



**UNIVERSIDAD NACIONAL AUTÓNOMA DE MEXICO**

**PROGRAMA DE MAESTRÍA Y DOCTORADO EN CIENCIAS QUÍMICAS**

**CONEXIÓN DE LOS MÉTODOS ALGEBRAICOS CON EL ESPACIO DE  
CONFIGURACIÓN EN MODELOS CON APLICACIÓN A SISTEMAS  
MOLECULARES**

**PROYECTO DE INVESTIGACIÓN  
PARA OPTAR POR EL GRADO DE**

**MAESTRO EN CIENCIAS**

**PRESENTA**

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**CIUDAD DE MÉXICO, MÉXICO, AGOSTO DE 2018**



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Este proyecto de investigación fue desarrollado en:

Departamento de Estructura de la Materia  
Cubículo F-2  
Instituto de Ciencias Nucleares  
Ciudad Universitaria  
Universidad Nacional Autónoma de México

Algunos de los resultados de este proyecto de investigación se presentaron en :

Decimoquinta Reunión Mexicana de Fisicoquímica Teórica

Decimosexta Reunión Mexicana de Fisicoquímica Teórica

Como parte de este proyecto de investigación se publicaron los siguientes artículos:

M. Estévez-Fregoso, M, Arias, J, Gómez Camacho, Joaquin, Lemus, R. (2018).  
An approach to establish a connection between algebraic and configuration spaces:  $su(\nu + 1)$  algebraic model for vibrational excitations. Molecular Physics. 1-16.  
10.1080/00268976.2018.1471229.

M. Estévez-Fregoso, Lemus, R. (2018).  
Connection between the  $su(3)$  algebraic and configuration spaces: bending modes of linear molecules. Molecular Physics. 1-22.  
10.1080/00268976.2018.1487599

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## AGRADECIMIENTOS

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A la Dirección General de Asuntos del Personal Académico (UNAM) por el apoyo a través del proyecto  
IN-227017.

Al Consejo Nacional de Ciencia y Tecnología por la beca número 433562 otorgada para la realización de mis  
estudios de maestría.

A los miembros de mi jurado por el tiempo invertido en la revisión de esta tesis.

Al Dr. Renato Lemus Casillas, por su gran apoyo, paciencia y dedicación. Toda mi admiración hacia usted.

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# INTRODUCCIÓN

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Las vibraciones y rotaciones moleculares han sido objeto de estudio desde mediados del siglo XX debido a que el análisis de los estados cuánticos de un espectro de rotación-vibración equivale a entender la dinámica cuántica de las moléculas [1, 2, 3, 4]. A inicios de 1945 ya se tenía una buena resolución en espectros puramente rotacionales con base en la tecnología de microondas, sin embargo, en el rango del infrarrojo, la resolución en los espectros era sólo suficiente para moléculas muy simples [1, 5]. En décadas recientes ha existido un avance sustancial en la espectroscopía IR y Raman alcanzando altas resoluciones aún en la región cercana a la disociación; esto ha hecho que la obtención del espectro de rotación- vibración de moléculas más complejas sea posible para el completo análisis de la estructura fina rotacional-vibracional de estas.[6, 7].

De forma paralela a los desarrollos experimentales, ha habido gran progreso en el desarrollo de modelos teóricos para la descripción de moléculas en el marco de la mecánica cuántica; en ellos se requiere obtener valores y funciones propias del sistema en estudio por lo que se debe construir una representación adecuada del Hamiltoniano molecular [8, 9].

El Hamiltoniano mecánico cuántico no relativista de una molécula puede escribirse en coordenadas cartesianas, sin embargo la ecuación de Schrödinger asociada resulta prácticamente irresoluble , una forma de abordar este problema es mediante la aproximación de Born- Oppenheimer, que separa los grados de libertad de la molécula en una parte electrónica y otra nuclear. Esta aproximación es posible debido a la diferencia másica entre núcleos y electrones, así, el movimiento nuclear es controlado por una superficie de energía potencial (SEP) que representa la energía electrónica [8, 9, 10]. La aproximación de Born-Oppenheimer utiliza 2 cambios de coordenadas; una a un sistema de referencia con origen en el centro de masa molecular para desacoplar los grados de libertad traslacionales y otro para desacoplar los electrónicos del resto en el centro de masa nuclear. La idea central de esta aproximación consiste en suponer una diferencia energética suficientemente grande entre la energía cinética electrónica y nuclear [11, 12].

El desarrollo de métodos teóricos que describan espectros vibracionales experimentales es fundamental, puesto que se necesitan datos espectroscópicos precisos para validar la SEP estimada a partir de modelos teóricos electrónicos, por ello, dada la aproximación de Born-Oppenheimer descrita, se desarrolla un Hamiltoniano vibracional [9, 13, 14].

Los modelos algebraicos para la descripción de vibraciones utilizan operadores de segunda cuantización; el más conocido se basa en el uso de operadores bosónicos de creación y aniquilación asociados al oscilador armónico [15, 16]. En un esquema de osciladores armónicos interactuantes la contribución diagonal del Hamiltoniano contiene las contribuciones de los osciladores independientes y términos anarmónicos proporcionales a potencias de los números cuánticos normales [17, 18]. Una gran ventaja de la representación algebraica es que cualquier elemento de matriz de un observable que dependa de las coordenadas y el momento, puede calcularse a través de manipulación algebraica que involucre las relaciones de conmutación de los operadores correspondientes; la acción de los operadores definidos sobre la base puede establecerse de manera exacta.

Una opción adicional son los modelos algebraicos basados en grupos unitarios. Los grupos unitarios son relevantes en la descripción de sistemas de muchos cuerpos pues los productos bilineales de operadores bosónicos y fermiónicos pueden ser identificados como generadores de grupos unitarios, los cuales se pueden identificar con el grupo dinámico de varios sistemas que involucran distintas escalas de energía: grados de libertad vibracionales [15, 19], electrónicos en átomos y moléculas [20, 21, 22], física nuclear [22, 23, 24, 25] y subnuclear [25, 26].

Cuando las excitaciones vibracionales son descritas en términos de una base de osciladores armónicos, los grupos unitarios aparecen de forma espontánea. Los productos bilineales de operadores de creación y aniquilación asociados con un conjunto de  $\nu$  osciladores  $n$ -dimensionales, constituyen los generadores del grupo de simetría del grupo de Lie  $U(\nu n)$ , mientras que el grupo simpléctico  $SP(2\nu n, R)$  es el correspondiente grupo dinámico [21, 27]. El hecho de que éstos últimos grupos sean no-compactos representa una desventaja desde el punto de vista práctico al tratar con estados ligados [28], pero es posible manejar grupos dinámicos compactos si restringimos el espacio de osciladores armónicos. Una forma de hacerlo es mediante la adición de un bosón escalar extra de manera que el número total de bosones del grupo unitario quede fijo [29, 30, 31, 32, 33].

Este nuevo enfoque es inspirado de trabajos anteriores [29]. En el año 1975, Arima y Iachello propusieron el llamado Modelo de Bosones Interactuantes (IBM) dentro del campo de la física nuclear para describir grados de libertad nucleares para núcleos par-par [34]; este modelo se basa en la deformación cuadrupolar en conexión con la vibración superficial de los núcleos [35]. El punto de partida consiste en la introducción de un bosón escalar extra al conjunto de bosones asociados a la deformación cuadrupolar nuclear con la restricción de tener un número fijo total de bosones. Aparte de que el grupo dinámico es compacto, el éxito de este modelo se debió a que el grupo resultante dio lugar a 3 simetrías dinámicas con sentido físico [24]. Años después Iachello *et al* propusieron aplicar esta misma idea a la descripción de grados de libertad ro-vibracionales de moléculas diatómicas, dando como resultado el modelo vibrónico  $U(4)$  donde el momento dipolar es el ingrediente físico dominante [36, 37]. En este contexto, el número total de bosones es un parámetro asociado a la profundidad del potencial, un hecho que provee de una descripción donde las anarmonicidades son tomadas en cuenta desde el inicio, sin la necesidad de introducir potenciales anarmónicos. El modelo fue extendido a moléculas poli-atómicas con claro éxito en moléculas lineales [32, 38]. La adición de un bosón escalar extra también fue usado en el contexto de excitaciones vibracionales puras donde un conjunto de osciladores equivalentes dan lugar al modelo propuesto por Michelot y Moret-Bailly, donde el grupo dinámico para un conjunto de  $\nu$ - osciladores equivalentes se vuelve  $U(\nu + 1)$  [39, 40].

La relevancia del modelo  $U(\nu + 1)$  es doble [22]. Por un lado, aparecen subgrupos ortogonales, dando como resultado variedad de simetrías dinámicas y por otro lado, las anarmonicidades del sistema pueden introducirse desde el planteamiento del problema. Las simetrías dinámicas representan aproximaciones a orden cero del problema completo; en algunos casos, añadir operadores de Casimir de diferentes cadenas puede ser suficiente para describir con la precisión deseada un sistema, sin embargo, cuando el número de osciladores aumenta, el número de interacciones se incrementa y los Casimires se vuelven insuficientes para proveer de una descripción completa. En física molecular, esta situación es muy común; las interacciones relevantes son en general numerosas y bien conocidas en el espacio de configuración. Como son conocidas, se puede plantear la realización algebraica de las interacciones especificadas en el espacio de coordenadas y momentos.

## 1.1. Objetivos

En el presente trabajo se estudia la conexión entre el espacio de configuración y el espacio algebraico en dos sistemas, en general se busca:

1. Establecer la conexión matemática formal entre el espacio algebraico  $U(\nu + 1)$  y el espacio de configuración para la descripción de modos locales equivalentes.
2. Establecer la conexión del grupo dinámico  $U(3)$  con el espacio de momentos y coordenadas para los grados de flexión de moléculas lineales aplicando los resultados a la molécula de acetileno.

Los objetivos particulares de este trabajo son:



- 1.1 Conectar el espacio de configuración con el espacio algebraico en el caso de dos osciladores a través del mapeo con oscilador armónico.
- 1.2 Obtener los momentos y las coordenadas para cada oscilador como una realización del álgebra dinámica.
- 1.3 Establecer la conexión entre espacios usando un mapeo con el producto directo de  $\nu$  osciladores de Morse restringido al subespacio caracterizado por un número máximo de cuantos.
- 2.1 Probar que la aproximación lineal previamente usada en el  $CO_2$  [41]. corresponde con la mejor aproximación cuando se propone un mapeo con oscilador armónico, obteniendo la representación de las coordenadas y momentos en el espacio algebraico  $U(3)$ .
- 2.2 En el caso de dos osciladores acoplados, establecer una manera de obtener constantes de fuerza cuando el sistema en estudio tiene un comportamiento normal.
- 2.3 Seguir la estrategia propuesta para estimar razonablemente las constantes de fuerza para acetileno.

## MODELO $SU(\nu + 1)$

---

### 2.1. Modelo algebraico $su(\nu + 1)$

#### 2.1.1. $\nu$ osciladores armónicos

Consideremos un sistema de  $\nu$  osciladores armónicos no interactuantes. A cada oscilador  $i$  se le puede asociar un operador de creación  $\hat{a}_i^\dagger$  y un operador de aniquilación  $\hat{a}_i$ , lo que nos permite expresar el Hamiltoniano como

$$\hat{H} = \frac{\hbar\omega}{2} \sum_{i=1}^{\nu} (\hat{a}_i^\dagger \hat{a}_i + \hat{a}_i \hat{a}_i^\dagger), \quad (2.1)$$

con vectores propios

$$|n_1, n_2, \dots, n_\nu\rangle = \frac{1}{\sqrt{\prod_j n_j!}} \prod_i (\hat{a}_i^\dagger)^{n_i} |0\rangle, \quad (2.2)$$

que están asociados a la cadena canónica

$$U(\nu) \supset U(\nu - 1) \supset U(\nu - 2) \supset \dots U(1), \quad (2.3)$$

donde  $n_i$  es el valor propio del operador de número  $\hat{n}_i = \hat{a}_i^\dagger \hat{a}_i$ :

$$\hat{n}_i |n_1, n_2, \dots, n_\nu\rangle = n_i |n_1, n_2, \dots, n_\nu\rangle. \quad (2.4)$$

El grupo de simetría de este sistema es  $U(\nu)$  y sus generadores están dados por

$$\hat{C}_i^j = \hat{a}_i^\dagger \hat{a}_j, \quad (2.5)$$

con relaciones de conmutación

$$[\hat{C}_i^j, \hat{C}_p^q] = \hat{C}_i^q \delta_{p,j} - \hat{C}_p^j \delta_{q,i}, \quad (2.6)$$

que definen al grupo unitario.

#### 2.1.2. Modelo $U(\nu + 1)$

En el marco de trabajo del modelo  $U(\nu + 1)$  un bosón adicional  $\hat{s}^\dagger(\hat{s})$  es añadido al conjunto de operadores bosónicos  $\hat{a}_i^\dagger(\hat{a}_i)$  con la restricción de fijar el número total de bosones a  $N$ . En este caso, la nueva cadena canónica del sistema es

$$U(\nu + 1) \supset U(\nu) \supset U(\nu - 1) \supset \dots U(1), \quad (2.7)$$

con su correspondiente base

$$|[N]; n_s, n_1, n_2, \dots, n_\nu\rangle = \frac{1}{\sqrt{n_s! \prod_j n_j!}} (\hat{s}^\dagger)^{n_s} \prod_i (\hat{a}_i^\dagger)^{n_i} |0\rangle, \quad (2.8)$$

que está caracterizada por el número total de cuantos  $N$ , cuyo operador es

$$\hat{N} = \hat{n} + \hat{n}_s \quad (2.9)$$

con

$$\hat{n} = \sum_{i=1}^{\nu} \hat{a}_i^\dagger \hat{a}_i; \quad \hat{n}_s = \hat{s}^\dagger \hat{s}. \quad (2.10)$$

El número total de bosones fija la representación totalmente simétrica  $[N]$  del grupo  $U(\nu + 1)$ , y como resultado de la ecuación (2.9), los estados en (2.8) pueden también expresarse en la forma

$$|[N], n; \mathbf{n}\rangle = |[N], n; n_1, n_2, \dots, n_\nu\rangle \equiv |[N]; n_s, n_1, n_2, \dots, n_\nu\rangle, \quad (2.11)$$

donde  $n$  juega el papel del pseudo número cuántico que definimos como poliada para el conjunto de  $\nu$  osciladores equivalentes [42]. Esta poliada resulta ser un buen número cuántico en moléculas con comportamiento local [43, 44].

El enfoque tradicional para describir  $\nu$  osciladores interactuantes consiste en desarrollar el Hamiltoniano en términos de los operadores de Casimir asociados con las diferentes cadenas del grupo dinámico  $U(\nu + 1)$ . Un aspecto importante de proponer una cadena es que provee una base que se obtiene de la diagonalización simultánea de operadores de Casimir.

La adición de un bosón extra  $\hat{s}$  junto con la restricción de tener la representación  $[N]$  fija, hace que el grupo unitario  $U(\nu + 1)$  sea un grupo dinámico para el conjunto de  $\nu$  osciladores.

La acción de estos operadores sobre los estados (2.11) se obtiene de forma inmediata:

$$\hat{a}_i^\dagger \hat{s} |[N], n; \dots, n_i, \dots\rangle = \sqrt{(n_i + 1)(N - n)} |[N], n + 1; \dots, n_i + 1, \dots\rangle, \quad (2.12a)$$

$$\hat{a}_i \hat{s}^\dagger |[N], n; \dots, n_i, \dots\rangle = \sqrt{n_i(N - n + 1)} |[N], n - 1; \dots, n_i - 1, \dots\rangle. \quad (2.12b)$$

Dentro de este modelo, cualquier variable dinámica incluido el Hamiltoniano, puede ser expresada en términos de los generadores del grupo  $U(\nu + 1)$  y los operadores dentro de (2.12) juegan un rol importante (en especial cuando la variable dinámica es el Hamiltoniano) debido a su conexión con el momento y las coordenadas [45, 46, 47, 48].

Con el propósito de obtener el límite armónico, es conveniente introducir operadores normalizados [45]

$$\hat{b}_i^\dagger \equiv \frac{\hat{J}_{i,+}}{\sqrt{N}}; \quad \hat{b}_i \equiv \frac{\hat{J}_{i,-}}{\sqrt{N}} \quad (2.13)$$

que satisfacen las relaciones de conmutación

$$[\hat{b}_i, \hat{b}_j^\dagger] = \delta_{ij} - \frac{1}{N} [\hat{n} \delta_{ij} + \hat{a}_j^\dagger \hat{a}_i]; \quad [\hat{b}_i^\dagger, \hat{b}_j^\dagger] = [\hat{b}_i, \hat{b}_j] = 0. \quad (2.14)$$

En particular

$$[\hat{b}_i, \hat{b}_i^\dagger] = 1 - \frac{1}{N} [\hat{n} + \hat{n}_i] = -\frac{2}{N} \hat{J}_{i_0}. \quad (2.15)$$

La acción de estos nuevos operadores normalizados sobre los estados (2.11) resulta ser

$$\hat{b}_i^\dagger |[N], n; \dots, n_i, \dots\rangle = \sqrt{(n_i + 1) \left(1 - \frac{n}{N}\right)} |[N], n + 1; \dots, n_i + 1, \dots\rangle, \quad (2.16a)$$

$$\hat{b}_i |[N], n; \dots, n_i, \dots\rangle = \sqrt{n_i \left(1 - \frac{n+1}{N}\right)} |[N], n-1; \dots, n_i-1, \dots\rangle. \quad (2.16b)$$

Si se comparan estos elementos de matriz con aquellos dados por los operadores bosónicos  $\hat{a}_i^\dagger(\hat{a}_i)$  en la base (2.2) se concluye que ambos operadores bosónicos coinciden en el límite armónico ( $N \rightarrow \infty$ ). Por tanto, con base en este análisis, un Hamiltoniano puede ser traducido a una representación algebraica en el espacio  $U(\nu + 1)$ , llevando a cabo la transformación  $\hat{a}_i^\dagger(\hat{a}_i) \rightarrow \hat{b}_i^\dagger(\hat{b}_i)$ . [45, 46, 47, 48]

$$\hat{Q}_i = \sqrt{\frac{\hbar}{2\mu\omega}}(\hat{b}_i^\dagger + \hat{b}_i); \quad \hat{P}_i = i\sqrt{\frac{\hbar\mu\omega}{2}}(\hat{b}_i^\dagger - \hat{b}_i). \quad (2.17)$$

El siguiente paso de este trabajo, consiste en presentar una aproximación que proporcione un fundamento formal a los resultados que hemos descrito, así como obtener la conexión entre el espacio de configuración y el espacio algebraico equivalente a (2.17).

### 2.1.3. Conexión entre el espacio algebraico y el espacio de configuración

En esta sección se seguirá el enfoque presentado en el capítulo para establecer la correspondencia formal (2.17). Como primer paso estableceremos el mapeo entre los estados algebraicos (2.8) y los estados asociados al producto directo de osciladores en el espacio de configuración

$$\psi_{\mathbf{j}, \mathbf{n}}(\mathbf{q}) = \psi_{j; n_1, \dots, n_\nu}(q_1, \dots, q_\nu) = \prod_{i=1}^{\nu} \langle q_i | j; n_i \rangle, \quad (2.18)$$

donde  $j$  es un parámetro relacionado con la profundidad del pozo de potencial de manera que se tome en cuenta tanto osciladores armónico como anarmónicos (Morse y Pöschl-Teller). Estos osciladores no interactuantes tienen asociado el Hamiltoniano  $\hat{H}_{cs}(q, p)$ , cuyo sistema propio de ecuaciones es

$$\hat{H}_{cs}(j; \mathbf{q}, \mathbf{p})\psi_{j; \mathbf{n}}(\mathbf{q}) = E_{j; \mathbf{n}}\psi_{j; \mathbf{n}}(\mathbf{q}), \quad (2.19)$$

En notación de segunda cuantización

$$\hat{H}_{Fock}|j; \mathbf{n}\rangle = E_{j; \mathbf{n}}|j; \mathbf{n}\rangle; \quad \psi_{j; \mathbf{n}}(\mathbf{q}) = \langle \mathbf{q} | j; \mathbf{n} \rangle, \quad (2.20)$$

Buscamos un Hamiltoniano algebraico equivalente  $\hat{H}_{alg}^{su(\nu+1)}$  en el espacio  $su(\nu + 1)$  que esté definido en términos de sus correspondientes generadores, de tal manera que se satisfaga

$$\hat{H}_{alg}^{su(\nu+1)}|[N]; n; \mathbf{n}\rangle = E_{N; \mathbf{n}}|[N]; n; \mathbf{n}\rangle; \quad \psi_{j; \mathbf{n}}(\mathbf{q}) = \langle \mathbf{q} | j; \mathbf{n} \rangle. \quad (2.21)$$

En este caso los estados propios de (2.21) son los estados (2.20) y por tanto, el mapeo natural entre estados es el siguiente

$$|j; \mathbf{n}\rangle \cong |[N]; n; \mathbf{n}\rangle; \quad n = 0, 1, \dots, N. \quad (2.22)$$

De esta manera vemos que el mapeo no necesariamente es un isomorfismo. Para el caso de oscilador armónico, por ejemplo, el espacio es infinito, mientras que en el espacio algebraico  $N$  es finita. La conexión entre  $j$  y  $N$  es determinada de acuerdo con la base específica en el espacio de configuración.

Para realizar el mapeo de operadores, introducimos el operador de densidad, en el espacio de configuración y en el espacio algebraico con la normalización  $\sum_{\mathbf{n}} p_{N;\mathbf{n}} = 1$ .

$$\hat{\rho}(\mathbf{q}, \mathbf{q}') = \sum_{\mathbf{n}} p_{\mathbf{n}} \Psi_{j,\mathbf{n}}^*(\mathbf{q}) \Psi_{j,\mathbf{n}}(\mathbf{q}'); \quad \hat{\rho} = \sum_{\mathbf{n}} p_{N;\mathbf{n}} |[N]; n; \mathbf{n}\rangle \langle [N]; n; \mathbf{n}|. \quad (2.23)$$

El siguiente paso consiste en considerar la realización algebraica de un operador general en el espacio de configuración  $\hat{F}_{cs}$  [49].

$$\hat{F}_{alg} \approx \sum_{s,m} \alpha_s^{(m)}(\hat{F}_{cs}) \hat{Y}_s \hat{P}_m, \quad (2.24)$$

donde  $\hat{Y}_s$  es el  $s$ -ésimo generador del grupo  $U(\nu + 1)$  y los operadores de proyección  $\hat{P}_m$  pertenecen a la base algebraica  $\hat{P}_m = |[N]; n; \mathbf{n}\rangle \langle [N]; n; \mathbf{n}|$ , los coeficientes  $\alpha_s^{(m)}(\hat{F}_{cs})$  son determinados bajo el criterio de optimizar el desarrollo (2.24). Para alcanzar esta meta, introducimos el operador  $\hat{\Delta}$  que corresponde a la diferencia entre el operador exacto y el operador algebraico aproximado  $\hat{\Delta} \equiv \hat{F}_{cs} - \hat{F}_{alg}$ :

$$\hat{\Delta} = \hat{F}_{cs} - \sum_{s,m} \alpha_s^{(m)}(\hat{F}_{cs}) \hat{Y}_s \hat{P}_m. \quad (2.25)$$

El error de la aproximación,  $\epsilon$ , se estima calculando el promedio de  $\hat{\Delta} \hat{\Delta}^\dagger$ , introduciendo el operador de densidad que nos proporciona pesos específicos.

$$\epsilon = Tr(\hat{\rho} \hat{\Delta} \hat{\Delta}^\dagger). \quad (2.26)$$

Los coeficientes  $\alpha$  se obtienen minimizando el error, esto es, derivando el error respecto a las  $\alpha$ ,

$$\frac{\partial \epsilon}{\partial \alpha_s^{*(m)}} = 0; \quad \forall s, m, \quad (2.27)$$

lo que conduce al conjunto de ecuaciones

$$\sum_{s,m} M_{s,r}^{(m,m')} \alpha_s^{(m)}(\hat{F}_{cs}) = D_r^{(m')}. \quad (2.28)$$

En esta base, la matriz  $M_{s,r}^{(m,m')}$  y  $D_r^{(m')}$ , definidos por (2.28), toman la forma

$$D_r^{(m')} = \langle m | \hat{Y}_r^\dagger \hat{\rho} \hat{F}_{cs} | m \rangle, \quad (2.29)$$

$$M_{s,r}^{(m,m')} = \langle m | \hat{Y}_r^\dagger \hat{\rho} \hat{Y}_s | m \rangle, \quad (2.30)$$

donde el estado  $|m\rangle$  designa el estado general  $|[N]; n; \mathbf{n}\rangle$ . Dado el mapeo (2.22), para determinar la acción del operador  $\hat{F}_{cs}$  es necesario hacer la sustitución  $|[N]; n; \mathbf{n}\rangle \rightarrow |j; \mathbf{n}\rangle$ .

Si consideramos un mapeo a través de funciones de oscilador armónico, tomando en cuenta la base (2.2), la forma de proceder es la siguiente. Como primer paso se establece un isomorfismo con el producto directo de los  $\nu$  estados del oscilador en el espacio de configuración  $\mathcal{C}$  y el espacio algebraico  $\mathcal{A}$ . Para hacer más sencillo el tratamiento, en lugar de considerar  $\nu$  grande, la consideraremos en adelante como 2, es decir, considerando sólo-

mente dos osciladores armónicos, por lo que el modelo a considerar para hacer la manipulación necesaria es  $U(3)$ .

El álgebra  $su(3)$  tiene cuatro cadenas relevantes en física molecular

$$a) \quad su(3) \supset su(2) \supset su(1), \quad (2.31a)$$

$$b) \quad su(3) \supset su(2) \supset so(2), \quad (2.31b)$$

$$c) \quad su(3) \supset so(3) \supset so(2), \quad (2.31c)$$

$$d) \quad su(3) \supset s\bar{o}(3) \supset so(2). \quad (2.31d)$$

La cadena canónica a) se usa en la descripción de 2 modos vibracionales equivalentes como el caso aquí descrito. La segunda cadena b) se usa para describir modos de flexión en moléculas lineales como se verá en otro capítulo [50]. La cadena c) proporciona una simetría dinámica para describir un oscilador desplazado (moléculas no lineales). La cadena d) es equivalente a la cadena c) en principio pues se aplican a los mismos sistemas, sin embargo en este trabajo se demostrará que tanto la cadena a), como la c) y la d) tienen una interpretación física diferente para el caso de osciladores equivalentes [50, 51].

Comencemos considerando los dos osciladores de estiramiento de una molécula triatómica. Estos osciladores tienen asociados operadores bosónicos de creación y aniquilación que a partir de ahora designaremos como  $\{\hat{t}_1^\dagger, \hat{t}_1, \hat{t}_2^\dagger, \hat{t}_2\}$ , en lugar de la notación con  $\hat{a}^\dagger, \hat{a}$ . Los productos bilineales de estos operadores son los que forman el álgebra  $u(2)$ , como lo indica (2.5), con un total de 4 generadores. La adición del bosón  $\hat{s}^\dagger(\hat{s})$  nos lleva al álgebra  $u(3)$  que, al hacer los productos bilineales, tiene un total de 9 generadores;

$$G_{u(3)} = \{\hat{t}_1^\dagger \hat{t}_1, \hat{t}_1^\dagger \hat{t}_2, \hat{t}_2^\dagger \hat{t}_1, \hat{t}_2^\dagger \hat{t}_2, \hat{s}^\dagger \hat{t}_1, \hat{t}_1^\dagger \hat{s}, \hat{s}^\dagger \hat{t}_2, \hat{t}_2^\dagger \hat{s}, \hat{s}^\dagger \hat{s}\}. \quad (2.32)$$

Los primeros 4 productos bilineales de (2.32) se identifican con la subálgebra  $u(2)$  mientras que los 9 generadores en conjunto forman el álgebra dinámica para dos osciladores equivalentes, donde hay que notar que la proyección del momento angular no se preserva pero sí lo hace el número total de bosones, como se había planteado anteriormente.

Los elementos de matriz de estos productos bilineales en la base canónica (2.11) se obtienen de la aplicación sucesiva de los operadores involucrados sobre la base.

$$\langle [N], n; n_1 | \hat{s}^\dagger \hat{s} | [N], n; n_1 \rangle = (N - n), \quad (2.33a)$$

$$\langle [N], n; n_1 | \hat{t}_i^\dagger \hat{t}_i | [N], n; n_1 \rangle = n_i, \quad (2.33b)$$

$$\langle [N], n + 1; n_1 + 1 | \hat{t}_1^\dagger \hat{s} | [N], n; n_1 \rangle = \sqrt{(N - n)(n_1 + 1)}, \quad (2.33c)$$

$$\langle [N], n + 1; n_1 | \hat{t}_2^\dagger \hat{s} | [N], n; n_1 \rangle = \sqrt{(N - n)(n - n_1 + 1)}, \quad (2.33d)$$

$$\langle [N], n - 1; n_1 - 1 | \hat{s}^\dagger \hat{t}_1 | [N], n; n_1 \rangle = \sqrt{(N - n + 1)(n_1)}, \quad (2.33e)$$

$$\langle [N], n - 1; n_1 | \hat{s}^\dagger \hat{t}_2 | [N], n; n_1 \rangle = \sqrt{(N - n + 1)(n - n_1)}, \quad (2.33f)$$

$$\langle [N], n; n_1 + 1 | \hat{t}_1^\dagger \hat{t}_2 | [N], n; n_1 \rangle = \sqrt{(n - n_1)(n_1 + 1)}, \quad (2.33g)$$

$$\langle [N], n; n_1 - 1 | \hat{t}_2^\dagger \hat{t}_1 | [N], n; n_1 \rangle = \sqrt{(n - n_1 + 1)(n_1)}, \quad (2.33h)$$

donde se ha dejado implícito el número cuántico  $n_2$  en la base y en la acción de los operadores sobre ella, pues se satisface,  $n_2 = n - n_1$ . Para realizar la conexión entre el espacio algebraico y el de configuración mediante

un mapeo, consideremos a los dos osciladores armónicos como el producto directo entre ellos

$$\langle q_1 q_2 | n_1 n_2 \rangle = \langle q_1 | n_1 \rangle \langle q_2 | n_2 \rangle \quad (2.34)$$

definidos en un subespacio que se caracteriza por el número de cuantos  $P$ :

$$n = n_1 + n_2; \quad n = 0, 1, \dots, P, \quad (2.35)$$

y la restricción del espacio con la definición de  $n$  es

$$\langle q_1 q_2 | n_1 n_2 \rangle = \langle q_1 q_2 | n; n_1 \rangle; \quad n = 0, 1, \dots, P. \quad (2.36)$$

Así pues, se propone el siguiente mapeo entre esta base y la algebraica

$$\langle q_1 q_2 | n; n_1 \rangle \approx |[N], n; n_1 \rangle; \quad N = P_{max}. \quad (2.37)$$

La representación del operador de densidad para este sistema es entonces

$$\hat{\rho} = \sum_{n_1, n-n_1}^{n=P} p_{n, n_1} |[N]; n; n_1 \rangle \langle [N]; n; n_1|; \quad n = n_1 + n_2; \quad n = 0, 1, \dots, P, \quad (2.38)$$

o de forma simplificada

$$\hat{\rho} = \sum_{n_1, n-n_1} p_{n, n_1} |n; n_1 \rangle \langle n; n_1|. \quad (2.39)$$

Con las consideraciones hechas, debemos preguntarnos por la mejor representación algebraica posible de un operador en el espacio de configuración  $\mathcal{C}$ ; de forma particular nuestro interés recae en los operadores de coordenadas y momentos para cada oscilador.

Como primer paso para esta descripción algebraica, proponemos un desarrollo hasta términos lineales para un operador en el espacio de configuración  $\hat{F}_{cs}$ , como en (2.24):

$$\hat{F}_{alg} \approx \sum_s \sum_m \alpha_s^{(m)} (\hat{F}_{cs}) \hat{Y}_s \hat{P}_m, \quad (2.40)$$

con las siguientes identificaciones

$$\hat{Y}_1 = \hat{t}_1^\dagger \hat{s}; \quad \hat{Y}_2 = \hat{s}^\dagger \hat{t}_1; \quad \hat{Y}_3 = \hat{t}_2^\dagger \hat{s}; \quad \hat{Y}_4 = \hat{s}^\dagger \hat{t}_2. \quad (2.41)$$

Siguiendo el procedimiento descrito de (2.11) a (2.12), considerando los elementos de matriz (2.33) y la acción de los momentos y las coordenadas de cada oscilador en el espacio de configuración en la base de oscilador armónico se propone para las coordenadas del oscilador 1 y 2, la realización lineal siguiente en términos de los generadores 2.41:

$$\hat{Q}_i \approx \alpha_1 \hat{t}_1^\dagger \hat{s} + \alpha_2 \hat{t}_1 \hat{s}^\dagger + \alpha_3 \hat{t}_2^\dagger \hat{s} + \alpha_4 \hat{t}_2 \hat{s}^\dagger; \quad i = 1, 2, \quad (2.42)$$

dando como resultado de esta realización

$$\hat{Q}_1 = \sqrt{\frac{\hbar}{2\mu\omega}} \left( \frac{\hat{t}_1^\dagger \hat{s}}{\sqrt{N}} + \frac{\hat{t}_1 \hat{s}^\dagger}{\sqrt{N}} \right) \quad \hat{Q}_2 = \sqrt{\frac{\hbar}{2\mu\omega}} \left( \frac{\hat{t}_2^\dagger \hat{s}}{\sqrt{N}} + \frac{\hat{t}_2 \hat{s}^\dagger}{\sqrt{N}} \right). \quad (2.43)$$

Pasemos ahora a la representación algebraica para los operadores de momento. Para los osciladores 1 y 2 proponemos el desarrollo lineal

$$\hat{\mathcal{P}}_i \approx \beta_1 \hat{t}_1^\dagger \hat{s} + \beta_2 \hat{t}_1 \hat{s}^\dagger + \beta_3 \hat{t}_2^\dagger \hat{s} + \beta_4 \hat{t}_2 \hat{s}^\dagger; \quad i = 1, 2. \quad (2.44)$$

Y siguiendo el procedimiento descrito en (2.11) a (2.12) [49], se llega a

$$\hat{\mathcal{P}}_1 = \sqrt{\frac{\hbar\mu\omega}{2}} \left( \frac{\hat{t}_1^\dagger \hat{s}}{\sqrt{N}} - \frac{\hat{t}_1 \hat{s}^\dagger}{\sqrt{N}} \right) \quad \hat{\mathcal{P}}_2 = \sqrt{\frac{\hbar\mu\omega}{2}} \left( \frac{\hat{t}_2^\dagger \hat{s}}{\sqrt{N}} - \frac{\hat{t}_2 \hat{s}^\dagger}{\sqrt{N}} \right). \quad (2.45)$$

Pudiendo generalizar con base en los resultados obtenidos en (2.43) y (2.45) la conexión del espacio de configuración de 2 osciladores a uno de  $\nu$  osciladores, es decir, bajo el modelo algebraico  $u(\nu + 1)$ . De esta forma definimos los siguientes operadores:

$$\hat{b}_i^\dagger = \frac{\hat{t}_i^\dagger \hat{s}}{\sqrt{N}}; \quad \hat{b}_i = \frac{\hat{t}_i \hat{s}^\dagger}{\sqrt{N}}, \quad (2.46)$$

que al usarse en la definición de coordenada  $\mathcal{Q}_i$  y momento  $\mathcal{P}_i$

$$\hat{\mathcal{Q}}_i = \sqrt{\frac{\hbar}{2\mu\omega}} (\hat{b}_i^\dagger + \hat{b}_i), \quad \hat{\mathcal{P}}_i = i\sqrt{\frac{\hbar\mu\omega}{2}} (\hat{b}_i^\dagger - \hat{b}_i). \quad (2.47)$$

Como una consecuencia de la aproximación lineal (2.47), los desarrollos no cumplen las relaciones de conmutación para el momento y coordenada  $[\hat{q}, \hat{p}] = i\hbar$ . En el espacio algebraico se tiene

$$[\hat{\mathcal{Q}}_i, \hat{\mathcal{P}}_j] = i\hbar\delta_{ij} \left( 1 - \frac{n}{N} \right) - \frac{i\hbar}{2N} (\hat{t}_i^\dagger \hat{t}_j + \hat{t}_j^\dagger \hat{t}_i). \quad (2.48)$$

Las relaciones de conmutación canónicas sólo se recuperan en el límite armónico,  $N \rightarrow \infty$ , cuando nos suscribimos a un subespacio fijo  $n$ . Otra característica de este enfoque es que las coordenadas y momentos de osciladores distintos no conmutan.

$$[\hat{\mathcal{Q}}_i, \hat{\mathcal{Q}}_j] = \frac{\hbar}{2\mu\omega} \left\{ \frac{\hat{t}_i^\dagger \hat{t}_j - \hat{t}_j^\dagger \hat{t}_i}{N} \right\}, \quad [\hat{\mathcal{P}}_i, \hat{\mathcal{P}}_j] = \frac{\hbar\mu\omega}{2} \left\{ \frac{\hat{t}_i^\dagger \hat{t}_j - \hat{t}_j^\dagger \hat{t}_i}{N} \right\}. \quad (2.49)$$

Este resultado tiene consecuencias a nivel práctico. Se debe asumir la no conmutatividad o se debe aplicar algún procedimiento de proyección de simetría cuando se traslada un Hamiltoniano a su representación algebraica. Estos resultados justifican de manera formal de [45, 46, 47, 48], donde se calcula la fuerza de transiciones dipolares.

#### *Interpretación física de las cadenas de grupos involucradas*

La cadena de subgrupo usada en todo este análisis corresponde con (2.31a); esta cadena tiene una interpretación física. Para convencernos de esto, el primer paso es escribir el Hamiltoniano de dos osciladores no interactuantes.

$$\hat{H}_{cs} = \frac{1}{2\mu} \sum_{i=1}^2 \hat{p}_i^2 + \frac{1}{2}k \sum_{i=1}^2 \hat{q}_i^2, \quad (2.50)$$

el cual tiene su correspondiente Hamiltoniano algebraico. Al sustituir la definición (2.47) de momentos y coor-



denadas se obtiene

$$\hat{H}_{alg} = \frac{\hbar\omega}{2} \sum_{i=1}^2 \left( \hat{b}_i^\dagger \hat{b}_i + \hat{b}_i \hat{b}_i^\dagger \right), \quad (2.51)$$

con valores propios

$$E(N, n_1, n_2) = \langle [N]; n, n_1 | \hat{H}_{alg} | [N]; n, n_1 \rangle = \hbar\omega \sum_{i=1}^2 \left\{ \left[ \left( 1 + \frac{1}{2N} \right) n_i + \frac{1}{2} \right] - \frac{n}{2N} - \frac{nn_i}{N} \right\}, \quad (2.52)$$

de donde es posible identificar una corrección anarmónica en el término  $nn_i$  que involucra la poliada  $n$  y otro factor que depende de forma lineal con la poliada,  $\frac{n}{2N}$ . En el límite  $N \rightarrow \infty$ , con  $n$  finita se recuperan las expresiones del caso armónico.

*Cadenas asociadas a dos osciladores equivalentes bajo el modelo  $U(3)$*

Dado que (2.52) es diagonal en la base de  $U(2)$ , se dice entonces que la cadena (2.31a) está asociada con la representación energética. Las demás cadenas, correspondientes a otras simetrías dinámicas, (2.31c) y (2.31d) están asociadas a las representaciones de coordenadas y momento, respectivamente, como veremos a continuación. Primero, se identifican los conjuntos

$$G_{so(3)} = \left\{ \hat{J}_x = \left( \hat{a}_1^\dagger \hat{s} + \hat{s}^\dagger \hat{a}_1 \right), \hat{J}_y = \left( \hat{a}_2^\dagger \hat{s} + \hat{s}^\dagger \hat{a}_2 \right), \hat{J}_z = i \left( \hat{a}_2^\dagger \hat{a}_1 - \hat{a}_1^\dagger \hat{a}_2 \right) \right\}, \quad (2.53)$$

$$G_{s\bar{o}(3)} = \left\{ \hat{J}'_x = i \left( \hat{a}_1^\dagger \hat{s} - \hat{s}^\dagger \hat{a}_1 \right), \hat{J}'_y = i \left( \hat{a}_2^\dagger \hat{s} - \hat{s}^\dagger \hat{a}_2 \right), \hat{J}'_z = i \left( \hat{a}_2^\dagger \hat{a}_1 - \hat{a}_1^\dagger \hat{a}_2 \right) \right\}, \quad (2.54)$$

como las relaciones de conmutación de los sendos grupos  $SO(3)$  y  $S\bar{O}(3)$ . Los correspondientes operadores invariantes son:

$$\hat{W}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2; \quad \hat{W}'^2 = \hat{J}'_x^2 + \hat{J}'_y^2 + \hat{J}'_z^2; \quad \hat{J}_z^2 = \hat{J}'_z^2, \quad (2.55)$$

e introduciendo las realizaciones de momentos y coordenadas (2.47) se tiene

$$\sum_{i=1}^2 \hat{Q}_i^2 = \frac{\hbar}{2\omega\mu N} \left( \hat{W}^2 - \hat{J}_z^2 \right), \quad \sum_{i=1}^2 \hat{P}_i^2 = \frac{\hbar}{2\omega\mu N} \left( \hat{W}'^2 - \hat{J}'_z^2 \right), \quad (2.56)$$

de donde concluimos que las cadenas  $c)U(3) \supset SO(3) \supset SO(2)$  y  $c)U(3) \supset S\bar{O}(3) \supset SO(2)$  están asociadas con las representación de la suma de los cuadrados de las coordenadas y los momentos, respectivamente. En la tabla 2.1 se resume el significado de las diferentes cadenas.

Tabla 2.1: Identificación de las simetrías dinámicas de acuerdo a las representaciones energética, de coordenadas y de momentos.

Cadena	Base	Representación
$U(3) \supset U(2) \supset SO(2)$	$ [N]; nl\rangle$	Energía
$U(3) \supset SO(3) \supset SO(2)$	$ [N]; \omega l\rangle$	Coordenadas
$U(3) \supset S\bar{O}(3) \supset SO(2)$	$ [N]; \bar{\omega} l\rangle$	Momentos

## MODELO $U(3)$

3

### 3.1. El enfoque algebraico $U(3)$ para un oscilador 2D

#### 3.1.1. Modelo algebraico $U(3)$

Consideremos los modos de flexión de una molécula lineal triatómica del tipo  $XY_2$  descrita en términos de coordenadas locales. Lo primero que se necesita hacer es escribir el Hamiltoniano en términos de las coordenadas de simetría internas y trasladarlo a segunda cuantización como función de operadores locales de creación y aniquilación por medio de la transformación canónica entre los bosones simetrizados y los locales. Este procedimiento es necesario para establecer la conexión con el modelo  $U_1(2) \times U(3) \times U_2(2)$ .

En términos de coordenadas internas,  $q_k$ , el Hamiltoniano en el espacio de configuración que describe las excitaciones vibracionales de una molécula tiene la forma

$$H = \frac{1}{2} \bar{\mathbf{p}} \mathbf{G}(\mathbf{q}) \mathbf{p} + V(\mathbf{q}), \quad (3.1)$$

donde  $\mathbf{q}$  y  $\mathbf{p}$  son vectores columna correspondientes al desplazamiento interno de coordenadas y su momento conjugado, respectivamente; los términos del potencial dependientes de la masa se omiten. La matriz de Wilson,  $\mathbf{G}(\mathbf{q})$ , conecta la expresión de la energía cinética del sistema en términos de las coordenadas internas y cartesianas; en el caso de las moléculas triatómicas se necesitan 2 conjuntos de coordenadas, el primero de ellos para las vibraciones de estiramiento y el segundo conjunto para las flexiones con las siguientes definiciones [52].

$$q_a = r_e \mathbf{e}_y \cdot \frac{\mathbf{r}_1 \times \mathbf{r}_2}{r_1 r_2}; \quad q_b = -r_e \mathbf{e}_x \cdot \frac{\mathbf{r}_1 \times \mathbf{r}_2}{r_1 r_2}, \quad (3.2)$$

donde  $\mathbf{r}_1$  y  $\mathbf{r}_2$  son vectores que van desde el átomo central  $X$  a cada uno de los átomos  $Y$ . Los vectores unitarios  $\mathbf{e}_x$  y  $\mathbf{e}_y$  están en las direcciones de los ejes  $X$  y  $Y$  del sistema de laboratorio con origen en el centro de masa molecular. Las coordenadas  $q_a$  y  $q_b$  están asociadas entonces a las coordenadas cartesianas y en consecuencia se tienen sus correspondientes momentos conjugados  $p_a$  y  $p_b$ .

Como en las moléculas lineales la proyección de momento angular  $l$  se preserva, es conveniente introducir las coordenadas circulares

$$Q_+ = -\frac{1}{\sqrt{2}}(q_a + iq_b); \quad Q_- = \frac{1}{\sqrt{2}}(q_a - iq_b); \quad (3.3)$$

con sus momentos lineales conjugados definidos a través de  $P_\alpha = \frac{\partial T}{\partial \dot{Q}_\alpha}$ :

$$P_+ = -\frac{1}{\sqrt{2}}(p_a - ip_b); \quad P_- = \frac{1}{\sqrt{2}}(p_a + ip_b). \quad (3.4)$$

El Hamiltoniano en el espacio de configuración hasta orden dos puede expresarse en términos de las coordenadas cartesianas desarrollando la matriz  $\mathbf{G}$  y  $V(\mathbf{q})$  hasta orden cuadrático, entonces éste toma la forma

$$\hat{H}_{cs} = \frac{1}{2} g_{aa}^\circ (p_a^2 + p_b^2) + \frac{1}{2} f_{aa}^\circ (q_a^2 + q_b^2), \quad (3.5)$$

donde  $g_{aa} = \frac{1}{\mu}$  es la constante de estructura del oscilador, siendo  $\mu$  la masa reducida y  $f_{aa}$  la constante de fuerza del oscilador. Si tomamos en cuenta (3.3) y (3.4) en el Hamiltoniano del espacio de configuración en coordenadas cartesianas (3.5), obtenemos el Hamiltoniano en términos de coordenadas circulares.

$$\hat{H}_{cs} = -g_{+-}^\circ P_+ P_- - f_{+-} Q_+ Q_-, \text{ donde } g_{+-}^\circ = g_{aa}^\circ \text{ y } f_{+-} = f_{aa}. \quad (3.6)$$

La estrategia para resolver la ecuación de Schrödinger consiste en transformar el Hamiltoniano (3.6) a la representación algebraica, por lo que introducimos las definiciones de los siguientes operadores bosónicos

$$\hat{\tau}_{\pm}^{\dagger} = \frac{1}{\sqrt{2}} \left[ \sqrt{\frac{\omega\mu}{\hbar}} Q_{\pm} + i \frac{P_{\mp}}{\sqrt{\hbar\omega\mu}} \right], \quad (3.7)$$

con sus respectivos operadores adjuntos. En este punto se ha introducido la frecuencia  $\omega = \sqrt{f_{aa}g_{aa}^2}$  de los dos osciladores degenerados. Esta correspondencia de operadores bosónicos en coordenadas circulares proviene de la transformación canónica a operadores bosónicos  $+/-$  que vienen de los correspondientes operadores de ascenso y descenso en coordenadas cartesianas:

$$\hat{\tau}_{+}^{\dagger} = -\frac{1}{\sqrt{2}}(a_b^{\dagger} + ia_a^{\dagger}); \quad \hat{\tau}_{-}^{\dagger} = \frac{1}{\sqrt{2}}(a_b^{\dagger} - ia_a^{\dagger}). \quad (3.8)$$

En este nuevo espacio, el Hamiltoniano (3.6) adquiere la forma

$$\hat{H}_{Fock} = \frac{\hbar\omega}{2} (\hat{\tau}_{+}^{\dagger}\hat{\tau}_{+} + \hat{\tau}_{+}\hat{\tau}_{+}^{\dagger} + \hat{\tau}_{-}^{\dagger}\hat{\tau}_{-} + \hat{\tau}_{-}\hat{\tau}_{-}^{\dagger}), \quad (3.9)$$

que es diagonal en la base

$$|n^l\rangle = N_{nl} (\hat{\tau}_{+}^{\dagger})^{\binom{n+l}{2}} (\hat{\tau}_{+})^{\binom{n-l}{2}} |0\rangle, \quad (3.10)$$

que es la base ocupada para describir las vibraciones (flexiones) del átomo central. Las definiciones que se usaron para construir esta base son

$$\hat{n} = \hat{\tau}_{+}^{\dagger}\hat{\tau}_{+} + \hat{\tau}_{-}^{\dagger}\hat{\tau}_{-}; \quad \hat{l} = \hat{\tau}_{+}^{\dagger}\hat{\tau}_{+} - \hat{\tau}_{-}^{\dagger}\hat{\tau}_{-}, \quad (3.11)$$

cuya constante de normalización es

$$N_{nl} = \frac{1}{\sqrt{\binom{n+l}{2}! \binom{n-l}{2}!}}. \quad (3.12)$$

La acción de los operadores bosónicos de flexión se obtiene por su acción sobre la base (3.10), dando lugar a

$$\hat{\tau}_{\pm}^{\dagger}|n^l\rangle = \sqrt{\frac{n \pm l}{2} + 1} |(n+1)^{l \pm 1}\rangle, \quad \hat{\tau}_{\pm}|n^l\rangle = \sqrt{\frac{n \pm l}{2}} |(n-1)^{l \mp 1}\rangle. \quad (3.13)$$

Los operadores

$$\left\{ \hat{J}_{+} = \hat{\tau}_{+}^{\dagger}\hat{\tau}_{-}, \quad \hat{J}_{-} = \hat{\tau}_{-}^{\dagger}\hat{\tau}_{+}, \quad \hat{J}_z = \frac{1}{2}\hat{l} \right\}, \quad (3.14)$$

satisfacen las relaciones de conmutación del momento angular, y en consecuencia son generadores del grupo  $SU(2)$ . El conjunto en (3.14) preserva el número total de cuantos, lo que implica a su vez que  $U(2)$  es el grupo de simetría de un oscilador armónico en 2D.

La expresión (3.9) y la definición de momentos y coordenadas provenientes de (3.7),

$$Q_{\pm} = \frac{1}{\sqrt{2}} \sqrt{\frac{\hbar}{\omega\mu}} (\hat{\tau}_{\pm}^{\dagger} - \hat{\tau}_{\mp}); \quad P_{\pm} = -\frac{i}{\sqrt{2}} \sqrt{\hbar\omega\mu} (\hat{\tau}_{\mp}^{\dagger} - \hat{\tau}_{\pm}), \quad (3.15)$$

son la representación en el espacio de Fock del Hamiltoniano y de coordenadas y momentos, respectivamente. Los elementos de matriz de esta representación reproducen de forma exacta los elementos de matriz del espacio de configuración.

El modelo  $SU(3)$  consiste en añadir un bosón escalar  $\hat{\sigma}^\dagger(\sigma)$  al espacio del oscilador 2D considerando todos los productos bilineales  $\{\xi_i^\dagger \xi_j; i, j = 1, 2, 3\}$  con  $\xi_1 = \hat{\sigma}$ , y  $\xi_2, \xi_3 = \hat{\tau}_+, \hat{\tau}_-$ . Esto nos da un total de 9 productos, que son los generadores del grupo  $U(3)$  [50]:

$$\hat{n}_\sigma = \hat{\sigma}^\dagger \hat{\sigma}, \quad (3.16a)$$

$$\hat{Q}_+ = \sqrt{2} \hat{\tau}_+^\dagger \hat{\tau}_-, \quad (3.16b)$$

$$\hat{Q}_- = \sqrt{2} \hat{\tau}_-^\dagger \hat{\tau}_+, \quad (3.16c)$$

$$\hat{D}_+ = \sqrt{2} (\hat{\tau}_+^\dagger \hat{\sigma} - \hat{\sigma}^\dagger \hat{\tau}_-), \quad (3.16d)$$

$$\hat{D}_- = \sqrt{2} (-\hat{\tau}_-^\dagger \hat{\sigma} + \hat{\sigma}^\dagger \hat{\tau}_+), \quad (3.16e)$$

$$\hat{R}_+ = \sqrt{2} (\hat{\tau}_+^\dagger \hat{\sigma} + \hat{\sigma}^\dagger \hat{\tau}_-), \quad (3.16f)$$

$$\hat{R}_- = \sqrt{2} (\hat{\tau}_-^\dagger \hat{\sigma} + \hat{\sigma}^\dagger \hat{\tau}_+), \quad (3.16g)$$

además de las expresiones dadas en (3.11). Este modelo introduce la restricción de mantener fijo el número total de bosones,

$$\hat{N} = \hat{n} + \hat{n}_\sigma, \quad (3.17)$$

por lo que  $U(3)$  es el grupo dinámico de un oscilador 2D al conectar todos los estados del sistema. Adicionalmente, el álgebra  $U(3)$  hace posible la existencia de 3 cadenas, como se mencionaba en la subsección 2.1.3, ecuación (2.31):

$$U(3) \supset U(2) \supset O(2), \quad (3.18a)$$

$$U(3) \supset O(3) \supset O(2), \quad (3.18b)$$

$$U(3) \supset \bar{O}(3) \supset O(2), \quad (3.18c)$$

cada una de las cuales proporciona una simetría dinámica distinta. La cadena (3.18a) contiene a la cadena física  $SU(2) \supset SO(2)$ . La cadena (3.18b) contiene el nuevo grupo  $O(3)$ , cuyos generadores son  $G_{O(3)} = \{\hat{D}_+, \hat{D}_-, \hat{l}\}$ , y la cadena de (3.18c) contiene al grupo  $\bar{O}(3)$ , con generadores  $G_{\bar{O}(3)} = \{\hat{R}_+, \hat{R}_-, \hat{l}\}$ .

La cadena que proporciona la base más simple para llevar a cabo cálculos es la  $U(3) \supset U(2) \supset O(2)$  ya que contiene a la cadena  $SU(2) \supset SO(2)$  del grupo de simetría, que involucra el número total de cuantos físicos. La forma explícita de los estados asociados a esta cadena se construye en términos de 3 osciladores armónicos de forma análoga a (3.10).

$$|[N]; n^l\rangle = N_{N_{nl}} (\sigma^\dagger)^{N-n} (\hat{\tau}_+^\dagger)^{\binom{n+l}{2}} (\hat{\tau}_+)^{\binom{n-l}{2}} |0\rangle, \quad (3.19)$$

con reglas de ramificación  $n = N, N-1, N-2, \dots, 0$  y  $l = \pm n, \pm(n-2), \dots, \pm 1$  o 0.

En el marco de este espacio algebraico, el Hamiltoniano, como cualquier variable dinámica puede desarrollarse

en potencias y productos de los generadores (3.16), de forma similar a como se realizó en el capítulo pasado. La tarea consiste en conectar los Hamiltonianos en el espacio de configuración dados por (3.5) y (3.6) con el espacio algebraico; esto se consigue obteniendo la representación algebraica de los momentos y las coordenadas en el espacio  $U(3)$ , que representa la clave para escribir cualquier operador dinámico en términos del espacio algebraico, permitiendo la obtención de los parámetros  $\alpha$  y  $\beta$  en términos de las constantes de fuerza y estructura,  $(f_{aa}, g_{aa})$ .

### 3.1.2. Conexión entre el espacio algebraico y el espacio de configuración

La correspondencia entre el espacio de configuración y el algebraico se consigue mediante el enfoque que presentamos en el capítulo pasado [49]. Primero se realiza el mapeo entre la simetría dinámica (3.18a) y un oscilador armónico en 2D. Siguiendo el método de las expresiones (2.11) a (2.12), con el uso de las definiciones

$$\hat{Y}_1 = \hat{\tau}_+^\dagger \hat{\sigma}; \quad \hat{Y}_2 = \hat{\sigma}^\dagger \hat{\tau}_-; \quad \hat{Y}_3 = \hat{\tau}_-^\dagger \hat{\sigma}; \quad \hat{Y}_4 = \hat{\sigma}^\dagger \hat{\tau}_+; \quad (3.20)$$

los elementos de matriz

$$\langle [N]; n+1, l+1 | \tau_+^\dagger \sigma | [N]; n, l \rangle = \sqrt{\frac{(N-n)(n+l+2)}{2}}, \quad (3.21a)$$

$$\langle [N]; n-1, l-1 | \sigma^\dagger \tau_+ | [N]; n, l \rangle = \sqrt{\frac{(N-n+1)(n+l)}{2}}, \quad (3.21b)$$

$$\langle [N]; n+1, l-1 | \tau_-^\dagger \sigma | [N]; n, l \rangle = \sqrt{\frac{(N-n)(n-l+2)}{2}}, \quad (3.21c)$$

$$\langle [N]; n-1, l+1 | \sigma^\dagger \tau_- | [N]; n, l \rangle = \sqrt{\frac{(N-n+1)(n-l)}{2}}, \quad (3.21d)$$

y los asociados al oscilador armónico 2D, se llega a realizaciones de los momentos y coordenadas:

$$\hat{Q}_\pm = \frac{1}{2} \sqrt{\frac{\hbar}{\mu\omega}} \frac{1}{\sqrt{N}} [\hat{D}_\pm], \quad \hat{P}_\pm = -\frac{i}{2} \sqrt{\hbar\mu\omega} \frac{1}{\sqrt{N}} [\hat{R}_\mp]. \quad (3.22)$$

Puesto que ya tenemos los operadores de momento y coordenada en el espacio algebraico, ahora podemos construir cualquier operador en el espacio algebraico que contenga a los momentos y coordenadas aquí descritos.

Si regresamos a las cadenas (3.18) asociadas al grupo dinámico  $U(3)$  y caracterizadas, cada una, por el subgrupo central, notamos que la cadena de (3.18a) está caracterizada por el subgrupo  $U(2)$ ; este grupo tiene un operador de Casimir asociado  $\hat{C}_{SU(2)} = \hat{n}$ . En el Hamiltoniano algebraico que se obtiene, salta a la vista la presencia del operador de número  $\hat{n}$ , por tanto podemos decir que esta cadena provee una base en la representación energética. El operador de Casimir asociado al subgrupo  $O(3)$  en (3.18b) está dado por  $\hat{C}_{SO(3)} = \hat{W}^2 = (1/2)(\hat{D}_+ \hat{D}_- + \hat{D}_- \hat{D}_+) + \hat{l}^2$ , que puede escribirse en términos de la coordenada:

$$\hat{W}^2 = -N \frac{4\mu\omega}{\hbar} Q^2 + \hat{l}^2, \quad (3.23)$$

y por tanto esta cadena nos da una base en la representación de coordenadas. Para el operador de Casimir asociado al subgrupo  $\bar{O}(3)$  en la tercera cadena en (3.18c) se tiene  $\hat{C}_{\bar{S}\bar{O}(3)} = \hat{W}^2 = (1/2)(\hat{R}_+ \hat{R}_- + \hat{R}_- \hat{R}_+) + \hat{l}^2$  de donde se deduce que

$$\hat{W}^2 = -N \frac{4}{\hbar\mu\omega} P^2 + \hat{l}^2, \quad (3.24)$$

dándonos una base en la representación de momentos. En la tabla 3.1 se resume el significado de las diferentes cadenas.

Tabla 3.1: Identificación de las simetrías dinámicas de acuerdo a las representaciones energética, de coordenadas y de momentos.

Cadena	Base	Representación
$U(3) \supset U(2) \supset SO(2)$	$  [N]; nl\rangle$	Energía
$U(3) \supset SO(3) \supset SO(2)$	$  [N]; \omega l\rangle$	Coordenadas
$U(3) \supset S\bar{O}(3) \supset SO(2)$	$  [N]; \bar{\omega} l\rangle$	Momentos

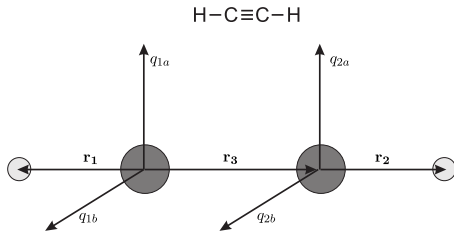
Hasta este momento nos hemos limitado a describir el modelo  $U(3)$  para un sólo oscilador en 2D, centrándonos en las representaciones de coordenadas, momentos y cómo llegar a ellas tanto en el espacio de configuración como en el algebraico así como en las consecuencias inmediatas de asociar este modelo con el espacio físico al referirnos a las cadenas. En la siguiente sección nos centraremos en cómo extender este modelo a más de un oscilador.

### 3.2. Enfoque algebraico $U(3)$ . Dos osciladores en 2D.

El modelo  $U(3)$  planteado es local; esto significa que puede aplicarse de manera directa sólo en moléculas que tengan un comportamiento local si se quiere tener una buena estimación de las constantes de fuerza. Para moléculas con comportamiento normal, se debe aplicar una transformación canónica al aplicar el modelo.

#### 3.2.1. Esquema local

Empecemos introduciendo las coordenadas para describir dos osciladores en 2D circunscribiéndonos a los grados de flexión de una molécula en particular: acetileno. De acuerdo con la notación introducida en la figura 3.1, tenemos las coordenadas



$$q_{1a} = \sqrt{r_{e1}r_{e3}} \mathbf{e}_y \cdot \frac{\mathbf{r}_1 \times \mathbf{r}_3}{r_1 r_3}; \quad q_{1b} = -\sqrt{r_{e1}r_{e3}} \mathbf{e}_x \cdot \frac{\mathbf{r}_1 \times \mathbf{r}_3}{r_1 r_3} \quad (3.25a)$$

$$q_{2a} = \sqrt{r_{e2}r_{e3}} \mathbf{e}_y \cdot \frac{(-\mathbf{r}_3) \times \mathbf{r}_2}{r_2 r_3}; \quad q_{2b} = -\sqrt{r_{e2}r_{e3}} \mathbf{e}_x \cdot \frac{(-\mathbf{r}_3) \times \mathbf{r}_2}{r_2 r_3}. \quad (3.25b)$$

Figura 3.1: Coordenadas para describir los modos de flexión del acetileno

Dadas estas coordenadas y sus momentos asociados, el Hamiltoniano para dos osciladores equivalentes (asociados a los carbonos del acetileno) toma la forma

$$\hat{H}_{cs} = \frac{1}{2} g_{aa}^o \sum_{i=1}^2 (p_{ia}^2 + p_{ib}^2) + \frac{1}{2} f_{aa} \sum_{i=1}^2 (q_{ia}^2 + q_{ib}^2) + g_{1a2a}^o (p_{1a} p_{2a} + p_{1b} p_{2b}) + \frac{1}{2} f_{1a2a} (q_{1a} q_{2a} + q_{1b} q_{2b}), \quad (3.26)$$

donde la primera parte contiene los términos de los osciladores individuales mientras que la segunda incluye interacciones. Incluyendo ahora para cada oscilador ( $i = 1, 2$ ) las coordenadas circulares definidas en (3.3) y (3.4), tenemos

$$Q_{i+} = -\frac{1}{\sqrt{2}}(q_{ia} + iq_{ib}); \quad Q_{i-} = \frac{1}{\sqrt{2}}(q_{ia} - iq_{ib}), \quad P_{i+} = -\frac{1}{\sqrt{2}}(p_{ia} - ip_{ib}); \quad P_{i-} = \frac{1}{\sqrt{2}}(q_{ia} + ip_{ib}), \quad (3.27)$$

y sustituyendo (3.27) en (3.26) a la vez de simplificar términos obtenemos

$$\hat{H}_{cs} = -[g_{aa}^o \sum_{i=1}^2 (P_{i+} P_{i-}) + f_{aa} \sum_{i=1}^2 (Q_{i+} Q_{i-})] - g_{1a2a}^o (P_{1+} P_{2-} + P_{1-} P_{2+}) - f_{1a2a} (Q_{1+} Q_{2-} + Q_{1-} Q_{2+}). \quad (3.28)$$

Este Hamiltoniano en el espacio de configuración, tiene su representación en el espacio de Fock, la cuál se obtiene al introducir los operadores bosónicos como en (3.15)

$$Q_{i\pm} = \sqrt{\frac{\hbar}{2\omega\mu}} (\tau_{i\pm}^\dagger - \tau_{i\mp}), \quad P_{i\pm} = -\frac{i}{\sqrt{2}} \sqrt{\hbar\omega\mu} (\tau_{i\mp}^\dagger + \tau_{i\pm}), \quad (3.29)$$

dando como resultado

$$\hat{H}_{Fock} = \frac{\hbar\omega}{2} \sum_{i=1}^2 (\tau_{i+}^\dagger \tau_{i+} + \tau_{i+} \tau_{i+}^\dagger + \tau_{i-}^\dagger \tau_{i-} + \tau_{i-} \tau_{i-}^\dagger) + \frac{\hbar\omega}{2} \lambda (\tau_{1+}^\dagger \tau_{2+} + \tau_{1-}^\dagger \tau_{2-} + H.c.) + \frac{\hbar\omega}{2} \lambda' (\tau_{1-}^\dagger \tau_{2+}^\dagger + \tau_{1+}^\dagger \tau_{2-}^\dagger + H.c.), \quad (3.30)$$

con

$$\omega = \sqrt{f_{aa} g_{aa}^o}, \quad \lambda = x_f + x_g, \quad \lambda' = x_f + x_g; \quad x_f = \frac{f_{1a2b}}{f_{aa}}, \quad x_g = \frac{g_{1a2a}^o}{g_{aa}^o}. \quad (3.31)$$

Si se introduce el concepto de poliada

$$P_L = n_1 + n_2; \quad n_i = \tau_{i+}^\dagger \tau_{i+} + \tau_{i-}^\dagger \tau_{i-}, \quad (3.32)$$

y aproximamos el Hamiltoniano (3.30) despreciando el término que no conserva el número total de cuantos obtenemos la simplificación

$$\hat{H}_{Fock}^{PL} = \frac{\hbar\omega}{2} \sum_{i=1}^2 (\tau_{i+}^\dagger \tau_{i+} + \tau_{i+} \tau_{i+}^\dagger + \tau_{i-}^\dagger \tau_{i-} + \tau_{i-} \tau_{i-}^\dagger) + \frac{\hbar\omega}{2} \lambda (\tau_{1+}^\dagger \tau_{2+} + \tau_{1-}^\dagger \tau_{2-} + H.c.) + \frac{\hbar\omega}{2} \lambda' (\tau_{1-}^\dagger \tau_{2+}^\dagger + \tau_{1+}^\dagger \tau_{2-}^\dagger + H.c.). \quad (3.33)$$

Con este esquema se puede llevar a cabo un ajuste y obtener estimados de las constantes de fuerza mediante  $\omega$  y  $\lambda$ . Sin embargo hasta este paso no se sabe qué tan importante resulta haber despreciado el término de (3.30) que no preserva la poliada, por lo que es importante cuestionarse la validez de las estimaciones de las constantes de fuerza obtenidas mediante este método. Para responder este punto se considerará el esquema normal.

### 3.2.2. Esquema normal

Debido a que el Hamiltoniano (3.30) sólo contiene términos cuadráticos, puede diagonalizarse en términos de 2 osciladores independientes. Para realizar esta diagonalización introduciremos coordenadas adaptadas por simetría. El sistema en estudio tiene una simetría puntual  $\mathcal{D}_{\infty h}$ . Con la introducción de coordenadas circulares, como se hizo en (3.27), se asegura que las coordenadas obtenidas tengan una buena proyección de momento angular, por lo que sólo resta asegurar que sean invariantes ante la aplicación de la inversión  $I$ . Esto es equivalente a aplicar el plano  $\sigma_h$  al sistema. Diagonalizando el operador  $\hat{I}$  se obtienen los vectores propios

$$Q_{g,\sigma} = \frac{1}{\sqrt{2}}(-Q_{1\sigma} + Q_{2\sigma}), \quad Q_{u,\sigma} = \frac{1}{\sqrt{2}}(Q_{1\sigma} + Q_{2\sigma}); \quad P_{g,\sigma} = \frac{1}{\sqrt{2}}(-P_{1\sigma} + P_{2\sigma}), \quad P_{u,\sigma} = \frac{1}{\sqrt{2}}(P_{1\sigma} + P_{2\sigma}). \quad (3.34)$$

Con estas nuevas coordenadas adaptadas por simetría, el Hamiltoniano (3.28) toma la forma

$$\hat{H}_{cs} = -[g_{gg}^o P_{g,+} P_{g,-} + f_{gg} Q_{g,+} Q_{g,-}] - [g_{uu}^o P_{u,+} P_{u,-} + f_{gg} Q_{u,+} Q_{u,-}]. \quad (3.35)$$

Es posible obtener también el Hamiltoniano en el espacio de Fock, al introducir la transformación de las coordenadas y momentos con los operadores bosónicos

$$Q_{r,\sigma} = \sqrt{\frac{\hbar}{2\omega_r \mu_r}} (\tau_{r,\sigma}^\dagger - \tau_{r,-\sigma}); \quad P_{r,\sigma} = -\frac{i}{\sqrt{2}} \sqrt{\hbar \omega_r \mu_r} (\tau_{r,-\sigma}^\dagger + \tau_{r,\sigma}), \quad r = g, u, \quad \sigma = +, -. \quad (3.36)$$

Esta transformación convierte a (3.35) en un Hamiltoniano que tiene la forma de dos osciladores independientes:

$$\hat{H}_{Fock} = \frac{\hbar \omega_g}{2} \sum_{\sigma} (\tau_{g,\sigma}^\dagger \tau_{g,\sigma} + \tau_{g,\sigma} \tau_{g,\sigma}^\dagger) + \frac{\hbar \omega_u}{2} \sum_{\sigma} (\tau_{u,\sigma}^\dagger \tau_{u,\sigma} + \tau_{u,\sigma} \tau_{u,\sigma}^\dagger). \quad (3.37)$$

El Hamiltoniano (3.37) en el esquema normal y el Hamiltoniano (3.30) en el esquema local, son equivalentes y generan el mismo espectro, sin embargo en el esquema local la poliada  $P_L$  debe romperse para recuperar las mismas constantes de fuerza. Ahora procederemos a analizar en qué casos el Hamiltoniano que preserva la poliada local, con sus parámetros espectroscópicos, puede usarse para obtener constantes de fuerza razonables; esto se logrará conectando el esquema local con el normal.

### 3.2.3. Transición local-normal

Si invertimos las expresiones (3.36), sustituimos la conexión entre coordenadas (3.34) e introducimos adicionalmente la definición de operadores bosónicos (3.29), obtendremos la conexión entre los operadores bosónicos en el esquema normal y en el esquema local.

$$\tau_{g,+}^\dagger = \frac{1}{\sqrt{2}} \{f_{1g}(\tau_{1,+}^\dagger + \tau_{2,+}^\dagger) + f_{2g}(\tau_{1,-} + \tau_{2,-})\}, \quad \tau_{u,+}^\dagger = \frac{1}{\sqrt{2}} \{f_{1u}(\tau_{1,+}^\dagger - \tau_{2,+}^\dagger) + f_{2u}(\tau_{1,-} - \tau_{2,-})\}. \quad (3.38)$$

Esta conexión se conoce como conexión del tipo Bogoliuvov entre operadores bosónicos locales y normales. Dentro del esquema normal, también es posible introducir el concepto de poliada, como un pseudonúmero cuántico que abarca el conjunto de estados conectados con las interacciones principales. En nuestro caso la poliada  $P_N$  en el esquema normal toma la forma

$$P_N = n_g + n_u; \quad n_\sigma = \tau_{g,+}^\dagger \tau_{g,+} + \tau_{g,-}^\dagger \tau_{g,-}, \quad \sigma = g, u. \quad (3.39)$$



En general, no hay coincidencia entre las poliadas (3.32) y (3.39), como puede verse si sustituimos la conexión de los operadores bosónicos normales (3.38) en (3.39):

$$\begin{aligned} \hat{P}_N = & \zeta_0 + \beta_0 \hat{P}_L + \beta_1 (\tau_{1,+}^\dagger \tau_{2,+} + \tau_{1,-} \tau_{2,-}^\dagger + \tau_{2,+}^\dagger \tau_{1,+} + \tau_{2,-} \tau_{1,-}^\dagger) \\ & + \gamma_1 (\tau_{1,+}^\dagger \tau_{1,-}^\dagger + \tau_{2,+}^\dagger \tau_{2,-}^\dagger + \tau_{1,+} \tau_{1,-} + \tau_{2,+} \tau_{2,-}) + \gamma_2 (\tau_{1,+}^\dagger \tau_{2,-}^\dagger + \tau_{1,-}^\dagger \tau_{2,+}^\dagger + \tau_{1,+} \tau_{2,-} + \tau_{1,-} \tau_{2,+}), \end{aligned} \quad (3.40)$$

donde se han factorizado términos que contienen operadores bosónicos semejantes. Como puede observarse,  $\hat{P}_N$  contiene a la poliada local  $\hat{P}_L$ , pues recordemos que para obtener esta última se despreciaron algunos términos que no conservaban el número total de cuantos, por tanto, en general  $\hat{P}_N \neq \hat{P}_L$ .

Si introducimos la siguiente transformación unitaria:

$$\tau_{g,+}^\dagger = \frac{1}{\sqrt{2}}(c_{1,+}^\dagger + c_{2,+}^\dagger), \quad \tau_{u,+}^\dagger = \frac{1}{\sqrt{2}}(c_{1,+}^\dagger - c_{2,+}^\dagger), \quad (3.41)$$

en (3.37), el Hamiltoniano es

$$\hat{H}_{Fock}^{PL} = \frac{\hbar \omega_{nor}}{2} \sum_{i=1}^2 (c_{i+}^\dagger c_{i+} + c_{i+} c_{i+}^\dagger + c_{i-}^\dagger c_{i-} + c_{i-} c_{i-}^\dagger) + \frac{\hbar \lambda_{nor}}{2} (c_{1+}^\dagger c_{2+} + c_{1-}^\dagger c_{2-} + H.c.). \quad (3.42)$$

Los operadores locales  $c_{i,\pm}^\dagger (c_{i,\pm})$  no son los operadores físicos  $\tau_{i,\pm}^\dagger (\tau_{i,\pm})$ , pero es posible elegir una base isomorfa local en la que la acción de estos operadores sea la misma. Dado este isomorfismo, los Hamiltonianos (3.33) y (3.42) son equivalentes en el sentido de que proporcionan el mismo espectro en la base local y sin embargo son distintos puesto que la conexión entre parámetros espectroscópicos con las constantes de fuerza es diferente.

La validez del Hamiltoniano (3.33) debería ser cuestionada dado el término que se había despreciado; se espera que haya coincidencia en los coeficientes espectroscópicos en moléculas con comportamiento local. Para elucidar las condiciones que se deben satisfacer, se lleva a cabo un desarrollo en series de Taylor de los parámetros espectroscópicos en (3.42)  $\omega_{nor}$  y  $\lambda_{nor}$  como función de las variables  $x_f$  y  $x_g$  alrededor de cero y quedándonos únicamente hasta 2do orden. De aquí notamos que el término cuadrático, que es idéntico para ambos parámetros espectroscópicos, debe ser mucho menor a uno para que los parámetros normales se aproximen a los que se obtuvieron en el esquema local,

$$\gamma \equiv \frac{1}{8}(x_g - x_f)^2 \ll 1, \quad \omega_{nor} = \frac{\omega}{2}, \quad \lambda = \omega(x_f + x_g). \quad (3.43)$$

Esta última condición debe ser consistente con el límite obvio  $|x_f| \rightarrow 0$ ;  $|x_g| \rightarrow 0$ , por lo que una manera de lograrlo es

$$|x_f| \ll 1; \quad |x_g| \ll 1. \quad (3.44)$$

Mediante estas condiciones, recuperamos los parámetros del esquema local de dos osciladores interactuantes. Las condiciones planteadas tienen ingerencia en la definición de poliada; si las aplicamos, los términos en (3.40) quedan de la siguiente forma:

$$\beta_0 \approx 1, \quad \zeta_0 = \beta_1 = \gamma_i \approx 0; \quad i = 1, 2. \quad (3.45)$$

Por tanto, después de aplicar el límite local  $\hat{P}_N \approx \hat{P}_L$ . De forma simultánea la transformación (3.38), se reduce a la transformación canónica (3.41).

La respuesta a la pregunta sobre la pertinencia de este modelo al estimar las constantes de fuerza a orden cero, está relacionada con las condiciones mencionadas. Es posible estimar las constantes de fuerza tanto en el esquema local como en el esquema normal en términos de las energías fundamentales  $E_g$  y  $E_u$  (acotándonos al análisis de los modos de flexión de la molécula de acetileno); en general, es de esperarse que los valores sean distintos. Las constantes de fuerza dado un esquema local son

$$f_{aa} = \frac{1}{\hbar g_{aa}^{\circ}} \left( \frac{E_g + E_u}{2} \right)^2; \quad f_{1a2a} = f_{aa} \left( \frac{E_u - E_g}{(E_u + E_g)/2} - \frac{\hbar g_{1a2a}^{\circ}}{\hbar g_{aa}^{\circ}} \right). \quad (3.46)$$

Para recalcar que estas son las constantes de fuerza del esquema local, se tomará  $f_{aa} \rightarrow F_{aa}$ ,  $f_{1a2a} \rightarrow F_{1a2a}$ . Por otro lado, dado el Hamiltoniano (3.37) en el esquema normal y las frecuencias asociadas, se obtienen las constantes de fuerza siguientes:

$$f_{aa} = \frac{(1 + \epsilon)}{2(1 - x_g)} \frac{E_g^2}{\hbar g_{aa}^{\circ}}; \quad f_{1a2a} = f_{aa} \left( \frac{\epsilon - 1}{\epsilon + 1} \right); \quad \epsilon = \left( \frac{E_u}{E_g} \right)^2 \left( \frac{1 - x_g}{1 + x_g} \right). \quad (3.47)$$

Las expresiones de las constantes de fuerza son diferentes, estas diferencias pueden ser medidas introduciendo el parámetro

$$\zeta = \left| \frac{2}{\pi} \arctan \left( \frac{E_g - E_u}{(E_g - E_u)/2} \right) \right|, \quad (3.48)$$

que provee una medida del grado de localidad [44]. Este análisis demuestra que empezando con un comportamiento local, debe existir una región de transición donde la igualdad entre poliadas  $\hat{P}_N = \hat{P}_L$  deje de ser válida, así como la estimación de constantes de fuerza mediante el esquema local a orden cero. Necesitamos entonces los estados fundamentales para estimar el grado de localidad de la molécula y proceder entonces de acuerdo al esquema que más se adecue para el cálculo de las constantes de fuerza.

### 3.3. Modos de flexión para la molécula de acetileno

La geometría de equilibrio del acetileno es lineal y presenta distancias entre sus átomos  $r_e^{\text{CH}} = 1.064 \text{ \AA}$  y  $r_e^{\text{CC}} = 1.206 \text{ \AA}$ . Su grupo puntual de simetría es  $\mathcal{D}_{\infty h}$  como se mencionaba en la sección anterior. El acetileno cuenta con 7 grados de libertad vibracionales, 2 de ellos asociados al estiramiento CH, con simetrías  $\Sigma_g^+$ ,  $\Sigma_u^+$  y notación estándar  $\nu_1$  y  $\nu_3$ ; uno asociado al modo de estiramiento CC,  $\Sigma_g^+$  con notación  $\nu_2$ , y 2 modos degenerados de flexión  $\Pi_g^{\pm}$  y  $\Pi_u^{\pm}$ , con notación  $\nu_4$  y  $\nu_5$ , respectivamente [1]. Los estados vibracionales de esta molécula toman la forma usual

$$|\nu\rangle = |\nu_1 \nu_2 \nu_3 \nu_4^l \nu_5^l\rangle. \quad (3.49)$$

Las frecuencias fundamentales son (en unidades de  $cm^{-1}$ ) [53]:

$$\omega_1 = 3372.87; \quad \omega_2 = 1974.32; \quad \omega_3 = 3288.68; \quad \omega_4 = 612.098; \quad \omega_5 = 726.835. \quad (3.50)$$

Las resonancias principales que se identifican con los modos de flexión son  $2\omega_4 \approx 2\omega_5$ , donde debe tomarse en cuenta que sólo modos con la misma simetría tienen resonancias asociadas. Estas son resonancias asociadas a interacciones efectivas, identificadas previamente [53]. El desarrollo que se muestra a continuación tiene el objetivo de ejemplificar el procedimiento mediante el cual es posible llegar a un estimado de las constantes de

fuerza dentro del modelo algebraico  $U(3)$ . Dado este esquema y las subsecciones desarrolladas anteriormente, sólo se consideran los grados de flexión de la molécula de acetileno, asociados a la resonancia  $2\omega_4 \approx 2\omega_5$ . La poliada vinculada con esta resonancia es [54],

$$P_N = \nu_4 + \nu_5. \quad (3.51)$$

Hasta este punto del desarrollo no conocemos la forma adecuada de estimar las constantes de fuerza del acetileno dentro del modelo  $U(3)$ , es decir, debemos elegir entre el esquema normal o local. Para ello se debe hacer una estimación del grado de localidad de la molécula. Si se usa el parámetro (3.48), este valor es de  $\zeta = 0.11$ . Al comparar este número con el obtenido para otros sistemas, se encuentra que éste es similar al de la molécula  $\text{SO}_2$  que presenta un comportamiento normal en el marco del análisis tradicional de la transición local-normal. Para obtener una comparación clara de qué tan grande o pequeño es este valor de  $\zeta$ , el cálculo para los modos de estiramiento del acetileno, arroja un valor de 0.016, que indica un comportamiento fuertemente local. Este breve análisis nos permite elegir como esquema para tratar al acetileno aquel de modos normales para continuar con la descripción local y finalmente llevar a cabo el proceso de anarmonización que nos situará en el modelo  $U(3)$ .

### 3.3.1. Hamiltoniano del acetileno en el esquema de modos normales

Dentro de un esquema de coordenadas generalizadas sin considerar términos que no contengan operadores de momento en la energía cinética, el Hamiltoniano mecánico-cuántico que describe las excitaciones vibracionales es, como en (3.1) [55]:

$$\hat{H} = \frac{1}{2} \mathbf{p}^\dagger \mathbf{G}(\mathbf{q}) \mathbf{p} + V(\mathbf{q}). \quad (3.52)$$

Los elementos de esta matriz así como los de la función que describe el potencial, pueden desarrollarse en términos de las variables a considerar, en este caso, las coordenadas normales [55]. En general, la forma explícita del desarrollo depende de la poliada a tomar en cuenta y para ser congruentes con la notación entre secciones se empleará  $Q_{g,\sigma} \rightarrow Q_{4\sigma}$ ;  $Q_{u\sigma} \rightarrow Q_{5,\sigma}$ , como indica la notación usual para los modos de flexión. Tomando en cuenta la poliada (3.51), los operadores de número  $\nu_\alpha$  están definidos por

$$\hat{\nu}_4 = \tau_{4,+}^\dagger \tau_{4,+} + \tau_{4,-}^\dagger \tau_{4,-}, \quad \hat{\nu}_5 = \tau_{5,+}^\dagger \tau_{5,+} + \tau_{5,-}^\dagger \tau_{5,-}. \quad (3.53)$$

Este trabajo no pretende la estimación con alta precisión del espectro energético del acetileno, trabajo que ya está descrito por Jacobson [54]. En contraparte se enfoca únicamente en la conexión entre los espacios algebraico y de configuración, por esta razón sólo se toman en consideración términos hasta orden cuártico que conserven la poliada (3.51). En este caso el Hamiltoniano se escribe como

$$\hat{H}_{cs} = \hat{H}^{[2]} + \hat{H}^{[4]}, \quad (3.54)$$

donde las interacciones de orden non son nulas porque no preservan los operadores de número;  $\hat{H}^{[4]}$  toma en cuenta interacciones de orden cuártico, y  $\hat{H}^{[2]}$  son los términos de interacción cuadráticos, descritos con detalle en la sección anterior

$$\hat{H}^{[2]} = -[g_{44}^o P_{4,+} P_{4,-} + f_{44} Q_{4,+} Q_{4,-}] - [g_{55}^o P_{5,+} P_{5,-} + f_{55} Q_{5,+} Q_{5,-}]. \quad (3.55)$$

Recordando que  $f_{rr} = \left( \frac{\delta^2 V}{\delta Q_{r+} \delta Q_{r-}} \right)_0$  mientras que  $g_{rr}^o$  corresponde a las constantes de estructura evaluadas en el equilibrio dadas por la matriz de Wilson.

Debido a la complejidad del estudio de los términos cuárticos es conveniente dividirlos en un término de energía cinética y otro de energía potencial. Así pues el potencial a orden cuártico toma la forma explícita

$$V^{[4]} = \frac{6}{4!} f_{4+4+4-4-} Q_{4+}^2 Q_{4-}^2 + \frac{6}{4!} f_{5+5+5-5-} Q_{5+}^2 Q_{5-}^2 + \frac{4!}{4!} f_{4+4-5+5-} Q_{4+} Q_{4-} Q_{5+} Q_{5-} + \frac{6}{4!} f_{4+4+5-5-} (Q_{4+} Q_{4+} Q_{5-} Q_{5-} + H.c.), \quad (3.56)$$

la cual considera todas las posibles combinaciones de coordenadas al momento de derivar.

Los términos cuárticos de la energía cinética se deben construir mediante el desarrollo en series de potencias de la matriz de Wilson y al tomar en cuenta términos de segundas derivadas. Dada la enorme cantidad de términos involucrados, se calculó explícitamente con ayuda del programa Mathematica la matriz de Wilson  $\mathbf{G}(\mathbf{q})$  así como sus primeras y segundas derivadas; muchos de los elementos son cero, y los que sobreviven son los siguientes:

$$\begin{aligned} T^{[4]} &= \frac{1}{4} \left( \frac{\partial^2 G_{4+,4+}}{\partial Q_{4+}^2} \right)_0 (P_{4+} Q_{4+}^2 P_{4+} + H.c.) + \frac{1}{4} \left( \frac{\partial^2 G_{5+,5+}}{\partial Q_{5+}^2} \right)_0 (P_{5+} Q_{5+}^2 P_{5+} + H.c.) \\ &+ \frac{1}{4} \left( \frac{\partial^2 G_{4+,4+}}{\partial Q_{5+}^2} \right)_0 (P_{4+} Q_{5+}^2 P_{4+} + H.c.) + \frac{1}{4} \left( \frac{\partial^2 G_{5+,5+}}{\partial Q_{4+}^2} \right)_0 (P_{5+} Q_{4+}^2 P_{5+} + H.c.) \\ &+ \frac{1}{2} \left( \frac{\partial^2 G_{4+,5-}}{\partial Q_{4+} \partial Q_{5-}} \right)_0 (P_{4+} Q_{4+} Q_{5-} P_{5-} + P_{5-} Q_{4+} Q_{5-} P_{4+}) + \frac{1}{2} \left( \frac{\partial^2 G_{4+,5+}}{\partial Q_{4+} \partial Q_{5+}} \right)_0 (P_{4+} Q_{4+} Q_{5+} P_{5+} + P_{5+} Q_{4+} Q_{5+} P_{4+}) \\ &+ \frac{1}{2} \left( \frac{\partial^2 G_{4+,5-}}{\partial Q_{4-} \partial Q_{5+}} \right)_0 (P_{4+} Q_{4-} Q_{5+} P_{5-} + P_{5-} Q_{4-} Q_{5+} P_{4+}). \end{aligned} \quad (3.57a)$$

El siguiente paso consiste en obtener la representación en el espacio de Fock introduciendo la transformación a operadores bosónicos (3.36), con lo que llegamos a

$$\begin{aligned} \hat{H}_{Fock} &= \frac{\hbar\Omega_4}{2} (\tau_{4,+}^\dagger \tau_{4,+} + \tau_{4,-}^\dagger \tau_{4,-}) + \frac{\hbar\Omega_5}{2} (\tau_{5,+}^\dagger \tau_{5,+} + \tau_{5,-}^\dagger \tau_{5,-}) \\ &+ x_{44} \hat{\nu}_4^2 + x_{55} \hat{\nu}_5^2 + x_{45} \hat{\nu}_4 \hat{\nu}_5 + g_{44} \hat{l}_4^2 + g_{55} \hat{l}_5^2 + g_{45} \hat{l}_4 \cdot \hat{l}_5 + K_{44/55} \hat{D}_{44/55} + L_{44/55} \hat{\Delta}_{44/55} + r_{45} \hat{R}_l, \end{aligned} \quad (3.58)$$

con los operadores de momento angular definidos como

$$\hat{l}_4 = \tau_{4,+}^\dagger \tau_{4,+} - \tau_{4,-}^\dagger \tau_{4,-}, \quad \hat{l}_5 = \tau_{5,+}^\dagger \tau_{5,+} - \tau_{5,-}^\dagger \tau_{5,-}, \quad (3.59)$$

y las contribuciones no diagonales

$$\hat{D}_{44/55} = \tau_{4,+}^\dagger \tau_{4,-}^\dagger \tau_{5,+} \tau_{5,-} + H.c., \quad \hat{\Delta}_{44/55} = \tau_{4,+}^{\dagger 2} \tau_{5,+}^2 + \tau_{4,-}^{\dagger 2} \tau_{5,-}^2 + H.c., \quad \hat{R}_l = \tau_{4,+}^\dagger \tau_{4,-} \tau_{5,-}^\dagger \tau_{5,+} + \tau_{4,-}^\dagger \tau_{4,+} \tau_{5,+}^\dagger \tau_{5,-}. \quad (3.60)$$

La primera interacción no diagonal  $\hat{D}_{44/55}$  es la resonancia de Darling Dennison de flexión I y  $\hat{\Delta}_{44/55}$  es la resonancia de Darling Dennison de flexión II.  $\hat{R}_l$  corresponde a la resonancia vibracional I. Sus elementos de matriz pueden encontrarse en la referencia [54]. Los parámetros espectroscópicos están dados en términos de la

estructura y las constantes de fuerza.

### 3.3.2. Hamiltoniano en el modelo $U_1(3) \otimes U_2(3)$

El Hamiltoniano (3.58) en el espacio de Fock está dado en el esquema normal mientras que el modelo  $U(3)$  está definido en un esquema local; por tanto debemos de realizar una transformación canónica del tipo (3.41) como primer paso para introducir operadores locales. Aplicando esta transformación canónica en (3.58) se consigue la forma funcional

$$\hat{H}_{Fock} = \hat{H}_{Fock}(c_{j,\sigma}^\dagger, c_{j,\sigma}); \quad j = 1, 2; \quad \sigma = \pm. \quad (3.61)$$

Los Hamiltonianos (3.58) y (3.61) son equivalentes pues proveen el mismo espectro de acuerdo con el isomorfismo  $c_{i,\pm}^\dagger \leftrightarrow \tau_{i,\pm}^\dagger$ . Nuestro sistema consta de 2 osciladores, por tanto el espacio algebraico asociado es  $su_1(3) \otimes su_2(3)$ . El Hamiltoniano correspondiente  $H_{alg}^{u_1(3) \otimes su_2(3)}$  se obtiene considerando  $\hat{b}_\pm^\dagger \equiv \frac{\hat{\tau}_\pm^\dagger \hat{\sigma}}{\sqrt{N}}$ , que representa la anarmonización en el nivel local.

De esta forma el Hamiltoniano algebraico se construye, primero, transformando de bosones normales a locales para después llevar a cabo la anarmonización a operadores dentro del modelo  $U(3)$ .

$$\hat{H}_{Fock}(\tau_{j,\sigma}^\dagger, \tau_{j,\sigma}) \Big|_{\tau_{j,\sigma} \rightarrow c_{j,\sigma}} = \hat{H}_{Fock}(c_{j,\sigma}^\dagger, c_{j,\sigma}) \Big|_{c_{j,\sigma} \rightarrow b_{j,\sigma}} = H_{alg}^{u_1(3) \otimes su_2(3)}(b_{j,\sigma}^\dagger, b_{j,\sigma}). \quad (3.62)$$

El enfoque tratado lleva a un formalismo tensorial donde el Hamiltoniano algebraico está dado en términos de acoplamientos sucesivos de tensores; en nuestro caso simplemente hicimos las sustituciones de (3.41) en (3.58). La expansión resultante de las interacciones se usa después para hacer el cómputo de los elementos de matriz del Hamiltoniano; esto puede hacerse mediante un código, sin tener que escribir de forma explícita las interacciones locales. La conexión con las constantes de fuerza y estructura se dan bajo el análisis de modos locales y se usa la conexión con los parámetros espectroscópicos para la estimación de las constantes de fuerza.

## CONCLUSIONES

4

Se realizó el mapeo del espacio de configuración con el algebraico dados dos osciladores  $2D$  mediante un mapeo de oscilador armónico y el espacio  $U(3)$  y se logró hacer una generalización para  $\nu$ -osciladores equivalentes en  $2D$  en el marco del modelo  $U(\nu + 1)$  para la descripción de excitaciones vibracionales, usando con éxito el método de minimización planteado [49].

Con el mapeo entre espacios, y en la base de oscilador armónico, se encontró que en el límite cuando  $N$  es muy grande, la realización algebraica del momento y la coordenada se reduce a tener coeficientes para estados independientes equivalentes a las expresiones obtenidas heurísticamente en otros trabajos [45, 46, 47, 48].

Se probó que el enfoque con el modelo  $U(\nu + 1)$  toma en cuenta efectos anarmónicos desde el inicio con la peculiaridad de que la poliada está involucrada en esta anarmonicidad

Se presentó la realización de momentos y coordenadas para osciladores  $2D$  en términos de un espacio algebraico dinámico  $U(3)$  encontrando varias ventajas; el grupo dinámico es compacto, emergen 3 simetrías dinámicas y se encuentra una anarmonización desde el inicio del enfoque dado el bosón  $N$ .

Se usó con éxito el método de minimización planteado [49], expresando a los momentos y coordenadas como una expansión lineal de los generadores del álgebra. La realización del Hamiltoniano involucra contribuciones anarmónicas  $(1/N)n^2$  que reflejan un efecto anarmónico en el modelo  $U(3)$ .

Se encontró que los estados asociados con las simetrías dinámicas corresponden a la representación algebraica de distintos observables; la cadena en 3.18a se asocia a la representación energética; la cadena 3.18b a la representación de coordenadas y la cadena 3.18c a la representación de momentos.

Se analizó con detalle el caso de 2 osciladores  $2D$  para conocer las condiciones en que se podían obtener constantes de fuerza confiables a orden cero dado que estas pueden estimarse mediante diferentes esquemas: local y normal, obteniendo distintos resultados para cada una.

Para el caso del acetileno, con un parámetro  $\zeta = 0.11$ , los 2 osciladores planteados tienen un comportamiento normal, por lo que se comenzó mediante el esquema normal y se conectó con el modelo local  $U_1(3) \otimes U_2(3)$ ; una transformación canónica de operadores bosónicos normales a operadores bosónicos locales y una posterior anarmonización a nivel local que permite obtener las ventajas del modelo  $U(3)$ .

Se aplicó de forma explícita el método planteado para los modos de flexión del acetileno, y se obtuvieron parámetros espectroscópicos que conectan con la estructura y las constantes de fuerza para después aplicar los pasos de transformación canónica y anarmonización.

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RESEARCH ARTICLE



# Connection between the $su(3)$ algebraic and configuration spaces: bending modes of linear molecules

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## ABSTRACT

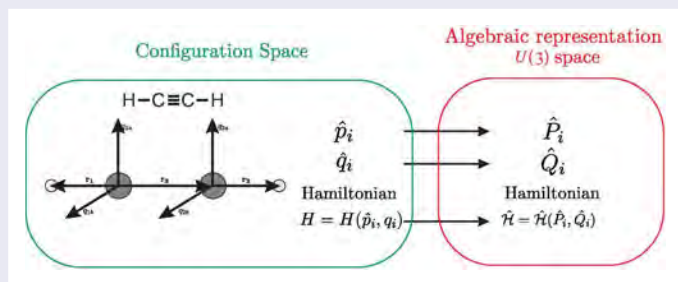
An approach to connect the  $su(3)$  dynamical group – used to describe the bending modes of linear molecules – with configuration space is discussed. The  $SU(3)$  group may be seen as a consequence of adding a scalar boson to the  $SU(2)$  space of two degenerate harmonic oscillators. The resulting  $SU(3)$  group becomes the dynamical group for 2D systems. The connection of the model with configuration space however is not obvious. Our approach is based on establishing a mapping between the algebraic and configuration states. The identification in the algebraic space of coordinates and momenta leads to a new identification of the group chains: they are associated with energy, coordinate and momentum representations. In addition an analysis of local-to-normal mode transition is presented. This provides a criterion to decide between a local or normal mode descriptions in an spectroscopic description. As an example we consider the situation of the bending modes of acetylene taking a Hamiltonian up to quartic order. The different results for the force constants obtained from the local and normal mode treatments leads to the conclusions that previous applications of the bending modes of acetylene dealing with a local mode treatment is on the verge of applicability.

## ARTICLE HISTORY

Received 7 March 2018  
 Accepted 30 May 2018

## KEYWORDS

$U(3)$  model; linear molecule; bending modes of acetylene; force constants; algebraic model versus configuration space



## 1. Introduction

Algebraic techniques practically emerge simultaneously with second quantisation formalism which allows the matrix elements in configuration space to be reproduced in Fock space [1]. Both spaces have advantages and disadvantages and consequently one usually considers the appropriate space for a given problem. May be the one dimensional harmonic oscillator represents the simplest system where we can deal with its description in both spaces at pedagogical level and see clearly the differences in the treatments [2]. The advantages of the algebraic representation manifest in the fact that every matrix element of any observable depending on coordinates and momentum can be calculated through algebraic manipulation involving the commutation relation

of the corresponding bosonic ladder operators. This situation is also the case when a set of interacting harmonic oscillators are considered for the vibrational description of polyatomic molecules. It is hardly overestimate the influence of the algebraic representation in dealing with the vibrational problem [3–5]. Indeed, it represents a straightforward approach for pattern recognition in vibrational spectroscopy since as a first approximation the Hamiltonian can be expanded in terms of powers of diagonal number operators with non-diagonal interactions easily constructed in accordance with the present resonances [6]. In fact, the polyad pseudo quantum number, crucial in establishing the relevant set of interacting states, can be established in a straightforward way [7].

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- 111 At the middle of the 70's, inspired from earlier works  
[8, 9] the algebraic model known as the  $U(6)$  Interacting  
Boson Model (IBM) was proposed by *Arima and*  
*F. Iachello* to describe the nuclear degrees of freedom  
for eve-even nuclei [10]. This model was based on the  
116 quadrupole deformation in connection with the surface  
vibration of the nucleus [11]. The starting point was the  
introduction of a scalar boson to the set of bosons asso-  
ciated with the nuclear quadrupole deformation with the  
constraint of a fixed total number of bosons. Besides the  
121 fact that the resulting dynamical group turns out to be  
compact, the success of this model was that the result-  
ing group  $U(6)$  provides three dynamical symmetries  
with a specific physical insight [12]. Later on F. Iachello  
*et al.* proposed to apply the same idea to describe the  
126 ro-vibrational degrees of freedom of diatomic molecules  
where the dipole moment is the dominant physical ingre-  
dient, leading to the  $U(4)$  vibron model [13, 14]. In this  
context, the total number of bosons plays the role of  
a parameter connected with the depth of the potential,  
131 a fact that provides a description where anharmonicities  
are taken into account from the outset. In the same  
venue the vibron model provides two dynamical sym-  
metries, recognised as  $O(4)$  and  $U(3)$ , associated with  
rigid and non-rigid molecules respectively, a fact that  
136 allows a mapping to be established between the kets  
associated with the  $O(4)$  chain and the Morse poten-  
tial [15, 16]. The model was extended to polyatomic  
molecules with definite success in linear molecules [17,  
18].
- 141 When an additional scalar boson is incorporated to  
the space of two degenerate harmonic oscillators, the  
 $U(3)$  model emerges as a dynamical group of **two-**  
**dimensional** systems with good angular momentum pro-  
jection  $l$  [19]. In this case also two dynamical sym-  
146 metries are given: the  $U(2)$  and the  $O(3)$ , identified  
with the bending modes of a linear and non linear,  
respectively. On the other hand, the one dimensional  
version of the vibron model corresponds to the  $U(2)$   
dynamical group [20], allowing the one dimensional  
151 oscillator to be treated as a Morse oscillator [21]. The  
**generalisation** to this algebraic treatment was immedi-  
ate: for each one dimensional variable a  $U(2)$  group is  
added, while a  $U(3)$  for each **two-dimensional** mode  
giving rise to a complete dynamical group expressed as  
156 the direct product for the full set of dynamical groups.  
In this context the Hamiltonian may be expanded in  
terms of powers and products of the generators of the  
groups, with the possibility of identifying the interactions  
associated with the energy resonances. The parameters  
161 involved in the Hamiltonian are then fitted to obtain  
the best description of the spectrum. This approach is  
phenomenological in the sense that the Hamiltonian is  
not clearly related to a Hamiltonian in configuration  
space, and consequently, the straightforward connec-  
tion between matrix elements of operators in algebraic  
and configuration spaces given in second **quantisation**  
is not present. However, based on the mapping between  
171 the dynamical symmetries and the eigenstates in con-  
figuration space it is possible to investigate the phys-  
ical meaning of the potential involved in a vibrational  
Hamiltonian through the use of coherent states [15,  
22]. Unfortunately this approach can be used only for  
176 molecules with local mode **behaviour** and does not pro-  
vide tools to predict spectroscopic properties of isotop-  
ologue species due to the fact that the kinetic energy  
is erased from the description, avoiding the possi-  
bility to estimate the potential energy surface (PES)  
181 [23].
- The need to establish a connection between unitary  
groups  $U(n + 1)$  and the standard molecular vibrational  
description enhances because it is possible to devise more  
than one Lie algebraic models based on unitary algebras  
providing the same description with the same level of  
186 accuracy, for example, two oscillators may be described  
either with a  $su(3)$  algebra or through the direct sum  
 $su_1(2) \oplus su_2(2)$  of algebras. This task was initiated in the  
one dimensional version of the vibron model by estab-  
lishing the isomorphism between the  $su(2)$  model and  
191 the Morse and Pöschl-Teller potentials [24, 25]. This con-  
nection was based on the comparison of matrix elements,  
following the same idea of second **quantisation**. Later  
on the  $U(3)$  model associated with the description of the  
bending modes in linear molecules was connected with  
196 configuration space in the framework of a linear approx-  
imation [26]. In similar way the connection between the  
spaces was carried out in the  $U(n + 1)$  model to describe  
correlated purely vibrational excitations [27]. This con-  
nections allowed PES's to be estimated [28]. In particular,  
201 this formalism permitted to describe the Raman spec-  
trum of  $\text{CO}_2$  beyond the linear approximation in the  
expansion of the internal coordinates [29].
- In both cases, the  $U(n + 1)$  model for correlated  
bosons and the  $U(3)$  model for bending modes, the  
206 algebraic coordinates and momenta realizations were *lin-*  
*ear* and carried out using criteria connected with the  
*harmonic limit*. This represents a limitation for many  
problems where anharmonic effects are preponderant.  
Recently an approach to establish the expansion of any  
211 dynamical variable in terms of generators of a given  
dynamical algebra in situations beyond the linear approx-  
imation was proposed [30]. Our approach is based on  
the **minimisation** method proposed in the description  
of molecular collisions [31, 32]. The basic idea consists  
216 in establishing a mapping between the eigenstates of the  
Hamiltonian in configuration space with the eigenstates

221 of the Hamiltonian in the algebraic space. The dynamic  
variables are then expanded in the algebraic space with  
coefficients determined through a **minimisation** method.  
The coefficients turn out to be given in terms of matrix  
elements of the dynamical operators in configuration  
226 space. This approach provides the best algebraic descrip-  
tion of the operators. Examples of this method were pre-  
sented for Morse and double Morse potentials as well as  
for the  $U(\nu + 1)$  model for correlated oscillators [33].  
One of our goals of this contribution **consists** in apply-  
231 ing this approach to the case of the  $U(3)$  dynamical group  
for linear molecules and prove that the linear approxima-  
tion previously used in the  $\text{CO}_2$  molecule corresponds  
to the best approximation when a mapping to the har-  
monic oscillator is proposed, but also to **analyse** the con-  
236 sequences of the identification of the coordinates and  
momenta in the algebraic space.

In linear triatomic molecules only one two-dimen-  
sional oscillator appears, and locality and normality con-  
cepts turn out to be relevant only for the stretching  
degrees of freedom. However when two oscillators are  
involved the arising new question is concerned about the  
locality degree of the coupled systems. This situation is  
present in acetylene for instance, where two 2D oscilla-  
tors are coupled. The  $U(3)$  model for bends, **however**,  
241 is local and consequently we are expected to obtain the  
force constants as long as a local **behaviour** is present.  
In this work, we shall show that this is not necessarily  
the case and in order to estimate correctly the PES it  
is appropriate to start with a normal mode scheme. In  
246 a recent paper, a **local-to-normal** mode transition has  
studied from the polyad breaking point of view, provid-  
ing criteria to establish the locality degree of two 1D  
interacting oscillators [34, 35]. We shall follow the same  
line to establish the strategy to obtain a reasonable esti-  
256 mation of the force constants for two interacting 2D  
oscillators.

This article is **organised** as follows. In Section 2 the  
main ingredients of the  $U(3)$  model to describe the bend-  
ing modes of a triatomic molecule are presented, as well  
261 as the connection with coordinates and momenta fol-  
lowing the approach presented in Ref. [30]. Section 3 is  
devoted to **analyse** two interacting oscillators, establish-  
ing the locality criterion. In Section 4 the Hamiltonian  
up to quartic order for two bending degrees of freedom  
266 is proposed, first in a local mode scheme and thereafter  
in the framework of a normal mode scheme. The con-  
nection between both schemes are considered through  
a canonical transformation. The  $U(3)$  model is applied  
after an anharmonization process. In Section 5 the the-  
271oretical framework is applied to the bending degrees of  
freedom of acetylene. Finally, in Section 6 the summary  
and our conclusions are presented.

## 2. The $U(3)$ algebraic approach

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In this section we present the main ingredients of the  
 $U(3)$  model to describe the bending degrees of free-  
dom of a triatomic molecule. The goal is to establish the  
expansion of the coordinates and momenta in terms of  
281 generators of the group, and provide the physical insight  
associated with the different subgroup chains. Although  
simple we need to start with the **2D-harmonic** oscillator.

### 2.1. 2D-harmonic oscillator

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Let us consider the bending modes of a linear triatomic  
molecule of type  $\text{XY}_2$  described in terms of the local  
coordinates [37]

$$q_a = r_e \mathbf{e}_y \cdot \frac{\mathbf{r}_1 \times \mathbf{r}_2}{r_1 r_2}; \quad q_b = -r_e \mathbf{e}_x \cdot \frac{\mathbf{r}_1 \times \mathbf{r}_2}{r_1 r_2}, \quad (1) \quad 291$$

where  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are vectors from the central X-atom to  
each one of the Y-atoms. The unit vectors  $\mathbf{e}_x$  and  $\mathbf{e}_y$  lie on  
the direction of the X- and Y-axis of the laboratory axis  
system, with its origin in the molecular's **centre** of mass. 296  
The coordinates  $q_a$  and  $q_b$  are then associated with Carte-  
sian coordinates with corresponding conjugate momenta  
 $p_a$  and  $p_b$  respectively. Since in linear molecules the angu-  
lar momentum projection  $l$  is preserved, it is convenient  
to introduce the circular coordinates  $Q_{\pm}$  with corre-  
299 sponding conjugate momenta defined by  $P_{\alpha} = \partial T / \partial \dot{Q}_{\alpha}$ :

$$Q_{\pm} = \mp \frac{1}{\sqrt{2}}(q_a \pm iq_b); \quad P_{\pm} = \mp \frac{1}{\sqrt{2}}(p_a \mp ip_b). \quad (2)$$

The Hamiltonian up to quadratic order may be expressed  
306 in terms of the Cartesian coordinates

$$\hat{H}_{cs} = \frac{1}{2}g_{aa}^o(p_a^2 + p_b^2) + \frac{1}{2}f_{aa}(q_a^2 + q_b^2). \quad (3)$$

where  $g_{aa} = 1/\mu$ , or in terms of the circular coordinates

$$\hat{H}_{cs} = -g_{+-}^o P_+ P_- - f_{+-} Q_+ Q_-, \quad (4) \quad 311$$

with the identification  $g_{+-}^o = g_{aa}^o$  and  $f_{+-} = f_{aa}$ . We can  
translate the Hamiltonian into Fock space by introducing  
the bosonic operators

$$\hat{\tau}_{\pm}^{\dagger} = \frac{1}{\sqrt{2}} \left[ \sqrt{\frac{\omega\mu}{\hbar}} Q_{\pm} + i \frac{P_{\mp}}{\sqrt{\hbar\omega\mu}} \right], \quad (5) \quad 316$$

with their corresponding adjoint conjugates. Here we  
have introduced the frequency  $\omega = \sqrt{f_{aa}g_{aa}^o}$  of the two  
degenerate oscillators. In this space the Hamiltonian  
takes thus the form

$$\hat{H}_{\text{Fock}} = \frac{\hbar\omega}{2} \sum_{\sigma} (\tau_{\sigma}^{\dagger} \tau_{\sigma} + \tau_{\sigma} \tau_{\sigma}^{\dagger}); \quad \sigma = \pm, \quad (6) \quad 321$$

which is diagonal in the basis

$$|n^l\rangle = N_{nl} (\tau_{+}^{\dagger})^{(n+l)/2} (\tau_{-}^{\dagger})^{(n-l)/2} |0\rangle; \quad 326$$

$$N_{nl} = \frac{1}{\sqrt{\binom{n+l}{2}! \binom{n-l}{2}!}} \quad (7)$$

where

$$\hat{n} = \tau_+^\dagger \tau_+ + \tau_-^\dagger \tau_-; \quad \hat{l} = \tau_+^\dagger \tau_+ - \tau_-^\dagger \tau_- \quad (8)$$

The operators

$$G_{SU(2)} = \left\{ \hat{j}_z = \frac{1}{2} \hat{l}; \quad \hat{j}_+ = \tau_+^\dagger \tau_-, \quad \hat{j}_- = \tau_-^\dagger \tau_+ \right\}, \quad (9)$$

satisfy the angular momentum commutation relations, and consequently are generators of the  $SU(2)$  group. The set (9) preserves the total number of quanta:  $[\hat{H}, \hat{n}] = 0$ , which means that  $U(2)$  is the symmetry group for a **2D-harmonic** oscillator. The states (7) are **labelled** according to the group chain

$$SU(2) \supset SO(2), \quad (10)$$

where  $\hat{l}$  is generator of the rotation subgroup  $SO(2)$ . The expression (6) together with coordinates and momenta

$$Q_\pm = \frac{1}{\sqrt{2}} \sqrt{\frac{\hbar}{\omega\mu}} (\tau_\pm^\dagger - \tau_\mp);$$

$$P_\pm = -\frac{i}{\sqrt{2}} \sqrt{\hbar\omega\mu} (\tau_\mp^\dagger + \tau_\pm), \quad (11)$$

are the representation in Fock space of the Hamiltonian, coordinates and momenta respectively. Their matrix elements given in Appendix 1 reproduce in exact form the matrix elements calculated in configuration space.

## 2.2. $U(3)$ algebraic space

The  $U(3)$  space is constructed by adding a scalar boson  $\sigma^\dagger(\sigma)$  to the 2D oscillator space by considering the nine possible bilinear products  $\{\xi_i^\dagger \xi_j; \quad i, j = 1, 3\}$  with  $\xi_1 = \sigma$  and  $\xi_2, \xi_3 = \tau_+, \tau_-$ . It is customary to write the generators of the  $U(3)$  group in the following form [19]:

$$\hat{Q}_\pm = \sqrt{2} \tau_\pm^\dagger \tau_\mp, \quad (12)$$

$$\hat{n}_\sigma = \sigma^\dagger \sigma, \quad (13)$$

$$\hat{D}_\pm = \sqrt{2} (\pm \tau_\pm^\dagger \sigma \mp \sigma^\dagger \tau_\mp), \quad (14)$$

$$\hat{R}_\pm = \sqrt{2} (\tau_\pm^\dagger \sigma + \sigma^\dagger \tau_\mp) \quad (15)$$

besides (8). The model introduces the constraint

$$\hat{N} = \hat{n} + \hat{n}_\sigma, \quad (16)$$

which makes the  $U(3)$  group the dynamical group for the system of a 2D oscillator. On the other hand the algebra

$U(3)$  contains the three angular momentum preserving chains

$$U(3) \supset U(2) \supset SO(2), \quad (17)$$

$$U(3) \supset SO(3) \supset SO(2), \quad (18)$$

$$U(3) \supset \overline{SO}(3) \supset SO(2), \quad (19)$$

each of them providing with a dynamical symmetry. Chain (17) contains the physical chain (10). Chains (18) contains the new group  $SO(3)$  with generators

$$G_{SO(3)} = \{D_+, D_-, \hat{l}\}, \quad (20)$$

while for the group **characterising** the chain (19) we have

$$G_{\overline{SO}(3)} = \{R_+, R_-, \hat{l}\}. \quad (21)$$

It is worth mentioning that a Hamiltonian involving chains (17) and (18) has been used to describe the linear-to-bent transition in triatomic molecules based on the transition between the dynamical symmetries [38]. As a consequence of our work, the linear-to-bent transition may be **analysed** starting from configuration space [39].

The simplest basis to carry out the calculations is the one associated with chain (17) because of its simplicity and nearness with the physical chain (10). In fact, the explicit form is constructed in terms of three harmonic oscillators

$$|[N]; nl\rangle = \mathcal{N}_{Nnl} (\sigma^\dagger)^{N-n} (\tau_+^\dagger)^{(n+l)/2} (\tau_-^\dagger)^{(n-l)/2} |0\rangle, \quad (22)$$

with **normalisation** constant

$$\mathcal{N}_{Nnl} = \frac{1}{\sqrt{(N-n)! \binom{n+l}{2}! \binom{n-l}{2}!}}, \quad (23)$$

and branching rules  $n = N, N-1, N-2, \dots, 0$  and  $l = \pm n, \pm(n-2), \dots, \pm 1$  or 0. The matrix elements of the generators (12) in the basis (22) are straightforward to calculate and are given in Appendix 2.

In the framework of this approach the Hamiltonian as well as any dynamical variable is expanded in terms of powers and products of the generators (8) and (12). On the other hand the algebraic representation of the Hamiltonian associated with a given system may be chosen as an expansion in terms of Casimir operators of groups associated with only one chain. In this case a dynamical symmetry is present and the eigenstates are **labelled** with the eigenvalues of the Casimir operators. For example the Casimir operators for chain (17) are  $\{N, \hat{n}, \hat{l}^2\}$  and consequently the simplest dynamical symmetry up to quadratic order is

$$\hat{H}_{\text{alg}}^{U(3)} = E_0 + \alpha \hat{n} + \beta \hat{n}^2 + \gamma \hat{l}^2. \quad (24)$$

From this point of view this dynamical symmetry may be broken by introducing additional Casimir operators

441 belonging to another chain in case we want to improve  
 the description of a given system. It is known that  
 chain (17) with its corresponding dynamical sym-  
 metry (24) is associated with the bending mode of linear  
 molecules, a fact that is reinforced because it contains  
 446 the chain (10) as remarked before. A reasonable question  
 which arises is concerned with the connection between  
 the Hamiltonians in configuration space (3) or (4) with  
 (24). The answer to this question is basically equivalent  
 to obtain the algebraic representation of coordinates and  
 451 momenta in the  $U(3)$  algebraic space  $\mathcal{A}$ , which represents  
 the key to translate any dynamical operator into  $\mathcal{A}$ ,  
 opening the possibility to obtain the parameters  $\{\alpha, \beta\}$  in  
 terms of the structure and force constant  $\{f_{aa}, g_{aa}\}$ . This  
 problem is addressed in next subsection.

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### 2.3. Connection between algebraic and configuration space

461 The main problem we are concerned about is how to  
 establish the correspondence between configuration and  
 algebraic spaces. In this subsection we shall follow the  
 approach presented in Ref. [30]. We achieve this goal we  
 should first establish the mapping between the dynamical  
 symmetry (17) and the **2D-harmonic** oscillator, which  
 466 is defined in configuration space by the Hamiltonian  
 $\hat{H}_{cs}(q, p)$  with eigensystem

$$\hat{H}_{cs}(\mathbf{q}, \mathbf{p})\psi_{n,l}(\mathbf{q}) = E_n\psi_{n,l}(\mathbf{q}), \quad (25)$$

471 where  $\mathbf{q}, \mathbf{p}$  denote the corresponding coordinates and  
 momenta, respectively, with  $\hat{H}_{cs}$  given by (3). The same  
 problem can be formulated in a second **quantised** form  
 (Fock space) as

$$476 \quad \hat{H}_{\text{Fock}}|n^l\rangle = E_n|n^l\rangle \quad \text{where} \quad \psi_{n,l}(\mathbf{q}) = \langle \mathbf{q} | n^l \rangle, \quad (26)$$

where  $|n^l\rangle$  is given by (7). We thus look for an equivalent  
 algebraic Hamiltonian  $\hat{H}_{\text{alg}}^{U(3)}$  in the  $U(3)$  space written in  
 terms of the corresponding algebra generators such that

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$$\hat{H}_{\text{alg}}^{U(3)}|[N]; nl\rangle = E_n|[N]; nl\rangle, \quad (27)$$

Comparing (26) with (27) the natural mapping (not  
 necessarily an isomorphism) between the eigenstates in  
 486 configuration and algebraic spaces can be proposed to be

$$|n^l\rangle \cong |[N]; nl\rangle; \quad n = 0, 1, \dots, N. \quad (28)$$

491 The importance of establishing this mapping stems from  
 the fact that the matrix elements of any operator can be  
 calculated indistinctly either in the algebraic  $\mathcal{A}$  or in the  
 physical (configuration)  $\mathcal{C}$  space.

Given the mapping (28), we start our approach by  
 496 introducing the density operator

$$\hat{\rho} = \sum_{nl} p_{nl} |n^l\rangle \langle n^l| = \sum_{n=0}^N \sum_l p_{nl} |[N]; nl\rangle \langle [N]; nl|, \quad (29)$$

with **normalisation**  $\sum_{n=0}^N \sum_l p_{nl} = 1$ . This density oper-  
 ator is general, with the only restriction that it is diagonal  
 in the eigenstates of the Hamiltonian. The weights  $p_{nl}$   
 may represent a thermal distribution according to the  
 Boltzmann distribution, but also may be used as a mathe-  
 506 matical tool. We now address the problem of establishing  
 an algebraic **realisation** of a general operator  $\hat{\mathcal{F}}_{cs}$  in con-  
 figuration space. Since we have established the mapping  
 involving the harmonic oscillator functions, it is enough  
 511 to propose the linear expansion

$$\hat{\mathcal{F}}_{\text{alg}} \approx \sum_{s,m} \alpha_s^{(m)}(\mathcal{F}_{cs}) \hat{Y}_s \hat{P}_m, \quad (30)$$

461 where  $\hat{Y}_s$  are generators of the  $U(3)$  group,  $\hat{P}_m$  are projec-  
 tion operators on the algebraic basis  $\hat{P}_m = |[N]nl\rangle \langle [N]nl|$ ,  
 while the coefficients  $\alpha_s^{(m)}(\mathcal{F}_{cs})$  are determined with the  
 criterion that they are to be the best given the proposed  
 expansion (30). Here we are interested in  $\hat{\mathcal{F}}_{cs}$  identified  
 521 with coordinates and momenta, but a more general sit-  
 uation may be considered [30]. The best selection of the  
 coefficients  $\alpha_s^{(m)}(\mathcal{F}_{cs})$  leads to solve the set of equations  
 [30]

$$\sum_s \alpha_s^{(m)}(\mathcal{F}_{cs}) \langle m | \hat{Y}_r^\dagger \hat{\rho} \hat{Y}_s | m \rangle = \langle m | \hat{Y}_r^\dagger \hat{\rho} \hat{\mathcal{F}}_{cs} | m \rangle, \quad (31)$$

476 where here the state  $|m\rangle$  denotes a general state  $|[N]; nl\rangle$ .  
 Notice that because of the mapping (28) to determine  
 the action of the operator  $\hat{\mathcal{F}}_{cs}$  we make the substitution  
 $|[N]; nl\rangle \rightarrow |n^l\rangle$ .

Let us now consider the coordinates  $Q_\pm$  and momenta  
 $P_\pm$  as the operator  $\hat{\mathcal{F}}_{cs}$  with a linear expansion in terms  
 536 of the generators

$$Y_1 = \tau_+^\dagger \sigma, \quad Y_2 = \sigma^\dagger \tau_-, \quad Y_3 = \tau_-^\dagger \sigma, \quad Y_4 = \sigma^\dagger \tau_+. \quad (32)$$

Taking into account the matrix elements given in  
 Appendix 2, the matrix elements involved in (31) turn out  
 541 to be diagonal

$$\langle m | \hat{Y}_r^\dagger \hat{\rho} \hat{Y}_s | m \rangle = p_\omega \delta_{r,s} |\langle \omega | \hat{Y}_r | m \rangle|^2, \quad (33)$$

491 If in addition we consider the matrix elements of  $Q_\pm$  and  
 $P_\pm$  in the harmonic oscillator basis given in Appendix 1,

551 we have that

$$\langle m | \hat{Y}^{\dagger r} \hat{\rho} \hat{\mathcal{F}}_{cs} | m \rangle = p_{\omega} \langle \omega | \hat{Y}_r | m \rangle^* \langle \omega | \hat{\mathcal{F}}_{cs} | m \rangle, \quad (34)$$

and consequently

$$\alpha_r^{(m)} = \frac{p_{\omega} \langle \omega | \hat{\mathcal{F}}_{cs} | m \rangle}{p_{\omega} \langle \omega | \hat{Y}_r | m \rangle} = \frac{\langle n' | \hat{\mathcal{F}}_{cs} | n' \rangle}{\langle [N]; n' | \hat{Y}_r | [N]; n \rangle}. \quad (35)$$

561 We should notice that the weights of the density matrix have been simplified. Substitution of the corresponding matrix elements in (35) yields

$$\begin{aligned} Q_{\pm} &= \sqrt{\frac{\hbar}{2\omega\mu}} \sum_m \left[ \frac{1}{\sqrt{N-n}} \tau_{\pm}^{\dagger} \sigma - \frac{1}{\sqrt{N-n+1}} \sigma^{\dagger} \tau_{\mp} \right] P_m, \quad (36) \end{aligned}$$

$$\begin{aligned} P_{\pm} &= -\frac{i}{\sqrt{2}} \sqrt{\hbar\omega\mu} \sum_m \left[ \frac{1}{\sqrt{N-n}} \tau_{\mp}^{\dagger} \sigma + \frac{1}{\sqrt{N-n+1}} \sigma^{\dagger} \tau_{\pm} \right] P_m. \quad (37) \end{aligned}$$

576 **Q3** The matrix elements of the operators (36) in the  $U(2)$  basis coincides with the matrix elements given in Appendix 1 for the **2D-harmonic** oscillator. Hence following this approach we have obtained a faithful representation for the harmonic oscillator in the algebraic space.

581 Let us now ask for a linear approximation with state-independent coefficients. To accomplish this end we have to select a particular state through the weight factors in the density matrix, for instance

$$p_{1,1} = 1; \quad \text{and } p_{nl} = 0 \quad \text{otherwise}, \quad (38)$$

591 a condition that establishes the dominance in the thermal distribution of the first excited state. Taking into account this condition in (31) we obtain the state-independent realizations

$$Q_{\pm} = \sqrt{\frac{\hbar}{2\omega\mu}} \left[ \frac{1}{\sqrt{N}} \tau_{\pm}^{\dagger} \sigma - \frac{1}{\sqrt{N-1}} \sigma^{\dagger} \tau_{\mp} \right], \quad (39)$$

$$P_{\pm} = -\frac{i}{\sqrt{2}} \sqrt{\hbar\omega\mu} \left[ \frac{1}{\sqrt{N}} \tau_{\mp}^{\dagger} \sigma + \frac{1}{\sqrt{N-1}} \sigma^{\dagger} \tau_{\pm} \right]. \quad (40)$$

601 If in addition we take into account that  $N$  is large compared to unity (a fact that latter will be evident), we may **Q4** simplify the coefficients in (39) to the form

$$\begin{aligned} Q_{\pm} &= \sqrt{\frac{\hbar}{2\omega\mu}} \frac{1}{\sqrt{N}} \left[ \tau_{\pm}^{\dagger} \sigma - \sigma^{\dagger} \tau_{\mp} \right] \quad 606 \\ &= \pm \frac{1}{2} \sqrt{\frac{\hbar}{\mu\omega}} \frac{1}{\sqrt{N}} \hat{D}_{\pm}, \quad (41) \quad 611 \end{aligned}$$

$$\begin{aligned} P_{\pm} &= -\frac{i}{\sqrt{2}} \sqrt{\hbar\omega\mu} \frac{1}{\sqrt{N}} \left[ \sigma^{\dagger} \tau_{\pm} + \sigma \tau_{\mp}^{\dagger} \right] \\ &= -\frac{i}{2} \sqrt{\hbar\omega\mu} \frac{1}{\sqrt{N}} \hat{R}_{\mp}, \quad (42) \quad 616 \end{aligned}$$

where we have identified the generators of the  $U(3)$  given in (14) and (15).

The results (41) can also be obtained considering a **Q26** state-independent expansion 621

$$\hat{\mathcal{F}}_{\text{alg}} \approx \sum_s \alpha_s(\mathcal{F}_{cs}) \hat{Y}_s, \quad (43)$$

leading to the set of equations [33]

$$\sum_s \alpha_s(\mathcal{F}_{cs}) \text{Tr}(\hat{\rho} \hat{Y}_s \hat{Y}_q^{\dagger}) = \text{Tr}(\hat{\rho} \hat{\mathcal{F}}_{cs} \hat{Y}_q^{\dagger}). \quad (44) \quad 626$$

We now consider the physical situation where in the distribution of states the ground state dominates, a fact that it is taken into account by considering 631

$$p_{00} = 1 - 2\epsilon; \quad p_{1,1} = p_{1,-1} = \epsilon, \quad (45)$$

and taking the limit  $\epsilon \rightarrow 0$ . The result is again (41), **Q6** identification that do not represent just a practical result that allows manipulation of expressions, but is crucial 636 to apply the  $U(3)$  model keeping the connection with configuration space.

The realizations (41) suggest the introduction of the **Q7** normalised operators 641

$$b_{\pm}^{\dagger} \equiv \frac{\tau_{\pm}^{\dagger} \sigma}{\sqrt{N}}; \quad b_{\pm} \equiv \frac{\tau_{\pm} \sigma^{\dagger}}{\sqrt{N}}, \quad (46)$$

in such a way that the coordinates and momenta takes the form 646

$$\begin{aligned} Q_{\pm} &= \frac{1}{\sqrt{2}} \sqrt{\frac{\hbar}{\omega\mu}} (b_{\pm}^{\dagger} - b_{\mp}); \\ P_{\pm} &= -\frac{i}{\sqrt{2}} \sqrt{\hbar\omega\mu} (b_{\mp}^{\dagger} + b_{\pm}), \quad (47) \quad 651 \end{aligned}$$

which can be obtained from (11) through the anharmonization procedure

$$Q_{\pm} |_{\tau_{\pm} \rightarrow b_{\pm}} \rightarrow Q_{\pm}; \quad P_{\pm} |_{\tau_{\pm} \rightarrow b_{\pm}} \rightarrow P_{\pm}. \quad (48)$$

The difference between the bosonic  $\tau_{\pm}^{\dagger}(\tau_{\pm})$  and  $b_{\pm}^{\dagger}(b_{\pm})$  operators manifests through the commutation relations 656

$$\begin{aligned}
 661 \quad [\hat{b}_{\sigma'}, \hat{b}_{\sigma}^{\dagger}] &= \left\{ 1 - \frac{\hat{n}}{N} \right\} \delta_{\sigma'\sigma} - \frac{\tau_{\sigma'} \tau_{\sigma}}{N}; & \hat{H}_{\text{alg}}^{\text{U}(3)} &= -\frac{1}{2}g_{+-} (\mathcal{P}_+ \mathcal{P}_- + \mathcal{P}_- \mathcal{P}_+) & 716 \\
 [\hat{b}_{\sigma'}^{\dagger}, \hat{b}_{\sigma}^{\dagger}] &= [\hat{b}_{\sigma'}, \hat{b}_{\sigma}] = 0, & & -\frac{1}{2}f_{+-} (\mathcal{Q}_+ \mathcal{Q}_- + \mathcal{Q}_- \mathcal{Q}_+). & (54)
 \end{aligned}$$

666 and the corresponding matrix elements. Commutation relations (49) reduces to the usual bosonic commutation relation in the  $N$  large limit as reflected in the matrix elements 721

$$\begin{aligned}
 671 \quad \langle [N]; n+1, l \pm 1 | b_{\pm}^{\dagger} | [N]; nl \rangle & & \hat{H}_{\text{alg}}^{\text{U}(3)} &= \hbar\omega \left\{ \left( 1 - \frac{1}{2N} \right) \hat{n} + 1 - \frac{\hat{n}^2}{N} \right\}. & (55) & 726 \\
 & = \sqrt{\frac{(1-n/N)(n \pm l + 2)}{2}}, & & & & 
 \end{aligned}$$

$$\begin{aligned}
 676 \quad \langle [N]; n-1, l \mp 1 \pm 1 | b_{\pm} | [N]; nl \rangle & & \lim_{N \rightarrow \infty} \hat{H}_{\text{alg}}^{\text{U}(3)} &= \hat{H}_{\text{Fock}}. & (56) & 731 \\
 & = \sqrt{\frac{(1-(n-1)/N)(n \pm l)}{2}}, & & & & 
 \end{aligned}$$

681 calculated considering the results given in Appendix 2. Here we can appreciate an outstanding feature. Even though the mapping was carried out using the harmonic oscillator basis, the final result does not reproduces the harmonic case. Indeed the matrix elements of the the coordinate are modified by an anharmonic correction, which vanishes in the limit  $N \rightarrow \infty$ . The matrix elements(50) were used in previous works although using phenomenological arguments [26, 29]. 741

686 Let us now turn our attention to the commutation Q8 relations of the conjugate variables (39): 746

$$691 \quad [\mathcal{Q}_{\pm}, \mathcal{P}_{\pm}] = i\hbar \left\{ 1 - \frac{3\hat{n}}{N} \right\}, \quad (52)$$

while for the coordinates and momenta

$$\begin{aligned}
 696 \quad [\mathcal{Q}_+, \mathcal{Q}_-] &= -\frac{\hbar}{2\omega\mu} \left\{ \frac{\hat{l}}{N} \right\}; & & & & 751 \\
 [\mathcal{P}_+, \mathcal{P}_-] &= -\frac{\hbar\omega\mu}{2} \left\{ \frac{\hat{l}}{N} \right\}, & (53) & & & 
 \end{aligned}$$

701 which means that only in the limit  $N \rightarrow \infty$  the correct results are recovered. This is a quite important Q9 result that allows (39) to be identified with coordinates and momenta without any association with a particular potential. However from the practical point of view this implies that symmetric expressions must be considered in the Hamiltonian [33]. 761

711 Given the relations (47) we may now obtain the algebraic representation of any operator depending on coordinates and momenta. In particular, we are interested in the algebraic representation of the Hamiltonian (4). The anharmonization procedure provides the expression

Substitution of (47) into the Hamiltonian (54), gives rise to

$$\hat{H}_{\text{alg}}^{\text{U}(3)} = \hbar\omega \left\{ \left( 1 - \frac{1}{2N} \right) \hat{n} + 1 - \frac{\hat{n}^2}{N} \right\}. \quad (55)$$

The algebraic Hamiltonian presents an anharmonic correction that vanishes for fixed  $n$  in the harmonic limit:

$$\lim_{N \rightarrow \infty} \hat{H}_{\text{alg}}^{\text{U}(3)} = \hat{H}_{\text{Fock}}. \quad (56)$$

This means that the  $U(3)$  algebraic model take into account anharmonicities from the outset, a significant property from the practical point of view.

Let us come back to the chains associated to the dynamical group  $U(3)$ . Each chain is characterised by the central subgroup. Hence chain (17) is characterised by the subgroup  $U(2)$ , whose first order Casimir operator is  $\hat{C}_{su(2)} = \hat{n}$ . Since the Hamiltonian (55) is given in terms of the number operator, we may say that chain (17) provides the basis in the energy representation. The Casimir operator associated with the  $O(3)$  subgroup characterising chain (18) is given by  $\hat{C}_{SO(3)} = \hat{W}^2 = (1/2)(\hat{D}_+ \hat{D}_- + \hat{D}_- \hat{D}_+) + \hat{l}^2$ , which can be written in terms of the coordinates 746

$$\hat{W}^2 = N \frac{2\omega\mu}{\hbar} \mathcal{Q}^2 + \hat{l}^2, \quad (57)$$

and consequently, we may say that chain (18) provides the basis in the coordinate representation. Finally the Casimir operator for the subgroup  $\overline{SO}(3)$  is  $\hat{C}_{\overline{SO}(3)} = \hat{W}^2 = (1/2)(\hat{R}_+ \hat{R}_- + \hat{R}_- \hat{R}_+) + \hat{l}^2$ , or

$$\hat{W}^2 = N \frac{2}{\hbar\omega\mu} \mathcal{P}^2 + \hat{l}^2, \quad (58) \quad 756$$

which means that chain (19) gives the basis in the momentum representation. These results are summarised in Table 1 with the following definition for the 761

**Table 1.** Identification of the dynamical symmetries according to the energy, coordinates and momenta representation.

Chain	Basis	Representation	
$U(3) \supset U(2) \supset SO(2)$	$ [N]; n\rangle$	Energy	766
$U(3) \supset SO(3) \supset SO(2)$	$ [N]; \xi l\rangle$	Coordinates	
$U(3) \supset \overline{SO}(3) \supset SO(2)$	$ [N]; \zeta l\rangle$	Momenta	



771 eigenkets

$$\hat{n}|[N]; nl\rangle = n|[N]; nl\rangle, \quad (59)$$

$$\hat{W}^2|[N]; \zeta l\rangle = \zeta(\zeta + 1)|[N]; \zeta l\rangle, \quad (60)$$

$$\hat{W}^{-2}|[N]; \bar{\zeta} l\rangle = \bar{\zeta}(\bar{\zeta} + 1)|[N]; \bar{\zeta} l\rangle, \quad (61)$$

776 with common eigenvalues for the angular momentum projection.

Here we should stress the importance of the identification displayed in Table 1. The fact that the states (60) define coordinate representation means for instance that any function of the coordinate  $Q^2$  (preserving the angular momentum projection) is diagonal in such basis. Suppose for instance that we have the general Hamiltonian preserving the projection  $l$ :

$$\hat{H} = \frac{1}{\mu} \hat{\mathbf{p}}^2 + V(\sqrt{\mathbf{Q}^2}). \quad (62)$$

The matrix elements of this Hamiltonian in the energy representation may be written in the form

$$\mathbf{H} = \frac{1}{\mu} \mathbf{W}^\dagger \Lambda^{(P)} \mathbf{W} + \mathbf{T}^\dagger \Lambda^{(Q)} \mathbf{T}, \quad (63)$$

791 where  $\Lambda^{(P)}$  and  $\Lambda^{(Q)}$  are diagonal matrices in the momentum and coordinates representations respectively, and  $\mathbf{W}$  and  $\mathbf{T}$  correspond to the transformation brackets connecting to the energy representation. This fact has important practical consequences that deserves special attention by itself and will be considered in a forthcoming contribution [39].

### 3. Two 2D oscillators

By construction the  $U(3)$  model is local. This means that it can be applied in a straightforward way in molecules presenting a local mode behaviour with a good estimation of the force constants. For molecules with normal mode behaviour it is still possible to apply the model but through a canonical transformation. It is necessary however establish the validity of the transformation when the force constants are expected to be well estimated. The next to subsections are rather standard but we decided to include them in order to introduce the notation to be used throughout this work.

#### 3.1. Local mode scheme

816 Let us start introducing the local coordinates to describe two 2D oscillators associated with the bending modes of acetylene for instance. Following the notation of Figure 1, we have

$$q_{1a} = \sqrt{r_{e1}r_{e3}} \mathbf{e}_y \cdot \frac{\mathbf{r}_1 \times \mathbf{r}_3}{r_1 r_3};$$

H-C≡C-H

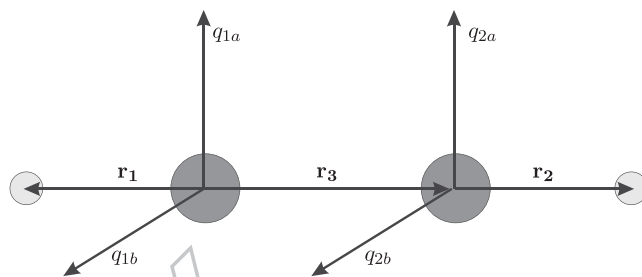


Figure 1. Coordinates chosen to describe the bending degrees of freedom of the acetylene molecule.

$$q_{1b} = -\sqrt{r_{e1}r_{e3}} \mathbf{e}_x \cdot \frac{\mathbf{r}_1 \times \mathbf{r}_3}{r_1 r_3} \quad (64)$$

$$q_{2a} = \sqrt{r_{e2}r_{e3}} \mathbf{e}_y \cdot \frac{(-\mathbf{r}_3) \times \mathbf{r}_2}{r_2 r_3};$$

$$q_{2b} = -\sqrt{r_{e2}r_{e3}} \mathbf{e}_x \cdot \frac{(-\mathbf{r}_3) \times \mathbf{r}_2}{r_2 r_3}. \quad (65)$$

In terms of these coordinates and associated momenta the Hamiltonian for two equivalent oscillators takes the form

$$\begin{aligned} \hat{H}_{cs} = & \frac{1}{2} g_{aa}^o \sum_{i=1}^2 (p_{ia}^2 + p_{ib}^2) + \frac{1}{2} f_{aa} \sum_{i=1}^2 (q_{ia}^2 + q_{ib}^2) \\ & + g_{1a2a}^o (p_{1a} p_{2a} + p_{1b} p_{2b}) + f_{1a2a} (q_{1a} q_{2a} + q_{1b} q_{2b}), \end{aligned} \quad (66)$$

while in terms of the circular coordinates

$$Q_{i\pm} = \mp \frac{1}{\sqrt{2}} (q_{ia} \pm i q_{ib});$$

$$P_{i\pm} = \mp \frac{1}{\sqrt{2}} (p_{ia} \mp i p_{ib}); \quad i = 1, 2, \quad (67)$$

we have

$$\begin{aligned} \hat{H}_{cs} = & - \left[ g_{aa}^o \sum_{i=1}^2 (P_{i+} P_{i-}) + f_{aa} \sum_{i=1}^2 (Q_{i+} Q_{i-}) \right] \\ & - g_{1a2a}^o (P_{1+} P_{2-} + P_{2+} P_{1-}) \\ & - f_{1a2a} (Q_{1+} Q_{2-} + Q_{1-} Q_{2+}). \end{aligned} \quad (68)$$

816 The representation in Fock space is obtained by introducing the bosonic operators through (11), but now for the two oscillators  $i = 1, 2$ :

$$Q_{i\pm} = \sqrt{\frac{\hbar}{2\omega\mu}} (\tau_{i\pm}^\dagger - \tau_{i\mp});$$

$$P_{i\pm} = -\frac{i}{\sqrt{2}} \sqrt{\hbar\omega\mu} (\tau_{i\mp}^\dagger + \tau_{i\pm}), \quad (69)$$

881 leading to

$$\begin{aligned}
 \hat{H}_{\text{Fock}} = & \frac{\hbar\omega}{2} \sum_{i=1}^2 (\tau_{i+}^\dagger \tau_{i+} + \tau_{i+} \tau_{i+}^\dagger + \tau_{i-}^\dagger \tau_{i-} + \tau_{i-} \tau_{i-}^\dagger) \\
 & + \frac{\hbar\omega}{2} \lambda (\tau_{1+}^\dagger \tau_{2+} + \tau_{1-}^\dagger \tau_{2-} + H.c.) \\
 & + \frac{\hbar\omega}{2} \lambda' (\tau_{1-}^\dagger \tau_{2+}^\dagger + \tau_{1+}^\dagger \tau_{2-}^\dagger + H.c.), \quad (70)
 \end{aligned}$$

891 where

$$\lambda = x_f + x_g; \quad \lambda' = x_g - x_f \quad (71)$$

with definitions

$$x_f = \frac{f_{1a2a}}{f_{aa}}; \quad x_g = \frac{g_{1a2a}^o}{g_{aa}^o}. \quad (72)$$

For the sake of convenience we now introduce the local polyad operator

$$\hat{P}_L = \hat{n}_1 + \hat{n}_2; \quad \hat{n}_i = \tau_{i+}^\dagger \tau_{i+} + \tau_{i-}^\dagger \tau_{i-}, \quad (73)$$

which in this case corresponds to the total number of quanta. The Hamiltonian (70) can be diagonalised using the basis of the direct product (7)

$$|n_1^{l_1} n_2^{l_2}\rangle = |n_1^{l_1}\rangle \otimes |n_2^{l_2}\rangle, \quad (74)$$

albeit with the problem of the non-preserving polyad. However, neglecting the third term that does not preserve the polyad  $P_L$ , the Hamiltonian may be approximated as

$$\begin{aligned}
 \hat{H}_{\text{Fock}}^{P_L} = & \frac{\hbar\omega}{2} \sum_{i=1}^2 (\tau_{i+}^\dagger \tau_{i+} + \tau_{i+} \tau_{i+}^\dagger + \tau_{i-}^\dagger \tau_{i-} + \tau_{i-} \tau_{i-}^\dagger) \\
 & + \frac{\hbar\omega}{2} \lambda (\tau_{1+}^\dagger \tau_{2+} + \tau_{1-}^\dagger \tau_{2-} + H.c.) \quad (75)
 \end{aligned}$$

921 with spectroscopic parameters given by

$$\omega = \sqrt{f_{aa} g_{aa}^o}; \quad \lambda = x_f + x_g. \quad (76)$$

926 We may thus carry out a fit of energy levels and estimate the force constant through (76). The question which arises is concerned with the validity of using (76) having neglected the non-preserving polyad contribution. This point is relevant since the standard treatment for a local-to-normal mode analysis consists in assuming the polyad preserving Hamiltonian (75). A detail analysis of this question needs the equivalence with the normal mode description.

### 3.2. Normal mode scheme

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The Hamiltonian (66) is quadratic and consequently it can be transformed to diagonal form in terms of two independent harmonic oscillators. To this end we introduce the symmetry adapted coordinates

$$Q_{g,\sigma} = \frac{1}{\sqrt{2}}(-Q_{1\sigma} + Q_{2\sigma}); \quad Q_{u,\sigma} = \frac{1}{\sqrt{2}}(Q_{1\sigma} + Q_{2\sigma}) \quad (77)$$

$$P_{g,\sigma} = \frac{1}{\sqrt{2}}(-P_{1\sigma} + P_{2\sigma}); \quad P_{u,\sigma} = \frac{1}{\sqrt{2}}(P_{1\sigma} + P_{2\sigma}), \quad (78)$$

where  $\sigma = \pm$  and  $g, u$  as an abbreviation of  $\Sigma_g^+, \Sigma_u^+$ , respectively. Taking into account (77) the Hamiltonian (66) acquires the diagonal form

$$\begin{aligned}
 \hat{H}_{\text{cs}} = & -[g_{gg}^o P_{g,+} P_{g,-} + f_{gg} Q_{g,+} Q_{g,-}] \\
 & - [g_{uu}^o P_{u,+} P_{u,-} + f_{uu} Q_{u,+} Q_{u,-}], \quad (79)
 \end{aligned}$$

where

$$g_{gg}^o = g_{aa}^o - g_{1a2a}^o; \quad g_{uu}^o = g_{aa}^o + g_{1a2a}^o; \quad (80)$$

$$f_{gg} = f_{aa} - f_{1a2a}; \quad f_{uu} = f_{aa} + f_{1a2a}. \quad (81)$$

We can obtain the Hamiltonian in the Fock space through the bosonic operators

$$\begin{aligned}
 \tau_{r,\sigma}^\dagger = & \frac{1}{\sqrt{2}} \left( \sqrt{\frac{\omega_r \mu_r}{\hbar}} Q_{r,\sigma} + i \frac{P_{r,-\sigma}}{\sqrt{\hbar \omega_r \mu_r}} \right); \\
 r = & g, u, \quad \sigma = +, -, \quad (82)
 \end{aligned}$$

which transform the Hamiltonian (79) into

$$\begin{aligned}
 \hat{H}_{\text{Fock}} = & \frac{\hbar\omega_g}{2} \sum_{\sigma} (\tau_{g,\sigma}^\dagger \tau_{g,\sigma} + \tau_{g,\sigma} \tau_{g,\sigma}^\dagger) \\
 & + \frac{\hbar\omega_u}{2} \sum_{\sigma} (\tau_{u,\sigma}^\dagger \tau_{u,\sigma} + \tau_{u,\sigma} \tau_{u,\sigma}^\dagger), \quad (83)
 \end{aligned}$$

where

$$\begin{aligned}
 \hbar\omega_g = & \hbar\omega \sqrt{(1 - x_g)(1 - x_f)}; \\
 \hbar\omega_u = & \hbar\omega \sqrt{(1 + x_g)(1 + x_f)}. \quad (84)
 \end{aligned}$$

981 Hamiltonians (70) and (83) are equivalent. They provide the same spectrum. However in the former Hamiltonian (70) the polyad  $P_L$  must be broken to recover the same force constants. In the next subsection we shall analyse the condition that allows the polyad preserving Hamiltonian (75) to be used with (76) in order to obtain reasonable force constants values [34, 35].

991 **3.3. Normal-to-local mode transition**

Taking into account the connection between the local and normal coordinates and momenta (69) and (82) in configuration space, we obtain the Bogoliubov-type transformation between the normal and local bosonic operators

$$\tau_{g,+}^\dagger = \frac{1}{\sqrt{2}} \{f_{1g}(-\tau_{1,+}^\dagger + \tau_{2,+}^\dagger) + f_{2g}(-\tau_{1,-} + \tau_{2,-})\}, \quad (85)$$

$$\tau_{u,+}^\dagger = \frac{1}{\sqrt{2}} \{f_{1u}(\tau_{1,+}^\dagger + \tau_{2,+}^\dagger) + f_{2u}(\tau_{1,-} + \tau_{2,-})\} \quad (86)$$

with coefficients

$$\begin{aligned} f_{1g} &= \frac{(r+1)}{2\sqrt{r}}; & f_{2g} &= \frac{(1-r)}{2\sqrt{r}}; \\ f_{1u} &= \frac{(s+1)}{2\sqrt{s}}; & f_{2u} &= \frac{(1-s)}{2\sqrt{s}}, \end{aligned}$$

where we have introduced the following definitions

$$r = \sqrt{\frac{1-x_f}{1-x_g}}, \quad s = \sqrt{\frac{1+x_f}{1+x_g}}. \quad (87)$$

The polyad concept, as a pseudo quantum number encompassing sets of states connected by the main interactions, is defined in the normal scheme. For acetylene for example the polyad for the bending modes is defined as the total number of quanta

$$\hat{P}_N = \hat{n}_g + \hat{n}_u; \quad \hat{n}_\alpha = \tau_{\alpha,+}^\dagger \tau_{\alpha,+} + \tau_{\alpha,-}^\dagger \tau_{\alpha,-}, \quad \alpha = g, u. \quad (88)$$

In general there is no coincidence with the local polyad (73), a fact that is reflected by their connection obtained by the substitution of (85) into (88) yielding

$$\begin{aligned} \hat{P}_N &= \zeta_0 + \beta_0 \hat{P}_L + \beta_1 (\tau_{1,+}^\dagger \tau_{2,+} + \tau_{1,-}^\dagger \tau_{2,-} \\ &\quad + \tau_{2,+}^\dagger \tau_{1,+} + \tau_{2,-}^\dagger \tau_{1,-}) \\ &\quad + \gamma_1 (\tau_{1,+}^\dagger \tau_{1,-}^\dagger + \tau_{2,+}^\dagger \tau_{2,-}^\dagger + \tau_{1,+} \tau_{1,-} + \tau_{2,+} \tau_{2,-}) \\ &\quad + \gamma_2 (\tau_{1,+}^\dagger \tau_{2,-}^\dagger + \tau_{1,-}^\dagger \tau_{2,+}^\dagger + \tau_{1,+} \tau_{2,-} + \tau_{1,-} \tau_{2,+}), \end{aligned} \quad (89)$$

where

$$\zeta_0 = \frac{4}{8rs} [s(r-1)^2 + r(s-1)^2], \quad (90)$$

$$\beta_0 = \frac{2}{8rs} [s(r^2+1) + r(s^2+1)], \quad (91)$$

$$\beta_1 = \frac{2}{8rs} [r(s^2+1) - s(r^2+1)], \quad (92)$$

$$\gamma_1 = \frac{2}{8rs} [s(1-r^2) + r(1-s^2)], \quad (93)$$

$$\gamma_2 = \frac{2}{8rs} [r(1-s^2) - s(1-r^2)]. \quad (94)$$

This shows that in general  $\hat{P}_N \neq \hat{P}_L$ . The question which arises is concerned with the condition under which  $\hat{P}_L \approx \hat{P}_N$  beyond the trivial condition

$$|x_f| \rightarrow 0; \quad |x_g| \rightarrow 0, \quad (95)$$

which implies  $r=s=1$ . As a first step to answer this question we introduce the unitary transformation:

$$\tau_{g,\sigma}^\dagger = \frac{1}{\sqrt{2}} (-c_{1,\sigma}^\dagger + c_{2,\sigma}^\dagger), \quad \tau_{u,\sigma}^\dagger = \frac{1}{\sqrt{2}} (c_{1,\sigma}^\dagger + c_{2,\sigma}^\dagger). \quad (96)$$

When (96) is inserted into the Hamiltonian (83) one obtains

$$\begin{aligned} \hat{H}_{\text{Fock}}^{PL} &= \frac{\hbar \omega_{\text{nor}}}{2} \sum_{i=1}^2 (c_{i+}^\dagger c_{i+} + c_{i+} c_{i+}^\dagger + c_{i-}^\dagger c_{i-} + c_{i-} c_{i-}^\dagger) \\ &\quad + \frac{\hbar \lambda_{\text{nor}}}{2} (c_{1+}^\dagger c_{2+} + c_{1-}^\dagger c_{2-} + H.c.), \end{aligned} \quad (97)$$

where

$$\omega_{\text{nor}} = \frac{\omega}{2} \left( \sqrt{(1-x_f)(1-x_g)} + \sqrt{(1+x_f)(1+x_g)} \right), \quad (98)$$

$$\lambda_{\text{nor}} = \omega \left( \sqrt{(1+x_f)(1+x_g)} - \sqrt{(1-x_f)(1-x_g)} \right). \quad (99)$$

Notice that the local operators  $c_{i,\pm}^\dagger (c_{i,\pm})$  do not correspond to the physical local operators  $\tau_{i,\pm}^\dagger (\tau_{i,\pm})$ , but their action on an isomorphic local basis may be chosen to be the same. Indeed, we may establish the isomorphism

$$c_{i,\pm}^\dagger \leftrightarrow \tau_{i,\pm}^\dagger, \quad c_{i,\pm} \leftrightarrow \tau_{i,\pm}. \quad (100)$$

The Hamiltonians (70) and (97) are equivalent in the sense that both provide the same spectrum in the local basis (74). However the connection between the spectroscopic parameters and the force and structure constants is different. Given the origin of the Hamiltonian (70) a coincidence of the spectroscopic coefficients for molecules with a local mode behaviour is expected. In order to elucidate the conditions to be satisfied without falling to the obvious case (95) a Taylor series expansion of the spectroscopic parameters (98) is carried out as a function of the variables  $x_f$  and  $x_g$  around zero [35]. Keeping only the

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1101 quadratic terms in  $x_f$  and  $x_g$ , we obtain

$$\omega_{\text{nor}} = \frac{\omega}{2}; \quad \lambda_{\text{nor}} = \omega(x_f + x_g), \quad (101)$$

as long as the condition

$$1106 \quad \gamma \equiv \frac{1}{8}(x_f - x_g)^2 \ll 1 \quad (102)$$

is satisfied. Since we know that (102) should be consistent with the strict local limit (95), this condition should be considered together with

$$1111 \quad |x_f| \ll 1; \quad |x_g| \ll 1. \quad (103)$$

Hence the conditions (102) and (103) assures the recovery of the spectroscopic parameters associated with the interacting local oscillators. This limit has consequences in the polyad definition. The expansion of the functions  $r$  and  $s$  in terms of the variables  $x_f$  and  $x_g$  are when

Q13 substituted into (90) reduces to

$$\beta_0 \approx 1; \quad \zeta_0 = \beta_i \approx 0; \quad i = 1, 2, 3. \quad (104)$$

1121 after applying the local limit (102–103), and consequently

$$\hat{P}_N \approx \hat{P}_L. \quad (105)$$

Under this situation the Bogoliubov-type transformation Q14 (85) reduces to the canonical transformation (96), widely applied in the analysis of the local-to-normal mode transition leading to the  $x_i$ - $K$  relations [40–48]. This analysis shows that there is a local-to-normal mode transition closely related with the preservation of the local polyad. In Refs. [34, 35] this transition has been studied for two equivalent stretching modes using tools of quantum mechanics like probability densities, fidelity and entropy, besides classical methods in the framework of Poincaré sections. A remarkable result is the existence of chaos in the region where the local polyad  $P_L$  stops being preserved.

1136 The suitability to estimate the force constants at the zeroth order is closely related to the condition (102). We may estimate the force constants either using the local or the normal mode descriptions in terms of the fundamental energies  $E_g$  and  $E_u$ . In general the obtained values are expected to be different. In the framework of the local description the one-quantum kets

$$1146 \quad |\Psi_g^\pm\rangle = \frac{1}{\sqrt{2}}(|1^\pm, 0\rangle - |0, 1^\pm\rangle), \quad (106)$$

$$|\Psi_u^\pm\rangle = \frac{1}{\sqrt{2}}(|1^\pm, 0\rangle + |0, 1^\pm\rangle), \quad (107)$$

are eigenkets of the Hamiltonian (75) with eigenvalues

$$1151 \quad E_g = \hbar\omega(1 - \lambda/2); \quad E_u = \hbar\omega(1 + \lambda/2), \quad (108)$$

where we have taken into account that the fundamentals are measured with respect to the ground state. From these

**Table 2.** Force constants as a function of the spectroscopic parameters for both local and normal mode schemes. 1156

Local mode scheme	Normal mode scheme
$f_{aa} = \frac{1}{h^2 g_{aa}^2} \left( \frac{E_g + E_u}{2} \right)^2$	$f_{aa} = \frac{(1+\epsilon)}{2(1-x_g)} \frac{E_g^2}{h^2 g_{aa}^2}$
$f_{1a2a} = f_{aa} \left( \frac{E_u - E_g}{(E_g + E_u)/2} - \frac{g_{1a2a}^0}{g_{aa}^0} \right)$	$f_{1a2a} = f_{aa} \left( \frac{\epsilon - 1}{\epsilon + 1} \right)$
$f_{aa} \rightarrow F_{aa}; \quad f_{1a2a} \rightarrow F_{1a2a}$	$\epsilon = \left( \frac{E_u}{E_g} \right)^2 \left( \frac{1-x_g}{1+x_g} \right)$

Notes: The definition of the parameter  $\eta$  in (109) involves the comparison of the force constants obtained from both schemes. For sake of clarity we map the force constants obtained from the local scheme to capital letters as indicated in the last row of the left column and used in (109). 1166

expressions and (76) we obtain the force constants given at the left column of Table 2. On the other hand from the Hamiltonian (83) and the frequencies (84) we obtain the force constants associated with the normal scheme and displayed at the right column of the same Table 2. The expressions for these force constants are different. This discrepancy may be measured by the parameters [35] 1171

$$1176 \quad \eta = \frac{\epsilon_1 + \epsilon_2}{2}; \quad \epsilon_1 = \left| 1 - \frac{f_{rr}}{F_{rr}} \right|, \quad \epsilon_2 = \left| 1 - \frac{f_{rr'}}{F_{rr'}} \right|. \quad (109)$$

where we have used the notation  $F_{rr}, F_{rr'}$  for the constants extracted from the local mode scheme to make the distinction from the constants  $f_{rr}, f_{rr'}$  obtained through the normal mode description. The parameter  $\eta$  represents a measure of confidence to calculate the force constants from a local model. It vanishes in the local limit and increases as the molecular system manifests a normal mode behaviour. In the same venue it is also convenient to introduce the parameter [34, 35] 1186

$$\zeta = \left| \frac{2}{\pi} \arctan \left( \frac{E_g - E_u}{(E_g + E_u)/2} \right) \right|, \quad (110)$$

1191 which provides a measure of locality degree. This is explained by the fact that in the pure local limit the splitting of the interacting levels vanishes and increases as the interaction becomes relevant [36].

This analysis shows that starting with a local mode behaviour there should be a transition region where the equality  $\hat{P}_L = \hat{P}_N$  stop being valid as well as the estimation of the correct force constants at zeroth order in a local model. We thus need the fundamentals in order to estimate the locality degree and proceed accordingly to choose the appropriate scheme for the calculation of the force constants [34, 35]. 1201

#### 4. An example: bending modes of acetylene

In this section, we analyse the approach to follow for two equivalent bending interacting oscillators in case we were interested in obtaining the corresponding force constants. As an example, we consider the bending modes 1206

1211 of the acetylene molecule. The bending modes of this  
 molecule **have** been extensively studied from the spec-  
 troscopic point of view [49–51] but also from the point  
 of view of dynamics in the context of bifurcation the-  
 ory [52]. Among the most recent contributions the works  
 1216 by R. Field *et al.* deserve special attention because of the  
 detection of improved dispersed fluorescence data set for  
 acetylene  $\tilde{A}^1A_u \rightarrow \tilde{X}^1\Sigma_g^+$  emission [53, 54]. In particular  
 detail studies of the bending modes has been presented  
 [55–57]. In this work, we do not intend to improve such  
 1221 spectroscopic description, but rather to focus on the cri-  
 terion to estimate the force constants. **Although** our the-  
 oretical model involves interactions up to quartic order  
 and an optimum spectroscopic description require sixth  
 order [55, 56], to estimate the force constants of second  
 1226 order is enough our approximation.

The equilibrium geometry of acetylene is linear with  
 structure parameters  $r_e^{\text{CH}} = 1.064$  and  $r_e^{\text{CC}} = 1.206$  Å  
 [58]. The symmetry group is  $D_{\infty h}$ . This molecule has 7  
 vibrational degrees of freedom, two of them associated  
 1231 with the CH stretching modes with symmetries  $\Sigma_g^+$  and  
 $\Sigma_u^+$  with standard notation  $\nu_1$  and  $\nu_3$ , one CC stretching  
 mode  $\Sigma_g^+$  with notation  $\nu_2$ , and two degenerate bending  
 modes  $\Pi_g^\pm$  and  $\Pi_u^\pm$ , with notation  $\nu_4$  and  $\nu_5$ , respec-  
 tively. In this standard notation the harmonic basis is then  
 1236 **labelled** by [59]

$$|v\rangle = |v_1 v_2 v_3 v_4^4 v_5^5\rangle. \quad (111)$$

The fundamental frequencies are (in  $\text{cm}^{-1}$ ) [55]:

$$\begin{aligned} \omega_1 &= 3372.87; & \omega_2 &= 1974.32; \\ \omega_3 &= 3288.68; & \omega_4 &= 612.098; & \omega_5 &= 726.835. \end{aligned} \quad (112)$$

1246 The following resonances associated with the stretching  
 modes have been identified

$$5\omega_2 \approx 3\omega_1; \quad 2\omega_1 \approx 2\omega_3, \quad (113)$$

1251 while for the bending modes

$$2\omega_4 \approx 2\omega_5. \quad (114)$$

Finally for the stretching-bending interactions the reso-  
 nances are

$$\begin{aligned} \omega_3 &\approx \omega_2 + \omega_4 + \omega_5; & \omega_1 &\approx \omega_2 + 2\omega_4; \\ \omega_1 &\approx \omega_2 + 2\omega_5; & \omega_1 + \omega_4 &\approx \omega_3 + \omega_5. \end{aligned} \quad (115)$$

1261 These resonances leads to the identification of the  
 polyads [7]

$$N_{\text{res}} = 5\nu_1 + 3\nu_2 + 5\nu_3 + \nu_4 + \nu_5;$$

$$N_s = \nu_4 + \nu_5; \quad l = l_4 + l_5. \quad (116) \quad 1266$$

Polyad  $N_{\text{res}}$  involves the stretching-bending interactions  
 while  $N_s$  reflects the preservation of the total number of  
 bending quanta. The last condition in (116) stands for the  
 conservation of the quantum numbers associated with  
 1271 the symmetry of the system. The interactions associated  
 with all these resonances have been identified in terms  
 of effective interactions [56]. The aim of our work is to  
 apply our analysis in the subspace of bending interactions  
 where the polyad  
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$$P_N = \nu_4 + \nu_5 \quad (117)$$

is preserved. To accomplish this end we need to carry out  
 the vibrational analysis in both local and normal mode  
 schemes. 1281

To start the spectroscopic description an estimation of  
 the locality degree must be done. Using the fundamental  
 bending frequencies (112) we obtain for the parameter  
 (110) the result  $\zeta = 0.11$ . This value is similar to the  
 parameter for  $\text{SO}_2$ , which is **characterised** by presenting  
 a normal mode **behaviour** in the framework of the tra-  
 ditional analysis of local-normal transition models. This  
 fact suggests that a local model is in on the verge of  
 estimating the force constants. Just for comparison, the  
 stretching modes of acetylene yields  $\zeta = 0.016$ , which  
 1291 reflects a strong local **behaviour**. From the fundamentals  
 and the matrix elements

$$\begin{aligned} g_{aa}^o &= \frac{r_e^{\text{CC}}}{r_e^{\text{CH}}} \frac{1}{m_H} + \frac{(r_e^{\text{CH}} + r_e^{\text{CC}})^2}{r_e^{\text{CH}} r_e^{\text{CC}}} \frac{1}{m_C}; \\ g_{1a2a}^o &= -\frac{2(r_e^{\text{CH}} + r_e^{\text{CC}})}{r_e^{\text{CC}}} \frac{1}{m_C}, \end{aligned} \quad (118) \quad 1296$$

we present in Table 3 the force constants estimated from  
 the expressions given in Table 2. The parameters intro-  
 duced in the previous section as a locality criterion are  
 also displayed. These results **indicate** that a local mode  
 description for the bending modes of acetylene induces  
 an error in the calculation of the forces at the level of har-  
 monic approximation. We shall proceed to carry out the  
 1306 analysis using a spectroscopic fit to prove the consistency  
 of our conclusion.

We proceed with a local mode description and then  
 move to the normal mode description to calculate the  
 force constants in both schemes in the full context of a  
 spectroscopic analysis. In this way we shall be in position  
 to see whether our conclusion is still valid. 1311

#### 4.1. Hamiltonian in the local mode scheme 1316

In the framework of **generalised** coordinates, omit-  
 ting terms not involving momentum operators in the

1321 **Table 3.** Force constants (units J/m<sup>2</sup>) estimated in accordance with Table 2 and the parameters (109) as well as the parameters providing the locality criterion. 1376

Mode	$f_{aa}$	$F_{aa}$	$f_{1a2a}$	$F_{1a2a}$	$\gamma$	$\eta$	$\zeta$
Bends	19.6912	18.0007	7.2927	6.9314	0.043	0.073	0.11
Stretches	603.83	603.92	-15.2627	-15.2627	0.079(-3)	0.079(-3)	0.016

1326 Notes: For comparison both bending and stretching modes are considered. Parenthesis means power of 10:  $x(-n) = x^{-n}$ . 1381

kinetic energy, the quantum mechanical Hamiltonian that describes the vibrational excitations takes the form [60]

$$\hat{H} = \frac{1}{2} \mathbf{p}^\dagger \mathbf{G}(\mathbf{t}) \mathbf{p} + V(\mathbf{t}), \quad (119)$$

where  $\mathbf{t}$  and  $\mathbf{p}$  are column vectors corresponding to the generalised coordinates and their conjugate momenta  $\hat{p}_k = -i\hbar(\partial/\partial t_k)$ , respectively, while  $\mathbf{G}(\mathbf{t})$  is matrix connecting the general coordinates  $\mathbf{t}$  and Cartesian coordinates  $x_{i\zeta}$  of the  $N$  atoms [61]:

$$g_{p,q}(\mathbf{t}) = \sum_{\zeta} \sum_i \frac{1}{m_i} \frac{\partial t_p}{\partial x_{i\zeta}} \frac{\partial t_q}{\partial x_{i\zeta}}; \quad \zeta = x, y, z; \quad i = 1, N, \quad (120)$$

where  $\mathbf{G}$  is intended to be calculated as a function of the local coordinates.

In our description, the matrix elements of the Wilson matrix, as well as the potential function, are calculated in terms of the local coordinates [62]. In general, the explicit form of the expansion depends on the polyad to be considered. The polyad however is strictly defined in the normal mode scheme as  $\hat{P}_N = \hat{v}_4 + \hat{v}_5$ , which have the translation

$$\hat{P}_L = \hat{n}_1 + \hat{n}_2 = \hat{P}_N, \quad (121)$$

as long as the approximations (102–103) are valid. One of the goals of our work consists in deriving the consequences of considering (105) in a local mode treatment in systems where the parameter  $\zeta$  does not manifest a clear local mode behaviour. In other words, is it valid to assume polyad preserving Hamiltonians in a local mode scheme? This has been the case in previous works where it is considered the approximation (121). This has been the case by Lehmann [43] and M. Jacobson *et al.* [57] for instance.

Since in our contribution we focus on showing the approach to connect the algebraic description with configuration space, we shall consider the simple case of taking up to quartic order in the Hamiltonian. We shall assume harmonic limit. Latter on in Section 4.3 the application of the algebraic model will be discussed. In this

case, the Hamiltonian may be written as

$$\hat{H}_{cs}^L = \hat{H}^{L[2]} + \hat{H}^{L[4]}, \quad (122)$$

where  $\hat{H}^{L[2]}$  involves the quadratic order interactions, while the contribution  $\hat{H}^{L[4]}$  carries the quartic order interactions in the local mode scheme. Because (121) is expected to be preserved, cubic terms do not appear. Hence, considering the discussion of the previous section we have for quadratic order

$$\begin{aligned} \hat{H}_{cs}^{L[2]} = & - \left[ g_{aa}^o \sum_{i=1}^2 (P_{i+} P_{i-}) + f_{aa} \sum_{i=1}^2 (Q_{i+} Q_{i-}) \right] \\ & - g_{1a2a}^o (P_{1+} P_{2-} + P_{2+} P_{1-}) \\ & - f_{1a2a} (Q_{1+} Q_{2-} + Q_{1-} Q_{2+}). \end{aligned} \quad (123)$$

On the other hand for quartic order it is convenient to split the contributions in kinetic and potential energies:

$$\hat{H}^{L[4]} = \hat{T}^{L[4]} + \hat{V}^{L[4]}. \quad (124)$$

For the kinetic energy we have

$$\begin{aligned} T^{L[4]} = & \frac{1}{4} \left( \frac{\partial^2 g_{1+,1+}}{\partial Q_{1+}^2} \right)_0 (P_{1+} Q_{1+}^2 P_{1+} + P_{2+} Q_{2+}^2 P_{2+} \\ & + H.c.) + \frac{1}{2} \left( \frac{\partial^2 g_{1+,1-}}{\partial Q_{1+} \partial Q_{1-}} \right)_0 (P_{1+} Q_{1+} Q_{1-} P_{1-} \\ & + P_{2+} Q_{2+} Q_{2-} P_{2-} + H.c.) + \frac{1}{2} \left( \frac{\partial^2 g_{1+,2+}}{\partial Q_{1+} \partial Q_{2+}} \right)_0 \\ & \times (P_{1+} Q_{1+} Q_{2+} P_{2+} + P_{2+} Q_{2+} Q_{1+} P_{1+} + H.c.) \\ & + \frac{1}{2} \left( \frac{\partial^2 g_{1+,2-}}{\partial Q_{1+} \partial Q_{2-}} \right)_0 (P_{1+} Q_{1+} Q_{2-} P_{2-} \\ & + P_{1-} Q_{1-} Q_{2+} P_{2+} + H.c.) \\ & + \frac{1}{2} \left( \frac{\partial^2 g_{1+,2-}}{\partial Q_{1-} \partial Q_{2+}} \right)_0 (P_{1+} Q_{1-} Q_{2+} P_{2-} \\ & + P_{1-} Q_{1+} Q_{2-} P_{2+} + H.c.) + \frac{1}{4} \left( \frac{\partial^2 g_{1+,2+}}{\partial Q_{1+}^2} \right)_0 \\ & \times (P_{1+} Q_{1+}^2 P_{2+} + P_{1-} Q_{1-}^2 P_{2-} + H.c.) \\ & + \frac{1}{2} \left( \frac{\partial^2 g_{1+,2-}}{\partial Q_{1+} \partial Q_{1-}} \right)_0 (P_{1+} Q_{1+} Q_{1-} P_{2-} \end{aligned} \quad (125)$$

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$$\begin{aligned}
1431 \quad & + P_{1-} Q_{1-} Q_{1+} P_{2+} + P_{2+} Q_{2+} Q_{2-} P_{1-} \\
& + P_{2-} Q_{2-} Q_{2+} P_{1+} + H.c.) \quad (125)
\end{aligned}$$

while for the potential energy

$$\begin{aligned}
1436 \quad V^{L[4]} &= \frac{6}{4!} f_{1+1+1-1-} (Q_{1+}^2 Q_{1-}^2 + Q_{2+}^2 Q_{2-}^2) \\
&+ \frac{6}{4!} f_{1+1+2-2-} (Q_{1+}^2 Q_{2-}^2 + Q_{2+}^2 Q_{1-}^2) \\
1441 \quad &+ \frac{4!}{4!} f_{1+1-2+2-} Q_{1+} Q_{1-} Q_{2+} Q_{2-} \\
&+ \frac{12}{4!} f_{1+1+1-2-} (Q_{1+}^2 Q_{1-} Q_{2-} \\
&+ Q_{2+}^2 Q_{2-} Q_{1-} + H.c.) \quad (126)
\end{aligned}$$

1446 We now proceed to obtain the algebraic representation of the Hamiltonian (122) by introducing the algebraic realizations (67). Proceeding in this manner we obtain

$$\begin{aligned}
1451 \quad \hat{H}_{\text{Fock}}^L &= \frac{\tilde{\omega}}{2} \sum_{i,\sigma} (\tau_{i,\sigma}^\dagger \tau_{i,\sigma} + \tau_{i,\sigma} \tau_{i,\sigma}^\dagger) + \lambda \hat{\Lambda}_+ \\
&+ x_{11} (\hat{n}_1^2 + \hat{n}_2^2) + x_{12} \hat{n}_1 \hat{n}_2 + x_{\mu\lambda} \hat{n} \hat{\Lambda}_+ \\
&+ g_{11} (\hat{l}_1^2 + \hat{l}_2^2) + g_{12} \hat{l}_1 \cdot \hat{l}_2 + g_{\lambda\mu} (\hat{l}_1 + \hat{l}_2) \hat{\Lambda}_- \\
1456 \quad &+ K_{11/22} \hat{D}_{11/22} + L_{11/22} \hat{\Delta}_{11/22} + r_{12} \hat{R}_I^{12}, \quad (127)
\end{aligned}$$

where we have introduced the definition

$$1461 \quad \hat{\Lambda}_\pm = \tau_{1,+}^\dagger \tau_{2,+} \pm \tau_{1,-}^\dagger \tau_{2,-} + H.c., \quad (128)$$

with the resonance operators

$$1466 \quad \hat{D}_{11/22} = \tau_{1+}^\dagger \tau_{1-}^\dagger \tau_{2+} \tau_{2-} + H.c., \quad (129)$$

$$\hat{\Delta}_{11/22} = \tau_{1+}^\dagger \tau_{1+}^\dagger \tau_{2+} \tau_{2+} + \tau_{1-}^\dagger \tau_{1-}^\dagger \tau_{2-} \tau_{2-} + H.c., \quad (130)$$

$$1471 \quad \hat{R}_I^{12} = \tau_{1+}^\dagger \tau_{1-} \tau_{2-}^\dagger \tau_{2+} + H.c. \quad (131)$$

The spectroscopic parameters involved in (127) are given in terms of the force and structure constants as shown in Appendix 3.

## 1476 4.2. Hamiltonian in the normal mode scheme

The description of two interacting oscillators may also be described in a normal mode scheme. We also start from Hamiltonian (119) but now the matrix  $\mathbf{G}$  will be considered as a function of normal coordinates, which in turn are given in terms of local coordinates. Calling  $G_{\alpha,\beta}$  the matrix elements in the normal scheme and  $g_{p,q}$  the matrix

elements in the local coordinates, and considering  $\mathbf{S}$  as the matrix connecting both schemes:

$$Q_\alpha = \sum_p s_{p,\alpha} t_p; \quad t_p = \sum_\alpha s_{p,\alpha}^* Q_\alpha; \quad (132)$$

we have that

$$G_{\alpha,\beta} = \sum_{p,q} s_{p,\alpha} g_{p,q} s_{q,\beta}, \quad (133)$$

with the relation

$$(Q_{4+}, Q_{4-}, Q_{5+}, Q_{5-}) = (q_{1a}, q_{1b}, q_{2a}, q_{2b}) \mathbf{S} \quad (134)$$

and explicit form for the  $\mathbf{S}$  matrix:

$$\mathbf{S} = \frac{1}{2} \begin{pmatrix} 1 & -1 & -1 & 1 \\ i & i & -i & -i \\ -1 & 1 & -1 & 1 \\ -i & -i & -i & -i \end{pmatrix}. \quad (135)$$

Our description consists in expanding the matrix elements of the Wilson matrix as well as the potential function in terms of the normal coordinates [62]. In general, the explicit form of the expansion depends on the polyad to be considered. For convenience in this section, we shall introduce the following notation for the coordinates and momenta

$$Q_{g,\sigma} \rightarrow Q_{4\sigma}; \quad Q_{u\sigma} \rightarrow Q_{5,\sigma}, \quad (136)$$

in accordance with the standard notation for the bending modes. As noticed before in our case the polyad to be considered is

$$\hat{P}_N = \hat{\nu}_4 + \hat{\nu}_5, \quad (137)$$

where the number operators  $\nu_\alpha$  are define by

$$\hat{\nu}_4 = \tau_{4,+}^\dagger \tau_{4,+} + \tau_{4,-}^\dagger \tau_{4,-}, \quad (138)$$

$$\nu_5 = \tau_{5,+}^\dagger \tau_{5,+} + \tau_{5,-}^\dagger \tau_{5,-}. \quad (139)$$

We again consider the simple case of taking up to quartic order in the Hamiltonian. In this case, the Hamiltonian may be written as

$$\hat{H}_{cs}^N = \hat{H}^{N[2]} + \hat{H}^{N[4]}, \quad (140)$$

where  $\hat{H}^{N[2]}$  involves the quadratic order interactions, while the contribution  $\hat{H}^{N[4]}$  carries the quartic order interactions. Again because the polyad (137) is expected to be preserved, cubic terms do not appear. Hence, considering the discussion of the previous section we have for quadratic order

$$\hat{H}^{N[2]} = -[g_{44}^o P_{4,+} P_{4,-} + f_{44} Q_{4,+} Q_{4,-}]$$

$$1541 \quad - [g_{55}^0 P_{5,+} P_{5,-} + f_{55} Q_{5,+} Q_{5,-}]. \quad (141)$$

On the other hand for quartic order it is **convenient** to split the contributions in kinetic and potential energies:

$$1546 \quad \hat{H}^{N[4]} = \hat{T}^{N[4]} + \hat{V}^{N[4]}. \quad (142)$$

For the kinetic energy we have

$$1551 \quad T^{N[4]} = \frac{1}{4} \left( \frac{\partial^2 G_{4+,4+}}{\partial Q_{4+}^2} \right)_0 (P_{4+} Q_{4+}^2 P_{4+} + H.c.)$$

$$1556 \quad + \frac{1}{4} \left( \frac{\partial^2 G_{5+,5+}}{\partial Q_{5+}^2} \right)_0 (P_{5+} Q_{5+}^2 P_{5+} + H.c.)$$

$$1556 \quad + \frac{1}{4} \left( \frac{\partial^2 G_{4+,4+}}{\partial Q_{5+}^2} \right)_0 (P_{4+} Q_{5+}^2 P_{4+} + H.c.)$$

$$1561 \quad + \frac{1}{4} \left( \frac{\partial^2 G_{5+,5+}}{\partial Q_{4+}^2} \right)_0 (P_{5+} Q_{4+}^2 P_{5+} + H.c.)$$

$$1561 \quad + \frac{1}{2} \left( \frac{\partial^2 G_{4+,5+}}{\partial Q_{4+} \partial Q_{5-}} \right)_0 (P_{4+} Q_{4+} Q_{5+} P_{5+}$$

$$1566 \quad + P_{5+} Q_{5+} Q_{4+} P_{4+} + H.c.)$$

$$1566 \quad + \frac{1}{2} \left( \frac{\partial^2 G_{4+,5-}}{\partial Q_{4+} \partial Q_{5-}} \right)_0 (P_{4+} Q_{4+} Q_{5-} P_{5-}$$

$$1571 \quad + P_{5-} Q_{5-} Q_{4+} P_{4+} + H.c.)$$

$$1571 \quad + \frac{1}{2} \left( \frac{\partial^2 G_{4+,5-}}{\partial Q_{5+} \partial Q_{4-}} \right)_0 (P_{4+} Q_{4-} Q_{5+} P_{5-}$$

$$1571 \quad + P_{5-} Q_{5+} Q_{4-} P_{4+} + H.c.), \quad (143)$$

while for the potential energy

$$1576 \quad V^{N[4]} = \frac{6}{4!} f_{4+4+4-4-} Q_{4+}^2 Q_{4-}^2$$

$$1581 \quad + \frac{6}{4!} f_{5+5+5-5-} Q_{5+}^2 Q_{5-}^2$$

$$1581 \quad + \frac{4!}{4!} f_{4+4-5+5-} Q_{4+} Q_{4-} Q_{5+} Q_{5-}$$

$$1581 \quad + \frac{6}{4!} f_{4+4+5-5-} (Q_{4+} Q_{4+} Q_{5-} Q_{5-} + H.c.). \quad (144)$$

1586 The derivatives are calculated using the chain rules, giving rise to the expression

$$1591 \quad \left( \frac{\partial^2 G_{\alpha,\beta}}{\partial Q_\gamma \partial Q_\delta} \right)_0 = \sum_{p,q,u,v} s_{p,\alpha} s_{q,\beta} s_{u,\gamma}^* s_{v,\delta}^* \left( \frac{\partial^2 g_{p,q}}{\partial t_u \partial t_v} \right)_0. \quad (145)$$

1591 Here the derivatives in the local scheme are calculated using the approach followed for linear triatomic molecules in Ref. [63]. In contrast to the sums involved

in (133), the sums over  $u,v$  involves both bending and stretching coordinates given by

$$q_1 = r_1; \quad q_2 = r_2; \quad q_3 = r_3; \quad (146)$$

with the corresponding symmetry adapted coordinates

$$Q_1 = \frac{1}{\sqrt{2}}(q_1 + q_2); \quad Q_2 = q_3; \quad Q_3 = \frac{1}{\sqrt{2}}(q_1 - q_2), \quad (147)$$

in accordance with Hertzberg's notation and Figure 1. The new transformation matrix  $\mathbf{S}$  is defined through the equation

$$(Q_1, Q_2, Q_3, Q_{4+}, Q_{4-}, Q_{5+}, Q_{5-}) = (q_1, q_2, q_3, q_{1a}, q_{1b}, q_{2a}, q_{2b}) \mathbf{S} \quad (148)$$

with

$$\mathbf{S} = \frac{1}{2} \begin{pmatrix} \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 \\ \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ 0 & 0 & 0 & \frac{i}{2} & \frac{i}{2} & -\frac{i}{2} & -\frac{i}{2} \\ 0 & 0 & 0 & -\frac{1}{2} & \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ 0 & 0 & 0 & -\frac{i}{2} & -\frac{i}{2} & -\frac{i}{2} & -\frac{i}{2} \end{pmatrix}. \quad (149)$$

The explicit form of the derivatives (145) were calculated in order to be able to simplify the kinetic energy.

The next step to establish the Hamiltonian in the algebraic space consists in obtaining the representation in Fock space by introducing in (140) the transformation to bosonic operators (82). The result is

$$1631 \quad \hat{H}_{\text{Fock}}^N = \frac{\hbar\Omega_4}{2} \sum_{\sigma} (\tau_{4,\sigma}^\dagger \tau_{4,\sigma} + \tau_{4,\sigma} \tau_{4,\sigma}^\dagger)$$

$$1636 \quad + \frac{\hbar\Omega_5}{2} \sum_{\sigma} (\tau_{5,\sigma}^\dagger \tau_{5,\sigma} + \tau_{5,\sigma} \tau_{5,\sigma}^\dagger)$$

$$1636 \quad + x_{44} \hat{v}_4^2 + x_{55} \hat{v}_5^2 + x_{45} \hat{v}_4 \hat{v}_5 + g_{44} \hat{l}_4^2$$

$$1636 \quad + g_{55} \hat{l}_5^2 + g_{45} \hat{l}_4 \cdot \hat{l}_5 + K_{44/55} \hat{D}_{44/55}$$

$$1636 \quad + L_{44/55} \hat{\Delta}_{44/55} + r_{45} \hat{R}_l, \quad (150)$$

with the angular momentum operators

$$1641 \quad \hat{l}_4 = \tau_{4,+}^\dagger \tau_{4,+} - \tau_{4,-}^\dagger \tau_{4,-}, \quad (151)$$

$$1646 \quad \hat{l}_5 = \tau_{5,+}^\dagger \tau_{5,+} - \tau_{5,-}^\dagger \tau_{5,-}, \quad (152)$$

while for the non-diagonal contributions

$$1646 \quad \hat{D}_{44/55} = \tau_{4,+}^\dagger \tau_{4,-}^\dagger \tau_{5,+} \tau_{5,-} + H.c., \quad (153)$$



$$1651 \quad \hat{\Delta}_{44/55} = \tau_{4,+}^{\dagger 2} \tau_{5,+}^2 + \tau_{4,-}^{\dagger 2} \tau_{5,-}^2 + H.c., \quad (154)$$

$$1652 \quad \hat{R}_I = \tau_{4,+}^{\dagger} \tau_{4,-} \tau_{5,-}^{\dagger} \tau_{5,+} + H.c. \quad (155)$$

1656 The spectroscopic parameters involved in (150) are functions of the structure and force constants, with explicit expressions given in Appendix 4. The first interaction  $\hat{D}_{44/55}$  is known as the Darling Dennison Bend Resonance I, while (154) is the Darling Dennison Bend Resonance II. Finally the (155) corresponds to the Vibrational-1-Resonance. Their corresponding matrix elements in the harmonic basis (111) can be found in [56]. The Hamiltonians (127) and (150) are equivalent from the practical point of view: both reproduce the same energy spectroscopic description. Indeed the normal and local interactions are related as shown in Appendix 5, from which the  $\chi$ - $K$  relations are obtained and given in the same appendix. Both Hamiltonians are equivalent, the difference stands in the identification with the structure and force constants.

### 1671 4.3. Hamiltonian in the $U_1(3) \otimes U_2(3)$ model

1676 In order to apply the  $U(3)$ -model we first introduce the correct degrees of freedom by introducing the direct product  $U_1(3) \otimes U_2(3)$  as the dynamical symmetry of the two bending oscillators. A remarked before the algebraic model is local, which means that the natural scheme to apply the model is given through the Hamiltonian (127). In this case we proceed to apply the transformation

$$1681 \quad \tau_{j,\sigma}^{\dagger} \rightarrow b_{j,\sigma}^{\dagger} = \frac{\tau_{j,\sigma}^{\dagger} s}{\sqrt{N}}; \quad \tau_{j,\sigma} \rightarrow b_{j,\sigma} = \frac{\tau_{j,\sigma} s^{\dagger}}{\sqrt{N}}, \quad (156)$$

in the Hamiltonian to obtain

$$1686 \quad \hat{H}_{\text{Fock}}^L(\tau_{j,\sigma}^{\dagger}, \tau_{j,\sigma}) \Big|_{\tau_{\alpha,\sigma} \rightarrow c_{j,\sigma}} = \hat{H}_{\text{alg}}^{su_1(3) \oplus su_2(3)}(b_{j,\sigma}^{\dagger}, b_{j,\sigma}). \quad (157)$$

1691 In this procedure we should remark that errors due to (52) and (53) are carried, which we shall neglect due to the fact that  $N$  is assumed to be large.

1696 When bending modes present a normal mode **behaviour** this approach leads to ill force constants. In this case we should proceed to carry out a canonical transformation of type (96) as a first step to introduce local operators. Applying (96) in (150) we obtain a Hamiltonian of the form

$$1701 \quad \hat{H}_{\text{Fock}}^N = \hat{H}_{\text{Fock}}^N(c_{j,\sigma}^{\dagger}, c_{j,\sigma}); \quad j = 1, 2; \quad \sigma = \pm. \quad (158)$$

Hamiltonians (150) and (158) are equivalent in the sense that they give rise to the same energy spectrum in accordance with the isomorphism (100). Because two oscillators are involved in our description, the algebraic space

is the direct sum  $su_1(3) \oplus su_2(3)$ . The corresponding Hamiltonian  $H_{\text{alg}}^{su_1(3) \oplus su_2(3)}$  is obtained when we consider the substitution

$$1711 \quad c_{j,\sigma}^{\dagger} \rightarrow b_{j,\sigma}^{\dagger} = \frac{\tau_{j,\sigma}^{\dagger} s}{\sqrt{N}}; \quad c_{j,\sigma} \rightarrow b_{j,\sigma} = \frac{\tau_{j,\sigma} s^{\dagger}}{\sqrt{N}}, \quad (159)$$

1716 representing the anharmonization at the local level. This means that in practice the operators involved in the algebraic Hamiltonian (150) takes the form of an expansion in terms of local operators given in Appendix 5. Hence the algebraic Hamiltonian is constructed through the following steps: the transformation from **normal-to-local** bosons and then the anharmonization to  $U(3)$  operators. Schematically these steps are

$$1721 \quad \hat{H}_{\text{Fock}}^N(\tau_{\alpha,\sigma}^{\dagger}, \tau_{\alpha,\sigma}) \Big|_{\tau_{\alpha,\sigma} \rightarrow c_{j,\sigma}} = \hat{H}_{\text{Fock}}^N(c_{j,\sigma}^{\dagger}, c_{j,\sigma}) \Big|_{c_{j,\sigma} \rightarrow b_{j,\sigma}} \\ 1726 \quad = \hat{H}_{\text{alg}}^{su_1(3) \oplus su_2(3)}(b_{j,\sigma}^{\dagger}, b_{j,\sigma}). \quad (160)$$

This approach leads to a tensorial formalism where the algebraic Hamiltonian is given in terms of successive coupling of tensors as explicitly shown in Appendix 6. The resulting expansion of the interactions are then used to compute the matrix elements of the Hamiltonian. A practical point to remark is that a symmetric representation of the operators must be constructed in (150) since the normal operators do not commute anymore.

1736 A code follows internally this procedure without the need to write down the explicit form of the interactions in the local mode scheme. However they may be extracted from Appendix 5, since the connection between both schemes is given by all the interactions. Because of the normal mode **behaviour** manifested by acetylene its is expected that the predicted force constants will not equal than the obtained through the Hamiltonian (127) in the normal scheme. This will be shown in next section.

## 1746 5. Results

1751 We now proceed to carry out the spectroscopic description of the bending modes of acetylene. To accomplish this goal we consider the first 70 experimental energies embracing states up to polyad  $P_N = 14$ . We have carried out the energy fit using the Hamiltonian (150) with  $N = 400$ , obtaining a root mean square deviation of  $rms = 4.7 \text{ cm}^{-1}$ . The spectroscopic parameters associated with the local Hamiltonian (127) are obtained with help of the  $\chi$ - $K$  relation provided in Appendix 5. The deviation obtained is basically the same, as expected since both Hamiltonians are equivalent. The

1761 **Table 4.** Spectroscopic parameters in  $\text{cm}^{-1}$  obtained in the fit of involving the first 70 bending energy levels of acetylene.

Local mode scheme		Normal mode scheme	
$\tilde{\omega}$	668.95	$\tilde{\omega}_4$	608.23
$\lambda$	62.03	$\tilde{\omega}_5$	732.298
$x_{11}$	-1.092	$x_{44}$	3.339
$x_{12}$	-2.214	$x_{55}$	-2.916
$x_{n\lambda}$	-3.128	$x_{45}$	-3.508
$g_{11}$	4.839	$g_{44}$	1.442
$g_{12}$	-0.113	$g_{55}$	3.004
$g_{l\lambda'}$	0.781	$g_{45}$	6.433
$K_{11/22}$	5.567	$K_{44/55}$	-2.272
$L_{11/22}$	2.285	$L_{44/55}$	3.598
$r_{12}$	0.349	$r_{45}$	-7.490

Note: The deviation obtained was  $rms = 4.7 \text{ cm}^{-1}$  with a total number of bosons  $N = 400$ .

1776 **Table 5.** Comparison between theoretical and experimental energy levels in  $\text{cm}^{-1}$  obtained with the parameters displayed in Table 4.

	Poly	Nor.	Comp.	Exp	Theo.	$\Delta$
	$\Sigma^+g$					
	2	1 <sub>2</sub>	1.00	1230.4	1229.84	0.559
	2	2 <sub>2</sub>	1.00	1449.1	1452.8	-3.704
1781	4	1 <sub>2</sub> 2 <sub>2</sub>	0.592	2648.	2643.22	4.778
	4	2 <sub>4</sub>	0.997	2880.2	2882.9	-2.698
	6	1 <sub>6</sub>	0.986	3770.3	3767.2	3.096
	6	1 <sub>4</sub> 2 <sub>2</sub>	0.859	3942.5	3941.76	0.735
	8	1 <sub>8</sub>	0.928	5068.8	5072.86	-4.057
	8	1 <sub>6</sub> 2 <sub>2</sub>	0.894	5216.	5220.71	-4.713
1786	10	1 <sub>8</sub> 2 <sub>2</sub>	0.428	6386.1	6384.39	1.710
	10	1 <sub>10</sub>	0.696	6423.	6415.01	7.991
	10	1 <sub>6</sub> 2 <sub>4</sub>	0.478	6462.1	6463.91	-1.808
	10	1 <sub>6</sub> 2 <sub>4</sub>	0.519	6658.5	6654.15	4.351
	12	1 <sub>10</sub> 2 <sub>2</sub>	0.322	7733.6	7722.78	10.817
	12	1 <sub>12</sub>	0.705	7773.3	7767.85	5.454
	12	1 <sub>8</sub> 2 <sub>4</sub>	0.414	7808.5	7812.85	-4.346
	12	1 <sub>6</sub> 2 <sub>6</sub>	0.192	7836.	7841.97	-5.972
1791	12	1 <sub>8</sub> 2 <sub>4</sub>	0.180	7951.5	7952.77	-1.271
	14	1 <sub>12</sub> 2 <sub>2</sub>	0.437	9041	9055.79	-14.792
	14	1 <sub>8</sub> 2 <sub>6</sub>	0.495	9073.4	9082.4	-9.003
	14	1 <sub>8</sub> 2 <sub>6</sub>	0.209	9090.3	9093.46	-3.164
	14	1 <sub>14</sub>	0.396	9136.2	9136.	0.197
	14	1 <sub>6</sub> 2 <sub>8</sub>	0.657	9162.5	9164.31	-1.809
1796	$\Sigma^-g$					
	4	1 <sub>2</sub> 2 <sub>2</sub>	1.000	2661.2	2660.51	0.688
	$\Sigma^+u$					
	2	1 <sub>1</sub> 2 <sub>1</sub>	1.000	1328.1	1327.94	0.158
	4	1 <sub>3</sub> 2 <sub>1</sub>	1.00	2560.6	2556.61	3.991
	4	1 <sub>1</sub> 2 <sub>3</sub>	1.00	2757.8	2754.73	3.075
	$\Sigma^-u$					
1801	2	1 <sub>1</sub> 2 <sub>1</sub>	1.000	1340.5	1342.8	-2.297
	4	1 <sub>3</sub> 2 <sub>1</sub>	0.997	2583.8	2585.76	-1.961
	4	1 <sub>1</sub> 2 <sub>3</sub>	0.997	2783.6	2785.	-1.395

Notes: Here  $\Delta = E_{exp} - E_{theor}$ . The labelling of the normal states corresponds to  $1_{1/2} 2_{1/2}$ , where 1 and 2 stand for the  $\Pi_g$  and  $\Pi_u$  oscillators, respectively. The component corresponds to the square of the maximum component of the given state.

1806 difference stands in the identification of the spectroscopic parameters. In Table 4 the spectroscopic parameters are displayed. As expected the parameters in the normal mode scheme are similar to the ones obtained in Ref. [55].

1811 In Table 6 the comparison between of the experimental and theoretical energy levels is presented. Using the

**Table 6.** Comparison between theoretical and experimental energy levels in  $\text{cm}^{-1}$  obtained with the parameters displayed in Table 4.

Poly	Nor.	Comp.	Exp	Theo.	$\Delta$
$\Pi_g$					
1	1 <sub>1</sub>	1.000	612.9	613.039	-0.139
3	1 <sub>3</sub>	0.999	1855.7	1855.92	-0.220
3	1 <sub>1</sub> 2 <sub>2</sub>	0.513	2049.1	2047.97	1.125
3	1 <sub>1</sub> 2 <sub>2</sub>	0.513	2067.	2069.17	-2.171
$\Pi_u$					
1	2 <sub>1</sub>	1.000	730.3	732.379	-2.079
3	1 <sub>2</sub> 2 <sub>1</sub>	0.670	1941.2	1940.35	0.852
3	1 <sub>2</sub> 2 <sub>1</sub>	0.670	1960.9	1962.49	-1.590
3	2 <sub>3</sub>	0.999	2170.3	2173.81	-3.513
$\Delta g$					
2	1 <sub>2</sub>	0.999	1233.5	1235.38	-1.876
2	2 <sub>2</sub>	0.999	1463.	1465.33	-2.328
4	1 <sub>2</sub> 2 <sub>2</sub>	0.551	2666.1	2662.34	3.759
4	2 <sub>4</sub>	0.997	2894.1	2895.42	-1.321
6	1 <sub>6</sub>	0.985	3770.3	3772.73	-2.435
6	1 <sub>4</sub> 2 <sub>2</sub>	0.558	3949.5	3947.67	1.832
8	1 <sub>8</sub>	0.931	5068.8	5078.48	-9.680
8	1 <sub>6</sub> 2 <sub>2</sub>	0.395	5221.	5226.11	-5.107
10	1 <sub>8</sub> 2 <sub>2</sub>	0.447	6386.1	6390.78	-4.679
10	1 <sub>10</sub>	0.684	6423.	6420.21	2.792
10	1 <sub>6</sub> 2 <sub>4</sub>	0.452	6511.	6503.45	7.550
10	1 <sub>6</sub> 2 <sub>4</sub>	0.456	6664.5	6661.35	3.155
12	1 <sub>10</sub> 2 <sub>2</sub>	0.274	7733.6	7728.34	5.264
12	1 <sub>8</sub> 2 <sub>4</sub>	0.284	7753.9	7750.15	3.751
12	1 <sub>12</sub>	0.686	7773.3	7772.43	0.870
12	1 <sub>8</sub> 2 <sub>4</sub>	0.425	7814.	7816.14	-2.141
12	1 <sub>6</sub> 2 <sub>6</sub>	0.302	7843.	7838.61	4.393
14	1 <sub>12</sub> 2 <sub>2</sub>	0.242	9046.	9054.34	-8.335
14	1 <sub>12</sub> 2 <sub>2</sub>	0.172	9073.4	9069.13	4.270
14	1 <sub>8</sub> 2 <sub>6</sub>	0.254	9090.3	9083.88	6.417
14	1 <sub>6</sub> 2 <sub>8</sub>	0.131	9102.6	9105.23	-2.626
14	1 <sub>14</sub>	0.302	9143.5	9140.69	2.814
14	1 <sub>8</sub> 2 <sub>6</sub>	0.226	9162.5	9154.56	7.942
14	1 <sub>6</sub> 2 <sub>8</sub>	0.372	9238.	9235.89	2.112
$\Delta u$					
2	1 <sub>1</sub> 2 <sub>1</sub>	1.000	1347.5	1348.46	-0.958
4	1 <sub>3</sub> 2 <sub>1</sub>	0.748	2561.5	2561.91	-0.409
4	1 <sub>3</sub> 2 <sub>1</sub>	0.746	2589.7	2591.11	-1.405
4	1 <sub>1</sub> 2 <sub>3</sub>	0.915	2773.2	2769.47	3.729
4	1 <sub>1</sub> 2 <sub>3</sub>	0.913	2795.5	2795.73	-0.225

Notes: Here  $\Delta = E_{exp} - E_{theor}$ . The labelling of the normal states corresponds to  $1_{1/2} 2_{1/2}$ , where 1 and 2 stand for the  $\Pi_g$  and  $\Pi_u$  oscillators, respectively. The component corresponds to the square of the maximum component of the given state.

spectroscopic parameters given in Table 4, the derivatives of the Wilson matrix given in Table 7 and the relation between the force constants and the spectroscopic parameters presented in Appendices C and D, we obtain Table 8, where the estimation of the force constants are given for both schemes. Since at zeroth order, the same force constant may be involved in more than one spectroscopic parameter the table includes several effective force constants indicating in parenthesis the origin from the spectroscopic parameter.

From Table 8 we confirm the difference between the local and normal mode treatments concerning the calculation of the force constants of second order. This manifested difference implies that we are in the verge of considering valid the canonical transformation (96)

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1871 **Table 7.** Second order derivatives of the **G** matrix involved in the Hamiltonian (124) associated with the local mode description.

	Local mode scheme		Normal mode scheme	
	$\left(\frac{\partial^2 g_{1+1+}}{\partial Q_{1+}^2}\right)_0$	-1.3393(47)	$\left(\frac{\partial^2 G_{4+A+}}{\partial Q_{4+}^2}\right)_0$	-7.8577(46)
1876	$\left(\frac{\partial^2 G_{1+1-}}{\partial Q_{1+} \partial Q_{1-}}\right)_0$	-8.5434(46)	$\left(\frac{\partial^2 G_{5+S+}}{\partial Q_{5+}^2}\right)_0$	-5.7581(46)
	$\left(\frac{\partial^2 G_{1+2+}}{\partial Q_{1+} \partial Q_{2+}}\right)_0$	-2.2291(45)	$\left(\frac{\partial^2 G_{4+A+}}{\partial Q_{5+}^2}\right)_0$	-7.3212(46)
	$\left(\frac{\partial^2 G_{1+2-}}{\partial Q_{1+} \partial Q_{2-}}\right)_0$	-2.2679(44)	$\left(\frac{\partial^2 G_{5+S+}}{\partial Q_{4+}^2}\right)_0$	-5.4030(46)
1881	$\left(\frac{\partial^2 G_{1+2-}}{\partial Q_{1+} \partial Q_{2+}}\right)_0$	-2.4559(45)	$\left(\frac{\partial^2 G_{4+S+}}{\partial Q_{4+} \partial Q_{5+}}\right)_0$	-6.8079(46)
	$\left(\frac{\partial^2 G_{1+2+}}{\partial Q_{1+}^2}\right)_0$	-1.0044(46)	$\left(\frac{\partial^2 G_{4+S-}}{\partial Q_{4+} \partial Q_{5-}}\right)_0$	-4.3501(46)
	$\left(\frac{\partial^2 G_{1+2-}}{\partial Q_{1+} \partial Q_{1-}}\right)_0$	-1.3595(46)	$\left(\frac{\partial^2 G_{4+S-}}{\partial Q_{5+} \partial Q_{4-}}\right)_0$	-4.0818(46)

Note: Units are in  $\text{Kg}^{-1} \text{m}^{-2}$ . The parenthesis indicates power of 10.

1886 **Table 8.** Zereth order force constants extracted from the fits.

	Local mode scheme		Normal mode scheme	
	$f_{aa}$	0.17087	$f_{aa}$	0.2022
	$f_{1a2a}$	0.07211	$f_{1a2a}$	0.0778
1891	$f_{1+1+1-}$ ( $X_{11}$ )	-0.4491*	$f_{4+4+4-}$ ( $X_{44}$ )	0.04471
	( $g_{11}$ )	1.1174	( $g_{44}$ )	-0.01234
	$f_{1+1-2+2-}$ ( $X_{12}$ )	-0.047*	$f_{5+5+5-}$ ( $X_{55}$ )	-0.0223
	( $g_{12}$ )	0.0305	( $g_{55}$ )	-0.03137
	( $K_{1122}$ )	+0.0777		
	$f_{1+1+1-2-}$ ( $X_{n\lambda}$ )	-0.0664*	$f_{4+4-5+5-}$ ( $X_{45}$ )	-0.05312
	( $g_{n\lambda}$ )	-0.0039	( $k_{4455}$ )	-0.3324
1896	$f_{1+1+2-2-}$ ( $L_{11/22}$ )	0.1445*	$f_{4+4+5-5-}$ ( $L_{4455}$ )	-0.4226
	( $r_{12}$ )	0.0222	( $r_{45}$ )	0.1811

Notes: Particular attention must be paid to the second order derivatives which are different because of the normal mode character of the bending modes of acetylene. Units are in  $\text{aJ} \text{Å}^{-2}$  and  $\text{aJ} \text{Å}^{-4}$  for second and quartic derivatives respectively. The asterisk indicates the force constants used in the calculation of the second order constants.

1901 with the identification (100), a result assumed by previous analysis [51, 57].

1906 Although in Appendix 7 the relation between the force constants of quartic order are given, it is not possible to establish the relation between both schemes since a one-to-one correspondence does not exist at zeroth order.

## 1911 6. Summary and conclusions

1916 In this manuscript we have presented a linear realisation of the coordinates and momenta for the 2D-oscillator system in terms of the dynamic  $U(3)$  algebraic space. To accomplish this goal we have used the minimisation method previously presented in [30], using a mapping between the 2D-harmonic oscillator and the  $U(2)$  dynamical symmetry (17). The realisation obtained coincide with the algebraic representation previously used in the description of linear molecules [28, 29]. Since the  $U(3)$  algebraic realisation of the 2D-harmonic oscillator turns out to be diagonal in the  $U(2)$  basis, the chain (17) has been identified with the energy representation. In

1926 addition the coordinates and momenta have been associated to chains (18) and (19), respectively. This is a remarkable results which is translated into a powerful method to obtain the solutions of 2D Hamiltonians associated with any potential as sketched in (63) [39]. The advantages of the  $U(3)$  model may be summarised in 1931 the following aspects: a) the dynamical group is compact, (b) three dynamical symmetries emerge and (c) the total number of bosons  $N$  provides a measure of the dimension of the harmonic oscillator basis, although may be used as a parameter expected to be large. 1936

In order to establish the procedure to apply the the  $U(3)$  model, two interacting 2D oscillators have been analysed in detail. The goal is to establish the conditions to be satisfied in order to obtain reliable force constants at zeroth order. This study consisted in connecting the normal and local mode descriptions of the 2D oscillators, leading to the condition under which both local and normal polyads coincides. A relevant result of our analysis corresponds to the fact that depending on the interaction strength the appropriate approach used to describe the system may be either the normal or the local scheme. The appropriate selection of the scheme leads to the correct estimation of the force constants. The scheme to follow may be chosen following the criterion (110) based on the splitting of the fundamentals as well as the parameter  $\eta$  concerned with the difference of the force constants calculated with both schemes. 1941 1946 1951

As an example of our analysis, we have considered the bending modes of the acetylene molecule. From the fundamentals and the structure constants the obtained dimensionless parameters are  $\zeta = 0.11$  and  $\eta = 0.004$ , the former of which indicates that we are in the verge of the local limit treatment. We thus proceeded to check if indeed this was the case through an spectroscopic analysis by fitting the first 70 levels including up to polyad  $P_N = 14$ . We obtained a deviation of  $rms = 4.7$  using a parameter  $N = 400$ . This high value for  $N$  is consistent with the fact that only in the limit  $N \rightarrow \infty$  the algebraic realisation of the coordinates and momenta are identified with the physical coordinates. 1956 1961 1966

The vibrational problem was thus set up in both local and normal mode schemes. In the local mode scheme the procedure is straightforward and given by (157). The application of the  $U_1(3) \otimes U_2(3)$  model for systems with normal mode behaviour was carried out through two extra steps as indicated in (160). First a canonical transformation (96) going from bosonic normal mode operators to local bosonic operators was applied and thereafter the anharmonization (159) at the local level was considered. The latter step is crucial to take advantage of the  $U(3)$ -model. This approach does not have analogue in configuration space and it may be taken as the main 1971 1976

1981 feature of the algebraic model from the practical point of view.

The spectroscopic analysis for the acetylene molecule confirms the preliminary results displayed in Table 3. The bending modes in acetylene present an enough strong interaction to induce a difference in the estimation of the force constants. This difference, **however**, is not considered to be large in analysis where the force constants **do** not play a preponderant role, like in predictions of spectra for isotopologue species. This fact **justifies** the use of the canonical transformation (96) as an approximation Q16 to the Bogoliubov transformation (85). This approximation is implicit but not justified in previous works [51, 52, 55–57]. This approximation is explained by the locality of the stretching modes. The energy transfer **from** the CH stretches to the bends is not so important to induce a strong coupling between the CC bonds.

We have developed the application to acetylene, but the present theoretical framework can be applied to any linear molecule involving interacting bending oscillators.

### Disclosure statement

Q17, No potential conflict of interest was reported by the authors.

### Funding

This work is partially supported by Dirección General de Asuntos del Personal Académico, Universidad Nacional Autónoma de México DEGAPA-UNAM, Mexico, under project IN-227017. First author is grateful for the scholarship (Posgrado en Ciencias Químicas) provided by CONACyT, Mexico.

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## Appendices

### Appendix 1

- 2116 Here we list the matrix elements of the coordinates and momenta operators (11) in the basis (7):

$$\langle (n+1)^{l+1} | Q_+ | n^l \rangle = \sqrt{\frac{\hbar}{2\mu\omega}} \sqrt{\frac{n+l+2}{2}}, \quad (\text{A1})$$

$$\langle (n-1)^{l+1} | Q_+ | n^l \rangle = -\sqrt{\frac{\hbar}{2\mu\omega}} \sqrt{\frac{n-l}{2}}, \quad (\text{A2})$$

$$\langle (n+1)^{l-1} | Q_- | n^l \rangle = \sqrt{\frac{\hbar}{2\mu\omega}} \sqrt{\frac{n-l+2}{2}}, \quad (\text{A3})$$

$$\langle (n-1)^{l-1} | Q_- | n^l \rangle = -\sqrt{\frac{\hbar}{2\mu\omega}} \sqrt{\frac{n+l}{2}}, \quad (\text{A4})$$

$$\langle (n+1)^{l-1} | P_+ | n^l \rangle = -\frac{i}{\sqrt{2}} \sqrt{\hbar\mu\omega} \sqrt{\frac{n-l+2}{2}}, \quad (\text{A5})$$

$$\langle (n-1)^{l-1} | P_+ | n^l \rangle = -\frac{i}{\sqrt{2}} \sqrt{\hbar\mu\omega} \sqrt{\frac{n+l}{2}}, \quad (\text{A6})$$

$$\langle (n+1)^{l+1} | P_- | n^l \rangle = -\frac{i}{\sqrt{2}} \sqrt{\hbar\mu\omega} \sqrt{\frac{n+l+2}{2}}, \quad (\text{A7})$$

$$\langle (n-1)^{l+1} | P_- | n^l \rangle = -\frac{i}{\sqrt{2}} \sqrt{\hbar\mu\omega} \sqrt{\frac{n-l}{2}}. \quad (\text{A8})$$

### Appendix 2

The basic matrix elements in the  $U(3)$  model associated with the basis (17) given by (22), are the following

$$\langle [N+1]; nl | \sigma^\dagger | [N]; nl \rangle = \sqrt{N-n+1}, \quad (\text{A9}) \quad 2146$$

$$\langle [N+1]; n+1, l \pm 1 | \tau_\pm^\dagger | [N]; nl \rangle = \sqrt{\frac{n \pm l + 2}{2}}, \quad (\text{A10})$$

from which we obtain

$$\langle [N]; n+1, l+1 | \tau_+^\dagger \sigma | [N]; nl \rangle = \sqrt{\frac{(N-n)(n+l+2)}{2}}, \quad (\text{A11}) \quad 2151$$

$$\langle [N]; n-1, l-1 | \sigma^\dagger \tau_+ | [N]; nl \rangle = \sqrt{\frac{(N-n+1)(n+l)}{2}}, \quad (\text{A12}) \quad 2156$$

$$\langle [N]; n+1, l-1 | \tau_-^\dagger \sigma | [N]; nl \rangle = \sqrt{\frac{(N-n)(n-l+2)}{2}}, \quad (\text{A13})$$

$$\langle [N]; n-1, l+1+1 | \sigma^\dagger \tau_- | [N]; nl \rangle = \sqrt{\frac{(N-n+1)(n-l)}{2}}. \quad (\text{A14}) \quad 2161$$

### Appendix 3

Relation between the spectroscopic parameters and the structure and force constants involved in the Hamiltonian (127) given in the local representation. 2166

$$\tilde{\omega} = \hbar\omega + \frac{6}{4!} \left( \frac{\hbar}{2\mu\omega} \right)^2 4f_{1+1+1-1-} \quad 2171$$

$$+ \left( \frac{\hbar}{2\mu\omega} \right)^2 f_{1+1-2+2-} - \frac{1}{4} \left( \frac{\partial^2 g_{1+,1+}}{\partial Q_{1+}^2} \right)_o 2\hbar^2$$

$$- \frac{1}{2} \left( \frac{\partial^2 g_{1+,1-}}{\partial Q_{1+} \partial Q_{1-}} \right)_o \hbar^2 \quad 2176$$

$$\lambda = \frac{\hbar\omega}{2} \left( \frac{g_{1a2a}^o}{g_{aa}^o} + \frac{f_{1a2a}}{f_{aa}} \right) + \frac{12}{4!} \left( \frac{\hbar}{2\mu\omega} \right)^2 \frac{5}{2} f_{1+1+1-2-}$$

$$- \frac{1}{4} \left( \frac{\partial^2 g_{1+,2+}}{\partial Q_{1+}^2} \right)_o \frac{\hbar^2}{2} \quad 2181$$

$$x_{11} = \frac{6}{4!} \left( \frac{\hbar}{2\mu\omega} \right)^2 2f_{1+1+1-1-} - \frac{1}{4} \left( \frac{\partial^2 g_{1+,1+}}{\partial Q_{1+}^2} \right)_o \frac{3\hbar^2}{8}$$

$$- \frac{1}{2} \left( \frac{\partial^2 g_{1+,1-}}{\partial Q_{1+} \partial Q_{1-}} \right)_o \frac{\hbar^2}{4} \quad 2186$$

$$x_{12} = \frac{3}{4} \left( \frac{\hbar}{2\mu\omega} \right)^2 f_{1+1-2+2-}$$

$$x_{n\lambda} = \frac{12}{4!} \left( \frac{\hbar}{2\mu\omega} \right)^2 \frac{3}{2} f_{1+1+1-2-} - \frac{1}{2} \left( \frac{\partial^2 g_{1+,2-}}{\partial Q_{1+} \partial Q_{1-}} \right)_o \frac{\hbar^2}{4} \quad 2191$$

$$- \frac{1}{4} \left( \frac{\partial^2 g_{1+,2+}}{\partial Q_{1+}^2} \right)_o \frac{\hbar^2}{2}$$

$$g_{11} = -\frac{6}{4!} \left( \frac{\hbar}{2\mu\omega} \right)^2 f_{1+1+1-1-} - \frac{1}{4} \left( \frac{\partial^2 g_{1+,1+}}{\partial Q_{1+}^2} \right)_o \frac{7\hbar^2}{8}$$

$$- \frac{1}{2} \left( \frac{\partial^2 g_{1+,1-}}{\partial Q_{1+} \partial Q_{1-}} \right)_o \frac{\hbar^2}{4} \quad 2196$$

$$2201 \quad g_{12} = \frac{1}{4} \left( \frac{\hbar}{2\omega\mu} \right)^2 f_{1+1-2+2-} + \frac{1}{2} \left( \frac{\partial^2 g_{1+,2+}}{\partial Q_{1+} \partial Q_{2+}} \right)_o \hbar^2 \quad 2256$$

$$K_{4\bar{4}/5\bar{5}} = \frac{\hbar^2}{\beta_5} \frac{4!}{4!} f_{4+4-5+5-} - \frac{1}{4} \left( \frac{\partial^2 G_{4+,5+}}{\partial Q_{4+} \partial Q_{5+}} \right)_o 2\hbar^2$$

$$2206 \quad g_{n\lambda'} = -\frac{12}{4!} \left( \frac{\hbar}{2\omega\mu} \right)^2 \frac{1}{2} f_{1+1+1-2-} - \frac{1}{2} \left( \frac{\partial^2 g_{1+,2-}}{\partial Q_{1+} \partial Q_{2-}} \right)_o \frac{\hbar^2}{4} \quad 2261$$

$$L_{44/55} = \frac{\hbar^2}{\beta_4 \beta_5} \frac{6}{4!} f_{4+4+5-5-} - \frac{1}{4} \left( \frac{\partial^2 G_{4+,4+}}{\partial Q_{5+}^2} \right)_o \frac{\hbar^2 \beta_4}{4\beta_5}$$

$$2211 \quad K_{1\bar{1}/2\bar{2}} = \left( \frac{\hbar}{2\omega\mu} \right)^2 f_{1+1-2+2-} - \frac{1}{2} \left( \frac{\partial^2 g_{1+,2+}}{\partial Q_{1+} \partial Q_{2+}} \right)_o \hbar^2 \quad 2266$$

$$r_{45} = 4 \frac{\hbar^2}{\beta_4 \beta_5} \frac{6}{4!} f_{4+4+5-5-} + \frac{1}{4} \left( \frac{\partial^2 G_{4+,4+}}{\partial Q_{5+}^2} \right)_o \frac{4\hbar^2 \beta_4}{4\beta_5}$$

$$2216 \quad L_{11/22} = \frac{6}{4!} \left( \frac{\hbar}{2\omega\mu} \right)^2 f_{1+1+2-2-} - \frac{1}{2} \left( \frac{\partial^2 g_{1+,2-}}{\partial Q_{1+} \partial Q_{2-}} \right)_o \frac{\hbar^2}{4} \quad 2271$$

$$r_{12} = \frac{6}{4!} \left( \frac{\hbar}{2\omega\mu} \right)^2 4 f_{1+1+2-2-}$$

## 2221 Appendix 4

Relation between the spectroscopic parameters and the structure and force constants. Here we have introduced the following definitions

$$2226 \quad \beta_p = 2\omega_p \mu_p; \quad \mu_p = 1/g_{pp}^0; \quad p = g, u; \quad (A15)$$

with corresponding frequencies given in (84). The relations are:

$$2231 \quad \hbar\Omega_4 = \hbar\omega_4 + \frac{6}{4!} \frac{\hbar^2}{\beta_4^2} f_{4+4+4-4-} + \frac{\hbar^2}{\beta_4 \beta_5} \frac{4!}{4!} f_{4+4-5+5-} \quad 2286$$

$$+ \frac{1}{4} \left( \frac{\partial^2 G_{4+,4+}}{\partial Q_{4+}^2} \right)_o \frac{\hbar^2}{2}$$

$$2236 \quad \hbar\Omega_5 = \hbar\omega_5 + \frac{6}{4!} \frac{\hbar^2}{\beta_5^2} f_{5+5+5-5-} + \frac{\hbar^2}{\beta_4 \beta_5} \frac{4!}{4!} f_{4+4-5+5-} \quad 2291$$

$$+ \frac{1}{4} \left( \frac{\partial^2 G_{5+,5+}}{\partial Q_{5+}^2} \right)_o \frac{\hbar^2}{2}$$

$$2241 \quad x_{44} = \frac{6}{4!} \frac{9}{2} \frac{\hbar^2}{\beta_4^2} f_{4+4+4-4-} + \frac{1}{4} \left( \frac{\partial^2 G_{4+,4+}}{\partial Q_{4+}^2} \right)_o \frac{\hbar^2}{4} \quad 2296$$

$$x_{55} = \frac{6}{4!} \frac{9}{2} \frac{\hbar^2}{\beta_5^2} f_{5+5+5-5-} + \frac{1}{4} \left( \frac{\partial^2 G_{5+,5+}}{\partial Q_{5+}^2} \right)_o \frac{\hbar^2}{4}$$

$$2246 \quad x_{45} = \frac{\hbar^2}{\beta_4 \beta_5} \frac{4!}{4!} f_{4+4-5+5-}$$

$$g_{44} = -\frac{6}{4!} \frac{7}{2} \frac{\hbar^2}{\beta_4^2} f_{4+4+4-4-} - \frac{1}{4} \left( \frac{\partial^2 G_{4+,4+}}{\partial Q_{4+}^2} \right)_o \frac{\hbar^2}{4} \quad 2301$$

$$2251 \quad g_{55} = -\frac{6}{4!} \frac{7}{2} \frac{\hbar^2}{\beta_5^2} f_{5+5+5-5-} - \frac{1}{4} \left( \frac{\partial^2 G_{5+,5+}}{\partial Q_{5+}^2} \right)_o \frac{\hbar^2}{4}$$

$$g_{45} = \frac{1}{4} \left( \frac{\partial^2 G_{4+,5+}}{\partial Q_{4+} \partial Q_{5+}} \right)_o 2\hbar^2 - \frac{1}{4} \left( \frac{\partial^2 G_{4+,5-}}{\partial Q_{4+} \partial Q_{5-}} \right)_o 2\hbar^2 \quad 2306$$

## Appendix 5. x-K relations

The interactions involved in the Hamiltonian in the normal mode scheme can be expressed in the local scheme in the following form. For linear terms

$$v_4 = \frac{1}{2} [\hat{n} - \hat{\Lambda}_+], \quad (A16)$$

$$v_5 = \frac{1}{2} [\hat{n} + \hat{\Lambda}_+], \quad (A17)$$

while for quadratic interactions

$$v_4^2 = \frac{1}{4} [\hat{n}^2 + \hat{\Delta}_{11/22} + 2(\hat{D}_{11/22} + \hat{R}_l^{12}) + \hat{n} + \hat{n}_1 \hat{n}_2 + l_1 \cdot l_2 - 2n\Lambda_+], \quad (A18)$$

$$v_5^2 = \frac{1}{4} [\hat{n}^2 + \hat{\Delta}_{11/22} + 2(\hat{D}_{11/22} + \hat{R}_l^{12}) + \hat{n} + \hat{n}_1 \hat{n}_2 + l_1 \cdot l_2 + 2n\Lambda_+], \quad (A19)$$

$$v_4 v_5 = \frac{1}{4} [\hat{n}^2 - (\hat{\Delta}_{11/22} + 2(\hat{D}_{11/22} + \hat{R}_l^{12}) + \hat{n} + \hat{n}_1 \hat{n}_2 + l_1 \cdot l_2)], \quad (A20)$$

$$\hat{l}_4^2 = \frac{1}{4} [(l_1 + l_2)^2 + \Delta_{11/22} - 2(\hat{D}_{11/22} + \hat{R}_l^{12}) + \hat{n} + \hat{n}_1 \hat{n}_2 + l_1 \cdot l_2 - 2(l_1 + l_2)\Lambda_-], \quad (A21)$$

$$\hat{l}_5^2 = \frac{1}{4} [(l_1 + l_2)^2 + \Delta_{11/22} - 2(\hat{D}_{11/22} + \hat{R}_l^{12}) + \hat{n} + \hat{n}_1 \hat{n}_2 + l_1 \cdot l_2 + 2(l_1 + l_2)\Lambda_-], \quad (A22)$$

$$\hat{l}_4 \cdot \hat{l}_5 = \frac{1}{4} [(l_1 + l_2)^2 - (\hat{\Delta}_{11/22} - 2(\hat{D}_{11/22} + \hat{R}_l^{12}) + \hat{n} + \hat{n}_1 \hat{n}_2 + l_1 \cdot l_2)], \quad (A23)$$

$$\hat{D}_{44/55} = \frac{1}{4} \left[ 2(\hat{D}_{11/22} - \hat{R}_l^{12}) + \frac{1}{2} [(\hat{n}_1^2 + \hat{n}_2^2) - (l_1^2 + l_2^2)] - \hat{n}_1 \hat{n}_2 + l_1 \cdot l_2 \right], \quad (A24)$$

$$\begin{aligned} 2311 \quad \hat{\Delta}_{44/55} = & \frac{1}{2} \left[ \hat{\Delta}_{11/22} + \frac{1}{2} [(\hat{n}_1^2 + \hat{n}_2^2) + (l_1^2 + l_2^2)] \right. \\ & \left. - 2(\hat{n}_1 \hat{n}_2 + l_1 \cdot l_2) - \hat{n} \right], \end{aligned} \quad (\text{A25})$$

$$\begin{aligned} 2316 \quad \hat{R}_l^{12} = & \frac{1}{2} \left[ \hat{R}_l^{12} - \hat{D}_{11/22} - \frac{1}{2}(\hat{n}_1 \hat{n}_2 - l_1 \cdot l_2) \right. \\ & \left. + \frac{1}{4}(\hat{n}_1^2 + \hat{n}_2^2 - (l_1^2 + l_2^2)) \right], \end{aligned} \quad (\text{A26})$$

which lead to the following  $x$ - $K$  relations:

$$\begin{aligned} 2321 \quad \tilde{\omega} = & \frac{1}{2}(\tilde{\omega}_4 + \tilde{\omega}_5 - L_{4455}) \\ & + \frac{1}{4}(g_{44} - g_{45} + g_{55} + x_{44} - x_{45} + x_{55}), \end{aligned} \quad (\text{A27})$$

$$2326 \quad \lambda = \frac{1}{2}(\tilde{\omega}_5 - \tilde{\omega}_4), \quad (\text{A28})$$

$$x_{11} = \frac{1}{8}(K_{4455} + r_{45}) + \frac{1}{4}(L_{4455} + x_{44} + x_{45} + x_{55}), \quad (\text{A29})$$

$$\begin{aligned} 2331 \quad x_{12} = & -L_{4455} + \frac{1}{4}(g_{44} - g_{45} + g_{55} - K_{4455} - r_{45} \\ & + 3x_{44} + x_{45} + 3x_{55}), \end{aligned} \quad (\text{A30})$$

$$x_{n\lambda} = \frac{1}{2}(x_{55} - x_{44}), \quad (\text{A31})$$

$$\begin{aligned} 2336 \quad g_{11} = & \frac{1}{4}(g_{44} + g_{45} + g_{55} + L_{4455}) \\ & - \frac{1}{8}(K_{4455} + r_{45}), \end{aligned} \quad (\text{A32})$$

$$\begin{aligned} 2341 \quad g_{12} = & (g_{44}/4 + g_{45}/4 + g_{55}/4 - K_{4455}/8 \\ & + L_{4455}/4 - r_{45}/8), \end{aligned} \quad (\text{A33})$$

$$g_{i\lambda'} = \frac{1}{2}(g_{55} - g_{44}), \quad (\text{A34})$$

$$\begin{aligned} 2346 \quad K_{11/22} = & \frac{1}{2}(-g_{44} + g_{45} - g_{55} + K_{4455} \\ & - r_{45} + x_{44} - x_{45} + x_{55}), \end{aligned} \quad (\text{A35})$$

$$\begin{aligned} 2351 \quad L_{11/22} = & \frac{1}{4}(g_{44} - g_{45} + g_{55} + x_{44} - x_{45} + x_{55}) \\ & + \frac{1}{2}L_{4455}, \end{aligned} \quad (\text{A36})$$

$$\begin{aligned} r_{12} = & \frac{1}{2}(-g_{44} + g_{45} - g_{55} - K_{4455} \\ & + r_{45} + x_{44} - x_{45} + x_{55}). \end{aligned} \quad (\text{A37})$$

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## Appendix 6

Explicit expressions for the operators involved in the Hamiltonian (150).

We start defining the basic tensor operators

$$\hat{T}_{4+}^\dagger = \frac{1}{\sqrt{2}}(-\hat{b}_{1+}^\dagger + \hat{b}_{2+}^\dagger); \quad \hat{T}_{5+}^\dagger = \frac{1}{\sqrt{2}}(\hat{b}_{1+}^\dagger + \hat{b}_{2+}^\dagger); \quad (\text{A38}) \quad 2371$$

$$\hat{T}_{4-}^\dagger = \frac{1}{\sqrt{2}}(-\hat{b}_{1-}^\dagger + \hat{b}_{2-}^\dagger); \quad \hat{T}_{5-}^\dagger = \frac{1}{\sqrt{2}}(\hat{b}_{1-}^\dagger + \hat{b}_{2-}^\dagger). \quad (\text{A39})$$

The number operators are then given by

$$\nu_4 = \hat{T}_{4+}^\dagger \hat{T}_{4+} + \hat{T}_{4-}^\dagger \hat{T}_{4-}; \quad \nu_5 = \hat{T}_{5+}^\dagger \hat{T}_{5+} + \hat{T}_{5-}^\dagger \hat{T}_{5-}, \quad (\text{A40}) \quad 2376$$

while for the angular momenta

$$\hat{l}_4^2 = (\hat{T}_{4+}^\dagger \hat{T}_{4+} - \hat{T}_{4-}^\dagger \hat{T}_{4-})^2, \quad (\text{A41})$$

$$\hat{l}_5^2 = (\hat{T}_{5+}^\dagger \hat{T}_{5+} - \hat{T}_{5-}^\dagger \hat{T}_{5-})^2, \quad (\text{A42}) \quad 2381$$

$$\hat{l}_4 \cdot \hat{l}_5 = (\hat{T}_{4+}^\dagger \hat{T}_{4+} - \hat{T}_{4-}^\dagger \hat{T}_{4-})(\hat{T}_{5+}^\dagger \hat{T}_{5+} - \hat{T}_{5-}^\dagger \hat{T}_{5-}). \quad (\text{A43})$$

Finally for the resonances

$$\hat{D}_{44/55} = \hat{T}_{4+}^\dagger \hat{T}_{4-}^\dagger \hat{T}_{5+} \hat{T}_{5-}, \quad (\text{A44})$$

$$\hat{\Delta}_{44/55} = (\hat{T}_{4+}^\dagger)^2 (\hat{T}_{5+})^2 + (\hat{T}_{4-}^\dagger)^2 (\hat{T}_{5-})^2 + H.c., \quad (\text{A45}) \quad 2386$$

$$\hat{R}_l^{45} = \hat{T}_{4+}^\dagger \hat{T}_{4-}^\dagger \hat{T}_{5-} \hat{T}_{5+} + H.c. \quad (\text{A46})$$

In practice, the explicit substitution of the tensor operators (A.31) is carried out in the code to compute the matrix elements in such a way that the matrix elements are computed at the local level. Q25, 2391

## Appendix 7

Explicit expressions for the operators involved in the Hamiltonian (150).

Relation between force constants given in the normal and the local schemes.

$$\begin{aligned} f_{4+4+4-4-} = & \frac{1}{2}f_{1+1+1-1-} + \frac{1}{2}f_{1+1+2-2-} \\ & + f_{1+1-2+2-} - 2f_{1+1+1-2-} \end{aligned} \quad (\text{A47}) \quad 2401$$

$$\begin{aligned} f_{4+4+4-4-} = & \frac{1}{2}f_{1+1+1-1-} + \frac{1}{2}f_{1+1+2-2-} \\ & + f_{1+1-2+2-} + 2f_{1+1+1-2-} \end{aligned} \quad (\text{A48})$$

$$f_{4+4+4-4-} = \frac{1}{2}f_{1+1+1-1-} - \frac{1}{2}f_{1+1+2-2-} \quad (\text{A49}) \quad 2406$$

$$\begin{aligned} f_{4+4+4-4-} = & \frac{1}{2}f_{1+1+1-1-} + \frac{1}{2}f_{1+1+2-2-} - f_{1+1-2+2-} \end{aligned} \quad (\text{A50})$$

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RESEARCH ARTICLE



# An approach to establish a connection between algebraic and configuration spaces: $su(\nu + 1)$ algebraic model for vibrational excitations

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## ABSTRACT

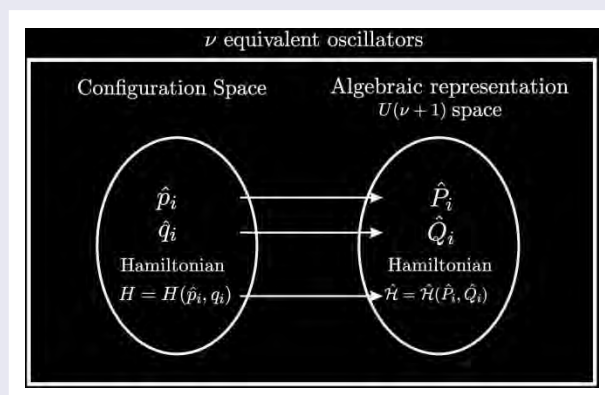
A realisation of coordinates and momenta in the  $su(\nu + 1)$  algebraic space to describe vibrational excitations of  $\nu$ -equivalent oscillators is obtained. The connection between algebraic and configuration spaces is carried out using the approach recently proposed [Mol. Phys. (2017), doi:10.1080/00268976.2017.1358829]. The realisation consists in an expansion in terms of the dynamical algebra generators with coefficients determined through a minimisation procedure and given in terms of matrix elements defined in configuration space. Two realisations are presented: one through an isomorphism with a harmonic oscillators basis and the second one using a mapping to Morse oscillators. In the case of the harmonic oscillator mapping, two chains associated with coordinate and momentum representation have been identified. Our approach allows us to establish the algebraic representation of any interaction and, consequently, of the Hamiltonian associated with  $\nu$ -interacting oscillators, providing a formal approach to estimate the potential energy surface.

## ARTICLE HISTORY

Received 21 February 2018  
Accepted 13 April 2018

## KEYWORDS

$U(\nu + 1)$  algebraic approach; configuration space; algebraic realisation; coordinates and momenta; harmonic oscillators; Morse oscillators



## 1. Introduction

Unitary groups are relevant in the description of many body systems since bilinear products of fermionic or bosonic operators can be identified as generators of unitary groups, which in turn may correspond to the dynamical group of a great variety of systems involving different energy scales: vibrational degrees of freedom [1,2], electronic degrees of freedom in atoms and molecules [3–7], nuclear physics [7–11] and subnuclear physics [11,12]. In this work, we are interested in the vibrational degrees of freedom.<sup>1</sup>

When molecular vibrational excitations are described in terms of a basis of harmonic oscillators, bilinear products of creation and annihilation operators associated with a set of  $\nu n$ -dimensional oscillators constitute the generators of the symmetry group of the system  $U(\nu n)$ , while  $Sp(2\nu n, R)$  is the corresponding dynamical group [6,13]. The non-compactness of the groups represents a disadvantage from the practical point of view when dealing with bound states [14]. It is possible, however, to deal with compact dynamical groups if the space of harmonic oscillators is constrained. A convenient way to achieve

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this task is through the addition of an extra boson in such a way that the totally symmetric representation (total number of bosons) of the unitary group is fixed. This approach was for the first time proposed in the context of the collective states in nuclei [15,16] and subsequently applied by Iachello *et al.* in the field of molecular physics to describe the ro-vibration excitations in molecular systems [1,17–21]. The addition of the scalar boson was also used in the context of purely vibrational excitations where a set of equivalent oscillators leads to the model proposed by Michelot and Moret-Bailly, where for a set of  $\nu$ -equivalent oscillators the dynamical group becomes  $U(\nu + 1)$ [22,23].

In general, the relevance of the  $U(\nu + 1)$  approach is twofold. On one hand, the mathematical formalism is enriched by the appearance of orthogonal subgroups, providing a variety of dynamical symmetries [7], and upon the other hand, anharmonicities are allowed to be introduced from the outset. Dynamical symmetries may represent zeroth-order approximations to the complete problem. In some cases, the addition of Casimir operators of different chains may be enough to describe the system with the desired level of accuracy. However, as the number of oscillators increases the number of interactions becomes so large that the Casimir operators are not enough to provide a complete set of interactions. This situation is present in molecular physics where the relevant interactions are numerous and well known in configuration space. Consequently, an approach to establish the algebraic realisation of the interactions in the space of coordinates and momenta is welcome.

The one-dimensional version of the  $U(\nu + 1)$  approach consists in treating one oscillator in terms of an  $su(2)$  algebra, a description which turns out to be equivalent to the algebraic treatment of either Morse [24–27] or Pöschl–Teller oscillators [27]. This connection allows the potential energy surface (PES) to be calculated [28–34]. The two-dimensional version corresponding to the dynamical algebra  $su(2 + 1)$  turns out to be particularly relevant in the description of the local degenerate bending modes of linear molecules, where degenerate local oscillators (preserving the projection of the angular momentum) are involved [1,20]. In this case the connection with configuration space was established from a heuristic point of view through the harmonic limit [35]. Recently, an alternative point of view for the  $U(\nu + 1)$  approach for vibrational excitations was proposed in such a way that every interaction can be translated into the  $U(\nu + 1)$  algebraic space [36–39]. The correspondence was based on the criterion that the matrix elements in the algebraic models reduce to the corresponding harmonic limit. This means that the expansion of coordinates and momenta was established up to linear

terms in the ladder operators. Although this step was quite important to calculate force constants useful to predict spectra of isotopologue species, the connection was restricted to linear terms without any clue to extend the connection to include higher order terms or even justify in a formal way the approximation. Although the relative success of these efforts permitted to estimate potential energy surfaces, the proposed connection was criticised because of its heuristic approach to establish the connection. The aim of this work is to establish formally this connection.

In a recent contribution [40], a general approach to establish the connection between configuration and algebraic spaces was proposed. The method is a generalisation of the approach presented in the field of molecular collisions, where it was needed to obtain an algebraic representation of the interaction potential [41–43]. The approach consists in establishing a mapping between the eigenstates of the system in configuration space and states associated with the algebraic space – not necessarily corresponding to a dynamical symmetry. The dynamic variable is expanded in the algebraic space with coefficients determined through a minimisation method. The coefficients turn out to be given in terms of matrix elements of the dynamical operators. A fundamental ingredient of the approach is the calculation of the matrix elements through the density operator, which involves parameters that may be used as a mathematical tool. In this work, the expansion of the coordinates and momenta in the  $su(\nu + 1)$  space is obtained for each oscillator. The application to 2D and 3D potentials involving angular momentum conservation will be presented elsewhere.

This article is organised as follows. In Section 2, a summary of the algebraic  $su(\nu + 1)$  approach to describe vibrational excitation is presented. Section 3 is devoted to present a summary of our general approach to establish the connection between algebraic and configuration spaces. In Section 4, the case of two oscillators is used to present the connection between algebraic and configuration spaces through a mapping to harmonic oscillators. Both momenta and coordinates are obtained for each oscillator as a realisation of the dynamical algebra. Keeping in mind an improvement going beyond linear terms in the expansion of the coordinates and momenta, in Section 5 the connection is established using a mapping with the direct product of  $\nu$ -Morse oscillators restricted to the subspace characterised by a maximum total number of quanta. In Section 6, a comparison between the  $U(3)$  model and the  $U_1(2) \otimes U_2(2)$  model representing two Morse oscillators is presented. Finally in Section 7 the summary and conclusions are given.

## 2. The $su(\nu + 1)$ -algebraic model

In this section, we shall present a summary of the  $U(\nu + 1)$  approach applied to vibrational excitations [22,23], albeit from a different viewpoint [36–39]. To achieve this goal, we shall start analysing a set of  $\nu$  harmonic oscillators, described by a  $U(\nu)$  approach, and compare it with: (i) a set of  $\nu$  independent anharmonic oscillators, described by a  $(SU(2))^\nu = SU_1(2) \otimes SU_2(2) \otimes \dots \otimes SU_\nu(2)$ , and (ii) a set of  $\nu$  correlated anharmonic oscillators, described by the  $U(\nu + 1)$  approach.

### 2.1. $\nu$ -Harmonic oscillators

Let us start considering a system of  $\nu$  equivalent non-interacting harmonic oscillators of mass  $\mu$  and frequency  $\omega$ , whose Hamiltonian in configuration space reads

$$\hat{H}_C(\vec{q}, \vec{p}) = \sum_{i=1}^{\nu} \left( \frac{p_i^2}{2\mu} + \frac{1}{2} \mu \omega^2 q_i^2 \right). \quad (1)$$

One can go to an algebraic space by associating to each  $i$ th oscillator creation  $\hat{a}_i^\dagger$  and annihilation  $\hat{a}_i$  operators, defined by

$$\begin{aligned} \hat{q}_i &= \sqrt{\frac{\hbar}{2\mu\omega}} (\hat{a}_i + \hat{a}_i^\dagger), \\ \hat{p}_i &= -i\sqrt{\frac{\hbar\mu\omega}{2}} (\hat{a}_i - \hat{a}_i^\dagger), \end{aligned} \quad (2)$$

such that the commutation relations for coordinates and momenta  $[\hat{q}_i, \hat{p}_j] = i\hbar\delta_{ij}$  are substituted by the equivalent  $[\hat{a}_i, \hat{a}_j^\dagger] = \delta_{ij}$ . With Equations (2), it is simple to write the algebraic image of  $\hat{H}_C$  (1)

$$\hat{H}_A = \frac{\hbar\omega}{2} \sum_{i=1}^{\nu} (\hat{a}_i^\dagger \hat{a}_i + \hat{a}_i \hat{a}_i^\dagger). \quad (3)$$

The  $\nu^2$  bilinear products (carets are displaced to the left)  $\mathcal{C}_i^j = \hat{a}_i^\dagger \hat{a}_j$  ( $i, j = 1, \dots, \nu$ ) fulfil the commutation relations (carets are displaced to the left)  $[\mathcal{C}_i^j, \mathcal{C}_p^q] = \mathcal{C}_i^q \delta_{p,j} - \mathcal{C}_p^j \delta_{q,i}$  and are the generators of the  $U(\nu)$  group, that is called the symmetry group of the system.

It is known that  $\hat{H}_A$  eigenkets are written as

$$|n_1, n_2, \dots, n_\nu\rangle = \frac{1}{\sqrt{\prod_{j=1}^{\nu} n_j!}} \prod_{i=1}^{\nu} (\hat{a}_i^\dagger)^{n_i} |0\rangle, \quad (4)$$

where  $n_i$  is the eigenvalue of the number operator  $\hat{n}_i = \hat{a}_i^\dagger \hat{a}_i$ :

$$\hat{n}_i |n_1, \dots, n_i, \dots, n_\nu\rangle = n_i |n_1, \dots, n_i, \dots, n_\nu\rangle. \quad (5)$$

The eigenkets (4) are associated with the  $U(\nu)$  canonical chain decomposition [5,7]

$$U(\nu) \supset U(\nu - 1) \supset U(\nu - 2) \supset \dots \supset U(1). \quad (6)$$

### 2.2. $(SU(2))^\nu$ : $\nu$ uncorrelated anharmonic oscillators

Let us consider now a system of  $\nu$  equivalent non-interacting anharmonic oscillators. One-dimensional anharmonic oscillators, for instance Morse or (it should be Pöschl-Teller) Poeschl–Teller oscillators, can be studied in an algebraic scheme by using the  $su(2)$  algebra. The system is characterised by an angular momentum  $J$  (that is linked to the depth of the potential) and the eigenstates are labelled by  $|J, M\rangle$ . The  $su(2)$  generators are  $J_+$ ,  $J_-$  and  $J_0$  that fulfil the angular momentum commutation relations. Thus, for  $\nu$  equivalent non-interacting anharmonic oscillators, one associates with the  $i$ th oscillator a  $su_i(2)$  algebra, with operators  $J_{i,+}$ ,  $J_{i,-}$ ,  $J_{i,0}$ , which satisfy the usual angular momentum commutation relations. Notice that operators associated with different oscillators  $i, j$  commute with each other. These operators act on a basis with dimension  $k\nu$ , where  $k = 2J + 1$  that is the dimension of the irreducible representation of each  $su(2)$  algebra. The states of this basis can be characterised by the eigenstates of the  $\nu$  operators  $J_{i,0}$ ,  $i = 1 \dots \nu$ , corresponding to eigenvalues  $M_i = -J \dots J$ . Alternatively, they can be labelled by eigenvalues of the operator that gives the number of anharmonic quanta,  $\hat{n}_i = J - J_{i,0}$ . It is convenient to define anharmonic operators  $\hat{b}_i^\dagger = J_{i,-}/\sqrt{k}$ ;  $\hat{b}_i = J_{i,+}/\sqrt{k}$ , that fulfil the commutation relation

$$[\hat{b}_i, \hat{b}_j^\dagger] = \delta_{ij} \left( 1 - \frac{2\hat{n}_i + 1}{k} \right). \quad (7)$$

These operators act on the basis according to

$$\begin{aligned} \hat{b}_i^\dagger |[\nu k]; n_1, \dots, n_i, \dots, n_\nu\rangle \\ = \sqrt{(n_i + 1) \left( 1 - \frac{n_i + 1}{k} \right)} \\ |[\nu k]; n_1, \dots, n_i + 1, \dots, n_\nu\rangle, \end{aligned} \quad (8)$$

$$\begin{aligned} \hat{b}_i |[\nu k]; n_1, \dots, n_i, \dots, n_\nu\rangle \\ = \sqrt{(n_i) \left( 1 - \frac{n_i}{k} \right)} \\ |[\nu k]; n_1, \dots, n_i - 1, \dots, n_\nu\rangle. \end{aligned} \quad (9)$$

In terms of these operators, the Hamiltonian of a set of independent anharmonic oscillators, such as Morse

oscillators, takes the form:

$$\hat{H} = \frac{\hbar\omega}{2} \sum_{i=1}^{\nu} (\hat{b}_i^\dagger \hat{b}_i + \hat{b}_i \hat{b}_i^\dagger). \quad (10)$$

The states  $|\nu k; n_1, \dots, n_i, \dots, n_\nu\rangle$  are eigenstates of the Hamiltonian, corresponding to the eigenvalues

$$\begin{aligned} E([\nu k]; n_1, \dots, n_i, \dots, n_\nu) \\ = \hbar\omega \sum_{i=1}^{\nu} \left( n_i + \frac{1}{2} - \frac{(n_i + 1/2)^2}{k} \right) - \nu \frac{\hbar\omega}{4k}, \end{aligned} \quad (11)$$

which are the eigenvalues of an anharmonic Hamiltonian except for an energy shift for each oscillator given by the last factor.

### 2.3. $U(\nu + 1)$ model: $\nu$ correlated anharmonic oscillators

In the  $U(\nu + 1)$  approach for  $\nu$  equivalent oscillators, an additional  $\hat{s}^\dagger(\hat{s})$  boson is added to the set of bosonic operators  $\hat{a}_i^\dagger(\hat{a}_i)$  with the constraint of a fixed total number of bosons  $N$ . The new canonical chain is

$$U(\nu + 1) \supset U(\nu) \supset U(\nu - 1) \supset \dots \supset U(1), \quad (12)$$

with the corresponding kets

$$\begin{aligned} |[N]; n_s, n_1, n_2, \dots, n_\nu) \\ = \frac{1}{\sqrt{n_s! \prod_j n_j!}} (\hat{s}^\dagger)^{n_s} \prod_i^{\nu} (\hat{a}_i^\dagger)^{n_i} |0), \end{aligned} \quad (13)$$

which are characterised by the total number of quanta  $N$ :

$$\hat{N} = \hat{n} + \hat{n}_s \quad \text{with} \quad \hat{n} = \sum_{i=1}^{\nu} \hat{a}_i^\dagger \hat{a}_i; \quad \hat{n}_s = \hat{s}^\dagger \hat{s}. \quad (14)$$

The total number of bosons fixes the totally symmetric representation  $[N]$  of the group  $U(\nu + 1)$ , and because of the relation (14) we can recast the kets (13) in the form

$$\begin{aligned} |[N], n; \mathbf{n}) &= |[N], n; n_1, n_2, \dots, n_\nu) \\ &\equiv |[N]; n_s, n_1, n_2, \dots, n_\nu), \end{aligned} \quad (15)$$

where here  $n$  plays the role of the polyad pseudo quantum number for the set of  $\nu$ -equivalent oscillators [44]. This polyad number turns out to be a good quantum number in molecules with local mode behaviour [45,46]. The generators of the group  $U(\nu + 1)$  are given by

$$\hat{C}_i^j = \hat{c}_i^\dagger \hat{c}_j; \quad \hat{c}_i = \hat{a}_i, \quad i = 1, \dots, \nu; \quad \hat{c}_{\nu+1} = \hat{s}, \quad (16)$$

with commutation relations  $([\hat{C}_i^j, \hat{C}_p^q] = \hat{C}_i^q \delta_{p,j} - \hat{C}_p^j \delta_{q,i})$  including the extra boson  $\hat{s}^\dagger(\hat{s})$ . The addition of the s-boson together with the fact that the representation  $[N]$

is fixed makes the unitary group  $U(\nu + 1)$  a dynamical group for the set of  $\nu$ -oscillators. From the generators (16), we can identify  $\nu$ - $su(2)$  subalgebras

$$\hat{J}_{i,+} = \hat{s} \hat{a}_i^\dagger, \quad (17a)$$

$$\hat{J}_{i,-} = \hat{s}^\dagger \hat{a}_i, \quad (17b)$$

$$\hat{J}_{i,0} = -\frac{1}{2} (\hat{s}^\dagger \hat{s} - \hat{a}_i^\dagger \hat{a}_i), \quad (17c)$$

with the usual angular momentum commutation relations [47,48]. The action of these operators over the kets (15) are obtained in a straightforward way

$$\begin{aligned} \hat{a}_i^\dagger \hat{s} | [N], n; \dots, n_i, \dots) &= \sqrt{(n_i + 1)(N - n)} \\ &\times |[N], n + 1; \dots, n_i + 1, \dots), \end{aligned} \quad (18a)$$

$$\begin{aligned} \hat{a}_i \hat{s}^\dagger | [N], n; \dots, n_i, \dots) &= \sqrt{n_i(N - n + 1)} \\ &\times |[N], n - 1; \dots, n_i - 1, \dots). \end{aligned} \quad (18b)$$

In the context of this model, any dynamical variable, including the Hamiltonian, can be expressed in terms of the generators (16), although the operators (17a) and (17b) turn out to play a preponderant role due to their connection with coordinates and momenta [36–39].

As in the preceding subsection, it is convenient to introduce the normalised operators [36]

$$\hat{b}_i^\dagger \equiv \frac{\hat{J}_{i,+}}{\sqrt{N}}, \quad \hat{b}_i \equiv \frac{\hat{J}_{i,-}}{\sqrt{N}} \quad \text{with } i = 1, \dots, \nu, \quad (19)$$

which satisfy the commutation relations

$$[\hat{b}_i, \hat{b}_j^\dagger] = \delta_{ij} - \frac{1}{N} [\hat{n} \delta_{ij} + \hat{a}_j^\dagger \hat{a}_i]. \quad (20)$$

The action of these normalised operators over the kets (15) turns out to be

$$\begin{aligned} \hat{b}_i^\dagger | [N], n; n_1, \dots, n_i, \dots, n_\nu) &= \sqrt{(n_i + 1) \left(1 - \frac{n}{N}\right)} \\ &\times |[N], n + 1; n_1, \dots, n_i + 1, \dots, n_\nu), \end{aligned} \quad (21a)$$

$$\begin{aligned} \hat{b}_i | [N], n; n_1, \dots, n_i, \dots, n_\nu) &= \sqrt{n_i \left(1 - \frac{n - 1}{N}\right)} \\ &\times |[N], n - 1; n_1, \dots, n_i - 1, \dots, n_\nu). \end{aligned} \quad (21b)$$

Comparing these matrix elements with the ones given by the bosonic operators  $\hat{a}_i^\dagger(\hat{a}_i)$  in the basis (4)

$$\begin{aligned} \hat{a}_i^\dagger | n_1, \dots, n_i, \dots, n_\nu) \\ = \sqrt{(n_i + 1)} | n_1, \dots, n_i + 1, \dots, n_\nu), \end{aligned} \quad (22a)$$

$$\hat{a}_i |n_1, \dots, n_i, \dots, n_\nu\rangle = \sqrt{n_i} |n_1, \dots, n_i - 1, \dots, n_\nu\rangle, \quad (22b)$$

we conclude that

$$\lim_{N \rightarrow \infty} \hat{b}_i^\dagger = \hat{a}_i^\dagger; \quad \lim_{N \rightarrow \infty} \hat{b}_i = \hat{a}_i; \quad \lim_{N \rightarrow \infty} [\hat{b}_i, \hat{b}_j^\dagger] = \delta_{ij}. \quad (23)$$

Hence, on the basis of this analysis, a Hamiltonian may be translated into an algebraic representation by carrying out the transformation  $\hat{a}_i^\dagger (\hat{a}_i) \rightarrow \hat{b}_i^\dagger (\hat{b}_i)$  [36–39]. In all these works, this transformation has been used with good results but without a theoretical support. The aim of this work is to present an approach that provides the required theoretical support to the cited studies and, in addition, to establish a connection between algebraic and configuration spaces beyond the linear approximation.

Here, we are treating a set of  $\nu$  equivalent oscillators. We would like to note, as a final point in this section, that the generalisation of this approach consists in considering the situation of several sets of equivalent oscillators. Following the convention that algebras are denoted in lower case while groups in upper case, for  $\alpha$  sets of  $\nu$  equivalent oscillators a  $su_i(\nu + 1)$  algebra is introduced for each equivalent set  $i$ , so that the dynamical algebra is given by the direct sum

$$su_1(\nu_1 + 1) \oplus su_2(\nu_2 + 1) \oplus \dots \oplus su_\alpha(\nu_\alpha + 1). \quad (24)$$

In this case, a total number of bosons  $N_i$  are associated with each  $i$ th space, which in turn is related to the dissociation limit of the corresponding internal coordinates [23].

### 3. Connection between algebraic and configuration spaces

Let us consider a configuration space Hamiltonian for a set of  $\nu$  oscillators,  $\hat{H}_{cs}(D; \mathbf{q}, \mathbf{p})$ , where  $\mathbf{q}, \mathbf{p}$  denote the corresponding coordinates and momenta, respectively. The Schrödinger equation provides eigenvalues and eigenstates

$$\hat{H}_{cs}(D; \mathbf{q}, \mathbf{p}) \psi_{D;\mathbf{n}}(\mathbf{q}) = E_{D;\mathbf{n}} \psi_{D;\mathbf{n}}(\mathbf{q}), \quad (25)$$

where here  $D$  is a parameter related to the depth of the potential in order to take into account both harmonic and anharmonic oscillators like Morse or Pöschl–Teller oscillators. The same problem can be formulated in a second quantised form (Fock space) as

$$\hat{H}_{Fock} |D; \mathbf{n}\rangle = E_{D;\mathbf{n}} |D; \mathbf{n}\rangle \quad \text{where } \psi_{D;\mathbf{n}}(\mathbf{q}) = \langle \mathbf{q} | D; \mathbf{n} \rangle. \quad (26)$$

Following the approach presented in Ref. [40], the initial point is to look for an equivalent algebraic  $SU(\nu + 1)$

Hamiltonian such that it provides the same eigenvalues

$$\hat{H}_{alg} |N; \mathbf{n}\rangle = E_{N;\mathbf{n}} |N; \mathbf{n}\rangle. \quad (27)$$

For anharmonic oscillators, the quantum number  $N$  is related to the depth  $D$  of the potential. The eigenstates in Equation (27) are just (4) for harmonic oscillators or Equation (13) for anharmonic oscillators. Next point is to establish a mapping between the  $\hat{H}_{Fock}$  and  $\hat{H}_{alg}$  eigenstates

$$|D; \mathbf{n}\rangle \cong |N; \mathbf{n}\rangle; \quad n_i = 0, 1, \dots, N \\ \forall i \text{ but keeping } n_s + \sum_{i=1}^{\nu} n_i = N. \quad (28)$$

The importance of establishing this mapping stems from the fact that the matrix elements of any operator can be calculated indistinctly either in the algebraic  $\mathcal{A}$  or in the physical (configuration)  $\mathcal{C}$  space. Once the state mapping is performed, one can introduce the density operator, that in the algebraic space is,

$$\hat{\rho} = \sum_{\mathbf{n}} p_{\mathbf{n}} |N; \mathbf{n}\rangle \langle N; \mathbf{n}| = \sum_{\mathbf{n}} p_{\mathbf{n}} \hat{P}_{\mathbf{n}}, \quad (29)$$

with normalisation  $\sum_{\mathbf{n}} p_{\mathbf{n}} = 1$ .  $\hat{P}_{\mathbf{n}}$  are the projection operators. This density operator is general, with the only restriction that it is diagonal in the eigenstates of the Hamiltonian.

Now, we have the ingredients needed to establish the algebraic realisation,  $\hat{\mathcal{F}}_{alg}$ , of a general configuration space operator  $\hat{\mathcal{F}}_{cs}$  [40]. We are interested in establishing the mapping involving the harmonic oscillator functions where a linear expansion in terms of the group generators,  $g_s$ , is used and then a mapping involving anharmonic functions for which an expansion beyond linear terms ( $g_s^\gamma$ ) is needed. Because of that, we formulate the problem in general using  $\hat{Y}_s^{(\gamma)}$ , which includes for  $\gamma = 1$  the  $s$ th generator of the  $U(\nu + 1)$  group or for other  $\gamma$ -values general operators that include the possibility of products or power expansion of generators going beyond the linear approximation. An operator in the algebraic space takes the form

$$\hat{\mathcal{F}}_{alg} \approx \sum_{\gamma} \sum_s \alpha_s^{(\gamma)} (\hat{\mathcal{F}}_{cs}) \hat{Y}_s^{(\gamma)}, \quad (30)$$

where the coefficients  $\alpha_s^{(\gamma)} (\mathcal{F}_{cs})$  are determined with the criterion that they are to be the best given the proposed expansion (30). To achieve this goal, we introduce the operator  $\hat{\Delta}$  corresponding to the difference between the

exact operator  $\hat{\mathcal{F}}_{cs}$  and the algebraic approximation:

$$\hat{\Delta} = \hat{\mathcal{F}}_{cs} - \sum_{\gamma} \sum_s \alpha_s^{(\gamma)}(\mathcal{F}_{cs}) \hat{Y}_s^{(\gamma)}. \quad (31)$$

The error of the approximation,  $\epsilon$ , is estimated by calculating the average of  $\hat{\Delta} \hat{\Delta}^\dagger$ :

$$\epsilon = \text{Tr}(\hat{\rho} \hat{\Delta} \hat{\Delta}^\dagger). \quad (32)$$

The coefficients  $\alpha$ 's are obtained by minimising the error

$$\frac{\partial \epsilon}{\partial \alpha_r^{(\gamma')}} = 0; \quad \forall r, \gamma', \quad (33)$$

which leads to the set of equations

$$\sum_{\gamma} \sum_s M_{s,r}^{(\gamma, \gamma')} \alpha_s^{(\gamma)}(\mathcal{F}_{cs}) = D_r^{(\gamma')}, \quad (34)$$

where

$$D_r^{(\gamma')} = \text{Tr}(\hat{\rho} \hat{\mathcal{F}}_{cs} \hat{Y}_r^{\dagger(\gamma')}); \quad M_{s,r}^{(\gamma, \gamma')} = \text{Tr}(\hat{\rho} \hat{Y}_s^{(\gamma)} \hat{Y}_r^{\dagger(\gamma')}). \quad (35)$$

and consequently the set (34) reduces to the equations system

$$\begin{aligned} \sum_{\gamma} \sum_s \alpha_s^{(\gamma)}(\mathcal{F}_{cs}) \sum_m \langle j, m | \hat{Y}_r^{\dagger(\gamma')} \hat{\rho} \hat{Y}_s^{(\gamma)} | j, m \rangle \\ = \sum_m \langle j, m | \hat{Y}_r^{\dagger(\gamma')} \hat{\rho} \hat{\mathcal{F}}_{cs} | j, m \rangle. \end{aligned} \quad (36)$$

The states  $|j, m\rangle$  ( $j$  is directly related to  $N$ ) are algebraic basis states and we denote  $|j, i\rangle$  the eigenstates of the algebraic Hamiltonian (27). With the state mapping proposed, the matrix elements of  $\hat{\mathcal{F}}_{cs}$  on the right-hand side can be translated into the configuration space (28) as

$$\begin{aligned} F_{m',m} &= \langle j, m' | \hat{\mathcal{F}}_{cs} | j, m \rangle = \sum_{i,i'} A_{m,i}^{(j)*} A_{m',i'}^{(j)} \langle j, i' | \hat{\mathcal{F}}_{cs} | j, i \rangle \\ &\equiv \sum_{i,i'} A_{m,i}^{(j)*} A_{m',i'}^{(j)} \langle N, i' | \hat{\mathcal{F}}_{cs} | N, i \rangle \\ &= \sum_{i,i'} A_{m,i}^{(j)*} A_{m',i'}^{(j)} F_{i',i}^{(cs)}, \end{aligned} \quad (37)$$

where  $A_{m,i}^{(j)} = \langle j, i | j, m \rangle$  are the expansion coefficients of the Hamiltonian eigenstates in the selected algebraic basis, and  $F_{i',i}^{(cs)}$  is to be evaluated in the configuration

space as

$$F_{i',i}^{(cs)} = \langle N, i' | \hat{\mathcal{F}}_{cs} | N, i \rangle = \int dq \psi_{N,i'}^*(q) \hat{\mathcal{F}}_{cs}(q, p) \psi_{N,i}(q). \quad (38)$$

Thus, Equation (36) is written as

$$\begin{aligned} \sum_{\gamma} \sum_s \alpha_s^{(\gamma)}(\mathcal{F}_{cs}) \sum_m \langle j, m | \hat{Y}_r^{\dagger(\gamma')} \hat{\rho} \hat{Y}_s^{(\gamma)} | j, m \rangle \\ = \sum_{m,m'} \langle j, m | \hat{Y}_r^{\dagger(\gamma')} \hat{\rho} | j, m' \rangle F_{m',m}, \end{aligned} \quad (39)$$

with  $F_{m',m}$  defined by Equation (37) with  $F_{i',i}^{(cs)}$  to be evaluated in configuration space as Equation (38). All the rest of matrix elements are evaluated in the algebraic space.

The solution of the set (39) provides us with the coefficients  $\alpha_s^{(\gamma)}(\mathcal{F}_{cs})$  that produce the best algebraic image of a given configuration space operator  $\hat{\mathcal{F}}_{cs}$ . The  $\alpha_s^{(\gamma)}(\mathcal{F}_{cs})$  coefficients will be functions of both the matrix elements of the operator in the configuration space ( $F_{i',i}^{(cs)}$ ) and the algebraic matrix elements  $m_{ij} = \|\mathbf{M}\|$ . We stress the fact that the matrix  $\mathbf{M}$  depends only on the algebraic structure, but not on the operator  $\hat{\mathcal{F}}_{cs}$  involved. This may suggest that the matrix  $\mathbf{M}$  is computed once and for all given an algebraic structure, but this is not completely true. The expansion (30) strongly depends on the physical situation, which determines the dynamical symmetry and consequently the basis of the Lie algebra to be considered.

The solution of the set (39) depends obviously on the selected form for the operators  $\hat{Y}_s^{(\gamma)}$ . A particular and relevant situation arises when these operators may be identified with ladder operators that connect an algebraic basis state  $|j, m\rangle$  to another  $|j, m + \gamma\rangle$

$$\hat{Y}_s^{(\gamma)} |j, m\rangle = C_s(j, m, \gamma) |j, m + \gamma\rangle, \quad (40)$$

where  $C_s(j, m, \gamma)$  are characteristic coefficients defined from  $C_s(j, m, \gamma) = \langle j, m + \gamma | \hat{Y}_s^{(\gamma)} | j, m \rangle$ . Notice that the label  $m$  corresponds to all the algebraic quantum numbers (but  $j$ ) required to specify the states in the algebraic basis  $|j, m\rangle$ , and  $s$  characterises the effect of the operator  $\hat{Y}_s^{(\gamma)}$  on all these quantum numbers. So, a ladder operator  $\hat{Y}_s^{(\gamma)}$  is an operator that changes all the  $m$  quantum numbers of the state  $|j, m\rangle$ , characterised by a vector  $\mathbf{m}$ , in quantities given by a vector  $\gamma$ , to produce a state  $|j, m'\rangle$  characterised by a vector  $\mathbf{m}'$ . In this case, and supposing a dynamical symmetry, which means that the Hamiltonian eigenstates are the basis states, Equation (39) can be simplified as

$$\begin{aligned} \sum_{\gamma} \sum_s \alpha_s^{(\gamma)}(\mathcal{F}_{cs}) \sum_m C_s(j, m, \gamma) C_r^*(j, m, \gamma') \\ \langle j, m + \gamma | \hat{\rho} | j, m + \gamma \rangle \end{aligned} \quad (41)$$

$$= \sum_{m,m'} \langle j, m + \gamma' | \hat{\rho} | j, m' \rangle C_r^*(j, m, \gamma') F_{m',m}, \quad (42)$$

and since the density operator is diagonal,  $\gamma = \gamma'$  on the lhs and  $m + \gamma' = m'$  on the rhs. In addition, the subindexes  $s$  and  $r$  stand for different independent group generators, consequently, on the left-hand side only  $s=r$  gives  $C_s(j, m, \gamma) C_r^*(j, m, \gamma) \neq 0$ . Then, we get

$$\begin{aligned} \alpha_r^{(\gamma)}(\mathcal{F}_{cs}) & \sum_m |C_r(j, m, \gamma)|^2 \rho_{m+\gamma} \\ & = \sum_m \rho_{m+\gamma} F_{m+\gamma,m} C_r^*(j, m, \gamma), \end{aligned} \quad (43)$$

where  $F_{m',m}$ , in this particular case of dynamical symmetry, is just  $F_{m',m}^{(cs)}$  which is to be evaluated in configuration space as Equation (38) and  $C_r(j, m, \gamma)$  are the coefficients defining the ladder operators in the considered algebra.

Now, considering the situation of low temperature, the expression above will be dominated, in both sides, by the state labelled by  $m + \gamma$  with the lowest possible energy. If  $\gamma$  is positive (the ladder operator increases the vibrational quantum number, and hence the energy), this state will be the one with  $m=0$ ,  $m + \gamma = \gamma$ . If  $\gamma$  is negative, the state will be the one with  $m = -\gamma$ ,  $m + \gamma = 0$ . In any case, only one contribution of the density matrix dominates the sum in both sides, so the value of the density matrix does not appear, and we get

$$\alpha_r^{(\gamma)}(\mathcal{F}_{cs}) = F_{\gamma,0}/C_r(j, 0, \gamma), \quad (44)$$

if  $\gamma$  is positive, and

$$\alpha_r^{(\gamma)}(\mathcal{F}_{cs}) = F_{0,-\gamma}/C_r(j, -\gamma, \gamma), \quad (45)$$

if  $\gamma$  is negative.

#### 4. Connection between the $su(\nu + 1)$ -algebraic and configuration spaces using a mapping through harmonic oscillator functions

In the preceding section, we have presented a summary of the proposed method to connect configuration and algebraic spaces for a general dynamical generating algebra [40]. Here, we present the situation where the mapping (28) is established through the set (4) corresponding to the harmonic oscillator basis, while in the next section it will be worked out when the mapping is established through the Morse anharmonic oscillator basis (15).

We then proceed to establish an isomorphism between the direct product of  $\nu$ -oscillator states in configuration space  $\mathcal{C}$  and the  $u(\nu + 1)$  algebraic space  $\mathcal{A}$ . For convenience, we shall first restrict ourselves to the case of two oscillators:  $U(3)$  model. The generalisation is obtained in

a straightforward way as it will be shown in due course. The  $U(3)$  group presents four relevant chains in molecular physics

$$(a) \quad U(3) \supset U(2) \supset U(1), \quad (46)$$

$$(b) \quad U(3) \supset U(2) \supset SO(2), \quad (47)$$

$$(c) \quad U(3) \supset SO(3) \supset SO(2), \quad (48)$$

$$(d) \quad U(3) \supset \overline{SO}(3) \supset SO(2). \quad (49)$$

In accordance with the standard point of view, the canonical chain (a) is used in the description of two equivalent vibrational modes like in the model we are concerned to. The second chain (b) is suitable to describe the bending modes of a linear molecule [20]. In this case, the associated kets are isomorphic to the 2D harmonic oscillator basis with good angular momentum projection. The corresponding dynamical symmetry corresponds to the description of the vibrational excitations of a 2D oscillator. Chain (c) provides a dynamical symmetry for a displaced oscillator (non-linear molecules). While the chain (d) is in principle equivalent to (c) in the framework of the same applications [20,49]. In this section, we show that the first and the last two chains become relevant in the physics of two equivalent oscillators. The chains associated with linear and non-linear triatomic molecules will be considered in a forthcoming work.

We start considering the stretching oscillators of a triatomic molecule. Associated with these oscillators we have the creation and annihilation bosonic operators  $\{\hat{a}_1^\dagger, \hat{a}_1, \hat{a}_2^\dagger, \hat{a}_2\}$ . Bilinear products of these bosonic operators form the  $u(2)$  algebra. The addition of the boson  $\hat{s}^\dagger(\hat{s})$  leads to the algebra  $u(3)$  with 9 generators given by

$$G_{u(3)} = \{\hat{a}_1^\dagger \hat{a}_1, \hat{a}_1^\dagger \hat{a}_2, \hat{a}_2^\dagger \hat{a}_1, \hat{a}_2^\dagger \hat{a}_2, \hat{s}^\dagger \hat{a}_1, \hat{a}_1^\dagger \hat{s}, \hat{s}^\dagger \hat{a}_2, \hat{a}_2^\dagger \hat{s}, \hat{s}^\dagger \hat{s}\}. \quad (50)$$

This is the dynamical algebra for two equivalent oscillators where the projection of the angular momentum is not preserved. The matrix elements of these operators in the canonical basis are:

$$\begin{aligned} \hat{n}_s |N, n; n_1, n_2\rangle & = (N - n) |N, n; n_1, n_2\rangle \\ & \text{with } n = n_1 + n_2 \end{aligned} \quad (51a)$$

$$\hat{n}_i |N, n; n_1, n_2\rangle = n_i |N, n; n_1, n_2\rangle, \quad (51b)$$

$$\begin{aligned} \hat{a}_i^\dagger \hat{s} |N, n; n_1, n_2\rangle & = \sqrt{(N - n)(n_i + 1)} \\ & \times |N, n; \dots, n_i + 1, \dots\rangle, \end{aligned} \quad (51c)$$

$$\begin{aligned} \hat{s}^\dagger \hat{a}_i |N, n; n_1, n_2\rangle & = \sqrt{(N - n + 1)n_i} \\ & \times |N, n; \dots, n_i - 1, \dots\rangle, \end{aligned} \quad (51d)$$

$$\hat{a}_1^\dagger \hat{a}_2 |N, n; n_1, n_2\rangle = \sqrt{(n_1 + 1)n_2} |N, n; n_1 + 1, n_2 - 1\rangle, \quad (51e)$$

$$\hat{a}_2^\dagger \hat{a}_1 |N, n; n_1, n_2\rangle = \sqrt{(N - n_2 + 1)n_1} \times |N, n; n_1 - 1, n_2 + 1\rangle. \quad (51f)$$

Let us now proceed to establish the mapping between the algebraic and configuration space bases. We shall consider the direct product of two harmonic oscillators

$$\langle q_1 q_2 | n_1, n_2 \rangle = \langle q_1 | n_1 \rangle \langle q_2 | n_2 \rangle, \quad (52)$$

defined in a subspace characterised by the total number of quanta  $P$ :

$$n = n_1 + n_2; \quad n = 0, 1, \dots, P. \quad (53)$$

In this way, we define the constraint space of harmonic oscillators as

$$\langle q_1 q_2 | n_1, n_2 \rangle = \langle q_1 q_2 | n; n_1, n_2 \rangle; \quad n = 0, 1, \dots, P. \quad (54)$$

We now propose the mapping

$$\langle q_1 q_2 | n; n_1, n_2 \rangle \approx |[N], n; n_1, n_2\rangle; \quad N = P_{\max}. \quad (55)$$

The density operator takes thus the form

$$\hat{\rho} = \sum_{n_1, n_2}^{n_1 + n_2 = P} p_{n_1, n_2} |[N], n; n_1, n_2\rangle \langle [N], n; n_1, n_2|; \quad n = n_1 + n_2; \quad n = 0, 1, \dots, P. \quad (56)$$

For convenience, we shall simplify this expression as

$$\hat{\rho} = \sum_{n_1, n_2} p_{n_1, n_2} |n_1, n_2\rangle \langle n_1, n_2|. \quad (57)$$

With this consideration, we wonder about the best algebraic description of an operator given in configuration space  $\mathcal{C}$ . In particular, we shall be interested in the coordinate and momenta of the individual oscillators. To this end, we may start proposing the following expansion up to linear order for operators  $\hat{\mathcal{F}}_{cs}^{(1)}$  (a superindex (1) is included so as to remind that here the case of linear approximation is treated) associated with the first oscillator (30), with  $\gamma = 1$  (we are not stating the  $\gamma$ -value for simplicity in this section):

$$\hat{\mathcal{F}}_{alg}^{(1)} \cong \sum_{s=1}^2 \alpha_s (\mathcal{F}_{cs}^{(1)}) \hat{Y}_s, \quad (58)$$

with the following identification:

$$\hat{Y}_1 = \hat{a}_1^\dagger \hat{s}; \quad \hat{Y}_2 = \hat{s}^\dagger \hat{a}_1. \quad (59)$$

We have not included operators involving quanta changes in both oscillators, since they cannot be expected to contribute in expansions associated with operators corresponding to individual oscillators, e.g. coordinates and

momenta of a given oscillator. Diagonal operators were not included either because the diagonal harmonic oscillators matrix elements vanish.

Based on the matrix elements (51), we notice that the operators (59) are ladder operators and consequently it is straightforward the result of Equation (44). We next proceed to identify the operators with the coordinate and momentum. For coordinates and momenta in phase space, we are using the notation  $(\hat{q}, \hat{p})$ , while in the algebraic space the notation  $(\hat{Q}, \hat{P})$  is used for the same observables.

#### Coordinate $Q_1$

The non-vanishing matrix elements of  $q_1$  in configuration space are ( $\mu$  and  $\omega$  are the reduced mass and the frequency of the oscillator, respectively)

$$\langle n_1 + 1, n_2 | \hat{q}_1 | n_1, n_2 \rangle = \sqrt{\frac{\hbar}{2\mu\omega}} \sqrt{n_1 + 1}, \quad (60a)$$

$$\langle n_1 - 1, n_2 | \hat{q}_1 | n_1, n_2 \rangle = \sqrt{\frac{\hbar}{2\mu\omega}} \sqrt{n_1}, \quad (60b)$$

which together with Equation (51) provide explicit values for  $\alpha_s$ . This means that we must take  $\{n_1 = 0, n_2 = 0\}$  for  $\alpha_1$  and  $\{n_1 = 1, n_2 = 0\}$  for  $\alpha_2$ . This substitution, using Equations (44) and (45), leads to

$$\alpha_1 = \sqrt{\frac{\hbar}{2\mu\omega}} \frac{1}{\sqrt{N}}; \quad \alpha_2 = \sqrt{\frac{\hbar}{2\mu\omega}} \frac{1}{\sqrt{N}}, \quad (61)$$

which have the same magnitude and are state independent. This is not just a practical result that allows manipulation of expressions, but is crucial to connect the configuration space with the  $U(3)$  realisation. The coordinate  $q_1$  takes now the simple algebraic realisation

$$\hat{Q}_1 = \sqrt{\frac{\hbar}{2\mu\omega}} \left( \frac{\hat{a}_1^\dagger \hat{s}}{\sqrt{N}} + \frac{\hat{s}^\dagger \hat{a}_1}{\sqrt{N}} \right), \quad (62)$$

with matrix elements

$$\begin{aligned} \langle [N], n; n_1 + 1, n_2 | \hat{Q}_1 | [N], n; n_1, n_2 \rangle \\ = \sqrt{\frac{\hbar}{2\mu\omega}} \sqrt{(n_1 + 1)} \left( 1 - \frac{n}{N} \right), \end{aligned} \quad (63a)$$

$$\begin{aligned} \langle [N], n; n_1 - 1, n_2 | \hat{Q}_1 | [N], n; n_1, n_2 \rangle \\ = \sqrt{\frac{\hbar}{2\mu\omega}} \sqrt{n_1} \left( 1 - \frac{n-1}{N} \right). \end{aligned} \quad (63b)$$

Here, we can appreciate the advantage of our approach. Even though the mapping was carried out to the harmonic oscillator basis, the final result does reproduce

the harmonic case only in the limit  $N \rightarrow \infty$ . Indeed, the matrix elements of the coordinate are modified by an anharmonic correction, which vanishes in that limit. This fact represents the key to apply the  $U(\nu + 1)$  model keeping the connection with configuration space.

#### Momentum $\mathcal{P}_1$

The only non-vanishing matrix elements for the momentum  $\hat{p}_1$  in configuration space are

$$\langle n_1 + 1, n_2 | \hat{p}_1 | n_1, n_2 \rangle = \frac{i}{2} \sqrt{2\hbar\mu\omega} \sqrt{n_1 + 1}, \quad (64a)$$

$$\langle n_1 - 1, n_2 | \hat{p}_1 | n_1, n_2 \rangle = -\frac{i}{2} \sqrt{2\hbar\mu\omega} \sqrt{n_1}. \quad (64b)$$

Using Equations (44) and (45) again and using for the coefficients notation now  $\beta$  instead of  $\alpha$ , it is obtained

$$\beta_1 = \frac{i}{2} \sqrt{2\hbar\mu\omega} \frac{1}{\sqrt{N}}; \quad \beta_2 = -\frac{i}{2} \sqrt{2\hbar\mu\omega} \frac{1}{\sqrt{N}}. \quad (65)$$

and consequently

$$\hat{\mathcal{P}}_1 \cong \frac{i}{2} \sqrt{2\hbar\mu\omega} \left( \frac{\hat{a}_1^\dagger \hat{s}}{\sqrt{N}} - \frac{\hat{s}^\dagger \hat{a}_1}{\sqrt{N}} \right), \quad (66)$$

with matrix elements

$$\begin{aligned} & \langle [N], n; n_1 + 1, n_2 | \hat{\mathcal{P}}_1 | [N], n; n_1, n_2 \rangle \\ &= \frac{i}{2} \sqrt{2\hbar\mu\omega} \sqrt{(n_1 + 1)} \left( 1 - \frac{n}{N} \right), \end{aligned} \quad (67a)$$

$$\begin{aligned} & \langle [N], n; n_1 - 1, n_2 | \hat{\mathcal{P}}_1 | [N], n; n_1, n_2 \rangle \\ &= -\frac{i}{2} \sqrt{2\hbar\mu\omega} \sqrt{n_1} \left( 1 - \frac{n - 1}{N} \right). \end{aligned} \quad (67b)$$

As in the case of the coordinate, anharmonic corrections appear characterizing the  $su(3)$  approach.

#### Generalization

On the basis of these results, we can generalize the connection with configuration space for the  $u(\nu + 1)$  algebraic model for  $\nu$ -oscillators. Defining the operators

$$\hat{b}_i^\dagger = \frac{\hat{a}_i^\dagger \hat{s}}{\sqrt{N}}; \quad \hat{b}_i = \frac{\hat{s}^\dagger \hat{a}_i}{\sqrt{N}}, \quad (68)$$

we have for the coordinates and momenta

$$\hat{\mathcal{Q}}_i = \sqrt{\frac{\hbar}{2\mu\omega}} (\hat{b}_i^\dagger + \hat{b}_i), \quad (69a)$$

$$\hat{\mathcal{P}}_i = \frac{i}{2} \sqrt{2\hbar\mu\omega} (\hat{b}_i^\dagger - \hat{b}_i). \quad (69b)$$

The matrix elements of these operators coincide with Equations (63) and (67) and are obtained from

Equation (21). The harmonic limit is recovered in the limit  $N \rightarrow \infty$ , as expected.

As a consequence of our approximation, the expansions (69) do not satisfy the commutation relations  $[q, \hat{p}] = i\hbar$ . In fact, we have

$$[\hat{\mathcal{Q}}_i, \hat{\mathcal{P}}_j] = i\hbar\delta_{ij} \left( 1 - \frac{n}{N} \right) - i\hbar \frac{a_i^\dagger a_j + a_j^\dagger a_i}{2N}, \quad (70)$$

from which we see that the canonical commutation relations are recovered only in the limit  $N \rightarrow \infty$ . Another feature of this approach is that the coordinates and momenta associated with different oscillators do not commute:

$$[\hat{\mathcal{Q}}_i, \hat{\mathcal{Q}}_j] = \frac{\hbar}{2\omega\mu} \left\{ \frac{\hat{a}_i^\dagger \hat{a}_j - \hat{a}_j^\dagger \hat{a}_i}{N} \right\}, \quad (71a)$$

$$[\hat{\mathcal{P}}_i, \hat{\mathcal{P}}_j] = \frac{\hbar\omega\mu}{2} \left\{ \frac{\hat{a}_i^\dagger \hat{a}_j - \hat{a}_j^\dagger \hat{a}_i}{N} \right\}. \quad (71b)$$

This fact implies significant practical consequences. Either a symmetry projection procedure should be required when translating a general Hamiltonian into the corresponding algebraic representation or non-commutativity has to be assumed.

The results in this section formally justify the proposal presented in Ref. [36–39], where the PES was estimated and dipole transition strengths were calculated using Equation (69).

The advantage of counting on the algebraic realization of coordinates and momenta is that any ambiguity concerning the representation of an interaction disappears. The Darling–Dennison (DD) interaction, for instance, may appear either in the kinetic or in the potential energy contributions. The lowest order in the potential where the DD interaction appears is given by

$$\hat{V}_{cs} = \frac{6}{4} q_1^2 q_2^2. \quad (72)$$

Because of Equation (71a), in order to translate this expression into the algebraic approach we have to recast the potential without assuming the commutation relation  $[q_i, q_j] = 0$ :

$$\begin{aligned} \hat{V}_{cs} &= \frac{1}{4} (q_1^2 q_2^2 + q_1 q_2 q_1 q_2 + q_2 q_1 q_2 q_1 \\ &+ q_1 q_2^2 q_1 + q_2 q_1^2 q_2 + q_2^2 q_1^2). \end{aligned} \quad (73)$$

Applying

$$\hat{q}_i \rightarrow \hat{\mathcal{Q}}_i; \quad \hat{p}_i \rightarrow \hat{\mathcal{P}}_i, \quad (74)$$

we obtain

$$\begin{aligned} \hat{V}_{alg} &= \frac{1}{4} (Q_1^2 Q_2^2 + Q_1 Q_2 Q_1 Q_2 + Q_2 Q_1 Q_2 Q_1 \\ &+ Q_1 Q_2^2 Q_1 + Q_2 Q_1^2 Q_2 + Q_2^2 Q_1^2) \end{aligned} \quad (75)$$



and introducing Equation (69) we identify the DD contribution  $\hat{D}_{alg}$  in the following form:

$$\hat{D}_{alg} = \frac{1}{4} \frac{\hbar^2}{4\mu\omega} (2\hat{b}_1^{\dagger 2}\hat{b}_2^2 + b_1^{\dagger}b_2^2b_1^{\dagger} + b_2^{\dagger}b_1^2b_2^{\dagger} + b_1^{\dagger}b_2b_1^{\dagger}b_2 + b_1b_2^{\dagger}b_1b_2^{\dagger} + H.c.). \quad (76)$$

For comparison, the same interaction in terms of Morse oscillators in the framework of the  $SU_1(2) \otimes SU_2(2)$  model takes the simple form [50]

$$\hat{D}_{alg}^{su(2)} = \frac{6}{4} \frac{\hbar^2}{4\mu\omega} (\hat{b}_1^{\dagger 2}\hat{b}_2^2 + H.c.), \quad (77)$$

since the variables for different oscillators commute.

In order to end this section, we shall identify now the physical insight contained in chain (46). We start writing the Hamiltonian of two non-interacting oscillators. In configuration space, we have

$$\hat{H}_{cs} = \frac{1}{2\mu} \sum_{i=1}^2 \hat{p}_i^2 + \frac{1}{2}k \sum_{i=1}^2 \hat{q}_i^2. \quad (78)$$

The algebraic Hamiltonian is obtained by the identification (74), and the substitution of Equation (69) into Equation (78). The result provides the algebraic Hamiltonian

$$\hat{H}_{alg} = \frac{\hbar\omega}{2} \sum_{i=1}^2 (\hat{b}_i^{\dagger}\hat{b}_i + \hat{b}_i\hat{b}_i^{\dagger}), \quad (79)$$

with eigenvalues

$$\begin{aligned} E(N, n_1, n_2) &= \langle [N]; n; n_1, n_2 | \hat{H}_{alg} | [N]; n; n_1, n_2 \rangle \\ &= \hbar\omega \sum_{i=1}^2 \left\{ \left[ \left( 1 + \frac{1}{2N} \right) n_i + 1/2 \right] - \frac{n}{2N} - \frac{n n_i}{N} \right\}, \end{aligned} \quad (80)$$

from which we identify the peculiar anharmonic contribution  $nn_i$  involving the polyad number  $n$  with anharmonicity  $\hbar\omega/N$  and the linear polyad dependent factor  $= -n/2N$ . When  $N \rightarrow \infty$  the harmonic limit is recovered. Notice the difference with respect to the individual Morse oscillators, where the anharmonicity has the form  $n_i^2$  (see Equation (11)). Since Equation (80) is diagonal in the  $U(2)$  basis we say that chain (46) is associated with the energy representation. In the Appendix, we will show that the dynamical symmetries based on chains (48) and (49) provide basis states that are associated with coordinate and momenta representations, respectively.

Here, we have developed the  $U(v+1)$  model assuming a mapping with a harmonic oscillator basis. We next discuss how to apply this model in order to reproduce the matrix elements of Morse oscillators.

## 5. Connection between the $su(v+1)$ -algebraic and configuration spaces using a mapping with Morse functions

In this section, we start considering a mapping of the  $U(3)$  algebraic model with two non-interacting Morse oscillators [51]. We intend to improve beyond the linear approximation the algebraic description of the coordinates and momenta obtained in the preceding section.

The Schrödinger equation associated with the 1D Morse potential

$$V_M(q) = D(1 - e^{-\beta q})^2 \quad (81)$$

has the following solutions:

$$\langle z | jv \rangle = N_v^j e^{-z/2} z^s L_v^{2s}(z), \quad (82)$$

where  $L_v^{2s}(z)$  are the associated Laguerre functions, the argument is related to the physical coordinate  $q$  by  $z = (2j+1)e^{-\beta q}$ ,  $N_v^j$  is the normalization constant

$$N_v^j = \sqrt{\frac{\beta(k-2v-1)\Gamma(v+1)}{\Gamma(k-v)}}, \quad (83)$$

and the variables  $j$  and  $s$  are related to the depth of the potential and the energy, respectively, through

$$\kappa = 2j+1 = \sqrt{\frac{8\mu D}{\beta^2 \hbar^2}}, \quad s = \sqrt{\frac{-2\mu E}{\beta^2 \hbar^2}}, \quad (84)$$

with the constraint condition  $s=j-v$  leading to the energy

$$E_M(j; v) = \hbar\omega \left[ (v+1/2) - \frac{1}{k}(v+1/2)^2 \right], \quad (85)$$

with

$$\hbar\omega = 2\hbar\beta \sqrt{\frac{D}{2\mu}}. \quad (86)$$

The matrix elements of the momentum  $\hat{p}$  are [52]

$$\langle jv + \gamma | \hat{p} | jv \rangle = (1 - \delta_{0\gamma}) \frac{i\hbar\beta}{2} (-1)^{\gamma+1} \zeta(v, \gamma), \quad (87)$$

while for the coordinate  $y = 1 - e^{-\beta q}$  we have [53]

$$\langle jv + \gamma | y | jv \rangle = \delta_{\gamma 0} - \frac{(-1)^\gamma}{k} \zeta(v, \gamma), \quad (88)$$

with  $\gamma = 0, 1, \dots, j-v-1$  and the function  $\zeta(v, \gamma)$  defined by

$$\zeta(v, \gamma) = \sqrt{\frac{(k-2v-1)(k-2v-2\gamma-1)(v+\gamma)!(k-v-\gamma-1)!}{v!(k-v-1)!}}. \quad (89)$$

Let us now consider the space  $\mathcal{C}'$  of the direct product of two equivalent Morse oscillators characterized by  $j$  bound states

$$\begin{aligned} \langle q_1, q_2 | j; v_1, v_2 \rangle &= \langle q_1 | j; v_1 \rangle \otimes \langle q_2 | j; v_2 \rangle; \\ v_i &= 0, 1, \dots, j-1. \end{aligned} \quad (90)$$

A subspace  $\mathcal{C} \subset \mathcal{C}'$  consists in considering the states up to polyad  $P_{max} = v_1 + v_2 = j-1$ . This means that in this subspace all the states with  $v_1 + v_2 > j-1$  are ignored. This is a reasonable physical situation since most of such states belong to the continuum [54].

We may thus establish the mapping between the  $U(3)$  algebraic states and the configuration space  $\mathcal{C}$  in the following form:

$$\begin{aligned} \langle q_1, q_2 | j; v_1, v_2 \rangle &\approx |[N], n; n_1, n_2]; \quad N = j-1; \\ n_i &\approx v_i = 0, 1, \dots, j-1. \end{aligned} \quad (91)$$

With this consideration, we proceed to realize the coordinates and momenta for each oscillator in the algebraic space.

#### Momentum $\mathcal{P}_i$

We intend to obtain the algebraic expansion of the momentum going beyond the linear approximation, using the form

$$\hat{\mathcal{P}}_i \approx \sum_s \sum_\gamma \beta_s^{(\gamma)}(\hat{p}_i) \hat{Y}_s^{(\gamma)}. \quad (92)$$

Taking into account that the operators  $\hat{Y}_s^{(\gamma)}$  involved are ladder operators with the following action:

$$\begin{aligned} \langle [N]; n + \gamma; \dots, n_i + \gamma, \dots | (a_i^\dagger s)^\gamma | [N]; n; \dots, n_i, \dots \rangle \\ = \sqrt{\frac{(N-n)!(n_i + \gamma)!}{(N-n-\gamma)!n_i!}}, \end{aligned} \quad (93)$$

the coefficients  $\beta_s^{(\gamma)}$  take the form (44) and (45)

$$\begin{aligned} \beta_r^{(\gamma)}(\hat{p}_i) &= \frac{i\hbar\beta}{2}(-1)^{\gamma+1} \\ &\times \sqrt{\frac{(k-\gamma-1)!(N-\gamma)!}{(k-1)!(N)!}}(k-1)(k-2\gamma-1), \end{aligned} \quad (94)$$

where we have taken into account Equation (87) and the identification  $v_i \rightarrow n_i$ . In addition, taking into account that

$$\frac{i}{2}\sqrt{2\hbar\omega\mu} = \frac{i}{2}\hbar\beta\sqrt{k}, \quad (95)$$

we recast the expression in a more suitable form for our purposes

$$\begin{aligned} \beta_r^{(\gamma)}(\hat{p}_i) &= \frac{i}{2}\sqrt{2\hbar\omega\mu}\frac{(-1)^{\gamma+1}}{\sqrt{k}}\sqrt{(k-2\gamma-1)(k-1)} \\ &\times \sqrt{\frac{(N-\gamma)!(k-\gamma-1)!}{(N)!(k-1)!}}. \end{aligned} \quad (96)$$

We now proceed to introduce a function that in the harmonic limit goes to unit. The following limit

$$\begin{aligned} \lim_{k,N \rightarrow \infty} \sqrt{\frac{(N-\gamma)!(k-\gamma-1)!}{(N)!(k-1)!}}(k-2\gamma-1)(k-1) \\ = \sqrt{k^{2-\gamma}N^{-\gamma}} \end{aligned} \quad (97)$$

suggests the definition

$$\begin{aligned} A_\gamma &= \frac{(-1)^{\gamma+1}}{\sqrt{k^{2-\gamma}N^{-\gamma}}} \\ &\times \sqrt{\frac{(N-\gamma)!(k-\gamma-1)!}{(N)!(k-1)!}}(k-2\gamma-1)(k-1), \end{aligned} \quad (98)$$

in such a way that the expansion of the momentum takes, in terms of the  $\hat{b}_i^\dagger$  defined in Equation (19), the final form

$$\begin{aligned} \hat{\mathcal{P}}_i &= \frac{i}{2}\sqrt{2\hbar\omega\mu} \\ &\times \left\{ \sum_{\gamma=1}^{N=j-1} \left(\frac{1}{\sqrt{k}}\right)^{\gamma-1} [A_\gamma(\hat{b}_i^\dagger)^\gamma - A_\gamma^*(\hat{b}_i)^\gamma] \right\}. \end{aligned} \quad (99)$$

The coefficient associated with the annihilation operators  $\beta_r'^{(\gamma)}(\hat{p}_i)$  has been found through the relation

$$\beta_r'^{(\gamma)}(\hat{p}_i) = \beta_r^{(\gamma)*}(\hat{p}_i). \quad (100)$$

The remarkable property of the coefficients is that the following limit is satisfied:

$$\lim_{k,N \rightarrow \infty} A_\gamma = (-1)^{\gamma+1}. \quad (101)$$

This result implies that Equation (99) is indeed a power expansion in  $(1/\sqrt{k})$ . In the large  $N$  limit, but finite, we may take the approximation

$$A_1 = 1, \quad (102)$$

when only linear terms are kept. In this case, the expansion (99) reduces to

$$\hat{\mathcal{P}}_i \cong \frac{i}{2}\sqrt{2\hbar\mu\omega} \left( \frac{\hat{a}_i^\dagger \hat{s}}{\sqrt{N}} - \frac{\hat{s}^\dagger \hat{a}_i}{\sqrt{N}} \right), \quad (103)$$

which is the result previously obtained using the mapping with harmonic oscillators.

### Coordinate $\mathcal{Y}_i$

Similarly to the momentum, we intend here to obtain the algebraic expansion of the coordinate going beyond the linear approximation. For that purpose, we use the form (30)

$$\hat{\mathcal{Y}}_i \approx \alpha_0(\hat{y}_i) + \sum_s \sum_\gamma \alpha_s^{(\gamma)}(\hat{y}_i) \hat{Y}_s^{(\gamma)}, \quad (104)$$

taking into account that the coordinate  $y_i = 1 - e^{-\beta q_i}$  does have a diagonal contribution given by

$$\langle jv_i | y_i | jv_i \rangle = \frac{1 + 2v_i}{k}. \quad (105)$$

We thus have for the coefficient  $\alpha_0$  a simple expression (44)

$$\alpha_0 = \frac{1}{k}. \quad (106)$$

Let us now turn our attention to the non diagonal contributions. Taking into account Equations (88) and (44), we obtain

$$\alpha_r^{(\gamma)} = \frac{(-1)^{\gamma+1}}{k} \sqrt{\frac{(N-\gamma)!(k-\gamma-1)!(k-2\gamma-1)(k-1)}{(N)!(k-1)!}} \quad (107)$$

Now, we consider the limit (97), which makes convenient to introduce the definition (98), in terms of which we obtain the final expression for the expansion of  $\mathcal{Y}_i$ :

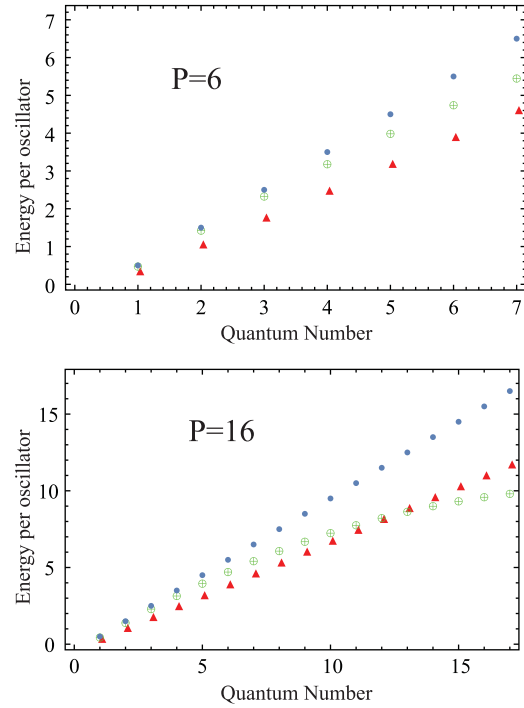
$$\frac{\mathcal{Y}_i}{\beta} = \sqrt{\frac{\hbar}{2\omega\mu}} \left\{ \frac{1}{\sqrt{k}} \delta_{\gamma,0} + \sum_{\gamma=1}^{N=j-1} \left( \frac{1}{\sqrt{k}} \right)^{\gamma-1} [A_\gamma (\hat{b}_i^\dagger)^\gamma + A_\gamma^* (\hat{b}_i)^\gamma] \right\}, \quad (108)$$

where Equation (95) was taken into account. By construction the expressions (99) and (108) reproduce the matrix elements for the Morse oscillators.

In a form similar to the approach followed for the momentum, we can obtain the linear approximation for the coordinate

$$\frac{\mathcal{Y}_i}{\beta} \approx \sqrt{\frac{\hbar}{2\omega\mu}} \left( \frac{\hat{a}_i^\dagger \hat{s}}{\sqrt{N}} + \frac{\hat{s}^\dagger \hat{a}_i}{\sqrt{N}} \right), \quad (109)$$

which is identical to the result previously obtained.

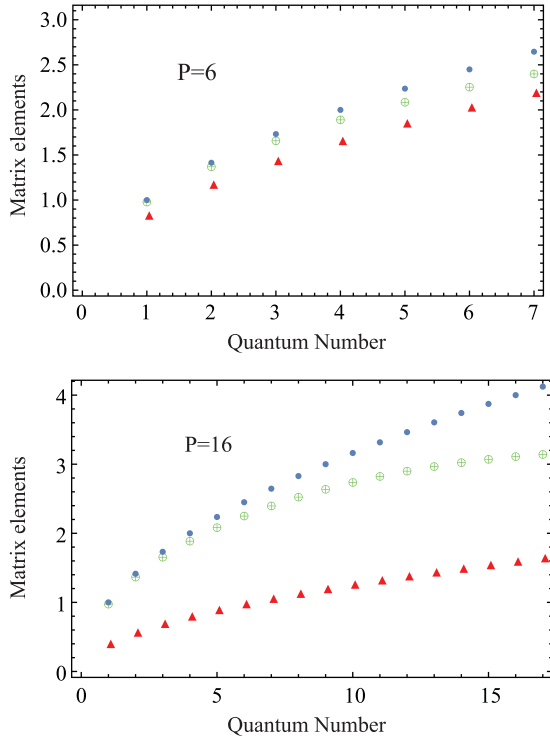


**Figure 1.** Energy per oscillator, in units of  $\hbar\omega$ , provided by the  $U(3)$  model, Equation (80) symbol  $\Delta$ , by the  $SU_1(2) \times SU_2(2)$  model, Equation (85) symbol  $\oplus$ , and by the harmonic oscillator approximation  $\bullet$ . The parameter fixing the dynamical space was taken to be  $j = 20$ , with a subspace corresponding to  $P = 6$  (upper panel) and  $P = 16$  (lower panel).

## 6. Comparison between the $U(3)$ and the $U_1(2) \otimes U_2(2)$ model

In the preceding sections, we have found the algebraic images of the coordinates and momenta with a mapping that uses either harmonic or anharmonic wavefunctions. We have seen that within the  $U(3)$  model anharmonic terms appear naturally. An alternative way of treating two equivalent anharmonic oscillators is to use an  $SU_1(2) \otimes SU_2(2)$  model, for example using Morse wavefunctions, that generates anharmonicity too. The natural question then is, when studying the stretching modes in two equivalent oscillators one can use either  $U(3)$  or  $SU(2) \otimes SU(2)$  models, How to compare the anharmonicities that arose from these two models? In this section, we analyse the differences between the  $U(3)$  model for two equivalent oscillators and the vibrational description in terms of two Morse oscillators considering the linear approximation.

The basic difference between the models is manifested in the energy and the matrix elements for the ladder operators. The energy expressions (80) and (85) establish the difference between the models in the anharmonicity correction. On the other hand for the matrix elements for



**Figure 2.** Dimensionless matrix elements provided by the  $U(3)$  model, Equation (110), symbol  $\Delta$ , by the  $SU_1(2) \times SU_2(2)$  model, Equation (111), symbol  $\oplus$ , and by the harmonic oscillator approximation  $\bullet$ . The parameter fixing the dynamical space was taken to be  $j = 20$ , with a subspace corresponding to  $P = 6$  (upper panel) and  $P = 16$  (lower panel).

the  $U(3)$  we have (21)

$$\begin{aligned} & \langle [N], n+1; n_1+1, n_2 | \hat{b}_i^\dagger | [N], n; n_1, n_2 \rangle \\ &= \sqrt{(n_i+1) \left(1 - \frac{n}{N}\right)}, \end{aligned} \quad (110)$$

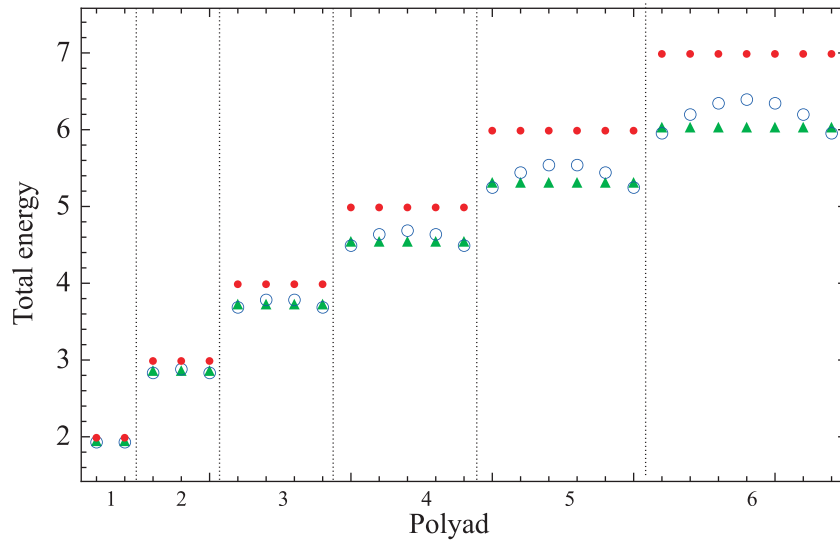
while in the  $U_1(2) \otimes U_2(2)$  model [34], the equivalent ladder operator  $b_1^\dagger$  is (8)

$$\langle j; n_1+1, n_2 | \hat{b}_i^\dagger | j; n_1, n_2 \rangle = \sqrt{(n_i+1) \left(1 - \frac{n_i+1}{2j+1}\right)}. \quad (111)$$

The difference, as noticed before, relies on the anharmonic correction. The  $U(3)$  model involves the polyad  $n$ , while the Morse oscillator is given in terms of the individual quantum numbers  $n_i$ . The relation between the parameters is  $N = 2j+1$ . We expect that as the polyad increases, the difference becomes more significant.

In Figure 1, the energy as a function of the quantum number for polyad  $P = 6$  is displayed in the upper panel while in Figure 2, upper panel, the matrix elements for the same polyad are given for both the  $U(3)$  and the  $SU_1(2) \otimes SU_2(2)$  model, as well as for the harmonic oscillator limit. In order to see the polyad number effect, in Figures 1 and 2 (lower panels) the energy and matrix elements are displayed but for polyad 16, in both cases taken  $j = 20$ . As noticed, as the quantum number increases, the difference between the models becomes more significant, providing the  $U(3)$  model a much significant anharmonicity. In Figure 3, the total energy for the two oscillators in different polyads (from  $P = 1$  to  $P = 7$ ) is presented.

The application of the  $U(v+1)$  approach starting with configuration space and invoking the transformations (74) leads to the peculiar expression (80) for the zeroth-order energy whose behaviour introduces polyad energy leaps. This anomalous behaviour has been



**Figure 3.** Polyad total energy, in units of  $\hbar\omega$ , from  $P = 1$  to  $P = 7$  for the two oscillators provided by the  $U(3)$  model, Equation (80) symbol  $\Delta$ , by the  $SU_1(2) \times SU_2(2)$  model, Equation (85) symbol  $\oplus$ , and by the harmonic oscillator approximation  $\bullet$ .

avoided from the applications where Equation (74) was used [38,39] but also in the original applications of the model [55–57], by taking the harmonic limit. In this way, the correspondence (74) is used in a selected way with preference to the resonances. Following the  $U(\nu + 1)$  algebraic approach with this consideration has not shown differences in the model of interacting Morse oscillators since the polyads involved are moderate. For instance, the pyramidal molecules stibine and arsine have been studied with both schemes without showing different results in the energy description [30,36–39].

## 7. Summary and conclusions

In this paper, we have presented a realization of the dynamical variables in the framework of the  $U(\nu + 1)$  model to describe the vibrational excitations of  $\nu$  equivalent oscillators. To accomplish this goal, we have followed the approach recently proposed where the algebraic realization is obtained through a minimization procedure [40].

A fundamental ingredient of our method consists in establishing a mapping between the algebraic and configuration spaces. Two mappings were proposed, to a harmonic oscillator basis and to a direct product of Morse oscillators. When the mapping with harmonic oscillators is considered with specific values for the weights involved in the density operator, the algebraic realization of coordinate and momenta reduces to state-independent coefficients, providing the scheme to apply the  $U(\nu + 1)$  model keeping the connection with configuration space, in a similar way to the previous applications based on heuristic arguments [36–39].

We have also shown the reliability of our approach to deal with a description of Morse oscillators for the realization of momenta and coordinates in the  $U(\nu + 1)$  algebraic approach. In this case, an expansion involving state-independent coefficients can be obtained too.

We have proved that the  $U(\nu + 1)$  approach takes into account anharmonicities from the outset with the peculiar feature that the polyad is involved in the anharmonic correction. This fact is a manifestation of the entanglement of the states belonging to the same polyad within this approximation.

In addition to the canonical chain associated with the states used in the mapping between configuration and algebraic spaces, two additional chains with physical significance emerge for the case of two oscillators containing the orthogonal groups (see Appendix). We have shown (Section 4 and Appendix) that the states associated with the dynamical symmetries correspond to representation of different observable operators. Hence, chain (46) is associated with the energy representation, chain (48)

to the coordinate representation and chain (49) to the momentum representation. This is indeed the case only for our approximation (69).

The application of this approach in the linear approximation has already been presented for the case of pyramidal molecules although in a hybrid manner: the zeroth-order interactions are considered in the harmonic limit, while higher order interactions and resonances are considered using the correspondence (74). The resulting spectroscopic parameters are connected to the structure and force constants. This approach allowed the force constants to be estimated.

The advantages of the  $U(3)$  model in the linear approximation may be summarized in the following aspects: (a) the dynamical group is compact, (b) three dynamical symmetries with physical meaning emerge and (c) the total number of bosons  $N$  provides a measure of the anharmonicity. In addition, counting on the connection with coordinates and momenta allows one to deal with the calculation of transition intensities following equivalent descriptions to those used in configuration space.

## Notes

1. Along this work, the usual convention of using upper-case roman letters for a Lie group and lower-case roman letters for the corresponding Lie algebra is used. In addition, it should be noted that special unitary and orthogonal groups/algebras appear when a scalar quantity in conserved due to the isomorphism  $U(n) \simeq SU(n) \otimes U(1)$ . Thus, since this is our case, the use of  $U(n)/u(n)$ ,  $O(n)/o(n)$  or  $SU(n)/su(n)$ ,  $SO(n)/so(n)$  is equivalent.
2. Notice that to describe a system in equilibrium with a thermal bath of temperature  $T$ , we can use  $p_\gamma = e^{-E_{N,\gamma}/K_B T} / Z$  with  $Z = \sum_\gamma e^{-E_{N,\gamma}/K_B T}$ .

## Disclosure statement

No potential conflict of interest was reported by the authors.

## Funding

This work is partially supported by DEGAPA-UNAM (Dirección General de Asuntos del Personal Académico, Universidad Nacional Autónoma de México), Mexico, under project IN-227017, by Spanish Consejería de Economía, Innovación, Ciencia y Empleo, Junta de Andalucía (Agencia de Innovación y Desarrollo de Andalucía) [grant numbers FQM-160, P11-FQM-7632] and by the Spanish Ministerio de Economía y Competitividad and FEDER funds under projects FIS2017-88410-P and FPA2016-77689-C2-1-R.

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## Appendix. Meaning of the different $U(3)$ chain reductions

In Section 4, we have identified that chain (46) provides basis states that diagonalize the Hamiltonian (79) and we say that this chain is associated with the energy representation of the problem. In this appendix, we shall identify the physical insight contained in chains (48) and (49). We start identifying the

following two sets:

$$G_{SO(3)} = \{\hat{J}_x = (\hat{a}_1^\dagger \hat{s} + \hat{s}^\dagger \hat{a}_1), \hat{J}_y = (\hat{a}_2^\dagger \hat{s} + \hat{s}^\dagger \hat{a}_2), \hat{J}_z = i(\hat{a}_2^\dagger \hat{a}_1 - \hat{a}_1^\dagger \hat{a}_2)\}, \quad (\text{A1})$$

$$G_{\overline{SO}(3)} = \{\hat{J}'_x = i(\hat{a}_1^\dagger \hat{s} - \hat{s}^\dagger \hat{a}_1), \hat{J}'_y = i(\hat{a}_2^\dagger \hat{s} - \hat{s}^\dagger \hat{a}_2), \hat{J}'_z = i(\hat{a}_2^\dagger \hat{a}_1 - \hat{a}_1^\dagger \hat{a}_2)\}, \quad (\text{A2})$$

as the commutation relations for the  $SO(3)$  and  $\overline{SO}(3)$  groups, respectively. The corresponding invariant operators are

$$\hat{W}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2, \quad (\text{A3})$$

$$\hat{W}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2; \quad \hat{J}_z^2 = \hat{J}_z^2, \quad (\text{A4})$$

and introducing the coordinate and momenta realization (69) we have

$$\sum_{i=1}^2 \hat{Q}_i^2 = \frac{\hbar}{2\omega\mu N} (\hat{W}^2 - \hat{J}_z^2), \quad (\text{A5a})$$

$$\sum_{i=1}^2 \hat{P}_i^2 = \frac{\hbar\omega\mu}{2N} (\hat{W}^2 - \hat{J}_z^2), \quad (\text{A5b})$$

from which we conclude that the chains

$$(c) \quad U(3) \supset SO(3) \supset SO(2), \quad (\text{A6})$$

$$(d) \quad U(3) \supset \overline{SO}(3) \supset SO(2), \quad (\text{A7})$$

are associated with the representation of the sum of squares of the coordinates and momenta, respectively. Thus, the basis

**Table A1.** Identification of the dynamical symmetries according to energy, coordinates and momenta representation.

Chain	Basis	Representation
$U(3) \supset U(2) \supset SO(2)$	$ [N]; n\rangle$	Energy
$U(3) \supset \overline{SO}(3) \supset SO(2)$	$ [N]; \omega\rangle$	Coordinates
$U(3) \supset \overline{SO}(3) \supset SO(2)$	$ [N]; \bar{\omega}\rangle$	Momenta

Note: The labels  $\omega$  and  $\bar{\omega}$  are associated with the irrep of  $SO(3)$  and  $\overline{SO}(3)$ , respectively.

states linked to the dynamical symmetries (c) and (d) are the eigenstates of the Hamiltonians

$$\hat{H}_{alg}^{(c)} = \frac{1}{2}k \sum_{i=1}^2 \hat{Q}_i^2 = \frac{\hbar\omega}{2} \frac{1}{N} (\hat{W}^2 - \hat{J}_z^2),$$

$$\hat{H}_{alg}^{(d)} = \frac{1}{2\mu} \sum_{i=1}^2 \hat{P}_i^2 = \frac{\hbar\omega}{2} \frac{1}{N} (\hat{W}^2 - \hat{J}_z^2),$$

respectively. And consequently, provide representations in terms of coordinates (chain c) and momenta (chain d).

In terms of Casimir operators the algebraic Hamiltonian can be recasted in the form

$$\hat{H}_{alg} = \frac{1}{2\mu} \sum_{i=1}^2 \hat{P}_i^2 + \frac{1}{2}k \sum_{i=1}^2 \hat{Q}_i^2 = \frac{\hbar\omega}{2} \frac{1}{N} (\hat{W}^2 + \hat{W}^2 - 2\hat{J}_z^2). \quad (\text{A8})$$

which reduces to Equation (80). In Table A1, we summarize the meaning of the different chains.