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# Freely jointed molecular chain: Dynamical variables, quantization, and statistical mechanics

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A freely rotating linear chain, formed by $N$ ($N \geq 2$) atoms with $N-1$ "bonds" of fixed lengths, is studied in three spatial dimensions. The classical ($c$) theory of that constrained system is formulated in terms of the classical transverse momentum $-\mathbf{a}_{j,c}$ and angular momentum $\mathbf{l}_{j,c}$ associated to the $j$th "bond" ($j=1,\ldots,N-1$). The classical Poisson brackets of the Cartesian components of $-\mathbf{a}_{j,c}$ and $\mathbf{l}_{j,c}$ are shown to close an algebra. The quantization of the chain in spherical polar coordinates is carried out. The resulting "curved-space" quantization yields modified angular momenta $\mathbf{l}_j$. Quantum-mechanical transverse momenta ($\mathbf{e}_j$) are constructed. The commutators of the Cartesian components of $\mathbf{e}_j$ and $\mathbf{l}_j$ satisfy a closed Lie algebra, formally similar to the classical one for Poisson brackets. Using $\mathbf{e}_j$'s and $\mathbf{l}_j$'s, the quantum theory is shown to be consistent by itself and, via the correspondence principle, with the classical one. Several properties of $\mathbf{e}_j$ and the modified $\mathbf{l}_j$ are given: some sets of eigenfunctions (modified spherical harmonics, etc.) and uncertainty relations. As an example, the case of $N=3$ atoms in two spatial dimensions is worked out. The peculiar properties of the chain regarding distinguishability at the quantum level play an important role in justifying the absence of a "Boltzmann counting" factor $[(N-1)!]^{-1}$ in its classical statistical distribution. The physical limitations and the methodological virtues of the model at the classical and quantum levels, and its relationship to previous works by different authors, are discussed.

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## I. INTRODUCTION

A freely jointed or freely rotating linear chain (or discretized string) is formed by $N$ ($\geq 2$) atoms so that the $N-1$ relative distances ("bonds" or "links") between any pair of successive neighbors along it are fixed. Such a system provides, for very large $N$, a simplified model for polymers (in the framework of classical statistical mechanics) [1–7] and, for $N=2$, a description of low-energy (rotational) degrees of freedom in diatomic molecules [8]. Internal rotations of successive "bonds" in a real linear polyatomic molecule are not absolutely free but hindered [2–4]. However, the idealized freely jointed chain, in which no internal rotation is hindered but free, constitutes a zeroth-order approximation, and its understanding continues to play an interesting role. A quantum theory of a freely jointed molecular chain appears to be interesting for, at least, the following reasons: (a) it may play a role in describing very-low-energy phenomena in small linear polyatomic molecules (say, for small $N>2$, and for energies smaller than vibrational and electronic ones), similar to that of the quantum theory of a rigid top in accounting for global (or overall) rotational spectra [8], (b) for $N \rightarrow \infty$ (very large molecules), it may happen that a proper understanding of certain features of the corresponding statistical distributions is reached only through the quantum-mechanical approach. Finally, we also remind the reader of the importance of dynamical variables, which satisfy simple relationships (and, in particular, give rise to closed algebras), either in the classical domain (via Poisson brackets) or at the quantum level (through commutators) [9–11].

This work will have several purposes: (1) to formulate the classical theory of the freely jointed molecular chain, from the standpoint provided by certain classical variables, the Poisson brackets of which enjoy rather remarkable properties; (2) to quantize the chain, using suitable quantum analogues of the above classical variables; (3) to discuss some features of its quantum and classical statistical mechanics. Interactions among non-neighboring atoms and excluded-volume forces will be disregarded in the present treatment (alternatively, the chain may be assumed to be near the $\Theta$ temperature [3]).

The contents of the work are the following. Section II deals with the classical theory: Sec. II A presents the dynamics of the chain in terms of the transverse momentum $-\mathbf{a}_{j,c}$ and of the angular momentum $\mathbf{l}_{j,c}$ for the $j$th "link," while Sec. II B displays the Poisson brackets of the Cartesian components of $\mathbf{a}_{j,c}$ and $\mathbf{l}_{j,c}$. Section III introduces the quantization of the chain. The quantum variables ($\mathbf{e}_j$ and the modified angular momentum $\mathbf{l}_j$) and the Hamiltonian are treated in Secs. III A and III B, respectively. The commutators of those variables are given in Sec. IV A. Section IV B discusses the correspondence principle for their expectation values. Several interesting or curious properties of $\mathbf{e}_j$ and $\mathbf{l}_j$ are collected in Sec. V: further representations for their algebra, modified spherical harmonics and other eigenfunctions, uncertainties, etc. Section VI discusses the case $N=3$ in two spatial dimensions. Distinguishability properties in a quantum chain, a discussion of the associated quantum and classical statistical mechanics for the chain, are given in Sec. VII. The quantization of a macromolecule with links of given lengths has attracted, in the past, a lot of activity. As a result of the latter, a conventional wisdom (based upon quantized vibrations of very stiff springs, as starting point) has arisen, with which the philosophy of this work (based upon rigid links at the classical level, from the outset) appears to bear some differences. Section VIII A discusses comparison with previous works (in particular, regarding classical statistical mechanics), the assumed absence of hindered rotations, the role of vibrations, and the conventional wisdom referred to above versus the standpoint of the present work. Finally, the conclusions are given in Sec. VIII B.

## II. CLASSICAL THEORY

### A. Dynamical variables and Hamiltonian

In three-dimensional space, we shall consider $N(\geq 2)$ classical nonrelativistic point particles with masses $m_i$ $(>0)$ and positions and momenta $\mathbf{x}_i$ and $\mathbf{p}_{i,c}$, $i=l,\ldots,N$. We shall introduce the center-of-mass (c.m.) and relative position vectors, $\mathbf{X}_{\mathrm{c.m.}}$ and $\mathbf{y}_s$, $s=1,\ldots,N-1$, through

$$\mathbf{X}_{\mathrm{c.m.}}=M^{-1}\sum_{i=1}^{N} m_i\mathbf{x}_i,\quad M=\sum_{i=1}^{N} m_i\ ,$$

$$\mathbf{y}_s=\mathbf{x}_{s+1}-x_s\ ,\quad s=1,\ldots,N-1\ .$$

The classical kinetic energy $T_c=\sum_{i=1}^{N}(2m_i)^{-1}\mathbf{p}_{i,c}^2$ reads, in terms of $\mathbf{X}_{\mathrm{c.m.}}$ and the $\mathbf{y}_s'$:

$$T_c=2^{-1}M\dot{\mathbf{X}}_{\mathrm{c.m.}}^2+2^{-1}\sum_{s,j=1}^{N-1}\dot{\mathbf{y}}_s(A^{-1})_{sj}\dot{\mathbf{y}}_j$$

(a dot denoting the first time derivative). One has

$$(A^{-1})_{sj}=(A^{-1})_{js}\ ,$$

$$(A^{-1})_{sj}=M^{-1}\left[\sum_{h=1}^{s} m_h\right]\left[\sum_{i=j+1}^{N} m_i\right]\ ,\quad s\leq j\ .$$

In spherical polar coordinates, let $\theta_s$ and $\varphi_s$ be the polar and azimuthal angles characterizing $\mathbf{y}_s$, according to standard conventions [10,11]. We shall also introduce the following unit vectors (which, for given $s$, are orthogonal to each other):

$$\mathbf{u}_s=\begin{bmatrix}\cos\varphi_s\sin\theta_s\\ \sin\varphi_s\sin\theta_s\\ \cos\theta_s\end{bmatrix}\ ,$$

$$\mathbf{u}_{\theta_s}=\begin{bmatrix}\cos\varphi_s\cos\theta_s\\ \sin\varphi_s\cos\theta_s\\ -\sin\theta_s\end{bmatrix}\ ,$$

$$\mathbf{u}_{\varphi_s}=\begin{bmatrix}-\sin\varphi_s\\ \cos\varphi_s\\ 0\end{bmatrix}\ , \tag{2.1}$$

as well as the row vectors $\mathbf{u}_s^T$, $\mathbf{u}_{\theta_s}^T$ and $\mathbf{u}_{\varphi_s}^T$, which are obtained by transposing $(T)$ the column vectors (2.1). One has $\mathbf{y}_s=y_s\mathbf{u}_s$, $y_s=|\mathbf{y}_s|$.

The following basic assumption characterizes the freely rotating chain: the distances $y_s$ between the $s$th and the $(s+1)$-th particles equal constants (the "bond lengths")

$$y_s=d_s\ ,\quad s=1,\ldots,N-1\ . \tag{2.2}$$

Notice that this discretized string is neither rigid nor closed. In fact, neither the distances between the $s$th and the $j$th particles, $|s-j|>1$ nor, in particular, the one between the first and the $N$th particles are constant. Having imposed (2.2), neither $y_s$ nor the corresponding conjugate (radial) momenta will appear any longer as dynamical variables. Then, when going to the quantum theory, no problem will arise in connection with the uncertainty principle for those (consistently disregarded) radial variables. In what follows, $H_c$ will denote the restriction of $T_c$ after having imposed (2.2). Since no further interaction [besides the holonomic constraint (2.2)] acts upon any particle, $H_c$ coincides with both the classical Lagrangian and Hamiltonian. By using $\dot{y}_s=0$, and $\dot{\mathbf{y}}_s=d_s(\dot{\theta}_s\mathbf{u}_{\theta_s}+\dot{\varphi}\sin\theta_s\mathbf{u}_{\varphi_s})$, one expresses $H_c$ as

$$H_c=\tfrac{1}{2}M\dot{\mathbf{X}}_{\mathrm{c.m.}}^2+\tfrac{1}{2}\Xi^T G\Xi\ ,\quad \Xi=\begin{bmatrix}\dot{\theta}_1\\ \dot{\varphi}_1\\ \vdots\\ \dot{\theta}_{N-1}\\ \dot{\varphi}_{N-1}\end{bmatrix}\ , \tag{2.3}$$

$\Xi^T$ being the transpose of $\Xi$. $G$ is a symmetric and nonsingular $[2(N-1)]\times[2(N-1)]$ matrix, which depends on $\theta_1,\varphi_1,\ldots,\theta_{N-1},\varphi_{N-1}$. On physical grounds, since the quadratic form $\sum_{s,j=1}^{N-1}\dot{\mathbf{y}}_s(A^{-1})_{sj}\dot{\mathbf{y}}_j$ is positive definite, it appears that the same should be true for $\Xi^T G\Xi$. All these are consistent with the methods known to deal with dynamical systems subject to holonomic constraints [12–14]. One introduces the classical momenta $\mathbf{\Pi}_{\mathrm{c.m.},c}$, $\pi_{\theta_s,c}$, $\pi_{\varphi_s,c}$, canonically conjugate to $\mathbf{X}_{\mathrm{c.m.}}$, $\theta_s$, $\varphi_s$, respectively, through

$$\mathbf{\Pi}_{\mathrm{c.m.},c}=\nabla_{\dot{\mathbf{X}}_{\mathrm{c.m.}}}H_c\ ,\quad \pi_{\theta_s,c}=\frac{\partial H_c}{\partial\dot{\theta}_s}\ ,\quad \pi_{\varphi_s,c}=\frac{\partial H_c}{\partial\dot{\varphi}_s}\ . \tag{2.4}$$

Upon expressing $H_c$ (2.3) in terms of $\overline{\mathbf{\Pi}}_{\mathrm{c.m.},c}$, $\pi_{\theta_s,c}$, $\pi_{\varphi_s,c}$ through (2.4), one finds

$$H_c=\frac{1}{2M}\mathbf{\Pi}_{\mathrm{c.m.},c}^2+\tfrac{1}{2}\Phi^T G^{-1}\Phi\ ,\quad \Phi=\begin{bmatrix}\pi_{\theta_1,c}\\ \pi_{\varphi_1,c}\\ \vdots\\ \pi_{\theta_{N-1},c}\\ \pi_{\varphi_{N-1},c}\end{bmatrix}\ , \tag{2.5}$$

$G^{-1}$ being the inverse of the matrix $G$. The classical transverse momentum associated with the $s$th "bond" is $-\mathbf{a}_{s,c}/d_s$, where

$$-\mathbf{a}_{s,c}=\mathbf{u}_{\theta_s}\pi_{\theta_s,c}+\mathbf{u}_{\varphi_s}(\sin\theta_s)^{-1}\pi_{\varphi_s,c}\ ,\quad \mathbf{u}_s\mathbf{a}_{s,c}=0\ . \tag{2.6}$$

For simplicity, we shall also call $-\mathbf{a}_{s,c}$ the transverse momentum thereby omitting $d_s^{-1}$. One also has

$$-\mathbf{a}_{s,c}=\mathbf{u}_s\times \boldsymbol{l}_{s,c},\boldsymbol{l}_{s,c}=\mathbf{y}_s\times\mathbf{\Pi}_{s,c}\ . \tag{2.7}$$

× denotes here vector product. $\boldsymbol{l}_{s,c}$ is the classical (orbital) angular momentum and

$$\mathbf{\Pi}_{s,c}=\nabla_{\dot{\mathbf{y}}_s}T_c=\sum_{i=1}^{N-1}(A^{-1})_{sj}\dot{\mathbf{y}}_j$$

is the classical momentum before imposing (2.2), both associated with the $s$th "link." By using (2.6), in order to introduce the **a**'s, (2.5) becomes $[-\mathbf{a}^T_{s,c}=\mathbf{u}^T_{\theta_s}\pi_{\theta_s,c}+\mathbf{u}^T_{\varphi_s}(\sin\theta_s)^{-1}\pi_{\varphi_s,c}]$:

$$H_c=\frac{1}{2M}\mathbf{\Pi}^2_{\text{c.m.},c}+\tfrac{1}{2}\sum_{s,j=1}^{N-1}(d_sd_j)^{-1}(-\mathbf{a}^T_{s,c})C_{sj}(-\mathbf{a}_{j,c})\ . \tag{2.8}$$

For each $s,j$, $C_{sj}$ is a 3×3 matrix, which depends on $\theta_1$, $\varphi_1,\ldots,\theta_{N-1}$, $\varphi_{N-1}$, is determined uniquely through (2.5) and (2.6) and (2.8) and fulfills $C_{sj}=C_{js}$. The general expressions will be omitted.

We consider the unique solution $\mathbf{X}_{\text{c.m.}}(t')$, $\theta_s(t'),\varphi_s(t'),s=1,\ldots,N-1$, in $0<t'<t$, of the Lagrange equations corresponding to (2.3) [of course, after having imposed (2.2)]. That solution is determined fully by two given sets of data: $(\mathbf{X}_{\text{c.m}}(0)$, $\theta_s(0),\varphi_s(0),s=1,\ldots,N-1)$ at $t'=0$ and $(\mathbf{X}_{\text{c.m.}},\ \theta_s,\varphi_s$, $s=1,\ldots,N-1)$ at $t'=t$. Let $H_c(t')$ be the kinetic energy (2.3) corresponding to that unique solution. Then, let

$$S_c=S_c(t;\mathbf{X}_{\text{c.m.}},\theta_1\varphi_1,\ldots,\theta_{N-1}\varphi_{N-1})$$
$$=\int_0^t dt'H_c(t')$$

be the corresponding action, for fixed initial data at $t'=0$, as the final data at $t'=t$ vary. Through general analytical dynamics [12], one derives the Hamilton-Jacobi equation:

$$\frac{\partial S_c}{\partial t}+(2M)^{-1}(\nabla_{\mathbf{X}_{\text{c.m.}}}S_c)^2+2^{-1}\sum_{s,j=1}^{N-1}(d_sd_j)^{-1}\left[\mathbf{u}^T_{\theta_s}\left[\frac{\partial S_c}{\partial\theta_s}\right]+\mathbf{u}^T_{\varphi_s}(\sin\theta_s)^{-1}\left[\frac{\partial S_c}{\partial\varphi_s}\right]\right]C_{sj}$$
$$\times\left[\mathbf{u}_{\theta_j}\left[\frac{\partial S_c}{\partial\theta_j}\right]+\mathbf{u}_{\varphi_j}(\sin\theta_j)^{-1}\left[\frac{\partial S_c}{\partial\varphi_j}\right]\right]=0\ . \tag{2.9}$$

### B. Poisson brackets

Let $a_{s,c,\alpha},l_{s,c,\alpha}$ denote the Cartesian components of $\mathbf{a}_{s,c}$, $\boldsymbol{l}_{s,c}$, respectively, $\alpha=1,2,3$. If $A_c$, $B_c$ are classical variables, which, at most, may depend on the Cartesian components $\Pi_{s,c,\alpha}$, $y_{s,\alpha}$ of $\mathbf{\Pi}_{s,c}$, $\mathbf{y}_s$, respectively, we remind the reader that their Poisson bracket is

$$\{A_c,B_c\}=\sum_{s=1}^{N-1}\sum_{\alpha=1}^{3}\left[\left[\frac{\partial A_c}{\partial\Pi_{s,c,\alpha}}\right]\left[\frac{\partial B_c}{\partial y_{s,\alpha}}\right]-\left[\frac{\partial A_c}{\partial y_{s,\alpha}}\right]\left[\frac{\partial B_c}{\partial\Pi_{s,c,\alpha}}\right]\right]\ . \tag{2.10}$$

We shall give the Poisson brackets for $a_{s,c,\alpha},l_{s,c,\alpha}$. A look at the first Eq. (2.7), indicates that those variables are independent on $y_s$, and then the constraints (2.2) will play no role in the computation of the Poisson brackets. Using the first equations (2.1) and (2.7), some lengthy, but straightforward calculations, yield ($\alpha,\beta,\gamma=1,2,3$):

$$\{a_{s,c,\alpha},a_{s,c,\beta}\}=\epsilon_{\alpha\beta\gamma}l_{s,c,\gamma},\{l_{s,c,\alpha},a_{s,c,\beta}\}$$
$$=-\epsilon_{\alpha\beta\gamma}a_{s,c,\gamma} \tag{2.11}$$

to which one should add the well-known ones

$$\{l_{s,c,\alpha},l_{s,c,\beta}\}=-\epsilon_{\alpha\beta\gamma}l_{s,c,\gamma}\ . \tag{2.12}$$

$\epsilon_{\alpha\beta\gamma}$ is the standard totally antisymmetric tensor with three indices ($\epsilon_{123}=+1$, etc.). The Poisson brackets for different values of $s$ vanish, clearly. The closed algebra (2.11) and (2.12) will provide an interesting consistency test for the quantum theory.

Let $A_{r,c}$ denote any Cartesian component of $-\mathbf{a}_{r,c}$ or $\boldsymbol{l}_{r,c}$. The time evolution, in differential form, for $A_{r,c}$ is given by

$$\dot{A}_{r,c}=\{H_c,A_{r,c}\}$$
$$=\left\{\frac{1}{2}\sum_{s,j=1}^{N-1}(d_sd_j)^{-1}(-\mathbf{a}^T_{s,c})C_{sj}(-\mathbf{a}_{j,c}),A_{r,c}\right\}, \tag{2.13}$$

which, as it stands, will be helpful in Sec. IV B in order to apply the correspondence principle for the freely jointed chain.

Finally, we notice the following consequences of (2.7):

$$\mathbf{a}_{s,c}\cdot\boldsymbol{l}_{s,c}=0\ ,\quad \mathbf{a}^2_{s,c}-\boldsymbol{l}^2_{s,c}=0\ . \tag{2.14}$$

## III. QUANTUM VARIABLES AND HAMILTONIAN

### A. Dynamical variables

We shall now assume that all particles in the freely rotating chain are microscopic and nonidentical, and undertake the task of quantizing (2.8). A quantum state of the chain, at time $t$, is represented by a complex wave function $\psi(t;\mathbf{X}_{\text{c.m.}}\mathbf{u}_1,\dots,\mathbf{u}_{N-1})$, which, by assumption, is periodic in each $\varphi_s(s=1,\dots,N-1)$ with period $2\pi$ [instead of $\theta_s$, $\varphi_s$ use is made of the equivalent $\mathbf{u}_s$, by virtue of the first equation (2.1)]. For any pair of wave functions $\psi_i=\psi_i(t;\mathbf{X}_{\text{c.m.}}\mathbf{u}_1,\dots,\mathbf{u}_{N-1})$ we introduce their scalar product ($[d\mathbf{u}]=\prod_{s=1}^{N-1}d\theta_s d\varphi_s$):

$$(\psi_1,\psi_2)=\int d^3\mathbf{X}_{\text{c.m.}}\int[d\mathbf{u}]g\psi_1^*\psi_2 \ . \tag{3.1}$$

The integrations in (3.1) extend over the whole configuration space for $\mathbf{X}_{\text{c.m}}$ and the whole solid angle for each pair $\theta_s,\varphi_s$, while $g=(\det G)^{1/2}$, $\det G$ being the determinant of the matrix that appears in (2.3). We recall that any acceptable quantum variable $B$ should be a Hermitian operator, that is, $(\psi_1,B\psi_2)=(B\psi_1,\psi_2)$ for any $\psi_1,\psi_2$. We shall consider the "naive" quantum analogs $-\mathbf{a}_s,\mathbf{l}_{0s}$ of the classical variables $-\mathbf{a}_{s,c},\mathbf{l}_{s,c}$. They are given by the direct quantum versions of (2.6) and (2.7) ($\hbar$ being Planck's constant)

$$\begin{gathered}\mathbf{a}_s=\mathbf{u}_s X\mathbf{l}_{0s}=i\hbar\left[\mathbf{u}_{\theta_s}\frac{\partial}{\partial\theta_s}+\mathbf{u}_{\varphi_s}(\sin\theta_s)^{-1}\frac{\partial}{\partial\varphi_s}\right] ,\\ \mathbf{l}_{0s}=\mathbf{y}_s X(-i\hbar\nabla_{\mathbf{y}_s}) \ .\end{gathered}\tag{3.2}$$

Clearly, $\mathbf{l}_{0s}$ is the standard orbital angular momentum, and its expression in terms of $\theta_s,\varphi_s$ and partial derivatives thereof is well known [10,11]. We emphasize that $\mathbf{a}_s$ are not Hermitian operators regarding the scalar product (3.1): $(\psi_1,\mathbf{a}_s\psi_2)\neq(\mathbf{a}_s\psi_1,\psi_2)$, as explicit computations show. The same negative result holds for $\mathbf{l}_{0s}$ also, with respect to (3.1) [although $\mathbf{l}_{0s}$ is certainly Hermitian if $g=(\det G)^{1/2}$ is replaced by $g=\prod_{s=1}^{N-1}\sin\theta_s$, but such a substitution cannot be carried out here]. Fortunately, by modifying the "naive" operators $-\mathbf{a}_s,\mathbf{l}_{0s}$ one can construct new "genuine" quantum variables $\mathbf{e}_s,\mathbf{l}_s$, which are indeed Hermitian regarding (3.1) and, so, can be regarded as acceptable quantum versions of $-\mathbf{a}_{s,c},\mathbf{l}_{s,c}$. Specifically, one imposes the condition that those modifications be such that $(\psi_1,B\psi_2)=(B\psi_1,\psi_2)$ holds for any $\psi_1,\psi_2$, when $B$ stands for either $\mathbf{e}_s$ or $\mathbf{l}_s$ (say, the Cartesian components thereof). Then, after some lengthy partial integrations, one finds

$$\begin{gathered}\mathbf{e}_s=g^{-1/2}\left[\mathbf{e}_{0s}+\frac{i\hbar}{2}(\cot\theta_s)\mathbf{u}_{\theta_s}\right]g^{1/2} ,\\ \mathbf{e}_{0s}=-\mathbf{a}_s+i\hbar\mathbf{u}_s\end{gathered}\tag{3.3}$$

$$\mathbf{l}_s=g^{-1/2}\left[\mathbf{l}_{0s}+\frac{i\hbar}{2}(\cot\theta_s)\mathbf{u}_{\varphi_s}\right]g^{1/2} \ . \tag{3.4}$$

The expressions for the Cartesian components $e_{0s,\alpha}$, $\alpha=1,2,3$, of $\mathbf{e}_{0s}$ in spherical polar coordinates read

$$\begin{gathered}e_{0s,1}=i\hbar\left[-\cos\theta_s\cos\varphi_s\frac{\partial}{\partial\theta_s}+\frac{\sin\varphi_s}{\sin\theta_s}\frac{\partial}{\partial\varphi_s}\right.\\ \left.+\sin\theta_s\cos\varphi_s\right] ,\\ e_{0s,3}=i\hbar\left[\sin\theta_s\frac{\partial}{\partial\theta_s}+\cos\theta_s\right] ,\end{gathered}\tag{3.5}$$

$$e_{0s,2}=i\hbar\left[-\cos\theta_s\sin\varphi_s\frac{\partial}{\partial\theta_s}-\frac{\cos\varphi_s}{\sin\theta_s}\frac{\partial}{\partial\varphi_s}+\sin\theta_s\sin\varphi_s\right] .$$

### B. Hamiltonian

By assumption, the quantum-mechanical Hamiltonian $H$ for the chain is given through the known recipe in curvilinear coordinates [15,10,11], including De Witt's correction [16]. Specifically, by recalling (2.5), it reads

$$\begin{gathered}H=\frac{1}{2M}\Pi_{\text{c.m.}}^2+\frac{1}{2g}\Lambda^T gG^{-1}\Lambda+\lambda\hbar^2 R ,\\ \Lambda=\begin{bmatrix}-i\hbar(\partial/\partial\theta_1)\\ -i\hbar(\partial/\partial\varphi_1)\\ \vdots\\ -i\hbar(\partial/\partial\theta_{N-1})\\ -i\hbar(\partial/\partial\varphi_{N-1})\end{bmatrix} ,\end{gathered}\tag{3.6}$$

where $\Pi_{\text{c.m.}}=-i\hbar\nabla_{\mathbf{X}_{\text{c.m.}}}$. The term $\lambda\hbar^2 R$ is just De Witt's correction. Let $g_{ij}$, $i,j=1,\dots,2(N-1)$ denote the elements of the matrix $G$ in (2.3) and let them be regarded as a metric in a curved space. Then, $R$ is just the curvature determined by that metric, through standard formulas [16,17]. $\lambda$ is a real dimensionless parameter. As De Witt pointed out [16], the precise value of $\lambda$ is the only ambiguity in the quantum Hamiltonian in curvilinear coordinates, in general. Comparisons with path-integral representations (closely related among themselves, but not exactly equivalent to one another) for the short-time propagator led [16] to either $\lambda=\frac{1}{12}$ or $\lambda=\pm\frac{1}{6}$. See also Schulman [17]. To the present author's knowledge, the ambiguity in $\lambda$ does not seem to have been settled as yet. Another comment seems in order here. The conventional justification [15,10,11] for the quantum Hamiltonian in curvilinear coordinates (with $\lambda=0$) relies upon its coincidence with the standard Laplacian in Cartesian coordinates, when the corresponding coordinate transformation is performed. Clearly, such a coincidence (or a search thereof) becomes meaningless after having imposed the constraints (2.2). Then, the structure $(2g)^{-1}\Lambda^T gG^{-1}\Lambda$ in (3.6) (with $\lambda\neq0$, possibly) is really an assumption and not the result of a transformation from Cartesian coordinates. Fortunately, De Witt's general work on quantum dynamics in curved space [16] (not restricted to the specific case of the chain) seems to imply that our assumption in (3.6) is consistent. Moreover, our specific work in this and later sections, based upon (3.6), the $\mathbf{e}$'s and $\mathbf{l}$'s and their algebra and the analysis of the classical limit will confirm that consistency.

By recalling the transformation which led from (2.5) to (2.8) and using (3.2), (3.6) can be trivially recast as

$$\begin{gathered}H=\frac{1}{2M}\Pi_{\text{c.m.}}^2+\frac{1}{2g}\sum_{s,j=1}^{N-1}(d_s d_j)^{-1}(-\mathbf{a}_s^\dagger)gC_{sj}(-\mathbf{a}_j)\\ +\lambda\hbar^2 R ,\end{gathered}\tag{3.7}$$

$$\mathbf{a}_s^{\dagger}=i\hbar\left[\frac{\partial}{\partial\theta_s}\mathbf{u}_{\theta_s}^T+(\sin\theta_s)^{-1}\frac{\partial}{\partial\varphi_s}\mathbf{u}_{\varphi_s}^T\right], \tag{3.8}$$

where $C_{sj}$ is the same as in (2.8). The orderings of operators are crucial and they have been carefully respected when going from (3.6) to (3.7) and (3.8). Although (3.7) resembles (2.8), it is still unsatisfactory, since neither $-\mathbf{a}_s^{\dagger}$, nor $-\mathbf{a}_j$ is Hermitian. Fortunately, by using (3.3), (3.7) becomes, after some cancellations ($\mathbf{e}_s^T=g^{-1/2}[-\mathbf{a}_s^T+i\hbar\mathbf{u}_s^T+i\hbar 2^{-1}(\cot\theta_s)\mathbf{u}_{\theta_s}^T]g^{1/2}$, $\mathbf{a}_s^T=i\hbar[\mathbf{u}_{\theta_s}^T(\partial/\partial\theta_s)+\mathbf{u}_{\varphi_s}^T(\sin\theta_s)^{-1}(\partial/\partial\varphi_s)]$):

$$H=\frac{1}{2M}\boldsymbol{\Pi}_{\mathrm{c.m.}}^2+\tfrac{1}{2}\sum_{s,j=1}^{N-1}(d_sd_j)^{-1}\mathbf{e}_s^TC_{sj}\mathbf{e}_j+V_0+\lambda\hbar^2R\ , \tag{3.9}$$

$$V_0=\tfrac{1}{2}\sum_{s,j=1}^{N-1}\{[\mathbf{b}_s^T-2i\hbar\mathbf{u}_s^T-i\hbar(\cot\theta_s)\mathbf{u}_{\theta_s}^T]C_{sj}\mathbf{b}_j+g^{-1}[\mathbf{a}_s^T(gC_{sj}\mathbf{b}_j)]\}(d_sd_j)^{-1}\ ,$$
$$\mathbf{b}_j=i\hbar[\mathbf{u}_j+2^{-1}(\cot\theta_j)\mathbf{u}_{\theta_j}]+g^{-1/2}(\mathbf{e}_{0j}g^{1/2})\ . \tag{3.10}$$

$V_0$, which is of order $\hbar^2$, is just a multiplicative function of $\mathbf{u}_1,\ldots,\mathbf{u}_{N-1}$ (as it contains no differential operator which would act upon wave functions). The interest of (3.9) is that, except for the "quantum correction" $V_0+\lambda\hbar^2R$, it does display a satisfactory analogy with (2.8), as the (Hermitian) **e**'s are the genuine quantum analogs of the $-\mathbf{a}_c$'s.

$H$ is a Hermitian operator. This follows easily from either (3.6) or (3.9). Moreover, $H$ is bounded below. In fact, (3.7) yields, for any normalized $\psi((\psi,\psi)=1)$

$$(\psi,H\psi)=\frac{1}{2M}(\psi,\boldsymbol{\Pi}_{\mathrm{c.m.}}^2\psi)+\int d^3\mathbf{X}_{\mathrm{c.m.}}\int[d\mathbf{u}]g\tfrac{1}{2}\sum_{s,j=1}^{N-1}(d_sd_j)^{-1}(-\mathbf{a}_s^T\psi)^*C_{sj}(-\mathbf{a}_j\psi)+(\psi,\lambda\hbar^2R\psi)\ . \tag{3.11}$$

Since $\Xi^TG\Xi$ in (2.3) should be positive definite, the same should be true for

$$\sum_{s,j=1}^{N-1}(d_sd_j)^{-1}(-\mathbf{a}_{s,c}^T)C_{sj}(-\mathbf{a}_{j,c})$$

for all possible values of $\mathbf{a}_c$'s, $\theta$'s, and $\varphi$'s. Then, the second term on the right-hand side of (3.11) is nonnegative. Since $(\psi,\boldsymbol{\Pi}_{\mathrm{c.m.}}^2\psi)\geq 0$ and the matrix $G$ is such that $R$ is bounded above and below, the boundedness below $H$ follows. All these properties imply that $H$ can always be regarded as (or, more precisely, extended so as to be) a self-adjoint operator. This can be fulfilled through the use of the associated quadratic form $(\psi_1,H\psi_2)$ and the so-called Friedrichs extension theorem [11].

The time-dependent Schrödinger equation reads

$$H\psi=i\hbar\frac{\partial}{\partial t}\psi\ . \tag{3.12}$$

Upon considering $\psi^*(H\psi)-\psi(H\psi)^*$, multiplying by $[d\mathbf{u}]g$, integrating over all $\theta_s,\varphi_s$, and using (3.9), (3.12), and the Hermiticity of the **e**'s, the continuity equation follows:

$$\frac{\partial}{\partial t}\int[d\mathbf{u}]g|\psi|^2=-\nabla_{\mathbf{X}_{\mathrm{c.m.}}}\frac{\hbar}{2iM}\int[d\mathbf{u}]g(\psi^*(\nabla_{\mathbf{X}_{\mathrm{c.m.}}}\psi)-\psi(\nabla_{\mathbf{X}_{\mathrm{c.m.}}}\psi^*))\ , \tag{3.13}$$

which expresses conservation of probability, etc. We shall outline the classical limit for (3.12), by setting $\psi=|\psi|\exp i\hbar^{-1}S$, applying (3.9) and keeping only the dominant terms as $\hbar\to 0$. As expected, lim $S$ satisfies (2.9) as $\hbar\to 0$, and so it can be identified with the classical action $S_c$.

## IV. ALGEBRA OF COMMUTATORS AND CORRESPONDENCE PRINCIPLE

### A. Derivation of the algebra of commutators for e's and l's

We shall study the commutation relations for the Cartesian components $e_{s,\alpha},l_{s,\alpha},\alpha=1,2,3$, of the Hermitian operators $\mathbf{e}_s,\mathbf{l}_s$ (3.3) and (3.4). By applying also (2.1), (3.5), and the well-known expressions for $\mathbf{l}_{0s}$ in terms of $\theta_s,\varphi_s$ [10,11] one gets ($\alpha,\beta,\gamma=1,2,3$; $[A,B]=AB-BA$)

$$[e_{s,\alpha},e_{s,\beta}]=-i\hbar\epsilon_{\alpha\beta\gamma}l_{s,\gamma},\quad [l_{s,\alpha},e_{s,\beta}]=i\hbar\epsilon_{\alpha\beta\gamma}e_{s,\gamma}\ , \tag{4.1}$$

$$[l_{s,\alpha},l_{s,\beta}]=i\hbar\epsilon_{\alpha\beta\gamma}l_{s,\gamma}\ . \tag{4.2}$$

Any two operators carrying different values of the subscript $s$ commute with each other. The set (4.1) and (4.2) goes over the set (2.11) and (2.12) by means of the replacement $i\hbar^{-1}[A,B]\to[A_c,B_c]$, in agreement with the correspondence principle [9] (about which more will be said in Sec. IV B). This also shows, *a posteriori*, that the introduction of $\mathbf{e}_s,\mathbf{l}_s$ through (3.3) and (3.4) is consistent. The set constitutes a Lie algebra; its mathematical characterization will be carried out elsewhere.

The set (4.1) and (4.2) is reminiscent of the so(4) algebra for the hydrogen atom [11,18]. The latter algebra is formed by the Cartesian components of the orbital angular momentum and of the Runge-Lenz vector (which would be the counterpart of **e**). However, both algebras are not completely identical: their differences arise from global signs on the right-hand sides of (4.1). The so(4) algebra does not correspond entirely (but only partially) to geometrical symmetries for the hydrogen atom, and so it is regarded as a signal of a dynamical symmetry. It is, by now, unclear whether (2.11) and (2.12) and (4.1) and (4.2) may indicate some sort of dynamical symmetry for the freely jointed chain.

### B. Time evolution of $(\psi,\mathbf{l}_{r,\alpha}\psi)$ and $(\psi,\mathbf{e}_{r,\alpha}\psi)$

Let $A_r$ represent any Cartesian component of $\mathbf{l}_r,\mathbf{e}_r$. For any normalized $\psi$ fulfilling (3.12), one has

$$\begin{aligned}&\frac{d}{dt}(\psi,A_r\psi)=(\psi,i\hbar^{-1}[H,A_r]\psi)=\left(\psi,i\hbar^{-1}\left[\frac{1}{2}\sum_{s,j=1}^{N-1}(d_sd_j)^{-1}\mathbf{e}_s^TC_{sj}\mathbf{e}_j,A_r\right]\psi\right)+\text{q.c.}\\&\text{q.c.}=(\psi,i\hbar^{-1}[V_0+\lambda\hbar^2R,A_r]\psi)\ .\end{aligned}\tag{4.3}$$

Notice that q.c. (the "quantum correction") is a function of $\mathbf{u}_1,\dots,\mathbf{u}_{N-1}$ simply, and so it does not contain differential operators acting on wave functions. In agreement with the correspondence principle [9–11]: (i) the structure of (4.2) is formally analogous, term by term, to that of (2.13), except for q.c.; (ii) in the classical ($\hbar\to0$) limit, q.c. tends to zero (as $V_0+\lambda\hbar^2R$ is of order $\hbar^2$), and so (4.1) appears to go over (2.13), term by term.

We stress that the existence of q.c. in (4.3) does not spoil its basic analogy with (2.13) and, hence, the correspondence principle. Actually, a related "quantum correction," also arising basically from the specific ordering of noncommuting operators in the quantum Hamiltonian, also occurs in other cases, as we shall exemplify with the symmetric top. We recall that the Hamiltonian (the kinetic energy) for the classical symmetric top is [19]

$$\begin{aligned}H_{ST,c}=&\frac{1}{2I_1}P_{\theta,c}^2+\frac{1}{2I_3}P_{\varphi,c}^2\\&+\frac{1}{2I_1(\sin\theta)^2}[P_{\varphi,c}-(\cos\theta)P_{\gamma,c}]^2\ ,\end{aligned}\tag{4.4}$$

where $I_1,I_3$ are moments of inertia; $\theta$, $\varphi$, and $\gamma$ are suitable Euler angles; and $P_{\theta,c}$, $P_{\varphi,c}$, and $P_{\gamma,c}$ are the corresponding conjugate classical momenta. The quantum Hamiltonian for the symmetric top is $[P_\lambda=-i\hbar(\partial/\partial\lambda)$, $\lambda=\theta,\varphi,\gamma]$

$$\begin{aligned}H_{ST}=&\frac{1}{2I_1(\sin\theta)}P_\theta((\sin\theta)P_\theta)+\frac{1}{2I_3}P_\varphi^2\\&+\frac{1}{2I_1(\sin\theta)^2}[P_\gamma-(\cos\theta)P_\varphi]^2\ .\end{aligned}\tag{4.5}$$

The scalar product is

$$(\psi_1,\psi_2)=\int_0^\pi d\theta\sin\theta\int_0^{2\pi}d\varphi\,d\gamma\,\psi_1^*(t;\theta,\varphi,\gamma)\psi_2(t;\theta,\varphi,\gamma)\ ,$$

and so the actual $g$ has been taken (up to an overall harmless constant) as $\sin\theta$. Thus (4.5) also agrees with the recipe for "curved-space" quantization, in terms of $\theta$, $\varphi$, $\gamma$. We now take $P_{\theta,c}$ and $P_\theta$ as the counterparts of $A_{r,c}$ and $A_r$. The quantum correction for the actual symmetric top, namely, the specific term that appears in

$$\frac{d}{dt}(\psi,P_\theta\psi)=(\psi,i\hbar^{-1}[H_{ST},P_\theta]\psi)$$

but does not have an analog in $\dot{P}_{\theta,c}=\{H_{ST,c},P_{\theta,c}\}$ is easily seen to be

$$-(\psi,i\hbar^{-1}(2I_1)^{-1}[P_\theta((\sin\theta)^{-1}(P_\theta\sin\theta))]P_\theta\psi)\ .$$

This "quantum correction" also approaches zero as $\hbar\to0$.

## V. PROPERTIES OF THE QUANTUM-MECHANICAL VARIABLES

### A. Some further representations of the algebra (4.1) and (4.2)

One can show that (4.1) and (4.2) are also satisfied if $l_{s,\alpha}$ is substituted by the Cartesian components $l_{0s,\alpha}$ of $\mathbf{l}_{0s}$ and, at the same time, $e_{s,\alpha}$ is replaced, respectively, by (i) $e_{0s,\alpha}$, (ii) $-a_{s,\alpha}$ (the Cartesian components of $-\mathbf{a}_s$), or (iii) $il_{0s,\alpha}$. Moreover, the algebra (4.1) and (4.2) is also fulfilled by the Cartesian components of (iv) $\mathbf{l}_{0s}$ and $\mathbf{e}_{0s,\alpha}+\hbar\lambda\mathbf{u}_s$ for any real $\lambda$, (v) $2^{-1}\hbar\sigma$ and $i2^{-1}\hbar\sigma,\sigma=(\sigma_1,\sigma_2,\sigma_3)$ being the standard Pauli matrices. These five possibilities provide (presumably only a small) part of the set of all further representations for (4.1) and (4.2) besides that given in (3.3) and (3.4). It is not guaranteed that the dynamical variable $\mathbf{e}_s$, as given by (3.1) and (3.2) is self-adjoint, even if it is hermitian (while $H$ and $\mathbf{l}_s$ share both properties). That suspicion is suggested by the fact that (4.1) and (4.2) allows for representations for the e's by operators and matrices that are not self-adjoint.

### B. FURTHER RELATIONSHIPS BETWEEN $\mathbf{l}_s$ and $\mathbf{e}_s$

Equations (3.3) and (3.4) imply

$$\mathbf{e}_s\mathbf{l}_s=\mathbf{l}_s\mathbf{e}_s=0\ ,\quad \mathbf{e}_s^2-\mathbf{l}_s^2=\hbar^2\ ,\tag{5.1}$$

which are the quantum analogs of (2.14) (again with "quantum corrections"). The first set of Eqs. (4.1) can also be interpreted as the statement that $\mathbf{e}_s$ is an irreducible first-order tensor operator, relative to $\mathbf{l}_s$.

### C. Study of the modified orbital angular momentum

The operators $\mathbf{l}_s$, $s=1,\dots,N-1$, as given by (3.4), do constitute orbital angular momenta, relative to the scalar product (3.1), and so $\mathbf{l}_s^2$ and $l_{s,3}$ can be diagonalized simultaneously. Hence, well-known general results [10,11] about eigenvalues and eigenvectors in the *standard* theory of angular momentum (namely, the one corresponding to $g=\prod_{s=1}^{N-1}\sin\theta_s$) also hold for the actual $\mathbf{l}_s^2$ and $l_{s,3}$ [with $g=(\det G)^{1/2}$]. However, due to the structure of (3.4), some specific formulas for $\mathbf{l}_{0s}$ cannot be taken over directly for $\mathbf{l}_s$, but they require certain modifications. We shall give some characteristic results for $\mathbf{l}_s$ (which differ from those for $\mathbf{l}_{0s}$), omitting derivations.

(a) The result

$$l_s^2=g^{-1/2}\left[l_{0s}^2+\hbar^2\left[(\cot\theta_s)\frac{\partial}{\partial\theta_s}-4^{-1}(\cot\theta_s)^2-2^{-1}\right]\right]g^{1/2} . \quad (5.2)$$

(b) Raising ( + ) and lowering ( − ) operators

$$l_{s\pm}=g^{-1/2}\hbar\exp(\pm i\varphi_s)\left[\pm\frac{\partial}{\partial\theta_s}+(\cot\theta_s)\left[i\frac{\partial}{\partial\varphi_s}\mp\frac{1}{2}\right]\right]g^{1/2} . \quad (5.3)$$

(c) Modified spherical harmonics: ($\tilde{Y}_l^m(\theta_s\varphi_s)$) ($l=L_s$, $m=M_s$, for simplicity), $l=0,1,2,\dots,m=-l,-l+1,\dots,+l$ ($Y_l^l$ being a standard spherical harmonics):

$$l_s^2\tilde{Y}_l^m=\hbar^2 l(l+1)\tilde{Y}_l^m , \quad l_{s,3}\tilde{Y}_l^m=\hbar m\tilde{Y}_l^m , \quad (5.4)$$

$$\tilde{Y}_l^l(\theta_s\varphi_s)=(2\pi^2)^{-(N-2)/2}g^{-1/2}(\sin\theta_s)^{1/2}Y_l^l(\theta_s\varphi_s) , \quad (5.5)$$

$$\tilde{Y}_l^m(\theta_s\varphi_s)=\{(l+m)!/[(2l)!(l-m)!]\}^{1/2}\times(l_{s-})^{l-m}\tilde{Y}_l^l(\theta_s\varphi_s) , \quad (5.6)$$

$$\sum_{l=0}^{+\infty}\sum_{m=-l}^{+l}\tilde{Y}_l^m(\theta_s\varphi_s)\tilde{Y}_l^m(\theta_s'\varphi_s')=g^{-1}\delta(\theta_s-\theta_s')\delta(\varphi_s-\varphi_s') . \quad (5.7)$$

Notice that $\tilde{Y}_l^m(\theta_s\varphi_s)$ also depends on all other $\theta_r,\varphi_r,r\neq s$, through $g$, but for simplicity the latter dependences have not been made explicit. Let $\psi_i,i=1,2$ depend only on $\mathbf{u}_1,\dots,\mathbf{u}_{N-1}$, but not on $\mathbf{X}_{\text{c.m.}}$, and let us introduce an internal scalar product as $(\psi_1,\psi_2)_{\text{in}}=\int[d\mathbf{u}]g\psi_1^*\psi_2$. One has

$$(\tilde{Y}_l^m,\tilde{Y}_{l'}^{m'})_{\text{in}}=\delta_{l,l'}\delta_{m,m'} , \quad (\tilde{Y}_l^m,l_{s,\alpha}\tilde{Y}_l^m)_{\text{in}}=0 , \quad \alpha=1,2 . \quad (5.8)$$

The composition or "vector addition" of $\tilde{Y}_{l_1}^{l_1}(\theta_1\varphi_1),\dots,\tilde{Y}_{l_{N-1}}^{l_{N-1}}(\theta_{N-1}\varphi_{N-1})$, annihilated by $\sum_{s=1}^{N-1}l_{s+}$, is $(g^{1/2})^{N-2}\prod_{s=1}^{N-1}\tilde{Y}_{l_s}^{l_s}(\theta_s\varphi_s)$, instead of $\prod_{s=1}^{N-1}\tilde{Y}_{l_s}^{l_s}(\theta_s\varphi_s)$. Further composed states are obtained upon applying $\prod_{s=1}^{N-1}l_{s-}$, finding new functions orthogonal to the previous ones, etc. We omit details. All such functions may be useful in order to carry out variational and perturbative studies of the set of eigenvalues of $H_{\text{in}}=H-(2M)^{-1}\mathbf{\Pi}_{\text{c.m.}}^2$. Such a set is expected to be discrete and denumerably infinite.

### D. Uncertainty relations

The uncertainty of the $\mathbf{X}_{\text{c.m.}}$ independent quantum variable $B$ in the $\mathbf{X}_{\text{c.m.}}$-independent and normalized state $\psi$ ($(\psi,\psi)_{\text{in}}=1$) is $\Delta B=[(\psi,B^2\psi)_{\text{in}}-(\psi,B\psi)_{\text{in}}^2]^{1/2}$. We shall apply the general uncertainty relation $\Delta B_1\Delta B_2\geq 2^{-1}|(\psi,[B_1,B_2]\psi)_{\text{in}}|$ to the case $\psi=\tilde{Y}_{L_s}^{M_s}(\theta_s)$, the $\tilde{Y}$'s being the modified spherical harmonics (5.6), for suitable choices of $B_1,B_2$ out of $e_{s,\alpha},l_{s,\alpha}$. By using (4.1) and (4.2), (5.8), and (5.4), one finds

$$\Delta e_{s,\alpha}\Delta e_{s,3}\geq 0 , \quad \Delta l_{s,\alpha}\Delta l_{s,3}\geq 0 , \quad \alpha=1,2$$
$$\Delta e_{s,\alpha}\Delta l_{s,\alpha}\geq 0 , \quad \alpha=1,2,3 \quad (5.9)$$

$$\Delta e_{s,1}\Delta e_{s,2}\geq 2^{-1}\hbar^2 M_s , \quad \Delta l_{s,1}\Delta l_{s,2}\geq 2^{-1}\hbar^2 M_s . \quad (5.10)$$

Thus, the pairs of variables related by an inequality like (5.9) [(5.10)] can (cannot) be measured simultaneously with arbitrary accuracy, in the above state, according to the standard probabilistic interpretation in quantum mechanics [9–11].

### E. Simultaneous diagonalization of $e_{s,3},l_{s,3}$

Besides diagonalizing $l_s^2,l_{s,3}$ as in Sec. V C, other possibilities exist. Specifically, we shall explore succinctly the one based upon the common eigenfunctions $\psi(\sigma_s,M_s)$ of $e_{s,3},l_{s,3}(M_s=0,\pm1,\pm2,\dots)$: $e_{s,3}\psi(\sigma_s,M_s)=\hbar\sigma_s\psi(\sigma_s,M_s)$, $l_{s,3}\psi(\sigma_s,M_s)=\hbar M_s\psi(\sigma_s,M_s)$. One finds

$$\psi(\sigma_s,M_s)=\psi_0(g\sin\theta_s)^{-1/2}\exp i\{-\sigma_s\ln[\tan(2^{-1}\theta_s)]+M_s\varphi_s\} , \quad (5.11)$$

$\psi_0$ being an arbitrary function of $\mathbf{X}_{\text{c.m.}},\mathbf{u}_1,\dots,\mathbf{u}_{s-1},\mathbf{u}_{s+1},\dots,\mathbf{u}_{N-1}$. $\sigma_s$ is an arbitrary real number. Notice that, for fixed $\mathbf{X}_{\text{c.m}},\mathbf{u}_1,\dots,\mathbf{u}_{s-1},\mathbf{u}_{s+1},\dots,\mathbf{u}_{N-1}$, $\psi(\sigma_s,M_s)$ is not square integrable in $\theta_s$, $\int_0^\pi d\theta_s g|\psi(\sigma_s,M_s)|^2=+\infty$, due to the singularities at $\theta_s=0,\pi$. For this reason, the functions $\psi(\sigma_s,M_s)$ are expected to be far less convenient than the above modified spherical harmonics, regarding the determination of eigenvalues and eigenfunctions of $H_{\text{in}}$. One also expects that the classical limit corresponds to large values of $\sigma_s,M_s$.

## VI. THE CASE $N=3$
## IN TWO SPATIAL DIMENSIONS

As an example, we shall analyze a simple, but not trivial, case. Let $N=3$, with equal masses $m_i=m,i=1,2,3$ and equal "bond" lengths $d_s=d,s=1,2$, in two spatial dimensions.

### A. Classical model

The classical kinetic energy, before imposing (2.2), reads

$$T_c=(3m/2)\dot{\mathbf{X}}_{\text{c.m.}}^2+(m/3)(\dot{\mathbf{y}}_1^2+\dot{\mathbf{y}}_2^2+\dot{\mathbf{y}}_1\dot{\mathbf{y}}_2) .$$

In planar polar coordinates, and after having imposed (2.2), one has $\mathbf{y}_s=d\mathbf{u}_s,\dot{\mathbf{y}}_s=d\dot{\varphi}_s\mathbf{u}_{\varphi_s}$, and the analogs of (2.1) and (2.3) are now

$$\mathbf{u}_s=\begin{bmatrix}\cos\varphi_s\\ \sin\varphi_s\end{bmatrix} , \quad \mathbf{u}_{\varphi_s}=\begin{bmatrix}-\sin\varphi_s\\ \cos\varphi_s\end{bmatrix} , \quad s=1,2 , \quad \Xi=\begin{bmatrix}\dot{\varphi}_1\\ \dot{\varphi}_2\end{bmatrix} ,$$
$$G=\frac{2md^2}{3}\begin{bmatrix}1 & 2^{-1}\cos(\varphi_2-\varphi_1)\\ 2^{-1}\cos(\varphi_2-\varphi_1) & 1\end{bmatrix} . \quad (6.1)$$

The analogs of (2.5), (2.6) and (2.8) are

$$H_c=\frac{1}{6m}\mathbf{\Pi}^2_{\mathrm{c.m.},c}+H_{c,\mathrm{in}}\ ,\quad \rho=\{4-[\cos(\varphi_2-\varphi_1)]^2\}^{-1}\ , \tag{6.2}$$

$$\begin{aligned}H_{c,\mathrm{in}}&=(md^2)^{-1}3\rho(\pi^2_{\varphi_1,c}+\pi^2_{\varphi_2,c}-\cos(\varphi_2-\varphi_1)\pi_{\varphi_1,c}\pi_{\varphi_2,c})\\&=(md^2)^{-1}3\rho\{(-\mathbf{a}^T_{1,c})(-\mathbf{a}_{1,c})+(-\mathbf{a}^T_{2,c})(-\mathbf{a}_{2,c})-2^{-1}[(-\mathbf{a}^T_{2,c})(-\mathbf{a}_{1,c})+(-\mathbf{a}^T_{1,c})(-\mathbf{a}_{2,c})]\}\ ,\end{aligned} \tag{6.3}$$

$$\mathbf{a}_{s,c}=-\mathbf{u}_{\varphi_s}\pi_{\varphi_s,c}\ . \tag{6.4}$$

Let $a_{s,c,\alpha},\alpha=1,2$ be the Cartesian components of $\mathbf{a}_{s,c}$. The Poisson brackets are

$$\begin{aligned}\{a_{s,c,1},a_{s,c,2}\}=\pi_{\varphi_s,c}\ ,\{a_{s,c,1},\pi_{\varphi_s,c}\}\\=a_{s,c,2}\ ,\{\pi_{\varphi_s,c},a_{s,c,2}\}=a_{s,c,1}\ .\end{aligned} \tag{6.5}$$

It is curious to see that the equations of motion for the actual model can be integrated completely, a simplifying feature that should not be expected for the general case treated in Sec. II A. We shall disregard $\mathbf{\Pi}_{\mathrm{c.m.},c}$, which is trivially conserved. The classical Hamilton equations of motion $\dot{\varphi}_s=\partial H_{c,\mathrm{in}}/\partial\pi_{\varphi_s,c}$, $\dot{\pi}_{\varphi_s,c}=-\partial H_{c,\mathrm{in}}/\partial\varphi_s$ together with the change of variables,

$$\begin{aligned}&\varphi=\varphi_2-\varphi_1\ ,\quad \Phi=2^{-1}(\varphi_1+\varphi_2)\ ,\\&L_c=\pi_{\varphi_1,c}+\pi_{\varphi_2,c}\ ,\quad l_c=2^{-1}(\pi_{\varphi_2,c}-\pi_{\varphi_1,c})\ ,\end{aligned} \tag{6.6}$$

give

$$\begin{aligned}&\dot{L}_c=0\ ,\quad \dot{\Phi}=(2md^2)^{-1}3\rho(2-\cos\varphi)L_c\ ,\\&\dot{\varphi}=(md^2)^{-1}6\rho(2-\cos\varphi)l_c\ ,\end{aligned} \tag{6.7}$$

plus another equation for $l_c$, which will not be needed, as we shall see [see (6.8)]. The first equation (6.7) implies that $L_c$ is conserved, which is not surprising, as it is precisely the total angular momentum (about an axis orthogonal to the plane in which the motions occur). The fact that energy is conserved ($\dot{H}_{\mathrm{in},c}=0$), (6.3) and (6.7) give, finally,

$$\begin{aligned}l_c=l_c(\varphi)=(2-\cos\varphi)^{1/2}\{3^{-1}md^2H_{c,\mathrm{in}}\\-[4(2+\cos\varphi)]^{-1}L_c^2\}^{1/2}\ ,\end{aligned} \tag{6.8}$$

$$\begin{aligned}&t-t_0=6^{-1}md^2\int_{\varphi_0}^{\varphi}\frac{d\varphi'(2-\cos\varphi')}{l_c(\varphi')}\ ,\\&\Phi-\Phi_0=4^{-1}L_c\int_{\varphi_0}^{\varphi}\frac{d\varphi'(2-\cos\varphi')}{l_c(\varphi')(2+\cos\varphi')}\ ,\end{aligned} \tag{6.9}$$

$\varphi_0$ and $\Phi_0$ being initial data at the initial time $t_0$. $L_c$ and $H_{c,\mathrm{in}}$ are constant.

### B. Quantization

We shall now quantize the model described in Sec. VI A by applying suitably the procedure described in Sec. III. We shall assume that the microscopic particles are nonidentical (even if they have the same mass), in order to avoid possible subtleties related to either indistinguishability or anyonic features in two spatial dimensions [20]. The scalar product of two arbitrary wave functions $\psi_i=\psi_i(t,\mathbf{X}_{\mathrm{c.m.}}\varphi_1\varphi_2)$, $i=1,2$ (periodic in both $\varphi_1\varphi_2$, with period $2\pi$) is

$$\begin{aligned}&(\psi_1,\psi_2)=\int d^3\mathbf{X}_{\mathrm{c.m.}}\int_0^{2\pi}d\varphi_1 d\varphi_2 g\psi_1^*\psi_2\ ,\\&g=(\det G)^{1/2}=3^{-1}md^2\rho^{-1/2}\ .\end{aligned} \tag{6.10}$$

The analogs of (3.2)–(3.4) are

$$\begin{aligned}&-\mathbf{a}_s=\mathbf{u}_{\varphi_s}\left[-i\hbar\frac{\partial}{\partial\varphi_s}\right]\ ,\\&\mathbf{e}_s=\mathbf{e}_{0s}-2^{-1}i\hbar\mathbf{u}_{\varphi_s}\frac{\partial\ln g}{\partial\varphi_s}\ ,\end{aligned} \tag{6.11}$$

$$\begin{aligned}&\mathbf{e}_{0s}=-\mathbf{a}_s+2^{-1}i\hbar\mathbf{u}_s\ ,\\&\pi_{\varphi_s}=-i\hbar\frac{\partial}{\partial\varphi_s}-2^{-1}i\hbar\frac{\partial\ln g}{\partial\varphi_s}\ .\end{aligned} \tag{6.12}$$

Notice that the notation $\pi_{\varphi_s}$ is used here, instead of $l_{s,3}$. The analogs of (3.6) and (3.7) are

$$H=(2M)^{-1}\mathbf{\Pi}^2_{\mathrm{c.m.}}+H_{\mathrm{in}}\ , \tag{6.13}$$

$$\begin{aligned}H_{\mathrm{in}}&=-3\hbar^2(md^2g)^{-1}\left[\sum_{s=1}^{2}\frac{\partial}{\partial\varphi_s}g\rho\frac{\partial}{\partial\varphi_s}-2^{-1}\left[\frac{\partial}{\partial\varphi_1}g\rho\cos(\varphi_2-\varphi_1)\frac{\partial}{\partial\varphi_2}+\frac{\partial}{\partial\varphi_2}g\rho\cos(\varphi_2-\varphi_1)\frac{\partial}{\partial\varphi_1}\right]\right]+\lambda\hbar^2R\\&=3(md^2g)^{-1}\left[\sum_{s=1}^{2}(-\mathbf{a}_s^\dagger)g\rho(-\mathbf{a}_s)-2^{-1}[(-\mathbf{a}_1^\dagger)g\rho(-\mathbf{a}_2)+(-\mathbf{a}_2^\dagger)g\rho(-\mathbf{a}_1)]\right]+\lambda\hbar^2R\ ,\end{aligned} \tag{6.14}$$

with $-\mathbf{a}_s^\dagger = -i\hbar(\partial/\partial\varphi_s)\mathbf{u}_{\varphi_s}^T$, $s=1,2$. Using the elements $g_{ij}$ of the matrix $G$ (6.1) as a metric, a rather lengthy calculation gives the curvature $R=18(md^2)^{-1}\cos(\varphi_2-\varphi_1)/2$. Some integrations by parts confirm that $\mathbf{e}_s$, $\pi_{\varphi_s}$, and $H$ are Hermitian operators with respect to the scalar product (6.10). One can also express $H_{\text{in}}$ as the counterpart of (3.9), that is, in terms of **e**'s, but this will be omitted, as it will be not necessary. The Cartesian components $e_{s,\alpha}$, $\alpha=1,2$ of $\mathbf{e}_s$ fulfill the analog of (4.1):

$$[e_{s,1},e_{s,2}]=-i\hbar\pi_{\varphi_s}, \quad [e_{s,1},\pi_{\varphi_s}]=-i\hbar e_{s,2} ,$$
$$[e_{s,2},\pi_{\varphi_s}]=i\hbar e_{s,1} . \tag{6.15}$$

One can show that the Lie algebra (6.15) is also satisfied if $e_{s,1},e_{s,2}$ and $\pi_{\varphi_s}$ are replaced, respectively, by (i) either $e_{0s,1},e_{0s,2}$ (the Cartesian components of $\mathbf{e}_{0s}$) and $-i\hbar(\partial/\partial\varphi_s)$, (ii) $-a_{s,1},-a_{s,2}$ (the Cartesian components of $\mathbf{a}_s$) and $-i\hbar(\partial/\partial\varphi_s)$, or (iii) $e_{0s,1}+\hbar\mu\cos\varphi_s$, $e_{0s,2}+\hbar\mu\sin\varphi_s$, $-i\hbar(\partial/\partial\varphi_s)$ for any real $\mu$. The commutation relations (6.15) are, precisely, those for the Lie algebra of so(2,1). They have also appeared in model studies of independent-particle systems having collective properties [21].

The eigenfunctions of $\pi_{\varphi_s}$ (the actual analogs of the modified spherical harmonics in Sec. V C) are easily seen to be $\psi_0 g^{-1/2}\exp iM_s\varphi_s$, where $M_s=0,\pm1,\pm2,\dots$, and $\psi_0$ may depend, at most, on $\varphi_{s'}, s'\neq s$.

Using the first two Eqs. (6.6), $H_{\text{in}}$ can be easily cast into the form

$$H_{\text{in}}=-\frac{3\hbar^2}{md^2}\left\{\frac{1}{4(2+\cos\varphi)}\frac{\partial^2}{\partial\Phi^2}+\frac{1}{2-\cos\varphi}\frac{\partial^2}{\partial\varphi^2}+2\rho^{1/2}\left[\frac{d}{d\varphi}\rho^{1/2}\left[1+\frac{\cos\varphi}{2}\right]\right]\frac{\partial}{\partial\varphi}\right\}+\lambda\hbar^2R . \tag{6.16}$$

Notice a simplifying feature: the functions multiplying $\partial^2/\partial\Phi^2$, $\partial^2/\partial\varphi^2$, and $\partial/\partial\varphi$ in (6.16) are singularity free in $0\le\varphi<2\pi$.

The total angular momentum is $L=\pi_{\varphi_1}+\pi_{\varphi_2}=-i\hbar(\partial/\partial\Phi)$, which is the quantum analog of $L_c$ (Sec. VI A) and commutes with $H_{\text{in}}$. Hence, the time-independent internal ($\mathbf{X}_{\text{c.m.}}$-independent) wave function can be factorized as

$$\psi(\varphi_1\varphi_2)=\exp iM_{\text{tot}}\Phi q(\varphi) ,$$

with $M_{\text{tot}}=0,\pm1,\pm2,\dots$, and

$$(H_{\text{in}}-E_{\text{in}})\psi(\varphi_1\varphi_2)=(L-M_{\text{tot}})\psi(\varphi_1\varphi_2)=0 .$$

The determination of $q(\varphi)$ and of the energy eigenvalue $E_{\text{in}}$ appears to require variational or perturbation methods.

The complete integrability of the classical model (Sec. VI A) together with (6.8) and (6.9) and the fact that $L_c$ is a constant of motion allow for the applicability of Bohr-Sommerfeld-Wilson (BSW) quantization rules to the approximate evaluation of $E_{\text{in}}$. The semiclassical BSW rules give ($h=2\pi\hbar$):

$$\int_0^{2\pi} d\Phi\, L_c=n_\Phi h , \quad \int_0^{2\pi} d\varphi\, l_c(\varphi)=n_\varphi h , \tag{6.17}$$

$n_\Phi$ and $n_\varphi$ being non-negative integers. If (6.17) are expected to be approximately reliable, both $n_\Phi$ and $n_\varphi$ should be large. One has $L_c=n_\Phi\hbar$, consistently with the allowed values for $M_{\text{tot}}$. On the other hand, an exact evaluation of the second integral in (6.17) seems to be hopeless. However a rather gross estimate of that integral proceeds by approximating $2\pm\cos\varphi$ by 2 in (6.8). Then, one gets the following approximate quantized formula for $E_{\text{in}}$:

$$E_{\text{in}}\approx\frac{3}{md^2}\left[\frac{\hbar^2}{8}n_\Phi^2+\frac{\hbar^2}{2}n_\varphi^2\right] . \tag{6.18}$$

## VII. DISTINGUISHABILITY VERSUS INDISTINGUISHABILITY IN A QUANTUM CHAIN AND STATISTICAL MECHANICS

Let us suppose that all atoms in the chain are identical, so that $m_i=m$, $i=1,\dots,N$, $d_s=d$, $s=1,\dots,N-1$. The very existence of the constraints (2.2), which force all identical atoms $1,2,\dots,N$ to lie successively along a chain, destroys unavoidably and permanently their indistinguishability, if not completely, at least to a very large extent, as we shall see. Take $N=3$ atoms and imagine three simultaneous measurements of their positions at time $t$, which, by assumption, yield, as results, $\mathbf{x}_a,\mathbf{x}_b,\mathbf{x}_c$, with $|\mathbf{x}_b-\mathbf{x}_a|=|\mathbf{x}_c-\mathbf{x}_b|=d$, $|\mathbf{x}_c-\mathbf{x}_a|\neq d$. By assumption, all experimental uncertainties in $|\mathbf{x}_b-\mathbf{x}_a|$, $|\mathbf{x}_c-\mathbf{x}_b|$, and $|\mathbf{x}_c-\mathbf{x}_a|$ either vanish (consistently with the existence of the constraints) or are much smaller than $d$. Which atom is at each of those positions? Clearly, the only possibilities are (i) atom 1 is at $\mathbf{x}_1=\mathbf{x}_a$ and atom 3 is at $\mathbf{x}_3=\mathbf{x}_c$, or (ii) atom 1 is at $\mathbf{x}_1=\mathbf{x}_c$ and atom 3 is at $\mathbf{x}_3=\mathbf{x}_a$ (atom 2 being at $\mathbf{x}_2=\mathbf{x}_b$ in both cases). Other possibilities are distinguishable and thus excluded by the very existence of (2.2) ($|\mathbf{x}_b-\mathbf{x}_a|=d$, etc.), but cases (i) and (ii) are indistinguishable from each other. Consequently, and invoking general quantum-mechanical ideas about identical particles, if the atoms are bosons (fermions), their wave function

$$\psi_1(t,\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)\equiv\psi(t,\mathbf{X}_{\text{c.m.}},\mathbf{u}_1,\mathbf{u}_2)$$

fulfills

$$\psi_1(t,\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)\equiv+\psi_1(t,\mathbf{x}_3,\mathbf{x}_2,\mathbf{x}_1)(-\psi_1(t,\mathbf{x}_3,\mathbf{x}_2,\mathbf{x}_1)) .$$

Upon applying similar arguments for any $N$, the wave function $\psi(t,\mathbf{X}_{\text{c.m.}},\mathbf{u}_1,\dots,\mathbf{u}_{N-1})$ for a quantum chain made up of $N$ identical atoms fulfills

$$\psi(t,\mathbf{X}_{\text{c.m.}},\mathbf{u}_1,\mathbf{u}_2,\ldots,\mathbf{u}_{N-1}) = \delta\psi(t,\mathbf{X}_{\text{c.m.}},-\mathbf{u}_{N-1},\ldots,-\mathbf{u}_2,-\mathbf{u}_1)\ , \qquad (7.1)$$

where $\delta=+1$ $(-1)$ for bosons (fermions). In the remainder of this section, let $\psi_{0,\alpha}=\psi_{0,\alpha}(\mathbf{u}_1,\ldots,\mathbf{u}_{N-1})$ be some normalized wave function in which both the $t$ and the $\mathbf{X}_{\text{c.m.}}$ dependences have been factored out $[(\psi_{0,\alpha},\psi_{0,\alpha})_{\text{in}}=1]$. $\alpha$ denotes a set of "quantum numbers." $\psi_{0,\alpha}$ may or may not be an eigenfunction of $H-\Pi^2_{\text{c.m.}}/2M$ and it does *not* fulfill (7.1). for instance, for $N=3$, $\psi_{0,\alpha}$ could correspond to

$$g^{1/2}\tilde{Y}_{L_1}^{L_1}(\theta_1\varphi_1)\tilde{Y}_{L_2}^{L_2}(\theta_2\varphi_2)\ ,$$

$(l_{1-}+l_{2-})[g^{1/2}\tilde{Y}_{L_1}^{L_1}(\theta_1\varphi_1)\tilde{Y}_{L_2}^{L_2}(\theta_2\varphi_2)]$, etc. (compare with the last paragraph in Sec. V C), up to suitable normalization factors. The important point is that the physically acceptable wave functions fulfilling (7.1) are

$$\psi_\alpha(\mathbf{u}_1,\ldots,\mathbf{u}_{N-1})\equiv n[\psi_{0\alpha}(\mathbf{u}_1,\mathbf{u}_2,\ldots,\mathbf{u}_{N-1}) + \delta\psi_{0\alpha}(-\mathbf{u}_{N-1},\ldots,-\mathbf{u}_2,-\mathbf{u}_1)] \qquad (7.2)$$

for both $\delta=+1$ and $-1$ (bosons and fermions, respectively). $n$ is a suitable normalization factor, associated to the peculiar statistics (7.2), which ensures that $(\psi_\alpha,\psi_\alpha)_{\text{in}}=1$. We shall now suppose that the set of all $\psi_\alpha$'s, as given through (7.2), becomes a complete orthonormal one regarding the dependences on $\mathbf{u}_1,\ldots,\mathbf{u}_{N-1}$, as $\alpha$ varies in its allowed range. Let us now assume that $N$ is very large and that the quantized chain of identical atoms is at thermodynamical equilibrium at absolute temperature $T$. Then, the quantum partition function is ($k_B$ being Boltzmann's constant)

$$\operatorname{Tr}\exp[-(k_BT)^{-1}(H-\Pi^2_{\text{c.m.}}/2M)] = \sum_\alpha \int [d\mathbf{u}]g\psi_\alpha^*\exp[-(k_BT)^{-1}(H-\Pi^2_{\text{c.m.}}/2M)]\psi_\alpha\ , \qquad (7.3)$$

$H$ being given in (3.7). Notice that the statistical behavior is associated with the large number of internal degrees of freedom but not with the motion of the center of mass.

Let all identical particles in the chain now be regarded as classical. Then, for a very large chain in thermodynamical equilibrium, the classical partition function is

$$\left[ [d\Pi_c]=\prod_{s=1}^{N-1} d\pi_{\theta_s}d\pi_{\varphi_s},[d\mathbf{u}]=\prod_{s=1}^{N-1}d\theta_s d\varphi_s \right] ,$$
$$Z_c=(2\pi\hbar)^{-2(N-1)}\int[d\mathbf{u}][d\Pi_c]\exp[-(k_BT)^{-1}][H_c-(2M)^{-1}\Pi^2_{\text{c.m.}c}]\ . \qquad (7.4)$$

Notice that no factor $[(N-1)!]^{-1}$ has been included in (7.4), as we shall justify below. Other classical approaches [23] to molecular chains (like DNA) using classical partition functions different from ours also *excluded* those "Boltzmann counting" factors.

Even if a detailed analysis of the classical high-temperature limit for (7.3) lies outside the scope of the present work, the following remarks will suffice to establish the absence of the Boltzmann counting factor $[(N-1)!]^{-1}$ in (7.4). In that regime [say, for $k_BT>\hbar^2(2md^2)^{-1}$] the right-hand side of (7.3) should go over that of (7.4) consistently as in the simpler case of the rotational partition function of a diatome molecule [4]. The key point to be emphasized here is that no factor $[(N-1)!]^{-1}$ can now appear at any stage. In turn, the reason is that the correctly symmetrized wave function $\psi_\alpha$ for the actual quantized chain appearing in (7.3) requires only two terms for any $N$, and, hence, the normalizing factor $n$ does not grow as $N$ increases, as (7.2) indicates correctly. This peculiarity is in sharp contrast with the usual recipe for $N$ free atoms in a quantum gas, where an adequately symmetrized sum over $N!$ permutations and, hence, a factor $(N!)^{-1}$ in the corresponding classical partition function are needed [22,4]. Like in the latter, one also expects that in the classical high-temperature limit complete distinguishability is established and, hence, that only one of the two possibilities in (7.2) contributes. Then, the right-hand side of (7.4) should have an additional factor $n^2$, but the latter has been disregarded, as it does not grow with $N$ and, hence, its influence disappears completely for large $N$. The quantitative study (omitted here) about how (7.3) becomes (7.4) would (i) use the functions $\tilde{Y}_L^M$ introduced in Sec. V C (and, eventually, their composed states and linear superpositions thereof), (ii) display cancellations among various factors $g^{\pm 1/2}$ contained in the $\tilde{Y}_L^M$'s and the factor $g$ in (3.1), and (iii) be based upon the replacement of quantum by classical variables (by neglecting the noncommutativity of the former as $\hbar\to 0$). It is easy to check that (7.3) becomes indeed (7.4) in the classical limit through the above steps (i)–(iii) in the special case treated in Sec. VI [namely, for (6.14) and (6.3)].

Equation (7.4) is believed to provide a less realistic description of a polymer than a classical partition function in which the rigid bonds considered here are replaced by stiff springs. A wide digression about these issues will be presented in Sec. VIII A. In spite of such a limitation, a summary of several consequences of (7.4) and their relationship to polymers may have a certain methodological interest. Let us add, for a while, external stretching forces $(0,0,-f)$ and $(0,0,f)$ acting upon $\mathbf{x}_N$ and $\mathbf{x}_1$, respectively and, accordingly, let $-(k_BT)^{-1}df\sum_{s=1}^{N-1}\cos\theta_s$ be included in Boltzmann's exponential factor in the classical distribution (7.4). Then, $Z_c=\exp[-(k_BT)^{-1}G_c]$, $G_c=G_c(T,f)$ being the classical Gibbs free energy. The classical Helmholtz free energy $A_c=A_c(T,D)$ is given through $A_c=fD+G_c$, $\partial G_c/\partial f=-D$, $\partial A_c/\partial D=f$. $D$ is interpreted here as a measure of the end-to-end distance in the chain, when both stretching forces act. The classical entropy ($S_c$) and internal energy ($U_c$) are $S_c=-(\partial A_c/\partial T)_D$, $U_c=A_c+TS_c$. One can prove directly that the equipartition principle, namely, $U_c=k_BT(N-1)$ holds exactly. Under suitable approximations [specifically, by approximating the determinant of the matrix in (2.5) by $(\prod_{s=1}^{N-1}\sin\theta_s)^2$], one can show that when $fd \ll k_BT$, then

$$f\cong 3Dk_BT[d^2(N-1)]^{-1}\ , \quad \left[\frac{\partial S_c}{\partial D}\right]_T<0\ . \tag{7.5}$$

Both (7.5) mean that the entropy decreases upon stretching, a property conventionally referred to as "rubber elasticity" [4,24]. We recall that the linearity between $f$ and $Dk_BT[d^2(N-1)]^{-1}$ turns out to be approximately valid for polymers [4,24]. The calculations yielding the equipartition principle and (7.5) are entirely similar to those outlined elsewhere [25] for a related (but somewhat different) model, which corresponds, formally, to the replacement of the $3\times 3$ matrix $C_{sj}$ (dependent on $\mathbf{u}_1,\dots,\mathbf{u}_{N-1}$) by the constant $A_{sj}$: in turn, the latter are the elements of the matrix $A$, the inverse of $A^{-1}$, which appeared in $T_c$, Sec. II A. For brevity, we shall omit those calculations. We believe that $(\partial S/D)_T<0$ may hold in more general situations. The above analysis suggests that the chain be regarded as composed by a very large number of independent elements (namely, the $N-1$ "bonds" between successive particles), subject to thermal motion. In turn, the above equipartition principle displays a basic property of a polymer, namely, that at a given temperature, the energy needed to add one element to the system is constant [3]. The approximations yielding (7.5) are similar to those discussed by Go and Scheraga [26]. See those authors and Fixman [7], for further discussion.

The same approximation yielding (7.5) also gives

$$S_c\cong k_B(N-1)\left\{1+\ln\left[\frac{8\pi k_BTmd^2}{(2\pi\hbar)^2}\right]\right\}-\frac{3}{2}\frac{k_BD^2}{d^2(N-1)}\ . \tag{7.6}$$

The last term on the right-hand side of (7.6) coincides exactly with the $D$-dependent contribution to the entropy of a polymer, as given in Kuhn's kinetic theory of rubber elasticity [24]. By using (7.6) and Boltzmann's relation, $S_c=k_B\ln W$, one can introduce the probability ($W$) for the end-to-end distance in the polymer, in thermodynamical equilibrium at temperature $T$, to be $D$. Clearly, $W$ is Gaussian. It is interesting to compare the above classical statistical mechanics for (2.8) with the probabilistic approach (basically, the random flight model [1–4], Kuhn's related kinetic theory [24], etc.). In the former, all thermodynamical functions were determined explicitly once a suitable approximation for the determinant appearing in the evaluation (via Gaussian integration) of (7.4) was used. However, it does not seem easy to derive from (7.4) (with stretching forces included) a probabilistic distribution (like the Gaussian one or Wiener's one) for an *arbitrary* pair of atoms in the chain, besides the one for the two end atoms [given through (7.6) and Boltzmann's relation]. On the other hand, in the probabilistic approach [1–4,24], the Gaussian or Wiener's distribution for any pair of atoms has indeed been obtained, but, thus far, the thermodynamical functions [like the equipartition principle or the $T$-dependent contribution to $S_c$ in the right-hand side of (7.6)] have not.

## VIII. DISCUSSION AND CONCLUSIONS

### A. Discussion

In principle, one expects that a model including vibrations should provide a better description of a molecular chain than another one without them. We remind the reader that, consistent with the Born-Oppenheimer philosophy, typical energies for individual internal rotations (about single bonds) are, at least, one order of magnitude smaller than those for vibrations (implying, say, bond stretching), at least at room temperatures. Alternatively, angular variables describing internal rotations evolve very slowly compared to those for vibrations. Then, for small energy (or room-temperature) phenomena, one expects physically that one can deal only with the relevant degrees of freedom, which are those pertaining to the slow internal rotations, and, so omit the vibrational ones. See, in this connection, the distinction between soft (slow) and hard (fast) variables made by Go and Scheraga [26]. Actually, some general features of their discussion can be taken over almost directly to the actual case: rotation angles (bond lengths) are regarded as soft (hard) variables.

The fixing of bond lengths and the direct restriction, from the outset, to angles for internal rotations are not the end of the story. Various calculations on the classical statistical mechanics of polymers with both rigid bonds and links modeled by very stiff springs have given rise to a controversy [27–29]. Further works shed more light [30–35] and it was considered that at the classical level the stiff spring computation [28] is more realistic than the one using rigid links [27]. Closely related to this viewpoint, a conventional wisdom emerged, which can be summarized as follows: (i) the best description of the actual molecular chain should be provided through a quantum-mechanical treatment; (ii) specifically, one should start with a quantized chain with flexible but stiff springs and, then take the limit in which the force constants become very large; (iii) at a later stage, one could proceed to the classical limit. The main trouble regarding this philosophy is practical: it turns out to be very difficult to carry through a treatment according to both (i) and (ii), unless a number of approximations are made, the validity of which is rather difficult to control. Thus, as Rallison [32] points out, the large quantum zero-point energies of the constrained degrees of freedom due to the very stiff springs may depend in general on the remaining unconstrained coordinates (regarded as classical). If such variations are taken into account, the subsequent analysis may be quite difficult, whereas if they are not, the resulting approximations are difficult to assess. Moreover [32], if those quantum zero-point energies are sufficiently large (as they will eventually become, for suitably large force constants), it may be necessary to treat the remaining unconstrained coordinates through quantum mechanics as well, a fact which may add even greater difficulties.

In the past, several works analyzed the possibility of treating constraints in quantum mechanics by introducing the potential that is responsible for that constraint [36–38]. The purpose was to find out, when the constraining potential becomes very large, a unique Schrödinger equation regarding the unconstrained coordinates. To this author's knowledge, the most general analysis was carried out by da Costa [36]: he found that a unique Schrödinger equation is arrived at if a certain "geometrical condition" [namely, Eq. (3) in his work] is fulfilled. Otherwise, different quantum-mechanical descriptions in the unconstrained coordinates are obtained. The other works [37,38] refer to simpler situations in which the geometrical condition [36] is fulfilled and, so, a unique Schrödinger equation (with well-defined curvature terms) is obtained. It appears that the various vectors $\mathbf{u}_s$ and $\mathbf{u}_{\theta_s}$, $\mathbf{u}_{\varphi_s}$ in Eq. (2.1) do not fulfill da Costa's geometrical condition [36]. This fact could be (more or less loosely) related to the term $\lambda\hbar^2 R$ in (3.6) (De Witt's correction).

In previous works [25,39], we have carried out a quantum-mechanical study of vibrations in a molecular chain, in the limit of large frequencies (in spherical polar coordinates); that is, from the standpoint of the accepted wisdom referred to above. Such an analysis, in the Born-Oppenheimer fashion, led to the quantum Hamiltonian (up to an additive finite constant),

$$(2M)^{-1}\mathbf{\Pi}_{\mathrm{c.m}}^2+2^{-1}\sum_{s,j=1}^{N-1}(d_s,d_j)^{-1}\mathbf{e}_{0s}\mathbf{e}_{0j}A_{sj}=H' ,$$

which is similar to (3.9), with three important differences: (a) instead of the functions $C_{sj}$, one finds the constants $A_{sj}$, which are the elements of the matrix $A$ (the inverse of $A^{-1}$ which, in turn, appeared in $T_c$, Sec. II A); (b) $\mathbf{e}_0$ (3.3) appears instead of $\mathbf{e}$; (c) neither $V_0$ nor $\lambda\hbar^2 R$ contributes. In turn, the classical limit $H'_c$ of $H'$ is similar to (2.8), again with $C_{sj}$ replaced by $A_{sj}$. Thus, such an approach [25,39], which starts directly from the quantum situation, and the one pursued in the present work [which originates in the classical constrained situation (2.2)] lead to similar but not exactly identical results. They also yield *partially* identical results in classical statistical mechanics, as commented upon in Sec. VII (but not fully identical, since their exact classical partition functions can easily be shown to be different from each other). A partially unsatisfactory feature in the calculation [25,39] was its *variational* character: that was the way and the price for bypassing Rallison's warning that the exact "quantum zero-point energies may depend on the unconstrained energies" [32]. That limitation as well as some appealing features (like the appearance of the $\mathbf{e}_0$'s and their closed algebra of commutators with $\mathbf{l}_0$'s) [39] indicated the interest and the convenience of carrying through an analysis with rigid links, as given in the present work.

We emphasize that the quantization method considered here follows the same philosophy as the one applied to the symmetric top [19,40]. In fact, the latter did start from classical mechanics for a rigid body (instead of from very stiff quantum oscillators), and it has allowed one to treat several molecules like $CH_3Cl$, $C_2H_4$, $C_2H_6$, . . . . Anyway, the peculiarities of the present work rely, most specifically, on the special properties (closed algebras, etc.) satisfied by the dynamical variables used (transverse momenta, etc.) Even if the quantization of the chain with rigid links does not coincide exactly with the quantum study based on very stiff springs (which is physically more acceptable), the former still has a certain interest since (a) it can be carried out, while the stiff-spring quantum analysis is, in general, very difficult and, so, the former could serve as a guide for the latter; (b) both procedures may be expected to lead to several *qualitatively* or formally similar results (like, for instance, the closed algebras for transverse momenta); (c) their quantitative differences, although not necessarily small, could, perhaps, be not too large generally (compare with the comments made by Van Kampen [31]).

In order to justify even further the interest in quantum-mechanical studies about internal rotations in small molecules, we recall that such treatments (together with quantum-statistical-mechanical ones) have already been carried out; for instance, in ethanelike molecules [41] (each being regarded as two tops rotating independently about a certain common axis), tetramethylmethane [42]. Moreover, those quantum-mechanical analyses were extended to a wider class of molecules, also consisting of rigid frameworks in which (symmetric and even unsymmetric) tops were attached [43].

Throughout this work we have made the simplifying assumption that all internal rotations are completely unhindered. Thus bond angles have not been held fixed, but are treated as independent variables; in other words, they have not been regarded as hard variables but as soft ones. A shortcoming of such an assumption is the following: in various cases of physical interest [24,4], the potential energies associated with the variations of bond angles could be comparable to vibrational energies. In order to justify, *a posteriori,* that assumption as a zeroth-order approximation, we shall add further arguments. First, we remind the reader that in any molecular chain (including hindered rotations for the bond angles), there is some length $d_{\mathrm{PL}}$ called persistent length, having the following basic property [24]: any two atoms in the chain separated by a distance $d'$ larger than $d_{\mathrm{PL}}$ are freely jointed, that is, they are capable of performing fully unhindered rotations independent of one another (while they behave as a rigid rod if $d' \leq d_{\mathrm{PL}}$). Then, our freely jointed chain with *unhindered rotations* and, say, fixed distance $d$ between "neighboring atoms" always has a potential usefulness since it turns out to be equivalent to another physical chain with (i) fixed bond length $d_{\mathrm{PH}}$ between real neighboring atoms; (ii) *hindered rotations* for bond angles; and (iii) persistent length $d_{\mathrm{PL}}$, with $d_{\mathrm{PH}} < d_{\mathrm{PL}} \cong d$. Second, the freely jointed chain is of a conceptual interest, since it has led to the biggest and tightest mathematical structure for the molecular chain, namely, to the (largest) sets of algebraic relations [(2.11), (2.12), (4.1) and (4.2)] for the relevant classical and quantum variables. Then, by invoking the existence of hindered rotations and keeping the bond angles fixed at a later stage, one would search for suitable variables and, eventually, for a more reduced mathematical structure (that is, for necessarily smaller sets of algebraic relations corresponding to (2.11), (2.12), (4.1) and (4.2).

### B. Conclusions

In spite of the various limitations discussed in Sec. VIII A, this work contains results and features that may have a certain physical interest. They are the following:

(1) The classical theory of the freely rotating chain is formulated in terms of $-\mathbf{a}_{j,c}$'s and $\boldsymbol{l}_{j,c}$'s. A closed algebra has been obtained for the Poisson brackets of the Cartesian components of those variables.

(2) In order to quantize the chain (in three spatial dimensions), the scalar product and the quantum Hamiltonian $H$ have been constructed, using spherical polar coordinates, in the framework of curved-space quantization. The quantum analogs $\mathbf{e}_j$ and $\boldsymbol{l}_j$ of $-\mathbf{a}_{j,c}$ and $\boldsymbol{l}_{j,c}$ have been obtained. We stress that $\boldsymbol{l}_j$ can be consistently regarded as the quantum orbital angular momentum for the $j$th "bond," even if its detailed expression in terms of angles differs from the standard formulas [10,11]. It has been shown that $\boldsymbol{l}_j$ and $\mathbf{e}_j$ are Hermitian and that $H$ is self-adjoint.

(3) The commutators of the Cartesian components of $\mathbf{e}_j$ and $\boldsymbol{l}_j$ have been shown to close a Lie algebra.

(4) The consistency (via the correspondence principle) between the classical and the quantum theories is established. In spite of the technical complications that have arisen in the quantum expressions, similar structures have been found for (i) the Hamiltonians $H_c$ and $H$, (ii) the algebras of Poisson brackets and commutators, (iii) relationships between $-\mathbf{a}_{j,c}$ and $\boldsymbol{l}_{j,c}$ and between $\mathbf{e}_j$ and $\boldsymbol{l}_j$, and (iv) the time evolutions of $-\mathbf{a}_{j,c}$, $\boldsymbol{l}_{j,c}$ and of $(\psi,\mathbf{e}_j\psi)$ and $(\psi,\boldsymbol{l}_j\psi)$. Except for (ii), some quantum corrections have been found that disappear as $\hbar\to 0$. Moreover, the classical limit of the Schrödinger equation has been shown to yield the Hamilton-Jacobi one. A quantum continuity equation for the motion of the center-of-mass has been obtained.

(5) Modified spherical harmonics, associated with the modified $\boldsymbol{l}_j$ (induced by the nonstandard scalar product) have been constructed. Uncertainty relations for $\mathbf{e}_j$ and $\boldsymbol{l}_j$ have been discussed. Simultaneous eigenfunctions of $e_{s,3}$ and $l_{s,3}$ have been found and discussed.

(6) An interesting example for $N=3$ particles in two spatial dimensions has been worked out in some detail. The corresponding classical model turned out to be completely integrable, while the quantum one was separable. The energy eigenvalues for the latter have been obtained approximately, in the regime of large quantum numbers, via semiclassical methods.

(7) The very existence of the constraints (2.2) implies that a quantum chain made up of identical particles has indistinguishability properties, which differ from the usual ones for $N$ free quantum particles. This fact implies that the classical partition function for the chain lacks any "Boltzmann counting" factor (like $[(N-1)!]^{-1}$). This feature may hold when other internal forces are also acting in the macromolecules or in other models based on stiff springs at the quantum level (in the framework of the conventional wisdom referred to in Sec. VIII A). Such a property and, at the classical level, other ones (like the exact validity of the equipartition principle and some approximate rubber elasticity features) may be of interest as well, at least methodologically.

The structure (3.9) and the Lie algebra (4.1) and (4.2) have been used *mainly* in order to provide powerful consistency tests for the quantization procedure, although several additional applications of them have also been made (Sec. V) or suggested (Sec. VII). The possibility that (3.9), (4.1) and (4.2) may lead to a more detailed understanding of eigenvalues and eigenfunctions of $H$ stands as an open problem.

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