Rayleigh-Schroedinger perturbation theory generalized to eigen-operators in non-commutative rings

Patrick Cassam-Chenaï

Rayleigh-Schrödinger perturbation theory generalized to eigen-operators in non-commutative rings

P. Cassam-Chenaï

Laboratoire J. A. Dieudonné, UMR 6621 du CNRS, Faculté des Sciences, Parc Valrose, 06108 Nice cedex 2, France. cassam@unice.fr

Abstract

A perturbation scheme to find approximate solutions of a generalized spectral problem is presented. The spectral problem is generalized in the sense that the "eigenvalues" searched for, are not real numbers but operators in a non-commutative ring, and the associated "eigenfunctions" do not belong to an Hilbert space but are elements of a module on the non-commutative ring. The method is relevant wherever two sets of degrees of freedom can be distinguished in a quantum system. This is the case for example in rotation-vibration molecular spectroscopy. The article clarifies the relationship between the exact solutions of rotation-vibration molecular Hamiltonians and the solutions of the effective rotational Hamiltonians derived in previous works. It also proposes a less restrictive form for the effective dipole moment than the form considered by spectroscopists so far.

1 Introduction

In two previous articles [1,2], we have presented and applied a method which generalizes Rayleigh-Schrödinger perturbation theory to the case where "eigenvalues" are not element of the field of real numbers but are element of a ring spanned by, non necessarily

commuting, operators, and where "eigenfunctions" are not elements of a Hilbert space but element of a module over a ring. The method was applied to the Watson Hamiltonian for the ro-vibrational motion of polyatomic molecules [3,4], however it is relevant wherever the perturbation, εH_1, depends upon extra degrees of freedom which do not appear in the unperturbed Hamiltonian, H_0. In particular, it can be used for other types of ro-vibrational Hamiltonians if the part that does not contain rotational coordinates and momenta in these Hamiltonians, is treated as the unperturbed Hamiltonian.

Numerical results for the rotational levels of methane in its vibrational ground state demonstrate the speed of convergence of our approach where the unperturbed Hamiltonian is the $(J = 0)$-Hamiltonian with respect to traditional approaches starting from the vibrational harmonic Hamiltonian [5–7], see Tab. 1.

The relative accuracy of our predicted energy levels obtained at order 4 of perturbation with respect to the levels of an effective Hamiltonian derived from observed spectra, was better than 2.10^{-5}, see Tab. 2. It was further shown in [2] that the Q-branch calculated from our energy levels was accurate enough to usefully complement the HITRAN database [8], in particular when extrapolating methane spectra at high temperature.

However, the relationship between the solutions of the effective, rotational Hamiltonian derived ab initio, and the exact eigenstates of the initial rotation-vibration Hamiltonian was not clearly established. The purpose of this article is to propose a theoretical frame which clarifies this relationship and allows one to develop a general, effective observable theory when two sets of degrees of freedom can be distinguished in a quantum system.

The rest of the paper is organised as follows: In Section II, we introduce the general theoretical setting of our new approach to obtain effective observables, including effective Hamiltonian. In section III, we derive perturbational formula for effective Hamiltonians in this setting. Other observables such as the electric dipole moment are also considered. We conclude that our generalized perturbation theory is on firm theoretical ground and future applications are outlined.

2 Effective observables

Let us consider a general problem where the degrees of freedom (dof) of a physical system can be splitted into two subsets. We assume that all the degrees of freedom are distinguishable, so the Hilbert space required for the quantum treatment of the system is a tensor product, $V = V_{\mathbf{x}} \otimes V_{\mathbf{y}}$ of two Hilbert spaces of square integrables functions, $V_{\mathbf{x}}$ and $V_{\mathbf{y}}$, corresponding respectively to the two sets of dof. In Dirac notation, kets on V (resp. on $V_{\mathbf{x}}$, $V_{\mathbf{y}}$) will be denoted by $|\cdots\rangle$, (resp. $|\cdots\rangle_{\mathbf{x}}$, $|\cdots\rangle_{\mathbf{y}}$). We denote by $H(X,Y)$ the Hamiltonian of the system, where X is a set of operators acting on the first family of dof associated with variables $\mathbf{x}$, and Y a set of operators acting on the other family of dof associated with variables $\mathbf{y}$. In the case of a molecular rotation-vibration Hamiltonian, X can be the set of vibrational coordinates and their conjugate momenta, $X = \{(Q_i)_i, (P_k)_k\}$, Y, the set of Euler angles in the Eckart frame and their conjugate momenta, $Y = \{\theta, \chi, \phi, P_\theta, P_\chi, P_\phi)\}$. The identity on $V_{\mathbf{x}}$ (respectively $V_{\mathbf{y}}$) is written $Id_{\mathbf{x}}$ (respectively $Id_{\mathbf{y}}$). Let $(\psi_n)_n$, (respectively $(\Psi_K)_K$), be a normalized Hilbertian basis set of $V_{\mathbf{x}}$ (respectively $V_{\mathbf{y}}$), we have: $Id_{\mathbf{x}} = \sum\limits_n |\psi_n\rangle\langle\psi_n|$, (respectively $Id_{\mathbf{y}} = \sum\limits_K |\Psi_K\rangle\langle\Psi_K|$). A basis of V is obtained by taking the tensor product of basis functions, $(\psi_n \otimes \Psi_K)_{n,K}$.

Let us assume that $H(X,Y)$ is dominated by a term of the form, $H_0(X) \otimes Id_{\mathbf{y}}$. By "dominated" we mean that the discrete spectrum eigenvalues of $H_0(X) \otimes Id_{\mathbf{y}}$ are only slightly modified by the operator $H_1(X,Y) := H(X,Y) - H_0(X) \otimes Id_{\mathbf{y}}$, so that they can be related to the eigenvalues of $H(X,Y)$ without ambiguities. We introduce a real parameter $\varepsilon \in [0,1]$, and define a parametrized Hamiltonian,

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

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

Since we are free to choose the basis set of $V_{\mathbf{x}}$, we can take for $(\psi_n)_n$ an orthonormal set of 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. The version of the method for (quasi-) degenerate eigenstates of $H_0(X)$ will

be explored in a forthcoming articles.

Our goal is to solve the eigenvalue equation,

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

For $\varepsilon = 0$, we have,

$$(H_0(X) \otimes Id_{\mathbf{y}})|\psi_n \otimes \Psi_K\rangle = \nu_n|\psi_n \otimes \Psi_K\rangle \quad \forall K, \tag{3}$$

so, the eigenspaces are degenerate of dimension, $dimV_{\mathbf{y}}$. We note that we can also write the following identity,

$$(H_0(X) \otimes Id_{\mathbf{y}})|\psi_n\rangle_{\mathbf{x}} \otimes Id_{\mathbf{y}} = \nu_n|\psi_n\rangle_{\mathbf{x}} \otimes Id_{\mathbf{y}}. \tag{4}$$

For some fixed n, suppose that the $dimV_{\mathbf{y}}$ eigenstates $(\psi_n \otimes \Psi_K)_K$ of $H_0(X) \otimes Id_{\mathbf{y}}$ are in one-to-one correspondance with $dimV_{\mathbf{y}}$ eigenstates of $H(X,Y)$, denoted by $(\phi_{n,K})_K$. The $\phi_{n,K}$'s can be expanded on the tensorial product basis set as,

$$\phi_{n,K} = \sum_{n',K'} c^{n,K}_{n',K'}\ \psi_{n'} \otimes \Psi_{K'}. \tag{5}$$

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

$$\forall n', \forall \Psi_K, \quad \Psi_{n'}(Y)\Psi_K := \sum_{K'} c^{n,K}_{n',K'}\ \Psi_{K'}, \tag{6}$$

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

$$\phi_n(Y) = \sum_{n'} \psi_{n'} \otimes \Psi_{n'}(Y), \tag{7}$$

Eq.(5) assumes a peudo-factored form,

$$\phi_{n,K} = \phi_n(Y)\Psi_K. \tag{8}$$

Then we see that solving Eq.(2) for the $dimV_{\mathbf{y}}$ eigenpairs $(E_{n,K}, \phi_{n,K})_K$ at once, amounts to finding the operator $\phi_n(Y)$ for some basis Ψ_K that need not be specified in the first

place, and an eigenvalue operator $E_n(Y)$ acting on $V_{\mathbf{y}}$ by $E_n(Y)\Psi_K = E_{n,K}\Psi_K$, such that,

$$H(X,Y)\phi_n(Y) = \phi_n(Y)E_n(Y). \tag{9}$$

Then, applying the operators of both members to the Ψ_K's basis functions, Eq.(2) is recovered for the $(E_{n,K}, \phi_{n,K})_K$ eigenpairs.

The effective wave operator, together with its Hermitic conjugate which satisfies,

$$\phi_n^\dagger(Y)H(X,Y) = E_n^\dagger(Y)\phi_n^\dagger(Y), \tag{10}$$

where the operators act on $V_{\mathbf{y}}$ on the left, allows one to derive for any "observable", i.e. Hermitian operator, $O(X,Y)$, acting on $V_{\mathbf{x}} \otimes V_{\mathbf{y}}$, an effective operator, $O_n(Y)$, acting solely on $V_{\mathbf{y}}$, by,

$$O_n(Y) = \langle \phi_n^\dagger(Y)O(X,Y)\phi_n(Y)\rangle_{\mathbf{x}}, \tag{11}$$

where we extend the notation $\langle\cdots\rangle_{\mathbf{x}}$ here to signify that integration is carried over the $\mathbf{x}$-variables only,

$$\langle \psi_1 \otimes \Psi_1(Y)|\psi_2 \otimes \Psi_2(Y)\rangle_{\mathbf{x}} := \left(\int d\mathbf{x}\ \bar{\psi}_1(\mathbf{x})\psi_2(\mathbf{x})\right)\Psi_1(Y)\Psi_2(Y) \equiv \langle\psi_1|\psi_2\rangle_{\mathbf{x}}\Psi_1(Y)\Psi_2(Y). \tag{12}$$

Note that $O_n(Y)$ is Hermitian by construction. For $O(X,Y) = H(X,Y)$, we have from Eqs.(9) and (10),

$$H_n(Y) = \langle \phi_n^\dagger(Y)\phi_n(Y)\rangle_{\mathbf{x}}E_n(Y) = E_n^\dagger(Y)\langle \phi_n^\dagger(Y)\phi_n(Y)\rangle_{\mathbf{x}}. \tag{13}$$

If the $(\phi_{n,K})_K$'s are orthonormal for the scalar product $\langle\cdots\rangle := \int\cdots d\mathbf{x}\ d\mathbf{y}$, and the Ψ_K's are orthonormal for the scalar product $\langle\cdots\rangle_{\mathbf{y}} := \int\cdots d\mathbf{y}$, then the $\phi_n(Y)$ of Eq.(7) satisfy,

$$\langle \phi_n^\dagger(Y)\phi_n(Y)\rangle_{\mathbf{x}} = Id_{\mathbf{y}}. \tag{14}$$

It is therefore legitimate to impose this constraint when solving Eq.(9) for $\phi_n(Y)$. Then, one obtains,

$$H_n(Y) = E_n(Y) = E_n^\dagger(Y), \tag{15}$$

and other effective observables $O_n(Y)$ are also properly normalized.

3 Explicit perturbational formulas

In the following, we set without loss of generality $n = 0$, and we drop the index n in all effective operators. We are now going to solve Eq.(9) in a Rayleigh-Schrödinger fashion, that is to say, we expand the effective eigenvalue and eigenfunction operators as a power series of ε,

$$E(Y) = \nu_0 Id_{\mathbf{y}} + \varepsilon E^{(1)}(Y) + \varepsilon^2 E^{(2)}(Y) + \varepsilon^3 E^{(3)} + \varepsilon^4 E^{(4)} + ..., \tag{16}$$

$$\phi(Y) = \psi_0 \otimes Id_{\mathbf{y}} + \varepsilon \phi^{(1)}(Y) + \varepsilon^2 \phi^{(2)}(Y) + \varepsilon^3 \phi^{(3)}(Y) + \varepsilon^4 \phi^{(4)}(Y) + ... \tag{17}$$

Inserting these expression in Eq. (9) and identifying the terms with the same power of ε, we obtain Eq.(4) for $k = 0$, and for all $k > 0$,

$$(H_0(X) - \nu_0) \otimes Id_{\mathbf{y}} \phi^{(k)}(Y) + H_1(X, Y)\phi^{(k-1)}(Y) = \sum_{i=0}^{k-1} \phi^{(i)}(Y) E^{(k-i)}(Y), \tag{18}$$

(with $\phi^{(0)}(Y) = \psi_0 \otimes Id_{\mathbf{y}}$ and $E^{(0)}(Y) = \nu_0 Id_{\mathbf{y}}$).

We do not impose the effective eigenvalue operator, $E(Y)$, to be diagonal in the first place. We have not attempted either, to impose a generalization of the widely used "intermediate" normalization conditions. Instead, in order to obtain normalized effective observables, we impose the set of conditions,

$$\forall k > 0, \qquad \langle \sum_{i=0}^{k} \varepsilon^i \phi^{(i)\dagger}(Y) | \sum_{i=0}^{k} \varepsilon^i \phi^{(i)}(Y) \rangle_{\mathbf{x}} = Id_{\mathbf{y}} + o(\varepsilon^k, Y). \tag{19}$$

where the notation $o(\varepsilon^k, Y)$ means that $\lim_{\varepsilon \to 0} \varepsilon^{-k} o(\varepsilon^k, Y) = 0_{\mathbf{y}}$, the null operator on $V_{\mathbf{y}}$. In addition, we choose the following "phase" conventions, which are actually, Hermiticity conditions for the operators tensorized with ψ_0 in the expansion, Eq.(7), of the corrective terms to the effective wave operator,

$$\forall k > 0, \qquad \langle \phi^{(0)\dagger}(Y) | \phi^{(k)}(Y) \rangle_{\mathbf{x}} = \langle \phi^{(k)\dagger}(Y) | \phi^{(0)}(Y) \rangle_{\mathbf{x}}. \tag{20}$$

Conditions Eqs. (19,20) are enough to determine unambiguously, by recursion, an effective wave operator, Eq. (17), satisfying Eq. (18) at any order. More precisely, Eq. (18) al-

lows one to determine the $E^{(k)}(Y)$'s and the operators tensorized with ψ_n, for $n \neq 0$ in the expansions, Eq.(7), of the $\phi^{(k)}(Y)$'s, whereas Eqs. (19,20) determine $\langle \phi^{(0)\dagger}(Y)|\phi^{(k)}(Y)\rangle_{\mathbf{x}}$ and $\langle \phi^{(k)\dagger}(Y)|\phi^{(0)}(Y)\rangle_{\mathbf{x}}$ which in turn determine the operators tensorized with ψ_0 in the same expansions.

Then, effective observables, $O(Y)$, as defined in Eq.(11), can be expanded as a series in ε,

$$O(Y) = O^{(0)}(Y) + \varepsilon O^{(1)}(Y) + \varepsilon^2 O^{(2)}(Y) + \cdots + \varepsilon^n O^{(n)}(Y) + \cdots , \tag{21}$$

where the n^{th}-order term has the following expression,

$$O^{(n)}(Y) = \sum_{k=0}^{n} \langle \phi^{(k)\dagger}(Y)|O(X,Y)|\phi^{(n-k)}(Y)\rangle_{\mathbf{x}}. \tag{22}$$

and is Hermitian. However, for $O(X,Y) = H(X,Y)$, taking into account Eqs. (18,19), one easily obtains

$$H^{(n)}(Y) = \sum_{i=0}^{n} \sum_{k=0}^{n-i} \langle \phi^{(k)\dagger}(Y)|\phi^{(n-i-k)}(Y)\rangle_{\mathbf{x}} E^{(i)}(Y) = E^{(n)}(Y), \tag{23}$$

which implies by the way that $E^{(n)}(Y)$ is Hermitian.

For $n = 0$, the above expressions are simply,

$$O^{(0)}(Y) = \langle \psi_0 \otimes Id_{\mathbf{y}}|O(X,Y)|\psi_0 \otimes Id_{\mathbf{y}}\rangle_{\mathbf{x}}, \tag{24}$$

$$H^{(0)}(Y) = \nu_0 Id_{\mathbf{y}}, \tag{25}$$

higher order expressions of $H^{(n)}(Y) = E^{(n)}(Y)$ and $\phi^{(n)}(Y)$ are derived below.

3.1 First order:

For $k = 1$, Eq. (18) becomes

$$(H_0(X) - \nu_0) \otimes Id_{\mathbf{y}} \phi^{(1)}(Y) + H_1(X,Y)\phi^{(0)}(Y) - \phi^{(0)}(Y)E^{(1)}(Y) = 0. \tag{26}$$

Multiplying by $\bar{\psi}_0(\mathbf{x}) \otimes Id_{\mathbf{y}}$ and integrating over $d\mathbf{x}$, i.e. projecting onto $\langle \phi^{(0)\dagger}(Y)| = \langle \phi^{(0)}(Y)|$, we obtain, since $\langle \phi^{(0)\dagger}(Y)|\phi^{(0)}(Y)\rangle_{\mathbf{x}} = Id_{\mathbf{y}}$,

$$E^{(1)}(Y) = \langle \phi^{(0)\dagger}(Y)|H_1(X,Y)|\phi^{(0)}(Y)\rangle_{\mathbf{x}} = \langle \psi_0 \otimes Id_{\mathbf{y}}|H_1(X,Y)|\psi_0 \otimes Id_{\mathbf{y}}\rangle_{\mathbf{x}}. \tag{27}$$

in agreement with our previous works [1,2].

Projecting onto $\langle \psi_k \otimes Id_{\mathbf{y}}|$, different from $\langle \psi_0 \otimes Id_{\mathbf{y}}|$, we obtain the operator $\Psi_k^{(1)}(Y)$ tensorized with ψ_k in the expansion, Eq.(7), of the first order correction to the effective wave operator, $\phi^{(1)}(Y)$,

$$\langle \psi_k \otimes Id_{\mathbf{y}}|\phi^{(1)}(Y)\rangle_{\mathbf{x}} = \frac{\langle \psi_k \otimes Id_{\mathbf{y}}|H_1(X,Y)|\psi_0 \otimes Id_{\mathbf{y}}\rangle_{\mathbf{x}}}{\nu_0 - \nu_k}. \tag{28}$$

The normalization and Hermiticity conditions impose that the operator $\Psi_0^{(1)}(Y)$ tensorized with ψ_0 is zero, so that,

$$\phi^{(1)}(Y) = \sum_{k\neq 0} \psi_k \otimes \frac{\langle \psi_k \otimes Id_{\mathbf{y}}|H_1(X,Y)|\psi_0 \otimes Id_{\mathbf{y}}\rangle_{\mathbf{x}}}{\nu_0 - \nu_k}. \tag{29}$$

3.2 Second order:

For $k = 2$, Eq. (18) becomes

$$(H_0(X) - \nu_0) \otimes Id_{\mathbf{y}}\phi^{(2)}(Y) + H_1(X,Y)\phi^{(1)}(Y) - \phi^{(1)}(Y)E^{(1)}(Y) = \phi^{(0)}(Y)E^{(2)}(Y). \tag{30}$$

Projecting onto $\langle \phi^{(0)\dagger}(Y)|$, we obtain,

$$\begin{aligned} E^{(2)}(Y) &= \langle \phi^{(0)\dagger}(Y)|H_1(X,Y)|\phi^{(1)}(Y)\rangle_{\mathbf{x}} \\ &= \sum_{k\neq 0} \langle \psi_0 \otimes Id_{\mathbf{y}}|H_1(X,Y)|\psi_k \otimes \frac{\langle \psi_k \otimes Id_{\mathbf{y}}|H_1(X,Y)|\psi_0 \otimes Id_{\mathbf{y}}\rangle_{\mathbf{x}}}{\nu_0 - \nu_k}\rangle_{\mathbf{x}} \\ &= \sum_{k\neq 0} \frac{\langle \psi_0 \otimes Id_{\mathbf{y}}|H_1(X,Y)|\psi_k \otimes Id_{\mathbf{y}}\rangle_{\mathbf{x}}\langle \psi_k \otimes Id_{\mathbf{y}}|H_1(X,Y)|\psi_0 \otimes Id_{\mathbf{y}}\rangle_{\mathbf{x}}}{\nu_0 - \nu_k}. \end{aligned} \tag{31}$$

So, $H^{(2)}(Y)$ agrees again with our previous works [1,2].

Projecting onto $\langle \psi_{k_1} \otimes Id_{\mathbf{y}}|$, gives

$$\langle\psi_{k_1}\otimes Id_{\mathbf{y}}|\phi^{(2)}(Y)\rangle_{\mathbf{x}} = \frac{\langle\psi_{k_1}\otimes Id_{\mathbf{y}}|H_1(X,Y)|\phi^{(1)}(Y)\rangle_{\mathbf{x}} - \langle\psi_{k_1}\otimes Id_{\mathbf{y}}|\phi^{(1)}(Y)\rangle_{\mathbf{x}}E^{(1)}(Y)}{\nu_0-\nu_{k_1}}$$
$$= \sum_{k_2\neq 0}\frac{\langle\psi_{k_1}\otimes Id_{\mathbf{y}}|H_1(X,Y)|\psi_{k_2}\otimes Id_{\mathbf{y}}\rangle_{\mathbf{x}}\langle\psi_{k_2}\otimes Id_{\mathbf{y}}|H_1(X,Y)|\psi_0\otimes Id_{\mathbf{y}}\rangle_{\mathbf{x}}}{(\nu_0-\nu_{k_1})(\nu_0-\nu_{k_2})} -$$
$$\frac{\langle\psi_{k_1}\otimes Id_{\mathbf{y}}|H_1(X,Y)|\psi_0\otimes Id_{\mathbf{y}}\rangle_{\mathbf{x}}\langle\psi_0\otimes Id_{\mathbf{y}}|H_1(X,Y)|\psi_0\otimes Id_{\mathbf{y}}\rangle_{\mathbf{x}}}{(\nu_0-\nu_{k_1})^2}. \quad (32)$$

From Eq.(19) at order 2,

$$\langle\phi^{(0)\dagger}(Y)|\phi^{(2)}(Y)\rangle_{\mathbf{x}} + \langle\phi^{(2)\dagger}(Y)|\phi^{(0)}(Y)\rangle_{\mathbf{x}} + \langle\phi^{(1)\dagger}(Y)|\phi^{(1)}(Y)\rangle_{\mathbf{x}} = 0 \quad (33)$$

and Eq.(20), we deduce,

$$\langle\phi^{(0)\dagger}(Y)|\phi^{(2)}(Y)\rangle_{\mathbf{x}} = -\frac{1}{2}\langle\phi^{(1)\dagger}(Y)|\phi^{(1)}(Y)\rangle_{\mathbf{x}}$$
$$= -\frac{1}{2}\sum_{k_1\neq 0}\frac{\langle\psi_0\otimes Id_{\mathbf{y}}|H_1(X,Y)|\psi_{k_1}\otimes Id_{\mathbf{y}}\rangle_{\mathbf{x}}\langle\psi_{k_1}\otimes Id_{\mathbf{y}}|H_1(X,Y)|\psi_0\otimes Id_{\mathbf{y}}\rangle_{\mathbf{x}}}{(\nu_0-\nu_{k_1})^2}. \quad (34)$$

So the second order effective wave function is,

$$\phi^{(2)}(Y) = \sum_{k_1\neq 0}\psi_{k_1}\otimes\left(\sum_{k_2\neq 0}\frac{\langle\psi_{k_1}\otimes Id_{\mathbf{y}}|H_1(X,Y)|\psi_{k_2}\otimes Id_{\mathbf{y}}\rangle_{\mathbf{x}}\langle\psi_{k_2}\otimes Id_{\mathbf{y}}|H_1(X,Y)|\psi_0\otimes Id_{\mathbf{y}}\rangle_{\mathbf{x}}}{(\nu_0-\nu_{k_1})(\nu_0-\nu_{k_2})} -\right.$$
$$\left.\frac{\langle\psi_{k_1}\otimes Id_{\mathbf{y}}|H_1(X,Y)|\psi_0\otimes Id_{\mathbf{y}}\rangle_{\mathbf{x}}\langle\psi_0\otimes Id_{\mathbf{y}}|H_1(X,Y)|\psi_0\otimes Id_{\mathbf{y}}\rangle_{\mathbf{x}}}{(\nu_0-\nu_{k_1})^2}\right)$$
$$-\frac{1}{2}\psi_0\otimes\sum_{k_1\neq 0}\frac{\langle\psi_0\otimes Id_{\mathbf{y}}|H_1(X,Y)|\psi_{k_1}\otimes Id_{\mathbf{y}}\rangle_{\mathbf{x}}\langle\psi_{k_1}\otimes Id_{\mathbf{y}}|H_1(X,Y)|\psi_0\otimes Id_{\mathbf{y}}\rangle_{\mathbf{x}}}{(\nu_0-\nu_{k_1})^2}. \quad (35)$$

We continue our careful derivation of the perturbation formulas at the next two orders, as new interesting details show up. Hereafter, we alleviate the notation by setting,

$$H_1(Y)_{i,j} := \langle\psi_i\otimes Id_{\mathbf{y}}|H_1(X,Y)|\psi_j\otimes Id_{\mathbf{y}}\rangle_{\mathbf{x}}, \quad (36)$$

so for example, we have

$$E^{(1)}(Y) = H_1(Y)_{0,0} \quad (37)$$
$$E^{(2)}(Y) = \sum_{k\neq 0}\frac{H_1(Y)_{0,k}H_1(Y)_{k,0}}{\nu_0-\nu_k}. \quad (38)$$

3.3 Third order:

Repeating the algebraic procedure outlined at the previous orders, we have,

$$(H_0(X)-\nu_0)\phi^{(3)}(Y)+H_1(X,Y)\phi^{(2)}(Y)-\phi^{(2)}(Y)E^{(1)}(Y)-\phi^{(1)}(Y)E^{(2)}(Y)=\phi^{(0)}(Y)E^{(3)}(Y), \tag{39}$$

from which we deduce,

$$\begin{aligned} E^{(3)}(Y) &= \langle\phi^{(0)\dagger}(Y)|H_1(X,Y)|\phi^{(2)}(Y)\rangle_{\mathbf{x}} - \langle\phi^{(0)\dagger}(Y)|\phi^{(2)}(Y)\rangle_{\mathbf{x}}E^{(1)}(Y) \\ &= \sum_{k_1,k_2\neq 0}\frac{H_1(Y)_{0,k_1}H_1(Y)_{k_1,k_2}H_1(Y)_{k_2,0}}{(\nu_0-\nu_{k_1})(\nu_0-\nu_{k_2})} \\ &-\frac{1}{2}\sum_{k_1\neq 0}\frac{H_1(Y)_{0,k_1}H_1(Y)_{k_1,0}H_1(Y)_{0,0}+H_1(Y)_{0,0}H_1(Y)_{0,k_1}H_1(Y)_{k_1,0}}{(\nu_0-\nu_{k_1})^2}. \end{aligned} \tag{40}$$

Note that $H_3(Y)$ may be different from our previous formula [1,2] or its corrected version [9], if $H_1(Y)_{0,0}$ does not commute with the $H_1(Y)_{0,k_1}$'s. However, in our previous application to the methane ground state, $H_1(Y)_{0,0}$ was a Casimir operator of the Lie algebra spanned by the angular momentum operators, and was actually commuting with the $H_1(Y)_{0,k_1}$'s. So, the formula in this context were correct and our numerical applications would be unaffected.

$$\begin{aligned} &\langle\psi_{k_1}\otimes Id_{\mathbf{y}}|\phi^{(3)}(Y)\rangle_{\mathbf{x}} = \\ &\frac{\langle\psi_{k_1}\otimes Id_{\mathbf{y}}|H_1(X,Y)|\phi^{(2)}(Y)\rangle_{\mathbf{x}} - \langle\psi_{k_1}\otimes Id_{\mathbf{y}}|\phi^{(2)}(Y)\rangle_{\mathbf{x}}E^{(1)}(Y) - \langle\psi_{k_1}\otimes Id_{\mathbf{y}}|\phi^{(1)}(Y)\rangle_{\mathbf{x}}E^{(2)}(Y)}{\nu_0-\nu_{k_1}} \\ &= \sum_{k_2,k_3\neq 0}\frac{H_1(Y)_{k_1,k_2}H_1(Y)_{k_2,k_3}H_1(Y)_{k_3,0}}{(\nu_0-\nu_{k_1})(\nu_0-\nu_{k_2})(\nu_0-\nu_{k_3})} \\ &-\sum_{k_2\neq 0}\frac{H_1(Y)_{k_1,k_2}H_1(Y)_{k_2,0}H_1(Y)_{0,0}+\frac{1}{2}H_1(Y)_{k_1,0}H_1(Y)_{0,k_2}H_1(Y)_{k_2,0}}{(\nu_0-\nu_{k_1})(\nu_0-\nu_{k_2})^2} \\ &-\sum_{k_2\neq 0}\frac{H_1(Y)_{k_1,k_2}H_1(Y)_{k_2,0}H_1(Y)_{0,0}+H_1(Y)_{k_1,0}H_1(Y)_{0,k_2}H_1(Y)_{k_2,0}}{(\nu_0-\nu_{k_1})^2(\nu_0-\nu_{k_2})} \\ &+\frac{H_1(Y)_{k_1,0}H_1(Y)_{0,0}H_1(Y)_{0,0}}{(\nu_0-\nu_{k_1})^3}, \end{aligned} \tag{41}$$

$$\langle\phi^{(0)\dagger}(Y)|\phi^{(3)}(Y)\rangle_{\mathbf{x}} = -\frac{1}{2}\left(\langle\phi^{(1)\dagger}(Y)|\phi^{(2)}(Y)\rangle_{\mathbf{x}} + \langle\phi^{(2)\dagger}(Y)|\phi^{(1)}(Y)\rangle_{\mathbf{x}}\right)$$
$$= -\sum_{k_1,k_2\neq 0}\frac{H_1(Y)_{0,k_1}H_1(Y)_{k_1,k_2}H_1(Y)_{k_2,0}}{2(\nu_0-\nu_{k_1})(\nu_0-\nu_{k_2})}\left(\frac{1}{\nu_0-\nu_{k_1}}+\frac{1}{\nu_0-\nu_{k_2}}\right)$$
$$+\sum_{k_1\neq 0}\frac{H_1(Y)_{0,k_1}H_1(Y)_{k_1,0}H_1(Y)_{0,0}+H_1(Y)_{0,0}H_1(Y)_{0,k_1}H_1(Y)_{k_1,0}}{2(\nu_0-\nu_{k_1})^3} \tag{42}$$

The third order effective wave function, $\phi^{(3)}(Y)$, is easily obtained from Eqs. (41) and (42).

3.4 Fourth order:

$$(H_0(X)\otimes Id_{\mathbf{y}}-\nu_0)\phi^{(4)}(Y)+H_1(X,Y)\phi^{(3)}(Y)-\phi^{(3)}(Y)E^{(1)}(Y)-$$
$$\phi^{(2)}(Y)E^{(2)}(Y)-\phi^{(1)}(Y)E^{(3)}(Y)=\phi^{(0)}(Y)E^{(4)}(Y). \tag{43}$$

At this order, we just give the expression of the effective Hamiltonian operator $E^{(4)}(Y)$,

$$E^{(4)}(Y)=\sum_{k_1,k_2,k_3\neq\phi_0}\frac{H_1(Y)_{0,k_1}H_1(Y)_{k_1,k_2}H_1(Y)_{k_2,k_3}H_1(Y)_{k_3,0}}{(\nu_0-\nu_{k_1})(\nu_0-\nu_{k_2})(\nu_0-\nu_{k_3})}$$
$$-\frac{1}{2}\sum_{k_1,k_2\neq\phi_0}\frac{H_1(Y)_{0,0}H_1(Y)_{0,k_1}H_1(Y)_{k_1,k_2}H_1(Y)_{k_2,0}+H_1(Y)_{0,k_1}H_1(Y)_{k_1,k_2}H_1(Y)_{k_2,0}H_1(Y)_{0,0}}{(\nu_0-\nu_{k_1})(\nu_0-\nu_{k_2})}\left(\frac{1}{\nu_0-\nu_{k_1}}+\frac{1}{\nu_0-\nu_{k_2}}\right)$$
$$-\left(\sum_{k_1\neq\phi_0}\frac{H_1(Y)_{0,k_1}H_1(Y)_{k_1,0}}{(\nu_0-\nu_{k_1})}\right)\left(\sum_{k_1\neq\phi_0}\frac{H_1(Y)_{0,k_1}H_1(Y)_{k_1,0}}{(\nu_0-\nu_{k_1})^2}\right)$$
$$+\frac{1}{2}\sum_{k_1\neq\phi_0}\frac{H_1(Y)_{0,0}^2H_1(Y)_{0,k_1}H_1(Y)_{k_1,0}+H_1(Y)_{0,k_1}H_1(Y)_{k_1,0}H_1(Y)_{0,0}^2}{(\nu_0-\nu_{k_1})^3}, \tag{44}$$

which shows that $H_4(Y)$ may be different from our previous formula in [1,2], if $H_1(Y)_{0,0}$ does not commute with the $H_1(Y)_{k_1,k_2}$'s. Again, this does not affect our previous application to the methane ground state, since in this case, $H_1(Y)_{0,0}$ was a Casimir operator commuting with all the $H_1(Y)_{k_1,k_2}$'s.

3.5 Effective electric dipole moment

Beside the Hamiltonian, an observable of prime interest in molecular spectroscopy is the electric dipole moment, as it serves to compute line intensities. It is a typical example of observable that can be expressed in terms of linear combination of tensor products of X and Y-dependent operators: if the X and Y-sets are those mentionned at the beginning of Section 2, it writes,

$$\mu_f(X,Y) = \sum_{\alpha=x,y,z} \mu_\alpha(X) \otimes \lambda_{f\alpha}(Y) \tag{45}$$

Where $\mu_f(X,Y)$ is the electric dipole moment operator along the f-axis in the laboratory frame, $\mu_\alpha(X)$, the electric dipole moment operator along the α-axis in the Eckart frame, and $\lambda_{f\alpha}(Y)$ the direction cosines depending upon the Euler angles, ($\hbar = 1$ in this article).

The first orders of the effective dipole moment $\mu_f(Y)$ follow from Eq.(22) and are given below:

Order 0

$$\mu_f^{(0)}(Y) = \sum_{\alpha=x,y,z} \langle \phi^{(0)\dagger}(Y) | \mu_\alpha(X) \otimes \lambda_{f\alpha}(Y) | \phi^{(0)}(Y) \rangle_{\mathbf{x}} = \sum_{\alpha=x,y,z} \langle \psi_0 | \mu_\alpha(X) | \psi_0 \rangle_{\mathbf{x}} \lambda_{f\alpha}(Y) \tag{46}$$

Order 1

$$\begin{aligned} \mu_f^{(1)}(Y) &= \sum_{\alpha=x,y,z} \langle \phi^{(1)\dagger}(Y) | \mu_\alpha(X) \otimes \lambda_{f\alpha}(Y) | \phi^{(0)}(Y) \rangle_{\mathbf{x}} + \langle \phi^{(0)\dagger}(Y) | \mu_\alpha(X) \otimes \lambda_{f\alpha}(Y) | \phi^{(1)}(Y) \rangle_{\mathbf{x}} \\ &= \sum_{\alpha=x,y,z} \sum_{k_1 \neq 0} \frac{\langle \psi_{k_1} | \mu_\alpha(X) | \psi_0 \rangle_{\mathbf{x}}}{\nu_0 - \nu_{k_1}} H_1(Y)_{0,k_1} \lambda_{f\alpha}(Y) + \frac{\langle \psi_0 | \mu_\alpha(X) | \psi_{k_1} \rangle_{\mathbf{x}}}{\nu_0 - \nu_{k_1}} \lambda_{f\alpha}(Y) H_1(Y)_{k_1,0} \end{aligned} \tag{47}$$

Order 2

$$\mu_f^{(2)}(Y) = \sum_{\alpha=x,y,z} \langle \phi^{(1)\dagger}(Y)|\mu_\alpha(X)\otimes\lambda_{f\alpha}(Y)|\phi^{(1)}(Y)\rangle_{\mathbf{x}} + \langle \phi^{(2)\dagger}(Y)|\mu_\alpha(X)\otimes\lambda_{f\alpha}(Y)|\phi^{(0)}(Y)\rangle_{\mathbf{x}} + \langle \phi^{(0)\dagger}(Y)|\mu_\alpha(X)\otimes\lambda_{f\alpha}(Y)|\phi^{(2)}(Y)\rangle_{\mathbf{x}}$$
$$= \sum_{\alpha=x,y,z}\left(\sum_{k_1,k_2\neq 0} \frac{1}{(\nu_0-\nu_{k_1})(\nu_0-\nu_{k_2})} \left(\langle\psi_{k_1}|\mu_\alpha(X)|\psi_{k_2}\rangle_{\mathbf{x}} H_1(Y)_{0,k_1}\lambda_{f\alpha}(Y)H_1(Y)_{k_2,0} + \right.\right.$$
$$\langle\psi_0|\mu_\alpha(X)|\psi_{k_1}\rangle_{\mathbf{x}}\lambda_{f\alpha}(Y)H_1(Y)_{k_1,k_2}H_1(Y)_{k_2,0} + \langle\psi_{k_1}|\mu_\alpha(X)|\psi_0\rangle_{\mathbf{x}}H_1(Y)_{0,k_2}H_1(Y)_{k_2,k_1}\lambda_{f\alpha}(Y)) -$$
$$\sum_{k_1\neq 0}\frac{\langle\psi_0|\mu_\alpha(X)|\psi_{k_1}\rangle_{\mathbf{x}}}{(\nu_0-\nu_{k_1})^2}\left(\lambda_{f\alpha}(Y)H_1(Y)_{k_1,0}H_1(Y)_{0,0} + H_1(Y)_{0,0}H_1(Y)_{0,k_1}\lambda_{f\alpha}(Y)\right) -$$
$$\left.\left.\frac{\langle\psi_0|\mu_\alpha(X)|\psi_0\rangle_{\mathbf{x}}}{2}\sum_{k_1\neq 0}\frac{1}{(\nu_0-\nu_{k_1})^2}\left(\lambda_{f\alpha}(Y)H_1(Y)_{0,k_1}H_1(Y)_{k_1,0} + H_1(Y)_{0,k_1}H_1(Y)_{k_1,0}\lambda_{f\alpha}(Y)\right)\right). \tag{48}$$

Clearly, any observable that can be decomposed as in Eq.(45) would give effective operator contributions of the same form as Eqs.(46-48).

Application to methane

In the case of a non linear molecule described by the Eckart-Watson Hamiltonian [3], one can set $H_0(X)$ to the $(J=0)$-Eckart-Watson Hamiltonian and,

$$H_1(X,Y) = \sum_{\alpha,\beta=x,y,z}\frac{1}{2}M_{\alpha\beta}\otimes\Pi_\alpha\Pi_\beta - M_{\alpha\beta}\pi_\alpha\otimes\Pi_\beta. \tag{49}$$

where M is a 3 by 3 symmetrical matrix depending only upon normal coordinates (it is usually denoted by μ but we have reserved this symbol for the dipole moment); π is the so-called "Coriolis coupling operator" depending upon normal coordinates and their conjugate momenta that is to say, only upon operators in set X; Π is the total angular momentum, the sole quantity depending upon operators in set Y.

If the molecule is a spherical top molecules such as methane main isotopologue, the matrix elements $\langle\psi_0|\mu_\alpha(X)|\psi_0\rangle_{\mathbf{x}} = 0$ for all α, for symmetry reasons, therefore there is no zero order effective dipole moment, and the last term in the second order contribution is also zero.

By symmetry, the x, y, z directions are equivalent, so, it is only necessary to determine the z-term of the Eq.(47) to obtain the first order contribution to the effective dipole moment, the x, y-terms being obtained by circular permutation of the x, y, z indices. Given the irreducible representations of the group Td carried by $\mu(X)$ and Π, the z-component has the simple form,

$$\sum_{k_1 \neq 0} \frac{\langle \psi_{k_1} | \mu_z(X) | \psi_0 \rangle_{\mathbf{x}} H_1(Y)_{0,k_1}}{\nu_0 - \nu_{k_1}} = \frac{\theta^z_{xy}}{2} (\Pi_x \Pi_y + \Pi_y \Pi_x), \tag{50}$$

where, θ^{xy}_z is just a real number. This expression is of the same form as the one obtained by Watson [10] and the notation θ^{xy}_z with the factor $\frac{1}{2}$ matches that of this author.

The first order expression has been used in all spectroscopic studies to date. Higher order corrections have been considered by Ozier [11], however, as far as we are aware, they have never been retrieved from experiment nor calculated. Ozier implicitly assumed that the dipole moment operator in the laboratory frame can be cast in the form,

$$\mu_f(Y) = \sum_{\alpha=x,y,z} \lambda_{f\alpha}(Y) \tilde{\mu}_\alpha(Y) + \tilde{\mu}_\alpha(Y) \lambda_{f\alpha}(Y) \tag{51}$$

and expanded $\tilde{\mu}_\alpha(Y)$ as a power series of the Π_x, Π_y, Π_z operators in [11]. However, if our first order expression can assume the form of Eq.(51) by setting $\tilde{\mu}_z(Y) = \frac{\theta^z_{xy}}{2}(\Pi_x \Pi_y + \Pi_y \Pi_x)$, and similarly for the other components, this is no longer the case at order 2. In particular, the first term in the right hand side of Eq.(48) has the $\lambda_{f\alpha}(Y)$'s operators in between two Y-dependent operators and the commutators that are needed to bring them on the sides do not necessarily cancel off. Furthermore, the remaining terms writes as $\sum_{\alpha=x,y,z} \lambda_{f\alpha}(Y) \tilde{\mu}_\alpha(Y) + \tilde{\mu}^\dagger_\alpha(Y) \lambda_{f\alpha}(Y)$ and $\tilde{\mu}^\dagger_\alpha(Y)$ can be different from $\tilde{\mu}_\alpha(Y)$.

In fact, symmetry considerations gives the following form for the z-term in Eq.(48),

$$\lambda_{fz}(Y)\Big[c_1(\Pi_x\Pi_y+\Pi_y\Pi_x)+ic_2\Pi_z(\Pi_x^2-\Pi_y^2)+ic_3(\Pi_x^2-\Pi_y^2)\Pi_z$$
$$ic_4(\Pi_x(\Pi_z\Pi_x+\Pi_x\Pi_z)-\Pi_y(\Pi_y\Pi_z+\Pi_z\Pi_y))+ic_5((\Pi_z\Pi_x+\Pi_x\Pi_z)\Pi_x-(\Pi_y\Pi_z+\Pi_z\Pi_y)\Pi_y)$$
$$+c_6(\Pi_x\Pi_y+\Pi_y\Pi_x)(\Pi_x^2+\Pi_y^2)+c_7(\Pi_x^2+\Pi_y^2)(\Pi_x\Pi_y+\Pi_y\Pi_x)+$$
$$c_8(\Pi_x\Pi_y+\Pi_y\Pi_x)\Pi_z^2+c_9\Pi_z^2(\Pi_x\Pi_y+\Pi_y\Pi_x)$$
$$+c_{10}((\Pi_z\Pi_x+\Pi_x\Pi_z)(\Pi_y\Pi_z+\Pi_z\Pi_y)+(\Pi_y\Pi_z+\Pi_z\Pi_y)(\Pi_z\Pi_x+\Pi_x\Pi_z))]$$
$$+c_{11}\Pi_x\lambda_{fz}(Y)\Pi_y+ic_{12}\Pi_z\lambda_{fz}(Y)(\Pi_x^2-\Pi_y^2)$$
$$+ic_{13}(\Pi_x\lambda_{fz}(Y)(\Pi_z\Pi_x+\Pi_x\Pi_z)-\Pi_y\lambda_{fz}(Y)(\Pi_y\Pi_z+\Pi_z\Pi_y))$$
$$+c_{14}(\Pi_x^2+\Pi_y^2)\lambda_{fz}(Y)(\Pi_x\Pi_y+\Pi_y\Pi_x)+c_{15}\Pi_z^2\lambda_{fz}(Y)(\Pi_x\Pi_y+\Pi_y\Pi_x)$$
$$+c_{16}((\Pi_z\Pi_x+\Pi_x\Pi_z)\lambda_{fz}(Y)(\Pi_y\Pi_z+\Pi_z\Pi_y)+hermitic\ conjugate, \tag{52}$$

where $c_1,\cdots,c_{16}$ are real coefficients. The commutation property of the angular momenta [3], $[\Pi_\alpha,\Pi_\beta]=-ie_{\alpha\beta\gamma}\Pi_\gamma$, with $e_{\alpha\beta\gamma}$ the unit antisymmetrical tensor, allows one to simplify the above expression, showing that there are six redundant coefficients among $c_1,\cdots,c_{10}$, since one obtains:

$$\lambda_{fz}(Y)\Big[(c_1-2c_3-3c_4-c_5-4c_6+4c_8+3c_{10})(\Pi_x\Pi_y+\Pi_y\Pi_x)$$
$$+i(c_2+c_3+2c_4+2c_5+4c_6-4c_8-8c_{10})\Pi_z(\Pi_x^2-\Pi_y^2)$$
$$+(c_6+c_7)(\Pi_x^2+\Pi_y^2)(\Pi_x\Pi_y+\Pi_y\Pi_x)+(c_8+c_9+4c_{10})\Pi_z^2(\Pi_x\Pi_y+\Pi_y\Pi_x)\Big]$$
$$+c_{11}\Pi_x\lambda_{fz}(Y)\Pi_y+ic_{12}\Pi_z\lambda_{fz}(Y)(\Pi_x^2-\Pi_y^2)$$
$$+ic_{13}(\Pi_x\lambda_{fz}(Y)(\Pi_z\Pi_x+\Pi_x\Pi_z)-\Pi_y\lambda_{fz}(Y)(\Pi_y\Pi_z+\Pi_z\Pi_y))$$
$$+c_{14}(\Pi_x^2+\Pi_y^2)\lambda_{fz}(Y)(\Pi_x\Pi_y+\Pi_y\Pi_x)+c_{15}\Pi_z^2\lambda_{fz}(Y)(\Pi_x\Pi_y+\Pi_y\Pi_x)$$
$$+c_{16}((\Pi_z\Pi_x+\Pi_x\Pi_z)\lambda_{fz}(Y)(\Pi_y\Pi_z+\Pi_z\Pi_y)+hermitic\ conjugate. \tag{53}$$

In the third line of expression (53), one could easily make appear $(\Pi_x^2+\Pi_y^2+\Pi_z^2)$ so that the fourth order terms in factor of $\lambda_{fz}(Y)$ would ressemble the related expression in [11]. However, expresion (53) is much more complex than that considered by Ozier. In particular there are third order terms that do not cancel off, either because there is a $\lambda_{fz}(Y)$ in the middle or because the expression that could be identified to $\tilde{\mu}_z(Y)$ is not Hermitian.

A numerical application using these expression up to second order with comparison to a recent experiment [12], is to appear soon [13].

V. CONCLUSION

We have presented and effective observable theory for quantum systems with two distinguishable sets of dof, which put on a firm ground the generalized perturbation method proposed and applied in previous studies. The present work shows that the eigenvalues of the effective Hamiltonian will converge to the exact energies of the complete Hamiltonian, when the perturbation series converges. Exact eigenstates can also be obtained from the effective eigen-operators, as defined in the theory, by applying them to the eigenfunctions of the effective Hamiltonian.

We have also derived explicit expressions for effective observable such as the dipole moment up to order 2. In the case of the methane vibrational ground state, it has been shown that the effective rotational dipole moment is a more complex operator than previously anticipated. At the first order of our perturbation theory, as in the case of a single contact transformation [10,14,15], we do find that the laboratory-fixed effective dipole moment operator is a symmetrized scalar product of a direction cosine vector and an other vector of Hermitian operators which can be interpreted as a body-fixed effective dipole moment. However, this interpretation seems no longer possible at order 2, because the operators that one could identify with body-fixed effective dipole components are not Hermitian, and in addition, there are also terms where direction cosine operators are in between angular momentum operators with no prospect of simplification by using their commutation relations [16].

A numerical test of our dipole moment formulas using ab initio data, with a careful assessment of the contributions of the different terms and of their convergence, is currently in progress. Given the high interest of methane in high resolution spectroscopy and in space sciences [17,18,12], our formulas could also be used by spectroscopists to refined their experimental data with a more detailed effective dipole moment expression.

4 ACKNOWLEDGEMENTS

The author acknoledge Dr. F. Patras for fruitful discussions and the suggestion of several improvements.

References

[1] P. Cassam-Chenaï and J. Liévin, Int. J. Quantum Chem. **93**, 245-264 (2003).

[2] P. Cassam-Chenaï, J. Quant. Spectrosc. Radiat. Transfer **82**, 251-277 (2003).

[3] J. K. G. Watson, Mol. Phys. **15**, 479-490 (1968).

[4] J. K. G. Watson, Mol. Phys. **19**, 465-487 (1970).

[5] H. H. Nielsen, Phys. Rev. **60**, 794 (1941).

[6] I. M. Mills, in "'Molecular Spectroscopy: Modern Reseach", K. Narahari Rao and C. W. Mathews, Eds., (Acadmic Press, New York, 1972), pp. 115-140.

[7] M. R. Aliev and J. K. G. Watson, in "Molecular Spectroscopy: Modern Reseach" (K. Narahari Rao, Ed.), Vol. 3 pp. 1-67, Acadmic Press, Orlando, FL, 1985.

[8] L.S. Rothman, I.E. Gordon, A. Barbe, D.Chris Benner, P.F. Bernath, M. Birk, V. Boudon, L.R. Brown, A. Campargue, J.-P. Champion, K. Chance, L.H. Coudert, V. Dana, V.M. Devi, S. Fally, J.-M. Flaud, R.R. Gamache, A. Goldmanm, D. Jacquemart, I. Kleiner, N. Lacome, W.J. Lafferty, J.-Y. Mandin, S.T. Massie, S.N. Mikhailenko, C.E. Miller, N. Moazzen-Ahmadi, O.V. Naumenko, A.V. Nikitin, J. Orphal, V.I. Perevalov, A. Perrin, A. Predoi-Cross, C.P. Rinsland, M. Rotger, M. Šimečkovà, M.A.H. Smith, K. Sung, S.A. Tashkun, J. Tennyson, R.A. Toth, A.C. Vandaele, J. Vander Auwera J. Quant. Spectrosc. Radiat. Transfer **82**, 251-277 (2008).

[9] P. Cassam-Chenaï, *Des fondements thoriques des concepts et mthodes de la chimie quantique l'analyse et la prdiction d'observations*, Habilitation thesis, Universit de Nice-Sophia Antipolis, (2003).

[10] J.K.G. Watson, J. Mol. Spectrosc. **40**, , (536).,1971

[11] I. Ozier, J. Mol. Spectrosc. **58**, , (39).,1975

[12] V. Boudon, O. Pirali, P. Roy, J.-B. Brubach, L. Manceron, J. Vander Auwera J. Quant. Spectrosc. Radiat. Transfer **111**, 1117 (2010).

[13] P. Cassam-Chenaï and J. Liévin, to be published

[14] M. Loete, Can. J. Phys. **66**, 17 (1988).

[15] A. Mourbat, A. Aboumajd and M. Loete, J. Mol. Spectrosc. **190**, 198 (1998).

[16] J. H. Van Vleck, Rev. Mod. Phys. **23**, 213 (1951).

[17] E.H. Wishnow, G.S. Orton, I. Ozier, H.P. Gush, J. Quant. Spectrosc. Radiat. Transfer **103**, 102 (2007).

[18] S. Albert, S. Bauerecker, V. Boudon, L.R. Brown, J.-P. Champion, M. Lote, A. Nikitin, M. Quack, Chem. Phys. **356**, 131 (2009).

[19] X. G. Wang et E. L. Sibert, Spectrochimica Acta A **58**, 863 (2002).

[20] C. Wenger and J. P. Champion, J. Quant. Spectrosc. Radiat. Transfer **59**, 471-480 (1998).

[21] S. Carter and J. M. Bowman, J. Phys. Chem. **A104**, 2355 (2000).

[22] X. G. Wang et T. Carrington,J. Chem. Phys **121**, 2937 (2004).

Tables

	Van Vleck Perturbation			Our method			STDS
	ord2	ord4	ord6	ord0	ord2	ord4	
$J=1$	10.59973	10.44174	10.44237	10.63296	10.48010	10.48008	10.481648
$J=2$	31.79918	31.32521	**31.32439**	31.89887	**31.43746**	**31.43742**	31.442121
	31.79918	31.32521	*31.32463*	31.89887	*31.43772*	*31.43769*	31.442387
$J=3$	63.59837	62.65041	**62.64064**	63.79775	**62.86645**	**62.86635**	62.875779
	63.59837	62.65041	62.64162	63.79775	62.86749	62.86742	62.876841
	63.59837	62.65041	*62.64285*	63.79775	*62.86879*	*62.86877*	62.878169

Table 1

Convergence of methane rotational levels (in cm^{-1}) in the vibrational ground state with perturbation order. Van Vleck Perturbation theory was applied to a PES with 12 force constants adjusted on experimental vibrational wave numbers [19], the computational effort to go beyond $J=3$ was found too heavy. Our generalized Rayleigh-Schrödinger perturbative predictions are purely ab initio and were made up to $J=18$ in [1], and up to $J=30$ in [2]. The last column coresponds to the levels derived from experiment, obtained with the STDS package [20].

	[21]	[22]	[19]	our work	STDS
$J = 1$	10.47	10.430	10.44237	10.48165	10.481648
$J = 2$	N/A	N/A	31.32439	31.44213	31.442121
	N/A	N/A	31.32463	31.44240	31.442387
$J = 3$	N/A	N/A	62.64064	62.87581	62.875779
	N/A	N/A	62.64162	62.87689	62.876841
	N/A	N/A	62.64285	62.87824	62.878169
$J = 4 - 18$	N/A	N/A	N/A	*largest relative difference* 2.10^{-5}	

Table 2

Energies in cm^{-1} of methane rotational levels in its vibrational ground state predicted by different approaches. In [19] 12 force constants were adjusted on experiment. In our work [1] (fifth column) a global scaling factor of 1.0002535 accounting for the error in the equilibrium distance was applied to all levels. The last column corresponds to the prediction of the STDS package [20] from an effective Hamiltonian, fitted on experimental transitions, accurate to 10^{-5} cm^{-1} .