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ORIGINAL PAPER

Enfolded conformational spaces: definition of the chemical quantum mechanical multiverse under Born–Oppenheimer approximation

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Abstract Starting from the Born–Oppenheimer approximation and the state density functions, which can be computed for any molecular structure, several conformational vector space enfoldments can be described, and configuring what can be described as well-defined molecular quantum mechanical universes. The collection of all imaginable molecular enfoldment universes, constitute the molecular multiverse. This study sets the basic definitions to describe such mathematical constructs.

Keywords Density functions · Born–Oppenheimer approximation ·
Vector space enfoldments · Conformational spaces ·
Conformational space enfoldment ·
Molecular quantum mechanical enfoldment universes ·
Chemical enfoldment Multiverse

1 Introduction

Since its publication in 1927, Born–Oppenheimer approximation [1] might be reckoned as a giant step influencing the development of quantum chemistry up to the present times. In the present study it will be tried to use the obvious vectorial molecular pattern, issuing from this old but fruitful approach, to produce a common mathematical framework encompassing all imaginable molecular frames.

One can start with this purpose in mind, first considering the structure of vector space enfoldment which has been recently described in some schematic way [2,3], using the large and varied set of mathematical properties Gaussian functions possess [4,5].

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On the other hand, it can be also indicated the interest of this laboratory about density functions (DF) and their properties has been shown along various recent publications [6–8], as DF are elements playing a fundamental role in quantum similarity; see for example [9–11]. Also, the subject of the present work can be related with studies performed about function extended vector spaces [12], which have been put forward when structuring a new way to plot molecular quantum mechanical functions, like DF [13].

Moreover, a recent publication was intended to critically analyze the current literature fuzzy descriptions of the concept of chemical space [14]. The present analysis corresponds to one of the possibilities in order to clarify this issue from the quantum mechanical point of view, by the way to setting up the new concept of quantum mechanical molecular universes, leading naturally to their aggregate: the chemical quantum mechanical multiverse.

In the present study, such possible definitions are based on the option to describe an enfoldment structure which might be developed, associated to any molecular DF obtained under the Born–Oppenheimer approximation [1]. The emerging picture can be promptly associated for each molecule to a mathematical construct, which can be considered as a molecular quantum mechanical universe by itself. Bearing in mind all the possible molecular structures, independently of their atomic composition or size, under such quantum mechanical approximation, then their individual DF enfoldment universes can be gathered together and contained into a superstructure which can be safely named the molecular multiverse.

To perform this task, first the obvious and trivial concept of conformational space will be described. Beyond this initial step, the quantum mechanical enfoldment of conformational spaces and their completeness will be set up. Hydrogen molecule will be used afterwards to illustrate the previous descriptions. Alternative enfoldment completeness options will be described next. Finally, the transformation of the molecular quantum mechanical enfoldment universes will close the present analysis.

2 Conformational spaces

In general, a molecular structure M within Born–Oppenheimer approximation [1] has to be associated to some set of nuclear coordinates: $\mathrm{N} = \{\mathbf{R}_I \,|I = 1, N\}$, which, for any nuclear conformation, outlines a vector belonging to some well-defined and real Euclidean $3N-$dimensional space: $\mathbf{R} = (\mathbf{R}_1; \mathbf{R}_2; \ldots \mathbf{R}_N) \in \mathrm{V}_{3N}$. Let me call such a space: conformational (or conformation) space.

3 Enfoldment in conformational spaces

Constructed within the aforementioned Born–Oppenheimer approximation, the quantum mechanical υth order density functions for some electronic state S, which can be associated to the molecular structure M, and attached in turn to the previously defined vector of nuclear coordinates, can be written formally as: $\rho_{SM}^{(\upsilon)}(\mathbf{r}\,|\mathbf{R})$. Now, besides the nuclear coordinate vector $\mathbf{R}$ one must take into account another vector $\mathbf{r}$, containing as elements the coordinates of the chosen number of electrons υ, attached to the DF of the molecular structure M. This might be written as: $\mathbf{r} = (\mathbf{r}_1; \mathbf{r}_2; \ldots \mathbf{r}_\upsilon) \in \mathrm{V}_{3\upsilon}$.

One can also consider each nuclear coordinate vector $\mathbf{R}$ as a possible molecular conformation point in the corresponding conformation space. Then, as a consequence, the density functions $\rho_{SM}^{(v)}(\mathbf{r}|\mathbf{R})$ can be seen as an enfoldment of the conformation space. From the theoretical point of view, at least this is so, because nothing opposes considering the fact to have a density function like $\rho_{SM}^{(v)}(\mathbf{r}|\mathbf{R})$, centered at each point of the nuclear coordinate space.

4 Completeness of the conformational space enfoldment

One can call an enfoldment *complete* if at every point of the background vector space, there is a function attached to it, as it is obviously the case in Gaussian enfoldments [2,3]. However, it must be taken into account that not all the points contained within conformation space can be enfolded with a proper DF, but some of them might be lacking of a properly defined DF; due to the possible infinity divergences of the point-like charge Coulomb nuclear repulsion model.

In order to have the enfoldment complete some points can be associated to a zero function, for instance. Such a DF enfoldment complement can be readily defined by means of: $\forall \mathbf{r}; \mathbf{R} : \Theta(\mathbf{r}|\mathbf{R}) = 0$.

When gathering information on conformation space points, some of these might be associated to collapsed nuclear coordinates, where at least: $\exists I, J : \mathbf{R}_I = \mathbf{R}_J$, like the obvious point: $\mathbf{R} = \mathbf{0}$. Provisionally, this kind of points can be collected into a set: R_0, say.

Therefore, considering all that has been said up to now, DF of any order can be undoubtedly seen as space enfoldments of the nuclear coordinate space of every molecular structure. Then, for completeness sake, one can define the enfoldment associated to a given DF, connected to a pair of conditions, in the following way:

$$\begin{aligned} &(a) \quad \forall \mathbf{R} \notin \mathrm{R}_0 \wedge \mathbf{r} \in \mathrm{V}_{3v} \rightarrow \exists \rho_{SM}^{(v)}(\mathbf{r}|\mathbf{R}) \\ &(b) \quad \forall \mathbf{R}_0 \in \mathrm{R}_0 \wedge \mathbf{r} \in \mathrm{V}_{3v} \rightarrow \exists I, J : \mathbf{R}_I = \mathbf{R}_J \rightarrow \exists \Theta(\mathbf{r}|\mathbf{R}_0) = 0 \end{aligned}$$

The two above described conditions become sufficient to define any complete DF enfoldment in conformation space. According to the association of a conformation space point to the condition (a) or (b) one can name respectively such points as *proper* or *collapsed* conformational space points.

The conformational space enfoldment will certainly present regions where the points belong to the collapsed point set: R_0. These collapsed conformation space points will appear practically as void, due to the presence of the zero function as the collapsed enfoldment element according to the completion condition (b), and they will be surrounded by proper enfoldment regions of conformation space.

5 Hydrogen molecule: schematic enfoldment example

In diatomic molecules the conformation space can be considered in practice as monodimensional, but the conformation points might be written as bidimensional vectors:$\langle D| = (-R; +R)$ which can be supposedly generated by a unique parameter R in such a way that the only collapsed point is located at: $R = 0$.

In a highly schematic case, the hydrogen molecule wave function might be defined with just two normalized 1s GTO functions $\{\gamma_a; \gamma_b\}$, centered at the hydrogen atoms, located in turn at the two parameter values conformational point: $\langle D|$. The ground state schematic MO, which at the same time coincides with the ground state wave function, can be written as:

$$|\psi\rangle = N\left(\gamma_a + \gamma_b\right)$$

where N is a normalization factor, and the subscripts are used to indicate the centering of each GTO in one of the coordinates of $\langle D|$, and thus the corresponding first order DF will have the following form:

$$\begin{aligned}\rho = |\psi\rangle\langle\psi| &= \nu N^2\left(|\gamma_a\rangle\langle\gamma_a| + |\gamma_b\rangle\langle\gamma_b| + 2\,|\gamma_a\rangle\langle\gamma_b|\right)\\ &= \nu N^2\left(\rho_{aa} + \rho_{bb} + 2\rho_{ab}\right)\end{aligned}$$

where ν corresponds to the number of electrons considered filling the ground state MO. Now, in order to define the density components, for example, one can construct the functions:

$$\rho_{ab} = |\gamma_a\rangle\langle\gamma_b| = n^2 \exp\left(-\alpha\left(|\mathbf{r} - \mathbf{R}_a|^2 + |\mathbf{r} - \mathbf{R}_b|^2\right)\right)$$

with n as the minimal basis set GTO normalization factor. In this manner a similar structure can be straightforwardly obtained for the other two monocentric terms, and also it can be used the following convention:

$$\mathbf{R}_a = (0; 0; +R) \wedge \mathbf{R}_b = (0; 0; -R)\,.$$

In the hydrogen molecule case, centered into a unique possible collapsed point, instead of a zero function the enfolding can be also safely associated to one GTO centered at the origin. So, as an alternative of the enfoldment zero function at the collapsed point, which has been previously defined, one can construct it with a collapsed DF, which might be written in turn within the chosen molecular hydrogen schematic framework as:

$$\rho_0\left(\mathbf{r}\,|\mathbf{0}\right) = \nu n^2 \exp\left(-\beta\,|\mathbf{r}|^2\right),$$

where now β is an appropriate exponent and n the adequate associated GTO normalization factor.

6 Alternative enfoldment of collapsed points in conformational space

Constructing the DF for collapsed points in a similar way, as it has been done in the hydrogen case, then the enfoldment, associated to the set R_0 of a given molecular structure, will not have to be compulsively the zero function, but can be a set of collapsed atom DF if possible. In one way or another, though, the conformational space enfoldment can be thus completed for molecular structures of reasonable size, but unlikely for large molecular structures.

From the hydrogen molecule schematic example, one can easily consider that an alternative to the collapsed points can be an appropriate DF, where the atoms, located at the same collapsed point coordinates, are transformed into a new unique atom with the characteristic nature, resulting from the addition of nuclear charges and electron number respectively. Thus, the former enfoldment completeness point (b) can be written in the following alternative way:

$$(b') \quad \forall \mathbf{R}_c \in \mathrm{R}_0 \wedge \mathbf{r} \in \mathrm{V}_{3v} \rightarrow \exists I, \quad J : \mathbf{R}_I = \mathbf{R}_J \in \mathbf{R}_c \rightarrow \exists \rho_c \left(\mathbf{r} \left| \mathbf{R}_c \right. \right),$$

where now $\rho_c \left(\mathbf{r} \left| \mathbf{R}_c \right. \right)$ corresponds to a collapsed DF centered at the collapsed conformational point: $\mathbf{R}_c$.

7 The enfoldment at the neighborhood of a conformational space point

Whenever the DF of any order is well defined at some proper conformation space point, in its neighborhood there can be easily described the DF behavior [15], as a consequence of the analytical way to express the holographic theorem on electronic density [16].

8 The result of quantum mechanical expectation value over an enfoldment

Any DF enfoldment can be submitted to transformations, which result into some augmented conformation vector space or another molecular enfoldment of conformational space.

Considering an appropriate Hermitian operator: $\Omega \left(\mathbf{r}_\omega \right) \wedge \mathbf{r}_\omega \in \mathrm{V}_{3\nu_\omega}$, say, where:$\mathbf{r}_\omega$ is the electron coordinate vector associated to the operator, which acting over the enfoldment DF provides an expectation value:

$$\left\langle \Omega \left(\mathbf{r}_\omega \right) \rho_{SM}^{(v)} \left(\mathbf{r} \left| \mathbf{R} \right. \right) \right\rangle = \int_{D_1} \Omega \left(\mathbf{r}_\omega \right) \rho_{SM}^{(v)} \left(\mathbf{r} \left| \mathbf{R} \right. \right) d\mathbf{r}_\omega = \omega_{SM} \left(\mathbf{r}' \left| \mathbf{R} \right. \right),$$

with the remnant electronic vector, after the expectation value integration, defined as:

$$\mathbf{r}' \in \mathrm{V}_{3\nu'},$$

whenever: $\nu' = \nu - v_\omega$.

Then, every time $v' = 0$, this leads to some vector $\mathbf{r}'$, which becomes void under the considered operator action. Therefore the enfoldment might transform into a conformational space just with a scalar extension or a higher dimension tensor depending of the nature of the operator, whose vectors can be written in the operator scalar case as:

$$\mathbf{W} = (\mathbf{R}, \omega_{SM}) \in \mathrm{V}_{3N+1};$$

or alternatively in case that $v' \neq 0$, transforming into another enfoldment, where the enfoldment function will be associated to the expectation value function $\omega_{SM}\left(\mathbf{r}'\,|\mathbf{R}\right)$. That is: the part (a) of the transformed enfoldment can be written now as:

$$(a) \quad \forall \mathbf{R} \notin \mathrm{R}_0 \wedge \mathbf{r}' \in \mathrm{V}_{3v'} \rightarrow \exists \omega_{SM}\left(\mathbf{r}'\,|\mathbf{R}\right).$$

9 Conclusions

Given a molecular structure quantum mechanically defined under Born–Oppenheimer approximation, a large enfoldment set of the associated conformational space can be defined simply using the generated state DF of the appropriate order, provided in turn by the considered electron number.

Furthermore, Hermitian operators transform every conformational space enfoldment set into another enfoldment or into an extended dimension conformational space, where the extra dimensions correspond to the scalar expectation value characteristics.

In principle, for every molecule a quantum mechanical enfoldment universe of electronic states over the vector space of conformational arrangements can be built up in the way explained in the present work.

The set of all possible molecular structures can be seen as constituting a quantum mechanical multiverse made of particular enfolded molecular conformational spaces.

9.1 Final remark

The naming of any molecular quantum mechanical DF enfoldment as a *molecular universe*, and the gathering of all the possible molecular enfoldment universes as a *molecular multiverse*, has to be considered fairly provisional. The author will not discuss any better semantic proposals coming from other authors about these names, which might be given to the same or slightly amended or further refined in deep mathematical elements as these described here.

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