

Comment

Molecular structure and Bader's theory

José R. Mohallem

Laboratório de Átomos e Moléculas Especiais, Departamento de Física, ICEx, Universidade Federal de Minas Gerais, CP 702, 30123-970 Belo Horizonte, MG, Brazil

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Abstract. It is shown that a supposed catastrophe of Bader's theory of atoms in molecules, suggested by Cassam-chenaï and Jayatilaka [*Theor Chem Acc* (2001) 105: 213] is merely a consequence of the approximate character of the adiabatic Born–Oppenheimer theory of molecular structure, and that nonadiabatic approaches could be in accordance with Bader's ideas.

Key words: Atoms in molecules – Zero flux partitioning – Molecular structure – Adiabatic approximation – Nonadiabatic approximation

The theory of atoms in molecules (AIM), based on the topological properties of electronic densities, developed by Bader and coworkers [1, 2], is a modern tool of analysis of electronic structure of molecules. In essence, it states that the one-electron density, ρ , of a molecule can be partitioned into atomic contributions delimited by surfaces of zero flux of $\nabla\rho$. Many applications confirm the usefulness of this theory for a variety of problems. Although there are many AIM theories, here AIM will be taken to mean Bader's theory.

Cassam-chenaï and Jayatilaka recently claimed, in this journal [3], to have found some fundamental problems with AIM theory. Most of them seem to concern ambiguities that could be accounted for by appropriate restrictions in the formal structure of the theory. Some have been analyzed by Bader himself in a recent article [4]. But a particular criticism in Ref. [3], namely that concerning excited vibrational levels of molecules, remains unanswered and seems quite significant, since it calls into question the applicability of the theory to these states. The purpose of this article is to show that the

authors of Ref. [3] are wrong in this particular point, and that a proper view of the problem is not in disagreement with AIM theory.

Summarizing the criticism, the authors of Ref. [3] assume that a state, n , of a molecule can be put exactly, or to a good approximation, in the common product form,

$$\Psi_n(\vec{r}, \vec{R}) = \phi_n(\vec{r}; \vec{R})\chi_n(\vec{R}) \quad (1)$$

where ϕ_n is the electronic wavefunction that depends dynamically on the electronic coordinates, \vec{r} , and parametrically on the nuclear coordinates, \vec{R} , and χ_n is the nuclear (ro) vibrational wavefunction. In this case, the density is the product

$$\rho = \rho_{\text{el}}\rho_{\text{nuc}} \quad (2)$$

The existence of a node in an excited nuclear function at some configuration \vec{R}^0 implies $\rho(\vec{R}^0) = 0$, so (according to the authors of Ref [3]), AIM theory predicts that the system has no atom, no bond and no structure at configuration \vec{R}^0 . It is further considered in Ref. [3] that if a sum of terms like Eq. (1) is needed, one term will always be dominant, so the problem of defining a molecular structure at \vec{R}^0 remains. It is shown, in what follows, that these arguments are wrong.

First, it has to be noted that Eq. (1) does not specify unambiguously what the authors mean by the total wavefunction, since there are various adiabatic approaches based on such product functions, the clamped-nuclei Born–Oppenheimer (BO) and the common adiabatic (BO plus diagonal corrections [5]) approximations being those that address the catastrophe, because of their strong restrictions. In particular, they admit a common potential-energy surface for various vibrational states, which generate orthogonal solutions with nodes.

The cases that must be considered are those that go beyond the BO and related adiabatic approximations. The question of whether a product function like Eq. (1) could be exact was considered some decades ago by Hunter [6, 7] and more recently by Mohallem and Tostes [8]. The approach of the last work, in which the reduc-

Correspondence to: J. R. Mohallem
e-mail: rachid@fisica.ufmg.br

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tion of a series of functions like Eq. (1) to a single term is discussed, in the case of a diatomic molecule, seems to be appropriate to the present analysis and is followed here. An appropriate starting point is to consider the Born–Huang (BH) [9] expansion of the total wavefunction,

$$\Psi(\vec{r}, \vec{R}) = \sum_k \phi_k(\vec{r}; \vec{R}) \chi_k(\vec{R}), \quad (3)$$

where $\phi_k(\vec{r}; \vec{R})$ are eigenfunctions of some electronic Hamiltonian and its parametric dependence on \vec{R} comes simply from demanding that it is normalized for all \vec{R} [10]. In the body-fixed coordinate system in which the electron positions are referred to the center of mass of the nuclei, the resulting internal Hamiltonian is

$$H = -\frac{\nabla_R^2}{2\mu_{AB}} - \sum_{i,j} \frac{1}{2M} \vec{\nabla}_i \cdot \vec{\nabla}_j + H_{BO}, \quad (4)$$

where $H_{BO} = -\sum_i \frac{1}{2m} \nabla_i^2 + V$ is the common BO Hamiltonian, (i,j) represent electrons of mass m , μ_{AB} is the reduced mass of the nuclei A and B and M is their total mass.

Following the common procedure of substituting Eqs. (3) and (4) into the Schrödinger equation, integrating over the electronic coordinates, and separating to the right the nondiagonal terms, the usual set of coupled equations is obtained [9],

$$\begin{aligned} & -\frac{\nabla_R^2}{2\mu_{AB}} \chi_k + U_k(R) \chi_k - E_k \chi_k \\ & = \sum_{l \neq k} \left(H_{kl} - \frac{1}{\mu_{AB}} (\vec{\nabla}_R)_{kl} \cdot \vec{\nabla}_R \right) \chi_l, \end{aligned} \quad (5)$$

with

$$U_k(R) = H_{kk}, \quad (6)$$

where the property that $(\vec{\nabla}_R)_{kk} = 0$ [10] has been used, with the notation $(O)_{kl} \equiv \langle \phi_k | O | \phi_l \rangle$ for a general operator O . Now, since the vibrational functions χ_k depend only on \vec{R} , the right-hand side of Eq. (5) can be manipulated, yielding

$$\begin{aligned} & -\frac{\nabla_R^2}{2\mu_{AB}} \chi_k + U_k(R) \chi_k - E_k \chi_k \\ & = \sum_{l \neq k} \left(H - \frac{1}{\mu_{AB}} \vec{\nabla}_R \chi_l \cdot \vec{\nabla}_R \right)_{kl}. \end{aligned} \quad (7)$$

Thus, complete decoupling of the BH equations will be accomplished only if the electronic functions satisfy the pseudoeigenvalue equation

$$\left(H - \frac{1}{\mu_{AB}} \vec{\nabla}_R \chi_k \cdot \vec{\nabla}_R \right) \phi_k = \epsilon_k \phi_k. \quad (8)$$

It becomes clear that the electronic functions ϕ_k will be (exact or approximate) eigenfunctions of some electronic part, H_{el} , of H ($H_{el} = H$ corresponding to the variational adiabatic approach [10]) only at the extrema of χ_k , or in their vicinity, where $\vec{\nabla}_R \chi_k \simeq 0$. These seem to be the cases that match the hypothesis of Ref. [3] that the product wavefunction, Eq. (1) is, respectively, exact or dominant in a BH series, and it is seen that they are far

from corresponding to nodes in the nuclear wavefunction. Near possible nodes of χ_k , $\vec{\nabla}_R \chi_k$ may be very large and the product function is no longer exact nor dominant.

This last conclusion might seem surprising, in view of the accuracy of most BO calculations based on productlike wavefunctions. Further, it brings out an interesting question that concerns the chemical meaning of a BH wavefunction made up of a series of nondominant terms. Although this still seems to be an open question, some insight was given some time ago by Czub and Wolniewicz [11]. They considered an exact factorization of the $v=3, \Sigma_g^+$ state of the H_2 molecule as $\Psi(\vec{r}, \vec{R}) = \phi(\vec{r}; \vec{R}) \chi(\vec{R})$, where the electronic factor, ϕ , is no longer restricted to be an eigenfunction of some electronic Hamiltonian. This ansatz was based on an older hypothesis of Hunter [6], concerning the factorization of the density into marginal, $\rho(\vec{R})$, and conditional, $\rho(\vec{r}; \vec{R})$, factors, suggested by probabilistic arguments. The authors of Ref. [11] showed that, in the nuclear configurations where the adiabatic BO vibrational function has nodes, the state-dependent nonadiabatic potential $U(R) = \int \phi^* H \phi d\vec{r}$ has sharp (deltalike) singularities, which turn it into a form critically different from the adiabatic BO one, but, on the other hand, modify the total energy and the wavefunction itself only in second order. They further showed that the nonadiabatic vibrational function has no nodes and no zeros. This work therefore suggests that the BH series of nondominant terms, in the vicinity of the nodes of the adiabatic vibrational wavefunction, retains the chemical picture of the molecule, as it must do.

Although not formally proved, it is expected that the nonadiabatic approach of Czub and Wolniewicz [11] corresponds to the exact solution of the coupled Eqs. (7) and (8). In fact, in the table of Ref. [11], it is seen that the differences between the adiabatic and nonadiabatic potentials vanish exactly where the vibrational function has maxima or minima. This theoretical prediction of the present work is thus numerically confirmed by the results of Ref. [11].

In conclusion, the catastrophe of AIM theory due to the factorization of the molecular wavefunction, suggested in Ref. [3], does not actually occur, if the appropriate molecular approach is considered. On the other hand, it is unlikely that large-scale beyond-BO calculations will be feasible in the near future. Thus, it seems that applications of AIM theory to conventional excited-state electronic structure calculations must be done with careful consideration of the points discussed here.

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