



# The theory of the canonical force field revisited

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## ABSTRACT

In a previous Letter, Kuczera's theory of the canonical force field was generalized to the case of redundant curvilinear internal coordinates related by non-linear constraints. A central issue in this theory is the projection from the space of internal coordinates onto the pure vibrational manifold. In this Letter we present a new mathematical treatment of the projection that solves some problems of inconsistency that have arisen when applying the theory to molecules with a central atom. In addition to solving these problems, this treatment greatly simplifies the attainment of the projection and, consequently, the calculation of canonical force constants.

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## 1. Introduction

The purpose of the canonical force field is to provide a well-defined way of expressing the molecular force field in terms of redundant internal coordinates and thus to avoid the problem of indeterminacy of the force constants [1–6]. Such theory was formulated in the 1980s in terms of rectilinear internal coordinates in the harmonic approach. In a previous Letter the theory was extended to anharmonic potentials in curvilinear coordinates [7]. In that Letter, some properties of the canonical force constants were proved: the sum of their squares is minimal and they are transferable to molecules with the same geometrical structure. The purpose of this new Letter is to solve some mathematical problems that arise when applying the theory to molecules with a central atom, such as  $XYZ_3$  ( $C_{3v}$ ),  $XY_4$  ( $C_{4v}$ ) and  $XY_2Z_2$  ( $C_{2v}$ ). Next, we display the main points of the theory and show these problems.

Let us consider a molecule with  $N$  atoms whose geometry is described by  $m$  curvilinear internal coordinates, where  $m > n = 3N - 6$ . The values of the coordinates are related by  $m - n$  redundancy relations,  $\varphi_s(\mathbf{r}) = 0$  ( $s = 1, 2, \dots, m - n$ ), whose power series expansions are<sup>1</sup>

$$\varphi_s(\mathbf{r}) = B_s^i r_i + \frac{1}{2!} B_s^{ij} r_i r_j + \frac{1}{3!} B_s^{ijk} r_i r_j r_k + \dots \quad (1)$$

where  $r_i$  ( $i = 1, 2, \dots, m$ ) are the displacements of the internal coordinates from their equilibrium values. In order to simplify subsequent mathematical developments we chose the coefficients of these expansions so that the linear coefficients are orthonormal:  $B_s^i B_t^i = \delta_{st}$ , where  $\delta_{st}$  is the Kronecker delta.<sup>2</sup>

The geometrical configuration of the molecule can be defined by a point with coordinates  $(r_1, r_2, \dots, r_m)$  in an  $m$ -dimensional Cartesian space  $\mathbf{R}^m$ . The points of such a space which satisfy the redundancy relation form the pure vibrational manifold,  $\mathbf{V}$ . An important subject in the theory of the canonical force field is the projection of the points of  $\mathbf{R}^m$  onto  $\mathbf{V}$ . Let  $\mathbf{p}$  be the point of  $\mathbf{V}$  with coordinates  $p_i$  ( $i = 1, 2, \dots, m$ ) which is obtained by projecting a point  $\mathbf{r} \in \mathbf{R}^m$ . In Ref. [7] the point  $\mathbf{p}$  was defined by the following three equations:

$$\varphi_s(\mathbf{p}) = 0 \quad (2a)$$

$$p_i(\mathbf{p}) = p_i(\mathbf{r}) \quad (2b)$$

$$\langle \nabla p_i | \nabla \varphi_s(\mathbf{p}) \rangle = 0 \quad (2c)$$

By expanding the coordinates of  $\mathbf{p}$  in power series of the coordinates of  $\mathbf{r}$ ,

$$p_i(\mathbf{r}) = C_i^j r_j + \frac{1}{2!} C_i^{jk} r_j r_k + \frac{1}{3!} C_i^{jkl} r_j r_k r_l + \dots \quad (3)$$

Eqs. (2a), (2b), and (2c) lead respectively to the following sets of linear equations [7]:

$$B_s^i C_j^i = 0 \quad (4a)$$

$$B_s^{kl} C_l^i C_j^i + B_s^{ij} C_k^i = 0 \quad (4b)$$

$$B_s^{lmn} C_l^i C_m^j C_n^k + B_s^{lm} (C_l^{ij} C_m^k + C_l^{ik} C_m^j + C_l^{jk} C_m^i) + B_s^l C_l^{ijk} = 0 \quad (4c)$$

...

$$C_i^j = C_i^k C_l^j \quad (5a)$$

$$C_i^{jk} = C_i^{lm} C_l^j C_m^k + C_i^l C_l^{ijk} \quad (5b)$$

$$C_i^{jkl} = C_i^{mno} C_m^j C_n^k C_o^l + C_i^{mn} (C_m^{jk} C_n^l + C_m^{jl} C_n^k + C_m^{kl} C_n^j) + C_i^m C_m^{jkl} \quad (5c)$$

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<sup>1</sup> We employ the convention according to which when an index is repeated in a term, it implies that we are summing over all possible values for that index.

<sup>2</sup> In this Letter, Kronecker delta may appear as  $\delta_{ij}$ ,  $\delta_i^j$  or  $\delta^{ij}$ .

$$C_i^j B_s^j = 0 \quad (6a)$$

$$C_i^{jk} B_s^k + C_i^k B_s^k = 0 \quad (6b)$$

$$C_i^{jkl} B_s^l + C_i^{jl} B_s^{kl} + C_i^{kl} B_s^{jl} + C_i^l B_s^{jkl} = 0 \quad (6c)$$

...

In principle, the linear coefficients  $C_i^j$  could be obtained by solving the system of linear equations given by Eqs. (4a), (5a), and (6a), the quadratic coefficients  $C_a^{ij}$  could be obtained by solving Eqs. (4b), (5b) and (6b), and so on. In the previous Letter, this method was applied in the methane molecule to obtain the linear, quadratic and cubic coefficients of the expansion power series of the projection. Later we applied this procedure to other tetracoordinate molecules finding that the systems of linear equations given by Eqs. (4b), (5b), (6b) and Eqs. (4c), (5c), (6c) are often inconsistent and, hence, there is no solution for the coefficients. This means that, in general, the three conditions together (Eqs. (2a), (2b) and (2c)) are incompatible with the power series expansion of the projection. In the next section we analyze the causes of this incompatibility and we present a consistent way to get the projection that overcomes this problem.

## 2. New treatment of the projection

Every projection must fulfil Eqs. (2a), (2b) because they are requirements that any projection must necessarily satisfy. However, Eq. (2c) is a further condition imposed in order that the projection be orthogonal to the level surfaces of the redundancies. Hence, if we express the projection as a power series, we should not require the fulfilment of the orthogonality condition in the same way as we did in Ref. [7]. We cannot dispense completely with this condition since the projection is not thoroughly determined by Eqs. (2a) and (2b).

In the case of linear redundancies, the point  $\mathbf{p}$  which is the orthogonal projection of a point  $\mathbf{r} \in \mathbb{R}^m$  can be written in matrix form as  $\mathbf{p} = (\mathbf{I} - \mathbf{B}\mathbf{B}^T)\mathbf{r}$  [1–6], where  $\mathbf{I}$  is the  $m$ -dimensional unit matrix,  $\mathbf{B}$  is the column matrix whose elements are the coefficients of the redundancies, and  $\mathbf{B}^T$  is the transpose matrix of  $\mathbf{B}$ . According to this, the  $i$  coordinate of  $\mathbf{p}$  is given by:

$$p_i(\mathbf{r}) = r_i - B_s^i B_s^j r_j, \quad (7)$$

It is easy to check that this expression satisfy Eqs. (2a), (2b), and (2c). It can also be written as:

$$p_i(\mathbf{r}) = r_i + \frac{\partial \varphi_s(\mathbf{r})}{\partial r_i} D_s^j r_j \quad (8)$$

where  $D_s^j = -B_s^j$ . The expression that we propose for the projection in the case of non-linear redundancies is a generalization of Eq. (8):

$$p_i(\mathbf{r}) = r_i + \frac{\partial \varphi_s(\mathbf{r})}{\partial r_i} \varphi_s(\mathbf{r}) \quad (9)$$

where  $\varphi_s$  is a power series of the coordinates of  $\mathbf{r}$ :

$$\varphi_s(\mathbf{r}) = D_s^i r_i + \frac{1}{2!} D_s^{ij} r_i r_j + \frac{1}{3!} D_s^{ijk} r_i r_j r_k + \dots \quad (10)$$

One advantage of this expression is that if it satisfies Eq. (2a), then Eq. (2b) is automatically satisfied. This is easy to show since, from Eq. (9),  $p_i(\mathbf{p})$  is given by

$$p_i(\mathbf{p}) = p_i + \frac{\partial \varphi_s(\mathbf{p})}{\partial p_i} \varphi_s(\mathbf{p}) \quad (11)$$

which transforms into  $p_i(\mathbf{p}) = p_i$  (Eq. (2b)) if  $\varphi_s(\mathbf{p}) = 0$  (Eq. (2a)) is satisfied.

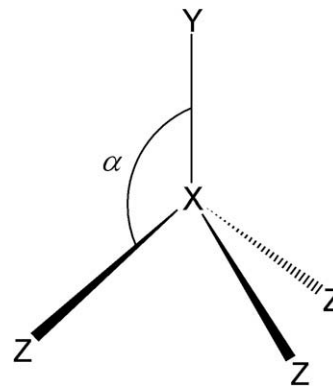


Fig. 1. XYZ<sub>3</sub> molecule (C<sub>3v</sub>).

The coefficients of the expansion,  $D_s^i$ ,  $D_s^{ij}$ ,  $D_s^{ijk}$ , ..., can be obtained by substituting Eqs. (9) and (10) into Eq. (2a). Thus we get<sup>3</sup>:

$$D_s^i = -B_s^i \quad (12a)$$

$$D_s^{ij} = -B_s^{kl} (\delta^{ik} - B_t^i B_t^k) (\delta^{jl} - B_u^j B_u^l) + B_s^k (B_t^i B_t^{jk} + B_t^j B_t^{ik}) \quad (12b)$$

$$D_s^{ijk} = -B_s^{lmn} (\delta^{il} - B_t^l B_t^l) (\delta^{jm} - B_u^j B_u^m) (\delta^{kn} - B_v^k B_v^n) - B_s^{lm} (D_t^{ij} B_t^l - B_t^i B_t^{jl} - B_t^j B_t^{il}) (\delta^{km} - B_u^k B_u^m) - B_s^{lm} (D_t^{ik} B_t^l - B_t^i B_t^{lk} - B_t^k B_t^{il}) (\delta^{jm} - B_u^j B_u^m) - B_s^{lm} (D_t^{jk} B_t^l - B_t^j B_t^{lk} - B_t^k B_t^{jl}) (\delta^{im} - B_u^i B_u^m) \times (\delta^{jm} - B_u^j B_u^m) - B_s^{lm} (D_t^{jk} B_t^l - B_t^j B_t^{lk} - B_t^k B_t^{jl}) (\delta^{im} - B_u^i B_u^m) - B_s^l (D_t^{ij} B_t^l + D_t^{ik} B_t^l + D_t^{jl} B_t^l - B_t^i B_t^{kl} - B_t^j B_t^{il} - B_t^k B_t^{jl}) \quad (12c)$$

...

On the other hand, by substituting Eq. (10) into Eq. (9) and comparing the obtained series with Eq. (3) we get:

$$C_i^j = \delta_i^j + B_s^i D_s^j \quad (13a)$$

$$C_i^{jk} = B_s^i D_s^j + B_s^j D_s^i + B_s^{ij} D_s^k \quad (13b)$$

$$C_i^{jkl} = B_s^i D_s^j + B_s^j D_s^i + B_s^{ij} D_s^k + B_s^{jk} D_s^l + B_s^{kl} D_s^i + B_s^{il} D_s^j + B_s^{jl} D_s^k + B_s^{kl} D_s^i \quad (13c)$$

...

Eqs. (12a), (12b), (12c), (13a), (13b), and (13c) ensure that the new way to obtain the projection is consistent and provides a unique solution for the coefficients  $C_i^j$ ,  $C_i^{jk}$ , ...

The fulfilment of Eq. (2c) requires certain conditions to be met by the redundancies. Such conditions can be obtained by equating to zero the coefficients of the polynomial resulting from substituting Eq. (9) into Eq. (2c). Thus we get:

$$(\delta^{ij} + B_t^i D_t^j) B_s^j = 0 \quad (14a)$$

$$(B_t^i D_t^j + B_t^j D_t^i + B_t^{ij} D_t^k) B_s^k + (\delta^{ik} + B_t^i D_t^k) B_s^k = 0 \quad (14b)$$

$$(B_t^i D_t^j + B_t^j D_t^i + B_t^{ij} D_t^k + B_t^{jk} D_t^l + B_t^{kl} D_t^i + B_t^{il} D_t^j + B_t^{jl} D_t^k + B_t^{kl} D_t^i) B_s^l + (B_t^i D_t^j + B_t^j D_t^i + B_t^{ij} D_t^k) B_s^k + (B_t^i D_t^k + B_t^k D_t^i + B_t^{ik} D_t^l) B_s^l + (\delta^{il} + B_t^i D_t^l) B_s^l = 0 \quad (14c)$$

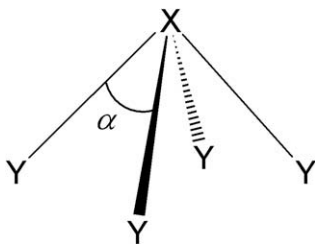
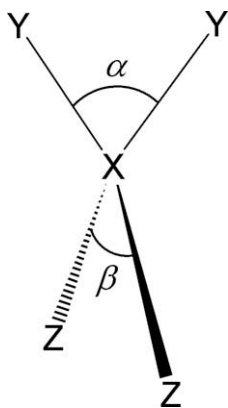
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Using Eq. (12a) it is easy to check that the left side of Eq. (14a) is identically zero. This result was expected because, as mentioned at the beginning of this section, Eq. (2c) is always fulfilled in the case of linear redundancies.

Now let us obtain the condition that the coefficients of the redundancies must fulfil in order that Eq. (2c) be satisfied by the quadratic terms of the power series expansion of the projection. It can be obtained by substituting Eqs. (12a) and (12b) into Eqs. (14b), thus we get:

$$B_s^j B_t^k B_u^l = B_s^i B_t^j \quad (15)$$

<sup>3</sup> The expression of  $D_s^{ijk}$  is too long to be shown here, so it is given as function of  $D_s^{ij}$ .

Fig. 2.  $XY_4$  molecule ( $C_{4v}$ ).Fig. 3.  $XY_2Z_2$  molecule ( $C_{2v}$ ).

This condition has no special physical significance and its fulfilment depends on the molecular geometry. In the case of  $XYZ_3$  ( $C_{3v}$ ) molecules (Fig. 1) we have found that such condition is met when  $\alpha = \pi - \alpha_0$ ,  $\alpha = \pi/2$  or  $\alpha = \alpha_0$ , where  $\alpha_0$  is the tetrahedral angle:  $\alpha_0 = \arccos(-1/3)$ . In  $XY_4$  ( $C_{4v}$ ) molecules (Fig. 2) it is satisfied when  $\alpha = \pi - \alpha_0$  or  $\alpha = \pi/2$ . For  $XY_2Z_2$  ( $C_{2v}$ ) molecules (Fig. 3) it is fulfilled if  $\alpha = \beta = \alpha_0$  or  $\alpha = \beta = \pi$ . The details of these calculations will be discussed in a future Letter.

By substituting Eqs. (12a), (12b) and (12c) into Eqs. (14c) and after a long mathematical development we obtain the condition for the fulfilment of Eq. (2c) by the cubic terms:

$$\begin{aligned} & B_s^l B_t^{ilm} B_u^j B_u^m B_u^k + B_s^l B_t^{ilm} B_u^i B_u^m B_u^k + B_s^l B_t^{ilm} B_u^i B_u^m B_u^{jk} + B_s^l B_t^{ilm} B_u^j B_u^m B_u^{ik} \\ & + B_s^{il} B_t^{lm} B_u^j B_u^m B_u^k + B_s^{il} B_t^{lm} B_u^i B_u^m B_u^k - B_s^l B_t^{ikl} B_u^j - B_s^l B_t^{jkl} B_u^i - B_s^{il} B_t^{kl} B_u^j \\ & - B_s^{jl} B_t^{kl} B_u^i - B_s^l B_t^{ilm} B_u^i B_u^m B_u^j B_u^k - B_s^l B_t^{ilm} B_u^i B_u^m B_u^j B_u^k = 0 \end{aligned} \quad (16)$$

This condition is more restrictive than Eq. (15) and is not satisfied by the above molecules. The mathematical developments required to obtain the conditions corresponding to higher terms are extremely laborious, and these conditions are more and more complicated and difficult to meet. This makes us suspect that Eq. (2c) can be only fulfilled by the first terms of the power series expansions whatever the molecule under consideration.

### 3. Canonical force constants

The canonical force constants are given as function of non-canonical ones by [7]:

$$F^{ii} = F^j C_j^i = 0 \quad (17a)$$

$$F^{*ij} = F^{kl} C_k^i C_l^j + F^{*k} C_k^{ij} \quad (17b)$$

$$F^{*ijk} = F^{lmn} C_l^i C_m^j C_n^k + F^{lm} (C_l^{ij} C_m^k + C_l^{ik} C_m^j + C_l^{jk} C_m^i) + F^l C_l^{ijk} \quad (17c)$$

The sum rule relationships obtained in Ref. [7] in which cubic and higher force constants appear (Eq. (28) of Ref. [7]) are wrong in general because they were obtained using Eq. (2c). The correct

sum rule relationships should be obtained by replacing the non-canonical force constants in the right members of Eqs. ((17a), (17b), (17c), ...) by canonical ones and then writing the coefficients  $C_i^j$ ,  $C_i^{jk}$ , ... in terms of  $B_s^i$ ,  $B_s^{ij}$ , ... using Eqs. (12a), (12b), (12c), (13a), (13b), and (13c). Thus, we get:

$$F^{*ij} B_s^j = 0 \quad (18a)$$

$$F^{*ijk} B_s^k + F^{*ik} B_s^{kj} + F^{*jk} B_s^{ik} + F^{*ik} B_t^{kl} B_s^l + F^{*jk} B_t^{kl} B_s^l = 0 \quad (18b)$$

Note that Eq. (18b) is not the same than Eq. (28b) of Ref. [7]. Fortunately, the remaining properties of the canonical force constants which were obtained in Ref. [7] are not affected by the new treatment of the projection because they were obtained without using the orthogonality condition.

### 4. Conclusions

A new procedure for obtaining the projection from the space of internal coordinates onto the vibrational manifold has been found that solves the problems of inconsistency that arise when the previous method has been applied to molecules with symmetry  $C_{2v}$ ,  $C_{3v}$  and  $C_{4v}$ , formed by a central atom surrounded by four atoms. The mathematical treatment here developed is a generalization of the procedure for the linear case to the case of non-linear redundancies. This method provides explicit expressions for the coefficients of the projection in terms of the coefficients of the redundancies, allowing us to perform direct calculation of these coefficients without solving complicated equation systems as occurs in the previous method [7].

The inconsistencies stem from applying the orthogonality condition, Eq. (2c), to obtain the quadratic and cubic coefficients of the projection. It has been shown that the linear coefficients are the only ones which must satisfy Eqs. (2a), (2b) and (2c); on the contrary, the higher-degree coefficients are uniquely determined by Eqs. (2a) and (2b) and do not necessarily satisfy Eq. (2c). The conditions that redundancies must satisfy for the fulfilment of the orthogonality condition by the quadratic and cubic terms of the projection have been obtained. The complexity of these conditions greatly increases with the degree of the terms (see Eq. (16)), which makes one think that, whatever the geometry of the molecule, it is unlikely that the orthogonality condition be satisfied by terms higher than cubic. This means that the trajectory of the projection can not be completely orthogonal to the level surfaces of the redundancies, but only up to a certain approximation. If a completely orthogonal projection exists, it cannot be written as a power series expansion like Eq. (3).

The new treatment of the projection does not affect the properties of the canonical force constants established in Ref. [7], according to which the sum of their squares is minimal and they are transferable to molecules with the same geometrical structure. However, the sum rule relationships involving anharmonic force constants are affected. The lack of general validity of the orthogonality condition makes these relationships more complicated.

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