 219.91357 | 219.89158 | 0.02199 | 219.91460 | 219.91389 | 0.00071 | 219.91505 |
| 6 | A2 | 219.91820 | 219.89610 | 0.02210 | 219.91939 | 219.91868 | 0.00071 | 219.91985 |
| 6 | F2 | 219.93464 | 219.91214 | 0.02250 | 219.93639 | 219.93557 | 0.00082 | 219.93677 |
| 6 | F1 | 219.93899 | 219.91639 | 0.02260 | 219.94090 | 219.94005 | 0.00085 | 219.94126 |
| 6 | A1 | 219.94284 | 219.92015 | 0.02269 | 219.94488 | 219.94402 | 0.00086 | 219.94523 |
| 7 | F1 | 293.12046 | 293.09415 | 0.02631 | 293.12258 | 293.12160 | 0.00098 | 293.12299 |
| 7 | F2 | 293.12389 | 293.09750 | 0.02639 | 293.12614 | 293.12515 | 0.00099 | 293.12655 |
| 7 | A2 | 293.15084 | 293.12381 | 0.02703 | 293.15396 | 293.15276 | 0.00120 | 293.15420 |
| 7 | F2 | 293.16085 | 293.13358 | 0.02727 | 293.16432 | 293.16311 | 0.00121 | 293.16457 |
| 7 | E | 293.16624 | 293.13884 | 0.02740 | 293.16989 | 293.16867 | 0.00122 | 293.17013 |
| 7 | F1 | 293.17455 | 293.14695 | 0.02760 | 293.17847 | 293.17720 | 0.00127 | 293.17868 |
| 8 | A1 | 376.72607 | 376.69667 | 0.02940 | 376.73023 | 376.72886 | 0.00137 | 376.73044 |
| 8 | F1 | 376.72923 | 376.69976 | 0.02947 | 376.73349 | 376.73214 | 0.00135 | 376.73372 |
| 8 | E | 376.73107 | 376.70156 | 0.02951 | 376.73541 | 376.73406 | 0.00135 | 376.73565 |
| 8 | F2 | 376.78015 | 376.74945 | 0.03070 | 376.78598 | 376.78422 | 0.00176 | 376.78587 |
| 8 | F1 | 376.79838 | 376.76724 | 0.03114 | 376.80480 | 376.80309 | 0.00171 | 376.80478 |
| 8 | E | 376.81450 | 376.78297 | 0.03153 | 376.82141 | 376.81958 | 0.00183 | 376.82129 |
| 8 | F2 | 376.81933 | 376.78769 | 0.03164 | 376.82640 | 376.82455 | 0.00185 | 376.82627 |
| 9 | F1 | 470.70936 | 470.67877 | 0.03059 | 470.71713 | 470.71525 | 0.00188 | 470.71696 |
| 9 | F2 | 470.71259 | 470.68192 | 0.03067 | 470.72047 | 470.71863 | 0.00184 | 470.72034 |
| 9 | E | 470.78964 | 470.75711 | 0.03253 | 470.79969 | 470.79717 | 0.00252 | 470.79897 |
| 9 | F1 | 470.79574 | 470.76307 | 0.03267 | 470.80598 | 470.80347 | 0.00251 | 470.80528 |
| 9 | A1 | 470.82044 | 470.78717 | 0.03327 | 470.83146 | 470.82912 | 0.00234 | 470.83096 |
| 9 | F1 | 470.84404 | 470.81021 | 0.03383 | 470.85572 | 470.85313 | 0.00259 | 470.85500 |
| 9 | F2 | 470.85384 | 470.81977 | 0.03407 | 470.86581 | 470.86317 | 0.00264 | 470.86506 |
| 9 | A2 | 470.86151 | 470.82725 | 0.03426 | 470.87369 | 470.87102 | 0.00267 | 470.87292 |
| 10 | E | 575.03852 | 575.00957 | 0.02895 | 575.05209 | 575.04952 | 0.00257 | 575.05127 |
| 10 | F2 | 575.03985 | 575.01086 | 0.02899 | 575.05346 | 575.05091 | 0.00255 | 575.05266 |
| 10 | A2 | 575.04271 | 575.01366 | 0.02905 | 575.05641 | 575.05392 | 0.00249 | 575.05567 |
| 10 | F2 | 575.15519 | 575.12343 | 0.03176 | 575.17179 | 575.16821 | 0.00358 | 575.17008 |
| 10 | F1 | 575.16895 | 575.13686 | 0.03209 | 575.18594 | 575.18242 | 0.00352 | 575.18430 |
| 10 | A1 | 575.20699 | 575.17398 | 0.03301 | 575.22494 | 575.22101 | 0.00393 | 575.22292 |
| 10 | F1 | 575.24246 | 575.20860 | 0.03386 | 575.26146 | 575.25782 | 0.00364 | 575.25978 |
| 10 | E | 575.25430 | 575.22015 | 0.03415 | 575.27362 | 575.26994 | 0.00368 | 575.27192 |
| 10 | F2 | 575.26755 | 575.23309 | 0.03446 | 575.28722 | 575.28343 | 0.00379 | 575.28542 |

Table 5

**Energies in cm^{-1} of the vibrational levels of methane
for increasing PES expansion order in rectilinear normal coordinates**

| Assignment | irreps. | ord 6 | ord 8 | ord 10 | NRT |
|---------------------|---------|--------------------|--------------------|--------------------|-----------------|
| ZPE | A1 | 9702.226768 | 9703.245519 | 9703.098960 | 9703.3981 |
| ν_4 | F2 | 1309.525446 | 1311.427855 | 1310.927299 | 1310.761 |
| ν_2 | E | 1532.468199 | 1534.053661 | 1533.438473 | 1533.332 |
| $2\nu_4$ | A1 | 2580.717572 | 2589.839545 | 2586.412638 | 2587.117 |
| $2\nu_4$ | F2 | 2609.953143 | 2615.686895 | 2614.130234 | 2614.240 |
| $2\nu_4$ | E | 2621.928428 | 2626.416225 | 2624.863233 | 2624.718 |
| $\nu_2 + \nu_4$ | F2 | 2826.362611 | 2832.816297 | 2829.928258 | 2830.477 |
| $\nu_2 + \nu_4$ | F1 | 2843.343893 | 2847.729869 | 2846.116077 | 2846.040 |
| ν_1 | A1 | 2915.547514 | 2916.520745 | 2916.639327 | 2916.483 |
| ν_3 | F2 | 3019.467966 | 3020.215269 | 3020.187468 | 3019.497 |
| $2\nu_2$ | A1 | 3060.822889 | 3065.989962 | 3063.557572 | 3063.792 |
| $2\nu_2$ | E | 3062.911523 | 3066.867957 | 3065.132466 | 3065.168 |
| $3\nu_4$ | F2 | 3859.063144 | 3879.029093 | 3870.195501 | 3870.757 |
| $3\nu_4$ | A1 | 3900.825363 | 3913.109308 | 3909.600258 | 3909.184 |
| $3\nu_4$ | F1 | 3915.273081 | 3924.989944 | 3921.990831 | 3920.529 |
| $3\nu_4$ | F2 | 3926.272865 | 3935.464430 | 3932.016176 | 3931.220 |
| $\nu_2 + 2\nu_4$ | E | 4092.419103 | 4110.851729 | 4101.136404 | 4101.782 |
| $\nu_2 + 2\nu_4$ | F1 | 4121.768210 | 4135.250256 | 4129.009970 | 4129.004 |
| $\nu_2 + 2\nu_4$ | A1 | 4126.761228 | 4139.980283 | 4133.104853 | 4133.379 |
| $\nu_2 + 2\nu_4$ | F2 | 4136.874475 | 4147.718981 | 4143.221974 | 4142.929 |
| $\nu_2 + 2\nu_4$ | E | 4146.910246 | 4155.888698 | 4152.016006 | 4151.384 |
| $\nu_2 + 2\nu_4$ | A2 | 4158.601906 | 4166.080415 | 4163.048539 | 4161.953 |
| $\nu_1 + \nu_4$ | F2 | 4220.885998 | 4225.296088 | 4224.945071 | 4223.629 |
| $\nu_3 + \nu_4$ | F2 | 4318.582645 | 4322.060844 | 4321.654303 | 4319.372 |
| $\nu_3 + \nu_4$ | E | <i>4321.640373</i> | <i>4325.557407</i> | <i>4324.439805</i> | <i>4322.669</i> |
| $\nu_3 + \nu_4$ | F1 | <i>4322.248522</i> | 4325.217615 | <i>4324.854518</i> | <i>4322.661</i> |
| $\nu_3 + \nu_4$ | A1 | <i>4320.681606</i> | <i>4325.215955</i> | <i>4323.958867</i> | 4323.031 |
| $2\nu_2 + \nu_4$ | F2 | 4341.955740 | 4356.378038 | 4348.200305 | 4349.131 |
| $2\nu_2 + \nu_4$ | F1 | 4358.834555 | 4368.672905 | 4363.915891 | 4363.833 |
| $2\nu_2 + \nu_4$ | F2 | 4375.015924 | 4383.510238 | 4379.587204 | 4379.076 |
| $\nu_1 + \nu_2$ | E | 4433.471555 | 4436.752603 | 4435.999202 | 4435.220 |
| $\nu_2 + \nu_3$ | F1 | 4537.378076 | 4540.417969 | 4539.559415 | 4537.625 |
| $\nu_2 + \nu_3$ | F2 | 4542.942703 | 4546.544470 | 4545.260400 | 4543.940 |
| $3\nu_2$ | E | 4587.592579 | 4597.792383 | 4592.239851 | 4592.426 |
| $3\nu_2$ | A2 | 4592.275444 | 4599.341362 | 4595.889548 | 4595.377 |
| $3\nu_2$ | A1 | 4592.384566 | 4599.650204 | 4596.028056 | 4595.664 |
| nb. basis functions | | 16086 | 16202 | 15809 | |
| nb. PES terms | | 1160 | 5696 | 21884 | |

Table 6

**Energies in cm^{-1} of the vibrational levels of methane
for increasing μ -expansion order**

| Assignment | irreps. | ord 0 | ord 1 | ord 2 | ord 4 |
|-----------------------------|---------|------------------------|-------------|-------------|-------------|
| ZPE | A1 | 9703.098960 | 9703.185496 | 9703.183153 | 9703.184993 |
| ν_4 | F2 | 1310.927299 | 1310.753844 | 1310.884071 | 1310.882416 |
| ν_2 | E | 1533.438473 | 1533.278814 | 1533.357656 | 1533.356351 |
| $2\nu_4$ | A1 | 2586.412638 | 2586.507977 | 2586.723627 | 2586.729369 |
| $2\nu_4$ | F2 | 2614.130234 | 2613.927557 | 2614.226307 | 2614.226072 |
| $2\nu_4$ | E | 2624.863233 | 2624.447363 | 2624.801377 | 2624.797887 |
| $\nu_2 + \nu_4$ | F2 | 2829.928258 | 2829.946722 | 2830.167101 | 2830.169972 |
| $\nu_2 + \nu_4$ | F1 | 2846.116077 | 2845.736709 | 2846.040115 | 2846.036894 |
| ν_1 | A1 | 2916.639327 | 2916.664325 | 2916.671492 | 2916.672933 |
| ν_3 | F2 | 3020.187468 | 3019.490741 | 3019.625077 | 3019.614050 |
| $2\nu_2$ | A1 | 3063.557572 | 3063.302664 | 3063.474918 | 3063.473842 |
| $2\nu_2$ | E | 3065.132466 | 3064.819023 | 3065.029711 | 3065.026585 |
| $3\nu_4$ | F2 | 3870.195501 | 3870.492710 | 3870.894713 | 3870.910306 |
| $3\nu_4$ | A1 | 3909.600258 | 3909.403775 | 3909.883837 | 3909.886014 |
| $3\nu_4$ | F1 | 3921.990831 | 3921.716320 | 3922.273060 | 3922.276211 |
| $3\nu_4$ | F2 | 3932.016176 | 3931.652683 | 3932.285535 | 3932.287769 |
| $\nu_2 + 2\nu_4$ | E | 4101.136404 | 4101.467830 | 4101.807398 | 4101.819023 |
| $\nu_2 + 2\nu_4$ | F1 | 4129.009970 | 4129.248500 | 4129.725405 | 4129.734759 |
| $\nu_2 + 2\nu_4$ | A1 | 4133.104853 | 4133.109290 | 4133.601985 | 4133.607444 |
| $\nu_2 + 2\nu_4$ | F2 | 4143.221974 | 4143.081860 | 4143.621528 | 4143.625496 |
| $\nu_2 + 2\nu_4$ | E | 4152.016006 | 4151.746837 | 4152.309114 | 4152.312282 |
| $\nu_2 + 2\nu_4$ | A2 | 4163.048539 | 4162.384095 | 4163.053460 | 4163.048908 |
| $\nu_1 + \nu_4$ | F2 | 4224.945071 | 4224.610686 | 4224.846117 | 4224.839439 |
| $\nu_3 + \nu_4$ | F2 | 4321.654303 | 4320.273893 | 4320.648401 | 4320.625937 |
| $\nu_3 + \nu_4$ | E | 4324.439805 | 4322.855425 | 4323.243001 | 4323.216368 |
| $\nu_3 + \nu_4$ | F1 | 4324.854518 | 4323.408556 | 4323.801743 | 4323.777575 |
| $\nu_3 + \nu_4$ | A1 | 4323.958867 | 4323.674256 | 4323.807826 | 4323.805353 |
| $2\nu_2 + \nu_4$ | F2 | 4348.200305 | 4348.361911 | 4348.714881 | 4348.722510 |
| $2\nu_2 + \nu_4$ | F1 | 4363.915891 | 4363.912331 | 4364.378640 | 4364.384372 |
| $2\nu_2 + \nu_4$ | F2 | 4379.587204 | 4379.071591 | 4379.583223 | 4379.579519 |
| $\nu_1 + \nu_2$ | E | 4435.999202 | 4435.823270 | 4435.983506 | 4435.981964 |
| $\nu_2 + \nu_3$ | F1 | 4539.559415 | 4538.039894 | 4538.366726 | 4538.341582 |
| $\nu_2 + \nu_3$ | F2 | 4545.260400 | 4544.220450 | 4544.486884 | 4544.468304 |
| $3\nu_2$ | E | 4592.239851 | 4591.898737 | 4592.218519 | 4592.217029 |
| $3\nu_2$ | A2 | 4595.889548 | 4595.424580 | 4595.819982 | 4595.815341 |
| $3\nu_2$ | A1 | 4596.028056 | 4595.564726 | 4595.960023 | 4595.954949 |
| nb. basis functions | | 15809 | 15812 | 15803 | 15809 |
| nb. Coriolis terms in H_0 | | 282 | 1458 | 5274 | 40223 |