The generalized mean field configuration interaction method

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Abstract

The mean field configuration interaction (MFCI) method is a variational approximation method that has been developed to solve the Schrödinger equation for molecular vibrations (VMFCI) and electrons (EMFCI). The Rayleigh-Schrödinger perturbation theory generalized to eigen-operators in non-commutative rings has been proposed to solve the Schrödinger equation for molecular rotation-vibration degrees of freedom. In the present work, the two approaches are merged in a unified method, the perturbative ansatz giving a "generalized mean field" for the MFCI approach. At order one of perturbation, the MFCI method is recovered. However, higher orders give more accurate mean fields taking better into account the coupling of the so-called "active" and "spectator" degrees of freedom (DOF) defined in a MFCI step. The new method has increased flexibility, since not only one can build any hierarchy of partitions of the system DOF as in the MFCI method, but one can also tune up the perturbation order at each MFCI step for each subset of DOF. An illustrative calculation of methane ro-vibrational spectrum is presented.

Keywords:

perturbative mean field, configuration interaction, contraction of degrees of freedom.

Suggested running head: GMFCI

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1 Introduction

The mean field configuration interaction (MFCI) method has been developed originally by Cassam-Chenaï and Liévin for molecular vibrations and was called vibrational MFCI (VMFCI) [1–3]. It has proved extremely powerful and flexible to solve the molecular, vibrational, stationary Schrödinger equation [4–6]. Combined with a generalized perturbation theory, it has given effective rotational observable [1,7,8], from which accurate rotational spectra were calculated [4,9].

In the present work, we recognize in the effective Hamiltonian of a MFCI step, a generalized pertubation first order Hamiltonian, and in the Hamiltonian of the original contraction method [10–13] a zero order one. Then, it is natural to propose a more general MFCI method, where one can adjust the order of perturbation to obtain an effective mean-field Hamiltonian of a targeted level of accuracy, assuming that the formal perturbative series of non necessarily commuting, effective operators, converges. The MFCI method is generalized in the sense that the mean-field due to spectator DOF, used to build the partial Hamiltonian of the active DOF, can include corrective terms of order greater than one, involving excitations to, or, from the reference spectator state. In this case, one will speak of a "generalized mean-field" and a generalized mean-field configuration interaction (GMFCI) method.

The article is organized as follows: We begin with a presentation of the main ideas and equations which the GMFCI method is based over. Then, we show that our previous ro-vibrational calculations can serve as an illustration of the GMFCI method. We give updated results for methane vibrational ground state rotational spectrum. We conclude on the new applications the generalization will permit to deal with.

2 The GMFCI method

A natural approximation strategy in physics, which follows Descartes second precept, consists in separating the system degrees of freedom into subgroups. In quantum physics, this translates in building the state space as a tensor product of DOF subgroup Hilbert spaces. However, physical wave functions are seldom exactly decomposable into a simple tensor product of factors pertaining to the different Hilbert subspaces, even when one

disregards spin statistics or EPR correlations.

The MFCI method has been proposed to separate DOF and contract wave functions, according to a hierarchy of DOF partitions, designed to capture the physics of the system while controling computational costs. More precisely, the MFCI method consists in performing configuration interactions (CI) of some DOF in the mean field of the others. The sizes of the finite basis sets used in successive CI, is kept within a manageable range, owing to a basis "truncation scheme" associated to the DOF partitioning or "contraction scheme". The power of the method comes from the mean field (MF) term added to the group Hamiltonians not present in the original contraction approach [10–13]. In the GMFCI method, the expression of this MF term is extented to include corrective terms according to a pertubative expansion.

2.1 Partitions of DOF

Consider a quantum system with N distinguishable DOF. A GMFCI step starts with a partition, P, of the N DOF into n_P subsets :

$$P = (I_1, I_2, \cdots, I_{n_P}) = (\{i_1^1, i_2^1, \cdots, i_{k_1}^1\}, \{i_1^2, i_2^2, \cdots, i_{k_2}^2\}, \cdots, \{i_1^{n_P}, i_2^{n_P}, \cdots, i_{k_{n_P}}^{n_P}\}) \quad (1)$$

Using partition P the Hamiltonian can be written as :

$$\begin{aligned}
H = h_0 &+ \sum_{\gamma_1=1}^{n_P} h_{\gamma_1}(I_{\gamma_1}) \\
&+ \sum_{1 \leq \gamma_1 < \gamma_2 \leq n_P} h_{\gamma_1,\gamma_2}(I_{\gamma_1}) h_{\gamma_1,\gamma_2}(I_{\gamma_2}) \\
&+ \cdots + h_{1,2,\cdots,n_P}(I_1) h_{1,2,\cdots,n_P}(I_2) \cdots h_{1,2,\cdots,n_P}(I_{n_P})
\end{aligned} \quad (2)$$

where $h_{\gamma_1,\gamma_2,\ldots,\gamma_k}(I_{\gamma_l})$ denotes an operator acting on DOF in subsets I_{γ_l}.

Then, one defines an equal or coarser partition, $Q = (J_1, J_2, \cdots, J_{n_Q})$, satisfying $n_Q \leq n_P$ and $\forall \gamma \in \{1, \cdots, n_P\}, \exists \alpha \in \{1, \cdots, n_Q\}$ such that $I_\gamma \subseteq J_\alpha$.

For the GMFCI step under consideration, we call "contractions" the subsets J_α, and "components of contraction J_α" the subsets I_γ such that $I_\gamma \subseteq J_\alpha$. When successive GMFCI steps are performed, the *components* of one step are the *contractions* of the

previous step.

2.2 Product basis sets

Let us assume that contraction J_α has β_α components :

$$
\begin{aligned}
J_\alpha &= I_{\gamma_1} \cup I_{\gamma_2} \cup \cdots \cup I_{\gamma_{\beta_\alpha}} \\
&= \left\{ i_1^{\gamma_1}, \cdots, i_{k_{\gamma_1}}^{\gamma_1}, \cdots, i_1^{\gamma_{\beta_\alpha}}, \cdots, i_{k_{\gamma_{\beta_\alpha}}}^{\gamma_{\beta_\alpha}} \right\} \\
&= \left\{ j_1^\alpha, \cdots, j_{l_\alpha}^\alpha \right\} \quad \text{with} \quad l_\alpha = k_{\gamma_1} + \cdots + k_{\gamma_{\beta_\alpha}}.
\end{aligned} \tag{3}
$$

For each component I_γ, we suppose that we have a basis set of orthonormalized functions, $\{\phi_{I_\gamma}^{m_\gamma}\}_{m_\gamma \in \{0,\dots,d_\gamma\}}$, spanning an Hilbert subspace of dimension $(d_\gamma + 1)$. We further assume that these functions are eigenfunctions of some model Hamiltonian, H_γ^{mod}, associated to the eigenvalues, $\{E_{I_\gamma}^{m_\gamma}\}_{m_\gamma \in \{0,\dots,d_\gamma\}}$, in increasing order, the indice $m_\gamma = 0$ corresponding to the ground state of H_γ^{mod}.

For contraction J_α, we build a so-called "product basis set", $\{\Phi_{J_\alpha}^{M_\alpha}\}_{M_\alpha}$, spanning an Hilbert subspace of dimension say, $(D_\alpha$, by constructing product functions of the form:

$$
\Phi_{J_\alpha}^{M_\alpha} = \bigotimes_{I_\gamma \subseteq J_\alpha} \phi_{I_\gamma}^{m_\gamma} \tag{4}
$$

or more explicitly, writing variable dependencies:

$$
\Phi_{J_\alpha}^{M_\alpha}(q_{j_1^\alpha}, \cdots, q_{j_{l_\alpha}^\alpha}) = \prod_{I_\gamma \subseteq J_\alpha} \phi_{I_\gamma}^{m_\gamma}(q_{i_1^\gamma}, \cdots, q_{i_{k_\gamma}^\gamma}),
$$

where $M_\alpha = (m_{\gamma_1}, \cdots, m_{\gamma_{\beta_\alpha}})$, is the multiplet of the indices "m_γ", appearing on the right-hand side of the equation. So, $M_\alpha = (0, ..., 0)$, will correspond to the product of ground state functions.

The dimension, D_α, of the basis set for contraction J_α can be different from the product of dimensions of its component's basis sets, $\prod_{I_\gamma \subseteq J_\alpha} (d_\gamma + 1)$, because of possible basis function truncations, usually performed according to some energy criteria, $E_{J_\alpha}^{max}, (E_{I_\gamma}^{max})_{I_\gamma \subseteq J_\alpha}$. Typically, we will select only product functions, $\Phi_{J_\alpha}^{(m_{\gamma_1}, \cdots, m_{\gamma_{\beta_\alpha}})}$, such that

$$
\sum_{I_\gamma \subseteq J_\alpha} E_{I_\gamma}^{m_\gamma} < E_{J_\alpha}^{max}, \tag{5}
$$

and/or, $\forall m_\gamma \in \{m_{\gamma_1}, \cdots, m_{\gamma_{\beta_\alpha}}\}$,

$$E_{I_\gamma}^{m_\gamma} < E_{I_\gamma}^{max}. \tag{6}$$

2.3   Mean field Hamiltonian

Now, we consider a given contraction J_α as "active", and call the other contractions "spectators". For the active contraction J_α, we define a partial Hamiltonian, H_α, by grouping all the terms in H involving the DOF in components I_γ of J_α:

$$H_\alpha = h_0 + \sum_{\substack{\gamma_1 \\ such\ that \\ I_{\gamma_1} \subseteq J_\alpha}} h_{\gamma_1}(I_{\gamma_1}) + \sum_{\substack{\gamma_1 < \gamma_2 \\ such\ that \\ I_{\gamma_1}, I_{\gamma_2} \subseteq J_\alpha}} h_{\gamma_1,\gamma_2}(I_{\gamma_1}) h_{\gamma_1,\gamma_2}(I_{\gamma_2})$$
$$+ \cdots + \sum_{\substack{\gamma_1 < \cdots < \gamma_{\beta_\alpha} \\ such\ that \\ I_{\gamma_1}, \cdots, I_{\gamma_{\beta_\alpha}} \subseteq J_\alpha}} h_{\gamma_1, \cdots, \gamma_{\beta_\alpha}}(I_{\gamma_1}) \cdots h_{\gamma_1, \cdots, \gamma_{\beta_\alpha}}(I_{\gamma_{\beta_\alpha}}) \tag{7}$$

Then we consider an eigenvalue equation for J_α:

$$[H_\alpha^{eff} - \epsilon_\alpha]\Phi_\alpha = 0, \tag{8}$$

where H_α^{eff} is an "effective" Hamiltonian determined according to perturbative expressions:

Order 0: Original contraction method Hamiltonian [10–13]

$$H_\alpha^{eff} = H_\alpha \tag{9}$$

Order 1: MFCI Hamiltonian [1–3]

$$H_\alpha^{eff} = H_\alpha + \langle \bigotimes_{I_\gamma \not\subseteq J_\alpha} \phi_{I_\gamma}^0 | H - H_\alpha | \bigotimes_{I_\gamma \not\subseteq J_\alpha} \phi_{I_\gamma}^0 \rangle \tag{10}$$

Order 2: second order GMFCI Hamiltonian

$$H_\alpha^{eff} = H_\alpha + \langle \bigotimes_{I_\gamma \nsubseteq J_\alpha} \phi_{I_\gamma}^0 |H - H_\alpha| \bigotimes_{I_\gamma \nsubseteq J_\alpha} \phi_{I_\gamma}^0 \rangle$$

$$+ \sum_{\substack{(m_{\gamma_1},\cdots,m_{\gamma_{(n_P-\beta_\alpha)}}) \neq (0,\cdots,0) \\ for\ \gamma_1,\dots,\gamma_{(n_P-\beta_\alpha)}\ such\ that\ I_{\gamma_l} \nsubseteq J_\alpha}} \frac{\langle \bigotimes_{I_\gamma \nsubseteq J_\alpha} \phi_{I_\gamma}^0 |H - H_\alpha| \bigotimes_{I_\gamma \nsubseteq J_\alpha} \phi_{I_\gamma}^{m_\gamma} \rangle \langle \bigotimes_{I_\gamma \nsubseteq J_\alpha} \phi_{I_\gamma}^{m_\gamma} |H - H_\alpha| \bigotimes_{I_\gamma \nsubseteq J_\alpha} \phi_{I_\gamma}^0 \rangle}{\sum_{\gamma\ /\ I_\gamma \nsubseteq J_\alpha} E_{I_\gamma}^0 - E_{I_\gamma}^{m_\gamma}},$$

(11)

and so on, up to an arbitrary order. These expressions are those given by the generalized perturbation theory of Refs. ([7–9]). They can also be derived through equivalent approaches [14–17]. Dirac bracket notation corresponds in these equations to integration over spectator variables only.

The summation on the m_γ's in Eq. (11) can be restricted according to constraints of the types given in expressions (5) and (6).

Note that, at orders more than zero, the corrective terms added to the original contraction method Hamiltonian, correspond, here, to mean field effects of the approximate ground states of the spectator modes. As explained in [3], it is not suitable to use an excited state mean field, (and that holds too for an excited state generalized mean field), if one intends to perform further GMFCI steps. In contrast, at the last step of a sequence of GMFCI calculations, one can modify the equations above to use a generalized mean field corresponding to an arbitrary spectator state. This is straightforward if the spectator approximate, reference state is non degenerate, that is to say, if it can be represented by $\bigotimes_{I_\gamma \nsubseteq J_\alpha} \phi_{I_\gamma}^{m_\gamma^0}$ and if this is the only product function of this type with approximate energy equal to $\sum_{\gamma\ /\ I_\gamma \nsubseteq J_\alpha} E_{I_\gamma}^{m_\gamma^0}$. It suffices to replace the "0" superscripts by the "m_γ^0" of the reference state, and to avoid the multiplet, $(m_{\gamma_1}^0, \cdots, m_{\gamma_{(n_P-\beta_\alpha)}}^0)$, in the GMFCI Hamiltonian summations over $(m_{\gamma_1}, \cdots, m_{\gamma_{(n_P-\beta_\alpha)}})$. In case of a k-fold degenerate or quasi degenerate excited spectator state, one should use a k-dimensional super-Hamiltonian for the active contraction, as explained elsewhere [18].

A nth-order GMFCI calculation consists in solving the eigen-equation (8) for a nth-order generalized mean field Hamiltonian, by performing a "configuration interaction" in the product basis sets, Eq. (4), that is to say, by diagonalizing the representation of the Hamiltonian in this finite dimensional Hilbert subspace basis (Galerkin method).

Thereby, we obtain for the active contraction a new basis set, $\{\phi_{J_\alpha}^{m_\alpha}\}_{m_\alpha\in\{0,\dots,d_\alpha\}}$, of dimension $(d_\alpha+1)$, made of eigenvectors of the generalized mean field Hamiltonians. So, the process can be iterated, the H_γ^{mod} of step $n+1$ being the H_α^{eff} of step n. The eigenvalues $\{E_{J_\alpha}^{m_\alpha}\}_{m_\alpha\in\{0,\dots,d_\alpha\}}$ associated to the $\{\phi_{J_\alpha}^{m_\alpha}\}_{m_\alpha\in\{0,\dots,d_\alpha\}}$ will serve to truncate the product basis sets according to energy criteria (5) and (6).

In practice, $(d_\alpha+1)$ can be less than D_α, as one needs not to calculate all the eigenpairs of H_α^{eff}. This is so, when some high energy states will not be required at all for the construction of the product basis sets of the next step according to the anticipated truncation criteria to be applied.

Note that, in the computer code CONVIV [19], a GMFCI is performed for each contraction of the Q-partition before updating the H_γ^{mod}. That is to say, the n_Q contractions of Q are treated simultaneously as active and the same n_P sets of eigenstates $\{E_{I_\gamma}^{m_\gamma},\phi_{I_\gamma}^{m_\gamma}\}_{m_\gamma\in\{0,\dots,d_\gamma\}}$ are used to build the spectator product functions appearing in the n_Q GMFCI Hamiltonians. However, the orders of the n_Q GMFCI Hamiltonians need not be the same, nor the truncation criteria for the spectator basis functions. Then, the n_Q new sets of eigenstates, $\{E_{J_\alpha}^{m_\alpha},\phi_{J_\alpha}^{m_\alpha}\}_{m_\alpha\in\{0,\dots,d_\alpha\}}$, are used to update the n_P sets, $\{E_{I_\gamma}^{m_\gamma},\phi_{I_\gamma}^{m_\gamma}\}_{m_\gamma\in\{0,\dots,d_\gamma\}}$. In other words, CONVIV performs n_Q GMFCI steps in parallel for each successive partition, instead of sequential GMFCI steps. This parallel treatment has been found more effective for vibrational MFCI calculations, whereas this is not the case for electronic MFCI [3].

2.4 calculation of observables

Whether one performs sequential or parallel GMFCI steps, after each step, one has to decide whether the Q-partition is sufficient, or if further contractions are necessary, to capture properly the important physical couplings between DOF. If eventually, all the DOF are contracted and $Q=(\{1,2,\cdots,N\})$, then eigenfunctions are obtained for the full system in the last GMFCI step, and, observable expectation values or transition matrix elements are calculated in the standard way. In contrast, if, at the last step, Q still contains more than one contraction, there are different ways to compute properties just as there are different orders to compute the effective Hamiltonian.

The eigenvalues of the effective Hamiltonian of each contraction can be interpreted as

energy levels of the subsystems corresponding to the DOF pertaining to the contraction. Assuming that the observable, O, can be expanded in the same fashion as the Hamiltonian, Eq.(2),

$$
\begin{aligned}
O = o_0 &+ \sum_{\alpha_1=1}^{n_Q} o_{\alpha_1}(J_{\alpha_1}) \\
&+ \sum_{1 \leq \alpha_1 < \alpha_2 \leq n_Q} o_{\alpha_1,\alpha_2}(J_{\alpha_1}) o_{\alpha_1,\alpha_2}(J_{\alpha_2}) \\
&+ \cdots + o_{1,2,\cdots,n_Q}(J_1) o_{1,2,\cdots,n_Q}(J_2) \cdots o_{1,2,\cdots,n_Q}(J_{n_Q}),
\end{aligned}
\tag{12}
$$

it is tempting to compute its matrix element between two total states represented by the product functions, $\bigotimes_{\alpha\in\{1,\ldots,n_Q\}} \phi_{J_\alpha}^{m_\alpha}$ and $\bigotimes_{\alpha\in\{1,\ldots,n_Q\}} \phi_{J_\alpha}^{m'_\alpha}$ according to the following equation,

$$
\begin{aligned}
&\langle \bigotimes_{\alpha\in\{1,\ldots,n_Q\}} \phi_{J_\alpha}^{m_\alpha} |O| \bigotimes_{\alpha\in\{1,\ldots,n_Q\}} \phi_{J_\alpha}^{m'_\alpha} \rangle = \\
&o_0 \prod_{\alpha\in\{1,\ldots,n_Q\}} \delta_{m_\alpha m'_\alpha} + \sum_{\alpha_1=1}^{n_Q} \langle \phi_{J_{\alpha_1}}^{m_{\alpha_1}} |o_{\alpha_1}(J_{\alpha_1})| \phi_{J_{\alpha_1}}^{m'_{\alpha_1}} \rangle \prod_{\alpha\in\{1,\ldots,n_Q\}\smallsetminus\{\alpha_1\}} \delta_{m_\alpha m'_\alpha} \\
&+ \sum_{1 \leq \alpha_1 < \alpha_2 \leq n_Q} \langle \phi_{J_{\alpha_1}}^{m_{\alpha_1}} |o_{\alpha_1,\alpha_2}(J_{\alpha_1})| \phi_{J_{\alpha_1}}^{m'_{\alpha_1}} \rangle \langle \phi_{J_{\alpha_2}}^{m_{\alpha_2}} |o_{\alpha_1,\alpha_2}(J_{\alpha_2})| \phi_{J_{\alpha_2}}^{m'_{\alpha_2}} \rangle \prod_{\alpha\in\{1,\ldots,n_Q\}\smallsetminus\{\alpha_1,\alpha_2\}} \delta_{m_\alpha m'_\alpha} \\
&+ \cdots + \prod_{\alpha\in\{1,\ldots,n_Q\}} \langle \phi_{J_\alpha}^{m_\alpha} |o_{1,2,\cdots,n_Q}(J_\alpha)| \phi_{J_\alpha}^{m'_\alpha} \rangle,
\end{aligned}
\tag{13}
$$

in particular, the expectation value over $\bigotimes_{\alpha\in\{1,\ldots,n_Q\}} \phi_{J_\alpha}^{m_\alpha}$ would be,

$$
\begin{aligned}
&\langle \bigotimes_{\alpha\in\{1,\ldots,n_Q\}} \phi_{J_\alpha}^{m_\alpha} |O| \bigotimes_{\alpha\in\{1,\ldots,n_Q\}} \phi_{J_\alpha}^{m_\alpha} \rangle = o_0 + \sum_{\alpha_1=1}^{n_Q} \langle \phi_{J_{\alpha_1}}^{m_{\alpha_1}} |o_{\alpha_1}(J_{\alpha_1})| \phi_{J_{\alpha_1}}^{m_{\alpha_1}} \rangle \\
&+ \sum_{1 \leq \alpha_1 < \alpha_2 \leq n_Q} \langle \phi_{J_{\alpha_1}}^{m_{\alpha_1}} |o_{\alpha_1,\alpha_2}(J_{\alpha_1})| \phi_{J_{\alpha_1}}^{m_{\alpha_1}} \rangle \langle \phi_{J_{\alpha_2}}^{m_{\alpha_2}} |o_{\alpha_1,\alpha_2}(J_{\alpha_2})| \phi_{J_{\alpha_2}}^{m_{\alpha_2}} \rangle \\
&+ \cdots + \prod_{\alpha\in\{1,\ldots,n_Q\}} \langle \phi_{J_\alpha}^{m_\alpha} |o_{1,2,\cdots,n_Q}(J_\alpha)| \phi_{J_\alpha}^{m_\alpha} \rangle.
\end{aligned}
\tag{14}
$$

However, this is not necessarily consistent with the derivation of the $\phi_{J_\alpha}^{m_\alpha}$'s if some of the latter correspond to an order 2 GMF, or, to an order 1 MF for a spectator reference state different from its counterpart in $\bigotimes_{\alpha\in\{1,\ldots,n_Q\}} \phi_{J_\alpha}^{m_\alpha}$ or $\bigotimes_{\alpha\in\{1,\ldots,n_Q\}} \phi_{J_\alpha}^{m'_\alpha}$.

A more rigorous expression can be derived when $(m_1, \cdots, m_{n_Q})$ and $(m'_1, \cdots, m'_{n_Q})$ differ by at most one component, say, without loss of generality, their first component. That is to say, $\forall\alpha \in \{2,\ldots,n_Q\}, m_\alpha = m'_\alpha$, and, we denote by, m_α^0, this common value. (In fact, if this condition is not met, further contractions should be made to achieve it and avoid using Eqs.(13) and (14) as such.) So, let us assume that the last GMFCI step

corresponds to contraction 1 being active, with a spectator reference state equal to the product function $\bigotimes_{\alpha \in \{2,...,n_Q\}} \phi_{J_\alpha}^{m_\alpha^0}$. The effective Hamiltonians of section 2.3 are related to effective wave operators, as described in [7]. For example, Eq.(11), generalized for the spectator reference state, $(m_2^0, \cdots, m_{n_Q}^0)$, is related to a first order effective wave operator, acting on J_1-states, of the form,

$$\hat{\phi}_{J_1}^{eff} = Id_{J_1} \otimes \phi_{J_2}^{m_2^0} \otimes \cdots \otimes \phi_{J_{n_Q}}^{m_{n_Q}^0}$$

$$+ \sum_{(m_2, \cdots, m_{n_Q}) \neq (m_2^0, \cdots, m_{n_Q}^0)} \frac{\langle \bigotimes_{\alpha=2}^{n_Q} \phi_{J_\alpha}^{m_\alpha} | H - H_{J_1} | \bigotimes_{\alpha=2}^{n_Q} \phi_{J_\alpha}^{m_\alpha^0} \rangle}{\sum_{\alpha=2}^{n_Q} E_{J_\alpha}^{m_\alpha^0} - E_{J_\alpha}^{m_\alpha}} \otimes \phi_{J_2}^{m_2} \otimes \cdots \otimes \phi_{J_{n_Q}}^{m_{n_Q}}, \qquad (15)$$

where Id_{J_1} denotes the identity operator on J_1-wave functions. Then, the matrix element of observable, O of Eq.(12), between two total states represented by the multiplets $(m_1, m_2^0, \cdots, m_{n_Q}^0)$ and $(m_1', m_2^0, \cdots, m_{n_Q}^0)$ is, up to order 1 in the wave operator expansion,

$$\langle \phi_{J_1}^{m_1} \hat{\phi}_{J_1}^{eff\,\dagger} | O | \hat{\phi}_{J_1}^{eff} \phi_{J_1}^{m_1'} \rangle = \langle \phi_{J_1}^{m_1} \otimes \phi_{J_2}^{m_2^0} \otimes \cdots \otimes \phi_{J_{n_Q}}^{m_{n_Q}^0} | O | \phi_{J_1}^{m_1'} \otimes \phi_{J_2}^{m_2^0} \otimes \cdots \otimes \phi_{J_{n_Q}}^{m_{n_Q}^0} \rangle$$

$$+ \sum_{(m_2, \cdots, m_{n_Q}) \neq (m_2^0, \cdots, m_{n_Q}^0)} \left(\langle \phi_{J_1}^{m_1} \otimes \phi_{J_2}^{m_2^0} \otimes \cdots \otimes \phi_{J_{n_Q}}^{m_{n_Q}^0} | O | \frac{\langle \bigotimes_{\alpha=2}^{n_Q} \phi_{J_\alpha}^{m_\alpha} | H - H_{J_1} | \bigotimes_{\alpha=2}^{n_Q} \phi_{J_\alpha}^{m_\alpha^0} \rangle \phi_{J_1}^{m_1'}}{\sum_{\alpha=2}^{n_Q} E_{J_\alpha}^{m_\alpha^0} - E_{J_\alpha}^{m_\alpha}} \otimes \phi_{J_2}^{m_2} \otimes \cdots \otimes \phi_{J_{n_Q}}^{m_{n_Q}} \rangle \right.$$

$$\left. + \langle \frac{\phi_{J_1}^{m_1} \langle \bigotimes_{\alpha=2}^{n_Q} \phi_{J_\alpha}^{m_\alpha} | H - H_{J_1} | \bigotimes_{\alpha=2}^{n_Q} \phi_{J_\alpha}^{m_\alpha^0} \rangle^\dagger}{\sum_{\alpha=2}^{n_Q} E_{J_\alpha}^{m_\alpha^0} - E_{J_\alpha}^{m_\alpha}} \otimes \phi_{J_2}^{m_2} \otimes \cdots \otimes \phi_{J_{n_Q}}^{m_{n_Q}} | O | \phi_{J_1}^{m_1'} \otimes \phi_{J_2}^{m_2^0} \otimes \cdots \otimes \phi_{J_{n_Q}}^{m_{n_Q}^0} \rangle \right) \qquad (16)$$

where $\hat{\phi}_{J_1}^{eff\,\dagger}$, (respectively, $\langle \Psi | H - H_{J1} | \Psi' \rangle^\dagger$), is the Hermitian conjugate of $\hat{\phi}_{J_1}^{eff}$, (respectively, $\langle \Psi | H - H_{J1} | \Psi' \rangle$) acting on the left on J_1-wave functions. Note that each term in the left-hand side of Eq. (16) is of the form of the right-hand side of Eq. (13), so, it can be expanded according to this equation. If observable O, itself, is expressed as a perturbative series, then the terms retained in the expansion must be determined according to the required, total, expansion order. Just like the Hamiltonian, the summation on components 2 to n_Q basis functions can be truncated according to energy criteria (5) and (6).

3 Application to methane rotation-vibration spectrum

The theory outlined in the previous section is directly applicable to any quantum system with distinguishable degrees of freedom, although, originally, it was intended to be used for the computation of rotation-vibration spectra of molecules. This theory is more general than what we have introduced in previous works, since it proposes the use of GMF at any step of a MFCI calculation, including intermediate steps. However, now, we are going to show that the calculation of the rotational spectrum of methane vibrational ground state, as performed in a former article [9], in fact, is a particular case of GMFCI calculation with a GMF of order more than 1 at the last step. Then, we will present numerical results of the same GMFCI scheme for an improved dipole moment surface (DMS) with respect to [9].

3.1 GMFCI calculation

The ro-vibrational Hamiltonian used to describe the rotation-vibration DOF of methane in the present study, as in [9], is the Eckart-Watson Hamiltonian for non-linear molecules [20,21]. This Hamiltonian may not be suitable to describe molecular states with significant amplitude along some floppy DOF. However, this is not the case of the low-lying vibrational states of methane, we are interested in. The potential energy surface (PES) in the Hamiltonian is the 10th order, normal coordinate PES used in our previous calculation [9]. It has been derived from the Nikitin-Rey-Tuyterev (NRT) PES [22]. For details on the PES and on Watson μ-matrix expansion order, we refer the reader to Ref. [9].

Let us number the twelve ro-vibrational DOF. Number 1 is the symmetric streching DOF of mode ν_1 carrying an A_1 irreducible representation (irrep.) of the group T_d, 2 and 3 the bending DOF of mode ν_2 carrying an E irrep., 4, 5 and 6 the stretching DOF of mode ν_3 carrying a F_2 irrep., 7, 8 and 9 the bending DOF carrying also a F_2 irrep., 10, 11 and 12 the three Euler angles. The GMFCI calculation we have performed can be denoted compactly as,

$$
(HO, HO, HO, HO, SYM-TOP)/
$$

$$
(\{1\}_{[14]}^{(1,1,1,0)}, \{2,3\}_{[16]}^{(1,1,1,0)}, \{4,5,6\}_{[14]}^{(1,1,1,0)}, \{7,8,9\}_{[16]}^{(1,1,1,0)}, \{10,11,12\})^2/
$$

$$
(\{1\}^{(1,1,1,0)}, \{2,3\}^{(1,1,1,0)}, \{4,5,6\}_{[598]}^{(1,1,1,0)}, \{7,8,9\}_{[691]}^{(1,1,1,0)}, \{10,11,12\})^6/
$$

$$
(\{1,4,5,6\}_{(48000)}^{(1,1,0)}, \{2,3\}^{(1,1,1,0)}, \{7,8,9\}^{(1,1,1,0)}, \{10,11,12\})/
$$

$$
(\{1,4,5,6\}_{(22000)}^{(1,1,0)}, \{2,3\}_{(20000)}^{(1,1,0)}, \{7,8,9\}^{(1,1,0)}, \{10,11,12\})/
$$

$$
(\{1,2,3,4,5,6,7,8,9\}_{(19318)}^{(0)}, \{10,11,12\})/
$$

$$
(\{1,2,3,4,5,6,7,8,9\}, \{10,11,12\}_{[J=30]}^{(4)(8281,8281,4160)}). \tag{17}
$$

The notation means the following:

- The first line specifies the basis sets used for the different DOF. Here we have used standard harmonic oscillator "HO" basis functions, whose frequencies were derived from the quartic force constant of the PES, for the 9 internal DOF. Other possible choices available in the CONVIV code include: general HO basis "HO(ω,λ)" corresponding to a HO potential of wave number ω with minimum shifted by λ, Kratzer potential basis "KRA(r_0,D_e)" eigenfunctions of a Kratzer potential [23] parametrized by equilibrium distance r_0, and dissociation energy D_e; Morse potential basis "MOR(a,D_e)" eigenfunctions of a Morse potential [24] parametrized by exponent a, and dissociation energy D_e; trigonometric Pösch-Teller potential basis "TPT(α,μ)" eigenfunctions [25] (the parameter ν being set to zero); Chebychev polynomials "CHE" and so on. For the Euler angles, we have used the "SYM-TOP" basis made of eigenfunctions of a symmetric rigid rotator Hamiltonian [26].

- Each of the other lines describes a parallel GMFCI step as performed in CONVIV, or, when an exponent, "n", follows the last closing parenthesis, as on lines 2 and 3 of expression (17), a parallel GMFCI step iterated n-times with identical partition, truncations and GMF orders. Iterating a GMFCI step permits to achieve MF self-consistency as in the vibrational self-consistent field method [27,28], but for more general DOF partitions, as in [29]. The partition of the step is given in parentheses, the subsets of DOF making the partition being given in curly brackets. For example, lines 2 and 3 correspond to contracting degenerate components of internal modes together, and Euler angles together. In lines 4 and 5, all the stretching modes are contracted together. Finally, in lines 6 and 7, all internal modes are contracted together, (it is an instance of the vibrational configuration interaction method [30]).

- The superscripts of a curly bracket correspond to the orders of the GMF due to DOF in spectator contractions, when the DOF inside the curly brackets are active. Since the GMF is given by the spectator ground states of the previous step, there are as many order indices as there are spectator contractions at the previous step. For example, on the third line, the contraction $\{2,3\}^{(1,1,1,0)}$ indicates that the GMFCI calculation, when the E-mode is active, is performed with order 1 GMF, (that is the usual MF), from spectator contractions $\{1\}$, $\{4,5,6\}$, $\{7,8,9\}$ and order 0, (that is no mean field), from contraction $\{10,11,12\}$. So, there are four orders specified, whereas there are only three spectator contractions, DOF $\{1\}$ and $\{4,5,6\}$ being contracted at this step.

- When a proper GMF is used, that is when the GMF order, m, is more than 1, such as in line 7, the order index may have $(m-1)$ numbers as subscript. These numbers describe the truncations on spectator states for the sums appearing in perturbative corrective terms. For example, if the order $m = 2$, the sum of Eq. (11), that is in principle infinite, will be truncated in practice, according to one number specified as subscript. By convention, when the numbers of the subscript are in square brackets, the truncation is done according to function indices, (that is to say, according to restrictions on general quantum numbers), when it is in parentheses, the truncation is done according to wave numbers, (that is to say, according to thresholds on eigenvalues). For example, on line 7, $\{10,11,12\}^{(4)(8281,8281,4160)}$ means that the sums in second and third order, effective Hamiltonian, corrective terms are limited to the 8281 first spectator (that is to say, vibrational, here,) functions above the ground state, while at order four, only 4160 basis functions are used.

- The same convention is used for the curly bracket subscripts. However, in this case, the numbers specify truncations on the product basis functions of the active contraction, defined by the curly brackets, as explained in Section 2.2. On line 2, the integers in square brackets correspond to the maximum number, $M_{J_\alpha}^{max}$, of degenerate HO quanta that appear in the product basis set of Eq.(4), $\sum_{I_\gamma \subseteq J_\alpha} m_\gamma < M_{J_\alpha}^{max}$, (in this particular case, this criteria is more convenient than the energy criterium of Eq.(5)). On line 3, the subscripts means that 599 product basis functions were retained for the stretching mode ν_3, and 692 for the bending mode ν_4, (recall that the ground states are always associated to quantum number 0). On line 4, 5 and 6, the subscrits refer to a truncation on the sum of eigenvalues, Eq. (5). However, we use in fact wave number thresholds in

cm^{-1} , for the eigenvalue differences with respect to the ground state eigenvalues. For example, at line 4, the subscrit of the stretching contraction means that we only retain in the product basis sets the functions whose sum of component wave numbers are less than 48000 cm^{-1} above the ZPE. Finally, on line 7, the subscript means that SYM-TOP basis functions up to rotational quantum number [$J = 30$] have been used.

- For the calculation of the effective dipole moment transition elements, a second order expansion has been used. The summations in both first (see Eq. (16)) and second order terms were truncated at the 8282th Hamiltonian eigenfunction.

All these details are required to fully specify a GMFCI calculation. All the adjustable parameters have clear physical meanings. Their large number is related to the great flexibility of such a calculation.

3.2 Numerical results

The previous section shows that the generalized perturbation calculation, presented in Ref. [9], was indeed a GMFCI calculation with non trivial GMF. So, the numerical results for the R-branch of methane ground state, obtained in [9], could serve to illustrate the GMFCI theory. However, in the present work, we have updated these results with a complete third order DMS. The new results will not only demonstrate the accuracy a GMFCI calculation can reach, but they will also permit to assess the influence of the third order terms that were omitted in Ref. [9].

The DMS of the present work does not differ from that of [9] by the level of electronic calculation, that is MRCI [31,32]/aug-cc-pCV5Z [33,34]. The equilibrium geometry and normal coordinates are those of our previous study. However, an augmented grid of 119 points has been used. It is provided as supplementary material [35]. These points have been fitted with a complete set of polynomial generators allowed by symmetry up to third order. It includes ten third order terms that were omitted in our previous fit of the body-fixed z-component of the dipole moment. The results are given in Appendix A.

Tab. 1, diplays the difference between the fitted dipole moment constants up to second order. The introduction of new grid points and new third order terms hardly affect the first and second order constants. This shows the stability of the least square fit, the

variations due to the new points being essentially absorbed by the new and some old third order terms. The comparison of the dipole moment z-component expansion given in Appendix with that of Ref. [9], shows that the third order constants involving Q_1 are unchanged. The new terms involving the E-mode coordinates have limited influence on the old ones. This is in contrast with what occurs for the F_2 modes, where the introduction of two new terms coupling Q_{3z} and Q_{4z} results in the change of sign of two old third order constants.

Tab. 2 presents the intensities obtained from the new DMS along those from the old one. The formulas used to derive them from the GMFCI dipole moment transition matrix element have been explained in details in [9]. The new intensities are systematically lower by about 1 percent with respect to the formerly published values. The average relative error with respect to the (reliable) observed intensities changes from 5.85% to 5.93%, which is unsignificant given the targeted level of accuracy. In particular, this is well within the experimental average relative uncertainty of 10.62%. So, this supports `a posteriori` the reliability of our DMS for the calculation of the vibrational ground state intensities, despite the fact that it is limited to third order. Updated Q- and R-branch line lists are given as supplementary material [35].

4   Conclusion

When strong resonances occur in a quantum system, perturbative approximations are usually inappropriate. Perturbative series are known to converge poorly even in some simple cases, where in addition, no resummation technique is able to cover efficiently the full range of the parameter space [41,42].

When small energy differences relative to total energy occur, that is to say, typically, when two well-separated energy scales are present in a physical problem, the CI method may encounter numerical instabilities, due to a possibly ill-conditionned CI matrix. However, in such a situation, one is usually able to find a small parameter amenable to a rapidly converging pertubative expansion. Perturbative approaches are also better suited when the Hamiltonian is not bounded from below, as is often the case in relativistic systems, but also in vibrational Hamiltonians, whenever the potential is fitted with polynomials [3]. Finally, of course, when a large number of eigenstates is sought after, the compu-

tational cost of a perturbation method can be more advantageous than that of CI, the latter scaling at best as the CI matrix dimension to the power 3.

The increased flexibility of the GMFCI method with respect to MFCI allows one to take the best of two worlds, the perturbative and the variational ones. Our implementation of what we had called the "generalized perturbation method to non-commutative rings", was in fact a particular case of GMFCI calculation with a GMF of order 4, as shown in section 3. The numerical results presented here, with an improved DMS, confirm the reliability of the predictions made with our approach.

In practice, beside the rotation-vibration DOF partitioning explored in this article, we expect GMFCI to perform better than the simple MFCI approach for floppy systems, with large amplitude motion, or more generally, when slow and rapid motions are coupled in the same system. Work is in progress on hydrogen peroxyde, where, beside rotational DOF, a torsional DOF is coupled to the bending and stretching internal motions.

APPENDIX A: BODY-FIXED DIPOLE MOMENT

We give below the result of a least square fit of the dipole moment z-component grid provided as supplementary material [35]. The dipole moment z-component expansion in Cartesian mass-weighted normal coordinates is in atomic units. Note that the arbitrary phase factors in the definition of the normal coordinates are those corresponding to Gray and Robiette's conventions (Tab. 1 of Ref. [36]). The x- and y-components can be deduced by symmetry.

$$
\begin{aligned}
D_z(ACV5Z) = \\
-3.54425 \cdot 10^{-3} Q_{3z} + 2.32658 \cdot 10^{-3} Q_{4z} - 5.09773 \cdot 10^{-5} Q_1 Q_{3z} - 5.44507 \cdot 10^{-5} Q_1 Q_{4z} \\
-3.05546 \cdot 10^{-5} Q_{2a} Q_{3z} + 1.75830 \cdot 10^{-5} Q_{2a} Q_{4z} \\
-9.14627 \cdot 10^{-5} Q_{3x} Q_{3y} - 5.76126 \cdot 10^{-5} (Q_{3x} Q_{4y} + Q_{3y} Q_{4x}) + 6.15606 \cdot 10^{-5} Q_{4x} Q_{4y} \\
+9.81662 \cdot 10^{-8} Q_1^2 Q_{3z} + 2.94314 \cdot 10^{-7} Q_1^2 Q_{4z} \\
-1.08833 \cdot 10^{-7} Q_1 Q_{2a} Q_{3z} + 8.69156 \cdot 10^{-6} Q_1 Q_{2a} Q_{4z} \\
-1.12720 \cdot 10^{-7} Q_1 Q_{3x} Q_{3y} - 1.72212 \cdot 10^{-7} Q_1 (Q_{3x} Q_{4y} + Q_{3y} Q_{4x}) - 5.27870 \cdot 10^{-7} Q_1 Q_{4x} Q_{4y} \\
+7.53758 \cdot 10^{-8} Q_{3z} \left(Q_{2a}^2 + Q_{2b}^2 \right) + 5.65204 \cdot 10^{-7} Q_{4z} \left(Q_{2a}^2 + Q_{2b}^2 \right) \\
+1.19100 \cdot 10^{-8} Q_{3z} \left(Q_{2a}^2 - Q_{2b}^2 \right) + 4.17843 \cdot 10^{-7} Q_{4z} \left(Q_{2a}^2 - Q_{2b}^2 \right) \\
-1.50088 \cdot 10^{-6} Q_{2a} Q_{3x} Q_{3y} - 5.95730 \cdot 10^{-8} Q_{2a} (Q_{3x} Q_{4y} + Q_{3y} Q_{4x}) - 1.30784 \cdot 10^{-8} Q_{2a} Q_{4x} Q_{4y} \\
-2.83012 \cdot 10^{-7} Q_{2b} (Q_{3x} Q_{4y} - Q_{3y} Q_{4x}) + 2.53769 \cdot 10^{-8} Q_{3z}^3 - 2.80844 \cdot 10^{-7} Q_{4z}^3 \\
+2.21245 \cdot 10^{-7} Q_{3z} \left(Q_{3x}^2 + Q_{3y}^2 + Q_{3z}^2 \right) - 5.93272 \cdot 10^{-7} Q_{4z} \left(Q_{3x}^2 + Q_{3y}^2 + Q_{3z}^2 \right) \\
-2.90606 \cdot 10^{-8} Q_{3z} (Q_{3x} Q_{4x} + Q_{3y} Q_{4y} + Q_{3z} Q_{4z}) + 1.35001 \cdot 10^{-7} Q_{3z}^2 Q_{4z} \\
+4.07208 \cdot 10^{-7} Q_{4z} (Q_{3x} Q_{4x} + Q_{3y} Q_{4y} + Q_{3z} Q_{4z}) - 1.14485 \cdot 10^{-6} Q_{3z} Q_{4z}^2 \\
+4.90883 \cdot 10^{-7} Q_{3z} \left(Q_{4x}^2 + Q_{4y}^2 + Q_{4z}^2 \right) + 4.11389 \cdot 10^{-7} Q_{4z} \left(Q_{4x}^2 + Q_{4y}^2 + Q_{4z}^2 \right)
\end{aligned}
$$

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	This work	[9]	[37]	[38]
$\frac{\partial D_z}{\partial q_{3z}}$	-0.075013	-0.075010	-0.07561(4)	-0.0754(17)
$\frac{\partial D_z}{\partial q_{4z}}$	+.0755477	+0.075561	+0.07950(8)	+0.0808(16)
$\frac{\partial^2 D_z}{\partial q_1 \partial q_{3z}}$	-0.009173	-0.009173	N/A	-0.0009(01)
$\frac{\partial^2 D_z}{\partial q_1 \partial q_{4z}}$	-0.015024	-0.015024	-0.01657	-0.0145(12)
$\frac{\partial^2 D_z}{\partial q_{2a} \partial q_{3z}}$	-0.007646	-0.007646	-0.00800	-0.0080(03)
$\frac{\partial^2 D_z}{\partial q_{2a} \partial q_{4z}}$	+0.006798	+0.006798	+0.01286	+0.0060(09)
$\frac{\partial^2 D_z}{\partial q_{3x} \partial q_{3y}}$	-0.016135	-0.016121	N/A	-0.0310(15)
$\frac{\partial^2 D_z}{\partial q_{3x} \partial q_{4y}}$	-0.015585	-0.015587	-0.01611	-0.0163(06)
$\frac{\partial^2 D_z}{\partial q_{4x} \partial q_{4y}}$	+0.025537	+0.025528	+0.02736	+0.0337(09)

Table 1

Electric dipole moment z-component first and second derivatives of ^{12}CH4 (in Debye) for adimensional normal coordinates. Values obtained from our new fit are compared to those of [9]. Note, that some of the latter were slightly wrong due to a "copy-paste" error and are corrected here. Similarly, the first derivatives given in D.Å^{-1} in our previous study should have been $\frac{\partial D_z}{\partial Q_{3z}}$ =-0.7264; $\frac{\partial D_z}{\partial Q_{4z}}$ = +0.4772 instead of the published values, so slightly closer to the values of [39]. The sign convention for the normal coordinates is that of Gray and Robiette [36], so the signs of the derivatives including q_{2a} and q_{2b} of Loete [37] have been changed accordingly, (see also Tab. 4 of Mourbat et al. [38]).

ν_ηη'			S_ηη'						J, irrep.			
Obs [1]	Cal.	$\frac{Obs-Cal}{Obs}$	Obs [40]	Unc. %	[9]	$\frac{Obs-Cal}{Cal}$ %	This work	$\frac{Obs-Cal}{Cal}$ %	η		η'	
83.56549	83.56381	2.01E-05	7.909E-26	18.0	7.965E-26	-0.7	7.881E-26	0.4	7	E	8	E
83.56913	83.56746	2.00E-05	1.366E-25	34.0	1.364E-25	0.2	1.349E-25	1.3	7	F2	8	F1
83.57622	83.57456	1.99E-05	2.940E-25	3.3	2.992E-25	-1.7	2.960E-25	-0.7	7	A2	8	A1
93.91555	93.91360	2.08E-05	1.851E-25	6.9	1.713E-25	8.0	1.695E-25	9.2	8	F1	9	F2
93.93107	93.92913	2.06E-05	2.259E-25	16.0	2.164E-25	4.4	2.141E-25	5.5	8	F2	9	F1
104.22470	104.22244	2.17E-05	3.375E-25	13.0	3.358E-25	0.5	3.322E-25	1.6	9	A1	10	A2
104.24737	104.24513	2.15E-05	2.187E-25	3.9	2.249E-25	-2.8	2.226E-25	-1.8	9	F1	10	F2
104.25229	104.25006	2.14E-05	1.326E-25	33.0	1.703E-25	-22.1	1.685E-25	-21.3	9	E	10	E
104.31507	104.31292	2.06E-05	2.432E-25	5.8	2.869E-25	-15.2	2.838E-25	-14.3	9	F1	10	F2
104.31924	104.31709	2.06E-05	2.579E-25	11.0	2.645E-25	-2.5	2.617E-25	-1.5	9	F2	10	F1
104.35000	104.34789	2.02E-05	5.639E-25	16.0	5.745E-25	-1.8	5.684E-25	-0.8	9	A2	10	A1
104.36479	104.36270	2.00E-05	5.884E-26	23.0	5.561E-26	5.8	5.503E-26	6.9	9	F1	10	F2
104.39473	104.39266	1.98E-05	5.951E-26	10.0	6.498E-26	-8.4	6.429E-26	-7.4	9	F2	10	F1
114.52344	114.52087	2.25E-05	2.267E-25	20.0	2.297E-25	-1.3	2.273E-25	-0.3	10	F1	11	F2
114.53532	114.53276	2.23E-05	2.576E-25	18.0	2.670E-25	-3.5	2.642E-25	-2.5	10	F2	11	F1
114.61438	114.61192	2.15E-05	1.686E-25	7.1	1.873E-25	-10.0	1.853E-25	-9.0	10	E	11	E
114.61714	114.61467	2.15E-05	2.930E-25	6.1	2.893E-25	1.3	2.862E-25	2.4	10	F1	11	F2
114.63941	114.63697	2.13E-05	7.343E-25	28.0	7.155E-25	2.6	7.079E-25	3.7	10	A1	11	A2
114.67144	114.66904	2.09E-05	3.632E-25	7.9	3.652E-25	-0.6	3.614E-25	0.5	10	F2	11	F1
114.69262	114.69025	2.07E-05	6.598E-26	24.0	5.628E-26	17.2	5.569E-26	18.5	10	F1	11	F2
114.87932	114.87718	1.86E-05	3.423E-26	16.0	4.862E-26	-29.6	4.811E-26	-28.9	10	F2	11	F1
124.76275	124.75985	2.33E-05	1.632E-25	7.8	1.575E-25	3.6	1.559E-25	4.7	11	E	12	E
124.77117	124.76827	2.32E-05	2.414E-25	7.6	2.434E-25	-0.8	2.409E-25	0.2	11	F2	12	F1
124.78389	124.78101	2.30E-05	4.350E-25	3.6	4.384E-25	-0.8	4.338E-25	0.3	11	A2	12	A1
124.86687	124.86407	2.25E-05	2.760E-25	8.7	2.710E-25	1.9	2.681E-25	2.9	11	F2	12	F1
124.90983	124.90707	2.21E-05	3.801E-25	5.4	3.856E-25	-1.4	3.815E-25	-0.4	11	F1	12	F2
124.95360	124.95089	2.17E-05	2.366E-25	5.2	2.315E-25	2.2	2.290E-25	3.3	11	E	12	E
124.95887	124.95616	2.17E-05	3.365E-25	2.9	3.253E-25	3.4	3.219E-25	4.5	11	F1	12	F2
125.28147	125.27915	1.85E-05	1.230E-25	16.0	1.097E-25	12.2	1.085E-25	13.4	11	A2	12	A1
134.95865	134.95539	2.41E-05	2.026E-25	5.1	2.118E-25	-4.3	2.096E-25	-3.3	12	F1	13	F2
134.97498	134.97175	2.40E-05	2.127E-25	1.7	2.196E-25	-3.2	2.173E-25	-2.1	12	F2	13	F1
135.06476	135.06157	2.36E-05	3.871E-25	2.1	3.934E-25	-1.6	3.893E-25	-0.6	12	A2	13	A1
135.12831	135.12520	2.30E-05	2.870E-25	1.8	2.811E-25	2.1	2.781E-25	3.2	12	F2	13	F1
135.13616	135.13306	2.30E-05	2.268E-25	4.5	2.255E-25	0.6	2.231E-25	1.7	12	E	13	E
135.18891	135.18584	2.27E-05	2.471E-25	6.8	2.579E-25	-4.2	2.552E-25	-3.2	12	F2	13	F1

20

135.24148	135.23846	2.23E-05	5.208E-25	4.6	5.334E-25	-2.4	5.278E-25	-1.3	12	A1	13	A2
135.29673	135.29379	2.17E-05	8.246E-26	12.0	7.948E-26	3.8	7.864E-26	4.9	12	F2	13	F1
135.65576	135.65325	1.85E-05	3.389E-26	4.9	4.019E-26	-15.7	3.977E-26	-14.8	12	F2	13	F1
135.73905	135.73659	1.81E-05	3.190E-26	2.4	3.023E-26	5.5	2.991E-26	6.7	12	A1	13	A2
145.09922	145.09559	2.50E-05	2.920E-25	1.1	2.833E-25	3.1	2.803E-25	4.2	13	A1	14	A2
145.11543	145.11182	2.49E-05	1.761E-25	9.1	1.729E-25	1.8	1.711E-25	2.9	13	F1	14	F2
145.12193	145.11832	2.48E-05	1.244E-25	16.0	1.173E-25	6.1	1.161E-25	7.1	13	E	14	E
145.29512	145.29162	2.41E-05	2.128E-25	5.0	2.125E-25	0.1	2.103E-25	1.2	13	F2	14	F1
145.31437	145.31088	2.40E-05	2.656E-25	6.7	2.653E-25	0.1	2.625E-25	1.2	13	F1	14	F2
145.38186	145.37839	2.39E-05	1.930E-25	4.4	1.956E-25	-1.3	1.936E-25	-0.3	13	F2	14	F1
145.38969	145.38624	2.38E-05	1.388E-25	11.0	1.445E-25	-3.9	1.430E-25	-2.9	13	E	14	E
145.44356	145.44016	2.33E-05	5.557E-25	2.8	5.658E-25	-1.8	5.599E-25	-0.8	13	A2	14	A1
145.45911	145.45571	2.34E-05	2.502E-25	9.6	2.519E-25	-0.7	2.492E-25	0.4	13	F1	14	F2
145.53228	145.52900	2.26E-05	7.812E-26	11.0	7.300E-26	7.0	7.223E-26	8.2	13	F2	14	F1
155.20508	155.20108	2.58E-05	1.174E-25	13.0	1.271E-25	-7.6	1.258E-25	-6.7	14	F1	15	F2
155.21702	155.21303	2.57E-05	1.238E-25	3.7	1.295E-25	-4.4	1.281E-25	-3.4	14	F2	15	F1
155.43277	155.42886	2.52E-05	1.694E-25	14.0	1.844E-25	-8.1	1.825E-25	-7.2	14	F1	15	F2
155.46268	155.45880	2.50E-05	3.485E-25	4.5	3.499E-25	-0.4	3.462E-25	0.7	14	A1	15	A2
155.51376	155.50982	2.53E-05	1.512E-25	6.9	1.522E-25	-0.6	1.506E-25	0.4	14	F1	15	F2
155.60915	155.60533	2.45E-05	2.216E-25	19.0	2.419E-25	-8.4	2.394E-25	-7.4	14	F2	15	F1
155.62286	155.61899	2.49E-05	1.143E-25	22.0	1.175E-25	-2.8	1.163E-25	-1.7	14	E	15	E
155.63624	155.63239	2.47E-05	1.896E-25	11.0	1.790E-25	5.9	1.771E-25	7.1	14	F2	15	F1
156.23286	156.22982	1.95E-05	5.215E-26	6.2	6.036E-26	-13.6	5.972E-26	-12.7	14	A1	15	A2
165.24669	165.24230	2.66E-05	6.758E-26	11.0	5.817E-26	16.2	5.756E-26	17.4	15	E	16	E
165.25216	165.24778	2.65E-05	9.349E-26	9.3	8.761E-26	6.7	8.669E-26	7.8	15	F2	16	F1
165.26211	165.25775	2.64E-05	1.488E-25	6.1	1.477E-25	0.8	1.461E-25	1.8	15	A2	16	A1
165.48246	165.47805	2.67E-05	1.189E-25	16.0	1.251E-25	-4.9	1.237E-25	-3.9	15	F2	16	F1
165.52922	165.52488	2.62E-05	1.403E-25	16.0	1.350E-25	3.9	1.336E-25	5.0	15	F1	16	F2
165.57721	165.57272	2.71E-05	1.793E-25	9.1	1.745E-25	2.7	1.727E-25	3.8	15	A1	16	A2
165.71246	165.70816	2.59E-05	1.466E-25	19.0	1.381E-25	6.2	1.366E-25	7.3	15	F1	16	F2
165.71962	165.71531	2.60E-05	1.055E-25	9.8	1.107E-25	-4.7	1.095E-25	-3.7	15	E	16	E
165.72524	165.72079	2.69E-05	1.011E-25	14.0	1.038E-25	-2.6	1.027E-25	-1.6	15	F1	16	F2
165.76086	165.75646	2.66E-05	1.348E-25	8.8	1.198E-25	12.5	1.186E-25	13.7	15	F2	16	F1
165.80353	165.79916	2.64E-05	2.266E-25	10.0	2.155E-25	5.2	2.132E-25	6.3	15	A2	16	A1
175.23026	175.22546	2.74E-05	6.572E-26	13.0	5.536E-26	18.7	5.478E-26	20.0	16	F1	17	F2
175.23920	175.23442	2.73E-05	5.148E-26	9.2	5.565E-26	-7.5	5.507E-26	-6.5	16	F2	17	F1
175.47690	175.47191	2.84E-05	1.414E-25	11.0	1.336E-25	5.8	1.322E-25	7.0	16	A2	17	A1
175.52873	175.52387	2.77E-05	8.728E-26	32.0	8.248E-26	5.8	8.161E-26	6.9	16	F2	17	F1

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175.54531	175.54047	2.76E-05	6.748E-26	42.0	5.762E-26	17.1	5.702E-26	18.3	16	E	17	E
175.75462	175.74976	2.77E-05	8.168E-26	20.0	8.286E-26	-1.4	8.199E-26	-0.4	16	F1	17	F2
175.77014	175.76523	2.79E-05	1.052E-25	3.7	1.003E-25	4.8	9.929E-26	6.0	16	F2	17	F1
175.77944	175.77428	2.94E-05	5.211E-26	14.0	6.232E-26	-16.4	6.166E-26	-15.5	16	F1	17	F2
175.80961	175.80452	2.89E-05	4.971E-26	21.0	4.844E-26	2.6	4.793E-26	3.7	16	E	17	E
175.88877	175.88369	2.89E-05	8.307E-26	10.0	7.934E-26	4.7	7.850E-26	5.8	16	F2	17	F1
175.91944	175.91453	2.79E-05	1.914E-25	7.6	1.996E-25	-4.1	1.975E-25	-3.1	16	A1	17	A2
185.14892	185.14369	2.82E-05	5.447E-26	2.2	5.432E-26	0.3	5.375E-26	1.3	17	A1	18	A2
185.15627	185.15108	2.81E-05	2.560E-26	4.7	3.269E-26	-21.7	3.235E-26	-20.9	17	F1	18	F2
185.15978	*185.15459*	*2.80E-05*	*3.178E-26*	*6.0*	*2.183E-26*	*45.6*	*2.161E-26*	*47.1*	*17*	*E*	*18*	*E*
185.72296	185.71736	3.01E-05	3.828E-26	3.0	3.538E-26	8.2	3.501E-26	9.3	17	E	18	E
185.75272	185.74712	3.01E-05	5.439E-26	3.8	5.619E-26	-3.2	5.560E-26	-2.2	17	F2	18	F1
185.77760	185.77164	3.21E-05	4.182E-26	5.6	4.018E-26	4.1	3.976E-26	5.2	17	F2	18	F1
185.81261	185.80712	2.95E-05	1.109E-25	5.7	1.125E-25	-1.4	1.114E-25	-0.4	17	A2	18	A1
185.95843	185.95276	3.05E-05	6.835E-26	16.0	6.932E-26	-1.4	6.859E-26	-0.3	17	F1	18	F2
195.36349	195.35732	3.16E-05	1.843E-26	5.1	1.842E-26	0.1	1.823E-26	1.1	18	E	19	E
195.38122	195.37512	3.12E-05	2.301E-26	4.3	2.789E-26	-17.5	2.760E-26	-16.6	18	F1	19	F2
195.41070	195.40470	3.07E-05	4.622E-26	10.0	4.793E-26	-3.6	4.743E-26	-2.6	18	A1	19	A2
195.69065	195.68368	3.56E-05	4.795E-26	3.3	3.738E-26	28.3	3.699E-26	29.6	18	A2	19	A1
195.74041	195.73417	3.19E-05	3.295E-26	1.8 [2]	3.493E-26	-5.7	3.457E-26	-4.7	18	F2	19	F1
Average of absolute values		2.46E-05		10.57		6.28		6.37				
Average of absolute values minus italicized transition				10.62		5.85		5.93				

Table 2

Comparison with experiment [40] of calculated transition wave numbers and intensities for the R-branch of methane vibrational ground state. Theoretical transition wave numbers, $\nu_{\eta\eta'}$ in cm^{-1} units, were calculated at fourth order of perturbation (second column). Order 2 of perturbation theory has been used to compute effective dipole moments, which in turn, were used to obtain theoretical intensities at 296 K, $S_{\eta\eta'}$ in cm^{-1} /(molecule.cm^{-2}). The underlined transition in italics is singled out because it was withdrawn from the fit of the observed spectra, its relative error of 42% being too large.

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[1] The line position are taken from Tab.A1 of [40] but actually they were obtained with the STDS code from an effective Hamiltonian fitted on experiments

[2] Jean Vander Auwera, private communication