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Electrons as a nuclear environment within molecules: a quantitative assessment of their contribution to a classical-like molecular structure

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Abstract

Molecular structure is often considered as emerging from the decoherence effect of the environment. Electrons are part of the environment of the nuclei in a molecule. Here, we investigate their contribution to the classical-like geometrical relationships often observed between nuclei in molecular systems. Our numerical computations of reduced density matrix (RDM) elements are made from accurate all-particle wave functions. However, we found that, as in the Born-Oppenheimer picture, the electrons play an essential rôle in localizing nuclei in specific "equilibrium" geometries. Although the electronic environment alone cannot explain molecular symmetry-broken isomers, it can contribute to their dynamical stability by significantly reducing off-diagonal RDM elements.

Keywords:

Suggested running head: Decoherence within molecules

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1 Introduction

The usual approach for reconstructing or recognizing molecular structural elements from a wave function follow the observation of Claverie and Diner [1], that classical structures can be identified with nuclear configurations for which appropriately defined density functions have maxima. Within such a view, based on Born's probabilistic interpretation of the square modulus of the wave function, molecules do exhibit clear structural features as demonstrated by accurate calculation of their full i.e. "all-particle" wave functions, in the sense that inter-nuclei geometrical parameter distributions are peaked at definite values [2,3].

Decoherence effects by the environment [4] are often invoked to explain why molecule behave as near classical objects with structural features related to those maximal density configurations, that chemists can use without having usually to worry about any quantum mechanical interference or tunelling phenomena. The environment of a molecular system has undoubtly some decoherence effects and something to do with the localization of the system in a state with "quasi-classical" characteristics. But when we are thinking about molecules, it is hard to imagine a completely generic environment. How to formulate in mathematical expressions such a general i.e non specific environment? There have been proposals to consider the photon vacuum field as an ubiquitously present environment, responsible for the stability of isolated, chiral molecules [5]. However, it has been shown that the proposed mechanism was only valid at zero temperature [6]. In the early years of the development of decoherence ideas in connection with the molecular structure problem, Claverie and Jona-Lasinio [7,8] used external random noise to simulate localization in a double potential well (which is a typical toy model for the ammonia "umbrella" inversion or molecular chirality-breaking). However, the reaction field mechanism of these authors is a collective effect, hard to invoked for quasi-isolated, single molecules, as can be found in astrophysical conditions, where densities of one molecule per cubic centimeters or less, are observed. Davies argued that, for a collection of identical molecules (at least two), there exists metastable approximate eigenstates in the form of a tensor product of one and the same molecular state, which are both close to the gen-

uine eigenstates of the whole collection of molecules, and symmetry-broken with respect to the individual molecule symmetry [9]. However, it remains to justify why the whole system would be in such an approximate product state rather than in a true eigenstate. The spin-boson model can encompass a variety of environements, such as the electromagnetic radiation field, as long as they can be represented by a set of model harmonic oscillators within some simplifying hypotheses [10]. Hornberger and co-workers simulated the stabilization of chiral molecules upon collisions [11,12,13]. Recent and more realistic decoherence simulations demonstrate that different environment models have different decoherence properties that affect different degrees of freedom differently [14]. These realistic simulations are very interesting, because the systematic and accurate calculation of the decoherence times for a variety of molecular processes, in interaction with a series of "standard" environment models, could be useful for controlling decoherence in real systems and designing better quantum computers (using molecular qubits).

In the present work, we prefer to confine ourself to the sole molecular system: we are seeking the furthermost point, one can reach in resolving the molecular structure conundrum, without explicitly considering any specific kind of environment. By molecular structure, we understand the relative localization of the nuclei in the three dimensional space. However, a molecule consist of not only nuclei but also of electrons. So, it is appropriate to ask to which extent the electrons play a rôle in the localization of the nuclei by their continuous monitoring. The idea is that nuclei are constantly "measured" by electrons through their Coulomb interactions. So, electrons should impose a decoherence time scale on nuclei of $\tau_{decoherence} \approx \frac{\hbar}{<V_{Coulomb}^{e-n}>}$ expected to be much shorter than that of the nuclei dynamics. This agrees with Ref. [15], where the initial decoherence time due to electrons is found to be of the order of a few femtoseconds, whereas the time scale for nuclear motion is rather of the order of the nanoseconds. However, using only two electronic basis functions obtained as eigenfunctions of a clamped nuclei Hamiltonian, as in [15], is questionable. Time propagation of an initial pure state would lead to the ground state of the system, as in Monte-Carlo simulation, and such a state should be decomposed on a complete, infinite dimensional basis set of electronic states. The purpose of this work is to study the localization and decoherence effects of the electrons on

the nuclei, by using highly accurate all-particle wave functions.

The article is organized as follows: In the next section, we introduce the concept of 'pointer states', define what we mean by a "classical-like" molecular structure and present the notion of "purity" of the reduced density matrix (RDM), for the nuclei of a molecule, the electrons, considered as the environment of the latter, being traced out. Since, this electronic environment corresponds only to a finite set of degrees of freedom, we cannot expect superselection rules to emerge, but we are curious about what kind of conclusions can be drawn within this setup. This is investigated in the third section, before concluding in the last section.

2 Theoretical tools to quantify the classicality of molecular structure

Let us first define in a very pedestrian way, the basic theoretical tools, we will rely on in the rest of the paper.

2.1 Pointer states

When measuring a property of a quantum system, the needle of an (idealized) measuring device points to one of the possible outcome values. In a satisfactory theory of quantum measurement, an experimental setup, although macroscopic, should be amenable to a quantum treatment. Hence, the idea to associate a quantum state to every position of the needle. These states were termed "pointer state" by Zurek [16], and their apparent classical behaviour was assumed to be due to the decoherence effect of the environement.

At present, in decoherence theory, the concept of "pointer states" has been extended to a wider context, where there is not necessarily a bona fide experimental setup. The environment of a quantum system is assumed for all practical purposes, to break the unitary invariance of the quantum mechanical representation of the system, by selecting a special basis in which the "coherences" i.e. the non diagonal elements of the density matrix, decrease exponentially with time. The "pointer states" are defined as the pure states

belonging to the basis set selected by the environment, the latter constantly destructing their superposition.

There is no general theory to determine the pointer states of a quantum system in a given environment. For each microscopic environment modelling, one has to tackle the task of finding the proper pointer states [16,13]. However, in many cases, such as macroscopic objects which appear perfectly localized in space, the representation selected by the environment is the so-called "direct representation", the pointer states corresponding to Dirac distributions in configuration space.

2.2 Reduced density and transition operator matrices for nuclear degrees of freedom (DOFs)

Let $|\Psi\rangle$ be a molecular, normalized wave function in Dirac ket notation. The associated (pure state) density operator, $|\Psi\rangle\langle\Psi|$, will be denoted as $\hat{\rho}$. The representation selected by an environment being often the "direct representation", let us consider it first to express the density operator matrix. In the direct representation, denoting collectively by $\mathbf{r}$ the electronic DOFs coordinates and by $\mathbf{R}$ the nuclear ones, we have,

$$\begin{aligned}\hat{\rho} &= \int d\mathbf{r}\ d\mathbf{R}\ |\mathbf{r}\ \mathbf{R}\rangle\langle\mathbf{r}\ \mathbf{R}| \cdot |\Psi\rangle\langle\Psi| \cdot \int d\mathbf{r}'\ d\mathbf{R}'\ |\mathbf{r}'\ \mathbf{R}'\rangle\langle\mathbf{r}'\ \mathbf{R}'| \\ &= \int d\mathbf{r}\ d\mathbf{R}\ d\mathbf{r}'\ d\mathbf{R}'\ |\mathbf{r}\ \mathbf{R}\rangle\langle\mathbf{r}\ \mathbf{R}|\Psi\rangle\langle\Psi|\mathbf{r}'\ \mathbf{R}'\rangle\langle\mathbf{r}'\ \mathbf{R}'| \\ &= \int d\mathbf{r}\ d\mathbf{R}\ d\mathbf{r}'\ d\mathbf{R}'\ \Psi^*(\mathbf{r}',\mathbf{R}')\Psi(\mathbf{r},\mathbf{R})\ |\mathbf{r}\ \mathbf{R}\rangle\langle\mathbf{r}'\ \mathbf{R}'|. \qquad (1)\end{aligned}$$

To study the nuclear structure, we integrate out the electronic degrees of freedom that are considered as the environment for the nuclei. The resulting reduced density matrix operator for the nuclear motion is

$$
\begin{aligned}
\hat{\rho}_{\text{nuc}} &= \text{Tr}_{\text{el}}\ [\hat{\rho}] \\
&= \int d\mathbf{r}''\ \langle \mathbf{r}''|\Psi\rangle\langle\Psi|\mathbf{r}''\rangle \\
&= \int d\mathbf{r}''\ d\mathbf{r}\ d\mathbf{R}\ d\mathbf{r}'\ d\mathbf{R}'\ \Psi^*(\mathbf{r}',\mathbf{R}')\Psi(\mathbf{r},\mathbf{R})\ \langle \mathbf{r}''|\mathbf{r}\ \mathbf{R}\rangle\langle \mathbf{r}'\ \mathbf{R}'|\mathbf{r}''\rangle \\
&= \int d\mathbf{r}''\ d\mathbf{r}\ d\mathbf{R}\ d\mathbf{r}'\ d\mathbf{R}'\ \Psi^*(\mathbf{r}',\mathbf{R}')\Psi(\mathbf{r},\mathbf{R})\ \delta_{r''r'}\delta_{r''r}|\mathbf{R}\rangle\langle\mathbf{R}'| \\
&= \int d\mathbf{R}\ d\mathbf{R}' \left(\int d\mathbf{r}''\ \Psi^*(\mathbf{r}'',\mathbf{R}')\Psi(\mathbf{r}'',\mathbf{R})\right)|\mathbf{R}\rangle\langle\mathbf{R}'|, \qquad (2)
\end{aligned}
$$

so that,

$$
\rho_{\text{nuc}}(\mathbf{R},\mathbf{R}') := \langle\mathbf{R}|\hat{\rho}_{\text{nuc}}|\mathbf{R}'\rangle = \int d\mathbf{r}''\ \Psi^*(\mathbf{r}'',\mathbf{R}')\Psi(\mathbf{r}'',\mathbf{R}) \qquad (3)
$$

If the wave function assumes a BO form, $\Psi_{BO}(\mathbf{r},\mathbf{R}) = \Psi_e(\mathbf{r},\mathbf{R})\Psi_N(\mathbf{R})$, then Eq. (3) becomes

$$
\langle\mathbf{R}|\hat{\rho}_{\text{nuc}}|\mathbf{R}'\rangle = \left(\int d\mathbf{r}''\ \Psi_e^*(\mathbf{r}'',\mathbf{R}')\Psi_e(\mathbf{r}'',\mathbf{R})\right)\Psi_N^*(\mathbf{R}')\Psi_N(\mathbf{R})\ , \qquad (4)
$$

that is to say, the interference amplitude between pointer states $|\mathbf{R}\rangle$ and $|\mathbf{R}'\rangle$ for the nuclear system depends upon the overlap of the BO electronic functions, $\int d\mathbf{r}''\ \Psi_e^*(\mathbf{r}'',\mathbf{R}')\Psi_e(\mathbf{r}'',\mathbf{R})$. In the case of Refs. [15,22,23] an all-particle wave function is written in a tensor product basis as, $\Psi_{TPB}(\mathbf{r},\mathbf{R}) = \sum_{i,I}\lambda_{i,I}\Psi_e^i(\mathbf{r})\Psi_N^I(\mathbf{R})$, (all basis sets are taken orthonormal). Then Eq. (3) reads

$$
\begin{aligned}
\langle\mathbf{R}|\hat{\rho}_{\text{nuc}}|\mathbf{R}'\rangle &= \sum_{i,I,j,J}\lambda_{i,I}^*\lambda_{j,J}\left(\int d\mathbf{r}''\ \Psi_e^{*i}(\mathbf{r}'')\Psi_e^j(\mathbf{r}'')\right)\Psi_N^{*I}(\mathbf{R}')\Psi_N^J(\mathbf{R}) \\
&= \sum_{i,I,j,J}\lambda_{i,I}^*\lambda_{j,J}\delta_{i,j}\Psi_N^{*I}(\mathbf{R}')\Psi_N^J(\mathbf{R}) \\
&= \sum_{I,J}\left(\sum_i\lambda_{i,I}^*\lambda_{i,J}\right)\Psi_N^{*I}(\mathbf{R}')\Psi_N^J(\mathbf{R})\ . \qquad (5)
\end{aligned}
$$

This shows that all electronic functions contribute to the interference amplitude between pointer states $|\mathbf{R}\rangle$ and $|\mathbf{R}'\rangle$ through $\sum_i\lambda_{i,I}^*\lambda_{i,J}$, which is nothing but the reduced density matrix element in the $\left(\Psi_N^I\right)_I$ basis:

$$\langle \Psi_N^J | \hat{\rho}_{\rm nuc} | \Psi_N^I \rangle = \sum_i \lambda_{i,I}^* \lambda_{i,J}, \tag{6}$$

as can be seen by comparing Eq. (5) with the change of representation formula:

$$\langle \mathbf{R} | \hat{\rho}_{\rm nuc} | \mathbf{R}' \rangle = \sum_{I,J} \langle \mathbf{R} | \Psi_N^J \rangle \langle \Psi_N^J | \hat{\rho}_{\rm nuc} | \Psi_N^I \rangle \langle \Psi_N^I | \mathbf{R}' \rangle \ . \tag{7}$$

We note in passing, that, would the pointer state basis be a general one, such as $\mathbf{B}_{nuc} := \left(\Psi_N^I\right)_I$, instead of $(|\mathbf{R}\rangle)_{\mathbf{R}}$, the corresponding reduced density matrix elements could be easily derived owing to this transformation.

Remark 1: One can define reduced transition matrices (RTM) in a similar fashion. Let $|\Psi_1\rangle\langle\Psi_2|$ be the transition operator from molecular state Ψ_2 to Ψ_1, the reduced transition matrix elements in the direct representation are,

$$\langle \mathbf{R} | RTM_{nuc} | \mathbf{R}' \rangle = \int d\mathbf{r}'' \ \Psi_2^*(\mathbf{r}'', \mathbf{R}') \Psi_1(\mathbf{r}'', \mathbf{R}) \ . \tag{8}$$

When Ψ_1 and Ψ_2 are decomposed on a tensor product basis set, $\Psi_1(\mathbf{r}, \mathbf{R}) = \sum_{i,I} \lambda_{i,I}^1 \Psi_e^i(\mathbf{r}) \Psi_N^I(\mathbf{R})$ and $\Psi_2(\mathbf{r}, \mathbf{R}) = \sum_{i,I} \lambda_{i,I}^2 \Psi_e^i(\mathbf{r}) \Psi_N^I(\mathbf{R})$, one obtains,

$$\langle \mathbf{R} | RTM_{nuc} | \mathbf{R}' \rangle = \sum_{I,J} \left(\sum_i \lambda_{i,I}^{2\ *} \lambda_{j,J}^1 \right) \Psi_N^{*I}(\mathbf{R}') \Psi_N^J(\mathbf{R}) \ . \tag{9}$$

In the case of two BO wave functions, $\Psi_1(\mathbf{r}, \mathbf{R}) = \Psi_e^1(\mathbf{r}, \mathbf{R}) \Psi_N^1(\mathbf{R})$ and $\Psi_2(\mathbf{r}, \mathbf{R}) = \Psi_e^2(\mathbf{r}, \mathbf{R}) \Psi_N^2(\mathbf{R})$ one has more simply,

$$\langle \mathbf{R} | RTM_{nuc} | \mathbf{R}' \rangle = \left(\int d\mathbf{r}'' \ \Psi_e^{2\ *}(\mathbf{r}'', \mathbf{R}') \Psi_e^1(\mathbf{r}'', \mathbf{R}) \right) \Psi_N^{2\ *}(\mathbf{R}') \Psi_N^1(\mathbf{R}) \ . \tag{10}$$

Time dependence has only been implicit, so far. If Ψ_1 and Ψ_2, are stationary eigenstates of the total Hamiltonian associated to eigenvalues E_1 and E_2, the RTM will oscillate as $e^{-\frac{i(E_1 - E_2)\cdot t}{\hbar}}$, while the RDM of a stationary state will be time independent.

Remark 2: For a molecule in a general environment, the definition of the reduced density

matrix operator for the nuclear motion, $\hat{\rho}_{\text{nuc}}$, is formally identical. We only need to start from the total wave function of the molecule plus its environment, and to integrate out both the electronic and environmental DOFs.

2.3 Classical-like molecular structure

We will say that a property of a quantum system is "classical-like", to distinguish it from "truly quantum" or from "chaotic", if the outcomes of its measurement have a narrow distribution, compatible with what one would expect for a plausible experimental uncertainty distribution of a classical property measurement.

This implies two constraints on the reduced density operator of the system after tracing out the environment degrees-of-freedom: (i) In the "pointer state" basis representation where the RDM is diagonal, all the significant eigenvalues (which give the probabilities to obtain the corresponding eigenstate) must correspond to eigenstates which gives expectation values for the property falling within a narrow distribution (ii) Decoherence must rapidly lead to the decay of any superposition of pointer states (related to the environment monitoring) back to the mixture of (i), after a perturbation of the system such as the measurement of the property of interest (which would project the system to a pointer state associated to the property measuring device, so *a priori* to a superposition of environment-selected pointer states).

2.4 Purity

The less pointer states with a significant probability, the easier to fulfill condition (i). The limit case, where one pointer state has probability close to one, and therefore all the others have a probability close to zero, is the most favorable to deal with, because then one can assume that the environment will select this pointer state and one has just to verify that the property has a narrow distribution of possible measurement outcomes for that pointer state.

The "purity" of a RDM is a number which provides a sufficient condition to demonstrate that the RDM is dominated by a single state. The purity concept is widely used in quantum information theory [17]. It can be used as both an entanglement and a decoherence assessment tool [18]. It is defined for the nuclear motion reduced density operator as

$$P = Tr[\hat{\rho}^2_{\text{nuc}}] \ . \tag{11}$$

We easily see that P can take values between 1, when a pointer state has probability one and all the others zero, and $\frac{1}{N_{dim}}$, when all pointer states are equiprobable.

Note that P does not depend upon the basis set, so it can be evaluated even if the pointer state basis has not been determined. A value close to one implies that one eigenvalue of $\hat{\rho}_{\text{nuc}}$ dominates all the others. The associated eigenstate can be considered as the dominant pointer state.

In the BO approach, for example, the purity of $\hat{\rho}_{\text{nuc}}$ is exactly 1, since only the Ψ_N appearing in Eq. (4) is populated. Such a state, at least the vibrational ground state (omitting rotational and translational DOFs), is usually well-localized in the neighbourhood of the so-called equilibrium geometry of the system. So, a molecular structure is recovered in this sense. However, it is often pointed out that recovering molecular structure from the BO approach is not a great achievement, since it is put in from the start.

2.5 Environment classes defined by pointer states

We have seen that decoherence theory associate to a given environment a set of pointer states (defined up to unitary transformations within equiprobable subsets). Here we consider the inverse mapping. Assume that we have a set of orthonormal states, $\mathcal{S}$, of an isolated quantum system, we define the class, $\mathcal{E}$, of environments of this system such that $\mathcal{S}$ is a set of pointer states for the system in each of these environments. That is to say, the nuclear RDM, $\hat{\rho}_{\text{nuc}}$, after tracing out the environment DOFs as explained in Remark 2, in set $\mathcal{S}$ representation, has non diagonal element decaying exponentially with time.

In the following, we will extend this definition to a set, $\mathcal{S}$, of Dirac distribution and assume that its associated environment class, $\mathcal{E}$, is non empty.

3 Decoherence by the electronic environment

In this section, we consider a stationary eigenstate of the total system (electrons plus nuclei) Hamiltonian, and study the decoherence effect on nuclear motion of the electrons, the latter being considered as the environment of the former. As noted above, the density operator and consequently, the reduced density matrices of such an eigenstate are time independent. Therefore, they are not appropriate to explore the dynamics of the system or to determine isomer lifetimes.

We will assess the decoherence effect in two complementary ways. First, we will consider the electrons as the sole environment of the nuclei. In this context, the pointer states of interest for the molecular structure problem, are the eigenstates of $\hat{\rho}_{\text{nuc}}$. They can be readily obtained and analysed. Second, we will assume that the molecule is in an external environment that localize the nuclei in space, so that the pointer states of interest are now the Dirac distributions of the direct representation. We will calculate the contribution of the electronic environment to the suppression of interferences between these pointer states.

We will limit our study to H_2 isotopologues, as we want to deal with accurate all-particle wave functions.

3.1 Purity of $\hat{\rho}_{nuc}$ for H_2 isotopologues

In this section, we consider a translation-free system whose rotational DOFs have been separated out and give only an effective, J-dependent term in the potential for the internal coordinate. The nuclear configuration $\mathbf{R}$ appearing in $\hat{\rho}_{\text{nuc}}$ is specified by the internuclear distance only.

In Electron-Nucleus Full Configuration Interaction (EN-FCI) calculations [22,23] a basis set of electronic states, obtained at one and the same clamped nuclei configuration, is used to build direct product, electron-nucleus basis sets. In Ref. [22,23], the basis set was not complete, but uses typically tens of thousands of electronic states for H_2, so many more than in [15]. Computing the vibration-reduced density matrix for electronic degrees of freedom, or the electron-reduced density matrix for the vibrational degrees of freedom, we find that the approximate ($J = 0$)-ground state basis function bears a population of about 99% for H_2, while the largest coherence between the approximate ground state and excited states basis functions are of the order of a few percents. For the second excited state, the approximate first excited vibrational basis function bears a population of about 97% for H_2.

Let us focus now on a representation-free quantity: The purity of the RDM for the vibrational DOF, $\hat{\rho}_{\rm nuc}$, (identical to that for the electrons by duality), is reported in Tab.1 for selected, molecular eigenstates. The latter are primarily those previously published in Ref.[22], for which we are confident, that the relative differences in the purity numbers are reliable with respect to the exact results. The entries in italics correspond to *a priori* less accurate, approximate molecular states. (Note that the label "$^1\Sigma_g^+ 0 \rightarrow 1$" in Tab.VI of [22] was somewhat misleading, it was referring to the transition $X^1\Sigma_g^+ \rightarrow B^1\Sigma_u^+$ in the notation used here).

The first observation is that all purity numbers are close to, but not equal to one, so that all the corresponding molecular eigenstates are reasonably, but not perfectly pure. There are two clear tendencies. Firstly, following every row, we note that purity numbers increase. This is not surprising: it is related to the decrease of the De Broglie wave length with increasing mass of the system, and the concomitant increase in state localization, well-illustrated in Fig.3 of Ref.[23]. Secondly, across every column, purity tends to decrease for successive excited ro-vibrational states of a given approximate electronic state, and for successive approximate electronic states of a given approximate ro-vibrational state. For example, for H_2, the purity is found to be 0.983 for the lowest ro-vibrational states of the first singlet, approximate, electronic, excited state, $B^1\Sigma_u^+$ $\nu = 0,\ J = 0$ and $J = 1$, while it is 0.989 for states $X^1\Sigma_g^+$ $\nu = 0,\ J = 0$ and $J = 1$. In fact, there are

States	H_2	D_2	T_2
$X^1\Sigma_g^+$ $\nu=0,\ J=0$	0.988841	0.992048	0.993479
$X^1\Sigma_g^+$ $\nu=0,\ J=1$	0.988830	0.992044	0.993476
$X^1\Sigma_g^+$ $\nu=0,\ J=2$	0.988807	0.992036	0.993472
$X^1\Sigma_g^+$ $\nu=0,\ J=3$	0.988773	0.992024	0.993466
$X^1\Sigma_g^+$ $\nu=0,\ J=4$	0.988728	0.992009	0.993458
$X^1\Sigma_g^+$ $\nu=1,\ J=0$	0.966507	0.976131	0.980428
$X^1\Sigma_g^+$ $\nu=1,\ J=1$	0.966473	0.976120	0.980420
$X^1\Sigma_g^+$ $\nu=1,\ J=2$	0.966406	0.976097	0.980409
$X^1\Sigma_g^+$ $\nu=1,\ J=3$	0.966306	0.976062	0.980390
$X^1\Sigma_g^+$ $\nu=1,\ J=4$	0.966173	0.976016	0.980365
$X^1\Sigma_g^+$ $\nu=2,\ J=0$	*0.944993*	0.960590	0.967589
$X^1\Sigma_g^+$ $\nu=2,\ J=1$	*0.944935*	0.960571	0.967579
$X^1\Sigma_g^+$ $\nu=2,\ J=2$	*0.944822*	0.960535	0.967558
$X^1\Sigma_g^+$ $\nu=2,\ J=3$	*0.944655*	0.960480	0.967527
$X^1\Sigma_g^+$ $\nu=2,\ J=4$	*0.944440*	0.960408	0.967486
$B^1\Sigma_u^+$ $\nu=0,\ J=0$	0.983095	*0.987301*	*0.989288*
$B^1\Sigma_u^+$ $\nu=0,\ J=1$	0.983104	*0.987308*	*0.989119*

Table 1
Purity of $\hat{\rho}_{\rm nuc}$ for selected molecular eigenstates. The values italicized are those that we find less reliable, and that are not used to draw any conclusion in the main text. J is the total angular momentum quantum number, ν an approximate vibrational quantum number, and the first label of each row designates the approximate electronic state.

exceptions to this trend, for example, for D_2, the purity of $B^1\Sigma_u^+$ $\nu=0,\ J=1$ is slightly larger than that of $B^1\Sigma_u^+$ $\nu=0,\ J=0$. The same phenomenon occurs between states (not reported here) of increasing vibrational quantum numbers for fixed approximate electronic state and angular momentum quantum number. However, all the exceptions encountered so far, involve molecular eigenstates whose accuracy is probably not sufficient to draw definite conclusions, and may be artefacts of an incomplete eigenstate description.

The purity of our $\hat{\rho}_{\rm nuc}$ is quite different to what is found in the simple dynamical model, reduced to the first two electronic states of Ref.[15]. [1] The purity of the $\hat{\rho}_{\rm nuc}$ of low-lying molecular eigenstates is always found to be quite high, so that the outcome of nuclear

[1] It seems that there is a normalization issue in this work, because χ_0 and χ_1 should not be normalized to one, as implicitly assumed in the formula for P (after Eq. (14) of [15]).

position measurements will be distributed according to the module square of the most populated eigenstate of $\hat{\rho}_{\text{nuc}}$ with high probability. The larger the mass of the system, the larger the probability and the localization of the distribution. So, the pointer states for the electronic environment alone, that is to say, the eigenstates of $\hat{\rho}_{\text{nuc}}$, will tend to Dirac distributions only at the infinite mass limit. The $(J = 0)$-pointer states of the main isotopologue are depicted in Fig.1. There are quite similar in shape to the vibrational eigenstates one would obtain in the BO approach.

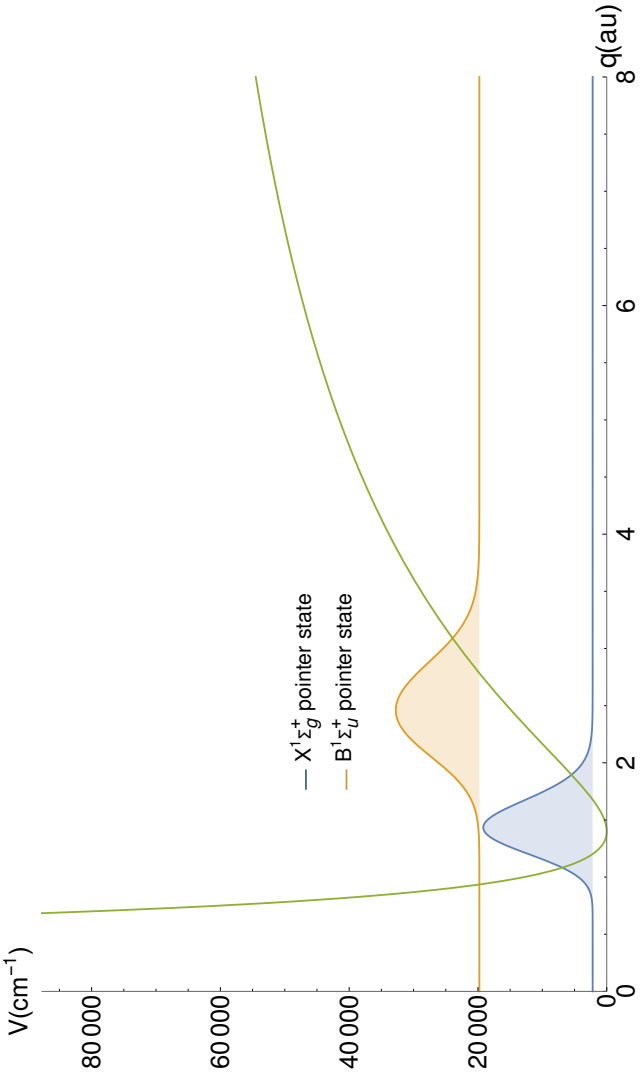

Figure 1. Main pointer state (in arbitrary units) of the two lowest "electronic" singlet states of H_2 as a function of the internuclear distance q (in Bohr). The Kratzer potential curve, V, (in cm^{-1}) of the vibrational Hamiltonian whose lowest eigenfunctions were used as the nuclear motion basis set, is also represented. Note that the positions of the pointer states with respect to the minimum of the potential curve, and with respect to each other, have been chosen ad hoc.

Such an analysis can be generalized to polyatomic molecules. One can obtain a nuclear motion RDM by tracing over electronic states. It is not always possible to separate out rotational motion from the other nuclear degrees of freedom [19]. However, one can leave out these very special systems for which a classical point of view is probably irrelevant.

So far, we have ignored nuclear spin DOFs, although they can prove important to take into account, when studying localization issues [24]. For dihydrogen, one can form two nuclear spin states, a singlet and a triplet, which by Pauli principle are only coupled to odd and even J-values, respectively. So, the $(J = 0)$-state is associated to the nuclear spin singlet ("parahydrogen") while the $(J = 1)$-state, which is higher by about 1.6 kJ/mol, is associated to the nuclear spin triplet ("orthohydrogen"). So, even at very low temperature, an ensemble density matrix instead of a pure state one, may be necessary to account for the three degenerate triplet components of orthohydrogen. However, in most common situations, the appropriate description of the three triplet components will be a the combination with equal weights of their three pure state density matrices. After integration over the electronic DOFs, the $\hat{\rho}_{\text{nuc}}$ so-obtained will also contain such a combination of pure state components. Even in this case, it is expected that by further reducing $\hat{\rho}_{\text{nuc}}$ over nuclear spin, the picture of a quasi pure vibrational state will still emerge, since the latter will be similar for all nuclear spin components.

In contrast, note that when the molecular state is degenerate because it is an electron-(rather than a nuclear)-spin multiplet, the ensemble, density matrix corresponding to the convex combination with equal weights of the degenerate components, will not necessarily produce such a sum after tracing over electronic DOFs, it may give a quasi-pure $\hat{\rho}_{\text{nuc}}$.

So, to conclude this section, the electronic environment is able to explain at least partially the classical-like internal structure of a molecule, since repeated measurements will find consistently, internuclear geometrical parameters within a reasonably narrow range of values. However, such an approach cannot explain the non observation of the superposition of parity-broken enantiomers, nor the breaking of molecular orientational symmetry, simply because a whole molecular system, electrons plus nuclei, does not break parity nor SO(3)-symmetry. An external environment has to be invoked to induce

superselection rules partitioning the Hilbert space of the system into different sectors.

3.2 Interference damping of rotational pointer states

So, we assume now that we have such an external environment. However, we do not specify it explicitly. We just consider that we know the set of pointer states, $\mathcal{S}$, for our system and that there exists at least one hypothetical environment leading to these pointer states, that is to say, the associated environment class, $\mathcal{E}$, is non-empty.

To evaluate the contribution of the electronic subsystem to nuclear position decoherence, we take the example of four-particle systems $\{m^{Z+}, m^{Z+}, e^-, e^-\}$ made of two electrons and two (possibly fictitious) particles of mass m and positive charge $+Z$. Real systems include $\mathrm{H}_2 = \{\mathrm{p}^+, \mathrm{p}^+, \mathrm{e}^-, \mathrm{e}^-\}$ and $\mathrm{Ps}_2 = \{\mathrm{e}^+, \mathrm{e}^+, \mathrm{e}^-, \mathrm{e}^-\}$. To quantify the decoherence effect of the electrons alone, we use the $\hat{\rho}_{\mathrm{nuc}}$ of the ground rovibronic eigenstate with zero total angular momentum of the isolated system, so that the molecular wave function is spherically symmetric, and only the relative angular difference between two pointer states matters. Then, fixing the internuclear distance between the two positively charged particles and a plane, $\mathcal{P}$, containing them, this allows us to restrict the set, $\mathcal{S}$ to the set of configuration-centered delta distributions corresponding to positively charged particle positions rotated around their center-of-mass within $\mathcal{P}$. They can be specified by a single angle parameter, α.

More precisely, we denote by $\pm\frac{\vec{R}_0}{2}$ the position vectors of the two positively charged particles with respect to their center of mass at some reference position, and by $|\xi_0\rangle := |\delta_{-\frac{\vec{R}_0}{2}}\rangle \otimes |\delta_{+\frac{\vec{R}_0}{2}}\rangle$ the pointer state corresponding to this reference nuclear configuration. Next, we define the pointer states $|\xi_\alpha\rangle := |\delta_{-\frac{\hat{O}_\alpha \vec{R}_0}{2}}\rangle \otimes |\delta_{+\frac{\hat{O}_\alpha \vec{R}_0}{2}}\rangle$ where $\hat{O}_\alpha$ is the rotation operator of angle α around the internuclear center in plane $\mathcal{P}$. We study orientational decoherence due to the electrons by calculating the damping of $\hat{\rho}_{\mathrm{nuc}}$ cross-terms between these pointer states as a function of their angular distance, see Fig.2.

The ground-state wave function of the four-particle systems was computed using an explicitly correlated Gaussian basis set and the QUANTEN computer program [25] (see

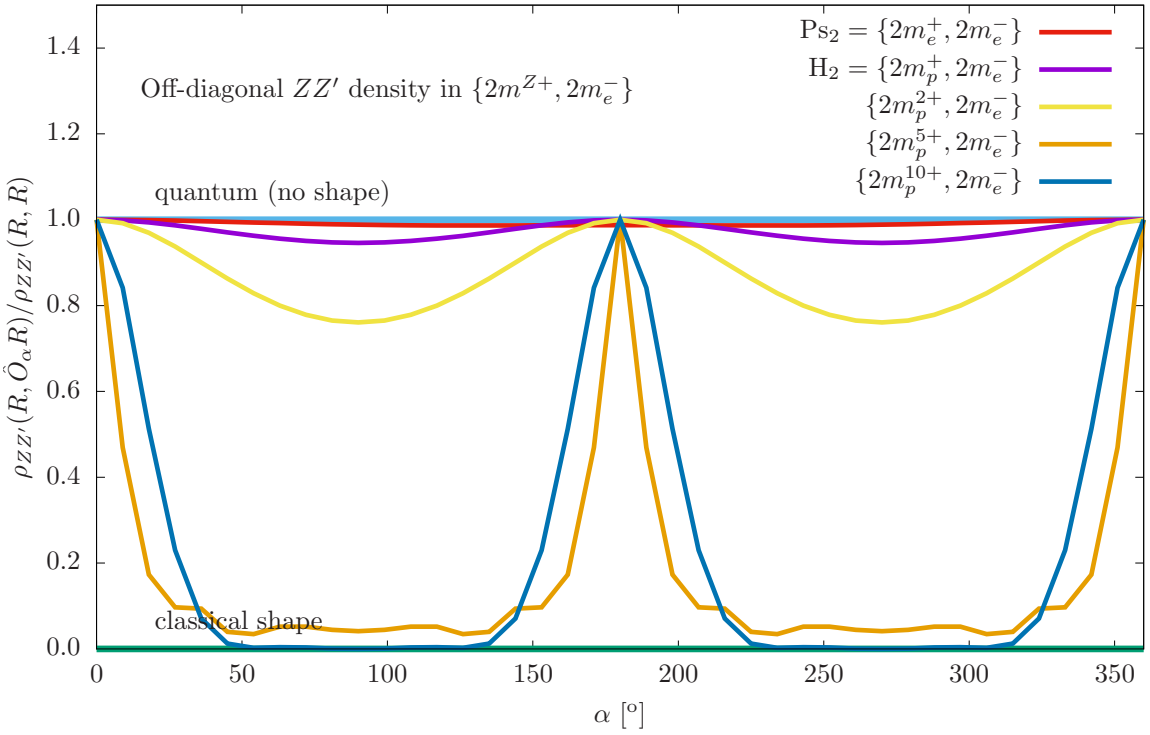

Figure 2. Measure for orientational localization in $\{2m^{Z+}, 2m_{\mathrm{el}}^-\}$-type four-particle systems including the H_2 and the Ps_2 molecules and a series of hypothetical systems. Increase of the mass and the electric charge leads to suppression of the interference terms among rotated structures. WARNING: this figure is a draft, there are convergence issues to be improved in a forthcoming version.

also Refs. [2,3] relevant for this work). The aim was to get accurate RDM matrix elements for the ground state of these system with zero total angular momentum ($N = 0$), natural parity ($p = +1$), and zero spin for the pair of electrons, and of positive particles. We managed to converge the corresponding energies up to the order of a 1 $\mathrm{mE_h}$ range and we believe that this is sufficient for the purpose of studying the RDM matrix elements as a function of particle masses and charges.

In Fig.2, we have displayed the off-diagonal elements of the nuclear reduced density matrix in the pointer state basis, $\langle \xi_0 | \rho_{\mathrm{nuc}} | \xi_\alpha \rangle$. For the sake of simplicity, we have fixed plane $\mathcal{P}$ to define the angle α, and the pointer states $|\xi_\alpha\rangle$. However, thank to the spherical symmetry, we may as well consider that the coordinates of the two positively charged particles are at antipodal points of a sphere centered around their midpoint. In practice, calculations were made by freezing two of the three Euler angles.

To understand when the interference terms get small and the localization of the nuclei

by the electrons efficient, it is convenient to return to the Born–Oppenheimer approximation, Eq. (4):

$$\langle \xi_0 | \rho_{\rm nuc}^{[\rm BO]} | \xi_\alpha \rangle =$$
$$\left[\int {\rm d}r'' \; \Psi_{\rm el}^*(r'', -\frac{\hat{O}_\alpha \vec{R}_0}{2}, +\frac{\hat{O}_\alpha \vec{R}_0}{2}) \Psi_{\rm el}(r'', -\frac{vecR_0}{2}, +\frac{\vec{R}_0}{2}) \right] \Psi_{\rm nuc}^*(-\frac{\hat{O}_\alpha \vec{R}_0}{2}, +\frac{\hat{O}_\alpha \vec{R}_0}{2}) \Psi_{\rm nuc}(-\frac{\vec{R}_0}{2}, +\frac{\vec{R}_0}{2}) \tag{12}$$

If the overlap of the electronic wave function corresponding to the rotated nuclear structures is small, then $\langle \xi_0 | \rho_{\rm nuc}^{[\rm BO]} | \xi_\alpha \rangle$ is also small. More generally, interferences are damped if the electronic cloud of the molecular wave function changes significantly between the rotated nuclear configurations.

The results of Fig.2, shows that for rotated H_2 structures the contribution of electrons to interference suppression is tiny, with only 5-10 % suppression at 90°. It is even less for the lighter Ps_2 system: the pair of positive (and symmetrically negative) particles retain full coherence with respect to orientational changes with a 1-2 % suppression only at 90°. .

To see a more significant effect, we have experimented with increasing the charge of the protons and computed hypothetical H_2-like ions with $\{{\rm p}^{Z+}, {\rm p}^{Z+}, {\rm e}^-, {\rm e}^-\}$. The increased nuclear charge makes the attractive potential energy and the electrons' monitoring effect stronger. For values $Z = 2, 5$ and 10 the interference between structures rotated by 90° is suppressed by 20 %, 90 %, and 99 % respectively.

Alternatively, we can play with the mass of the positive particles to increase their localization by decreasing their kinetic energy.

4 Conclusion

As concluding remarks, it is important to recall that the concept of the structure of a molecule with fixed values of geometrical parameters, makes no sense in traditional

quantum mechanics. The only thing that can make sense, is the structure attached to a given molecular state. Because, even for the simplest molecules, the average geometrical parameters can depend drastically upon the molecular state considered. For example, the equilibrium geometry of HeH^+, the first molecule to have appeared in the universe, is ≈ 1.43 bohr whereas in its first excited $^1\Sigma^+$ electronic state, it is ≈ 5.53.

One could argue that the concept of stable excited states makes no sense in QED, since, because of spontaneous emission, only the GS is potentially stable. However, invoking QED to focus on GS-only structural properties, is quite far-fetched, given the fruitfulness of the concept of excited state in molecular sciences.

In this work, we have attempted to better understand the contribution of the electronic subsystem to the internal nuclear structure of molecules, by starting out from accurate molecular (electrons plus nuclei) wave function, beyond the BO-approximation. "Pathological" systems for which it is difficult to assign a classical-like structure experimentally, are out-of-the scope of our study. We only consider molecules that appear classical-like to chemists.

We have used two complementary ways to assess the electronic influence to the apparent classical character of molecular structure. First, we have shown on symmetrical H_2-isotopologues that isolated, semi-rigid molecules in their low-lying states are dominated by a single pointer state providing nuclear geometrical parameter distributions with well defined peaks. Then, assuming that there exist at least one environment of a molecule giving a set of fully localized pointer states, we have quantified the suppression of the non-diagonal density matrix elements between these pointer states due to the electronic part of the wave function. We have shown that, both increasing the potential energy through a charge effect, or decreasing the kinetic energy through a mass effect, can facilitate localization by damping interference terms, hence limiting the dynamical instability due to the superpositions.

It is obvious from electrostatic considerations, that without electrons, the nuclei would not be bound. Their wave functions would be plane waves, and no structure would emerge. In this paper, we have been one step further, showing that, in general, electrons

help to project nuclei in an almost pure vibrational state, closely related to their apparent classical molecular structure.

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