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Comment

A comment on "Some fundamental problems with zero-flux partitioning of electron densities"

R. F. W. Bader

Department of Chemistry, McMaster University, Hamilton Ont., L8S 4M1, Canada

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Abstract. It is shown that the statement made by Cassam-Chenai and Jayatilaka regarding the atoms of AIM to the effect that "In particular, we shall demonstrate that these atoms are not a consequence of the Schwinger variation principle, as has been claimed" is false.

Key words: Zero-flux surface – Electron density

There recently appeared in this journal an article by Cassam-Chenai and Jayatilaka (C-J) [1] criticizing the fundamental nature of the quantum theory of atoms in molecules. A paper by the present author in the following issue of this journal [2] and written before the appearance of their paper, deals with many of the criticisms they put forth. However, C-J present a particular variational argument in section 3, one that is readily demonstrated to be incorrect.

The essential point in Schwinger's principle of stationary action as applied to an *open* system (an atom in a molecule) is the variation of the wave function Ψ on the *finite* zero-flux surface bounding the system, as well as a variation of the surface itself, variations $\delta\psi$, that are ultimately associated with generators of infinitesimal unitary transformations [2–4]. C-J base their criticism on one particular choice of trial function Φ for the ground state of the hydrogen atom whose sole zero-flux surface is at infinity. When the surface variation is applied, the surface is not transformed in a continuous manner into the corresponding surface defined by the state function Ψ, as required for the application of Schwinger's variation principle. Their example deals not with an *open* system, but instead considers the variations associated with a *closed isolated* system – the surface infinitely removed from the nucleus of a hydrogen atom. Not only does their example have nothing to do with the application of Schwinger's variational principle to an open system, their variation of Ψ on the boundary of a closed system is both mathematically and physically incorrect. It is not possible to retain variations on the surface of a closed system at infinity if one wishes to obtain the quantum equations of motion. As stated by both Schrödinger [5] and Schwinger [4], the surface term involving $\delta\psi$ on an infinite boundary is required to vanish to obtain Schrödinger's equation as the Euler equation in the variation of the Hamilton integral for a stationary state or in the variation of the action integral for a time-dependent system. Any attempt to retain variations on an infinite boundary precludes the obtainment of the wave equation and hence, of quantum mechanics. There are no contributions to the mathematical or physical properties of a closed system from its infinitely removed surface. *The absence of surface contributions for a closed system and their presence for an open system is the source of the difference in their mechanics* [6].

Schwinger's principle of stationary action requires the use of a class of trial functions whose variation corresponds to continuous changes in the coordinates of the physical system caused by the action of generators of infinitesimal unitary transformations, the very requirement that ensures the applicability of the zero-flux surface condition as the defining constraint of a proper open system. Indeed, the generators responsible for the most important of the atomic theorems are all demonstrated to exhibit the property of continuous deformability of a region $\Omega(\Phi, t)$ into the region $\Omega(\Psi, t)$ [2]. The C-J example fails on two counts: (i) it refers to variations on the surface of a closed isolated system, variations that, along with the variations of both the energy functional and action integral, must vanish to obtain the equation of motion, and (ii) their trial function does not belong to the class of functions whose variation corresponds to the action of generators of infinitesimal unitary transformations, as required by Schwinger's identification of the variations $\delta\psi$ with such generators.

Correspondence to: R. F. W. Bader
e-mail: bader@mcmaster.ca

Comment to the article "Some fundamental problems with zero-flux partitioning of electron densities" by P. Cassam-Chenai and D. Jayatilaka, Theor Chem Acc (2001) 105: 213–218

In fact, the effect of their proposed variation is equivalent to an electronic excitation and to a change in quantum state. Thus the conclusion of C-J, that their example of a single trial function Φ is sufficient to prove their statement quoted in the Abstract is false. Their further contention that one can choose trial functions exhibiting ''spike-like' features is also incorrect, as such functions bear no relation to the class of functions whose variation corresponds to the action of generators of infinitesimal unitary transformations.

The opening statement of their reply, to the effect that it 'has attracted many comments from the quantum chemistry community' is undocumented. The few comments that I am aware of were in any case, critical. It is pointless to continue the discussion, but one feels forced to respond to the more startling of the their statements. Schwinger is noted for his terseness in writing and for not stating the obvious. He once described the two-tome treatise on the ''Methods of Mathematical Physics'' by Morse and Feshbach as a road map for physics, written to the scale of one inch to the mile. He does not spell out necessary restrictions on the variations, as these are clear from their having to represent (this being the very *raison d'être* of his approach) the generators of infinitesimal unitary transformations; linear Hermitian operators expressed in terms of the dynamical variables, $\hat{q}$ and $\hat{p}$, the latter being a differential operator and thus all variations must be differentiable. The use of the calculus of variations in physics is discussed in Goldstein 'Classical Mechanics', where the special type of variation termed the 'Δ-variation' is introduced in the derivation of the principle of least action; the one that involves the variation of the time end-points and employed by Schwinger in his classic paper 'The Theory of Quantized Fields. I' to obtain a restatement of physics. One finds (page 365 of Goldstein, 2nd edn) the following statement regarding the nature of the variations; ''*All that is required is that they be continuous and differentiable*.'' Thus my criticisms of their counter example stands: their variation induces a discontinuous change and their variation is *applied* to an infinite surface where all contributions to the variation necessarily vanish. The equations of motion *are of course obtained* in the open system approach where they are derived as in the original works: in Schrödinger's case by setting $\Omega = R^3$ and in Schwinger's case by his principle that requires the variations over the space-time volume vanish. The proof of the pudding is in its eating and the quantum theory of atoms in molecules recovers all measurable properties of any system that are defined in terms of linear Hermitian operators.

References

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