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Quantum entropic ambiguities: Ethylene

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In a quantum system, there may be many density matrices associated with a state on an algebra of observables. For each density matrix, one can compute its entropy. These are, in general, different. Therefore, one reaches the remarkable possibility that there may be many entropies for a given state [R. Sorkin (private communication)]. This ambiguity in entropy can often be traced to a gauge symmetry emergent from the nontrivial topological character of the configuration space of the underlying system. It can also happen in finite-dimensional matrix models. In the present work, we discuss this entropy ambiguity and its consequences for an ethylene molecule. This is a very simple and well-known system, where these notions can be put to tests. Of particular interest in this discussion is the fact that the change of the density matrix with the corresponding entropy increase drives the system towards the maximally disordered state with maximum entropy, where Boltzman's formula applies. Besides its intrinsic conceptual interest, the simplicity of this model can serve as an introduction to a similar discussion of systems such as colored monopoles and the breaking of color symmetry.

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I. INTRODUCTION

Many years ago, Balachandran *et al.* [1,2] and Nelson and Manohar [3] discovered that color symmetry is spontaneously broken in the presence of non-Abelian GUT monopoles [4].

Subsequently, we discovered that this phenomenon is quite common [5,6]. It can happen whenever wave functions are sections of a twisted bundle over a configuration space $\mathcal{Q}$. If the group H associated with the bundle is non-Abelian, then it is broken for the same reason that the above mentioned monopole breaks color. Examples are diverse and include the following:

(a) Molecules such as ethylene with non-Abelian symmetry H [6].
(b) Systems of N identical particles with the representation of a braid or permutation group of dimension 2 or more [5].
(c) QCD [4,7,8] and GUT theories [9] with their gauge groups as H.
(d) Non-Abelian mapping class diffeomorphism groups H of quantum gravity [10–13].

It is often the case that such anomalous quantum breakdown of a classical symmetry is not desirable. With that in mind, Balachandran and Queiroz [14] had suggested the use of appropriate mixed states which restore the symmetry.

Summarizing, if H is a twisted non-Abelian gauge symmetry, then it is anomalous on pure states. The use of appropriate mixed states removes this anomaly.

The contribution of the present paper is to show that *such mixed states necessarily emerge in quantum theory.* We will show the result here for the simple quantum mechanical system of the ethylene molecule C_2H_4. That can be the basis for the future treatment of GUT monopoles and QCD.

The framework best adapted for this analysis is the Gel'fand-Naimark-Segal (GNS) theory. It formulates quantum theory using unital C^* algebras of observables $\mathcal{A}$ and states ω on $\mathcal{A}$. The usual Hilbert space formulation emerges from this theory. All results of physical interest can be formulated in the latter, but certain ideas and approaches become less transparent. With this in mind, in Sec. II, we explain the aspects of the GNS theory of interest here using the Hilbert space language.

Section III recalls the basic quantum theory of ethylene. It then deals with the algebra $\mathcal{A}$ of observables of this system. It shows that a ground-state wave function induces a *mixed* state on $\mathcal{A}$. It is not unique. That reflects the fact that the (convex) set of states is not a simplex [15,16].

The final Sec. IV examines what happens upon appropriately including the electronic observables in $\mathcal{A}$. Then one can actually prepare the molecule in one of the above mixed states. Further time evolution becomes a stochastic map, steadily increasing entropy towards its fixed point, which is its maximum [16].

II. THE GNS CONSTRUCTION

In elementary quantum theory, a general state is identified with a density matrix ρ. It is represented in terms of rank-1 (pure) orthogonal density matrices ρ_α:

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$$\rho = \sum_\alpha \lambda_\alpha \rho_\alpha, \qquad \lambda_\alpha > 0, \qquad \sum_\alpha \lambda_\alpha = 1, \tag{2.1}$$

$$\rho_\alpha \rho_\beta = \delta_{\alpha\beta} \rho_\alpha. \tag{2.2}$$

These ρ and ρ_α, as the (unital C^*) algebra of observables $\mathcal{A}$, are regarded as operators on a Hilbert space $\mathcal{H}$. The expectation value of $a \in \mathcal{A}$ in the state specified by ρ is then

$$\langle a \rangle_\rho = \mathrm{Tr}\, \rho a. \tag{2.3}$$

The entropy of ρ is

$$S(\rho) = -\mathrm{Tr}\, \rho \log \rho = -\sum_\alpha \lambda_\alpha \log \lambda_\alpha. \tag{2.4}$$

We now deduce the GNS language using the density matrix description, first for the rank-1 density matrices and then for general rank matrices.

A. Rank-1 density matrix

In this case,

$$\rho = |\psi\rangle\langle\psi|, \qquad \psi \in \mathcal{H}, \qquad \langle\psi|\psi\rangle = 1. \tag{2.5}$$

The expectation value of the product $a_1 \cdot \ldots \cdot a_N$ of N observables for this density matrix is

$$\mathrm{Tr}\, \rho(a_1 \cdot \ldots \cdot a_N) = \langle\psi|a_1 \cdot \ldots \cdot a_N|\psi\rangle. \tag{2.6}$$

Further, for any observable a,

$$\langle\psi|a^* a|\psi\rangle \geq 0. \tag{2.7}$$

From Eq. (2.7) we see that the set of vector states in $\mathcal{H}$ excited by $\mathcal{A}$ from $|\psi\rangle$ is

$$\mathcal{A}|\psi\rangle \subseteq \mathcal{H} = \{|a\rangle_\psi := a|\psi\rangle : a \in \mathcal{A}\}. \tag{2.8}$$

The inner product on these vectors is given by Eq. (2.7).

It may happen that certain observables n annihilate $|\psi\rangle$. Such n have zero norm,

$$\langle\psi|n^* n|\psi\rangle = 0, \tag{2.9}$$

and generate a left-ideal $\mathcal{N}$ in the algebra, as is readily shown using the Schwarz inequality. We must remove this "Gel'fand ideal" $\mathcal{N}$ from $\mathcal{A}$ to convert Eq. (2.8) to a Hilbert space. Thus, we consider

$$(\mathcal{A}/\mathcal{N})|\psi\rangle = \{|[a]\rangle_\psi := (a + \mathcal{N})|\psi\rangle : a \in \mathcal{A}\}, \tag{2.10}$$

where $\mathcal{N}|\psi\rangle$ denotes the set $\{n|\psi\rangle : n \in \mathcal{N}\}$. The scalar product for these vectors is given by

$$\langle [a] | [b] \rangle_\psi = \langle\psi|a^* b|\psi\rangle. \tag{2.11}$$

Note that $[a] = [a']$, if $a - a' \in \mathcal{N}$. Also, by Schwarz inequality, $\langle\psi|a^* n|\psi\rangle = 0$ for $a \in \mathcal{A}$, so that the rhs of Eq. (2.11) does not depend on the chosen elements a, b from $[a]$, $[b]$.

We can now complete $(\mathcal{A}/\mathcal{N})|\psi\rangle$ using the norm of Eq. (2.11) to obtain a variant $\tilde{\mathcal{H}}_{\mathrm{GNS}}$ of the canonical GNS Hilbert space.

On $\tilde{\mathcal{H}}_{\mathrm{GNS}}$, there is also a $*$ representation $\tilde{\pi}$ of $\mathcal{A}$ (the star becoming the adjoint operator in the representation):

$$\tilde{\pi}(b)|[a]\rangle_\psi = |[ba]\rangle_\psi. \tag{2.12}$$

The image of the density matrix ρ in $\tilde{\mathcal{H}}_{\mathrm{GNS}}$ is the vector

$$|[\mathbb{1}]\rangle_\psi. \tag{2.13}$$

(Recall that by assumption $\mathcal{A}$ is unital; that is, $\mathbb{1} \in \mathcal{A}$). The density matrix

$$\tilde{\rho}_{\mathrm{GNS}} = |[\mathbb{1}]\rangle_{\psi\,\psi}\langle[\mathbb{1}]| \tag{2.14}$$

for the algebra $\tilde{\pi}(\mathcal{A})$ is entirely equivalent to the density matrix ρ of $\mathcal{A}$:

$$\mathrm{Tr}_{\tilde{\mathcal{H}}_{\mathrm{GNS}}} \tilde{\rho}_{\mathrm{GNS}} \tilde{\pi}(a) = \mathrm{Tr}_{\mathcal{H}} \rho a, \quad \text{for all } a \in \mathcal{A}. \tag{2.15}$$

B. Rank-N density matrix

In this case,

$$\rho_\alpha = |\psi_\alpha\rangle\langle\psi_\alpha|, \qquad \psi_\alpha \in \mathcal{H}, \qquad \langle\psi_\alpha|\psi_\beta\rangle = \delta_{\alpha\beta}, \tag{2.16}$$

while Eqs. (2.6) and (2.7) are replaced by

$$\mathrm{Tr}\, \rho(a_1 \cdot \ldots \cdot a_N) = \sum_\alpha \lambda_\alpha \langle\psi_\alpha|a_1 \cdot \ldots \cdot a_N|\psi_\alpha\rangle, \tag{2.17}$$

$$\sum_\alpha \lambda_\alpha \langle\psi_\alpha|b^* b|\psi_\alpha\rangle \geq 0. \tag{2.18}$$

The space $\mathcal{A}|\psi\rangle$ is replaced by the direct sum

$$\bigoplus_\alpha \mathcal{A}|\psi_\alpha\rangle. \tag{2.19}$$

This space inherits the following inner product $(\cdot,\cdot)$ from Eq. (2.18):

$$(a|\psi_\alpha\rangle, b|\psi_\beta\rangle) = \sum_\alpha \lambda_\alpha \delta_{\alpha\beta} \langle\psi_\alpha|a^* b|\psi_\alpha\rangle. \tag{2.20}$$

Let us first assume that there are no vectors of zero norm for this inner product. Then the completion of $\bigoplus_\alpha \mathcal{A}|\psi_\alpha\rangle$ using this scalar product gives the full Hilbert space $\bigoplus_\alpha \tilde{\mathcal{H}}_\alpha$, with $\tilde{\mathcal{H}}_\alpha$ being the completion of $\mathcal{A}|\psi_\alpha\rangle$. Thus, $\bigoplus \tilde{\mathcal{H}}_\alpha$ *is an orthogonal direct sum with the weighted inner product* [Eq. (2.20)].

Also, while $\mathcal{A}|\psi_\alpha\rangle$ are subspaces $\iota(\tilde{\mathcal{H}}_\alpha)$ of $\mathcal{H}$ *as vector spaces*, the scalar product [Eq. (2.20)] differs from that inherited by $\iota(\tilde{\mathcal{H}}_\alpha)$ from $\mathcal{H}$. That is because as subspaces $\iota(\tilde{\mathcal{H}}_\alpha)$ of $\mathcal{H}$, they would in general have nontrivial intersection for $\alpha \neq \beta$:

$$\iota(\tilde{\mathcal{H}}_\alpha) \cap \iota(\tilde{\mathcal{H}}_\beta) \neq \{0\}, \tag{2.21}$$

and hence they would have vectors with nonzero scalar product. Therefore, it is not appropriate to regard $\bigoplus_\alpha \tilde{\mathcal{H}}_\alpha$ as a subspace of $\mathcal{H}$.

Suppose next that there are null vectors. Then we must remove them first from $\bigoplus_\alpha \mathcal{A}|\psi_\alpha\rangle$. They come from the $n \in \mathcal{A}$ such that

$$\langle\psi_\alpha|n^*n|\psi_\alpha\rangle = 0, \quad \text{for all } \alpha. \tag{2.22}$$

Such n form the Gel'fand ideal $\mathcal{N}$ of $\mathcal{A}$.

The space $\bigoplus_\alpha(\mathcal{A}/\mathcal{N})|\psi_\alpha\rangle$, with

$$(\mathcal{A}/\mathcal{N})|\psi_\alpha\rangle := \{(a+\mathcal{N})|\psi_\alpha\rangle \equiv |[a]\rangle_\alpha\}, \tag{2.23}$$

has the scalar product

$$\langle[a]|[b]\rangle = \sum_\alpha \lambda_\alpha\langle\psi_\alpha|a^*b|\psi_\alpha\rangle. \tag{2.24}$$

On completion it gives a variant $\tilde{\mathcal{H}}_{\text{GNS}}$ of the canonical GNS Hilbert space.

We can write

$$\mathbb{1} = \sum_\alpha |\psi_\alpha\rangle\langle\psi_\alpha| = \sum_\alpha \rho_\alpha \tag{2.25}$$

so that the component of $|[\mathbb{1}]\rangle$ in $\mathcal{A}/\mathcal{N}|\psi_\alpha\rangle$ is

$$|[\mathbb{1}]\rangle_\alpha := |[|\psi_\alpha\rangle\langle\psi_\alpha|]\rangle_\alpha = |[\rho_\alpha]\rangle_\alpha. \tag{2.26}$$

The Hilbert space $\tilde{\mathcal{H}}_{\text{GNS}}$ carries a $*$ representation $\tilde{\pi}$ of $\mathcal{A}$:

$$\tilde{\pi}(a)|[b]\rangle = |[ab]\rangle, \tag{2.27}$$

$$\tilde{\pi}(b)|[\mathbb{1}]\rangle := |[b]\rangle. \tag{2.28}$$

Since

$$_\beta\langle[c]|\tilde{\pi}(a)|[b]\rangle_\alpha = \delta_{\alpha\beta}\langle\psi_\beta|c^*ab|\psi_\alpha\rangle, \tag{2.29}$$

so that each subspace $|[\mathcal{A}]\rangle_\alpha$ is invariant under $\tilde{\pi}$, the density matrix

$$\tilde{\rho}_{\text{GNS}} = \sum_\alpha |[\mathbb{1}]\rangle_\alpha \sum_\beta {}_\beta\langle[\mathbb{1}]| \tag{2.30}$$

is entirely equivalent to ρ:

$$\text{Tr}_{\tilde{\mathcal{H}}_{\text{GNS}}} \tilde{\rho}_{\text{GNS}}\tilde{\pi}(a) = \text{Tr}_{\mathcal{H}}\, \rho a, \quad \text{for all } a \in \mathcal{A}. \tag{2.31}$$

The density matrix $\tilde{\rho}_{\text{GNS}}$ can in fact be rewritten discarding the cross terms in Eq. (2.31) in view of Eq. (2.29):

$$\tilde{\rho}_{\text{GNS}} = \sum_\alpha |[\mathbb{1}]\rangle_{\alpha\,\alpha}\langle[\mathbb{1}]|. \tag{2.32}$$

Since

$$_\alpha\langle[\mathbb{1}]|[\mathbb{1}]\rangle_\alpha = \lambda_\alpha, \tag{2.33}$$

in terms of density matrices

$$\tilde{\rho}_{\text{GNS},\alpha} \equiv \frac{1}{\lambda_\alpha}|[\mathbb{1}]\rangle_{\alpha\,\alpha}\langle[\mathbb{1}]|, \tag{2.34}$$

Eq. (2.32) reads

$$\tilde{\rho}_{\text{GNS}} = \sum_\alpha \lambda_\alpha\,\tilde{\rho}_{\text{GNS},\alpha}. \tag{2.35}$$

C. A shift in perspective

A *state* ω on a unital $*$-algebra $\mathcal{A}$ is a non-negative linear map from $\mathcal{A}$ to $\mathbb{C}$ normalized to 1 on $\mathbb{1}$ and compatible with the $*$ operation:

$$\omega(a^*a) \geq 0, \qquad \omega(a^*) = \overline{\omega(a)}, \tag{2.36}$$

$$\omega(\mathbb{1}) = 1, \qquad a, \mathbb{1} \in \mathcal{A}. \tag{2.37}$$

Hence, a density matrix ρ defines a state ω_ρ:

$$\omega_\rho(a) = \text{Tr}\,\rho a. \tag{2.38}$$

It can and does happen in quantum theory that many density matrices ρ_i give the same state:

$$\text{Tr}\,\rho_j a = \text{Tr}\,\rho_k a, \qquad \rho_j \neq \rho_k \quad \text{for } j \neq k, \tag{2.39}$$

so that

$$\omega_{\rho_j} = \omega_{\rho_k}. \tag{2.40}$$

But their entropies can be different:

$$-\text{Tr}\,\rho_j \log\rho_j \neq -\text{Tr}\,\rho_k \log\rho_k, \quad \text{for } j \neq k. \tag{2.41}$$

We can capture such subtleties more elegantly by not starting with a density matrix, but with a state ω on $\mathcal{A}$, presented now as a unital $*$ algebra, shifting the focus away from its representation on $\mathcal{H}$ by a density matrix.

In the original GNS approach, one introduces a vector space $\mathcal{A}|\mathbb{1}\rangle$ labeled by elements of $\mathcal{A}$:

$$\mathcal{A}|\mathbb{1}\rangle := \{a|\mathbb{1}\rangle = |a\rangle : a \in \mathcal{A}\}. \tag{2.42}$$

Then one uses ω to define inner products:

$$(|b\rangle, |a\rangle) = \omega(b^*a). \tag{2.43}$$

If $\omega = \omega_\rho$, then this coincides with $\text{Tr}\,\rho(b^*a)$:

$$\omega_\rho(b^*a) = \sum_\alpha \lambda_\alpha\langle\psi_\alpha|b^*a|\psi_\alpha\rangle. \tag{2.44}$$

As in the earlier approach, here too there can be null vectors $|n\rangle$:

$$\langle n|n\rangle = \omega(n^*n) = 0. \tag{2.45}$$

The set $\mathcal{N}$ of $n \in \mathcal{A}$ creating the space $\mathcal{N}|\mathbb{1}\rangle$ of null vectors is the Gel'fand ideal. We remove them by considering

$$(\mathcal{A}/\mathcal{N})|\mathbb{1}\rangle := \{|[a]\rangle\}, \tag{2.46}$$

where, as before, by $[a]$ we mean the equivalence class of elements in $\mathcal{A}$ differing by an element of $\mathcal{N}$:

$$[a]=[b]\Leftrightarrow a-b\in\mathcal{N}. \tag{2.47}$$

The scalar product in $(\mathcal{A}/\mathcal{N})|\mathbb{1}\rangle$ is also given by ω:

$$\langle[b]|[a]\rangle=\omega(b^{*}a). \tag{2.48}$$

As before, by Schwarz inequality, the rhs does not depend on the choice of the representatives b and a from their equivalence classes. The completion of $(\mathcal{A}/\mathcal{N})|\mathbb{1}\rangle$ gives the standard presentation of the GNS Hilbert space $\mathcal{H}_{\mathrm{GNS}}$.

We emphasize that this process of completion can be important, as it is for the ethylene molecule treated below in Secs. III and IV.

As before, $\mathcal{H}_{\mathrm{GNS}}$ carries a representation π of $\mathcal{A}$:

$$\pi(a)|[b]\rangle=|[ba]\rangle. \tag{2.49}$$

We can generate a dense subset of $\mathcal{H}_{\mathrm{GNS}}$ by acting with $\pi(a)$'s on $|[\mathbb{1}]\rangle$. For this reason, $|[\mathbb{1}]\rangle$ is called a "cyclic vector."

It is an easy check that the density matrix

$$\hat{\rho}_{\mathrm{GNS}}=|[\mathbb{1}]\rangle\langle[\mathbb{1}]| \tag{2.50}$$

defines exactly the same state as ω:

$$\omega(a)=\mathrm{Tr}_{\mathcal{H}_{\mathrm{GNS}}}\hat{\rho}_{\mathrm{GNS}}\pi(a). \tag{2.51}$$

We can now quickly recover the decomposition of $\hat{\rho}_{\mathrm{GNS}}$ in pure states. Let us reduce $\pi(a)$ into a direct sum of irreducible representation (IRR),

$$\pi=\bigoplus_{\alpha,r}\pi^{(\alpha,r)} \tag{2.52}$$

with the corresponding orthogonal direct sum decomposition of $\mathcal{H}_{\mathrm{GNS}}$:

$$\mathcal{H}=\bigoplus_{\alpha,r}\mathcal{H}^{(\alpha,r)}. \tag{2.53}$$

Here, if $\alpha\neq\beta$, $\pi^{(\alpha,r)}$ and $\pi^{(\beta,s)}$ are inequivalent:

$$\pi^{(\alpha,r)}\neq\pi^{(\beta,s)},\quad \text{if } \alpha\neq\beta, \tag{2.54}$$

while for fixed α, $\pi^{(\alpha,r)}$ and $\pi^{(\alpha,s)}$ are equivalent:

$$\pi^{(\alpha,r)}\simeq\pi^{(\alpha,s)},\qquad r,s=1,\dots N_{\alpha}, \tag{2.55}$$

where N_α is the multiplicity of the representation α.

If $P^{(\alpha,r)}$ are projectors to $\mathcal{H}^{(\alpha,r)}$, then

$$|[\mathbb{1}]\rangle=\sum_{\alpha,r}P^{(\alpha,r)}|[\mathbb{1}]\rangle=\sum_{\alpha,r}|[P^{(\alpha,r)}]\rangle. \tag{2.56}$$

Therefore

$$\mathrm{Tr}\,\hat{\rho}_{\mathrm{GNS}}\pi(a)=\sum_{\alpha,r}\mathrm{Tr}\,|[P^{(\alpha,r)}]\rangle\langle[P^{(\alpha,r)}]|\,\pi(a), \tag{2.57}$$

so that as *states*, we can write

$$\hat{\rho}_{\mathrm{GNS}}\simeq\rho_{\mathrm{GNS}}:=\sum_{\alpha,r}\sigma^{(\alpha,r)}, \tag{2.58}$$

$$\sigma^{(\alpha,r)}:=|[P^{(\alpha,r)}]\rangle\langle[P^{(\alpha,r)}]|, \tag{2.59}$$

with the corresponding entropy

$$S(\rho_{\mathrm{GNS}})=-\mathrm{Tr}\,\rho_{\mathrm{GNS}}\log\rho_{\mathrm{GNS}}. \tag{2.60}$$

The vectors $|[P^{(\alpha,r)}]\rangle$ may not be of norm 1, which is to be computed using ω. Let

$$\lambda_{\alpha,r}=(|[P^{(\alpha,r)}]\rangle,|[P^{(\alpha,r)}]\rangle)=\omega((P^{(\alpha,r)})^{2})=\omega(P^{(\alpha,r)}). \tag{2.61}$$

Then, in terms of normalized density matrices

$$\rho^{(\alpha,r)}=\frac{1}{\lambda_{\alpha,r}}\sigma^{(\alpha,r)}, \tag{2.62}$$

we can write

$$\rho_{\mathrm{GNS}}=\sum_{\alpha,r}\lambda_{\alpha,r}\rho^{(\alpha,r)} \tag{2.63}$$

and

$$S(\rho_{\mathrm{GNS}})=-\sum\lambda_{\alpha,r}\log\lambda_{\alpha,r}. \tag{2.64}$$

But if the same IRR α occurs more than once, then the decomposition in Eq. (2.53) is not unique. We can replace the subspace $\mathcal{H}^{(\alpha,r)}$ by

$$\mathcal{H}^{(\alpha,r)}(u)=\mathcal{H}^{(\alpha,s)}u_{sr}\equiv\{\eta^{(\alpha,s)}u_{sr}\colon\,\eta^{(\alpha,s)}\in\mathcal{H}^{(\alpha,s)}\},$$
$$u^{\dagger}u=\mathbb{1}. \tag{2.65}$$

As $u=e^{i\theta}\mathbb{1}$ gives the same orthogonal decomposition for all θ, we have $U(N_\alpha)/U(1)\simeq SU(N_\alpha)/\mathbb{Z}_{N_\alpha}$ worth of distinct decompositions in the above.

Here if $\{|[\xi_j^{(\alpha,r)}]\rangle\}$ is an orthonormal basis for $\mathcal{H}^{(\alpha,r)}$, then an orthonormal basis for $\mathcal{H}^{(\alpha,r)}(u)$ is

$$\{|[\xi_j^{(\alpha,s)}]\rangle u_{sr}\}. \tag{2.66}$$

In quark model language, one says that if α is a color index, then r is a flavor index.

Since

$$\pi(a)\mathcal{H}^{(\alpha,r)}(u)\subseteq\mathcal{H}^{(\alpha,r)}(u), \tag{2.67}$$

we can repeat the construction of ρ_{GNS} using projectors $P^{(\alpha,r)}(u)$ on $\mathcal{H}^{(\alpha,r)}(u)$, getting generically a new density matrix $\rho_{\mathrm{GNS}}(u)$,

$$\hat{\rho}_{\mathrm{GNS}}\simeq\rho_{\mathrm{GNS}}(u), \tag{2.68}$$

and the new entropy

$$S(\rho_{\mathrm{GNS}}(u))=-\mathrm{Tr}\,\rho_{\mathrm{GNS}}(u)\log\rho_{\mathrm{GNS}}(u). \tag{2.69}$$

Reference [16] discusses the dependence of the entropy on u in detail. We shall return to it later.

We have now captured the relevant features of states using the original GNS approach as well.

D. The emergent "gauge" symmetry

For the IRR α with degeneracy N_α, the set of unitary transformations $\{u\}$ modulo $U(1)$ forms the group $SU(N_\alpha)/\mathbb{Z}_{N_\alpha} \equiv \mathcal{G}_\alpha$. It commutes with the algebra of observables $\mathcal{A}$. It is therefore a "gauge" symmetry. The full gauge symmetry is $\times_\alpha \mathcal{G}_\alpha$.

Each $\mathcal{G}_\alpha$ generates an algebra $\mathbb{C}\mathcal{G}_\alpha$, the group algebra of $\mathcal{G}_\alpha$, in the commutant $\mathcal{A}'$ of $\mathcal{A}$. We identify $\mathcal{A}'$ with $\bigoplus_\alpha \mathbb{C}\mathcal{G}_\alpha$.

Remark: It is worth pointing out an important subtlety related to the role of $P^{(\alpha,r)}$'s, the projectors to the $\mathcal{H}^{(\alpha,r)}$. Considerations based purely on $\mathcal{A}$ allow us to construct only the central projectors $P^{(\alpha)} \equiv \sum_r P^{(\alpha,r)}$. Their further "splitting" into different $P^{(\alpha,r)}$'s is impossible to construct if one makes use of only elements $a \in \mathcal{A}$. To decompose $P^{(\alpha)}$ further, we need to enlarge the algebra $\mathcal{A}$ to a larger algebra $\bar{\mathcal{A}}$ containing the commutant $\mathcal{A}' = \bigoplus_\alpha \mathbb{C}\mathcal{G}_\alpha$. Using $u \in \mathcal{A}'$, we can construct the noncentral projectors $P^{(\alpha,r)}$ and subsequently subspaces $\mathcal{H}^{(\alpha,r)}(u)$ of Eq. (2.65). The u dependence of the entropy [Eq. (2.69)] then follows easily.

The above considerations will play an important role in understanding the example of the ethylene molecule discussed in the next section.

Alternatively, if we were to restrict ourselves just to the algebra $\mathcal{A}$, we would still be able to deduce if the state is mixed or pure by computing the trace of the central projector $P^{(\alpha)}$. So if

$$\frac{\operatorname{Tr} P^{(\alpha)}}{\dim \pi^\alpha} > 1, \tag{2.70}$$

then the associated state is mixed, or else it is pure. This trace can be computed just from the representation of $\mathcal{A}$ on the Hilbert space.

The emergence of a gauge symmetry and $\mathcal{A}'$ are among the remarkable insights from the GNS approach and the Tomita-Takesaki theory [17].

We will see that the twisted gauge symmetries in the conventional sense are transmuted to the role of $U(N_\alpha)$. Further, since only the elements of $\mathcal{A} \cap \mathcal{A}'$, which are contained in the center of $\mathcal{A}$, are observable, mixed states of the sort in Refs. [14,18] naturally emerge, eliminating the gauge anomalies.

III. CONFIGURATION SPACE OF ETHYLENE

Polyatomic molecules can be approximated by rigid shapes in three dimensions at energies much smaller than, say, the dissociation energy of the molecule. The success of molecular spectroscopy, which uses the quantum theory of molecular shapes, bears out the validity of this approximation. Molecular shapes possessing some symmetry [subgroups of the rotation group $SO(3)$] are of particular interest, not only because of the simplification that group theory offers, but also because a large number of interesting molecules possess some symmetry.

Let us briefly describe the configuration space of a molecular shape that has $H \subset SO(3)$ as its symmetry group [6]. A conveniently chosen configuration $\mathcal{C}_0$ will be denoted as its standard configuration. Then all its other configurations can be obtained from $\mathcal{C}_0$ by applying all rotations to it. It is easy to see that its configuration space $\mathcal{Q}$ obtained in this manner is

$$\mathcal{Q} = SO(3)/H. \tag{3.1}$$

It is multiply connected if H is discrete. Since ethylene, the molecule we focus on, has a discrete H, we assume henceforth that H is discrete. For concreteness, we think of $\mathcal{Q}$ as the set of *right* cosets of H in $SO(3)$.

A convenient way to think of $\mathcal{Q}$ is to recognize that the universal cover of $SO(3)$ is $SU(2)$, which allows one to write

$$\mathcal{Q} = SU(2)/H^*, \tag{3.2}$$

where H^* is the double cover of H. Since $SU(2)$ is simply connected, $\pi_1(\mathcal{Q}) = H^*$.

The universal cover $\bar{\mathcal{Q}}$ of $\mathcal{Q}$ is $SU(2)$.

The observables for this system are generated by two types of observables:

1. Functions on $\mathcal{Q}$.
2. Generators of translations on $\mathcal{Q}$ (i.e. generators of physical rotations), or more generally, the group algebra $\mathbb{C}SU(2)$ associated with physical rotations.

To construct the Hilbert space of wave functions for the molecule, it is convenient to start with $\bar{\mathcal{Q}} = SU(2)$ and functions on it. These are spanned by components of the rotation matrices $D^j_{\lambda\mu}$, with $j \in \mathbb{Z}^+/2$, and λ, $\mu \in \{-j, -j+1, \ldots, j-1, j\}$. The scalar product is

$$(D^{j'}_{\lambda'\mu'} | D^j_{\lambda\mu}) = \int_{s \in SU(2)} d\mu(s) \bar{D}^{j'}_{\lambda'\mu'}(s) D^j_{\lambda\mu}(s), \tag{3.3}$$

where $d\mu(s)$ is the invariant $SU(2)$ measure.

The group $\pi_1(\mathcal{Q})$ acts on $\bar{\mathcal{Q}}$ by *right* multiplication:

$$g \to gh^* \quad \text{for } g \in SU(2), \quad h^* \in H^*. \tag{3.4}$$

On the other hand, a physical rotation (see item 2 above) induced by $g \in SU(2)$ acts on the left:

$$(U(g) D^j_{\lambda\mu})(s) = D^j_{\lambda\mu}(gs). \tag{3.5}$$

Since left and right multiplications commute, we see that physical rotations (and more generally, all physical observables) commute with the action of H^*. *Thus, H^* is the gauge group for this system.*

Thus, molecules provide realistic examples of physical systems with discrete gauge groups.

In quantum theory, wave functions are thus functions on $SU(2)$ that transform by a fixed unitary irreducible representation Γ of H^*, different Γ describing different intrinsic states of the molecule. These are spanned by the matrix elements $D^j_{\lambda\mu}$, with the index μ now restricted to a subset of $\{-j\dots,j\}$. We will henceforth denote the restricted values of μ by m. On this basis, the action of H^* is

$$D^j_{\lambda m}(s) \to D^j_{\lambda m}(sh^*) = D^j_{\lambda m'}(s)\Gamma_{m'm}(h^*). \tag{3.6}$$

It is easily seen that functions on $\mathcal{Q}$ are generated by $\sum_m \bar{D}^j_{\lambda m} D^{j'}_{\nu m}$: they are invariant under the H^* action [Eq. (3.6)].

(The above paragraphs are only meant to indicate how wave functions and functions on Q are constructed in general. The unitary irreducible representation Γ may occur more than once for a fixed j, and that is not shown here. Also, the above presentation is a version with no gauge fixing. The ethylene case, including the problem of gauge fixing, is worked out in full detail below, so that such issues are covered there.)

The Hamiltonian for the system is proportional to the square of the angular momentum, or more realistically,

$$\mathcal{H} = \sum_{i=1}^{3} \frac{J_i^2}{2I_i}, \tag{3.7}$$

where I_i are the three principal moments of inertia and J_i are angular momentum operators which generate rotations on the *left* of g [cf. Eq. (3.5)]:

$$(e^{i\theta J_i} D^j_{\lambda m})(g) = D^j_{\lambda m}(e^{-i\theta\frac{\tau_i}{2}} g), \qquad \tau_i = \text{Pauli matrices.} \tag{3.8}$$

They hence commute with elements of H^*.

The Hamiltonian [Eq. (3.7)] is unbounded, and hence defined only on a dense domain in the Hilbert space. It is determined by the linear span of $D^j_{\lambda m}$, as we explicitly see below for the ethylene.

Our interest is in situations when H^* is non-Abelian. We will restrict our attention to the case of ethylene C_2H_4, which is a planar molecule with H^* as the binary dihedral group D_8^*:

$$D_8^* = \{\pm\mathbf{1}_2, \pm i\tau_i\colon i = 1, 2, 3\}. \tag{3.9}$$

The configuration space is $\mathcal{Q} = SU(2)/D_8^*$ with the non-Abelian fundamental group $\pi_1(\mathcal{Q}) = D_8^*$. The domain of the Hamiltonian is fixed to come from the two-dimensional representation of this group. (Here we do not consider the one-dimensional representations of H^*.)

This domain can be constructed by starting from the complex linear span in σ of the $SU(2)$ rotation matrices,

$$D^j_{\sigma\pm m}, \qquad \sigma \in \{-j, \dots, j\}, \qquad j \in \mathbb{Z}^+/2. \tag{3.10}$$

If $h \in D_8^*$, then h acts on these functions by

$$D^j_{\sigma m}(g) \to D^j_{\sigma m}(gh) = \sum_{m'\in\{m,-m\}} D^j_{\sigma m'}(g) D^j_{m'm}(h). \tag{3.11}$$

These are, for fixed j, σ, two-dimensional representations of D_8^* acting on the indices $\pm m$. They are all isomorphic to Eq. (3.9). For fixed j, there are $(2j+1)/2$ such representations. As explained earlier, physical rotations act on the left and commute with the action of D_8^*, and are hence gauge invariant.

In the Hamiltonian [Eq. (3.7)], we assume hereafter for simplicity that all I_i are equal to a common I. Then the ground-state wave functions are obtained from $D^{1/2}_{\sigma,\pm 1/2}$ after gauge fixing (see below).

A. The algebra $\mathcal{A}$

It consists of two parts:

(a) Continuous functions $C^0(\mathcal{Q})$ on $\mathcal{Q}$. They are generated by

$$\sum_{m'\in\{m,-m\}} \bar{D}^j_{\sigma m'} D^{j'}_{\sigma' m'}, \tag{3.12}$$

with the bar denoting complex conjugation.

As they are invariant under D_8^* (the two-dimensional matrices are arranged to transform by the same Γ for all j, σ), they are functions on $\mathcal{Q}$. Other functions are obtained by taking products of linear combinations of Eq. (3.12).

Note that the first m' can take on $(2j+1)/2$ values, while the second can take on $(2j'+1)/2$ values.

(b) The group algebra $\mathbb{C}SU(2)$.

The algebra $\mathcal{A}$ is generated by $C^0(\mathcal{Q})$ and $\mathbb{C}SU(2)$.

1. Gauge fixing

After gauge fixing, the domain of the Hamiltonian should come from functions of $\mathcal{Q}$. If global gauge fixation is possible, then there will exist a map $\varphi\colon \mathcal{Q} \to SU(2)$ such that if Π is the projection map $SU(2) \to \mathcal{Q} \simeq SU(2)/D_8^*$, then

$$\Pi \circ \varphi = \text{identity map on } \mathcal{Q}. \tag{3.13}$$

Then we can fix the gauge as follows: Restrict $D^j_{\sigma\lambda}$ to $\varphi(\mathcal{Q})$; then the domain would be spanned by $D^j_{\sigma\lambda}|_{\varphi(\mathcal{Q})}$. But for the case at hand, there is no such *smooth* global map φ. Instead, as explained in Ref. [14], we will cover $\mathcal{Q}$ by open sets $\mathcal{Q}_\alpha$ and find maps $\varphi_\alpha\colon \mathcal{Q}_\alpha \to SU(2)$ such that $\Pi \circ \varphi_\alpha = \mathrm{id}|_{\mathcal{Q}_\alpha}$, the identity map on $\mathcal{Q}_\alpha$. Then, on $\mathcal{Q}_\alpha \bigcap \mathcal{Q}_\beta$, we get transition functions $h_{\alpha\beta} \in D_8^*$: if $q \in \mathcal{Q}_\alpha \bigcap \mathcal{Q}_\beta$, then $\varphi_\beta(q) = h_{\beta\alpha}\varphi_\alpha(q)$.

Let us return to Eq. (3.12) and restrict $D^j_{\sigma,\pm m}$ to $\varphi_\alpha(\mathcal{Q}_\alpha)$. In this patch, we can mix $\pm m$ by an action of $h \in D_8^*$ as in Eq. (3.6). It changes the local section and mixes $\pm m$. Thus, there is a quantum internal multiplicity of 2 even though there is no such internal multiplicity indicated in $\mathcal{A}$ [5].

But this h *cannot* be globally defined, since, D_8^* being non-Abelian, it does not commute in general with $h_{\beta\alpha}$. So in general, $h_{\beta\alpha} h h_{\beta\alpha}^{-1} \neq h$, and h cannot be used to implement the D_8^* action in $\mathcal{Q}_\beta$.

Another way to say this is that D_8^* changes the domain.

Now the puzzle arises: what "symmetry" group, preserving the domain of $\mathcal{H}$ and commuting with it, mixes the indices m?

We approach the problem using a state and GNS construction.

In Ref. [5], while discussing quantization on configuration spaces with non-Abelian fundamental groups, the emergence at the quantum level of a multiplicity of states, all localized at the same point of the configuration space, has been discussed using an approach equivalent to, but not identical with the GNS one. That discussion adapted to ethylene reaches conclusions similar to the present one.

B. The GNS construction for C_2H_4

The ground-state wave functions have $j = 1/2$ when all the I_i's in Eq. (3.7) are equal. As said earlier, we will assume this condition.

Recall that an automorphism γ of $\mathcal{A}$ acts on any state ω via duality:

$$\omega(\gamma(a)) := \omega_\gamma(a), \quad \forall\ a \in \mathcal{A}. \tag{3.14}$$

In the present case, since the algebra is invariant under the action of the gauge group, it also acts trivially on ω. Its apparent lack of gauge invariance (if any) when written in terms of wave functions is misleading and should be ignored.

If $d\mu(g)$ is the invariant volume form on $SU(2)$ normalized to $8\pi^2$,

$$\int_{SU(2)} d\mu(g) = 8\pi^2, \tag{3.15}$$

then with the scalar product given by

$$\begin{aligned}(D^j_{\lambda\mu}|D^{j'}_{\lambda'\mu'}) &= \frac{1}{8\pi^2}\int d\mu(g)\bar{D}^j_{\lambda\mu}(g) D^{j'}_{\lambda'\mu'}(g)\\ &= \delta_{jj'}\delta_{\lambda\lambda'}\delta_{\mu\mu'},\end{aligned} \tag{3.16}$$

we see that

$$\omega_{++}(\mathbb{1}) = (D^{\frac{1}{2}}_{++}|D^{\frac{1}{2}}_{++}) = 1. \tag{3.17}$$

We can therefore start with the following rank-1 density matrix ρ_{++} of a ground state for our GNS construction:

$$\omega_{++}(\cdot) = \mathrm{Tr}\,\rho_{++}(\cdot), \tag{3.18}$$

$$\rho_{+\pm} = \left|\frac{1}{2}; +\pm\right)\left(\frac{1}{2}; +\pm\right|, \tag{3.19}$$

$$\left|\frac{1}{2}; +\pm\right) \equiv |D^{\frac{1}{2}}_{+\pm}). \tag{3.20}$$

Remark: The Hilbert space with the scalar product given by Eq. (3.16) is $\mathcal{H}_{SU(2)} \equiv L^2(SU(2); d\mu(g))$. We denote its kets and bras by $|\cdot)$ and $(\cdot|$.

The vectors and scalar product of the GNS Hilbert space $\mathcal{H}_{\mathrm{GNS}}$ are different. The definition of the scalar product in particular involves the state. We denote kets and bras of $\mathcal{H}_{\mathrm{GNS}}$ by $|\cdot\rangle$ and $\langle\cdot|$.

Thus, in this section, we are working with two Hilbert spaces $\mathcal{H}_{SU(2)}$ and $\mathcal{H}_{\mathrm{GNS}}$. Their corresponding "traces" are distinguished by subscripts on Tr.

The algebra $\mathcal{A}$ of observables is invariant under the action of the symmetry group $SU(2)$ acting on the right of g [cf. Eq. (3.11)]. Hence, for $a \in \mathcal{A}$,

$$\omega_{++}(a) = \mathrm{Tr}_{\mathcal{H}_{SU(2)}}\rho_{++}a = \mathrm{Tr}_{\mathcal{H}_{SU(2)}}\rho_{+-}a \equiv \omega_{+-}(a), \tag{3.21}$$

where ω_{+-} is the state defined by ρ_{+-}.

The states

$$\omega = \lambda\omega_{++} + (1-\lambda)\omega_{+-}, \qquad 0 \le \lambda \le 1 \tag{3.22}$$

are thus entirely equivalent to ω_{++} when restricted to $\mathcal{A}$. It is here that the remark of Sec. II D assumes significance. By enlarging the algebra $\mathcal{A}$ to $\bar{\mathcal{A}}$, which includes the commutant $\mathcal{A}'$, we can distinguish between the $+$ and the $-$ of the second index in $\omega_{+\pm}$.

We have

$$\begin{aligned}\omega(a) &= \lambda(1/2; ++|a|1/2; ++)\\ &\quad + (1-\lambda)(1/2; +-|a|1/2; +-),\end{aligned} \tag{3.23}$$

so that ω seems a *mixed* state invariant under the symmetry or gauge group $SU(2)$. It is represented by the density matrix

$$\begin{aligned}\rho &= \lambda|1/2; ++)(1/2; ++|\\ &\quad + (1-\lambda)|1/2; +-)(1/2; +-|.\end{aligned} \tag{3.24}$$

We can now proceed with the GNS construction using the state in Eq. (3.22). Its next step is the determination of the null space $\mathcal{N}$. If $n \in \mathcal{N}$, then

$$\mathrm{Tr}_{\mathcal{H}_{SU(2)}}\rho(n^* n) = 0 \tag{3.25}$$

or

$$n|1/2; +\pm) = 0. \tag{3.26}$$

Hence, if

$$\mathbb{P}_+ = |1/2; ++)(1/2; ++| + |1/2; +-)(1/2; +-| \tag{3.27}$$

is the projector to the subspace spanned by $|1/2; +\pm)$, then

$$n = n(\mathbb{1} - \mathbb{P}_+). \tag{3.28}$$

Thus, the full null space is

$$\mathcal{N} = \mathcal{A}(\mathbb{1} - \mathbb{P}_+). \tag{3.29}$$

Note that $\mathcal{N}$ is a left ideal, as it should be.

It follows that the component of $\mathbb{1} \in \mathcal{A}$ in $\mathcal{A}/\mathcal{N}$ is

$$[\mathbb{P}_+] = \mathbb{P}_+ + \mathcal{N}, \tag{3.30}$$

and the cyclic vector of GNS is

$$|[\mathbb{P}_+]\rangle. \tag{3.31}$$

1. Impurity from gauge invariance

We just saw from Eq. (3.31) that the cyclic vector or "ground state" in the GNS construction is $|[\mathbb{P}_+]\rangle$. The mean value of $a \in \mathcal{A}$ in this "ground state" is

$$\begin{aligned}\langle[\mathbb{P}_+]|a|[\mathbb{P}_+]\rangle &= \mathrm{Tr}_{\mathcal{H}_{SU(2)}}\,\rho\mathbb{P}_+ a\mathbb{P}_+ \\ &= \lambda(1/2;++|a|1/2;++) \\ &\quad + (1-\lambda)(1/2;+-|a|1/2;+-).\end{aligned} \tag{3.32}$$

Thus, the cyclic vector gives an *impure* state on $\mathcal{A}$ when we take into account the gauge invariance of $\mathcal{A}$.

This state is a prototype of the mixed states proposed in Ref. [14] to restore gauge symmetry. The projector P_+ is of rank 2. It suggests a two-fold multiplicity of state vectors localized at a point of the configuration space. This observation is confirmed by the analysis of Ref. [5] as well.

Remark: Although $\mathbb{P}_+ \in \mathcal{A}$, that is not the case for ρ_{++} and ρ_{+-} on the rhs of Eq. (3.32). This expression for precision should be understood as follows: We first replace $|1/2;+\pm)$ with sections of the H^* bundle. They will then not be smooth functions on $SU(2)/D_8^*$. But the corresponding $[\rho_{++}]$ and $[\rho_{+-}]$ generate vectors contained in $\mathcal{H}_{\mathrm{GNS}}$, which involves the completion in norm of $\mathcal{A}/\mathcal{N}|[\mathbb{1}]\rangle$. The state ω trivially extends to this completion. It is in this sense that Eq. (3.32) is to be understood. Note that since $\mathcal{A}$ commutes with gauge transformations, the above rhs is independent of the sections used to define $|1/2;+\pm)$. For the same reason, the use of functions on $SU(2)$ and not sections in $\rho_{+,\pm}$ does not lead to errors.

2. Entropic ambiguities

The representation of $\mathcal{A}$ on $\pi(\mathcal{A})|[\mathbb{P}_+]\rangle$ is reducible, each subspace

$$\mathcal{H}_m \equiv \mathcal{H}_m(\mathbb{1}) = \pi(\mathcal{A})|[|1/2;+m)(1/2;+m|]\rangle, \quad m = \pm \tag{3.33}$$

being invariant under $\pi(\mathcal{A})$. The GNS Hilbert space

$$\mathcal{H}_{\mathrm{GNS}} = \bigoplus_m \mathcal{H}_m \tag{3.34}$$

is an orthogonal direct sum. Further, the representations π of $\mathcal{A}$ on $\mathcal{H}_m$ are both isomorphic.

We note that there are no projectors in the algebra of observables $\mathcal{A}$ projecting to $\mathcal{H}_m$. So we cannot prepare a quantum state by observations of elements of $\mathcal{A}$. But P_+ is in $\mathcal{A}$, and we can find its rank, namely 2, from Eq. (2.70). We can thus tell using just $\mathcal{A}$ that the state it defines is mixed. For preparing states associated with $\mathcal{H}_m$, we must introduce new operators—that is, projectors onto $\mathcal{H}_m$, and thereby enlarge $\mathcal{A}$. We thereby introduce new degrees of freedom. Their meaning for ethylene is discussed in the following section: they are associated with the electronic degrees of freedom.

For these reasons, we can make another orthogonal direct sum decomposition

$$\mathcal{H}_{\mathrm{GNS}} = \bigoplus \mathcal{H}_m(u), \tag{3.35}$$

$$\mathcal{H}_m(u) = \pi(\mathcal{A})\sum_s u_{ms}|\xi_s(\mathbb{1})\rangle \equiv \pi(\mathcal{A})|\xi_m(u)\rangle, \tag{3.36}$$

$$\begin{gathered}\xi_+(\mathbb{1}) = \frac{1}{\sqrt{\lambda}}\rho_{++}, \qquad \xi_-(1) = \frac{1}{\sqrt{1-\lambda}}\rho_{+-}, \\ \langle\xi_m(\mathbb{1})|\xi_n(\mathbb{1})\rangle = \delta_{mn},\end{gathered} \tag{3.37}$$

with $u^\dagger u = 1$, where s is summed over $\pm$. Each $\mathcal{H}_m(u)$ is invariant under $\pi(\mathcal{A})$. Also,

$$\begin{aligned}\langle\xi_m(u)|\xi_n(u)\rangle &= \mathrm{Tr}_{\mathcal{H}_{SU(2)}}\,\rho\,\xi_m(u)^*\xi_n(u) \\ &= \langle\xi_m(\mathbb{1})|\xi_n(\mathbb{1})\rangle = \delta_{mn},\end{aligned} \tag{3.38}$$

as follows from Eq. (3.36).

Now

$$\omega(a) = \mathrm{Tr}_{\mathcal{H}_{\mathrm{GNS}}}\,\rho(\mathbb{1})a, \quad a \in \mathcal{A}, \tag{3.39}$$

where

$$\rho(\mathbb{1}) = \lambda_+(\mathbb{1})|\xi_+(\mathbb{1})\rangle\langle\xi_+(\mathbb{1})| + \lambda_-(\mathbb{1})|\xi_-(\mathbb{1})\rangle\langle\xi_-(\mathbb{1})|, \tag{3.40}$$

$$\lambda_+(\mathbb{1}) = \lambda, \qquad \lambda_-(\mathbb{1}) = 1 - \lambda. \tag{3.41}$$

Using the above results, we have also proved elsewhere [16] that

$$\langle[\mathbb{P}_+]|a|[\mathbb{P}_+]\rangle = \sum_m \lambda_m(u)\langle\xi_m(u)|a|\xi_m(u)\rangle, \tag{3.42}$$

$$\lambda_m(u) = \sum_n |u_{mn}|^2\lambda_n(\mathbb{1}), \tag{3.43}$$

and hence that the density matrix

$$\rho(u) = \sum_m \lambda_m(u)|\xi_m(u)\rangle\langle\xi_m(u)| := \sum_m \lambda_m(u)\rho_m(u) \tag{3.44}$$

for all u defines the same state on $\mathcal{A}$.

But in general,

$$\lambda_m(u) \neq \lambda_m(1). \tag{3.45}$$

We can write

$$\rho(u) = \sum_m \lambda_m(u)\rho_m(u), \qquad \mathrm{Tr}_{\mathcal{H}_{\mathrm{GNS}}}\, \rho_m(u) = 1, \tag{3.46}$$

where $\rho_m(u)$ are rank-1 density matrices. Hence, the entropy

$$S(\rho(u)) = -\sum_m \lambda_m(u) \log \lambda_m(u) \tag{3.47}$$

depends on u.

When u is changed to, say, vu, we get from Eq. (3.43)

$$\lambda_m(vu) = \sum_s |v_{ms}|^2 \lambda_s(u) = T_{rs}(v)\lambda_s(u). \tag{3.48}$$

Accordingly, the entropy is in general changed when u is changed.

In fact, it generally increases, as $T(v)$ is a stochastic map [16].

The $\rho(\mathbb{1})$ for $\lambda = 1/2$ [see Eq. (3.24)] in our example is an exception. It has $\lambda_s(\mathbb{1}) = 1/2$ for both s. It is the maximally disordered state where the Boltzmann formula for entropy applies. It is the fixed point of the stochastic map.

IV. DYNAMICS ON u: THE ELECTRON CLOUD

It is clearly interesting to see if we can put dynamics on u. If that can be done, the molecular entropy will undergo stochastic maps, tending to increase steadily in time. It will be constant only at the exceptional fixed points. Thus, we would have a version of Boltzmann's theorem that entropy in general keeps increasing.

We claim that such dynamics can be induced from that of the electronic cloud. The observations are based on the work of Balachandran and Vaidya [19].

We assume as usual that all I_i's in the Hamiltonian [Eq. (3.7)] are equal, and that the symmetry group D_8^* has the two-dimensional spinorial representation for the molecule.

For definiteness, we assume that the molecule is in the ground state. Then a full eigenstate of the Hamiltonian including the electronic part is

$$\Psi_r = \sum_m D^{\frac{1}{2}}_{rm} \chi^m(\cdots), \qquad r = \pm\frac{1}{2}, \tag{4.1}$$

where $\cdots$ denote the electronic variables.

The index m in χ^m denotes the component of total angular momentum of electrons along the "third axis" of the body-fixed frame of the molecule.

The normalization condition on Ψ_r shows that

$$\sum_m \mu_m = 1, \tag{4.2}$$

$$\mu_m = \int |\chi^m(\cdots)|^2, \tag{4.3}$$

where the integral is over the variables not shown.

If we now perform only molecular observations, we get the mixed state

$$\sum_{m=\pm} \mu_m \rho_{r,m}. \tag{4.4}$$

Comparing with Eq. (3.46), we see that μ_m plays the role of $\lambda_m(u)$.

Under a rotation v of the electrons by total angular momentum,

$$\chi^m(\cdots) \mapsto v_{mr}\chi^r(\cdots) \tag{4.5}$$

and

$$\mu_m \mapsto \mu_m(v) = |v_{mr}|^2 \mu_r. \tag{4.6}$$

This matches Eq. (3.48).

Thus, by dynamically rotating the electronic angular momentum by electric or magnetic fields, and then restricting observables to the molecular variables, we can steadily evolve the molecular entropy.

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[1] A. P. Balachandran, G. Marmo, N. Mukunda, J. S. Nilsson, E. C. G. Sudarshan, and F. Zaccaria, Phys. Rev. D **29**, 2919 (1984).

[2] A. P. Balachandran, G. Marmo, N. Mukunda, J. S. Nilsson, E. C. G. Sudarshan, and F. Zaccaria, Phys. Rev. D **29**, 2936 (1984).

[3] P. C. Nelson and A. Manohar, Phys. Rev. Lett. **50**, 943 (1983).

[4] A. P. Balachandran, G. Marmo, N. Mukunda, J. S. Nilsson, E. C. G. Sudarshan, and F. Zaccaria, Phys. Rev. Lett. **50**, 1553 (1983).

[5] A. P. Balachandran, G. Marmo, B. S. Skagerstam, and A. Stern, *Classical Topology and Quantum States* (World Scientific, Singapore, 1991).

[6] A. P. Balachandran, A. Simoni, and D. M. Witt, Int. J. Mod. Phys. A **07**, 2087 (1992).

[7] A. P. Balachandran, A. R. de Queiroz, and S. Vaidya (to be published).
[8] A. P. Balachandran and S. Vaidya, arXiv:1302.3406.
[9] A. P. Balachandran, G. Marmo, B. Skagerstan, and A. Stern, *Gauge Theories and Fiber Bundles: Applications to Particle Dynamics*, Lecture Notes in Physics Vol. 188 (Springer-Verlag, Berlin, 1983).
[10] J. L. Friedman and R. D. Sorkin, Phys. Rev. Lett. **44**, 1100 (1980).
[11] J. L. Friedman and R. D. Sorkin, Phys. Rev. Lett. **45**, 148 (1980).
[12] A. P. Balachandran and A. R. de Queiroz, J. High Energy Phys. 11 (2011) 126.
[13] A. P. Balachandran, A. R. de Queiroz, and S. Vaidya (to be published).
[14] A. P. Balachandran and A. R. Queiroz, Phys. Rev. D **85**, 025017 (2012).
[15] B. Schroer, arXiv:hep-th/9805093.
[16] A. P. Balachandran, A. R. de Queiroz, and S. Vaidya, arXiv:1212.1239.
[17] R. Haag, *Local Quantum Physics: Fields, Particles, Algebras*, Texts and Monographs in Physics (Springer-Verlag, Berlin, 1992).
[18] A. P. Balachandran, T. R. Govindarajan, and A. R. de Queiroz, Eur. Phys. J. Plus **127**, 118 (2012).
[19] A. P. Balachandran and S. Vaidya, Int. J. Mod. Phys. A **12**, 5325 (1997).