

ARTICLES

Stress, virial, and pressure in the theory of atoms in moleculesA. Martín Pendás^{a)}*Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, E-33006-Oviedo, Spain*

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The quantum theory of stress is developed within the atoms in molecules framework. The complete local stress field is introduced and integrated within atomic basins, and it is shown that the kinetic term gives rise to the atomic virial theorem. The role of the potential part of the stress field in the AIM theory is discussed, and its necessary consideration in order to define atomic pressures presented. These atomic pressures are shown to tend to the thermodynamic limit as the size of the system grows. A link between the AIM theory and the theory of electronic separability has also been found. A set of simple examples illustrates our results. © 2002 American Institute of Physics. [DOI: 10.1063/1.1484385]

I. INTRODUCTION

The virial theorem (VT) has played a prominent role in the development of molecular quantum mechanics, as it provides, together with the Hellmann–Feynman theorem (HFT), a bridging tool that connects the prevailing energetic point of view with the classical force concepts.¹ It is this connection that makes interpretations based on the VT particularly clear, being Slater's emblematic discussion of the chemical binding in diatomics a vivid example of it.² The one-particle nature of the virial operator was also soon recognized as one of the few clean roads to partition global properties in real space. Virial partitions were, indeed, one of the germs of the theory of atoms in molecules.³

All of the original derivations of the quantum VT considered unconfined systems, from the first by Born, Heisenberg, and Jordan⁴ using the Heisenberg equations of motion, to those by Fock⁵ through scaling and variational arguments, or the ones by Filkenstein⁶ and Slater⁷ using Schrödinger wave functions. Nevertheless, the neat correspondence between the classical and quantum VT's demanded a proper account of the quantum equivalent of wall forces, whose classical virial is the $3p\Omega$ term, Ω being the volume of the system. The failure of the initial formulations to incorporate these effects was first noticed by Cottrell and Paterson⁸ in Slater's derivation, and ascribed to a surface integral that vanishes upon extending the integration region to infinity. Similar surface contributions were found within the equations of motion framework (EOM) by Epstein,⁹ and by Srebrenik and Bader¹⁰ on recognizing the problems associated with the assumed hermiticity of the quantum mechanical operators in the derivation of the EOM expressions. Analogous problems are also encountered on generalizing the HFT. Actually, surface terms permeate all attempts of extending quantum mechanics to finite subsystems.

Over the years, several attempts were published trying to

demonstrate that the surface contributions were in fact equal to the classical $3p\Omega$ term, and, furthermore, that this pressure was equivalent to the thermodynamic pressure. This equivalence was finally presented by Marc and McMillan in an interesting review devoted to the VT.¹¹ These authors also gave very elegant expressions which combined the surface terms coming from the VT and the HFT into a unified formulation.

Infinite systems pose additional interpretive difficulties, as special care must be taken whenever a summation with indices running over the particles of the system appear. In these cases, one must approach the thermodynamic limit while maintaining the N/V ratio fixed. Fock's scaling arguments are, however, easily applied to show that the excess virial is $3p\Omega$. If periodic boundary conditions (PBC) are imposed, additional complications arise, since the simple formulation of the HFT theorem breaks, as Kleinman showed.¹² A long discussion about the proper form of the microscopic surface terms arose in the 1970s,^{13–15} and the initial expressions proposed by Liberman, which did only include kinetic terms, were progressively refined until a general consensus about the need of including potential terms was achieved. In the meantime, the computational methods in solid-state Physics had developed to the point that virial equations of state (VEOS), i.e., those obtained by finding pressures through the virial relation, $2T + V = 3p\Omega$, were starting to be used routinely. The success of the density functional theory (DFT) also generated a considerable amount of work devoted to examine the VT in the DFT frame.¹⁶ The introduction in 1984 of the local thermodynamic transcription of DFT by Ghosh, Berkowitz, and Parr¹⁷ was followed by a renewed interest that has led to a number of interesting local formulations of the VT.

Extensions of the VTs have also been routine. On the one hand, the hypervirial theorem (HVT) of Hirschfelder,¹⁸ whose generalization to systems made of several subsystems introduces surface terms that may be written as generalized

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operator dependent current densities.³ On the other hand, tensor theorems, like that of McLellan,¹⁹ which recover the VT as the trace of a stress tensor. The latter are formulations of the quantum mechanical theory of stress, which in local form is associated to one of the earliest physical interpretations of the Schrödinger equation. In 1926, Madelung²⁰ put forward a hydrodynamic analogy by writing the complex wave function in polar form. The resulting equations describe the classical hydrodynamics of a fluid characterized by a stress tensor derivable from Born's probability density, and give the force concept a fundamental role.²¹ Work along these lines has shown the intimate relation between this formulation and Bohmian mechanics, the quantum nature of matter introducing a quantum potential into otherwise classical-like physics.²² It has also introduced the quantum fluid dynamics (QFD) framework, widely used in nuclear physics,²³ in molecular quantum mechanics. This effort is associated, among others, to the names of Ghosh, Deb, and Bamzai,²⁴ who have derived microscopic stress tensors whose derivatives yield local force densities in real space that vanish for stationary states due to the cancellation of classical and quantum forces.

The global stress tensors of quantum systems were already considered by Schrödinger and Pauli,²⁵ and constitute the nucleus of the second part of Feynman's PhD thesis.²⁶ However, a form both amenable to calculation and directly relating the stress fields to the VT only appeared after the work of Nielsen and Martin.²⁷ Subsequent papers by Folland,²⁸ Needs,²⁹ Vanderbilt,³⁰ Ziesche, Gräfenstein, and Nielsen,³¹ and Gräfenstein and Ziesche,³² finally left the subject in a mature state.

From the chemical point of view, the theory of atoms in molecules (AIM) developed by Bader *et al.*³ provides a physically sounded theory of quantum subsystems, and has reconciled the empirical background of transferable atomic properties with the roots of quantum mechanics. It is very well known in molecular quantum mechanics and it is starting to be applied to condensed matter problems.³³ It is to be noticed that the set of atomic theorems derived over the years by Bader *et al.*³⁴ is large, and that it includes atomic Pauli stress tensors which are just the kinetic parts of the quantum mechanical stress field we shall derive. The Pauli stress tensor has been used by Bader and Austen³⁵ to propose an expression for subsystem pressures that lacks potential contributions. This expression is equivalent to that of Liberman¹³ for complete systems, and is subject to the same criticisms previously commented, though it is relatively easy to compute and may be a rather good approximation to the correct result in some circumstances. Moreover, one of the original supports of the theory was the regional virial theorem.¹⁰ However, since the modern theory of stress in quantum systems has been developed by condensed matter physicists, a full discussion of stress in the AIM context is lacking.

The purpose of this paper is to develop the quantum theory of stress within the AIM framework. The quantum theory of stress (QTS) provides us with the rigorous magnitudes to construct stress-related properties. The AIM theory allows us to partition the physical space into subsystems that

obey the quantum laws. These spatial subsystems are the atoms and functional groups of chemistry. Both theories interweave when the local QTS fields are examined within the AIM groups.

In this process we will interpret what is already known about the atomic virial theorem as the atomic theorem corresponding to the kinetic part of the complete atomic stress tensor. The equivalent result for the potential stress will be obtained and physically interpreted. This will give rise to several interesting connections between the physical partitions of the AIM theory and the electronic partitions coming from the theory of electronic separability (TES). This last framework was formulated by McWeeny³⁶ and Huzinaga³⁷ in a completely different context, being a means to simplify the electronic structure problem in systems where weakly correlated electronic groups exist. We will also present a consistent definition of pressure within the AIM theory that lacks the problems of the one presented in Ref. 35.

We will illustrate our results with some toy examples, like the exactly soluble homodiatom molecule, and we will also present some simple results on heterodiatomics. However, as several approximate implementations of the TES exist in the literature, including our own *ab initio* perturbed ion method (A/PI),³⁸ particularly suited to study ionic systems, qualitative conclusions about the behavior of atomic stresses and pressures in both molecular and condensed phase systems may be safely done.

The rest of the paper is organized as follows: First, and in order to guarantee that the argumentation is self-contained, we will briefly summarize the basic results of the QTS. Our presentation is based both on that of Ziesche, Gräfenstein, and Nielsen,³¹ for their use of reduced density matrices is particularly useful in our context, and on the original derivation by Nielsen and Martin.²⁷ Section III will be devoted to develop the QTS results in the AIM spirit, paying particular attention to those results that are already part of the common AIM background and to those that cannot be understood without the potential part of the stress tensor. Section IV will present some of our preliminary results on simple systems of academic interest. We will summarize our conclusions in Sec. V.

II. THE QUANTUM THEORY OF STRESS

A. Total stress and macroscopic stress

A system is in a stressed state if net forces are acting upon it. These forces may be internal, acting within it, or external, acting on its surface. We are interested here in the stress exerted by external influences. For stationary states, Nielsen and Martin²⁷ (NM) showed that essentially the same scaling-variational argument used by Fock⁵ in his derivation of the virial theorem could be used with a general homogeneous scaling applied to the coordinates of all particles. Let

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + V_{\text{int}} + V_{\text{ext}} \quad (1)$$

be the Hamiltonian of our system, where V_{int} is the potential of the internal interactions, V_{ext} is the potential that is producing the stressed state, and i runs over all particles, nuclei,

and electrons. Let us also suppose that the Born–Oppenheimer approximation is valid. If we subject all the particles of the system to an infinitesimal homogeneous scaling defined by a symmetric strain tensor $\vec{\epsilon}$, $\mathbf{r}' = \mathbf{r} + \vec{\epsilon}\mathbf{r}$, then the properly normalized scaled wave function turns out to be $\Psi_{\epsilon}(\mathbf{r}) = \det(\vec{\mathbb{1}} + \vec{\epsilon})^{-1/2} \Psi((\vec{\mathbb{1}} + \vec{\epsilon})^{-1}\mathbf{r})$. Requiring that the energy expectation value for this scaled state be stationary with respect to variations of the independent components of the strain tensor leads to

$$\sum_i \langle \Psi | \frac{\mathbf{p}_i \otimes \mathbf{p}_i}{m_i} - \nabla_i (V_{\text{int}} + V_{\text{ext}}) \otimes \mathbf{r}_i | \Psi \rangle = 0. \quad (2)$$

Identifying the stress due to the external forces as

$$\vec{\Sigma} = - \sum_i \langle \Psi | \nabla_i V_{\text{ext}} \otimes \mathbf{r}_i | \Psi \rangle. \quad (3)$$

The NM stress theorem read as

$$\begin{aligned} \vec{\Sigma} &= \vec{\Sigma}_k + \vec{\Sigma}_p, \\ \vec{\Sigma}_k &= - \sum_i \langle \Psi | \frac{\mathbf{p}_i \otimes \mathbf{p}_i}{m_i} | \Psi \rangle, \\ \vec{\Sigma}_p &= + \sum_i \langle \Psi | \nabla_i V_{\text{int}} \otimes \mathbf{r}_i | \Psi \rangle, \end{aligned} \quad (4)$$

where the total kinetic, $\vec{\Sigma}_k$, and potential, $\vec{\Sigma}_p$, stresses have also been introduced. It is to be noticed that the magnitudes here defined are total stresses, or energetic quantities. In macroscopic systems, where volumes are well defined, it is common to introduce stresses per unit volume, $\vec{\sigma}$, with dimensions of pressure. By realizing that the trace of a dyadic product is a scalar product, the negative trace of Eq. (4) is the virial theorem. In macroscopic systems, the right-hand side of Eq. (3) may be obtained explicitly,²⁷ turning out to be $-3p\Omega$.

As NM clearly pointed out, a stressed macroscopic system is never modeled by imposing external potentials that warrant the final stressed state of interest. On the contrary, one obtains the ground state of an isolated but constrained system. For example, by fixing the strain, the nuclear positions, or the volume. This view solves the problem posed by infinite crystals modeled with PBCs. The latter lead to stressed states with no internal forces and without easily detectable external ones. Minimization of an energy expectation value using a Lagrange multiplier per independent constraint is then equivalent to obtain the conjugate forces of constraint. In the case of fixed total volume, the conjugate force is the pressure (minus the derivative of the energy expectation with respect to the volume), and the Lagrangian functional, $F = \langle H \rangle + p\Omega$. An isotropic scaling of the coordinates by a factor λ , $\mathbf{r}' = \lambda\mathbf{r}$, gives a scaled functional,

$$F_{\lambda} = \lambda^{-2} \langle T \rangle + \langle \Psi_{\lambda} | V_{\text{int}} | \Psi_{\lambda} \rangle + \lambda^3 p\Omega, \quad (5)$$

which is stationary with respect to λ at $\lambda = 1$ if

$$\left. \frac{dF_{\lambda}}{d\lambda} \right|_{\lambda=1} = 0 = -2 \langle T \rangle + \sum_i \langle \Psi | \mathbf{r}_i \cdot \nabla_i V_{\text{int}} | \Psi \rangle + 3p\Omega. \quad (6)$$

This argument clearly shows that the $3p\Omega$ term may be equally identified with the virial of the external forces [Eq. (3)] that generate the stressed state, or with the virial of the forces of constraint if the external forces are simulated by imposing constraints. Analogously, the excess virial in Slater’s classical derivation² may also be understood as the virial of the forces that maintain a constrained nuclear configuration, as can be easily shown by the Lagrangian multiplier’s method just introduced.

B. Microscopic stress

At the microscopic level, a theory of stress is defined in analogy with classical elasticity. In this way, a stress density $\vec{\sigma}(\mathbf{r})$ is associated to each point of real space such that its tensor divergence is the (microscopic) force density field:

$$\nabla \cdot \vec{\sigma}(\mathbf{r}) = \mathbf{f}_{\text{tot}}(\mathbf{r}). \quad (7)$$

As it is clear from this definition, microscopic stress fields are not unique, and arbitrary divergenceless tensor fields may be added to them. This fact was already noticed by Feynman,²⁶ and has been the source of continuous discussion through the years. In the case of Coulombic systems, Maxwell’s theory of electromagnetic stress provides a possible solution to the form of the potential stress field. This is accompanied by a rich classical interpretation.³⁹ A general solution, valid for arbitrary potentials, has also been proposed by Kugler.⁴⁰ Folland²⁸ has argued that the expressions found using the EOM method, which coincide with Maxwell’s form, should uniquely represent the dynamics of a system. Maxwell stresses have also been used by Ghosh *et al.* in their molecular extension of QFD. Anyway, an intrinsic arbitrariness in the stress fields exists,⁴¹ and it is a matter of convenience or interpretive power what should guide us to choose a particular form for them.

Following Ziesche, Gräfenstein, and Nielsen³¹ (ZGN), let us introduce reduced first and second order density operators for both the nuclear, $\rho_n^1(\mathbf{r}), \rho_n^2(\mathbf{r}_1, \mathbf{r}_2)$, and electron fields, $\rho_e^1(\mathbf{r}), \rho_e^2(\mathbf{r}_1, \mathbf{r}_2)$. Let us also use roman indices for electron coordinates and Greek indices together with capital letters for nuclear ones. Only Coulombic interactions will be considered in the following. Within the clamped nuclei approximation, the nuclear density operators adopt classical expressions,

$$\rho_n^1(\mathbf{r}) = \sum_{\alpha} Z_{\alpha} \delta(\mathbf{r} - \mathbf{R}_{\alpha}), \quad (8)$$

$$\rho_n^2(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\alpha \neq \beta} Z_{\alpha} Z_{\beta} \delta(\mathbf{r}_1 - \mathbf{R}_{\alpha}) \delta(\mathbf{r}_2 - \mathbf{R}_{\beta}).$$

The electronic densities, on the contrary, are quantum mechanical in nature, and are supposed to emerge from an adequate solution of the quantum equations of motion. With this compact notation, a total pair density operators may be introduced such that the total potential operator acquires a very simple real-space structure,

$$v(\mathbf{r}_1, \mathbf{r}_2) = \rho_n^2(\mathbf{r}_1, \mathbf{r}_2) - \rho_n^1(\mathbf{r}_1)\rho_e^1(\mathbf{r}_2) - \rho_e^1(\mathbf{r}_1)\rho_n^1(\mathbf{r}_2) + \rho_e^2(\mathbf{r}_1, \mathbf{r}_2), \quad (9)$$

$$V = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 v(\mathbf{r}_1, \mathbf{r}_2) \frac{1}{r_{12}}.$$

With these definitions, it is easy to show that the electromagnetic force density $\mathbf{f}_{\text{el}}(\mathbf{r})$ may be written as

$$\mathbf{f}_{\text{el}}(\mathbf{r}) = \mathbf{f}_e(\mathbf{r}) + \mathbf{f}_n(\mathbf{r}),$$

$$\mathbf{f}_e(\mathbf{r}) = -\rho_e^1(\mathbf{r})\mathbf{E}_n(\mathbf{r}) + \int d\mathbf{r}_2 \rho_e^2(\mathbf{r}, \mathbf{r}_2) \frac{\mathbf{r} - \mathbf{r}_2}{|\mathbf{r} - \mathbf{r}_2|^3}, \quad (10)$$

$$\mathbf{f}_n(\mathbf{r}) = +\rho_n^1(\mathbf{r})\mathbf{E}_e(\mathbf{r}) + \int d\mathbf{r}_2 \rho_n^2(\mathbf{r}, \mathbf{r}_2) \frac{\mathbf{r} - \mathbf{r}_2}{|\mathbf{r} - \mathbf{r}_2|^3},$$

where $\mathbf{E}_e(\mathbf{r})$ and $\mathbf{E}_n(\mathbf{r})$ are the electric fields created by electrons and nuclei at point \mathbf{r} , respectively. The \mathbf{f}_e and \mathbf{f}_n fields have direct interpretations as the electrostatic force densities acting on electrons and nuclei, and are consequently known as the Ehrenfest and the Hellmann–Feynman force densities, respectively. Notice that the nuclear force density field may be written as

$$\mathbf{f}_n(\mathbf{r}) = \sum_{\alpha} \mathbf{F}_{\alpha} \delta(\mathbf{r} - \mathbf{R}_{\alpha}), \quad (11)$$

where \mathbf{F}_{α} is the total force exerted on nucleus α . From these expressions, a Maxwellian potential stress field may be derived,

$$\tilde{\sigma}_p(\mathbf{r}) = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 v(\mathbf{r}_1, \mathbf{r}_2) \frac{1}{4\pi} \left(\frac{\mathbf{r} - \mathbf{r}_1}{|\mathbf{r} - \mathbf{r}_1|^3} \otimes \frac{\mathbf{r} - \mathbf{r}_2}{|\mathbf{r} - \mathbf{r}_2|^3} + \frac{\mathbf{r} - \mathbf{r}_2}{|\mathbf{r} - \mathbf{r}_2|^3} \otimes \frac{\mathbf{r} - \mathbf{r}_1}{|\mathbf{r} - \mathbf{r}_1|^3} - \frac{\mathbf{r} - \mathbf{r}_1}{|\mathbf{r} - \mathbf{r}_1|^3} \cdot \frac{\mathbf{r} - \mathbf{r}_2}{|\mathbf{r} - \mathbf{r}_2|^3} \right), \quad (12)$$

whose divergence is the electromagnetic force density,

$$\nabla \cdot \tilde{\sigma}_p(\mathbf{r}) = \mathbf{f}_{\text{el}}(\mathbf{r}), \quad (13)$$

and which integrates to the total potential stress of Eq. (4).

The total force field is made up of an electrostatic term, that we have just considered, and a *quantum* force component, $\mathbf{f}_q(\mathbf{r})$. This is minus the gradient of the quantum potential of Bohmian mechanics, and was shown by Schrödinger and Pauli^{3,25} to come from the divergence of the kinetic or Pauli stress field. In the Born–Oppenheimer case, this is purely electronic:

$$\tilde{\sigma}_k = \frac{\hbar^2}{4m_e} (\nabla' - \nabla) \otimes (\nabla' - \nabla) \rho_e^1(\mathbf{r}; \mathbf{r}')|_{\mathbf{r}=\mathbf{r}'},$$

$$\nabla \cdot \tilde{\sigma}_k(\mathbf{r}) = \mathbf{f}_q(\mathbf{r}). \quad (14)$$

Notice that we have used here a nondiagonal first order density operator. The tensor just defined integrates to the total kinetic stress of Eq. (4). Actually, in the single particle case it is very easy to show that

$$m \partial \mathbf{j} / \partial t = \nabla \cdot \tilde{\sigma}_k + \Psi^* (-\nabla V) \Psi, \quad (15)$$

where \mathbf{j} is the particle's current density. This is also the Euler equation of QFD,²⁴ and the total, quantum (kinetic), and electrostatic force terms can be easily identified in it.

In stationary states, which are the only ones we are going to consider, the quantum force density balances the electrostatic one, and the total force density vanishes. By means of either direct evaluation of the divergence of the Pauli stress tensor, or through a many electron generalization of the above Euler equation, the quantum force density turns out to be minus the electron force density:

$$\nabla \cdot \tilde{\sigma}_k(\mathbf{r}) = \mathbf{f}_q(\mathbf{r}) = -\mathbf{f}_e(\mathbf{r}). \quad (16)$$

This relation shows us that the total stress field, $\tilde{\sigma}(\mathbf{r}) = \tilde{\sigma}_k(\mathbf{r}) + \tilde{\sigma}_p(\mathbf{r})$ satisfies the following relation:

$$\nabla \cdot \tilde{\sigma}(\mathbf{r}) = \mathbf{f}_n(\mathbf{r}). \quad (17)$$

This central result has a clear interpretation. The total stress field is only related to the forces on the nuclei, which under the clamped nuclei hypothesis may only differ from zero if external constraints are imposed. The persuasive arguments of the previous subsection show that these forces should exactly compensate with those coming from the external potentials that force the stressed state.

In analogy with classical thinking, we introduce a local pressure field,

$$p(\mathbf{r}) = -\frac{1}{3} \text{Tr} \tilde{\sigma}(\mathbf{r}), \quad (18)$$

which integrates out to the macroscopic $p\Omega$ product (just a scaled total stress). Let us notice that either in a global or in a local formulation, pressures include both kinetic and potential terms. Ignoring the potential terms has been one of the most common sources of theoretical problems in the development of the QTS since the kinetic surface integrals of Liberman,¹³ a heritage that Bader and Austen,³⁵ introduced in their AIM subsystem pressures. This will be further commented on below.

A note of caution is necessary at this point. Neither the partition of the stress field that we have made here, nor that of the force density, are the only ones available in the literature. In fact, when these results are applied in the DFT context, it is usually to combine the kinetic stress field and the one coming from the exchange–correlation functionals into a *quantum* stress density, leaving the classical electrostatic stress alone. The quantum mechanical contributions to the potential stress are hidden in our presentation in the structure of ρ_e^2 .

III. THE THEORY OF ATOMS IN MOLECULES AND THE MICROSCOPIC STRESS

The AIM theory developed by Bader *et al.*³ has become a rigorous quantum mechanical theory of subsystems rooted in one of the most general formulations of the quantum theory: Schwinger's principle of stationary action.⁴² The theory has shown that a quantum system may be partitioned into subsystems that obey the general quantum laws. These subsystems are unique objects defined in the physical space, and any observable of the whole system (or global observables) may be obtained as a sum over the subsystems of

well-defined contributions due to each group. Of paramount relevance, the AIM subsystems coincide with the atoms and functional groups of chemistry.

A. Relation to QTS

On examining the hermiticity problem associated to the use of operators in finite subsystems, Epstein⁹ and Srebrenik and Bader¹⁰ have shown that Hirschfelder's hypervirial theorem adopts the following generalized form:

$$\frac{i}{\hbar} \langle [H, A] \rangle_{\Omega} + \text{c.c.} = \oint_{\partial\Omega} \mathbf{j}_A \cdot d\mathbf{S} + \text{c.c.}, \quad (19)$$

where Ω is the integration region bounded by the $\partial\Omega$ surface, and A and \mathbf{j}_A are, respectively, an arbitrary operator and its current density with respect to the electron field, $\mathbf{j}_A = (i\hbar/2m_e)\{\Psi^*(\vec{\nabla} - \nabla)A\Psi\}$. Only when the subsystem is surrounded by a local zero flux surface, $\nabla\rho_e^1(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0$, \mathbf{n} being an exterior normal vector, does a variational statement of the hypervirial theorem [Eq. (19)] follow.^{43,44} Several choices for the arbitrary A give rise to the different atomic theorems that have been put forward over the years.³⁴ Two of them are of particular interest here, the atomic force law and the atomic virial theorem.

The first one is obtained by setting $A = \mathbf{p}$, the linear momentum operator of an arbitrary given electron. This leads to

$$\begin{aligned} \mathbf{F}_e(\Omega) &= \int_{\Omega} d\mathbf{r} (-\nabla V)\rho_e^1(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} \\ &= - \oint_{\partial\Omega} \vec{\sigma}_k \cdot d\mathbf{S} = \int_{\Omega} d\mathbf{r} (-\nabla \cdot \vec{\sigma}_k), \end{aligned} \quad (20)$$

which gives the total Ehrenfest force exerted on the electrons of the region Ω , and that may also be obtained by integrating our Eq. (16). The complete force field in unconstrained molecular systems, null at every point by the cancellation of \mathbf{f}_q and \mathbf{f}_{e1} , is completely specified by the divergence of the Pauli stress tensor, determined in turn by the first-order electronic density matrix.

Similarly, using $A = \mathbf{r} \cdot \mathbf{p}$ yields

$$2T(\Omega) + \mathcal{V}_b(\Omega) = - \oint_{\partial\Omega} \vec{\sigma}_k \cdot \mathbf{r} \cdot d\mathbf{S}, \quad (21)$$

where the basin virial, \mathcal{V}_b , defined as

$$\begin{aligned} \mathcal{V}_b(\Omega) &= \int_{\Omega} d\mathbf{r} (-\mathbf{r} \cdot \nabla V)\rho_e^1(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} \\ &= \int_{\Omega} d\mathbf{r} (-\mathbf{r} \cdot \nabla \cdot \vec{\sigma}_k), \end{aligned} \quad (22)$$

is identified with the atomic average of the virial of the Ehrenfest force. The surface integral in Eq. (21) is also called the surface virial, $\mathcal{V}_s(\Omega)$, so the above equation can be written as $2T(\Omega) + \mathcal{V}_b(\Omega) + \mathcal{V}_s(\Omega) = 0$. This relation may also be obtained from Eq. (16) through the use of the tensor and vector identities,

$$\begin{aligned} \vec{\alpha} &= \nabla \cdot (\vec{\alpha} \otimes \mathbf{r}) - (\nabla \cdot \vec{\alpha}) \otimes \mathbf{r}, \\ \text{Tr} \vec{\alpha} &= \nabla \cdot (\vec{\alpha} \cdot \mathbf{r}) - (\nabla \cdot \vec{\alpha}) \cdot \mathbf{r}, \end{aligned} \quad (23)$$

after recognizing the atomic integral of the trace of the kinetic stress tensor as minus twice the atomic kinetic energy. This is clearly shown in the AIM framework, for $\text{Tr} \vec{\sigma}_k = -2G + (\hbar^2/4m_e)\nabla^2\rho_e^1$, where G is the positive definite kinetic energy density. The indefiniteness problems of the kinetic densities are avoided by the zero flux condition.

Actually, the original variational derivation of the atomic virial theorem^{10,43} imposes the vanishing of the surface virial as a necessary condition, in such a way that $2T(\Omega) + \mathcal{V}_b(\Omega) = 0$. This demand can be satisfied, as both the basin and the surface atomic virials depend on the choice of reference frame. It is not difficult to obtain an explicit decomposition of the basin virial into easy to identify components:¹⁰

$$\mathcal{V}_b(\Omega) = V_{en}(\Omega) + V_n(\Omega) + V_{ee}(\Omega) + V(\Omega, \Omega'), \quad (24a)$$

$$V_{en}(\Omega) = - \sum_{\alpha} Z_{\alpha} \int_{\Omega} d\mathbf{r} \frac{\rho_e^1(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_{\alpha}|}, \quad (24b)$$

$$V_n(\Omega) = \sum_{\alpha} \mathbf{R}_{\alpha} \cdot \mathbf{f}_{\alpha}(\Omega), \quad (24c)$$

$$\mathbf{f}_{\alpha}(\Omega) = -Z_{\alpha} \int_{\Omega} d\mathbf{r} \rho_e^1(\mathbf{r}) \frac{\mathbf{r} - \mathbf{R}_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|^3}, \quad (24d)$$

$$V_{ee}(\Omega) = \frac{1}{2} \int_{\Omega} d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\rho_e^2(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}, \quad (24e)$$

$$\begin{aligned} V(\Omega, \Omega') &= \frac{1}{2} \int_{\Omega} d\mathbf{r}_1 \int_{\Omega'} d\mathbf{r}_2 (\mathbf{r}_2 \cdot \nabla_2 - \mathbf{r}_1 \cdot \nabla_1) \\ &\quad \times r_{12}^{-1} \rho_e^2(\mathbf{r}_1, \mathbf{r}_2). \end{aligned} \quad (24f)$$

In these expressions, V_{en} is identified with the interaction of all nuclei with the electrons in Ω ; V_{ee} is the repulsion of the electrons in Ω with themselves, plus half the repulsion of these electrons with those in the rest of the system, Ω' ; \mathbf{f}_{α} is the force exerted by nucleus α on all the electrons in Ω ; and $V(\Omega, \Omega')$ is a measure of the degree of sharing in the *electronic* interaction between the subsystem under consideration and the rest of the system. Only the last term and that involving the nuclear coordinates in Eq. (24f) are origin dependent, and this dependence was found to come from the arbitrary choice of scaling origin in the variational procedure. It was also numerically shown that in the reference frame that makes the surface virial vanish the $V(\Omega, \Omega')$ term is also null.⁴³ In this case, the atomic virial theorem reads as $-2T(\Omega) = V_{en}(\Omega) + V_n(\Omega) + V_{ee}(\Omega)$, a form which will be useful in what follows.

B. QTS atomic theorems

All the above arguments teach us that the QTS applied in the AIM framework recovers the fundamental force related theorems obtained by Bader and co-workers. We believe that the variational generality of the AIM theory thus enriches the QTS viewpoint, and that in the same way, the clear image of the microscopic force fields given by the QTS may help clarify some particular AIM results that have been surrounded by some interpretive problems.

Let us then use Eqs. (13), (16), and (17), together with the tensorial relations in Eq. (23), to transform and integrate over an atomic basin the several stress fields defined. We can write

$$-\tilde{\Sigma}_k(\Omega) = - \int_{\Omega} d\mathbf{r} \tilde{\sigma}_k = - \int_{\Omega} d\mathbf{r} \mathbf{f}_e \otimes \mathbf{r} - \oint_{\partial\Omega} \tilde{\sigma}_k \otimes \mathbf{r} \cdot d\mathbf{S}, \quad (25a)$$

$$-\tilde{\Sigma}_p(\Omega) = - \int_{\Omega} d\mathbf{r} \tilde{\sigma}_p = + \int_{\Omega} d\mathbf{r} \mathbf{f}_{el} \otimes \mathbf{r} - \oint_{\partial\Omega} \tilde{\sigma}_p \otimes \mathbf{r} \cdot d\mathbf{S}, \quad (25b)$$

$$-\tilde{\Sigma}(\Omega) = - \int_{\Omega} d\mathbf{r} \tilde{\sigma}(\mathbf{r}) = + \int_{\Omega} d\mathbf{r} \mathbf{f}_n \otimes \mathbf{r} - \oint_{\partial\Omega} \tilde{\sigma} \otimes \mathbf{r} \cdot d\mathbf{S}, \quad (25c)$$

relations that define the kinetic, potential, and total atomic stresses, respectively. By taking the trace of these tensor formulas, and after some simple manipulations, we can transform them into

$$2T(\Omega) = -\mathcal{V}_b(\Omega) - \oint_{\partial\Omega} \tilde{\sigma}_k \cdot \mathbf{r} \cdot d\mathbf{S}, \quad (26a)$$

$$V(\Omega) = \sum_{\alpha \in \Omega} \mathbf{R}_{\alpha} \cdot \mathbf{F}_{\alpha} + \mathcal{V}_b(\Omega) - \oint_{\partial\Omega} \tilde{\sigma}_p \cdot \mathbf{r} \cdot d\mathbf{S}, \quad (26b)$$

$$\mathcal{V}(\Omega) = \sum_{\alpha \in \Omega} \mathbf{R}_{\alpha} \cdot \mathbf{F}_{\alpha} - \oint_{\partial\Omega} \tilde{\sigma} \cdot \mathbf{r} \cdot d\mathbf{S}, \quad (26c)$$

where we have defined the atomic potential, $V(\Omega)$, and the atomic virial relation, $\mathcal{V}(\Omega)$.

Equation (26a) is nothing but a statement of the atomic virial theorem that we have commented on the last subsection, Eq. (21). The atomic virial theorem of the standard AIM theory is then recovered in our development of the QTS in the AIM framework. From our present point of view, it is a kinetic theorem. Since in the clamped nuclei approximation all kinetic terms are electronic, it is also an electronic relation. Equation (26b) is a potential theorem. It contains the virial of the electron and nuclear force densities integrated over the atomic basin, plus the corresponding surface term. The nuclear component has usually just one term, as only one nucleus commonly lies inside an atomic basin. In cases where a pseudoatom appears,⁴⁵ however, this term will be present. Finally, Eq. (26c) is a virial relation. Let us notice that all the terms on the right hand sides of the above expressions are origin dependent, while the left hand sides are not.

The atomic energetic quantities of Eq. (26) clearly add up to the global molecular (or macroscopic) properties, and in our opinion enrich the interpretation of the atomic theorems.

In the first place, it is important to obtain an explicit expression for the atomic potential, $V(\Omega)$, in the spirit of Eq. (24). To do this, let us use the trace of Eq. (25b) and directly integrate $\mathbf{f}_{el} \cdot \mathbf{r}$ over an atomic basin. After taking the divergence of Eq. (12), the first term in our expression for $V(\Omega)$ becomes

$$\begin{aligned} \int_{\Omega} d\mathbf{r} \mathbf{f}_{el} \cdot \mathbf{r} &= \int_{\Omega} d\mathbf{r} \nabla \cdot \tilde{\sigma}_p \cdot \mathbf{r} \\ &= \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 v(\mathbf{r}_1, \mathbf{r}_2) \\ &\quad \times \int_{\Omega} d\mathbf{r} \left(\delta(\mathbf{r} - \mathbf{r}_1) \frac{\mathbf{r} - \mathbf{r}_2}{|\mathbf{r} - \mathbf{r}_2|^3} \cdot \mathbf{r} \right. \\ &\quad \left. + \delta(\mathbf{r} - \mathbf{r}_1) \frac{\mathbf{r} - \mathbf{r}_2}{|\mathbf{r} - \mathbf{r}_1|^3} \cdot \mathbf{r} \right). \end{aligned} \quad (27)$$

When Ω extends to infinity, one can make profit of the identity

$$\mathbf{r}_1 \cdot \frac{\mathbf{r}_1 - \mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|^3} + \mathbf{r}_2 \cdot \frac{\mathbf{r}_2 - \mathbf{r}_1}{|\mathbf{r}_1 - \mathbf{r}_2|^3} = \frac{1}{r_{12}}, \quad (28)$$

to immediately transform Eq. (27) into the total potential of the system using Eq. (9). In our case, however, we write the last integral of Eq. (27) as

$$\mathbf{r}_1 \cdot \frac{\mathbf{r}_1 - \mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|^3} \delta_{\mathbf{r}_1, \Omega} + \mathbf{r}_2 \cdot \frac{\mathbf{r}_2 - \mathbf{r}_1}{|\mathbf{r}_2 - \mathbf{r}_1|^3} \delta_{\mathbf{r}_2, \Omega}, \quad (29)$$

where $\delta_{\mathbf{r}, \Omega} = 1$ if $\mathbf{r} \in \Omega$, and zero otherwise. Four cases have to be considered according to the position of the $\mathbf{r}_1, \mathbf{r}_2$ coordinates with respect to the Ω region, and Eq. (27) splits into four terms. When both vectors lie outside Ω , Eq. (29) vanishes. This is a clearly desirable property, since there should be no contribution to the atomic potential from pairs of particles that are interacting outside our region. When both coordinates lie inside Ω , Eq. (28) can be used to obtain the net atomic potential,

$$V_{\text{net}}^{\Omega, \Omega} = \frac{1}{2} \int_{\Omega} d\mathbf{r}_1 \int_{\Omega} d\mathbf{r}_2 v(\mathbf{r}_1, \mathbf{r}_2) \frac{1}{r_{12}}, \quad (30)$$

i.e., the potential contribution coming from interactions between pairs of particles that lie inside the Ω region. The two remaining terms, with one particle inside, and one particle outside Ω (Ω'), are interaction potentials. They are identical, given the exchange symmetry of the total pair density function v , and add up to

$$I = \int_{\Omega} d\mathbf{r}_1 \int_{\Omega'} d\mathbf{r}_2 v(\mathbf{r}_1, \mathbf{r}_2) \frac{\mathbf{r}_1 - \mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|^3} \cdot \mathbf{r}_1.$$

Using once again Eq. (28), a symmetric expression arises:

$$\begin{aligned} I &= \frac{1}{2} \int_{\Omega} d\mathbf{r}_1 \int_{\Omega'} d\mathbf{r}_2 v(\mathbf{r}_1, \mathbf{r}_2) r_{12}^{-1} \\ &\quad + \frac{1}{2} \int_{\Omega} d\mathbf{r}_1 \int_{\Omega'} d\mathbf{r}_2 v(\mathbf{r}_1, \mathbf{r}_2) (\mathbf{r}_2 \cdot \nabla_2 - \mathbf{r}_1 \cdot \nabla_1) r_{12}^{-1}. \end{aligned} \quad (31)$$

The first term in this formula is recognized as half the interaction energy of the Ω region with its environment Ω' , $V_{\text{int}}^{\Omega, \Omega'}$. The second one is the generalization of the $V(\Omega, \Omega')$ contribution in Eq. (24) to the total pair density operator. Adding all the pieces together, we get

$$V(\Omega) = V_{\text{net}}^{\Omega, \Omega} + \frac{1}{2} V_{\text{int}}^{\Omega, \Omega'} + \frac{1}{2} \int_{\Omega} d\mathbf{r}_1 \int_{\Omega'} d\mathbf{r}_2 v(\mathbf{r}_1, \mathbf{r}_2) \times (\mathbf{r}_2 \cdot \nabla_2 - \mathbf{r}_1 \cdot \nabla_1) r_{12}^{-1} - \oint_{\partial\Omega} \vec{\sigma}_p \cdot \mathbf{r} \cdot d\mathbf{S}. \quad (32)$$

The notation above tries to avoid a possible confusion between the previously used $V(\Omega, \Omega')$ term, and the newly defined $V_{\text{int}}^{\Omega, \Omega'}$.

An inspection of the last expression shows that all origin dependent terms are found in the last two terms of Eq. (32), and that the net and interaction atomic potentials are OI. Let us emphasize that the full atomic potential is also an OI magnitude. This situation is different from that found in the kinetic atomic stress, Eq. (24), for in that case the potential term (or basin virial) did contain an origin dependent contribution in $V_n(\Omega)$. It may be traced back to the need of nuclear virials in order to obtain the potential from the virial of the forces.

There exist a number of hints, both numerical and theoretical, pointing towards a cancellation of the origin dependent terms in Eq. (32). At this point we are in a similar position to that faced in the original derivations of the atomic virial theorem. For example, ZGN (Ref. 31) were able to show that this is true when integrating a periodic cell. We will recover this argument later, but for the time being, let us notice that in the unit cell case, the cancellation guarantees that $V(\Omega)$ takes the correct form,

$$V(\Omega = \text{unit cell}) = V_{\text{net}}^{\Omega, \Omega} + \frac{1}{2} V_{\text{int}}^{\Omega, \Omega'} = V,$$

where V is the total potential per unit cell. In homonuclear diatomic molecules, on the other hand, the reference frame centered at the midpoint of the internuclear axis annihilates both origin dependent contributions simultaneously. Moreover, in simple heterodiatomics we also have numerical evidence of the cancellation. We will accept this results as of general validity in what follows.

The third identities in Eqs. (25) and (26) are particularly neat statements of the virial theorem. In unconstrained molecular systems, the force exerted on any nucleus vanishes, so one can write

$$-\vec{\Sigma}(\Omega) = - \oint_{\partial\Omega} \vec{\sigma} \otimes \mathbf{r} \cdot d\mathbf{S}, \quad (33)$$

$$\mathcal{V}(\Omega) = - \oint_{\partial\Omega} \vec{\sigma} \cdot \mathbf{r} \cdot d\mathbf{S},$$

and the total atomic stress adopts a purely classical expression. The surface term may be identified with the virial of the wall forces that would maintain an atomic subsystem, suddenly isolated from its molecular environment, in internal equilibrium. Let us notice that Eqs. (33) are manifestly origin independent (OI), and that the apparent origin dependence of the surface integral vanishes upon taking into account that $\nabla \cdot \vec{\sigma} = 0$ in Ω . Moreover, if we assume that the cancellation of the second and third lines of Eq. (32) holds, then the surface integral may be written in terms of linear momentum fluxes (coming from the kinetic part of the stress tensor), and interactions among particles *inside* Ω and particles *outside*

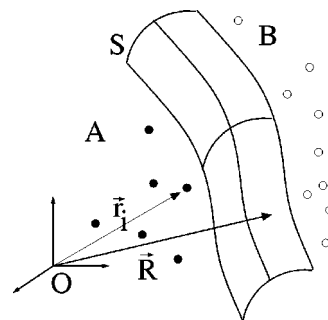


FIG. 1. Partition of a system of classical particles commented in the text into two subsystems separated by a surface S . \mathbf{R} is an arbitrary fixed point of the surface.

Ω . No contribution from interactions among particles fully inside or fully outside the subsystem appear. As an atomic surface is the union of the bi-dimensional attraction basins associated with the bond critical points whose bond paths end up at the atom under study,³ the total atomic virial relation may also be understood as a sum of bonding contributions.

In constrained molecules, on the other hand, a virial of the forces of constraint, or nuclear virial, is to be added per nucleus. Slater's result is recovered if the system is extended to infinity and we notice that all the surface terms cancel each other.

Actually, an analogous result can be obtained for a classical system of particles subjected to internal action–reaction forces \mathbf{f}_{ij} . In this case, the virial is written as $\mathcal{V} = \sum_i \mathbf{r}_i \cdot \mathbf{f}_i$, where $\mathbf{f}_i = \sum_{j \neq i} \mathbf{f}_{ij}$. If we try to partition the system into several subsystems (A, B for simplicity), additive virials are easily defined as $\mathcal{V}(A) = \sum_{i \in A} \mathbf{r}_i \cdot \mathbf{f}_i - \mathbf{R} \cdot \sum_{i \in A, j \in B} \mathbf{f}_{ij}$, where \mathbf{R} is an arbitrary vector. A similar expression holds for $\mathcal{V}(B)$. It is straightforward to show that these regional virials are OI and add up to the total virial of the system of particles. With the help of Fig. 1, we see that the two terms above are the discrete equivalent to the volume and surface terms in Eq. (25). We think that this analogy clarifies substantially the role of the surface terms and their cancellation upon summation.

C. Atomic pressure and thermodynamic pressure

A local pressure field was introduced in Eq. (18). This is a highly nonhomogeneous field that presents strong shell-type variations near core atomic regions.

The integration of this $p(\mathbf{r})$ scalar within an atomic basin defines the atomic $p\Omega$ product. With the aid of Eq. (26) this turns to be

$$3p\Omega = \mathcal{V}(\Omega). \quad (34)$$

This definition complies with all microscopic and macroscopic requirements. In the first place, the average pressure is an OI magnitude, so no arbitrary origins need be chosen. In unconstrained systems it adopts the form of the surface virial of the complete stress field which, as we have stated in the last subsection, has only contributions from interactions that cross the subsystem's boundaries.

If we consider the partition of a complete molecular system into atomic basins, Ω_i , such that $\Omega = \sum_i \Omega_i$ is the total

volume, the global $3p\Omega$ product of Eq. (6) is recovered by the addition of the contributions of each subsystem in such a way that

$$p = \sum_i p_i \frac{\Omega_i}{\Omega} = \sum_i f_i p_i. \quad (35)$$

In this expression f_i is the fractional volume occupancy of subsystem Ω_i , and p_i its atomic pressure as given by Eq. (34). This equation provides a partition of the macroscopic pressure into atomic or group contributions. A similar partition of other intensive properties in periodic crystals has already been presented,⁴⁶ and has provided meaningful insights into the microscopic origin of the compressibility in a macroscopic body.

Let us also notice that the atomic pressures involve both the kinetic and the potential parts of the microscopic stress field. As we have already commented, it has been usual practice to present just the kinetic (or quantum) contributions to the pressure as new methodological advances were introduced (see, for example, Ref. 13). This fact has been the source of much confusion.

In the present AIM context, Bader and Austen³⁵ (BA in the following) have presented atomic pressures that contain only the kinetic part of the stress field:

$$3p_{\text{BA}}\Omega = -\mathcal{V}_s(\Omega) = -\oint_{\partial\Omega} \vec{\sigma}_k \cdot \mathbf{r} \cdot d\mathbf{S}. \quad (36)$$

BA have criticized the introduction of a local quantum pressure through the trace of a stress tensor, as done in Eq. (18), by appealing to its large local variations, and used a scaling argument due to Marc and McMillan¹¹ to introduce a $p\Omega$ operator that leads to the pressure definition of Eq. (36). However, the use of an electron-only scaling to study stressed situations, where the virials due to the nuclear system cannot be neglected, is not a very consistent procedure. Moreover, BA's definition of the $p\Omega$ product is intimately coupled to the atomic virial theorem [Eq. (26a)], and is clearly not OI. This means that a change of origin changes both the basin and the surface virials. If applied to whole molecules, BA's expression gives always null total stress ($p\Omega$ product), independently of the actual stress state of the molecule, and is not able to recover Slater's excess virial. Another simple example of the problems derived from ignoring the potential terms on defining atomic pressures is that posed by systems of constant and isotropic density (and kinetic stress tensor), like the homogenous electron gas. Using Eq. (26a), and taking into account that the divergence of a constant tensor is null, BA's assignment gives $2T=3p\Omega$, the ideal equation of state. This result is independent of the existence or not of electron-electron interactions, but is only correct in their absence. The application of Eqs. (26) and (34) gives the correct result $2T+V=3p\Omega$, which includes the ideal equation of state as a limiting case. Other examples will be considered below. Despite this limitations, BA's pressure is not too difficult to compute, and being a part of our definition, will approach the actual pressure when the origin is taken at the nucleus position (as is usually done), and the pressure reaches a large enough value, so that the kinetic

energy outweighs any potential contribution. We want to emphasize that the atomic pressures given by Eq. (34) are manifestly OI.

Infinite systems modeled by imposing PBCs to a given unit cell pose a number of problems that are worth mentioning. On one hand, it is easy to show that the boundary of any unit cell is a global zero flux surface. This suffices for the kinetic energies to be well defined when integrating within the cell. One can also demonstrate that a simply connected periodic cell may be constructed by adequate juxtaposition of atomic basins, so the results below apply equally well to a common parallelepipedic cell or to a group of atomic basins that replicate the crystal.

If no volume constraints are forced, and electrons and nuclei are allowed to relax, no forces will be exerted on the nuclear subsystem, just as in finite molecular cases. Equations (33) and (34) define the pressure, and periodicity forces the mutual cancellation of the third and fourth terms of Eq. (32). In these conditions, the total atomic potential is the intensive potential (total potential per unit cell), and the surface virials of the kinetic and potential terms cancel each other in such a way that the pressure is null. Notice that this last result cannot be obtained if only the kinetic stress is used to evaluate the surface virial, as it is well known that the surface virials of the kinetic stress tensor are not generally zero at equilibrium. This means that BA's pressures computed for a unit cell in a crystal will not vanish at equilibrium, violating the thermodynamic definition of pressure. It is also useful to remember that, in infinite bodies, all atomic basins are necessarily finite, so the atomic volumes are well defined and the atomic pressures may be safely found. Equation (35) makes it then necessary that, at equilibrium ($p=0$), and given that the f_i factors are positive definite by construction, either all atomic pressures are null, or some of them are positive and others negative. The second option has been found to be true whenever two or more nonequivalent AIM groups are necessary to define a unit cell in the system.

When the volume is constrained, but nuclei and electrons are still allowed to relax (this condition is known as the absence of *inner strain*), we will eventually arrive at a constrained infinite crystal with no forces exerted upon its nuclear system. The situation is just as before, but now the total surface virial will not vanish. The arguments leading to Eq. (6) guarantee that the pressure defined by the $3p\Omega$ product is the derivative of the energy per unit cell with respect to the volume at each volume, so it is the thermodynamic pressure.

There is still another argument that may help clarify the situation. Let us model a crystallite by considering a molecular system as large as we like, but finite. Let us relax "almost" all the system, and constrain the nuclear positions of a number of atoms in its "surface." The actual number of constrained nuclei is irrelevant, provided that they confine the inner atoms and force them to adopt some relaxed configuration compatible with their positions. Forces act only on the fixed nuclei, so applying Eq. (26) to the whole system leads to $\mathcal{V} = \sum_{\alpha} \mathbf{R}_{\alpha} \cdot \mathbf{F}_{\alpha}$, just as in a normal constrained molecule. If the crystallite is large enough, the contribution of the surface (constrained) atoms to the total energetic quantities of the

system is an $\mathcal{O}(L^2)$ magnitude, where L is a measure of the linear dimensions of the crystallite. This is negligible with respect to the $\mathcal{O}(L^3)$ contribution of the inner components. If this system is used to model a periodic crystal, the relaxed positions of the inner atoms will approach periodicity in the limit of large L . Taking an (approximate) unit cell in the bulk of the crystallite, with volume Ω_u , and using Eqs. (33) and (34), we observe that

$$\lim_{L \rightarrow \infty} \frac{1}{3\Omega_u} \mathcal{V}(\Omega_u) = \lim_{L \rightarrow \infty} \frac{1}{3\Omega} \sum_{\alpha} \mathbf{R}_{\alpha} \cdot \mathbf{F}_{\alpha} = p. \quad (37)$$

In our opinion, this is a very intuitive way to prove that the imposition of periodic boundary conditions at fixed volume transforms Slater's nuclear virial into the unit cell surface virial of the total stress field.

D. Relation to the theory of electronic separability

There have been many attempts to relate the quantum dynamics of a system with that of some externally defined constituent groups. An extremely successful one is the Theory of Electronic Separability (TES), formulated by McWeeny, Huzinaga, and others^{36,37} in the late 1950's and early 1960's. According to it, a system's wave function, Ψ , is written as a linear combination of antisymmetrized products of group functions, Φ^R . If these groups interact weakly, then the strong orthogonality⁴⁷ relations of Parr *et al.* should apply, $\int d\mathbf{r}_1 \Phi^{*R}(\mathbf{r}_1, \dots, \mathbf{r}_{N_R}) \Phi^S(\mathbf{r}_1, \dots, \mathbf{r}_{N_S}) = \delta_{RS}$. If only one determinant of group functions is used, the electronic first-order density matrix of the complete system is the sum of those of each group, and the second-order density matrix adopts a Dirac–Fock form in terms of the first-order densities of the groups. Restricted variational principles may be applied to each group in the field of the others, much as when considering an orbital in standard Hartree–Fock theory, and very simplified computational schemes have been devised using this construct.^{38,48} The TES is a partitioning theory in Fock space.

One of the most relevant results for our purposes that emerge from this theory is that each interacting group, R , has a proper energy (effective energy in TES parlance) which includes all intragroup contributions (kinetic, T^R , potential, V_{intra}^R), and all the interactions with the rest of the groups, V_{intra}^R . This magnitude is a minimum if all the other group functions are kept frozen in the minimization process. The total energy of the system is obtained by adding the so-called additive energies, which include the intragroup contributions and half the interactions with the rest of the groups: $E_{\text{add}}^R = T^R + V_{\text{intra}}^R + (1/2)V_{\text{int}}^R$. Notice that the additive potential is exactly that defined in Eq. (32).

A simple TES in AIM may be obtained by back-engineering techniques. Given the atomic partition of a molecular system, we can conceive a basis set for each atom that vanishes outside the atomic basin. Actually, similar prescriptions (in spherical environments) have been recently proposed as an efficient way to achieve linear scaling in electronic structure codes.⁴⁹ The group wave functions obtained in this manner are strongly orthogonal by construction, and yield the correct atomic densities confined in the atomic ba-

sins. If our cancelling conjecture holds in all situations, then the additive energies derived from QTS–AIM, $E_{\text{add}}(\Omega) = T(\Omega) + V_{\text{add}}(\Omega)$, are nothing but the additive energies of a TES framework in which each group is an AIM atom. It would be of far reaching practical importance if the conditions defining an AIM atom could be introduced self-consistently in the TES structure. Such a scheme could make profit of linear scaling concepts and AIM transferabilities simultaneously, likely providing a very fast and reliable methodology for the solution of the electronic structure problem.

Existing TES implementations, like our own *ab initio* perturbed ion method (A/PI),³⁸ rely on more or less crude approximations. The A/PI methodology is tailored to work properly in very ionic situations. A group contains just one atom (ion), and its wave function is made up from an exponential, monocentric basis set centered at its nuclear position. The atomic wave function is further forced to maintain spherical symmetry. These requirements do not comply with those presented in the above paragraph, but approach them.

To understand this, we must first notice that the AIM atoms of very ionic systems are almost spherical entities with interatomic surfaces located in regions of very small electron density.³³ This, incidentally, does not mean that the atomic surfaces resemble spheres.³³ The atomic-like exponentially decaying basis functions of the A/PI scheme do not vanish at the atomic surfaces, but take almost negligible values outside the atomic basins. Differences between the two TES schemes are therefore expected to be found in very low density regions, and the A/PI energetic magnitudes should at least give a qualitative image of those that we would obtain from a full calculation of the atomic additive energies.

As a simple example, it has been found using the A/PI methodology that the main contribution to binding in very ionic crystals is cationic. In fact, the (spherical) densities of cations are almost *in vacuo* densities, in such a way that the sum $E_{\text{intra}} = T^R + V_{\text{intra}}^R$ differs very slightly from the isolated cation's energy. As the interaction potential is basically a negative (stabilizing) contribution to the energy, the cationic binding energy is large. On the contrary, the A/PI anionic densities are usually quite deformed with respect to those of the isolated cations, showing a radial contraction that grows as the pressure increases. Thus the intragroup energy differs considerably from the *in vacuo* energy, unstabilizing the system. This image has also been found in our AIM analyses of ionic crystals.³³ In every case studied, the interatomic surfaces separating anionic and cationic basins are concave from the cation's perspective, and convex from the anion's point of view. This means a contraction of the anionic densities along the fundamental anion–cation bond path directions. An exam of the A/PI kinetic and additive energies shows that the pressures found using Eq. (34)—which should be compatible with those defined in this paper, as the arguments of the preceding paragraphs show—are positive for anions and negative for cations at the equilibrium configurations. Actual numerical evidence of this behavior for simple heterodiatomics will be presented in the next section. We delay further discussion about the implications of this result until then.

E. QTS energy densities

The trace of the total potential stress has been seen to equal the minus total potential of a molecular system. Using one of the possible prescriptions emerging from the non-uniqueness of the stress field, it is shown that the total potential stress is generated by integration of the Maxwell local potential stress field. This means that we can construct a local potential density:

$$v(\mathbf{r}) = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 v(\mathbf{r}_1, \mathbf{r}_2) \frac{1}{4\pi} \frac{\mathbf{r}-\mathbf{r}_1}{|\mathbf{r}-\mathbf{r}_1|^3} \cdot \frac{\mathbf{r}-\mathbf{r}_2}{|\mathbf{r}-\mathbf{r}_2|^3}. \quad (38)$$

Since the total pair density operator $v(\mathbf{r}_1, \mathbf{r}_2)$ defined in Eq. (9) is a sum of physically meaningful terms, we can easily define local potential fields associated to the different interactions among the particles of our system: electron–electron, $v_{ee}(\mathbf{r})$; nuclear–electron, $v_{ne}(\mathbf{r})$; and nuclear–nuclear, $v_{nn}(\mathbf{r})$, fields. All these densities integrate to the global potential contributions of the system.

Particularly interesting is the $v_{nn}(\mathbf{r})$ scalar field,

$$v_{nn}(\mathbf{r}) = \frac{1}{8\pi} \sum_{\alpha \neq \beta} Z_\alpha Z_\beta \frac{\mathbf{r}-\mathbf{R}_\alpha}{|\mathbf{r}-\mathbf{R}_\alpha|^3} \cdot \frac{\mathbf{r}-\mathbf{R}_\beta}{|\mathbf{r}-\mathbf{R}_\beta|^3}, \quad (39)$$

as it is not common in conventional quantum–chemical wisdom to associate an energy density to the nuclear repulsion. This procedure is, nevertheless, perfectly valid, and we just have to think in the electromagnetic energy as being stored in the field and not in the pairwise Coulombic interactions among point charges. The general behavior of this density may be explored analytically in a diatomic molecule. It is a rather interesting exercise to compute the contribution of several regions to the internuclear repulsion energy. By using Green's first identity,

$$\begin{aligned} \int_\Omega d\mathbf{r} v_{nn}(\mathbf{r}) &= \frac{Z_\alpha Z_\beta}{4\pi} \int_\Omega d\mathbf{r} \frac{\mathbf{r}-\mathbf{R}_\alpha}{|\mathbf{r}-\mathbf{R}_\alpha|^3} \cdot \frac{\mathbf{r}-\mathbf{R}_\beta}{|\mathbf{r}-\mathbf{R}_\beta|^3} \\ &= -\frac{1}{4\pi} \int_{\partial\Omega} \frac{\mathbf{r}-\mathbf{R}_\beta}{|\mathbf{r}-\mathbf{R}_\alpha| |\mathbf{r}-\mathbf{R}_\beta|^3} \cdot d\mathbf{S} \\ &\quad + \frac{1}{R_{\alpha\beta}} \delta_{\mathbf{R}_\beta \cdot \Omega}. \end{aligned} \quad (40)$$

This expression allows us to easily discuss the following examples: (i) If Ω is a sphere of radius $R_s < R_{\alpha\beta}$ centered at one of both nucleus, $V_{nn}(\Omega) = 0$; (ii) if $R_s \geq R_{\alpha\beta}$, $V_{nn}(\Omega) = R_{\alpha\beta}^{-1} - R_s^{-1}$; (iii) if a plane orthogonal to the internuclear axis cuts the space into two regions, each one containing one of the two nuclei, each semispace contributes equally, $(1/2)R_{\alpha\beta}^{-1}$, to the repulsion energy.

These examples show us that in the most general cases, the behavior of these densities may be rather nonintuitive. However, as example (iii) puts forward, in situations where the regions may resemble quantum atoms, the results are easy to rationalize.

Equation (40) also illustrates another important characteristic of the Maxwell potential energy densities. Although we have considered here in detail only the weird v_{nn} density, it is easy to show that all Maxwell potential densities decay

as r^{-4} at large distances.²⁸ Moreover, when integrating within a subsystem and transforming the integrand by Green-like manipulations, the surface integrals decay as r^{-1} . This means that if we try to integrate Maxwell potential densities within atomic basins, using either volume or surface integrals, we face a very difficult to surmount r^{-1} computational tail problem. The barrier lies in the practical inability to determine confidently the surface of an atomic basin at large distances if the basin extends to infinity (as it is the usual case in isolated molecules). Current molecular packages use Gaussian basis sets, and these can never adequately represent the exponentially decaying limit of a molecule's electron density. Thus, in isolated molecules it is not feasible to integrate Maxwell densities within atomic basins, and only the likely fulfillment of our cancelling conjecture provides a clear way to the integrated potential densities. These arguments do not apply to infinite systems, where every atom is necessarily finite.

IV. EXAMPLES AND DISCUSSION

In this section, we present the application of the ideas worked so far to very simple systems. Our aim is to develop a sort of intuition about the performance of the QTS framework in the AIM description of rather uninteresting, but difficult to misinterpret, examples. We will start by examining the kinetic and potential contributions to the stress in some analytically soluble, academic systems. A brief consideration of a couple of heterodiatom molecules will follow, and a discussion of the behavior of the potential densities in a selected molecule will close the section.

A. Exactly soluble models

1. Infinite systems

Let us first consider a single electron confined in a cubic cage of volume $\Omega = a^3$, and let us impose PBCs to it. In this elementary case, which is a model of the noninteracting electron gas, the free-electron wave function, $\Psi = \Omega^{-1/2} e^{i\mathbf{k} \cdot \mathbf{r}}$, survives with quantized momentum, $\mathbf{k} = \mathbf{n}2\pi/a$, where \mathbf{n} is a triplet of arbitrary integers. The energy, $E = T = \hbar^2 k^2 / (2m_e)$, scales as a^{-2} , so

$$2T = -a \partial E / \partial a = -3\Omega \partial E / \partial \Omega, \quad (41)$$

and the virial theorem, as expressed in Eq. (6), is beautifully fulfilled, recovering the ideal equation of state (EOS).

Let us analyze this system in light of Eqs. (26). The surface of any closed region in this system, including that of the cubic cell, is a zero flux surface. There is no potential stress density, and the kinetic stress field adopts a particularly simple constant form,

$$\vec{\sigma}_k(\mathbf{r}) = \frac{\hbar^2}{m_e \Omega} \mathbf{k} \otimes \mathbf{k}. \quad (42)$$

Two properties of $\vec{\sigma}_k$ emerge from this formula: (i) the trace of the kinetic stress density is constant and equals twice the kinetic energy per unit volume; (ii) the surface virial of $\vec{\sigma}_k$ defines the pressure, $\mathcal{V}_s = -2T = -3p\Omega$. This is again the ideal EOS, matching the previous thermodynamic relation.

In this simple case, the absence of potential terms guarantees that BA's pressure definition is identical to ours, both giving the correct result.

The proper counterpoise to these relations is obtained if we examine what is usually called the empty lattice model. Now we have a periodic array of clamped nuclei with no electrons. In order to simplify as much as possible, let us imagine a simple primitive cubic lattice of volume $\Omega = a^3$, with one nucleus per cell. There are no kinetic energy terms, the potential energy is purely electrostatic, and no force acts on any nucleus. If the infinite repulsions are of concern, a jellium-like negative background may be added in order to renormalize the energies, as done in Ewald's method⁵⁰ on computing Madelung's potentials in ionic crystals. Anyway, the energy of this model scales as a^{-1} , so

$$E = V = -a \partial E / \partial a = -3\Omega \partial E / \partial \Omega, \quad (43)$$

and now it is the surface virial coming from the potential stress field which, upon integration to the cubic cell surface, generates the pressure:

$$V = - \oint_{\partial\Omega} \tilde{\sigma}_p \cdot \mathbf{r} \cdot d\mathbf{S} = 3p\Omega, \quad (44)$$

a result that matches again the thermodynamic relations. No pressure is obtained in this model if BA's definition is applied, since no kinetic terms exist.

These examples show that in actual systems kinetic and potential contributions to the pressure (stress) do exist. Moreover, they provide simple intuitions about the origin of stress in PBC infinite systems as simple generalizations of the molecular results. The total virial of a system in the clamped nuclei approximation is made up of an electronic component with kinetic and potential terms, and of a nuclear component that lacks kinetic contributions, $\mathcal{V} = \mathcal{V}_e + \mathcal{V}_n$. When stress is introduced by means of constraints, and the total virial does not vanish, we may talk of (i) electronically constrained systems, if only the electronic virial is nonzero; (ii) nuclearly constrained systems, if the only nonvanishing virial is the nuclear one; (iii) generically constrained, or just constrained systems, when both terms add to the nonzero total virial.

Isolated molecules may only be nuclearly constrained, for the electron subsystem is allowed to relax in \mathcal{R}^3 . The total virial is then nuclear: null at equilibrium, different from zero in other cases. A molecule can also be electronically constrained, and a great amount of work has been done in the last years to explore the consequences of confining molecular systems within hard walls of different shapes. Actually, Ludeña *et al.*⁵¹ studied in the 1970s the solution of the spherically confined atomic problem. Since then, many others have generalized and applied their ideas.⁵² In these cases one can relax the nuclear positions inside the walls, ending up with an electronically, but not nuclearly, constrained system. The total virial will not vanish, but will be completely electronic, or one can also fix the nuclei at some preassigned positions, creating a generally constrained system. In either case, Eqs. (26) hold.

Similar comments may be made when considering subsystems. For instance, an atomic basin in a completely re-

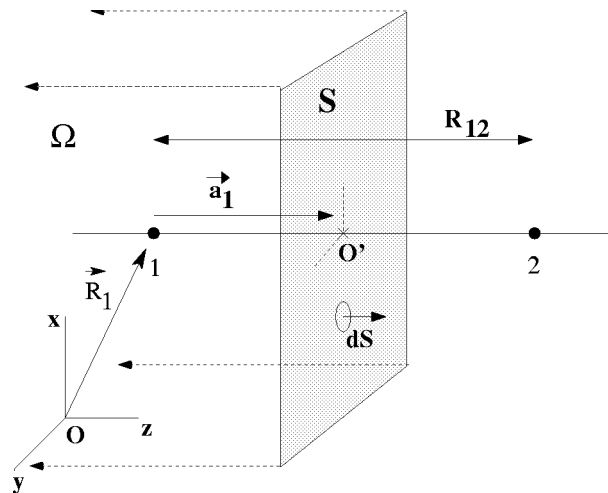


FIG. 2. Notation and reference systems of the homonuclear diatomic molecule discussed in the text. The Ω region is the left semispace defined by the planar interatomic surface S , and corresponds to atom 1.

laxed system is electronically constrained in the sense that from the QTS point of view, stress fields acting on its surface are needed to maintain the electronic situation.

2. Homodiatomics

The basic results coming from the integration of stress densities in the two identical atomic basins of homonuclear diatomic molecules may be obtained without actually solving the electronic problem. Let us use the reference systems and the notation of Fig. 2. Some features simplify the problem: (i) the interatomic surface is the infinite plane shown in the figure; (ii) any volume integral within one of the atomic basins must give half the complete molecular value; (iii) any two rank tensor density $\tilde{\alpha}$ has a simplified structure, forced by symmetry, at any point lying in the interatomic surface,

$$\tilde{\alpha}(\mathbf{r} \in S) \equiv \begin{pmatrix} a(\mathbf{r}) & b(\mathbf{r}) & 0 \\ b(\mathbf{r}) & a(\mathbf{r}) & 0 \\ 0 & 0 & c(\mathbf{r}) \end{pmatrix}, \quad (45)$$

so the product $\tilde{\alpha} \cdot d\mathbf{S}$ is a vector parallel to the internuclear axis, z .

Focusing our attention on atom 1,

$$\mathcal{V}(1) = \mathcal{V}/2 = -\mathbf{a}_1 \cdot \mathbf{F}_1 = \mathbf{R}_1 \cdot \mathbf{F}_1 - \oint_S \tilde{\sigma} \cdot \mathbf{r} \cdot d\mathbf{S}.$$

If the reference frame is set at the nucleus position, the nuclear virial term is zero, and the surface integral may be transformed to

$$\begin{aligned} \oint_S \tilde{\sigma} \cdot \mathbf{r}_O \cdot d\mathbf{S} &= \mathbf{a}_1 \cdot \oint_S \tilde{\sigma} d\mathbf{S} + \oint_S \tilde{\sigma} \cdot \mathbf{r}_{O'} \cdot d\mathbf{S} \\ &= \mathbf{a}_1 \cdot \int_{\Omega} d\mathbf{r} \nabla \cdot \tilde{\sigma} = \mathbf{a}_1 \cdot \mathbf{F}_1, \end{aligned}$$

where we have used the above mentioned property of tensors at the interatomic surface to show that the surface virial com-

TABLE I. Relevant atomic properties in the HF and LiF molecules. Hartree–Fock results obtained with 6-311+G** basis sets and self-consistent virial scaling. A refers to the nonfluorine atom, and $\rho_b, \nabla^2 \rho_b$ to the density and the Laplacian of the density at the bond point, respectively. Q is the atomic net charge. Columns two and three correspond to the theoretical equilibrium distance. The last column refers to a compressed state of LiF. All data in atomic units.

	HF	LiF	LiF
r	1.6958	2.9756	2.3000
$T(A)$	0.2683	7.3455	7.5252
$V_{\text{add}}(A)$	-0.7065	-14.7298	-14.8772
$\mathcal{V}(A)$	-0.1699	-0.0388	0.1732
$T(F)$	99.7851	99.6296	100.0305
$V_{\text{add}}(F)$	-199.4003	-199.2196	-199.5813
$\mathcal{V}(F)$	0.1698	0.0396	0.4797
ρ_b	0.3964	0.0713	0.2115
$\nabla^2 \rho_b$	-3.4333	0.7193	2.6850
$Q(A)$	0.7528	0.9387	0.8980

puted from the O' reference frame vanishes. Had we chosen O' as the coordinates origin, only the nuclear term would have contributed to the same final result.

This trivial exercise demonstrates that the virial relation for each atom in a homonuclear diatomic molecule is half Slater's excess virial for the whole molecule, and that if we identify it with the $3p\Omega$ product, each atomic pressure is identical to that of the whole molecule at any internuclear distance. At equilibrium, it is the cancellation of the kinetic and potential surface virials which guarantees a null atomic virial relation.

These results, based on the additivity of equal atomic properties for equivalent atoms, cannot be derived if the pressure is defined using only the Pauli stress density. In this case, the atomic stress ($3p\Omega$) is obtained by computing $-\mathcal{V}_s$ in a given basin. This term is not OI, and if we choose the nucleus belonging to the basin under study as the position of the reference frame, it may be transformed to yield the total Ehrenfest force of the basin's electrons. This force does not vanish at the equilibrium nuclear geometry, so it cannot be used to guess the stress state of the molecule.

B. Heterodiatomics

Here we present a very brief account of some preliminary results in the HF and LiF heterodiatomics. The purpose of these calculations is illustrative, so standard Hartree–Fock calculations have been done with the GAMESS⁵³ code, employing 6-311+G** Gaussian basis sets. Atomic integrations have been done using Biegler–König's PROAIM code.⁵⁴ Usage of PROAIM has forced us to ignore electron correlation, since only Fock–Dirac second-order electronic density matrices are properly accounted for in this code.

We have luckily found that it is possible to construct our additive potentials $V_{\text{add}}(\Omega)$ with the default integrated magnitudes offered by PROAIM. It is not possible, however, to resolve the net electron–electron interaction into an intra-atomic and an interaction contribution, as the self-consistent orbital energies are used to bypass the extremely expensive integrations of the exchange components of ρ_e^2 .

In order to avoid spurious effects in atomic properties if

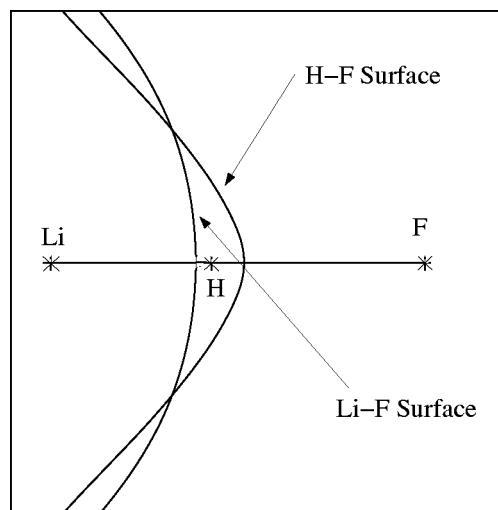


FIG. 3. Interatomic surfaces of the HF and LiF molecules at the Hartree–Fock/6-311+G** level. Both molecules are on a common scale, with coincident fluorines, and at their respective equilibrium geometries. Notice the difference in bond distance and overall curvature of the surfaces.

the whole molecular VT is not adequately satisfied, self-consistent virial scaling (SCVS) techniques⁵⁵ have been used in order to assure deviations of $2T+V-\sum_{\alpha} \mathbf{R}_{\alpha} \cdot \mathbf{F}_{\alpha}$ smaller than 10^{-8} atomic units. The SCVS equilibrium distance of HF and LiF will be reported, together with a compressed state of LiF.

The results are shown in Table I. As originally expected, the atomic virials relations at the equilibrium geometries do not vanish, and the global null result comes from the cancellation of a positive and a negative term. The incomplete cancellation of the atomic virial relations to yield the total molecular excess virial at equilibrium is due to errors in the basin integrations. Let us comment some interesting results.

First, it is to be noticed that the positive virial relation at equilibrium is that of the fluorine atom. As these two systems are highly charged, we may call this species a fluoride anion. This is in complete qualitative agreement with the intuitions gained through the TES analogy of the last section. Cations are responsible for the compression of anions. For unstressed configurations the latter shrink, and end up subjected to a positive pressure. In highly enough stressed situations, as the last LiF column teaches us, both cations and anions contribute positively to the total stress, though it is always the anionic species the one with a bigger contribution. We think that these results are of general applicability. A similar analysis in LiH shows that now it is the hydrogen atom (the anion again) the one with a positive virial relation at equilibrium.

Another interesting fact comes from examining the absolute values of the total equilibrium atomic stresses in the two compounds. It is rather clear that these magnitudes are much larger in the HF molecule than in LiF. This behavior is clearly related to the very different bonding character in these two systems. HF exhibits a typical shared shell interaction with large density and large negative Laplacian at the bond critical point, whereas LiF has a closed-shell interaction with small density and a small positive Laplacian at the bond critical point. As the total virial at equilibrium may be

obtained from the total stress surface virial, the values of the electron density and of its derivatives at the surface play an important role in the final value adopted by the total atomic virial. On examining Fig. 3, one can also see the different curvatures of the interatomic surfaces. As commented before, convex interatomic surfaces correspond to cations, and concave ones to anions. We can actually see that the fluoride is quite more compressed in the HF molecule than in LiF. This is particularly clear in the mostly relevant region surrounding the internuclear axis.

C. Maxwell stress densities

As a final example, we are going to present the main features of the several Maxwell densities previously introduced. We have coded a new computer program, PROMOLDEN, that among other tasks, obtains and integrates kinetic and potential stress densities in isolated molecules. The code is fed by wave function files written in a conventional format available from most standard quantum chemical packages. We have chosen the H_2O molecule as a simple system with no revolution symmetry. We will center our comments by referring to Fig. 4. It contains contour plots of the most important Maxwell densities as calculated with PROMOLDEN using Hartree–Fock/6–311+G** wave functions obtained at the theoretical geometry.

The nuclear–nuclear density, v_{nn} [Eq. (39)], to which we have devoted some comments above, displays an interesting structure. Each nuclear position is a singular point of this field, and it is surrounded by regions of arbitrarily large positive and negative densities. It is easy to show that in a homodiatom molecule the negative density region is a sphere centered at the midpoint between the two nuclei with a diameter equal to the internuclear separation. In this less symmetrical case, the negative nuclear–nuclear density surrounds the bonding regions associated to the O–H bonds. It is also interesting to point out that the positive isosurfaces surrounding the nuclear regions seem like caps that extend around the inner negative zone. In the plane shown in Fig. 4, the cap above the oxygen atoms resembles the form usually associated to the lone pairs of this molecule.

All the other fields, defined in Eq. (38) and its following paragraph, contain electronic terms and are therefore dominated by the oxygen's contribution. Their aspect is thus much more spherical. The electron–nuclear potential density is negative in almost all regions, with clear positive contributions near the hydrogen along the O–H line. Notice that the O–H bond point lies almost exactly on one of the zero isosurfaces. The electron–electron potential field is positive everywhere, and the hydrogens' positions are hardly critical points of it. This is due to the small interelectronic repulsion that exists near the positively charged hydrogen atoms. The total energy density is basically a negative magnitude with small positive regions near the cores that are clearly asymmetric around the hydrogen nuclei.

Let us also notice the quasi homomorphism that exists between the full potential field [$v(r)$, Eq. (38)], and the electron density field. This fact has been noticed many times in similar contexts (see, for instance, Ref. 56). Finally, the total stress field, $\mathcal{V}(r) = -\text{Tr} \vec{\sigma} = 3p(r)$, has positive regions near

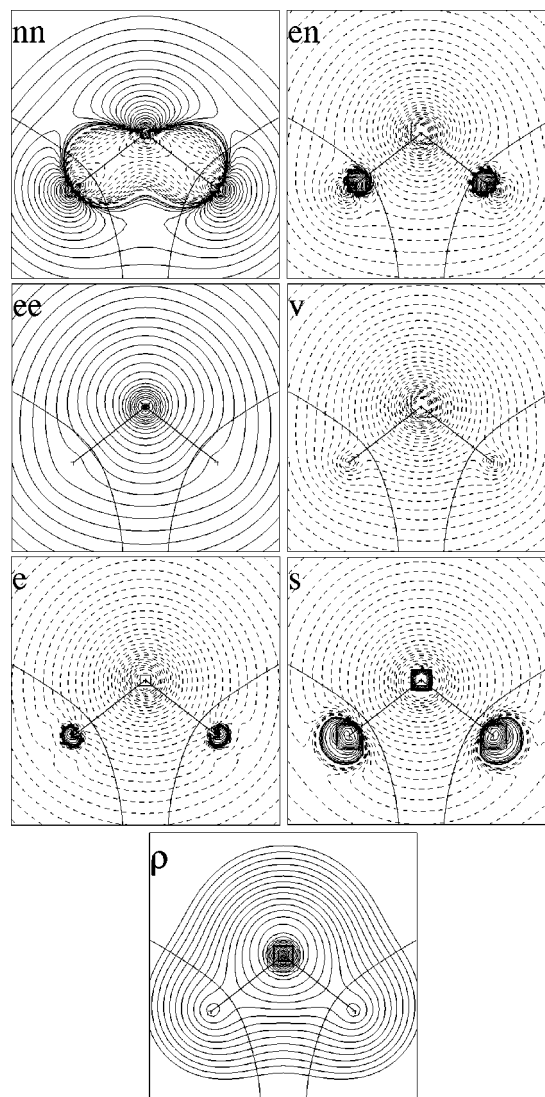


FIG. 4. Contour maps of the Maxwell energy densities in the molecular plane of the H_2O molecule in a Hartree–Fock/6–311+G** calculation at the theoretical equilibrium geometry. The labels nn , en , ee , and v stand for the $v_{nn}(\mathbf{r})$, $v_{en}(\mathbf{r})$, $v_{ee}(\mathbf{r})$, and $v(\mathbf{r})$ fields as defined in the text [Eq. (38) and the following paragraph]. The labels e and s stand for the total energy field, $e(\mathbf{r}) = -(1/2)\text{Tr} \vec{\sigma}_k(\mathbf{r}) + v(\mathbf{r})$, and the total stress field, $\mathcal{V}(\mathbf{r}) = -\text{Tr} \vec{\sigma}(\mathbf{r})$. Full lines are used for positive isocurve values, and dotted lines for negative ones. All plots are linear and in atomic units. There are 35 isolines in the range 0.01–1000 a.u. in both the positive and negative regions. The final, central figure shows the electron density for comparison purposes. Bond paths and projections of the interatomic surfaces have also been included for clarity.

the nuclear positions (the kinetic energy overtaking the potential contributions), being negative in the rest of the space. The integral of this field within the atomic basins yields the total atomic relations presented in this paper. By its relation to the pressure field, similar conclusions to those presented in the last subsection are apparent. The atomic cores, which act like *subatomic* cationic regions, are compressed by the interstitial electrons, that play the role of anionic counterparts. It is interesting to notice that when integrating this field over the atomic basins, it is the oxygen which finally acquires a positive atomic stress, as corresponds to its anionic role. The local stress field is not easily transferable

among systems, and bond formation or bond breaking should greatly alter the pictures here discussed. The AIM theory has shown, however, that interatomic surfaces are very stable objects, and that quantum subsystems are actually transferable. This means that we should expect atomic virial relations to behave, like other AIM atomic properties, in a rather controllable way.

V. CONCLUSIONS AND PERSPECTIVES

We have developed in this paper the quantum theory of stress^{27,31} in the AIM context. The QTS shows that the total stress field is made up of kinetic and potential terms, and that both are necessary to understand stressed molecular systems in general situations. Our analysis shows in a particularly clear way the intimate relationships among atomic stress, atomic pressure, and atomic virial.

The AIM theory teaches us that a variational statement of the hypervirial theorem in finite regions is only possible when the subsystem is surrounded by a local zero-flux surface. Integration of hypervirial commutators within atomic basins yields the AIM atomic theorems. If the virial operator is used as a generator of a hypervirial relation, the atomic virial theorem of Srebrenik and Bader^{10,43} appears. Integration of the stress densities of QTS within atomic basins gives rise to atomic kinetic, potential, and total virial relations. We have shown that the atomic virial theorem is the kinetic QTS atomic theorem. Our atomic potential relation provides an origin independent atomic potential that can be written in terms of physically sound magnitudes and origin dependent terms. In selected analytical situations and in some preliminary calculations, the origin dependent terms cancel each other. We have not been able to prove the generality of this result, but we do conjecture its universal validity. The remaining origin independent potential terms are immediately identified with the additive potential of the theory of electronic separability of McWeeny and Huzinaga. The potential of an atom would consist of all intra-atomic potential terms and half the interactions among the atom under study and all the others. We have also given arguments relating the AIM theory with the TES.

A rather important part of our arguments has been devoted to clarify the role of the atomic pressure and the thermodynamic pressure in the AIM framework. We have shown that the definition of atomic pressure requires the total stress field, and that the magnitudes so defined are governed by classical relations. We have also shown that the atomic pressures defined by Bader and Austen³⁵ within the AIM framework contain only the kinetic part of the stress field, and that they should be understood as approximations to the physically correct expressions. The thermodynamic pressure in infinite systems is given by our expressions if the AIM subsystem is a unit cell of the whole system. Arguments that help clarify the problems posed by periodic boundary conditions, as well as *gedanken* examples analyzing the relation between the nuclear virials in macroscopic and molecular cases, have also been given. The atomic pressures behave as other atomic properties with intensive macroscopic counterparts, being additive if a weight factor accounting for the fraction of the total volume occupied by each atom is used.

Our expressions show that in an unstressed system, there will coexist positively and negatively stressed atomic basins.

Several toy problems have been examined. In a couple of heteronuclear diatomics we have shown that atomic stresses are basically borne by the anion (the negatively charged component of the diatomic), and that cations generate the anionic stress. We have also given theoretical support to this finding, that we think has quite general validity. A relation between the curvature of the interatomic surface and the atomic stress has also been found. If Maxwell potential stress tensors are chosen to describe the local stress fields, a plethora of energy densities appear. To our knowledge, these magnitudes have not been fully explored in molecules, and we have presented preliminary results concerning their overall features in the water molecule.

Much work remains to be done, in the theoretical and the computational fronts. On the one hand, it would be highly desirable to derive in a variational context the results presented here. Such a goal would be fully consistent with the pure core of the AIM theory. Moreover, our cancellation conjecture would much benefit from a definite proof. We are quite confident about its validity, anyhow. On the other hand, a world of practical usage is open. There are many places where these ideas might be applied, ranging from the stability of crystalline structures to the characterization of the different components of the additive potentials in families of compounds. Work along this lines is being undertaken in our group.

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¹B. M. Deb, *Rev. Mod. Phys.* **45**, 22 (1973); B. M. Deb, in *The Force Concept in Chemistry* (Van Nostrand Reinhold, New York, 1981).

²J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1963), Vol. I

³R. F. W. Bader, *Atoms in Molecules: A Quantum Theory* (Oxford University Press, Oxford, 1990).

⁴M. Born, W. Heisenberg, and P. Jordan, *Z. Phys.* **35**, 557 (1926).

⁵V. Fock, *Z. Phys.* **63**, 855 (1930).

⁶B. Filkenstein, *Z. Phys.* **50**, 293 (1928).

⁷J. C. Slater, *J. Chem. Phys.* **1**, 687 (1933).

⁸T. L. Cottrell and S. Paterson, *Philos. Mag.* **42**, 391 (1955).

⁹S. T. Epstein, *J. Chem. Phys.* **63**, 3573 (1975).

¹⁰S. Srebrenik and R. F. W. Bader, *J. Chem. Phys.* **61**, 2536 (1974).

¹¹G. Marc and W. G. McMillan, *Adv. Chem. Phys.* **58**, 209 (1985).

¹²L. Kleinman, *Phys. Rev. B* **1**, 4189 (1970).

¹³D. A. Liberman, *Phys. Rev. B* **2**, 244 (1970); **3**, 2081 (1971).

¹⁴L. J. Sham, *Phys. Rev. B* **6**, 2509 (1972).

¹⁵E. Weislinger and G. Olivier, *Int. J. Quantum Chem., Symp.* **8**, 389 (1974); J. Schweitz, *J. Phys. A* **10**, 507 (1977).

¹⁶N. H. March, *Phys. Rev.* **110**, 604 (1958); P. N. Argyres, *ibid.* **154**, 410 (1967); N. H. March, *Mol. Phys.* **88**, 1039 (1996); L. J. Bartolotti and R. G. Parr, *J. Chem. Phys.* **72**, 1593 (1980).

¹⁷S. K. Ghosh, M. Berkowitz, and R. G. Parr, *Proc. Natl. Acad. Sci. U.S.A.* **81**, 8028 (1984).

¹⁸J. O. Hirschfelder, *J. Chem. Phys.* **33**, 1462 (1960); **69**, 5151 (1977).

- ¹⁹A. G. McLellan, *Am. J. Phys.* **42**, 239 (1973).
- ²⁰E. Madelung, *Z. Phys.* **40**, 322 (1926).
- ²¹T. Takabayashi, *Prog. Theor. Phys.* **8**, 143 (1952).
- ²²P. R. Holland, *The Quantum Theory of Motion* (Cambridge University Press, Cambridge, 1993).
- ²³C. Y. Wong, J. A. Mahrung, and T. A. Welton, *Nucl. Phys. A* **253**, 469 (1975); K. K. Kan and J. J. Griffin, *Phys. Rev. C* **15**, 1126 (1977).
- ²⁴A. S. Bamzai and B. M. Deb, *Rev. Mod. Phys.* **53**, 95 (1981); S. K. Ghosh and B. M. Deb, *Int. J. Quantum Chem.* **22**, 871 (1982); see also B. M. Deb and S. K. Ghosh, *J. Chem. Phys.* **77**, 342 (1982); S. K. Ghosh and R. G. Parr, *ibid.* **82**, 3307 (1984); S. K. Ghosh and M. Berkowitz, *ibid.* **83**, 2976 (1985).
- ²⁵E. Schrödinger, *Ann. Phys.* **82**, 265 (1927); W. Pauli, in *Handbuch der Physik*, Band XXIV, Teil 1 (Springer-Verlag, Berlin, 1933).
- ²⁶R. P. Feynman, Thesis, Massachusetts Institute of Technology, 1939 (unpublished).
- ²⁷O. H. Nielsen and R. M. Martin, *Phys. Rev. Lett.* **50**, 697 (1983); O. H. Nielsen and R. M. Martin, *Phys. Rev. B* **32**, 3780 (1985); **32**, 3792 (1985).
- ²⁸N. O. Folland, *Phys. Rev. B* **34**, 8296 (1986); **34**, 8305 (1986).
- ²⁹R. J. Needs, *Phys. Rev. Lett.* **58**, 53 (1987).
- ³⁰D. Vanderbilt, *Phys. Rev. Lett.* **59**, 1456 (1987).
- ³¹P. Ziesche, J. Gräfenstein, and O. H. Nielsen, *Phys. Rev. B* **37**, 8167 (1988).
- ³²J. Gräfenstein and P. Ziesche, *Phys. Rev. B* **53**, 7143 (1996).
- ³³A. Martín Pendás, A. Costales, and V. Luaña, *Phys. Rev. B* **55**, 4275 (1997); V. Luaña, A. Costales, and A. Martín Pendás, *ibid.* **55**, 4285 (1997); A. Martín Pendás, A. Costales, and V. Luaña, *J. Phys. Chem. B* **102**, 6937 (1998).
- ³⁴R. F. W. Bader and P. L. A. Popelier, *Int. J. Quantum Chem.* **45**, 189 (1993).
- ³⁵R. F. W. Bader and M. A. Austen, *J. Chem. Phys.* **107**, 4271 (1997).
- ³⁶See for a review, R. McWeeny and B. T. Sutcliffe, *Methods of Molecular Quantum Mechanics* (Academic, London, 1969).
- ³⁷S. Huzinaga and A. A. Cantu, *J. Chem. Phys.* **55**, 5543 (1971); S. Huzinaga, D. McWilliams, and A. A. Cantu, *Adv. Quantum Chem.* **7**, 187 (1973).
- ³⁸V. Luaña and L. Pueyo, *Phys. Rev. B* **41**, 3800 (1990); V. Luaña, A. Martín Pendás, J. M. Recio, E. Francisco, and M. Bermejo, *Comput. Phys. Commun.* **77**, 107 (1993); M. A. Blanco, A. Martín Pendás, and V. Luaña, *ibid.* **103**, 297 (1997).
- ³⁹See, for instance, J. D. Jackson, *Classical Electrodynamics*, 2nd ed. (Wiley, New York, 1975).
- ⁴⁰A. Kugler, *Z. Phys.* **198**, 236 (1967).
- ⁴¹O. H. Nielsen and N. M. Martin, *Phys. Rev. B* **37**, 10905 (1988); N. O. Folland, **37**, 10908 (1988).
- ⁴²J. Schwinger, *Phys. Rev.* **82**, 914 (1951).
- ⁴³S. Srebrenik and R. F. W. Bader, *J. Chem. Phys.* **63**, 3945 (1975); S. Srebrenik, R. F. W. Bader, and T. T. Nguyeng-Dang, *ibid.* **68**, 3667 (1978).
- ⁴⁴R. F. W. Bader, *Pure Appl. Chem.* **60**, 145 (1988).
- ⁴⁵See, for instance, W. L. Cao, R. F. W. Bader, C. Gatti, and P. J. Macdougall, *Chem. Phys. Lett.* **141**, 380 (1987); R. F. W. Bader and J. A. Platts, *J. Chem. Phys.* **107**, 8545 (1997); A. Martín Pendás, Miguel A. Blanco, A. Costales, Paula Mori-Sánchez, and V. Luaña, *Phys. Rev. Lett.* **83**, 1930 (1999).
- ⁴⁶A. Martín Pendás, A. Costales, M. A. Blanco, J. M. Recio, and V. Luaña, *Phys. Rev. B* **62**, 13970 (2000).
- ⁴⁷R. G. Parr, F. O. Ellison, and P. G. Lykos, *J. Chem. Phys.* **24**, 1106 (1956); P. G. Lykos and R. G. Parr, *ibid.* **24**, 1166 (1956).
- ⁴⁸Z. Barandiarán and L. Seijo, *J. Chem. Phys.* **89**, 5739 (1988).
- ⁴⁹P. Ordejón, E. Artacho, and J. M. Soler, *Phys. Rev. B* **53**, 10441 (1996); D. Sánchez-Portal, P. Ordejón, E. Artacho, and J. M. Soler, *Int. J. Quantum Chem.* **65**, 453 (1997).
- ⁵⁰P. P. Ewald, *Ann. Phys. (N.Y.)* **64**, 253 (1921).
- ⁵¹E. V. Ludeña, *J. Chem. Phys.* **69**, 1770 (1978); E. V. Ludeña and M. Gregori, *ibid.* **71**, 2235 (1979).
- ⁵²E. Ley-Koo and A. Flores-Flores, *Int. J. Quantum Chem.* **66**, 123 (1998); C. Zicovich-Wilson, J. Planelles, and W. Jaskólski, *ibid.* **50**, 429 (1994); C. Zicovich-Wilson, W. Jaskólski, and J. Planelles, *ibid.* **54**, 61 (1995); W. Jaskólski, *Phys. Rep.* **271**, 1 (1996).
- ⁵³M. W. Schmidt, *et al.* *J. Comput. Chem.* **14**, 1347 (1993).
- ⁵⁴F. W. Biegler-König, R. F. W. Bader, and T. H. Tang, *J. Comput. Chem.* **3**, 317 (1982).
- ⁵⁵M. Lehd and F. Jensen, *J. Comput. Chem.* **12**, 1089 (1991).
- ⁵⁶Y. Tal, R. F. W. Bader, and J. Erkkü, *Phys. Rev. A* **21**, 1 (1980).