

## A mathematical definition of molecular structure – open problem

P. Cassam-Chenaï

*Laboratoire d'Étude Théorique des Milieux Extrêmes, École Normale Supérieure, 24 rue Lhomond,  
75231 Paris Cedex 05, France*

A conjecture is proposed whose interest lies in the fact that, if false, it tells us what a molecule is not, if true, it is the basis for a rigorous definition of molecular structure in quantum mechanics.

A mathematical definition of a molecule, based on theorems by Weyl and Hunzinger–Van Winter–Zhislin, has been given by Löwdin [4] in the context of non-relativistic quantum mechanics: a molecule is a coulombic system of electrons and nuclei whose Hamiltonian with the center of mass translational degrees of freedom removed, has at least a bound state. (A comprehensive discussion on how to remove the center of mass translational degrees of freedom has been given by Fröman [1].) As noted by various authors [5], such a definition can only correspond bi-uniquely to a molecular formula and not to a specific isomer when several occur. So, following Löwdin's line of thought, one cannot expect to associate the notion of a single molecular structure to a molecule. However, if one seeks for a mathematical definition of molecular structure, it is natural to first look for it in the translationless, normalized wave function of a bound state of a Löwdin molecule,  $\Psi$  (since “everything is in the wave function”<sup>1</sup>). The quantity

$$\Psi^*((r_i)_i, (R_k)_k) \Psi((r_i)_i, (R_k)_k),$$

where the  $r_i$  (respectively,  $R_k$ ) are the electronic (respectively, nuclear) variables, has the physical meaning of the probability of finding the electrons at positions  $(r_i)_i$  and nuclei at positions  $(R_k)_k$ , and is in principle measurable (even if it is not the case in practice). Setting

$$\mathbf{r} = (r_i)_i, \quad \mathbf{R} = (R_k)_k, \quad d\mathbf{r} = \prod_i dr_i, \quad (1)$$

<sup>1</sup> Common saying in quantum mechanics.

then

$$P(\mathbf{R}) \equiv \int \Psi^*(\mathbf{r}, \mathbf{R})\Psi(\mathbf{r}, \mathbf{R}) \, d\mathbf{r} \quad (2)$$

is the probability of finding the nuclei in the configuration defined by  $(R_k)_k$ .

Let us first assume that  $\Psi$  is non-degenerate (thus, in particular, invariant within a phase factor under global rotation of the system  $\rho$ , i.e., it is an eigenfunction of the angular momentum operator  $J^2$  associated to the eigenvalue 0).

$$\Psi(\rho.\mathbf{r}, \rho.\mathbf{R}) = D(\rho)\Psi(\mathbf{r}, \mathbf{R}) = \exp(i\theta)\Psi(\mathbf{r}, \mathbf{R}), \quad (3)$$

where  $\rho$  denotes the action of the rotation on both the electrons and nuclei variables, and  $D(\rho)$ , the action on the wave function. It follows that  $P(\rho.\mathbf{R}) = P(\mathbf{R})$  for all global rotation  $\rho$ , therefore we can define a function, also denoted by  $P$ , of the set of all rotationally equivalent nuclear configurations,  $\dot{\mathbf{R}} \equiv \{\rho.\mathbf{R}\}_\rho$ , by

$$P(\dot{\mathbf{R}}) = P(\mathbf{R}), \quad \mathbf{R} \in \dot{\mathbf{R}}. \quad (4)$$

Then, it is tempting to associate a molecular structure to each local maximum of  $P(\dot{\mathbf{R}})$  corresponding to permutation–inversion symmetry [3] non-equivalent nuclear configurations. (Note that  $P(\mathbf{R})$  being positive, non constant, and vanishing at infinity,  $P(\dot{\mathbf{R}})$  has at least one maximum.) However, such a definition would not be satisfactory because there might be accretions of maxima of vibrational origin in certain regions which we would like to assign to one and the same isomer. Moreover, this does not give us any information about the mean lifetime of a given, such defined isomer. So, let us consider another quantity that is invariant under global rotation and, in principle, derivable from experiment (since  $\Psi^*(\mathbf{r}, \mathbf{R})\Psi(\mathbf{r}, \mathbf{R})$  is):

$$V(\mathbf{R}) \equiv \frac{\int \Psi^*(\mathbf{r}, \mathbf{R})V(\mathbf{r}, \mathbf{R})\Psi(\mathbf{r}, \mathbf{R}) \, d\mathbf{r}}{\int \Psi^*(\mathbf{r}, \mathbf{R})\Psi(\mathbf{r}, \mathbf{R}) \, d\mathbf{r}}, \quad (5)$$

where  $V(\mathbf{r}, \mathbf{R})$  is the Coulomb potential<sup>2</sup> of the system. As above, we define a function of  $\dot{\mathbf{R}}$ , also denoted by  $V$ , by

$$V(\dot{\mathbf{R}}) = V(\mathbf{R}), \quad \mathbf{R} \in \dot{\mathbf{R}}. \quad (6)$$

This is nothing but a generalisation of the Born–Oppenheimer potential energy surface: if  $\Psi(\mathbf{r}, \mathbf{R})$  can be written as a product  $\Phi_e(\mathbf{r}, \dot{\mathbf{R}})\Phi_n(\mathbf{R})$ , with  $\Phi_e$  normalized as a function of  $\mathbf{r}$  for all  $\dot{\mathbf{R}}$ , then

$$V(\dot{\mathbf{R}}) = \int \Phi_e^*(\mathbf{r}, \dot{\mathbf{R}})V(\mathbf{r}, \mathbf{R})\Phi_e(\mathbf{r}, \dot{\mathbf{R}}) \, d\mathbf{r}, \quad \mathbf{R} \in \dot{\mathbf{R}}. \quad (7)$$

So, defining a molecular structure of a Löwdin molecule to be a local minimum of  $V$  as a function of  $\dot{\mathbf{R}}$  corresponding to permutation–inversion symmetry non-equivalent nuclear configurations, we expect that the accreted maxima of  $P$  due to vibrational

<sup>2</sup> A proof of the fact that the Schrödinger Hamiltonian operator of a system composed of a finite number of particles interacting through a Coulomb potential is essentially self-adjoint, has been given in [2].

nodes of the wave function, will all fall in the basin of this minimum. More precisely, we would like to propose:

**Proposition 1.** For each maximum  $P(\dot{\mathbf{R}}_0)$  of the function  $P$  associated to a bound state of a Löwdin molecule by equations (2) and (4) there exists a neighbourhood  $N$  of  $\dot{\mathbf{R}}_0$  such that:

- (i) the function  $V$  defined by equation (6) has a minimum in  $N$ ;
- (ii) the restriction  $V|_N$  of  $V$  to  $N$  is convex.

The largest such neighbourhood,  $N_0$ , is called an “isomer” of the molecule, the nuclear configuration corresponding to the minimum of  $V|_{N_0}$  is the “molecular structure” of the isomer.

As far as we are aware, the validity of proposition 1 is an open problem and offer it to the readers to prove or disprove.

In the case of degeneracy, the above definitions of an isomer and its molecular structure can be generalised by considering the mixed state with equal weight of a set of orthonormal degenerate components,  $(\Psi_k)_k$ . Let us consider for instance a state with a non-zero angular momentum quantum number  $J$ , then

$$P(\mathbf{R}) \equiv \frac{1}{2J+1} \sum_{k=-J}^{+J} \int \Psi_k^*(\mathbf{r}, \mathbf{R}) \Psi_k(\mathbf{r}, \mathbf{R}) \, d\mathbf{r}, \quad (8)$$

$$V(\mathbf{R}) \equiv \frac{\sum_{k=-J}^{+J} \int \Psi_k^*(\mathbf{r}, \mathbf{R}) V(\mathbf{r}, \mathbf{R}) \Psi_k(\mathbf{r}, \mathbf{R}) \, d\mathbf{r}}{\sum_{k=-J}^{+J} \int \Psi_k^*(\mathbf{r}, \mathbf{R}) \Psi_k(\mathbf{r}, \mathbf{R}) \, d\mathbf{r}} \quad (9)$$

are rotationally invariant and define according to equations (4) and (6), respectively, the suitable functions of  $\dot{\mathbf{R}}$  for a generalised proposition 1.

As concluding remarks, we note that our definitions are relative to a given molecular bound state but do not imply a Born–Oppenheimer approach, and that assessing proposition 1 is more than a frivolous mind-game, because if it can be proved the function  $V(\dot{\mathbf{R}})|_{N_0}$  can be used to predict theoretically the mean lifetime of an observed or yet to be observed isomer, for instance, by comparing the values at the minimum and at the border of  $N_0$ .

## References

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