

On the connections between the quantum theory of atoms in molecules (QTAIM) and density functional theory (DFT): a letter from Richard F. W. Bader to Lou Massa

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Received: 24 February 2017 / Accepted: 28 March 2017 / Published online: 9 May 2017
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Abstract A 31-year-old letter from Professor Richard F. W. Bader to Professor Lou Massa outlining the connections between the quantum theory of atoms in molecules (QTAIM) and density functional theory (DFT) especially with regard to the first Hohenberg-Kohn theorem is brought to light. This connection has not often been the topic of such a focused review by Bader and is presented here for the first time. The scientific importance of this letter is, in the opinion of the presenter, as timely today as it was back then in 1986. In Bader's own opening words: "... *that if I sent you a summary of what I think are the important connections between our work and density functional theory, ...*". He then takes us in a grand tour of the foundations of QTAIM culminating into the antecedents of a paper he later published with Professor Pierre Becker, whereby the Hohenberg-Kohn theorem is shown to operate at the level of an atom-in-a-molecule. Bader closes his letter by suggesting to Massa: "*Study these two charge distributions – they are proof of the theorem of Hohenberg and Kohn*". By that Bader meant that when the charge distributions of two atoms or groups are identical within a given precision, then the kinetic and total energy contributions of these atoms to the corresponding molecular

quantities are also identical. It is revealing to follow the intellectual threads weaved by Bader which provides us with a glimpse of his thought processes and intuition that guided him to some of his key discoveries. The lucidity, rigor, and clarity characteristic of Bader and the informality of style of a letter makes it of pedagogic and historic interest.

Keywords The quantum theory of atoms in molecules (QTAIM) · Density functional theory (DFT) · Quantum stress tensor · Ehrenfest force · Transferability · Hohenberg-Kohn theorem

Introductory remarks

On 15 January 2012, Professor Richard F. W. Bader (1931–2012) [1] passed away. In August of the same year of his death, Bader's family asked three of his close friends (Dr. Todd A. Keith, Professor Paul W. Ayers, and the presenter) to classify, preserve, and take charge of his scientific archives representing a 60-year career. The Bader archives include, for example, copies of all the theses he has supervised, earlier drafts of manuscripts of papers, correspondence with editors, and a great number of letters to colleagues on scientific topics. The family authorized the three of us to use the archive at our discretion when we see fit for the benefit of science.

Below is an important letter that was written by Bader to Professor Lou Massa in 1986 that is brought to light from the dusty archives boxes for the first time. The letter acquires its importance, in my (the presenter's) opinion, for at least the following reasons:

- (1) The letter is of current and timely *scientific importance*, since it is an early condensed review of what became to be known in later literature as the quantum theory of

This article is dedicated to Professor Lou Massa and to the memory of Professor Richard F. W. Bader.

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atoms in molecules (QTAIM) [2–4]. More importantly, it seems to be one of the earliest statements by Bader that focuses primarily on the relation between QTAIM and density functional theory (DFT) [5] (in addition to relatively few original studies slanted primarily toward DFT, e.g., [6, 7] and a late definitive paper [8]). Bader “gives in words the essential idea that is formally developed in the papers”, to quote him from the tenth page of his letter. As he often does, Bader does not use atomic units in this letter, so all fundamental constants are explicitly written in the equations, which adds clarity by readily revealing physical dimensions.

- (2) As a former graduate student of Professor Bader, I became immediately aware of the mutual esteem and admiration between him and Professor Massa. As a new student in his research group, Bader has given me the assignment of summarizing Lou Massa’s work with Bill Clinton on the reconstruction, from X-ray structure factors, of idempotent density matrices that are consistent with the scattering data. Bader asked me to present it in his research group meeting and, later, this became the topic of my first graduate seminar at McMaster University. In 2011, *The Journal of Physical Chemistry A* devoted a special issue to honor Richard F. W. Bader [9]. Out of the 80 articles that appeared in the Bader festschrift, three were coauthored by Lou Massa including the opening article that gave tribute to Bader’s scientific accomplishments [1]. My 17 years of close friendship with Richard Bader allow me to be almost certain that should he had been alive today he would have desired to contribute in honoring and celebrating Lou Massa’s career by contributing to his festschrift.
- (3) The letter has *historical interest* since Bader gives an insight to what motivated him to explore certain questions, his intuition at “smelling the answer” (quoting Walter H. G. Lewin of MIT) before being able to actually prove it, and his process of thought in formulating key concepts that underpin his theory of atoms in molecules. These aspects cannot usually find their way into print. Furthermore, this letter summarizes some core concepts, predates, and leads the way to the principal themes of Bader’s now classic 1990 Oxford University Press book: *Atoms in Molecules: A Quantum Theory* [2].

In the following reproduction of the letter, the following conventions have been observed:

- (1) Equation numbers have been added (which were not in the original letter) to facilitate future referencing and scientific use of this letter.
- (2) In his letter, Bader refers to a number of enclosed reprints. Since only a photocopy of the letter itself is what was recovered and not any of its enclosures, we have no

way to be certain of the references that accompanied the letter. Bader refers specifically to a “*Reprint A*” and a “*Reprint B*”. The information given in the body of the letter about these reprints, and considering the date of the letter and the page numbers referred to at various parts of the letter, etc., it is determined beyond a reasonable doubt by the presenter that *Reprint A* is Ref. [10] and *Reprint B* is Ref. [11]. These references (in addition to two more that were published after the letter) were inserted in the body of the letter for the convenience of the reader. (There was neither bibliographic citations nor a list of references in the original text, the only citations were to *Reprints A* and *B*).

- (3) Text underlined for emphasis in the original text is italicized in the transcription to conform with current publication standards.
- (4) Any other alteration to—or insertion in—the original text (e.g., one instance of capitalization after a period, explanation of an abbreviation, etc.) is included in square brackets, as customary.

The informality of the letter and the usual rigor and precision of Bader’s style combined with his characteristic passion make it a revelation to read. To give the reader a visual sense of the actual letter, Fig. 1 reproduces the first paragraph of the first page and the signed last page. It is the hope of the presenter that this recently discovered letter will be incorporated into the body of literature on Bader’s quantum theory of atoms in molecules (QTAIM).

Text of Richard F. W. Bader’s 1986 letter to Lou Massa

November 1, 1986

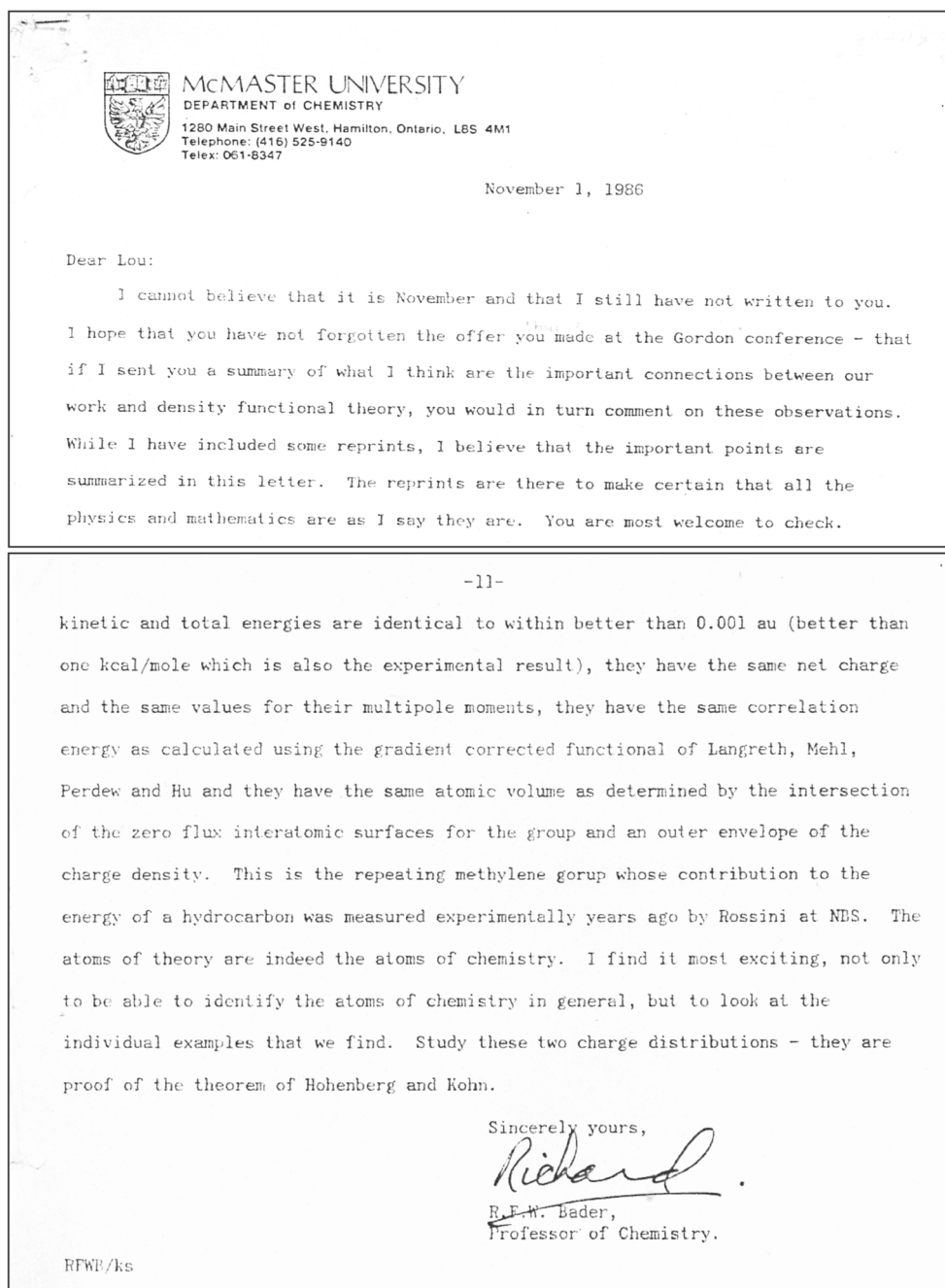
Dear Lou:

I cannot believe that it is November and that I still have not written to you. I hope that you have not forgotten the offer you made at the Gordon conference – that if I sent you a summary of what I think are the important connections between our work and density functional theory, you would in turn comment on these observations. While I have included some reprints, I believe that the important points are summarized in this letter. The reprints are there to make certain that all the physics and mathematics are as I say they are. You are most welcome to check.

Perhaps you wouldn’t mind however, to start by reading the reprint labelled A [10]. This is a two page summary of the theory of atoms in molecules which recently appeared in JCP. It emphasizes what is most important, that the whole theory is derived from a single fundamental principle of physics. It is not a model and most important of all, it is not arbitrary.

The theory is the result of extensive studies we have made on the properties of molecular charge distributions. We made

Fig. 1 First paragraph of the first page of the 11-page letter of Richard F. W. Bader to Lou Massa (*top*) and the signed last page (*bottom*)



the discovery that regions of space bounded by a surface of zero flux in the gradient vector of the charge density,

$$\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) = 0 \quad (1)$$

as well as yielding a disjointed partitioning of a molecule into atoms, were the most transferable pieces of some total system that one can define. We were at the same time studying the properties of kinetic energy densities $G(\mathbf{r})$ and $K(\mathbf{r})$ where

$$G(\mathbf{r}) = \frac{\hbar^2}{2m} \nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{r}'} \Gamma^{(1)}(\mathbf{r}, \mathbf{r}') \Big|_{\mathbf{r}=\mathbf{r}'} \quad (2)$$

and

$$K(\mathbf{r}) = -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 \Gamma^{(1)}(\mathbf{r}, \mathbf{r}') \Big|_{\mathbf{r}=\mathbf{r}'} \quad (3)$$

We observed that when the distribution of charge of an atom could be transferred between different molecules with little or no change (and this can happen for a spatial region bounded by zero flux surfaces) then the kinetic energy density, either K or G exhibited the same degree of transferability. Not only can this happen, it happens even though the neighbouring atoms are totally different

in the different systems. (Please see reprint B [11], page 72), for a diagram of some of the original examples of diatomic charge densities containing a Li atom with nearly transferable properties). Thus when $\rho(\mathbf{r})$ is transferable locally over the basin of an atom up to its bounding zero flux surface, so are the kinetic energy densities $G(\mathbf{r})$ and $K(\mathbf{r})$ and thus so is the average kinetic energy of the atom defined as (call the atom Ω)

$$T(\Omega) = \int_{\Omega} G(\mathbf{r}) d\mathbf{r} = \int_{\Omega} K(\mathbf{r}) d\mathbf{r} \quad (4)$$

This identity between the integrated values of the two kinetic energies, which of course is also obtained over all space, is a result of the zero flux boundary constraint since locally

$$K(\mathbf{r}) - G(\mathbf{r}) = -\frac{\hbar^2}{4m} \nabla^2 \rho(\mathbf{r}) \quad (5)$$

and thus

$$\begin{aligned} \int_{\Omega} K(\mathbf{r}) d\mathbf{r} - \int_{\Omega} G(\mathbf{r}) d\mathbf{r} &= -\frac{\hbar^2}{4m} \int_{\Omega} \nabla^2 \rho(\mathbf{r}) d\mathbf{r} \\ &= -\frac{\hbar^2}{4m} \int dS \nabla \rho \cdot \mathbf{n} = 0 \end{aligned} \quad (6)$$

We reasoned (in 1971) that if there was a virial theorem for an atom in a molecule then not only would the kinetic energy of the atom be transferable when its charge density was the same in two different molecules, so would its total energy, for by the virial theorem one has $E(\Omega) = -T(\Omega)$. Such a result would be interesting for a number of reasons: a) one would have a partitioning of E , the total energy of a molecule (including nuclear-nuclear and electron-electron repulsions) into a sum of spatially additive contributions,

$$E = -\sum_{\Omega} T(\Omega) = \sum_{\Omega} E(\Omega) \quad (7)$$

b) the potential energy contribution to the total energy of an atom would necessarily be defined as the virial of the forces exerted on the electron, the virial of the Ehrenfest force. (As discussed in more detail later, it is this definition of a potential energy that makes possible the spatial partitioning of potential energies of interactions such as nuclear-nuclear and electron-electron repulsions). c) [F]inally, the observation that the transferability of the charge density over an atom results in a transferable total energy of the atom is in complete accord with the theorem of Hohenberg and Kohn which states that E is a functional of ρ [12]. It would appear that the theorem is true not only for some total system, but also for an atom in a molecule, *i.e.* a quantum subsystem. Furthermore, the energy that exhibits this transferability is defined by the virial theorem

to be $E(\Omega) = T(\Omega) + V(\Omega)$, where the potential energy $V(\Omega)$ is the virial of the electronic forces. Only this definition of a potential energy (which as discussed below, contains the nuclear-nuclear repulsion energies and the virials of the net forces exerted on the nuclei) has the property of yielding a total energy that is unchanged when the charge density is transferable. Corresponding kinetic and potential energy densities can be defined and it is these densities, both the potential and as already noted above, the kinetic, that exhibit the property of transferability in parallel with that for the charge density itself. These are the energy densities of density functional theory and this is an observation, not an opinion. More about the parallelism between $\rho(\mathbf{r})$, $G(\mathbf{r})$ and $V(\mathbf{r})$ is given below after the quantum mechanical basis for all of this has been outlined.

Because of these observations (and how well they accounted for the fundamental chemical idea of atomic and group properties), I became convinced that it should be possible to obtain a definition of the atoms and their properties from quantum mechanics – that it should be possible to extend quantum mechanics to obtain a description of the average properties [of] an open subsystem of some total system and that the subsystem itself would be uniquely defined – because our observations applied only to a region bounded by a surface of zero flux in grad ρ . This has proved possible through a generalization of Schwinger's principle of stationary action.

You have probably seen the operational statement of this principle given in texts on field theory, that the variation in the system Lagrangian as caused by the action of some generator \hat{A} on the state function is given by

$$\delta \hat{L} [\hat{A}\Psi] = \frac{i}{\hbar} \langle [\hat{H}, \hat{A}] \rangle, \quad (8)$$

where

$$\delta \Psi = -i\varepsilon \hat{A}\Psi \quad (8')$$

(In the texts you read the principle is probably given in the operator representation, where the operators are varied but that is not important.) This statement can be generalized to a subsystem Ω of the total system if the subsystem is bounded by a surface through which the flux in the gradient vector of the charge density is zero. The generalized statement of the principle reads

$$\delta L [\hat{A}\Psi, \Omega] = \left(\frac{\varepsilon}{2} \right) \left\{ \frac{i}{\hbar} \langle \Psi | [\hat{H}, \hat{A}] | \Psi \rangle_{\Omega} + \text{complex conjugate} \right\} \quad (9)$$

The symbol $\langle \rangle_{\Omega}$ denotes a particular form of averaging. One integrates the coordinates of all the electrons but one over all

space [followed by a sum over both spins] and the coordinates of the remaining electron over the space of subsystem,

$$\langle \hat{A} \rangle_{\Omega} = \int_{\Omega} d\mathbf{r} \int d\tau' \Psi^* \hat{A} \Psi \quad (10)$$

This definition of a subsystem average is determined by the atomic statement of the principle of stationary action.

Just a brief word about the principle being unique to a subsystem bounded by a zero flux surface. In the variation of the Lagrangian, one must include a variation of the surface of the subsystem. This leads to the term

$$\int_{t_1}^{t_2} dt \int dS(\mathbf{r}) L(\mathbf{r}) \delta S(\mathbf{r}) \quad (11)$$

appearing in the general result. Its presence prevents any further progress in the general case and Schwinger's principle is not recovered in the general case. At the point of variation, where this term is obtained, the Lagrangian density of a many-particle system (including interactions between indistinguishable particles, a true many-body system) reduces to

$$L(\mathbf{r}) = -\frac{\hbar^2}{4m} \nabla^2 \rho(\mathbf{r}) \quad (12)$$

(see p. 76 of reprint B [11]) and the troublesome term may be replaced by the corresponding variations

$$\begin{aligned} \frac{\hbar^2}{4m} \int dS(\mathbf{r}) \nabla^2 \rho(\mathbf{r}) \delta S(\mathbf{r}) &= \delta \left\{ \frac{\hbar^2}{4m} \int_{\Omega} d\mathbf{r} \nabla^2 \rho(\mathbf{r}) \right\} \\ -\frac{\hbar^2}{4m} \int dS(\mathbf{r}) \int d\tau' [(\nabla \Psi^*) \delta \Psi + \Psi^* \nabla(\delta \Psi) + \nabla(\delta \Psi^*) \Psi + \delta \Psi^* \nabla \Psi] \cdot \mathbf{n}(\mathbf{r}) \end{aligned} \quad (13)$$

Demanding the variation of the first term on rhs [right hand side] vanish at every stage of the variation is mathematically equivalent to imposing the zero flux boundary condition on every trial density and this is how the zero flux surface condition enters.

The result is a great simplification in the variation of the Lagrangian – the remaining surface terms combine to yield an integral of the varied quantum mechanical current density. This physical result may be combined with the remaining terms to yield an expression free of all surface terms (a characteristic of the general statement of Schwinger's principle) and it leads to the final statement as given above, a statement which is the analogue of the all space result and which reduces to the all space result when the bounding surface is taken to infinity.

The two most important equations governing the mechanics of an atom in a molecule are obtained by setting the operator \hat{A} in the atomic statement of the principle of stationary action equal respectively to $\hat{\mathbf{p}}$, the momentum operator for an electron and to $\hat{\mathbf{r}} \cdot \hat{\mathbf{p}}$, the virial operator, $\hat{\mathbf{r}}$ being the electronic position operator. The former operator gives the Ehrenfest

force and thus yields the equation of motion for an atom in a molecule. The latter yields the atomic statement of the virial theorem and through it, a definition of the potential, kinetic and total electronic energies of an atom in a molecule. All of these properties are expressible in terms of the quantum mechanical stress tensor, a quantity introduced by Pauli. This tensor is totally determined by the one-density matrix. *Thus every property, including the potential energy, is expressible in terms of a corresponding three-dimensional density distribution which is then integrated over the atom to obtain its average value.* These atomic values, when summed over all the atoms in a molecule, yield the average values for the total molecule. This additivity of atomic properties is a necessary requirement for the existence of additivity schemes which result from the transferability of atomic properties between molecules as is observed for the energy and other properties.

It is to be stressed that only for a quantum subsystem can the theorems of quantum mechanics and in particular the virial theorem be derived variationally from the principle of stationary action. While one can partially integrate Heisenberg's equation of motion for the operator $\hat{\mathbf{r}} \cdot \hat{\mathbf{p}}$ over any arbitrarily defined region of space, this does not yield an expression which is the analogue of the virial theorem for the total system for two reasons: the kinetic energy is not uniquely defined for a subsystem with arbitrarily defined boundaries and the virial for an arbitrary subsystem contains a spurious contribution, either positive or negative in sign, arising from the nonvanishing of the integral of $(\hbar^2/4m) \nabla^2 \rho$. The vanishing of this integral and the unique definition of a kinetic energy for an atom are both consequences of the quantum boundary condition of zero flux. Thus only a quantum subsystem has a uniquely defined energy.

The quantum stress tensor is

$$\vec{\sigma}(\mathbf{r}) = \frac{\hbar^2}{4m} [(\nabla \nabla + \nabla' \nabla') - (\nabla \nabla' + \nabla' \nabla)] \Gamma^{(1)}(\mathbf{r}, \mathbf{r}') \Big|_{\mathbf{r}=\mathbf{r}'} \quad (14)$$

The equation for the Ehrenfest force is

$$\mathbf{F}(\Omega, t) = m \int_{\Omega} d\mathbf{r} \left(\frac{\partial \mathbf{J}(\mathbf{r})}{\partial t} \right) - \int dS(\mathbf{r}) \vec{\sigma}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) \quad (15)$$

and the corresponding differential statement or density expression obtained from the divergence equation satisfied by the energy-momentum tensor is

$$\mathbf{F}(\mathbf{r}, t) = m \frac{\partial \mathbf{J}(\mathbf{r})}{\partial t} - \nabla \cdot \vec{\sigma}(\mathbf{r}), \quad (16)$$

where

$$\mathbf{F}(\mathbf{r}, t) = \int d\tau' \Psi^* (-\nabla \hat{V}) \Psi \quad (17)$$

\hat{V} is the total potential energy operator and ∇ is the gradient operator for an electron of coordinate \mathbf{r} . ($\int d\tau'$ means integration over coordinates of all electrons but one [and summation over all spins]).

For a stationary state, the atomic statement of the virial theorem is

$$-2T(\Omega) = v(\Omega) \quad (18)$$

where the potential is defined as the virial of the Ehrenfest force, $-\mathbf{r} \cdot \nabla \cdot \vec{\sigma}$. It includes the virial of the forces acting over the surface of the atom.

$$v(\Omega) = v_b(\Omega) + v_s(\Omega)$$

$$= \int_{\Omega} d\mathbf{r} \int d\tau' (-\mathbf{r} \cdot \nabla \hat{V}) \Psi^* \Psi + \int dS(\mathbf{r}) \mathbf{r} \cdot \vec{\sigma}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) \quad (19)$$

The local expression of this law obtained from the divergence relationships is

$$-2G(\mathbf{r}) = -\mathbf{r} \cdot \nabla \cdot \vec{\sigma}(\mathbf{r}) + \nabla \cdot [\mathbf{r} \cdot \vec{\sigma}(\mathbf{r})] - \frac{\hbar^2}{4m} \nabla^2 \rho(\mathbf{r}) \quad (20)$$

Since the integral of $\nabla^2 \rho(\mathbf{r})$ over an atom vanishes, the integration of this local expression yields the atomic statement of the virial theorem. All energy densities and integrated values are expressible in terms of $\vec{\sigma}$.

$$v(\mathbf{r}) = -\mathbf{r} \cdot \nabla \cdot \vec{\sigma} + \nabla \cdot (\mathbf{r} \cdot \vec{\sigma}) = \text{Tr} \vec{\sigma}(\mathbf{r}) \quad (21)$$

and

$$K(\mathbf{r}) + G(\mathbf{r}) = -\text{Tr} \vec{\sigma}(\mathbf{r}) \quad (22)$$

where $\text{Tr} \vec{\sigma}(\mathbf{r})$ denotes the trace of $\vec{\sigma}$. Because of the atomic virial theorem, all of the following expressions integrate to the same total energy for an atom Ω or for the total system

$$\int_{\Omega} [K(\mathbf{r}) + v(\mathbf{r})] d\mathbf{r} = \frac{1}{2} \int_{\Omega} \text{Tr} \vec{\sigma}(\mathbf{r}) d\mathbf{r} = - \int_{\Omega} G(\mathbf{r}) d\mathbf{r} = E(\Omega) \quad (23)$$

When Ω equals all space the energy E is

$$E = \int \text{Tr} \vec{\sigma}(\mathbf{r}) d\mathbf{r} = T + v \quad (24)$$

This differs from the usual molecular energy W in that the virial v equals the average of the usual potential energy operator \hat{V} (which includes the nuclear-nuclear repulsions) plus the virial of the net force exerted on the nuclei

$$v = \langle \hat{V} \rangle + \sum_{\alpha} \mathbf{X}_{\alpha} \cdot \nabla_{\alpha} W \quad (25)$$

When the forces are zero – an equilibrium geometry, $v = \langle \hat{V} \rangle$ and $E = W$. For an isolated atom $v = \langle \hat{V} \rangle$.

Thus transferability of the one-density matrix over a spatial region bounded by a zero flux surface yields transferability of the stress tensor $\vec{\sigma}(\mathbf{r})$ (which in turn yields a transferable energy $E(\Omega)$ for the atom) and transferability of the charge density $\rho(\mathbf{r})$, the diagonal elements of the one-density matrix. It is only necessary that the properties of the one-matrix, $I^{(1)}(\mathbf{r}, \mathbf{r}')$ be transferable in the immediate neighbourhood of its diagonal elements $\mathbf{r} = \mathbf{r}'$ for the kinetic energy density to be transferable. We have shown that all of the information necessary for the definition of the charge and current densities and of the kinetic and potential energies are obtained from a Taylor series of expansion of $I^{(1)}(\mathbf{r}, \mathbf{r}')$ about a point $\mathbf{r} = \mathbf{r}'$ by retaining terms only up to second-order.

Transferability of group properties is not a consequence of a corresponding constancy in the orbitals or geminals that are used to construct the density matrices. By their very nature, orbitals and geminals extend over the total space of a system and even when chosen in some localized form will have “tails” that belong to different environments of the group in question as the group is transferred between systems. An atom on the other hand, can exhibit a transferability of form in the one-density matrix (in the neighbourhood of its diagonal elements) over its entire basin up to its atomic surface of zero flux sufficient to insure a change in energy between systems of less than one kcal/mole (less than 0.001 au). Atoms have no tails and what is most remarkable is that this consistency in their properties is obtained in spite of changes in their neighbouring fragments. This essential property of the chemical atom has its basis in the observation that an atom of theory responds only to changes in the *total (Ehrenfest) force* exerted on its charge distribution and not to changes in the individual contributions to this force, changes which are large even between closely related systems, be they members of a homologous series or chemically similar in structure. If it was not for this property of responding only to the total force, there would be no chemically recognizable atoms or functional groups.

One does not in general, encounter such near perfect examples of transferability. They simply serve to illustrate that the constancy in the total energy that is obtained when the charge density $\rho(\mathbf{r})$ is transferable is a consequence of the transferability of the stress tensor $\vec{\sigma}(\mathbf{r})$. This implies that the potential energy that is thus defined by a transferable $\rho(\mathbf{r})$ is necessarily the virial of the Ehrenfest force, $v(\mathbf{r})$ locally and $v(\Omega)$ over an atom.

That the potential is defined as the virial of the force on an electron is significant for there is no other way of obtaining a physically unique partitioning of potential energies of interaction. First of all, one cannot partition the Hamiltonian as this violates the indistinguishability of the electrons from the start and is therefore, physical unacceptable. It is the potential energy of interaction between two systems that is difficult to partition. How much of an energy of repulsion between two systems belongs to one and how much to the other? Physics does provide an answer to this problem. A force *is* local – the Ehrenfest force acting on an electron is the force at the

position of the electron. The virial of the force then gives a local potential energy. The virial of the Ehrenfest force for one electron gives the share of the total potential energy belonging to that electron. This gives in words the essential idea that is formally developed in the papers – a development which includes a proof that such a definition of the potential energy leads to a variational definition of the corresponding total energy.

I shall close with one final example of a chemical group that is essentially completely transferable both experimentally and theoretically – the methylene group of a saturated straight chain hydrocarbon. Professor Wiberg of Yale and my group have just completed a study of the atomic properties in hydrocarbon molecules and we have used the theory to identify the fragments that are responsible for the additivity of the energy in the normal alkanes and to find the physical origin of “strain energy” in small ring organic compounds [this study appeared the following year in Ref. [13]]. The two charge distributions shown in the figure are for the central methylene group (CH_2) in pentane and one of the two equivalent such groups in hexane. Their charge distributions are identical, their kinetic and total energies are identical to within better than 0.001 au (better than one kcal/mole which is also the experimental result), they have the same net charge and the same values for their multipole moments, they have the same correlation energy as calculated using the gradient corrected functional of Langreth, Mehl, Perdew and Hu and they have the same atomic volume as determined by the intersection of the zero flux interatomic surfaces for the group and the outer envelope of the charge density. This is the repeating methylene group whose contribution to the energy of a hydrocarbon was measured experimentally years ago by Rossini at NBS. The atoms of theory are indeed the atoms of chemistry. I find it most exciting, not only to be able to identify the atoms of chemistry in general, but to look at the individual examples that we find. Study these two charge distributions – they are proof of the theorem of Hohenberg and Kohn.

Sincerely yours,

Signed: Richard [See Figure 1]

R.F.W. Bader,
Professor of Chemistry
RFBW/ks

Acknowledgements The presenter thanks Professor Lou Massa for the careful reading of this manuscript and for approving its publication, Professor Tina Harriott (Mount Saint Vincent University) and Dr. Todd A. Keith (Semichem, Inc.) for their comments on the manuscript and helpful suggestions, and Ms. Carrie Armsworthy (Mount Saint Vincent University) for carefully transcribing the letter. Funding for this project was obtained from the Natural Sciences and Engineering Research Council of Canada (NSERC), Canada Foundation for Innovation (CFI), and Mount Saint Vincent University.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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