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The Jacobi–Wilson method: A new approach to the description of polyatomic molecules

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We present a new method adapted to the calculation of excited rovibrational states of semirigid molecules. It first relies on a description of the molecule in terms of polyspherical coordinates of Jacobi vectors, in order to obtain a compact expression for the kinetic energy operator $\hat{T}(\mathbf{q})$. This general description is then adapted to the molecule considered by defining *curvilinear* normal modes from the corresponding zero order harmonic Hamiltonian $\hat{H}^0 = \hat{T}(\mathbf{q}_{\text{eq}}) + V_{\text{harm}}(\mathbf{q})$, the solutions of which are being used as the working basis set. The residual kinetic term $\Delta\hat{T}$ is treated mainly analytically in this basis, and displays no radial contribution. Anharmonic coupling $\Delta V(\mathbf{q})$ is handled by means of a pseudospectral scheme based on Gauss Hermite quadratures. This method is particularly adapted to *direct* iterative approaches which only require the action of \hat{H} on a vector, without the need of the associated matrix, thus allowing ultralarge bases to be considered. An application to the excited vibrational states of the HFCO molecule is presented. It is shown in this example that energy levels can be trivially assigned from the leading expansion coefficient of the associated eigenvector. © 2001 American Institute of Physics. [DOI: 10.1063/1.1337048]

I. INTRODUCTION

Calculation of rovibrational energy levels of polyatomic molecules, beyond the normal modes approximation, still represents a challenging task. A powerful tool, the vibrational self-consistent field (VSCF) method, has been introduced by Bowman¹ to this aim. The SCF step *per se* allows the calculation to take into account both the anharmonic behavior of each mode and part of the intermode couplings through a mean-field definition. The subsequent configuration interaction procedure explicitly brings the full correlation between the modes. In its usual implementation, this method relies on a rectilinear definition of the normal modes,² due to its simplicity. However, this formulation reduces the efficiency of the method when excited states are of interest, or if overall rotation is explicitly considered. Consequently, many studies of small excited polyatomics ($N = 4-5$) made use so far of a curvilinear description of the molecules, be it in valence³ or Jacobi type.⁴⁻⁷

For semirigid molecules, valence coordinates are usually considered to be more physically grounded as they closely resemble the actual stretch or bend motions. In fact, this is true essentially at high energy in the local modes regime, but it is not so well verified at low energy when normal modes prevail. However, the kinetic energy operator (KEO) displays an intricate expression, with numerous coupling terms contributing both to the vibration and rotation–vibration

components.³ Such a large number of terms first makes more involved the actual implementation of the method. It also means that it will be more difficult to define a zero-order Hamiltonian \hat{H}^0 from which the working basis set is to be built, usually as its eigenstates. On the other hand, Jacobi coordinates display an extremely simple KEO with cross-derivative terms only appearing between angular coordinates. Such a property makes its implementation very easy but does not provide a good zero-order description of bound molecular states: Jacobi coordinates do not correspond to actual physical motions, except in limiting cases such as H_2O_2 ⁸ where they almost coincide with valence coordinates.

In this paper, we present a new method which combines the simplicity of the Jacobi description with the efficiency of the Wilson normal modes approach. It first consists of recasting the problem in a collision-type formulation by means of polyspherical coordinates.⁹ This formulation leads to a very compact form of the KEO and allows for an easy implementation of the rotational terms. This general description is then *adapted* to the molecule of interest by defining *curvilinear* normal modes from a zero-order harmonic Hamiltonian \hat{H}^0 , the solutions of which are being used as the working basis set. As a result, only the difference $\hat{H} - \hat{H}^0$ has to be explicitly considered, \hat{H}^0 being trivially handled. Such a scheme is particularly efficient when used in conjunction with an iterative direct method.¹⁰⁻¹² Indeed, defining a physically adapted basis set from the eigenstates of \hat{H}^0 is equivalent to preconditioning the iterative method by means of \hat{H}^0 . It is well known that such a preconditioning step greatly enhances or even makes possible the convergence of these methods.

One should also mention the use of curvilinear normal

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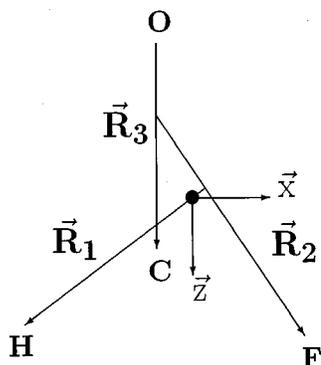


FIG. 1. Definition of the three Jacobi vectors \mathbf{R}_3 , \mathbf{R}_2 , and \mathbf{R}_1 used to describe the HFCO molecule.

coordinates by Sibert and co-workers¹³ and Quade.¹⁴ In their case, these normal modes were defined from a Hamiltonian operator written in terms of internal coordinates, and expanded around the equilibrium geometry. Subsequent calculations then relied on perturbation theory.

The outline of this paper is as follows. In Sec. II, we recall the Jacobi polyspherical parametrization of a molecule, and then present the resulting KEO. Section III gives an example of the new approach as applied to a six dimensional study of the bound states of the HFCO molecule. Finally, Sec. IV concludes on further possible improvements of this approach.

II. KINETIC ENERGY OPERATOR IN A JACOBI POLYSPHERICAL PARAMETRIZATION

In this approach, an N atom system is initially parametrized by $N-1$ Jacobi vectors ($\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N-1}$) in a space-fixed (SF) frame. By definition, a Jacobi vector relies on either 2 atoms, or the center of mass of a fragment and an atom, or the centers of mass of 2 fragments of the system. In order to simplify the notations later on, these vectors are defined sequentially in reverse order, i.e., \mathbf{R}_{N-1} is the first one, followed by \mathbf{R}_{N-2} until \mathbf{R}_1 . Also, by convention in the following formulation, the \mathbf{z} body fixed (BF) axis is taken parallel to \mathbf{R}_{N-1} . For example, Fig. 1 displays the set of Jacobi vectors used to describe the HFCO molecule to be considered in the next section. The interest of this formulation stems from the well-known simplicity¹⁵ of the KEO expressed in terms of the momenta ($\mathbf{P}_1, \mathbf{P}_2, \dots, \mathbf{P}_{N-1}$) conjugate to the Jacobi vectors

$$\hat{T} = \sum_i^{N-1} \frac{\hat{\mathbf{P}}_i^\dagger \cdot \hat{\mathbf{P}}_i}{2\mu_i}, \quad (1)$$

where μ_i is the reduced mass associated to \mathbf{R}_i . The Jacobi vectors are initially characterized by their spherical coordinates ($R_i, \Theta_i^{\text{SF}}, \Phi_i^{\text{SF}}$) in the SF frame.

In order to separate out molecular rotation, a BF frame is defined accordingly to Chapuisat and Lung:⁹ the \mathbf{z} axis is taken parallel to \mathbf{R}_{N-1} . Consequently, the first two Euler rotations $D_z(\alpha)$ and $D_y(\beta)$ to define G_z^{BF} axis correspond to $D_z(\Phi_{N-1}^{\text{SF}})$ and $D_y(\Theta_{N-1}^{\text{SF}})$. The frame obtained after these

two rotations is called E_2 . A last rotation $D_z(\gamma = \Phi_{N-2}^{E_2})$ around $G_z^{E_2} = G_z^{\text{BF}}$ is defined such that the xz half plane ($x > 0$) is parallel to \mathbf{R}_{N-2} .

Consequently, the system can be parametrized by the three Euler angles ($\alpha = \Phi_{N-1}^{\text{SF}}, \beta = \Theta_{N-1}^{\text{SF}}, \gamma = \Phi_{N-2}^{E_2}$), and the $(3N-6)$ BF spherical coordinates of the Jacobi vectors

- (i) $N-1$ distances $r_i = R_i, i = 1, \dots, N-1$;
- (ii) $N-2$ plane angles θ_i between vectors \mathbf{R}_{N-1} and \mathbf{R}_i ;
- (iii) $N-3$ dihedral angles $\phi_i = \Phi_i^{E_2} - \Phi_{N-2}^{E_2}, i = 1, \dots, N-3$.

By definition of the BF frame, θ_{N-1}, ϕ_{N-1} , and ϕ_{N-2} are fixed to zero. Furthermore, different recent studies¹⁶⁻¹⁸ have shown the interest of introducing the variables $u_i = \cos \theta_i$ instead of θ_i . The final parametrization thus consists of the three Euler angles and $3N-6$ internal variables denoted collectively by

$$\{q_n\}_{n=1}^{3N-6} = \{r_i, i = 1, \dots, N-1; u_i, i = 1, \dots, N-2; \phi_i, i = 1, \dots, N-3\}. \quad (2)$$

In the past, this parametrization was used as a starting point in order to express the KEO in terms of $N-1$ angular momenta,¹⁹ adapted to large amplitude motions. We derive below a *new and general* expression of the KEO aimed at describing the rovibrational motion of semirigid molecules as it is expressed in terms of

- (i) the $3N-6$ operators \hat{p}_n conjugate to the spherical coordinates: $\hat{p}_n = -i\hbar \partial / \partial q_n$;
- (ii) the BF Hermitian projections ($\hat{J}_x, \hat{J}_y, \hat{J}_z$) of the total angular momentum $\hat{\mathbf{J}}$.

Only the general strategy is sketched here; details of the calculation and generalization to any set of vectors (Jacobi, valence, satellite, \dots , or a combination of them) are given elsewhere.²⁰

The main steps of the calculation are the following:

- (i) first, the $\hat{\mathbf{P}}_i$ vectors [Eq. (1)] are substituted by their expression in terms of angular momenta $\hat{\mathbf{L}}_i$ and radial conjugate momenta \hat{p}_{r_i} , using

$$\mathbf{P}_i = \hat{p}_{r_i} \mathbf{e}_i - \frac{1}{r_i} \mathbf{e}_i \times \hat{\mathbf{L}}_i,$$
 where \mathbf{e}_i denotes the unit vector along the \mathbf{R}_i direction;
- (ii) $\hat{\mathbf{L}}_{N-1}$ is then substituted by $\hat{\mathbf{J}} - \sum_{i=1}^{N-2} \hat{\mathbf{L}}_i$ in order to introduce $\hat{\mathbf{J}}$;
- (iii) the angular momenta $\hat{\mathbf{L}}_i (i = 1, \dots, N-3)$, which are not linked to the BF frame, are substituted by their known expression in terms of \hat{p}_{u_i} and \hat{p}_{ϕ_i} ;²¹
- (iv) then, the angular momentum $\hat{\mathbf{L}}_{N-2}$, partially linked to the BF frame, is substituted by the following expression, previously derived by Gatti *et al.*:²²

$$\hat{L}_{(N-2)x} = -\cot \theta_{N-2} \left(\hat{J}_z - \sum_{i=1}^{N-3} \hat{p}_{\phi_i} \right)$$

$$\hat{L}_{(N-2)y} = -\sin \theta_{N-2} \hat{p}_{u_{N-2}} \quad (3)$$

$$\hat{L}_{(N-2)z} = \hat{J}_z - \sum_{i=1}^{N-3} \hat{p}_{\phi_i},$$

which leads to the following general expression for the KEO:

$$\hat{T} = \hat{T}_{\text{vib}} + \hat{T}_{\text{Cor}} + \hat{T}_{\text{Rot}}, \quad (4)$$

with

$$\hat{T}_{\text{vib}} = \frac{1}{2} \sum_{nm}^{3N-6} \hat{p}_n G_{nm} \hat{p}_m, \quad (5)$$

$$\hat{T}_{\text{cor}} = \frac{1}{2} \sum_{n=1}^{3N-6} \sum_{\alpha=x,y,z} \hat{p}_n C_{n\alpha} \hat{J}_\alpha + \hat{J}_\alpha C_{n\alpha} \hat{p}_n, \quad (6)$$

$$\hat{T}_{\text{rot}} = \sum_{\alpha\beta=x,y,z} \hat{J}_\alpha \Gamma_{\alpha\beta} \hat{J}_\beta + \hat{J}_\beta \Gamma_{\alpha\beta} \hat{J}_\alpha, \quad (7)$$

associated with the volume element

$$dV = \sin \beta \, d\alpha \, d\beta \, d\gamma \prod_{i=1}^{N-3} d\phi_i \prod_{i=1}^{N-2} du_i \prod_{i=1}^{N-1} dr_i.$$

The \mathbf{G} , \mathbf{C} , and $\mathbf{\Gamma}$ matrix elements are given in Appendix A. The expressions [Eqs. (4)–(7)] apply for any number N of atoms and include in a very simple way the Coriolis couplings. The general expression [Eq. (5)] can be further simplified due to the fact that the $\mathbf{G}^{(rr)}$ block is diagonal and constant, and the $\mathbf{G}^{(ru)}$ and $\mathbf{G}^{(r\phi)}$ ones are identically zero

$$2\hat{T}_{\text{vib}} = \sum_{i=1}^{N-1} G_{ii}^{(rr)} \hat{p}_{r_i}^2 + \sum_{i,j}^{N-2} \hat{p}_{u_i} G_{ij}^{(uu)} \hat{p}_{u_j}$$

$$+ \sum_{i,j}^{N-3} \hat{p}_{\phi_i} G_{ij}^{(\phi\phi)} \hat{p}_{\phi_j}$$

$$+ \sum_{i=1}^{N-2} \sum_{j=1}^{N-3} \{ \hat{p}_{u_i} G_{ij}^{(u\phi)} \hat{p}_{\phi_j} + \hat{p}_{\phi_j} G_{ij}^{(\phi u)} \hat{p}_{u_i} \}. \quad (8)$$

For reasons which will be discussed in the next section, we explicitly retain the above *symmetrical* formulation.

As emphasized in the Introduction, this formulation allows us to define a zero-order vibrational Hamiltonian \hat{H}_{vib}^o

$$\hat{H}_{\text{vib}}^o = \frac{1}{2} \sum_{n,m=1}^{3N-6} (q_n F_{nm} q_m + \hat{p}_n G_{nm}^o \hat{p}_m), \quad (9)$$

where \mathbf{G}^o represents the \mathbf{G} matrix of Appendix A evaluated at the equilibrium geometry \mathbf{q}_{eq} , and the \mathbf{F} matrix corresponds to the harmonic approximation for the potential:

$F_{nm} = \partial^2 V / \partial q_n \partial q_m |_{\mathbf{q}_{\text{eq}}}$. One can then proceed along the Wilson \mathbf{G} matrix formulation,² and define *curvilinear* normal modes $\{Q_\alpha\}$ in terms of the Jacobi coordinates

$$Q_\alpha = \sum_n^{3N-6} L_{\alpha n}^{-1} q_n. \quad (10)$$

Such a relationship enables one to use the harmonic basis set $\{|v_1 v_2, \dots, v_{3N-6}\rangle\}$ diagonalizing \hat{H}_{vib}^o as the working basis set. We can split \hat{H}_{vib} into

$$\hat{H}_{\text{vib}} = \hat{H}_{\text{vib}}^o + \Delta \hat{T}_{\text{vib}} + \Delta V(\mathbf{q}), \quad (11)$$

where $\Delta \hat{T}_{\text{vib}}$ is obtained by substituting in Eq. (8) G_{ij} by $\Delta G_{ij} = G_{ij} - G_{ij}^o$, and $\Delta V(\mathbf{q})$ is defined as $V(\mathbf{q}) - V_{\text{harm}}(\mathbf{q})$. It should be noted that $\Delta \hat{T}_{\text{vib}}$ does not contain any \hat{p}_{r_i} contribution as the $G_{ii}^{(rr)}$ matrix elements does not depend on \mathbf{q} .

The structure of $\Delta \hat{T}_{\text{vib}}$ allows this term to be treated partly analytically by means of the relations

$$\frac{\partial}{\partial q_n} = \sum_\alpha L_{\alpha n}^{-1} \frac{\partial}{\partial Q_\alpha}. \quad (12)$$

The inside term $\Delta G_{ij}(\mathbf{q})$ and the residual potential $\Delta V(\mathbf{q})$ can easily be handled by means of Gauss–Hermite quadratures associated to the harmonic basis set, as will be explained in the next section.

It is important to mention that the choice of the \mathbf{z} BF axis is crucial but not really restrictive. First, the higher the mass μ_n , the smaller the Coriolis couplings as shown by Eq. (A3). Second, analysis of the singularities of the G_{ij} expressions [Eq. (A1)] reveals that none of the plane angles θ_i^{BF} should be equal to zero or π in the space explored near the equilibrium geometry. As a consequence, one must choose the \mathbf{z} axis to avoid such singularities. This is the case of the parametrization adopted for HFCO, as shown in Fig. 1. Finally, this method is not restricted to systems initially parametrized by Jacobi vectors: any set of orthogonal coordinates (Radau coordinates, for instance) can also be considered. The use of nonorthogonal coordinates is possible and treated elsewhere.^{20,19}

III. APPLICATION TO THE HFCO MOLECULE

In order to test the new formulation presented above, we apply it in this section to a six dimensional ($J=0$) calculation of the bound states of the HFCO molecule. This molecule was recently studied by two of us in the framework of the adiabatic pseudospectral (APS) formulation.¹⁶ The HFCO molecule has been described by the set of Jacobi vectors shown in Fig. 1. The BF frame has been defined as \mathbf{z} parallel to \mathbf{OC} and the O, C, and F atoms laying in the xz plane. Specialization of Eqs. (8) and (9) to the present case leads to the following expressions:

$$\begin{aligned} \hat{T}_{\text{vib}} = & \frac{-\hbar^2}{2\mu_1} \frac{\partial^2}{\partial r_1^2} - \frac{\hbar^2}{2\mu_2} \frac{\partial^2}{\partial r_2^2} - \frac{\hbar^2}{2\mu_3} \frac{\partial^2}{\partial r_3^2} - \frac{\hbar^2}{2} \left[\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_3 r_3^2} \right] \left[\frac{\partial}{\partial u_1} (1-u_1^2) \frac{\partial}{\partial u_1} + \frac{1}{1-u_1^2} \frac{\partial^2}{\partial \phi^2} \right] \\ & - \frac{\hbar^2}{2} \left[\frac{1}{\mu_2 r_2^2} + \frac{1}{\mu_3 r_3^2} \right] \left[\frac{\partial}{\partial u_2} (1-u_2^2) \frac{\partial}{\partial u_2} + \frac{1}{1-u_2^2} \frac{\partial^2}{\partial \phi^2} \right] + \frac{\hbar^2}{\mu_3 r_3^2} \frac{\partial}{\partial \phi} (1 + \cot \theta_1 \cot \theta_2 \cos \phi) \frac{\partial}{\partial \phi} \\ & - \frac{\hbar^2}{2\mu_3 r_3^2} \left[\frac{\partial}{\partial u_1} \sin \theta_1 \sin \theta_2 \cos \phi \frac{\partial}{\partial u_2} + \sum_{i=1,2;i' \neq i} \frac{\partial}{\partial u_i} \sin \theta_i \cot \theta_{i'} \sin \phi \frac{\partial}{\partial \phi} \right] + \text{sym}, \end{aligned} \quad (13)$$

$$\mu_3 = \frac{m_C \cdot m_O}{m_C + m_O}, \quad \mu_2 = \frac{m_F \cdot m_{CO}}{m_F + m_{CO}}, \quad \mu_1 = \frac{m_H \cdot m_{FCO}}{m_H + m_{FCO}}, \quad (14)$$

associated with the volume element $dV = dr_1 dr_2 dr_3 du_1 du_2 d\phi$, and where sym means that the last line has to be completed by its symmetric Hermitian $\partial/\partial q_i G_{ij} \partial/\partial q_j \rightarrow \partial/\partial q_j G_{ij} \partial/\partial q_i$. The importance of writing the KEO in symmetrical form has been stressed in the past by Wei and Carrington.²³

Following the formulation described in Sec. II, one can define normal coordinates \mathbf{Q} from Eqs. (9) and (10), expressed in terms of the reduced variables

$$\begin{aligned} q_i &= r_i - r_{i_{\text{eq}}}, \quad i=1,2,3 \\ q_{i+3} &= u_i - u_{i_{\text{eq}}}, \quad i=1,2 \\ q_6 &= \phi - \phi_{\text{eq}}, \end{aligned}$$

in order to set up the working basis set

$$\{\Phi_{n_1, \dots, n_6}(\mathbf{Q})\} = \{\varphi_{n_1}(Q_1) \times \dots \times \varphi_{n_6}(Q_6)\}. \quad (15)$$

The above basis set is truncated such that only the states located below some energy threshold E_{Sp} are kept: $E_{\mathbf{n}}^o \leq E_{Sp}$. This results in a nondirect product basis set which is handled as described in Appendix B.

We give below the missing contribution to $\hat{H}_{\text{vib}}^{J=0}$ [Eq. (11)]

$$\begin{aligned} \Delta \hat{H} \equiv \Delta \hat{T}_{\text{vib}} + \Delta V(\mathbf{q}) = & -\frac{\hbar^2}{2} \sum_{n,m=4}^6 \frac{\partial}{\partial q_n} [G_{nm}(\mathbf{q}) \\ & - G_{nm}(\mathbf{q}_{\text{eq}})] \frac{\partial}{\partial q_m} + V - V_{\text{harm}}, \end{aligned} \quad (16)$$

where the G_{nm} matrix elements are defined from Eq. (13) above. One can first note that no radial derivative term appears in this expression as they are exactly handled in the \hat{H}^o description. Furthermore, the terms in Eq. (16) display small amplitudes at moderate energies as they all appear as correc-

tions with respect to the equilibrium geometry \mathbf{q}_{eq} . As mentioned previously [Eq. (12)], all the derivative terms can be evaluated analytically in the normal modes basis set

$$\begin{aligned} \frac{\partial}{\partial q_i} \varphi_{n_\alpha}(Q_\alpha) = & \sum_\alpha L_{\alpha i}^{-1} \sqrt{\frac{\mu_\alpha \omega_\alpha}{2\hbar}} \{ \sqrt{n_\alpha} \varphi_{n_\alpha-1}(Q_\alpha) \\ & - \sqrt{n_\alpha+1} \varphi_{n_\alpha+1}(Q_\alpha) \}. \end{aligned} \quad (17)$$

We now make explicit the pseudospectral scheme to be used for handling both the $\Delta \mathbf{G} \equiv \mathbf{G}(\mathbf{q}) - \mathbf{G}(\mathbf{q}_{\text{eq}})$ matrix and the potential term $\Delta V(\mathbf{q}) \equiv V(\mathbf{q}) - V_{\text{harm}}(\mathbf{q})$. As the working basis set [Eq. (15)] is defined in terms of normal modes $\{\mathbf{Q}\}$, it is easier to use the same coordinates in order to express the residual terms: $\Delta f(\mathbf{q}) \rightarrow \Delta f(\mathbf{q}(\mathbf{Q}))$. Namely, this term is computed on the six-dimensional grid $\{Q_{1a} \times \dots \times Q_{6f}\}$, the points of which correspond to the abscissas of Gauss Hermite quadratures associated to the different coordinates $\{Q_\alpha\}$. In order to reduce its overall size, this grid is truncated to keep only points corresponding to a potential energy lower than some threshold E_{Gr} defined later on.

The action of the residual Δf on a wave function

$$\Psi(\mathbf{Q}) = \sum_{\mathbf{n}} \psi_{\mathbf{n}} \Phi_{\mathbf{n}}(\mathbf{Q}) \quad (18)$$

is then performed by switching to the grid representation by means of the sequential transformations

$$\begin{aligned} \psi_{an_2, \dots, n_6} &= \sum_{n_1} R_{an_1}^{(1)} \psi_{n_1, \dots, n_6} \\ \dots \dots \dots & \dots \dots \dots \\ \psi_{ab, \dots, f} &= \sum_{n_6} R_{fn_6}^{(6)} \psi_{ab, \dots, n_6}. \end{aligned}$$

In the above relations, $\mathbf{R}^{(\alpha)}$ stands for the unitary collocation matrix associated with the Gauss quadrature.²⁴ After acting Δf , diagonal in the grid representation, one switches back to the spectral representation by means of the inverse (transposed) transformations. Dealiasing²⁵ can be enforced by using rectangular collocation matrices $\mathbf{R}^{(\alpha)}$ associated with a larger number of grid points. This was achieved by setting the threshold E_{Gr} at a value somewhat larger than the one E_{Sp} used for the basis set: $E_{Gr} = \eta \cdot E_{Sp}$. The η parameter has to be varied until convergence of the energy levels of interest, typically up to half the energy threshold E_{Sp} . As a

TABLE I. Root-mean-square deviation as defined by Eq. (19), and maximum deviation observed.

	$\eta=1.0$	$\eta=1.1$	$\eta=1.2$	$\eta=1.3$	$\eta=1.4$
rms (cm ⁻¹)	0.60	0.14	0.07	0.04	0.01
Max($E_{\mathbf{n}}^{\eta'} - E_{\mathbf{n}}^{\eta}$) (cm ⁻¹)	14.7	4.1	0.3	0.2	0.05

TABLE II. Comparison of experimental levels (in cm^{-1}) with those obtained in the present formulation. The coefficient given corresponds to the leading term in the expansion of the eigenvector onto the normal modes basis set. All the *assigned* experimental levels are reported in this table.

Exp. (Ref. 28)	$E_{Sp}=2.4$	$\Delta E(E_{Sp}=2.6)$	Coef.	n_1	n_2	n_3	n_4	n_5	n_6
662.6	660.9	-0.02	0.98	0	0	0	0	1	0
1011.2	1020.4	-0.06	0.98	0	0	0	0	0	1
1064.9	1047.3	-0.03	0.94	0	0	0	1	0	0
1324.1	1323.8	-0.04	0.96	0	0	0	0	2	0
1342.3	1392.2	-0.02	0.97	0	0	1	0	0	0
1719.3	1697.1	-0.04	0.90	0	0	0	1	1	0
1836.8	1830.0	-0.02	0.96	0	1	0	0	0	0
2115.6	2076.2	-0.15	0.85	0	0	0	2	0	0
2412.0	2432.3	-0.19	0.91	0	0	1	1	0	0
2494.2	2487.8	-0.16	0.93	0	1	0	0	1	0
2841.0	2845.3	-0.08	0.94	0	1	0	0	0	1
2895.0	2877.8	-0.31	0.88	0	1	0	1	0	0
2981.2	3021.7	-5.26	0.89	1	0	0	0	0	0
3150.6	3147.8	-0.16	0.91	0	1	0	0	2	0
3652.8	3642.2	-1.16	0.88	0	2	0	0	0	0
3838.1	3859.5	-0.43	0.91	0	1	0	0	0	2
4302.9	4297.3	-1.34	0.81	0	2	0	0	1	0
4307.5	4346.0	-2.29	0.86	1	0	0	0	2	0
4493.9	4509.1	-6.02	0.66	0	1	0	0	1	2
4653.1	4652.4	-1.38	0.85	0	2	0	0	0	1
4705.2	4691.7	-2.07	0.77	0	2	0	1	0	0
4817.6	4854.0	-1.88	0.87	1	1	0	0	0	0
4955.0	4955.2	-1.79	0.84	0	2	0	0	2	0

test, for a given basis set defined from $E_{Sp}=1.8$ eV, we selected all the eigenvalues $\{E_n^{(\eta)}\}$ up to $E_n \leq 1.1$ eV. We report in Table I how this changes the root-mean-square (rms) deviation between two sets corresponding to successive values η and $\eta' = \eta + 0.1$

$$\text{rms} = \sqrt{\frac{1}{N} \sum_{\mathbf{n}} (E_{\mathbf{n}}^{(\eta')} - E_{\mathbf{n}}^{(\eta)})^2}. \quad (19)$$

It can be seen that an η value of 1.2 leads to a convergence on the rms better than 0.1 cm^{-1} , and a maximum deviation of the order of 0.3 cm^{-1} .

The HFCO system has been described by the global potential energy surface of Yamamoto and Kato.²⁶ The formulation, as presented above, is basically designed to be used within an iterative scheme such as Lanczos¹⁰ or the filter diagonalization method.²⁷ The basic operation consists of applying the Hamiltonian operator \hat{H} on a wave function expressed in the $\{\Phi_{\mathbf{n}}\}$ basis set. In the study presented here, we were essentially interested in the low-lying levels in order to compare to experimental results. For simplicity of the calculations, we chose to directly generate the Hamiltonian matrices, of A' (n_6 even) and A'' (n_6 odd) symmetries, by applying \hat{H} onto each element of the basis set. These bases were defined by keeping all the states located below an energy threshold of 2.4 eV. The resulting matrices, of dimensions 6538 and 4709, respectively, have then been diagonalized by the standard QL algorithm. Due to the high quality of the working basis set, labeling of the energy levels can be done from the leading expansion coefficient. Table II below presents a comparison of the assigned experimental levels²⁸ with the ones calculated in our new formulation.

In order to test the convergence of the reported energy levels with respect to the basis set size, we also display in Table II their energy changes as computed with an energy threshold E_{Sp} set at 2.6 eV. The resulting A' and A'' bases were of dimensions 10466 and 7771, respectively. For such large values, direct diagonalization was no longer an option due to core memory restriction. We used instead a straight Lanczos algorithm¹⁰ in order to converge the energy levels of interest. One can check that states below 2000 and 4000 cm^{-1} of internal excitation energy are converged within 0.1 and 1 cm^{-1} , respectively. The main exception concerns the $1 \nu_1$ level (C–H stretch): this mode is strongly anharmonic, $x_{11} \sim -60 \text{ cm}^{-1}$, and is badly represented in a pure harmonic basis set as done presently. This problem can be easily fixed by contracting the $\{\varphi_{n_1}\}$ basis set in order to include most of the anharmonicity, or preferably to perform vibrational SCF on the whole basis set.

IV. DISCUSSION

We have presented in this study a new formulation aimed at computing the energy levels of a semirigid molecule. Based on an initial description of the system in terms of Jacobi vectors, it leads to a very compact expression of the KEO. By defining curvilinear normal modes from these Jacobi coordinates, one can then set up an efficient zero-order harmonic Hamiltonian \hat{H}^o , similar to the Wilson formulation. The main advantage comes from the simplicity of the residual contribution $\Delta \hat{H} = \Delta \hat{T}_{\text{vib}} + \Delta V(\mathbf{q})$.

It was shown that the calculations can be entirely conducted in the associated normal basis set, and then benefit from an exact (analytic) treatment of the residual derivative

terms $\partial/\partial Q_\alpha$. Use of a *pseudospectral* scheme based on Gauss Hermite quadratures allowed us to compute any residual function type term $\Delta f(\mathbf{q})$ to an arbitrary accuracy. It also permits us to consider ultralarge basis sets as no Hamiltonian matrix representation is ever performed. It must be stressed here that due to using different representations (spectral and grid), hermiticity is only achieved if one retains the *symmetrical* formulation of Eqs. (8) and (16).

The advantage of using a normal mode basis set has been shown when labeling the energy levels: mere inspection of the leading coefficient in the eigenvector expansion directly gives the associated labels. This is in contrast with a straight Jacobi formulation where assignment proceeds by visual inspection or by fitting the energy levels to some spectroscopic Hamiltonian.^{16,29}

Not considered in this preliminary study is the possibility of performing $J \neq 0$ calculations. In that case, one can define a zero-order rovibrational Hamiltonian \hat{H}_{vr}^o by including the rotational energy term \hat{T}_{rot} [Eq. (7)] evaluated at the equilibrium geometry, and possibly some Coriolis contributions.

In the present study, symmetry could be straightforwardly taken into account as it was governed by the sole $Q_6 \equiv \phi - \phi_{eq}$ coordinate. For more involved cases, symmetry can be implemented by switching from Jacobi to symmetry-adapted coordinates. In the case of H_2CO , for example, Bramley and Carrington⁵ have thus recast the formulation in terms of Radau coordinates for the 2 hydrogen atoms.

In its present formulation, this approach cannot handle large amplitude motion as its efficiency relies on an equilibrium reference geometry \mathbf{q}_{eq} . However, its extension to such a case can be envisioned by means of the reaction path Hamiltonian approach of Miller,^{30,31} which makes use of normal modes defined locally along some reaction coordinate.

Finally, the main improvement to the present method should come from a vibrational SCF¹ treatment of the primary harmonic basis set. This, for example, should cure the anharmonicity problem associated with the C–H stretch mode as encountered in this preliminary study. It should also help to improve the basis set at higher energy if a normal to local mode transition occurs. Further work along this direction is in progress.

APPENDIX A: KINETIC ENERGY COEFFICIENTS

We give below the coefficients appearing in the KEO expression [Eqs. (5)–(7)]. These expressions are valid for any N -atom molecule described in terms of $N-1$ Jacobi vectors, μ_i being the reduced mass associated with \mathbf{R}_i . These vectors are defined sequentially in reverse order, i.e., \mathbf{R}_{N-1} is the first one, followed by \mathbf{R}_{N-2} until \mathbf{R}_1 . Also, by convention, the \mathbf{z} BF axis is taken parallel to \mathbf{R}_{N-1} , and the xz half plane ($x > 0$) is parallel to \mathbf{R}_{N-2} . The G submatrices are symmetrical, i.e., $G_{ij}^{(u\phi)} = G_{ji}^{(\phi u)}$, and by definition $\phi_{N-2} = 0$.

1. Vibrational terms

$$G_{ii}^{(rr)} = \frac{1}{\mu_i}; \quad G_{ij}^{(rr)} = 0 (j \neq i), \quad i = 1, \dots, N-1,$$

$$G_{ij}^{(uu)} = \frac{1}{\mu_{N-1} r_{N-1}^2} \sin \theta_i \cos(\phi_i - \phi_j) \sin \theta_j \\ + \frac{\delta_{ij}}{\mu_i r_i^2} (\sin \theta_i)^2, \quad i, j = 1, \dots, N-2,$$

$$G_{ij}^{(u\phi)} = \frac{1}{\mu_{N-1} r_{N-1}^2} \sin \theta_i \{ \cot \theta_j \sin(\phi_i - \phi_j) \\ - \sin \phi_i \cot \theta_{N-2} \}, \\ i = 1, \dots, N-2, j = 1, \dots, N-3,$$

$$G_{ij}^{(\phi\phi)} = \frac{1}{\mu_n r_{N-1}^2} \{ \cot \theta_i \cot \theta_j \cos(\phi_i - \phi_j) + \cot^2 \theta_{N-2} \\ - \cot \theta_{N-2} (\cos \phi_j \cot \theta_j + \cos \phi_i \cot \theta_i) \} \\ + \frac{\delta_{ij}}{\mu_i r_i^2 \sin^2 \theta_i} + \frac{1}{\mu_{N-2} r_{N-2}^2 \sin^2 \theta_{N-2}}, \\ i, j = 1, \dots, N-3. \quad (A1)$$

2. Rotational terms

$$\Gamma_{xx} = \Gamma_{yy} = \frac{1}{\mu_{N-1} r_{N-1}^2}, \\ \Gamma_{zz} = \frac{\cot^2 \theta_{N-2}}{\mu_{N-1} r_{N-1}^2} + \frac{1}{\mu_{N-2} r_{N-2}^2 \sin^2 \theta_{N-2}}, \\ \Gamma_{xy} = \Gamma_{yx} = \Gamma_{yz} = \Gamma_{zy} = 0, \\ \Gamma_{xz} = \Gamma_{zx} = \frac{\cot \theta_{N-2}}{\mu_{N-1} r_{N-1}^2}. \quad (A2)$$

3. Coriolis terms

$$C_{i\alpha}^{(r)} = 0, \\ C_{ix}^{(u)} = \frac{\sin \theta_i \sin \phi_i}{\mu_{N-1} r_{N-1}^2}, \\ C_{iy}^{(u)} = - \frac{\sin \theta_i \cos \phi_i}{\mu_{N-1} r_{N-1}^2}, \\ C_{iz}^{(u)} = \frac{\sin \theta_i \sin \phi_i \cot \theta_{N-2}}{\mu_{N-1} r_{N-1}^2}, \\ C_{ix}^{(\phi)} = \frac{-\cot \theta_{N-2} + \cos \phi_i \cot \theta_i}{\mu_{N-1} r_{N-1}^2}, \\ C_{iy}^{(\phi)} = \frac{\sin \phi_i \cot \theta_i}{\mu_{N-1} r_{N-1}^2}, \quad (A3)$$

TABLE III. $M \log M$ scaling law displayed by the whole scheme as a function of the basis set size M .

Energy threshold E_{Sp} (eV)	1.4	1.9	2.2	2.4	2.6
Basis set size M	255	1619	3895	6538	10 466
CPU time T (s)	1.03	9.97	29.5	39.2	64.8
$T/(M \log M)$	1.7(-3)	1.9(-3)	2.1(-3)	1.6(-3)	1.6(-3)

$$C_{iz}^{(\phi)} = \frac{\cot \theta_{N-2} (-\cot \theta_{N-2} + \cos \phi_i \cot \theta_i)}{\mu_{N-1} r_{N-1}^2}.$$

APPENDIX B: NONDIRECT PRODUCT BASIS SET

In order to benefit from the physical meaning of the normal modes, we chose to use a nondirect product basis set defined by keeping only states $\{\Phi_{\mathbf{n}}(\mathbf{Q})\}$ [Eq. (15)] below some given threshold E_{Sp} : $E_{\mathbf{n}}^o \leq E_{Sp}$. The idea behind such a strategy relies on the fact that for moderate excitation energies, the coupling should be weak. From perturbation theory, it is well known that states located far from the perturbed level should play a minor role.

This choice allows for a drastic reduction in the basis set size as compared to a direct product definition. For example, in the case of the HFCO molecule considered here, the size is reduced from about 780 000 down to 6538 for an energy threshold set at $E_{Sp} = 2.4$ eV. A second improvement concerns the energy spread of the basis, as this is crucial for the efficiency of any iterative scheme used in a direct method. For the example given above, the direct product basis displays an upper energy threshold of about 10 eV.

The drawback is that handling a nondirect product basis generally results in more bookkeeping when applying the Hamiltonian operator on a wave function expressed in such a basis set. In order to minimize this extra cost, we have used the following strategy.

Associated with the truncated basis set $\{\Phi_{\mathbf{n}}(\mathbf{Q})\}$ is a list $\{R_{\mathbf{n}}\}$, where $R_{\mathbf{n}}$ stands for the rank of \mathbf{n} in the virtual direct product basis set:

$$R_{\mathbf{n}} = (((((n_1 \cdot (N_2 + 1) + n_2) \cdot (N_3 + 1) + n_3) \cdot (N_4 + 1) + n_4) \cdot (N_5 + 1) + n_5) \cdot (N_6 + 1) + n_6),$$

and N_{α} stands for the maximum occupation number in mode Q_{α} . The $\{\Phi_{\mathbf{n}}(\mathbf{Q})\}$ basis set is naturally ordered by increasing values of $R_{\mathbf{n}}$.

The action of an operator such as $\partial/\partial Q_1$ on a function Ψ known by its expansion coefficients $\{\psi_{\mathbf{n}}\}$ [Eq. (18)] produces two arrays $\{\psi_{\mathbf{n}}^{(-)}\}$ and $\{\psi_{\mathbf{n}}^{(+)}\}$ such as [see Eq. (17)]

$$\left\{ \psi_{n_1-1 n_2 \dots}^{(-)} \equiv \sqrt{\frac{\mu_1 \omega_1}{2\hbar}} \sqrt{n_1 - 1} \psi_{n_1 n_2 \dots} \right\},$$

and a similar expression for $\{\psi_{\mathbf{n}}^{(+)}\}$.

The important point is that these two new arrays will still be ordered by increasing values of their associated ranks $\{R_{\mathbf{n}}^{(-)}\}$ and $\{R_{\mathbf{n}}^{(+)}\}$, respectively, even for a nondirect product basis set. Furthermore, these new values can be straightforwardly computed as

$$R_{n_1 \pm 1 n_2 \dots}^{(\pm)} = R_{n_1 n_2 \dots} \pm \prod_{\alpha=2}^6 (N_{\alpha} + 1).$$

The result of $\partial/\partial Q_1 \{\psi_{\mathbf{n}}\}$ is finally obtained by merging each list $\{\psi_{\mathbf{n}}^{(\pm)}\}$ to a unique accumulation list. For the calculations presented in this study, less than 2% of the CPU time is spent in merging.

In order to show that using a nondirect product basis set does not hamper the efficiency of the whole scheme, we report in Table III the cost of applying the Hamiltonian operator \hat{H} on a function $\Psi(\mathbf{Q})$ for different basis set sizes M . Each of these bases corresponds to a given energy threshold E_{Sp} , ranging from 1.4 to 2.6 eV. The last line of this table reveals that the scheme displays an $M \log M$ scaling law.

¹J. M. Bowman, Acc. Chem. Res. **19**, 202 (1986).

²E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).

³M. J. Bramley and N. C. Handy, J. Chem. Phys. **98**, 1378 (1993).

⁴X. Chapuisat, A. Belafhal, and A. Nauts, J. Mol. Struct. **149**, 274 (1991).

⁵M. J. Bramley and T. Carrington, J. Chem. Phys. **101**, 8494 (1994).

⁶F. Gatti, J. Chem. Phys. **111**, 7225 (1999).

⁷M. Mladenovic, J. Chem. Phys. **112**, 1070 (2000).

⁸J. Antikainen, R. A. Friesner, and C. Leforestier, J. Chem. Phys. **102**, 1270 (1995).

⁹X. Chapuisat and C. Iung, Phys. Rev. A **45**, 6217 (1992).

¹⁰C. Lanczos, J. Res. Natl. Bur. Stand. **45**, 255 (1950).

¹¹H. Tal-Ezer and R. Kosloff, J. Chem. Phys. **81**, 3967 (1984).

¹²Y. Saad and M. H. Schultz, SIAM (Soc. Ind. Appl. Math.) J. Sci. Stat. Comput. **7**, 856 (1986).

¹³A. B. McCoy and E. L. Sibert, in *Dynamics of Molecules and Chemical Reactions*, edited by R. E. Wyatt and J. Z. H. Zhang (Dekker, New York, 1996), p. 151.

¹⁴C. R. Quade, J. Chem. Phys. **64**, 2783 (1976).

¹⁵D. W. Jepsen and J. O. Hirschfelder, Proc. Natl. Acad. Sci. U.S.A. **45**, 249 (1959).

¹⁶A. Viel and C. Leforestier, J. Chem. Phys. **112**, 1212 (2000).

¹⁷T. Carrington, J. Chem. Phys. **112**, 4413 (2000).

¹⁸J. Makarewicz and A. Skalozub, Chem. Phys. Lett. **306**, 352 (1999).

¹⁹C. Iung, F. Gatti, A. Viel, and X. Chapuisat, Phys. Chem. Chem. Phys. **1**, 3377 (1999).

²⁰F. Gatti, C. Munoz, and C. Iung (unpublished).

²¹R. N. Zare, *Angular Momentum* (Wiley, New York, 1988).

²²F. Gatti *et al.*, J. Chem. Phys. **108**, 8804 (1998).

²³H. Wei and T. Carrington, J. Chem. Phys. **101**, 1343 (1994).

²⁴J. C. Light, I. P. Hamilton, and J. V. Lill, J. Chem. Phys. **82**, 1400 (1985).

²⁵R. A. Friesner, J. Chem. Phys. **85**, 1462 (1986).

²⁶T. Yamamoto and S. Kato, J. Chem. Phys. **107**, 6114 (1997).

²⁷D. Neuhauser, J. Chem. Phys. **93**, 2611 (1990).

²⁸C. B. Moore and R. Tadday (private communication).

²⁹M. Menou and C. Leforestier, Chem. Phys. Lett. **210**, 294 (1993).

³⁰W. H. Miller, N. C. Handy, and J. E. Adams, J. Chem. Phys. **72**, 99 (1980).

³¹T. Carrington and W. H. Miller, J. Chem. Phys. **81**, 3942 (1984).