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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 Hamiltonians including centrugal distortion effects of arbitrary high orders. These methods are compared for the first time in this article with regard to calculations of the rotational levels of methane vibrational ground state.

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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], Soliverez [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 with 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 10^{th} order.

Throughout this article, "methane" will designate the main isotopologue, $^{12}CH_4$, 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 mentionned 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 with 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,

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

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-Chenaï [19]. However, a very similar formulation and notation for the separation of $\mathbf{x}$ and $\mathbf{y}$ dof by CT has 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,

$$H(X,Y)\phi = E\phi, \tag{2}$$

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

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

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 $(\psi_n)_n$,

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

The eigenspaces are degenerate of dimension, $dimV_\mathbf{y}$.
Note that we use the same symbols, $\langle\cdots|$ and $|\cdots\rangle$, 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,

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

We will assume that, for some fixed n, in the interval $\varepsilon \in [0,1]$, the $dimV_{\mathbf{y}}$ eigenstates $(\psi_n \otimes \Psi_K)_K$ of $H(X,Y,0)$ are in one-to-one correspondance with $dimV_{\mathbf{y}}$ 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,

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

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

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

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

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

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 $H(X,Y,\varepsilon)$,

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

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,

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

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

$$H(X,Y,\varepsilon)\phi_n(Y,\varepsilon)\Psi_K = \phi_n(Y,\varepsilon)E_n(Y,\varepsilon)\Psi_K. \tag{11}$$

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

$$H(X,Y,\varepsilon)\phi_n(Y,\varepsilon) = \phi_n(Y,\varepsilon)E_n(Y,\varepsilon). \tag{12}$$

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

$$\phi_n^\dagger(Y,\varepsilon)H(X,Y,\varepsilon) = E_n^\dagger(Y,\varepsilon)\phi_n^\dagger(Y,\varepsilon), \tag{13}$$

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

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

Note that, if we impose the normalization condition,

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

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

$$E_n(Y,\varepsilon) = E_n^\dagger(Y,\varepsilon). \tag{16}$$

2.2 Perturbational solution of the eigen equation for effective operators

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

$$H(X,Y,\varepsilon)\phi(Y,\varepsilon) = \phi(Y,\varepsilon)E(Y,\varepsilon). \tag{17}$$

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 hypotheses. 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:

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

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

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

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

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

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

where $\phi^{(0)}(Y) = \psi_n \otimes Id_{\mathbf{y}}$ and the notation $o(\varepsilon^k, Y)$ means that $\lim\limits_{\varepsilon \to 0} \varepsilon^{-k} o(\varepsilon^k, Y) = 0_{\mathbf{y}}$, 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,

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

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

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

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

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

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

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, $\lambda V_1 + \lambda^2 V_2 + ...$, 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 [5,8,9,11,13,35–44]:

$$\widetilde{H} = ...e^{i\lambda^2 S_2} e^{i\lambda S_1} H e^{-i\lambda S_1} e^{-i\lambda^2 S_2} ... = H_0 + \lambda\{V_1 + [iS_1, H_0]\} + ... \tag{27}$$

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 preserve 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 $H^k = \sum_n \lambda^n H^k_n$. Using the Hausdorff commutator expansion, recursive formulas have been established [8,9,11,13,37,45] which link the n-th order term of the k-times transformed Hamiltonian, H^k_n, with CT-generators S_1, $...S_k$ and the expansion terms, H^{k-1}_m, 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 "simpification" 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 [13,37,43,45].

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 $\widetilde{H} =< \widetilde{H} >$ where the notation $< O >$ 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,

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

The general solutions of these equations for degenerate or quasi-degenerate zeroth-order states are given in [8,9] in terms of operations $< \cdots >$ (taking the block-diagonal part with respect to H_0 eigenstates partitioning) and the inverse of operation, $[H_0, \cdots]$, consisting in taking the commutator with H_0. Some mathematical aspects of these solutions are considered in [9,35,39]. With an appropriate choice of $\mathcal{A}$ eqs.(28) are invariant under the substitution $S_n => S_n + < Z_n >$, where $Z_n \backsim \lambda^n$ 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 perturbation 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 [9,39]. 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 [40,41].

A separation of variables permits 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 [42,45], Aliev and Watson [13], Camy-Peyret and Flaud [37], Sarka and Demaison [43] and others [9,15,46]. It has been developed for polyatomic molecules by Sibert [47] and applied to methane by Wang and Sibert [44]. The irreducible tensor formulation of CT for methane was discussed in [15,48]. For nonrigid molecules the CT method has been extended by Starikov and Tyuterev [9,46,49] with application to inversion in ammonia and large-amplitude bending vibration in water molecule, whereas a classic-mechanical version of Birkhoff-Gustavson transformations similar to CT has been reviewed and employed for floppy molecules by Sugny and Joyeux [50]. Most implementations start from an harmonic vibrational approximation in H_0, through anharmonic terms can be included in the zeroth-order approximation [46,51] as well. With the notation of the previous section, this method yields 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 [40,41,52].

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.

If one denotes, $X = \{(Q_i)_i, (P_k)_k\}$, 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 zeroth-order operator and perturbation. The generalized perturbation theory will take the full $(J = 0)$-vibrational hamiltonian as a zeroth-order approximation written in atomic units as follows,

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

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

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

where, I_e^{-1} is the inverse of the inertia tensor $I(Q_1,...,Q_n)$ at equilibrium and $(a_{k_i})_i$ the derivatives of the latter with respect to the normal coordinates,

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

π is the vibrational angular momentum operator determined by the Coriolis coupling constants and only depending upon the operators in the set X. The term U represents 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

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

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

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

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

where, $U^{(2)}$ is the PES truncated at second order. In the latter case, anharmonicity, the vibrational Coriolis term and the 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. [53].

By construction, an effective Hamiltonian shares the same eigenvalues as the original one. So, in principle, if the radius of convergence of their expansion series is non zero, both 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 needs 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 [54]. The method will not be described in details. It suffices to say here, that it is a variational method that encompasses as particular cases the vibrational self-consistent field (VSCF) method [55–57] and the vibrational configuration interaction (VCI) [58,59]. 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 [60–64], 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 [65]. However, in contrast with [65], 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 three things. First, that we started 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. Secondly, that 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 thirdly, 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 2×10^{-5} 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 vibrational 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 [16,54,66–70], 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 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

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 cm^{-1} .

Moreover, preliminary studies of our 10^{th} order polynomial PES shows that it has artefactual barriers. In particular, it is not reliable in the range higher than 10600 cm^{-1} above the ZPE in the direction of the bending dof. Since the highest initial HO basis functions have already non negligeable weight in these pathological regions of the potential expansion, 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. [71], 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 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. [32,33,44,72–77] 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 1.5×10^{-4} 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 $X_i = \{C^i_{jk...rt...} Q_j Q_k ... P_r P_t ...\}$ and of a rotational operator $Y_j \in \{1, \Pi_\alpha, \Pi_\beta \Pi_\gamma, ...\}$. Following the previously developed CT-algorithm [40] 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 $X'_i = V^{\theta,\Gamma}_{\mathbf{nm}}$ of creation and annihilation operators $(a_1^+)^{n_1}(a_2^+)^{n_2}...(a_1)^{m_1}(a_2)^{m_2}...$ for vibration normal modes and symmetrized combinations $Y'_j = R^{\theta,\Gamma}_{k_1,k_2,k_3}$ 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 [40]. The vector indices $\mathbf{n} = (n_1, n_2, \cdots)$ and $\mathbf{m} = (m_1, m_2, \cdots)$ 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, $V^{\theta,\Gamma}_{\mathbf{nm}}$, 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, $R^{\theta,\Gamma}_{k_1,k_2,k_3}$, expressed in terms of ladder operators are performed by following the technique described by Rey et al. [53] for symmetric molecules.

In order to perform CT of the full vibration-rotation Hamiltonian and 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 [40,52]. 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 a classification of Hamiltonian terms based on C_s-symmetry (provided the molecular symmetry group contains a subgroup isomorphic to C_s, such as in methane, where $C_s \subset T_d$) and also it allows a complete characterisation of the commutator/anti-commutator algebra for vibrational $V^{\theta,\Gamma}_{\mathbf{nm}}$ and rotational $R^{\theta,\Gamma}_{k_1,k_2,k_3}$ operators [40]. 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 [45]. Even though the algorithm of MOL_CT based on the exact analytical formulas for all contributions in commutators and anti-commutators $\left[V^{\theta,\Gamma}_{\mathbf{nm}}, V^{\theta',\Gamma'}_{\mathbf{n'm'}}\right]_{\pm}$ and $\left[R^{\theta,\Gamma}_{\mathbf{k}}, R^{\theta',\Gamma'}_{\mathbf{k'}}\right]_{\pm}$ is very fast, the huge number of combinations 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 [45], Oka [78], 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 follows[1]) depends on the type of terms which are expected to be important in the effective Hamiltonian.

It is known that, the 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 [9,13,45]. In this paper we present two ansätze, denoted A1 and A2, for CT calculations of methane rotational Hamiltonian in the ground vibrational state. These ordering-selection schemes were found to give optimum accuracy/CPU time ratio for the 2^{nd} order and 4^{th} order CT respectively.

More precisely, denoting by N(CT) the number of S-generators and by o(CT) the CT order according to the algorithm as explained in refs. [8,9,40], the A1 ansatz corresponds to a standard Amat-Nielsen ordering scheme for effective rotational Hamiltonian derivation at second order: N(CT)=1, o(CT)=2, PES expanded up to cubic terms $\sim K_3Q^3$ and reciprocal inertia tensor μ up to quadratic terms $\sim \mu_2Q^2$ in the centrifugal distortion part $\mu\Pi\Pi$ with only constant term $\sim \mu_0$ kept in the vibration-rotation Coriolis coupling operator $\mu\pi\Pi$. In the A2 ansatz, higher terms were accounted for: N(CT)=2, o(CT)=4 and the PES was expanded up to quartic terms $\sim K_4Q^4$. The off-diagonal part of the μ tensor was expanded up to quadratic terms $\sim \mu_2Q^2$ in the centrifugal distortion operator and up to linear terms $\sim \mu_1Q$ in the the vibration-rotation Coriolis coupling operator with only constant term $\sim \mu_0$ kept in the pure vibrational Coriolis operator $\mu\pi\pi$. The expansion of the diagonal part of the μ tensor was taken into account up to quartic terms $\sim < \mu_4Q^4 >$ in the centrifugal distortion operator.

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.

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

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 results of the STDS methane database [79], obtained with the parameters of [80]. 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 vibrational anharmonicity up to 10^{th} power of normal coordinates, 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 only. However, the CT(1,2) calculation was much easier to perform with respect to Pert(2), since the full vibrational eigenvalue problem did not have to be solved prior to the effective Hamiltonian derivation.

The results of CT(2,4) using A2 scheme improves greatly with respect to those of CT(1,2) and becomes of comparable accuracy 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.

The differences in columns 5 and 8 of Tab.4 are all positive. Whether this is general or not, would require further studies. CT results systematically underestimate the empirical values, as do those of Pert(2), whereas Pert(3) results underestimate the empirical values up to $J = 8$, and overestimate them above. This J-dependent variation is probably related to differences in high order centrigugal distorsion effects which only become significant at sufficiently high J-values.

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 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, besides our previous works [16,33], only one theoretical calculation by Wang and Sibert [74] 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 a 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 endeaviour 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 the ν_4 mode 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 $Z = 14918$ 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 [66–68]. 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.* [33] 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 resource 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. Z is the truncation threshold (in cm^{-1}) as explained in the text.

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 values 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 values 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 give 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 give 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 database [79], with the parameters of Roche and Champion [80] obtained from the fit of experimental spectra 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. Abbreviations 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 10^{th} order, and the VCI truncation thresholds are all equal to 14918 cm^{-1} giving about 16000 basis functions in this last VMFCI step. Abbreviations 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		4					5			
max k in sums		1052	2086	4161	8282	16864	1052	2086	4161	8282
J	irreps.									
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

		H_{rot} up to $\Pi^{(4)}$			**H_{rot} up to $\Pi^{(6)}$**			
J	irreps.	Pert(2)	CT(1,2)	Pert(2)-CT(1,2)	Pert(3)	CT(2,4)	Pert(3)-CT(2,4)	Empirical
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	*4321.640373*	*4325.557407*	*4324.439805*	*4322.669*
$\nu_3 + \nu_4$	F1	*4322.248522*	4325.217615	*4324.854518*	*4322.661*
$\nu_3 + \nu_4$	A1	*4320.681606*	*4325.215955*	*4323.958867*	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