

A note on the initial condition of the differential equation which defines Proper Quantum Topological Subspaces

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Received 3 November 2003; revised 8 March 2004

We analyze Bader's variational procedure (BVP) to define Proper Quantum Topological Subspaces (PQTS) in multiatomic systems (MAS). In particular, we explicitly treat the problem of the initial condition of the partial differential equation resulting from BVP and defining the boundary of PQTS. We show that in general for MAS where nuclei correspond to spherical regions of constant (uniform) distribution the proper initial condition associated with the equation defining single atoms automatically emerges from the fundamental physical and mathematical hypothesis on which BVP is based. Our results justify the uniqueness of Bader's partition of atoms in molecules on the basis of an a priori mathematical argument implicitly contained in the theory rather than on an a posteriori chemical one as done so far.

KEY WORDS: Quantum Topological Subspaces, interatomic surface, partial differential equation, proper initial condition

AMS classification: 82-XX, 49Q99, 35Q40

1. Introduction

By combining Dirac's transformation theory and the action principle, J. Schwinger developed a self-contained formulation of quantum mechanics which does not require the conventional correspondence principle and the related assumptions [1]. Within such a theoretical framework, Bader and coworkers derived via a variational approach the definition of PQTS. This definition leads to quantum subsystems in real space for each of which equations of motion and commutation relations are the same as for the whole system [2–5]. In simple words (and in the most known application) this is Bader's theory of "Atoms in Molecules" [5]. Although this theory is well established in chemistry, did not produce much interest in the theoretical physics community, this probably because the trend in modern quantum theory is to never consider atoms and molecules as objects strictly bounded in space by some surface. We find

this point of view understandable, but not sufficient to justify the lack of interest towards a theoretical apparatus which is elegant and somehow rigorous. A detailed analysis of Bader's procedure can clearly lead to a deeper understanding of the quantum theory and how it applies to real systems, moreover the theory is supported by evident experimental results. For this reason we turned our attention to this subject, this work is part of a series of papers which try to analyze the theory from different points of view beyond chemistry. For the matter strictly connected with the current work, some points of the theory are not clearly stated in mathematical terms. Actually the very central point of the theory shows an evident incompleteness from a mathematical point of view; here we analyze this point in order to indicate a way for a more consistent formulation of the theory.

2. Bader's variational condition

We do not analyze the whole procedure followed by Bader but focus the attention on the final and crucial part of it, i.e. the variational problem whose solution leads to a differential equation defining the bounding surface $S(\mathbf{r})$ of the PQTS $\Omega(\mathbf{r})$. $\Omega(\mathbf{r})$ is a subspace in real space thus $S(\mathbf{r})$ must be a closed surface, or, as for the case of a diatomic molecule, together with the bounding surface at infinity should define a subspace of the whole space. The problem is defined in the following terms. In order to obtain for a subsystem $\Omega(\mathbf{r})$, via Schwinger's principle of stationary action, commutation relations and equations of motion which are the same as for the whole system, Bader shows [4] that is equivalent to require that the variation in the subsystem $\Omega(\mathbf{r})$ of the Laplacian of the electron density $\rho(\mathbf{r})$ vanishes:

$$\delta \left[\int_{\Omega} \nabla^2 \rho(\mathbf{r}) d\mathbf{r} \right] = 0. \quad (1)$$

For this problem $S(\mathbf{r})$ is considered dependent on $\rho(\mathbf{r})$, i.e. for a variation $\delta\rho(\mathbf{r})$ a variation $\delta S(\mathbf{r})$ is produced. Next he states and proves [2] that a necessary and sufficient condition to solve equation (1) is

$$\nabla \rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0; \quad \forall \mathbf{r} \in S(\mathbf{r}), \quad (2)$$

where $\mathbf{n}(\mathbf{r})$ is the unit vector normal to $S(\mathbf{r})$. This is the condition used to define atoms in multiatomic systems. Carefully reading equation (2) one can easily see that represents an incomplete statement. In fact this is a partial differential equation of explicit form [6–8]:

$$\frac{\partial \rho(\mathbf{r})}{\partial x} \frac{\partial S(\mathbf{r})}{\partial x} + \frac{\partial \rho(\mathbf{r})}{\partial y} \frac{\partial S(\mathbf{r})}{\partial y} + \frac{\partial \rho(\mathbf{r})}{\partial z} \frac{\partial S(\mathbf{r})}{\partial z} = 0 \quad (3)$$

which can be solved *if and only if* an initial condition or a class of initial conditions are specified; this is not the case of the current formulation of the theory. This is the crucial point of this contribution; in a self-contained theory, as Bader theory is supposed to be, where atoms are rigorously and uniquely topologically defined, informations about the initial condition of equation (2) should automatically emerge from the procedure adopted. In practical applications in chemistry and chemical physics this problem is solved by saying that the separatrix surface (SEP) of $\nabla\rho(\mathbf{r})$, i.e. the surface along which gradients paths, related to different nuclear sites, proceed parallel to each other, is the one to search for because leads to single topological entities which recover the chemical characteristics of atoms and molecules (see for example [12]). Using this chemically a posteriori motivated argument solutions of the equation built with trajectories of $\nabla\rho(\mathbf{r})$ generating (or terminating) at a nuclear site (along these trajectories equation (2) is always satisfied; we will refer to these kind of solutions as TGN) are excluded although in principle this does not emerge from any mathematical statement. This fact has been already pointed out in the literature [13] and in a previous work we gave a qualitative explanation [14]. It is important to point out that although the statement that the boundary between the atoms in a molecule does not pass through the nuclei seems rather obvious to a physicist, within a self consistent theory which does not consider a priori the separation in atoms of the whole quantum system, this separation should automatically emerge as a result of the basic physical principles and the mathematical procedure adopted; only in this case we can refer to the quantum subsystems as *proper* subsystems without any chemical or physical artifact which may give an empirical character to the procedure. We believe that this point is not a mere formal question but involves the very basis of the theory; a first principles theory cannot make ad hoc use of empirical considerations thus an analysis of how a class of initial conditions can automatically emerge from the theory itself would represent substantial contribution. As we have shown in some recent work [9–11], SEP shows interesting physical properties which could lead to a statistical interpretation of chemical properties, of course a mathematical analysis which shows the uniqueness of such a surface as an atomic interface will increase the validity of such conclusions.

3. Initial conditions consistent with the hypothesis of the variational problem

In a MAS the total distribution of matter can be written as

$$\rho_{\text{tot}}(\mathbf{r}) = \rho_e(\mathbf{r}) + \rho_n(\mathbf{r}), \quad (4)$$

where $\rho_e(\mathbf{r})$ is the electron distribution and $\rho_n(\mathbf{r})$ is the distribution of particles forming nuclei. Let us restrict to the case usually considered in practical applications, i.e. nucleus considered as a spherical region of constant (uniform)

distribution of particles and $\rho_{\text{tot}}(\mathbf{r})$ continuous and differentiable at every point. Of course this implies that the differentiable condition holds at the juncture between the electron and nuclear density as well; this is the basic principle which allows, in electronic calculations, the use of a pseudopotential for the nucleus and the non valence electrons. It follows that equation (4) on the whole domain $\Omega(\mathbf{r})$ can be rewritten as

$$\rho_{\text{tot}}(\mathbf{r}) = \rho_{\mathbf{r} \in \Omega_a}(\mathbf{r}) + \rho_{\mathbf{r} \in \Omega_b}(\mathbf{r}), \quad (5)$$

where Ω_b is the spherical region of the nucleus and $\Omega_a = \Omega - \Omega_b$, while $\rho_n(\mathbf{r}) = \text{const}; \forall \mathbf{r} \in \Omega_b$ and zero elsewhere; consequently $\rho_e(\mathbf{r}) = 0; \forall \mathbf{r} \in \Omega_b$. At this point we can transform equation(1) into

$$\delta \left[\int_{\Omega} \nabla^2 \rho(\mathbf{r}) d\mathbf{r} \right] = \delta \left[\int_{\Omega_a} \nabla^2 \rho(\mathbf{r}) d\mathbf{r} + \int_{\Omega_b} \nabla^2 \rho(\mathbf{r}) d\mathbf{r} \right]. \quad (6)$$

Clearly $\int_{\Omega_b} \nabla^2 \rho(\mathbf{r}) d\mathbf{r} = 0; \forall \mathbf{r} \in \Omega_b$ by definition and considering that Ω_b is fixed, the variational problem is reduced to

$$\delta \left[\int_{\Omega} \nabla^2 \rho(\mathbf{r}) d\mathbf{r} \right] = \delta \left[\int_{\Omega_a} \nabla^2 \rho(\mathbf{r}) d\mathbf{r} \right]. \quad (7)$$

The variation can be performed separately, first on a class of Ω s which entirely contain the spherical nucleus (see figure 1), and then on Ω s where the nucleus is on the border (see figures 2 and 3). In case Ω entirely contains Ω_b (which may be interpreted as the fact that the spherical nucleus is a solution of the variational problem as well being a particular subsystem (nuclear) (see figure 1)) the SEP of the field $\nabla \rho(\mathbf{r})$ is the only solution of equation (2). This because equation (2) expresses the condition that the surface S must be parallel to $\nabla \rho(\mathbf{r})$ at every point; such a condition is satisfied by two kind of solutions: (1) the SEP of the field $\nabla \rho(\mathbf{r})$. (2) Surfaces built with trajectories of $\nabla \rho(\mathbf{r})$ originating from (terminating at) the nucleus (TGN): this type of solutions imply that the nucleus is on the surface bounding Ω , as it is possible to see in figures 2 and

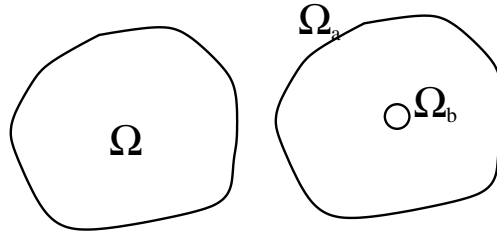


Figure 1. The plot shows the domain Ω over which the variation is performed. This corresponds to the case when the bounding surface of Ω does not pass through the nuclear region Ω_b .

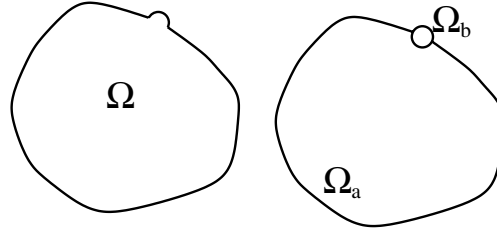


Figure 2. The plot shows the domain Ω over which the variation is performed. This corresponds to the case when the bounding surface of Ω passes through the nuclear region Ω_b and Ω_b belongs to Ω .

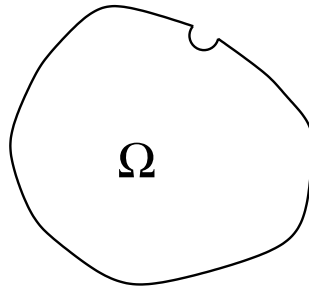


Figure 3. The plot shows the domain Ω over which the variation is performed. This corresponds to the case when the bounding surface of Ω passes through the nuclear region Ω_b and Ω_b does not belong to Ω .

3, and so far we are restricting the variation over Ω s which entirely contain the spherical nucleus, thus TGN are not in the class of surfaces we are considering in this case. Now, as a second case, we are going to consider the Ω s where the nucleus is on the border. From simple geometrical considerations from figures 2–4, one can argue that, if a solution exists for the case where the nuclear surface (or part of it) belongs to the global surfaces solution, this will be a TGN surface-like. At the same time a solution valid on the whole domain Ω should satisfy equation (2) at every point; we state that under the hypothesis we have done, this is not possible. In fact, as the only solutions of equation (2) are SEP and TGN, the latter inevitably presents cusps around the region of the spherical surface of the nucleus which is part of the solution because by definition around the nucleus $\rho(\mathbf{r})$ decreases along the radial direction so that $\nabla\rho(\mathbf{r})$ is perpendicular to the nuclear surface at every point (see figure 4). In conclusion this class of solutions is not acceptable on the basis of the fundamental mathematical and physical hypothesis of the problem and as a consequence, combining this results with those of Ref. [8], one can state that the separatrix surface is the only and unique surface solution of Bader's theory according to the fundamental mathematical and physical hypothesis on which the theory is based. For “fundamental mathematical and physical hypothesis of the problem” we mean that the surface

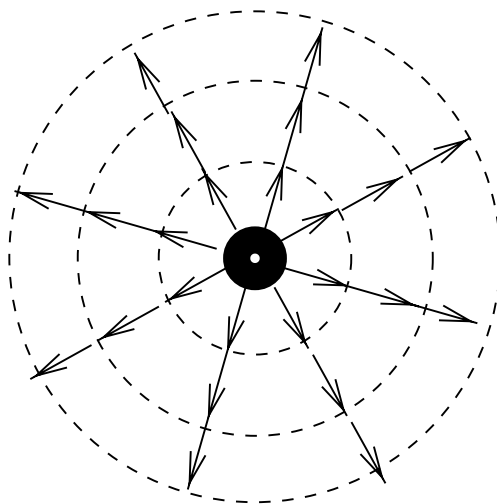


Figure 4. The plot shows gradient paths (bold lines) in the immediate neighboring of the nuclear spherical region. Dashed circles represent isodensity curves of decreasing value of $\rho(\mathbf{r})$ as one proceeds outward along the radial direction. This is a two-dimensional simplification, the extension to the three-dimensional case is trivial.

must be closed (in some cases together with the bounding surface at infinity) and must not present singularity at any point, i.e. each point belonging to Ω must be uniquely assigned to a subspace. The case of point-like nuclei representing cusps of $\rho(\mathbf{r})$ (as studied in [12]) can be studied by simply doing the limit to zero of Ω_b , and noticing that this does not eliminate the discontinuity at the surface, while the other considerations we have done for the spherical region remain the same. The case we have considered applies to many real cases; as previously argued, the most common example is the *ab initio* pseudopotential approaches, where the nucleus is considered as a uniform spherical entity, so that the topology of the whole system corresponds to the one we have treated.

4. Conclusion

The equation for defining atoms in MAS, as stated in Bader's procedure is formally incomplete, since is not related to an initial condition. Although this fact does not have consequences on practical applications of Bader's theory, we believe is an important point for showing the validity of the theory as a self-consistent first principles approach. We analyzed the procedure which leads to the central equation and from the fundamental mathematical and physical hypothesis of the problem derived properties which necessarily characterize a class of initial conditions for the equation. We have shown that the SEP of $\nabla\rho(\mathbf{r})$ is consistent with the mathematical and physical requirements of the problem and as a consequence a class of initial conditions is defined. In spite of the unjustified

lack of interest of most of the physical community, the physics behind this equation is very rich and need to be developed in several directions beyond chemistry, our pioneering statistical [9–11] and mathematical [8] analysis is an example.

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