Theor Chem Acc (2001) 105:213–218
DOI 10.1007/s002140000201

Theoretical
Chemistry Accounts

Regular article

Some fundamental problems with zero flux partitioning of electron densities

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Received: 9 March 2000 / Accepted: 13 August 2000 / Published online: 21 December 2000

Abstract. A number of fundamental problems with the topological analysis of molecular electron densities using the atoms in molecules (AIM) theory developed by Bader and coworkers are highlighted. In particular, contrary to statements made in the literature, we show that the local zero flux condition used in the AIM theory to define an atom in a molecule does not follow from the Schwinger variation principle, nor does it define unambiguously the atomic domains. Serious limitations of the definition of an atom in AIM theory also arise due to vibrational effects. A general definition of the structure of a molecular isomer based on a generalisation of the Born-Oppenheimer potential energy surface allow these limitations to be overcome.

Key words: Atoms in Molecules – Zero flux partitioning – Atomic partitioning – Zero flux surface – Electron density – Atomic variational principle – Schwinger variation principle

Introduction

Since the original article by Moffitt [18] entitled "Atoms in molecules and crystals" many atoms in molecules (AIM) theories have appeared in quantum chemistry. However, hereafter the term AIM theory will be reserved for what is commonly referred to as Bader analysis.

The theory of atoms in molecules put forward by Bader and coworkers is currently widely used for analysing molecular electronic charge distributions obtained from experiment or theory. The main thesis of the theory is that the electron distribution can be used to define "the atoms of chemistry" and to decompose property expectation values into additive atomic contributions. There are many publications which support the view that the atoms of the AIM theory rationalise the empirical behaviour that a chemist might expect of an atom in a molecule and thus the AIM analysis is an attractive tool for diagnosing important chemical information (see, for example, the monograph [6]).

One of the significant claims of the AIM theory is that the boundaries of the atoms in that theory are uniquely dictated by the Schwinger variational formulation of quantum theory. That is, the atoms of AIM theory are claimed to be the atoms of Chemistry and these atoms are in turn a unique consequence of quantum theory. Apart from the remarkable aesthetic importance of such a result, this claim is significant because it naturally suggests the idea of modelling chemistry directly and rigorously using these quantum atoms instead of the more cumbersome wavefunction.

The purpose of the present article is to rectify some ambiguous or incorrect statements which have appeared in the literature regarding the fundamental nature of the so-called zero flux surface which defines the boundary of an atom in the AIM theory. In particular, we shall demonstrate that these atoms are not a consequence of the Schwinger variation principle, as has been claimed. We also illustrate further difficulties encountered when applying the AIM theory to define atoms in the case of excited electronic and vibrational states.

Although our results are somewhat negative, our intention in bringing these points to the attention of the reader is to offer an explanation of why the AIM analysis has remained a post facto form of analysis rather than a new a priori atomic formulation of quantum theory, and we hope that our work will trigger constructive progress in extending the AIM theory to allow a truly atom-based treatment of quantum theory.

1. Local zero flux surfaces do not define unambiguously atomic domains

The idea of local zero flux surfaces for partitioning the one-electron density ρ of a molecule into atomic contributions was introduced by Bader and Beddall [1].

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A surface $\partial\Omega$ delimiting a domain Ω is called a local zero flux surface if it satisfies the following condition:

$$\nabla\rho(\mathbf{r}) \cdot \boldsymbol{n}(\mathbf{r}) = 0, \quad \forall\, \mathbf{r} \in \partial\Omega \qquad (1)$$

where $\boldsymbol{n}(\mathbf{r})$ is the outward normal to $\partial\Omega$ at point $\mathbf{r}$.

It is stated on p 31 of [6] that "the interatomic surfaces, along with the surfaces found at infinity, are the only closed surfaces of R^3 which satisfy the zero-flux condition of Eq. (1)". This is not true because any surface that originates from a nucleus and follows the gradient of the density satisfies Eq. (1) since the normal is orthogonal to $\nabla\rho(\mathbf{r})$ at every point. That is to say that Eq. (1) has an infinite number of solutions of the form depicted in Fig. 1 which is undesirable from the perspective of defining atomic domains.

In [5] (footnote, p 307) it is acknowledged that nuclei must be excluded from boundary surfaces but on the ground that the normal is not defined at these points because of the cusps in the density. This view is questionable on two grounds. First, in a real system, the size of the nucleus is finite, and there is no cusp [11]. The extension of the point nucleus model to the more realistic extended nucleus model, an extension which should cause no discernible effect as far as chemistry is concerned, appears here to have an unjustifiably exaggerated effect on the allowed form of an atom in a molecule, if that atom is to be bounded by a local zero flux surface. Second, even in the case where there is a cusp, Bader has shown (p 40, [6]) that there always exists a function "homeomorphic" to the density (i.e. nearly the same as the density, to any desired accuracy), and this function does not have cusps. Such homeomorphic functions are used to justify that the nuclear positions can be considered as so-called (3, −3) critical points, i.e. local maxima with well-defined gradient equal to the null vector. It is inconsistent to allow the treatment of the cusp as a well defined critical point with derivatives in one circumstance but not in another.

Our point here is not to invalidate the use of AIM as a practical tool but to emphasise that the spurious solutions of Eq. (1) cannot be excluded by using the cusp argument.

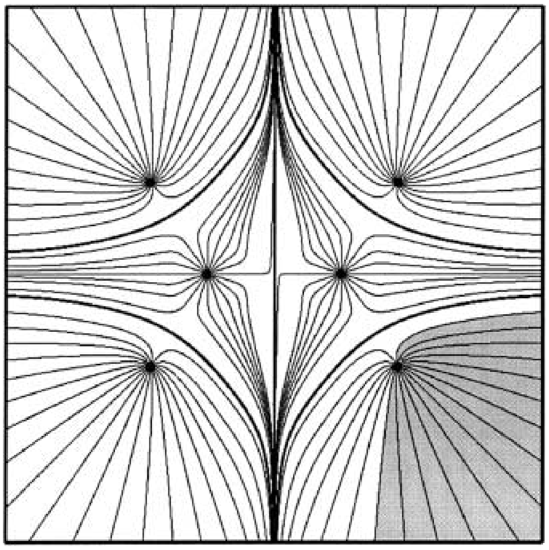

Fig. 1. The gradient vector field of the density for ethene, C_2H_4, in the σ_h plane, showing a shaded region whose boundary satisfies the zero flux condition, Eq. (1)

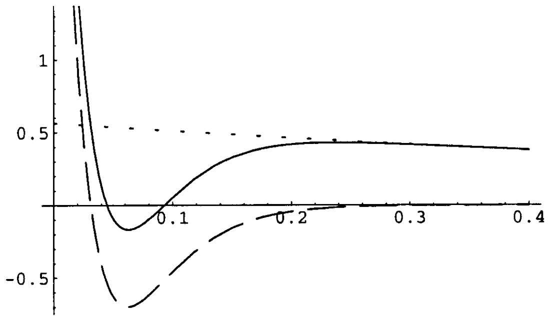

Fig. 2. Radial dependence of the 1s-like function $\Psi(r)$ [*dotted line*; see Eq. (2)], the 2s-like function $\varepsilon\Psi'(r)$ [*dashed line*; see Eq. (4)] for the value $\varepsilon = 0.1$ and the a less than $\frac{1}{2}$ solution of Eq. (7), and the function $\Phi(r)$ [*solid line*, see Eq. (3)] showing the zero at $r = 3a \approx 0.093$. Φ is only distinct from the variational solution Ψ in the small region $r < 0.25$ which is the reason why in terms of the distance (defined by square integration) it is only within ε of this function

2. Atomic domains do not always partition space uniquely

It is stated in [5] (footnote, p 307) regarding local zero-flux surfaces that "the partitioning obtained by excluding nuclei or attractors, in general, from a boundary surface is always unique, disjoint and exhaustive and the surfaces of bound and free atoms are continuously transformable one into the other". This is not true for the isolated hydrogen atom in its ns-state ($n > 1$) since $\nabla\rho(\mathbf{r})$ has $n{-}1$ finite radii nodal spheres plus one of infinite radius (e.g. see $\varepsilon\Psi'$ in Fig. 2 for a picture of a typical 2s-like function) which satisfy Eq. (1) and do not correspond to attractors. These nodal zero flux surfaces are contained within each other, so it is not clear which of the regions bounded by them is to represent an "atom".

The existence of maxima in the charge density for excited states was pointed out for one electron systems on p 43 of [6]. However, the consequences for an atomic partitioning of the density based on the zero-flux condition were not emphasised.

Moreover, it might be expected that ns-like nodal surfaces also appear for the Rydberg-like states of any neutral molecule.

3. The Schwinger subsystem variation principle cannot be applied to zero flux atomic domains

A subsystem variational principle has been invoked to justify the use of local zero flux surfaces to define atomic domains (see [5] and references cited therein). It is based on the Hilbert and Courant generalisation of variation calculus to the case of variable domains [9] (p 260). The applicability of this generalisation requires that there exists a family of mappings g_Φ of the local zero flux surface, $\partial\Omega(\Phi)$, defined by the wave functions Φ of a neighbourhood of a given wave function Ψ, onto that defined by Ψ, $\partial\Omega(\Psi)$, with the following properties:

1. g_Φ bijective for all Φ
2. $\lim_{\Phi\to\Psi} g_\Phi = \text{Identity}$
3. g_Φ differentiable for all Φ

We contend that these conditions are not necessarily fulfilled for the zero flux surfaces of the AIM theory, and now give a counter example.

Consider a hydrogen atom in its ground state and choose

$$\Psi(\mathbf{r}) = \frac{\mathrm{e}^{-r}}{\sqrt{\pi}} \tag{2}$$

where r denotes the modulus of $\mathbf{r}$ (atomic units are used throughout this paper). The only solution $\partial\Omega(\Psi)$, of Eq. (1) which does not include the nucleus is the surface at infinity. We will show that no matter how small the neighbourhood of Ψ is, there exists Φ in this neighbourhood such that $\partial\Omega(\Phi)$ cannot be deformed continuously by a bijective mapping (so a fortiori by a differentiable bijective mapping) into $\partial\Omega(\Psi)$. Let us fix $\varepsilon < 1$, and set

$$\Phi(\mathbf{r}) = \Psi(\mathbf{r}) + \varepsilon\Psi'(\mathbf{r}) \tag{3}$$

with

$$\Psi'(\mathbf{r}) = \frac{1}{2\sqrt{\pi}a^{3/2}}\left(1 - \frac{r}{a}\right)\mathrm{e}^{-\frac{r}{a}} \tag{4}$$

so that Φ belongs to the open ball of radius ε, i.e. $||\Phi - \Psi|| < \varepsilon$ for all a. The corresponding density at point $\mathbf{r}$ is

$$\rho(\mathbf{r}) = \frac{\Phi(\mathbf{r})^2}{N_\rho} \tag{5}$$

where N_ρ is a normalisation factor, and the gradient is

$$\nabla\rho(\mathbf{r}) = \frac{\partial\rho(\mathbf{r})}{\partial r}\hat{\mathbf{r}} = \frac{2}{N_\rho}\Phi(\mathbf{r})\frac{\partial\Phi(\mathbf{r})}{\partial r}\hat{\mathbf{r}} \tag{6}$$

denoting by $\hat{\mathbf{r}}$ the unit vector along $\mathbf{r}$. Let us choose $r = 3a$ and solve $\Phi(\mathbf{r}) = 0$ for a. The result is

$$\mathrm{e}^{-3(a-1)}a^{3/2} = \varepsilon \quad . \tag{7}$$

The left hand side of Eq. (7) is 0 for $a = 0$, reaches its maximum value of $\left(\frac{\mathrm{e}}{2}\right)^{3/2}$ at $a = \frac{1}{2}$ then decreases towards 0 as a tends to infinity. This means that no matter how small ε is chosen there are always at least two values of a such that $\Phi(3a\hat{\mathbf{r}}) = 0$ and so, where $\nabla\rho(3a\hat{\mathbf{r}}) = 0$, for all $\hat{\mathbf{r}}$. Therefore for either one of these values of a there is, in addition to the surface at infinity, a surface of finite radius at $r = 3a$ satisfying Eq. (1) (inherited from the $2s$-like component of Φ). This surface does not correspond to an attractor since it is a node of the density and it is not connected to the surface at infinity. Since a continuous mapping maps a connected set to a connected set, $\partial\Omega(\Psi)$ cannot be mapped continuously onto the two unconnected surfaces obtained for Φ. In other words, assuming that the surfaces at infinity are mapped one onto the other (as seems to be understood in AIM; however this mathematical problem has not been addressed by Bader and Coworkers), there is nothing left to map continuously onto the surface at finite distance. Hence there can be no mapping, g_Φ, from $\partial\Omega(\Phi)$ onto $\partial\Omega(\Psi)$ that is bijective and differentiable, i.e. satisfying properties 1 and 3.

Figure 2 depicts the three functions Ψ, $\varepsilon\Psi'$ and Φ for the particular choice $\varepsilon = 0.1$ and the $a < \frac{1}{2}$ solution of Eq. (7). There is a nodal surface in $\Phi(\mathbf{r})$ at $r = 3a \approx 0.093$ as expected, and another one closer to the nucleus at $r \approx 0.045$.

Although a single counter example is sufficient to prove our claim, the problem encountered is general because one can always find in the Hilbert space of square integrable functions a spike-like function whose square integral is arbitrarily small but whose density dominates locally that of a given reference wave function (not necessarily the ground state solution of the variational equation). In the case of, say, a $2n$ electron closed-shell wave function, one can create n extra zero flux surfaces in n different locations by adding a Slater determinant of orbitals spiked in n different regions where the reference wave function density is small compare to that of the spiked orbitals.

4. Non equivalence of net and local zero flux atomic domains

One of the original purposes for introducing the local zero flux condition, Eq. (1), was to define boundary surfaces such that the operators $\boldsymbol{P}^2$ and $\boldsymbol{P}^\dagger\cdot\boldsymbol{P}$ would have the same average over the so-delimited regions as they have over all space because of the Hermiticity of the linear momentum operator $\boldsymbol{P}$ [1]. It was clearly stated in [1] that only the net zero flux condition,

$$\int_\Omega \nabla^2\rho(\mathbf{r})\mathrm{d}\mathbf{r} = 0 \quad , \tag{8}$$

was required to achieve this aim and that the local zero flux condition at Eq. (1) was a stronger, sufficient but not necessary condition. However in later publications where an attempt was made to use the subsystem variational principle of Sect. 3, it was argued (p 78 of [3], p 158 of [6], equivalence between Eqs. (17) and (18) in [5] and between Eqs. (21) and (22) in [19] where it is stated that the steps from Eq. (20) to Eq. (26) can be reversed) that the local zero flux condition was necessary. This is clearly false since the more general local condition for all Φ

$$\nabla\rho(\mathbf{r})\cdot\boldsymbol{n}(\mathbf{r}) = \nabla\times\boldsymbol{A}(\mathbf{r})\cdot\boldsymbol{n}(\mathbf{r}), \quad \forall\,\mathbf{r}\in\partial\Omega \tag{9}$$

where $\boldsymbol{A}(\mathbf{r})$ is an arbitrary vector field, is sufficient to obtain net zero flux for all Φ. This is because when one applies the Green-Ostrogradsky formula to transform the surface integral over $\partial\Omega$ of the right hand side of Eq. (9) into a volume integral over Ω, the divergence of the expression $\nabla\times\boldsymbol{A}$ appears, and this equals zero at all points.

It has also been claimed that only the local zero flux surface has the property that, at all times, the net zero flux condition is maintained (p 379 of [6], p 77 of [3]). This, also, is false, since a zero flux surface satisfying

Eq. (9) at all times can be defined regardless of whether A is constant (local zero flux) or not (general net zero flux), the set form of A playing no particular rôle.

5. Vanishing of atomic domains at vibrational nodes

Consider a bound state of a given molecular system. Assuming that the translational degrees of freedom have been taken care of rigorously as described, for example in [12], the wave function Ψ is a function of the electronic variables $\mathbf{r} = (\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_{N_e})$ and the nuclear co-ordinates $\mathbf{R} = (\mathbf{R}_1, \ldots, \mathbf{R}_{N_n})$, integrable over the rovibrational degrees of freedom. Note that the symbols for the sets of vectors $\mathbf{r}$ and $\mathbf{R}$ are distinguished from vector positions in that they are not in italic font. More specifically, in the frame of the adiabatic approximation the wave function can be written in the form

$$\Psi(\mathbf{r}, \mathbf{R}) = \Psi_e(\mathbf{r}, \mathbf{R})\Psi_n(\mathbf{R}) \tag{10}$$

with Ψ_n normalised with respect to $\mathbf{R}$ and Ψ_e normalised with respect to $\mathbf{r}$ for all $\mathbf{R}$. Then the one-electron reduced density ρ of the system for a given nuclear configuration is also the product of two factors:

$$\rho(\mathbf{r}, \mathbf{R}) = \rho_e(\mathbf{r}, \mathbf{R})\rho_n(\mathbf{R}) \tag{11}$$

where

$$\rho_e(\mathbf{r}, \mathbf{R}) = N_e \int \Psi_e^*(\mathbf{r}, \mathbf{R})\Psi_e(\mathbf{r}, \mathbf{R})\ \Pi_{i=2}^{N_e} \mathrm{d}\mathbf{r}_i \tag{12}$$

$$\rho_n(\mathbf{R}) = \Psi_n^*(\mathbf{R})\Psi_n(\mathbf{R}) \tag{13}$$

Remember [15] (or [9] p 451) that as soon as there exist two distinct orthogonal states then one of them at least will have a nodal surface. So if there is more than one bound vibrational state in the system there exists a nuclear configuration $\mathbf{R}^0$ and a bound state Ψ_n such that

$$\Psi_n(\mathbf{R}^0) = 0 \tag{14}$$

This implies

$$\rho(\mathbf{r}, \mathbf{R}^0) = 0, \ \ \forall \mathbf{r}\ . \tag{15}$$

So according to the AIM theory, such a system has no atom, no bond and no structure at configuration $\mathbf{R}^0$. This configuration can be the equilibrium configuration: think of the first excited vibrational state in the harmonic approximation, or close to it when anharmonicity is taken into account. To our knowledge, this type of catastrophe has not been addressed before.

If the exact wave function cannot be cast in the form of a single product as in Eq. (10), but is instead a linear combination of such products, one term will generally dominate the expansion and the problem of getting a meaningful structure at a nodal point of the nuclear function of this term will remain.

6. Multiple atomic domains in vibrational excited states

One can think of two ways to circumvent the difficulty within the AIM theory. First, it can be acknowledged that the theory is limited in its application to approximate wave functions of the form of Eq. (10), and that the genuine one-electron density $\rho(\mathbf{r}, \mathbf{R}^0)$ must be replaced by $\rho_e(\mathbf{r}, \mathbf{R}^0)$. Second, as mentioned on p 68 of [3], one can average over nuclear co-ordinates and use $\bar{\rho}$ to define the structure, with

$$\bar{\rho}(\mathbf{r}) = \int \rho(\mathbf{r}, \mathbf{R})\mathrm{d}\mathbf{R} \tag{16}$$

where $\mathrm{d}\mathbf{R} = \Pi_i \mathrm{d}\mathbf{R}_i$. In fact, this equation is incorrect. In addition to removing the translational degrees of freedom, the rotational part of the wave function must be factored out because averaging over the rotational degrees of freedom gives a density that is not suitable for the AIM analysis, a difficulty not acknowledged in [3].

In Fig. 3 we present a plot of $\bar{\rho}(\mathbf{r})$ for the dinitrogen molecule N_2 calculated in the Born-Oppenheimer approximation. $\Psi_e(\mathbf{r}, \mathbf{R})$ was obtained at the SCF level using Dunning's DZP basis set [10], and $\Psi_n(\mathbf{R})$ was the first excited vibrational state in the harmonic approximation using the experimental equilibrium separation $r_e = 2.067$ atomic units and vibrational frequency, $\omega = 2359.61\ \mathrm{cm}^{-1}$. The density was calculated by using an adaptive Simpson's rule quadrature, integrating the dimensionless vibrational normal coordinate q from −4 to 4, and ensuring each density point was converged to 10^{-4} electrons per cubic bohr. This required approximately 12,000 individual SCF calculations. It is clear from the figure that the AIM analysis would find 4 "atoms" in this molecule. The width of the plot is 0.5 atomic units, so the separation of the two atomic peaks is about 0.04 Å.

Conclusion: local zero flux surfaces are not fundamental according to quantum theory

Bader and co-workers have made a claim in an abundant literature that local zero-flux surfaces are fundamental according to quantum theory. They argue that only local

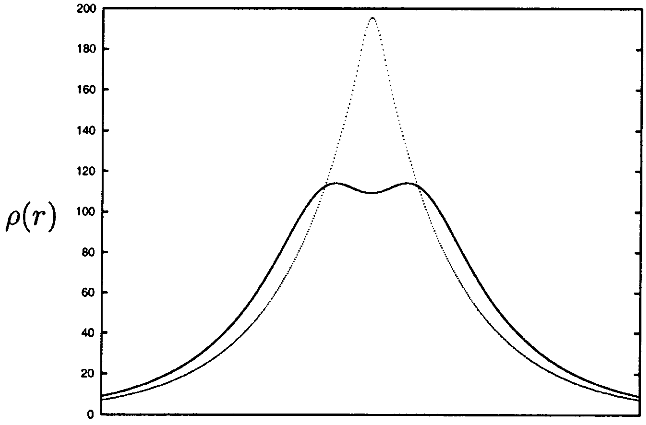

Fig. 3. The electron density along the bond axis in $X\ {}^1\sum_g^+ N_2$ molecule, showing a 0.5 atomic units slice around one N atom for the static charge density ρ_e (*dotted line*), and for the vibrationally averaged charge density, $\bar{\rho}$, in the $v = 1$ state (*solid line*)

zero-flux boundaries permit to derive the hypervirial theorem for a subsystem from what they call "a generalisation of Schwinger variational principle". For example we find in [4] the following statement: "What is remarkable and physically important is that this final generalisation [the generalisation to a subsystem of a total system of Schwinger's derivation of Schrödinger's wave equation and the hypervirial theorem from a variational principle] is possible only for a particular class of subsystem, those which satisfy a variational constraint [the zero flux condition]".

We note that, if one follows the traditional philosophy that the best derivation is the one which requires fewer assumptions, the Schrödinger equation derivation of the subsystem hypervirial theorem is to be preferred to the derivation via the Schwinger principle, since no assumption is required on the bounding surface ([6] Sect. 5.2). It might also be noted that this derivation which places no emphasis on zero flux surface is far more economical than the variational one. It seems strange to try to justify the zero-flux constraint by invoking a weaker demonstration of a general theorem (i.e. valid for all cases), that is only applicable under this particular restriction.

In any case, we have shown in Sect. 4 that the condition such a reasoning could possibly justify is not that of local zero-flux but only that of net zero-flux. However, in Sect. 3 we have proved with a counter example that the whole approach is problematic because the application of Schwinger principle under the conditions of Courant and Hilbert is not valid for a subsystem delimited by a zero-flux surface. Taken together, these points show that Bader and coworkers' use of the Schwinger variational principle fails to demonstrate that atomic domains defined by the local zero flux surface are implied by the principles of quantum mechanics.

Therefore, it is not surprising that this condition must be supplemented by additional conditions to represent meaningfully an atom (Sect. 1), that the local zero flux surface does not provide a well defined separation into atomic domains for electronic excited states (Sect. 2) and that the AIM theory is limited to the vibrational ground state (Sects. 5 and 6). Note also that the latter point cannot be simply fixed by defining an atomic domain as an attractor and its basin [8].

It might be possible to extend the Hilbert and Courant variation calculus to overcome the problem exposed in Sect. 3; however, the common use of the AIM analysis is not contingent on it being derivable from first principle quantum theory. Indeed, physics and chemistry being empirical sciences, it is perfectly legitimate to impose ad hoc additional conditions, such as the condition that the local zero flux surface should not pass through a nuclear position, or that the theory should be limited to the vibrational ground state in order to retrieve "the atoms of chemistry". Similarly, for electronic excited states one might extend the taxonomy of the AIM theory by proposing that an atom be defined by the outermost enclosing local zero flux surface, although this is a topic which requires further analysis and is not as straightforward as the case of the non-nuclear attractors called "pseudo-atoms" discussed in [6].

The difficulties raised by excited vibrational states are not exclusive to the partitioning by zero flux surfaces. These problems also hinder the generalisation to the complete molecular system (electrons plus nuclei) of many analyses based on purely electronic wavefunctions or densities, such as those of Li and Parr [16], Hunter [14], Gill [13] to quote a few. Such a generalisation is of course desirable because molecules in excited vibrational states are omnipresent in nature (except in the interstellar medium) or in the flask of the chemist. This has already led one of us to prefer the reduced Coulombian potential plus electronic kinetic energy operator[1] as a basis for defining molecular structure [7]. This quantity is expressed for a translation free, totally symmetrical with respect to rotations, bound state (see [7] for details and generalisation) as

$$v(\mathbf{R}) \equiv \frac{\int \Psi^*(\mathbf{r},\mathbf{R})(T_e + V(\mathbf{r},\mathbf{R}))\Psi(\mathbf{r},\mathbf{R})\mathrm{d}\mathbf{r}}{\int \Psi^*(\mathbf{r},\mathbf{R})\Psi(\mathbf{r},\mathbf{R})\mathrm{d}\mathbf{r}} \qquad (17)$$

where $V(\mathbf{r},\mathbf{R})$ is the Coulomb potential of the system, T_e is the electronic kinetic energy operator and $\mathrm{d}\mathbf{r} = \Pi_i \mathrm{d}\mathbf{r}_i$. Denote by $\dot{\mathbf{R}}$ the set of all rotationally equivalent nuclear configurations. Because we are dealing with a state that is totally symmetrical with respect to rotations, v has the same value for any configuration in $\dot{\mathbf{R}}$ and we shall call this value $v(\dot{\mathbf{R}})$.

The nuclear kinetic energy operator is left out in Eq. (17) in order that in the Born-Oppenheimer approximation, $v(\dot{\mathbf{R}})$ reduces to the usual potential energy surface (PES), and thus it can be used to generalise Mezey's view of isomers as a catchment region in the PES [17].

The latter definition retains the topological character of Bader's definition and allows us to follow Bader et al. [2] when they disagree with Woolley's statement that "if we do not make molecular structure part of the input of our theory it will never emerge in the output" [20]. Moreover, the drawbacks of Bader's definition addressed above are avoided and one has the additional advantage that the shape of the well in $v(\dot{\mathbf{R}})$ is related to the lifetime of the so-defined isomer.

Acknowledgements. We acknowledge stimulating discussion with Yvan Castin and Claude Le Bris (PCC) and with Stephen Wolff and Ian Bytheway (DJ). Graham Chandler and Yves Ellinger are acknowledged for discussions, and hospitality. The Australian Research Council is acknowledged for funding.

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[1] In fact the latter has been forgotten in the published version and we take this opportunity to correct this mistake.

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