7966 J. Phys. Chem. A 2007, 111, 7966−7972

Everyman's Derivation of the Theory of Atoms in Molecules

Richard F. W. Bader

Department of Chemistry, McMaster University, Hamilton, ON L7L 2T1, Canada

Received: April 25, 2007; In Final Form: May 23, 2007

This paper demonstrates that it is straightforward to develop the theory of an atom in a molecule—the extension of quantum mechanics to an open system—by deriving the necessary equations of motion from Schrödinger's equation, followed by a comparison of the predicted properties with experiment to determine the correct boundary condition. Although less fundamental than the variational derivation of the quantum theory of atoms in molecules, this heuristic approach makes the quantum mechanics of an atom in a molecule accessible to "everyman" possessing a knowledge of Schrödinger's equation, aiding its general acceptance by experimental chemists.

Extending Quantum Mechanics to an Atom in a Molecule

It is just over two hundred years since Dalton[1] proposed his atomic theory and just over 80 years since Schrödinger derived his wave equation.[2] The purpose of the present paper is to demonstrate that it is relatively simple to combine Dalton's idea of the atomic nature of matter with Schrödinger's equation by showing that quantum mechanics applies to an atom bound in a molecule or in a crystal. An atom bound to other atoms may exchange energy and/or charge with its neighbors when it undergoes motion relative to the other atoms. A bound atom is thus described as an open system.

The derivation of the physics of an open system is accomplished in two steps. One first uses Schrödinger's equation to determine the time rate-of-change of the average value of a property, the property's "equation of motion". This is done for the total system and for any of its possible fragments, bringing one to the second step. Out of all possible partitionings of a system, how does one determine the one that yields open systems corresponding to the atoms of chemistry? It is at this point that experiment comes to the aid of theory. Just as one invokes boundary conditions to delimit the mathematically acceptable solutions found for Schrödinger's equation to those that describe physically realizable states, so it is equally necessary to apply a boundary condition to delimit the equations of motion derived for arbitrary fragments of some total system, to the open systems whose predicted properties yield agreement with experiment. By applying a boundary condition such that the properties predicted for the resulting open systems recover the experimentally measured additive properties associated with an atom in a molecule, one obtains a unique partitioning of any system into atoms. The uniqueness of the partitioning is assured once this condition is satisfied, because the experimental predictions of quantum mechanics are unique.

This heuristic approach to defining the physics of an atom in a molecule—theory followed by appeal to experiment—is less elegant than its variational derivation[3−5] from Schwinger's principle of least action,[6] but it has two distinct advantages: it makes the physical validity of the theory accessible to "everyman" and demonstrates its rooting in experiment.

From Schrödinger's Equation to an Equation of Motion

An equation of motion completely determines the physics associated with any measurable property. It is worthwhile recalling that in the Heisenberg approach,[7] one that preceded Schrödinger's "wave mechanics", quantum mechanics is expressed in terms of the equations of motion for the observables, emphasizing the ties that link theory to observation. Thus developing the physics of an atom in a molecule entails the two basic concepts of quantum mechanics: Schrödinger's equation and the equations of motion for the observables.[8]

Although this is not the path generally followed in studies of quantum chemistry that tend to focus on the orbital approach, it is the path that links chemistry with physics. Molecular orbital theory is clearly essential to understanding chemistry, but why should one stop there when the world of physics lies at its doorstep? In seeking the physics of an atom in a molecule, one is obliged to cross the threshold from orbital theories and their associated models and step deeper into the world of physics. Besides, the physically sound models derived from orbital arguments, those that relate to measurable properties, are recovered by the physics of an atom in a molecule. These include the hybridization model as applied to atomic stability,[9,10] homoaromatic conjugation,[11,12] "resonance"[13] and strain energies,[10] NMR deshielding of an aromatic proton,[14] confirmation of the presence of the Chatt−Duncanson model of dπ−pπ* back-bonding[15] in the quadrupolar polarization of the ligand density[16] and the predictions of frontier orbital theory,[17] to cite a few examples. So one is not asked to give up orbital models, but rather to relate them more directly to the underlying physics.[16] If hybridization predicts planar nitrogen to be more stable than pyramidal in some reaction, why not make the argument quantitative by calculating the change in the energy of the nitrogen atom incurred in the reaction?

The Equation of Motion. The change with time of the average value of some property A (the expectation value of its associated operator $\hat{A}$, the quantity $\langle\Psi, \hat{A}\Psi\rangle$) is given by the Heisenberg equation of motion. When expressed in the language of wave functions, the Heisenberg equation is given by eq 1.

$$d\langle\Psi, \hat{A}\Psi\rangle/dt = (i/\hbar)\langle\Psi, [\hat{H},\hat{A}]\Psi\rangle \qquad (1)$$

10.1021/jp073213k CCC: $37.00

Equation 1 is expressed in terms of the "bra-ket" notation to take advantage of its compact nature. It is rewrittenbelow in terms of the more usual integral notation

$$\mathrm{d}\int \Psi^* \hat{A}\Psi \,\mathrm{d}\tau/\mathrm{d}t = (\mathrm{i}/\hbar)\int \Psi^*[\hat{H},\hat{A}]\Psi \,\mathrm{d}\tau \tag{1}$$

When the system is in a stationary state described by the function ψ, eq 1 becomes

$$\langle \psi, [\hat{H},\hat{A}]\psi\rangle = \int \psi^*[\hat{H},\hat{A}]\psi \,\mathrm{d}\tau = 0 \tag{2}$$

The vanishing of the commutator in eq 2 may be derived independently. Expanding the commutator and averaging yields

$$\langle \psi|\hat{H}\hat{A} - \hat{A}\hat{H}|\psi\rangle = \langle \psi|\hat{H}\hat{A}|\psi\rangle - \langle \psi|\hat{A}\hat{H}|\psi\rangle = 0 \tag{3}$$

This result follows from the hermitian nature of $\hat{H}$, which may act to the left to yield $\langle \psi|\hat{H}\hat{A}|\psi\rangle = \langle \hat{H}\psi|\hat{A}\psi\rangle = E\langle \psi|\hat{A}|\psi\rangle$ or to the right to yield the equivalent result, $\langle \psi|\hat{A}\hat{H}|\psi\rangle = E\langle \psi|\hat{A}|\psi\rangle$. Whether or not an operator has this property of acting to the left or to the right depends upon the domain of integration, and in general, when the domain is restricted, as it is in delineating the boundaries of an open system, this property is lost. One may prove this to oneself by considering the momentum operator $-\mathrm{i}\,\mathrm{d}/\mathrm{d}x$ in one-dimension. One finds that

$$\int (-\mathrm{i}\,\mathrm{d}\psi/\mathrm{d}x)^*\psi \,\mathrm{d}x = \int \psi^*(-\mathrm{i}\,\mathrm{d}\psi/\mathrm{d}x)\,\mathrm{d}x + \mathrm{i}\,\mathrm{d}(\psi^*\psi)/\mathrm{d}x|_{-\infty}^{+\infty} \tag{4}$$

The product $\psi^*\psi = \rho$, and the density together with its derivatives, vanish on the boundaries at infinity, but not when the boundary has a finite value. In three dimensions, the nonvanishing remainder is an integral over the surface that encloses the open system. This simple example demonstrates the feature that distinguishes the physics of an open system from that of the total system of which it is a part: the loss of the Hermitian character of operators and the resulting appearance of surface integrals.

We are now ready to consider the extension of the stationary state expression of the equation of motion, eq 2, to an open system Ω; that is, we wish to evaluate the quantity $\langle \psi|[\hat{H},\hat{A}]|\psi\rangle_\Omega$, where the subscript implies that the averaging is taken over the region of the open system. Concomitant with the loss of hermiticity is the necessity of now requiring the expectation value of an operator to be real. Thus one must always consider the sum of the operator average and its complex conjugate (cc) over an open system to be certain that the expectation values are real numbers. Thus we consider the quantity $^1/_2\{\langle \psi|[\hat{H},\hat{A}]|\psi\rangle_\Omega + \mathrm{cc}\}$. We shall in the derivation consider just one term in the expression, the cc being readily added at the end of the derivation.

Equation of Motion for an Open System. The procedure followed here is given in the book *The Quantum Theory of Atoms in Molecules, a Quantum Theory*.[18] Expanding the commutator as in eq 3 and averaging over an open system Ω yields

$$\langle \psi|\hat{H}\hat{A} - \hat{A}\hat{H}|\psi\rangle_\Omega = \langle \psi|\hat{H}\hat{A}|\psi\rangle_\Omega - \langle \psi|\hat{A}\hat{H}|\psi\rangle_\Omega \tag{5}$$

To proceed, one puts the expression in maximum correspondence with the total system result by adding and subtracting the term $\langle \hat{H}\psi|\hat{A}|\psi\rangle_\Omega$ to eq 5 to obtain

$$\langle \psi|\hat{H}\hat{A} - \hat{A}\hat{H}|\psi\rangle_\Omega = \langle \hat{H}\psi|\hat{A}|\psi\rangle_\Omega - \langle \psi|\hat{A}\hat{H}|\psi\rangle_\Omega + \langle \psi|\hat{H}\hat{A}|\psi\rangle_\Omega - \langle \hat{H}\psi|\hat{A}|\psi\rangle_\Omega \tag{6}$$

The first two terms on the RHS of eq 6 cancel because both equal $E\langle \psi|\hat{A}|\psi\rangle_\Omega$, as is the case of a total system, leaving

$$\langle \psi|\hat{H}\hat{A} - \hat{A}\hat{H}|\psi\rangle_\Omega = \langle \psi|\hat{H}\hat{A}|\psi\rangle_\Omega - \langle \hat{H}\psi|\hat{A}|\psi\rangle_\Omega \tag{7}$$

At this point and without the any loss of generality (as demonstrated below) one assumes a one-electron Hamiltonian $\hat{H} = -(\hbar^2/2m)\nabla^2 + \hat{V} = \hat{T} + \hat{V}$. In addition, the potential energy operator $\hat{V}$ is assumed to be of the form for an atomic or molecular Hamiltonian consisting of electron−nuclear and electron−electron interactions and not containing any gradient terms. This being the case, the only terms that survive the differencing in eq 7 are those involving the kinetic energy operator $\hat{T}$ and the operator $\hat{A}$ to yield eq 8,

$$\langle \psi|\hat{H}\hat{A} - \hat{A}\hat{H}|\psi\rangle_\Omega = \int_\Omega \mathrm{d}\mathbf{r}(-\hbar^2/2m)\nabla\cdot\{\psi^*\nabla(\hat{A}\psi) - \nabla\psi^*(\hat{A}\psi)\} \tag{8}$$

a step that is amplified in the Appendix. One now makes use of Gauss' theorem stating that the volume integral of the divergence of a vector as found in eq 8 may be expressed in terms of a surface integral bounding the volume Ω, transforming the RHS of eq 8 into a surface integral,[19,20]

$$\langle \psi|[\hat{H},\hat{A}]|\psi\rangle_\Omega = (-\hbar^2/2m)\oint \mathrm{d}S(\mathbf{r}_s;\Omega)\,\{\psi^*\nabla(\hat{A}\psi) - \nabla\psi^*(\hat{A}\psi)\}\cdot\mathbf{n}(\mathbf{r}) \tag{9}$$

The unit vector $\mathbf{n}(\mathbf{r})$ is normal to the surface at the point $\mathbf{r}$. Only components of the vector in the curly brackets that are parallel to $\mathbf{n}(\mathbf{r})$ survive in the scalar product.

The term appearing in the surface integral is proportional to the quantum mechanical current density for the operator $\hat{A}$, making eq 9 a result of physical importance. That is, eq 9 may be expressed as

$$\langle \psi|[\hat{H},\hat{A}]|\psi\rangle_\Omega = -\mathrm{i}\hbar \oint \mathrm{d}S(\mathbf{r}_s;\Omega)\,\mathbf{j}_A(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) \tag{10}$$

where the current density for property A is defined as

$$\mathbf{j}_A(\mathbf{r}) = (\hbar/2m\mathrm{i})\{\psi^*\nabla(\hat{A}\psi) - \nabla\psi^*(\hat{A}\psi)\} \tag{11}$$

The vector current $\mathbf{j}_A(\mathbf{r})$ has the dimensions of a velocity, giving the velocity of the density of the property A at some point $\mathbf{r}$ in space. The component of the surface integral of the current normal to the surface of the open system, the term described by $\mathbf{j}_A(\mathbf{r})\cdot\mathbf{n}(\mathbf{r})$, is termed the "flux". This result is demanded by physics, because, in the general time-dependent case, there will be a flow of matter and energy across the surface of an open system. Now of course in a stationary state, there is no current flow, but the surface term remains as an essential component of the properties of an open system, appearing as it does on an equal footing with the commutator average. The name "flux" is retained even in this case following Feynman's suggestion: "Although it is not the flow of anything, we still call it the 'flux'. ... We generalize the word 'flux' to mean the "surface integral of the normal component' of a vector."[20]

We can now state the equation of motion for operator $\hat{A}$ for an open system Ω in a stationary state, multiplying the results in eq 10 by (i/$\hbar$) to obtain

$$^1/_2\{(\mathrm{i}/\hbar)\langle \psi|[\hat{H},\hat{A}]|\psi\rangle_\Omega + \mathrm{cc}\} = {^1/_2}\oint \mathrm{d}S(\mathbf{r}_s;\Omega)\,\mathbf{j}_A(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) + \mathrm{cc} \tag{12}$$

Unlike the total system, for which the commutator average vanishes, eq 2, the corresponding quantity for an open system equals the surface integral of the normal component of the current of the property *A*, the flux in the current of *A*. It is this very property that makes the properties of an open system—of an atom in a molecule—different from the corresponding properties for the entire molecule. The same mathematical procedures may be employed to generalize the time-dependent expression of the equation of motion to an open system to yield eq 13.[18] The quantity $\rho_A(\mathbf{r})$ is the density of property *A*, equal

$$\mathrm{d}\int_\Omega \mathrm{d}\mathbf{r}\ \rho_A(\mathbf{r})/\mathrm{d}t = {}^1/_2\{(\mathrm{i}/\hbar)\langle\Psi|[\hat{H},\hat{A}]|\Psi\rangle_\Omega + \mathrm{cc}\} - {}^1/_2\{\oint \mathrm{d}S(\Omega)\ \mathbf{j}_A\cdot\mathbf{n} + \mathrm{cc}\} + \{\oint \mathrm{d}S(\Omega)\ (\partial S/\partial t)\rho_A(\mathbf{r}) + \mathrm{cc}\} \quad (13)$$

to ${}^1/_2\{(\hat{A}\Psi)^*\Psi + \Psi^*\hat{A}\Psi\}$, and its integral over Ω gives the open system average of A. Equation 13 relates the time rate-of-change of this average value to the commutator, to the flux in the property current, and to a surface term that takes into account the contribution to the change in the average value of *A* arising from the change in the surface with time, the term $\partial S/\partial t$. In a stationary state, the commutator average is balanced by the current flux, eq 12.

From the One- to the Many-Electron Case

Schrödinger's Definition of the Electron Density and Its Current. Extending the equation of motion for an open system to the many-electron case brings forth a very important tie with observation, as the mathematical procedure involved is identical to that used to define the measurable electron density, as done by Schrödinger in the fourth and final of the papers he published in 1926.[21] It is worth one's while to consider Schrödinger's remarks concerning the reasons he gives for defining the electron density. He initially ascribed physical meaning to the "ψ-function", having referred to "ψ-vibrations" "as something quite real." However, in the fourth paper he notes that "We have repeatedly called attention to the fact that the ψ-function itself cannot and may not be interpreted directly in terms of three-dimensional space—however much the one-electron problem tends to mislead us on this point—because it is in general a function in configuration space (now referred to as Hilbert space), not real space." Thus in the fourth paper he discards the idea of using the "ψ-function" in favor of the "weight-function $\psi^*\psi$", which, when subjected to the appropriate integration, yields the "density of electricity" at an arbitrary point in space, relegating the ψ-function to the role of determining the "weight-function $\psi^*\psi$". He obtained the "density of electricity" (the electron density ρ) by integrating the product $\psi^*\psi$ over the coordinates of all the electrons but one, whose position is fixed at a point in space, a procedure he denotes by the symbol $\int\psi^*\psi\ \mathrm{d}x'$, and then repeats for all *N* electrons.

Schrödinger's definition of ρ needs to be modified only to take into account electron spin, something that is done by simply including a summation over all spins, in addition to the integration over the coordinates of all electrons but one (whose coordinates are denoted by the vector **r**), a procedure presently denoted for all *N* electrons by the RHS of eq 14. One must

$$\rho(\mathbf{r}) = N\int \mathrm{d}\tau'\ \psi^*\psi \quad (14)$$

realize that one is not simply "integrating over the coordinates of the remaining electrons" in taking this average but is instead averaging the interactions of the density at **r** over the motions of the remaining electrons throughout "configuration space". To quote Schrödinger (his italics): "The *wave mechanical* configuration of the system is a *superposition* of many, strictly speaking, of *all*, point-mechanical configurations kinematically possible. Thus, each point-mechanical configuration contributes to the true wave-mechanical configuration with a certain *weight*, which is given precisely by $\psi^*\psi$."[21]

Schrödinger realized that in addition to the definition of the "electric density" as a single-particle concept in real space, it was equally necessary to describe its flow. Hence his derivation in the same paper of the "equation of continuity of electricity" through the definition of the single-particle current density. This equation, which applies equally to the classical flow of current, states that the change in density of charge per unit volume of space is given by the net outflow or flux of $\mathbf{j}(\mathbf{r})$ per unit volume in the neighborhood of the point **r**, a flow that is described mathematically by the divergence of the vector current, that is,

$$\mathrm{d}\rho(\mathbf{r})/\mathrm{d}t = \nabla\cdot\mathbf{j}(\mathbf{r}) \quad (15)$$

His definition of the current $\mathbf{j}(\mathbf{r})$ is identical to that derived above in eq 11 with the operator $\hat{A}$ set equal to unity and with the extension to the many-electron case determined by the same averaging as used in the definition of the density, in eq 14,

$$\mathbf{j}(\mathbf{r}) = N(\hbar/2mi)\int \mathrm{d}\tau'\ \{\psi^*\nabla_\mathbf{r}\psi - \psi\nabla_\mathbf{r}\psi^*\} \quad (16)$$

It is important to note that although ψ is the many-electron wave function, the derivative is taken with respect to the coordinates of the single electron denoted by **r**: it is a one-electron operator averaged over the motions of the remaining electrons, as is the density whose flow it describes.

Generalization of the Definition of the Density and Its Current to All Properties. The physics of an open system requires that one extend Schrödinger's definition of the electron and current densities to all properties, as is evident in eq 10 that equates the commutator average for the property *A* to the flux in its vector current through the surface of the open system. Thus, in anticipation of its averaging over an open system, the density of a property defined by the Hermitian operator $\hat{A}$ is given in its real form by

$$\rho_A(\mathbf{r}) = {}^1/_2\{\int \mathrm{d}\tau'\ (\psi^*\hat{A}(\mathbf{r})\psi + (\hat{A}(\mathbf{r})\psi)^*\psi)\} \quad (17)$$

and its associated current as

$$\mathbf{j}_A(\mathbf{r}) = N(\hbar/2mi)\int \mathrm{d}\tau'\ \{\psi^*\nabla_\mathbf{r}(\hat{A}(\mathbf{r})\psi) - \nabla_\mathbf{r}\psi^*(\hat{A}(\mathbf{r})\psi)\} \quad (18)$$

Both expressions differ from their one-electron system counterparts only in being averaged over the coordinates of the remaining electrons. It is important to note that the operator $\hat{A}(\mathbf{r})$, as does the gradient $\nabla_\mathbf{r}$, acts only on the particle with coordinate **r**.

Many-Electron Equation of Motion for an Open System. We are now in a position to rewrite the equation of motion for the operator $\hat{A}$ for an open system Ω for the many-electron case

$$\mathrm{d}\int_\Omega \rho_A(\mathbf{r})/\mathrm{d}t = {}^1/_2\{(\mathrm{i}/\hbar)\langle\Psi|[\hat{H},\hat{A}]|\Psi\rangle_\Omega + \mathrm{cc}\} - {}^1/_2\{\oint \mathrm{d}S(\Omega)\ \mathbf{j}_A\cdot\mathbf{n} + \mathrm{cc}\} + {}^1/_2\{\oint \mathrm{d}S(\Omega)\ \partial(S/\partial t)\rho_A(\mathbf{r})\} \quad (19)$$

This result is no different in form nor physical content to that given previously for the one-electron case, eq 13, other than that the property density and its current involve averages over the coordinates of the remaining electrons. The abbreviated notation used for the commutator in eq 19 is given explicitly below, emphasizing once again that the operator $\hat{A}$ acts only on the coordinates of the electron with position vector **r,** the coordinate that is integrated over the open system Ω.

$$(\mathrm{i}/\hbar)\langle\Psi|[\hat{H},\hat{A}]|\Psi\rangle_{\Omega} + \mathrm{cc} \equiv (\mathrm{i}/\hbar)N\int_{\Omega}\mathrm{d}\mathbf{r}\int \mathrm{d}\tau'\,\{\Psi[\hat{H},\hat{A}(\mathbf{r})]\Psi\} + \mathrm{cc} \quad (20)$$

The corresponding statement of the equation of motion for a system in a stationary state is identical to that given previously for the one-electron case in eq 12 with the understanding that the current refers to the definition given in eq 18 for the many-electron case and the operator $\hat{A}$ acts on the particle whose coordinates denoted by **r,** are integrated over the open system Ω as specified in eq 21.

$$^1/_2\{(\mathrm{i}/\hbar)\langle\psi|[\hat{H},\hat{A}(\mathbf{r})]|\psi\rangle_{\Omega} + \mathrm{cc}\} = {}^1/_2\oint \mathrm{d}S(\mathbf{r}_s;\Omega)\,\mathbf{j}_A(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) + \mathrm{cc} \quad (21)$$

The similarity in form and physical content of the expressions for the equations of motion for the one- and many-electron case are striking. *This brings to the fore that the single-particle nature of quantum mechanics in a many-particle system is the result of following the Heisenberg approach, transforming Schrödinger's equation into an equation of motion.* The Heisenberg approach brings one directly to the physics of the measurable *expectation* values. We shall find that this approach enables one to define *all* properties, including those that depend upon interparticle coordinates such as the energy, in terms of real-space density distributions.

One notes that all of this requires that the operator $\hat{A}$ refer only to the coordinates of the particle whose properties are averaged over the open system. Though this step follows naturally from the field theoretic approach employed in deriving the physics of an open system from Schwinger's principle, one that emphasizes the single-particle nature of matter, it is recovered in the present approach by defining the density and its current, as done by Schrödinger. These are the tools necessary for the application of his equation to predicting and understanding the properties of matter. Schrödinger concludes his fourth paper by expressing his hope that the density and its current prove useful in the elucidation of the electric and magnetic properties of atoms and molecules. It is clear to the reader at this point that with the four papers published in 1926, Schrödinger provided all of the physics required to extend quantum mechanics to an open system.[22,23]

Using the Equation of Motion To Define an Atom in a Molecule

Determining Properties from the Equation of Motion. The equations of motion for an open system, eqs 19 and 21, define all measurable properties A of an open system. Some properties are determined directly by the simple averaging of the corresponding operator, whereas others, such as the energy of an open system, require the evaluation of the appropriate commutator in the associated equation of motion. Two of the most important of these resulting theorems are obtained by setting $\hat{A}$ equal to the momentum operator $\hat{\mathbf{p}}$ of an electron whose time rate-of-change determines the force acting on the electron, the Ehrenfest force, and the virial operator $\hat{\mathbf{r}}\cdot\hat{\mathbf{p}}$, the product of the position and momentum operators for an electron, whose equation of motion yields the virial theorem.[18] The evaluation of the associated commutators and surface integrals for the resulting Ehrenfest force and virial theorems may be found elsewhere. We draw attention here only to the appearance in these expressions of the third and final single-particle densities introduced by Schrödinger, the energy density tensor, $\overleftrightarrow{\sigma}(\mathbf{r})$ defined in eq 22.[24] This quantity, with dimensions of energy per unit volume or equivalently, force per unit area, is termed a stress tensor. It is in fact the current of the momentum density and it thus appears as the flux in the Ehrenfest force theorem determining the force acting on the surface of an open system.

$$\overleftrightarrow{\sigma}(\mathbf{r}) = (\hbar^2/4m)\int \mathrm{d}\tau'\,\{\nabla(\nabla\psi^*)\psi + \psi^*\nabla\nabla\psi - \nabla\psi^*\nabla\psi - \nabla\psi\nabla\psi^*\} \quad (22)$$

The stress tensor is a most remarkable quantity. Its divergence, the quantity $-\nabla\cdot\overleftrightarrow{\sigma}(\mathbf{r})$ determines the force acting on the electron density at the point **r**.[18,25] Thus the interactions of an electron at a point in space with all of the remaining electrons, together with its interactions with the nuclear framework, are all condensed into a density expressible in real space. The virial of this force, the quantity $-\mathbf{r}\cdot\nabla\cdot\overleftrightarrow{\sigma}(\mathbf{r})$, determines the electronic potential energy of the electrons, a quantity that once again condenses the many-electron interactions and those with the nuclei into an energy density expressible in real space. Clearly, one may determine the force acting on a region of space or determine its potential energy simply by integrating the appropriate density. A most remarkable result!

The open system statement of the virial theorem is given by

$$-2T(\Omega) = \mathcal{V}_\mathrm{b}(\Omega) + \mathcal{V}_\mathrm{s}(\Omega) + L(\Omega) = \mathcal{V}(\Omega) + L(\Omega) \quad (23)$$

$T(\Omega)$ is the kinetic energy of the electrons, the terms $\mathcal{V}_\mathrm{b}(\Omega)$ and $\mathcal{V}_\mathrm{s}(\Omega)$ are the virials of the forces acting over the basin and the surface of the atom, which sum to yield the total $\mathcal{V}(\Omega)$, the potential energy of the electrons. The final term $L(\Omega)$ is foreign to the virial theorem for the total system which states that $-2T = \mathcal{V}$. It is the open system average of a quantity proportional to the Laplacian of the density, the term $-(\hbar^2/4m)\nabla^2\rho(\mathbf{r})$. The stage is now set to complete the derivation of the quantum theory of atoms in molecules by determining the boundary of the open system such that its properties including its energy, as determined by the equations of motion, agree with the measured values assigned to atoms in molecules.

Choosing the Boundary of the Open System. It is best to begin with the property that would appear to be the most difficult, if not perhaps impossible to spatially partition, the energy. How can one partition the energy of repulsion between the electrons and between the nuclei into atomic contributions? The literature records many failed attempts, but of course physics provides the answer by providing single-particle densities of all properties, including the energy. So we begin with the virial theorem, as did the historical development of the theory of atoms in molecules.[26] The study of the kinetic energy of the electrons leads immediately to a quantum constraint on the definition of the boundary. There are two ways of defining the kinetic energy density and hence the kinetic energy of some region Ω. One is the "Schrödinger kinetic energy", the form appearing in his equation and labeled $K(\mathbf{r})$,

$$\int_{\Omega}\mathrm{d}\mathbf{r}\,K(\mathbf{r}) = -(\hbar^2/4m)\int_{\Omega}\mathrm{d}\mathbf{r}\,\{\psi^*\nabla^2\psi + \psi\nabla^2\psi^*\} = K(\Omega) \quad (24)$$

and the other, the positive definite form used by him in the functional he varied to obtain his wave equation, labeled $G(\mathbf{r})$,

$$\int_{\Omega}\mathrm{d}\mathbf{r}\,G(\mathbf{r}) = (\hbar^2/2m)\int_{\Omega}\mathrm{d}\mathbf{r}\,\nabla\psi^*\cdot\nabla\psi = G(\Omega) \quad (25)$$

Though both kinetic energy densities integrate to the same value over all space, they differ locally by a term proportional to the Laplacian of the density, as indicated in eq 26. Gauss' theorem is again used in the final two terms of this equation to transform

$$K(\Omega) - G(\Omega) = L(\Omega) = -(\hbar^2/4m)\int_\Omega d\mathbf{r}\,\nabla^2\rho(\mathbf{r}) = -(\hbar^2/4m)\oint dS(\Omega)\,\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) \quad (26)$$

a volume integral of the gradient of a vector, $\nabla\cdot\nabla\rho(\mathbf{r})$, the term $L(\Omega)$ in eq 23, into a surface integral of the flux in the vector $\nabla\rho(\mathbf{r})$. The kinetic energies yield identical values when integrated over all space because the flux in $\nabla\rho(\mathbf{r})$ vanishes at every point on the boundary at infinity. For finite regions with arbitrary boundaries this will in general not be the case. However, if the region Ω is bounded by a surface though which the *net* flux in $\nabla\rho(\mathbf{r})$ vanishes, then $L(\Omega) = 0$, $K(\Omega) = G(\Omega)$, and the kinetic energy is well-defined, as it is for the total system.

Constraining the integral $L(\Omega)$ to vanish is, however, not a satisfactory way of defining the open system because the condition is not relatable to any observed property of the density and an infinitesimal motion of the nuclei will in general result in a non-vanishing flux making such a choice unsuitable. What is required is a boundary condition that is defined by the electron density and evolves with any and all changes in this physically measurable distribution function.

It is at this stage in the development that one realizes the physics we have uncovered up to this point is already rooted in the properties of the charge distribution, in that one finds that the necessary boundary condition is a natural result of the dominant topological property exhibited by the electron density—that it exhibits maxima at the positions of the nuclei.[18,27] The maxima are a result of the dominance of the attractive force exerted by the pointlike nuclei on the diffuse distribution of electronic charge and in a manner now well-documented, this topological feature results in an exhaustive partitioning of real space into a set of atomic domains Ω, each of which is bounded by a surface $S(\mathbf{r};\Omega)$, characterized by a *local* zero flux in the gradient vector field of the electron density, eq 27. The region

$$\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) = 0 \qquad \text{for all } \mathbf{r} \text{ on the surface of } \Omega \quad (27)$$

Ω is bounded by a surface of local "zero-flux in grad ρ".[26] The theory of open systems using the boundary condition given in eq 27 is called the quantum theory of atoms in molecules (QTAIM).

The portion of the atomic surface $S(\mathbf{r};\Omega)$ that lies at infinity, where both $\rho(\mathbf{r})$ and $\nabla\rho(\mathbf{r})$ vanish, clearly satisfies the zero-flux condition. The remainder of an atomic surface is composed of surfaces the atom shares with its neighboring atoms, called interatomic surfaces. Each such surface is defined by the set of trajectories of $\nabla\rho(\mathbf{r})$ that terminate at a "bond critical point" in ρ, a point where $\nabla\rho(\mathbf{r}) = \mathbf{0}$. The vector $\nabla\,\rho(\mathbf{r})$ is tangent to its trajectory at every point $\mathbf{r}$ and is thus necessarily perpendicular to the normal surface vector $\mathbf{n}(\mathbf{r})$. Equation 27 is therefore, satisfied for every point on an interatomic surface.[18,28,29]

The zero-flux boundary condition ensures that $L(\Omega) = 0$, that $K(\Omega) = G(\Omega)$, and that the atomic statement of the virial theorem, eq 23, reduces to a form identical to that for the total system, eq 28.

$$-2\mathrm{T}(\Omega) = \mathcal{V}(\Omega) \quad (28)$$

Equation 28 applies to any and all regions bounded by a zero-flux surface, and one may use the theorem to define the energy of an atom in a molecule. The theorem may be recast in its more usual form by adding $T(\Omega)$ to both sides of eq 28 to yield

$$-T(\Omega) = T(\Omega) + \mathcal{V}(\Omega) = E_e(\Omega) \quad (29)$$

The atomic virial $\mathcal{V}(\Omega)$, the virial of all of the forces acting on the atom, is the electronic potential energy of the atom. It defines the electronic energy $E_e(\Omega)$. $\mathcal{V}(\Omega)$ differs from the usual definition of the potential energy in a molecular system, the quantity V, that equals the electron−nuclear attractive energy, and the electron−electron and nuclear−nuclear energies of repulsion, in that it contains in addition to these contributions, the virials of the external forces (the Feynman forces) acting on the nuclei. These forces vanish in an equilibrium geometry and in this case $\mathcal{V}(\Omega) = V(\Omega)$. In this situation, eq 29 becomes

$$-T(\Omega) = T(\Omega) + V(\Omega) = E(\Omega) \quad (30)$$

and $E_e(\Omega)$ now equals $E(\Omega)$, the usual fixed-nucleus energy of the B−O approximation.[30,31]

Comparison with Experiment. We may now begin our ultimate test of the zero-flux boundary condition: Does it predict properties in agreement with experiment? Shortly after chemistry was organized into disciplines, it was recognized that atoms, and in particular "functional" groupings of atoms, exhibited characteristic properties that enabled one to detect their presence in any molecule and to predict the properties resulting from their presence. Indeed, it was early on discovered that atomic and group properties were not only classifiable as characteristic they could in some cases be transferable, as found for molar volume, molar refraction, electric and diamagnetic susceptibilities and thermodynamic functions H, S, and C_p etc. These properties obeyed "additivity rules"; that is, the molecular value of some property equalled the sum of the additive contributions from its constituent atoms or functional groups. It is these measured properties that are used to test the zero-flux boundary condition.

As important as the recovery of measured, additive properties, is the recovery of the *concept* of a functional group, the central building block of experimental chemistry. The concept of a functional group has been displaced in theoretical approaches to chemistry, from the central position it continues to play in experimental chemistry by the inability of molecular orbital theory to account for either its existence or properties, a failure admirably stated by Libit and Hoffmann: "Nothing like this logic (of substitutent effects) comes out of molecular orbital calculations. Every molecule is treated as a whole and no set of transferable properties associated with a functional group emerges."[32] QTAIM, on the other hand, recovers the concept of a functional group in its entirety, defining both its form and properties, reflecting the rooting of QTAIM in experiment. Thus QTAIM provides the link between molecular orbital theory and this most fundamental of all chemical concepts.

As has now been documented many times over, the atomic and group properties predicted by QTAIM agree with the additive group contributions measured experimentally. A recent publication[33] reviews the examples from thermodynamic properties such as molar volumes, heats of formation and the related properties of strain and resonance energies, to field induced properties such as electric and magnetic susceptibilities including Pascal's aromatic exaltation, to properties (infrared and Raman intensities and related transition probabilities) induced by the absorption or emission of light. A compendium of articles submitted by workers applying QTAIM to problems ranging across chemistry and solid-state physics has recently appeared.[34]

The most important of all the physical verifications of QTAIM is the common sense observation that "atoms that look the same have the same properties". Atoms that look the same have the same distribution of charge and *all* properties of the atom are found to be transferable to the same extent as is its electron density. This is widely documented for densities derived from both theory and experiment, particularly in biological molecules, as recently summarized.[33] It was the finding of the paralleling transferability of the densities of the electrons and their kinetic energy for regions of space bounded by zero-flux surfaces that led to the hypothesis that the virial theorem might apply to an atom in a molecule: if $T(\Omega)$ is transferable, then so is $E(\Omega)$ and one has in a single stroke defined an atom with transferable, additive properties.[26]

Conclusions

The equation of motion for any property A is rewritten in eq 31 with the time derivative placed inside the atomic boundary, leaving only the physically most relevant commutator and current terms, terms that survive even in the case of a stationary state.

$$\int_\Omega \partial\rho_A(\mathbf{r})/\partial t = {}^1/_2\{(\mathrm{i}/\hbar)\langle\Psi|[\hat{H},\hat{A}]|\Psi\rangle_\Omega + \mathrm{cc}\} - {}^1/_2\{\oint \mathrm{d}S(\Omega)\ \mathbf{j}_A\cdot\mathbf{n} + \mathrm{cc}\} \quad (31)$$

Every reader, upon reaching this point, has derived eq 31 from Schrödinger's equation and knows that it is mathematically correct. It is physically correct when the region Ω is bounded by a surface of local zero flux in the gradient vector of the electron density, satisfying Bethe's experimental dictum that "In science you know you know".[35] *Thus eq 31 predicts what can be measured, and in doing so, it extends quantum mechanics to an open system.* The case of $\Omega = R^3$ now appears as a special limiting case of the more general one where Ω is any region bounded by a zero-flux surface. A recent article provides a narrative account of the variational development of QTAIM, tracing its development from studies on the properties of the electron density.[36]

QTAIM, by providing the quantum basis for an atom in a molecule, necessarily recovers all of the related concepts of experimental chemistry. In addition to the atoms exhibiting additive, characteristic, and measurable properties, the theory yields definitions of molecular structure and structural stability in terms of the dynamics of the gradient vector field of $\rho(\mathbf{r})$,[27] and of electron localization/delocalization determined by the atomic expectation value of the exchange density[37,38] and given physical expression in the topology of the Laplacian of the electron density.[39]

The definition of a bond path and hence of molecular structure are inseparable from the definition and existence of an interatomic surface, both of which are defined by the topological behavior associated with the presence of a (3,−1) critical point.[40] It has recently been demonstrated that QTAIM is "robust" when extended to the relativistic domain and the entire theory can be applied with the same zero-flux boundary condition across the periodic table—including the actinides.[41] It is difficult to understand anyone doubting that the zero-flux boundary is a fundamental property of matter, providing the basis for the generalization of physics to its atomic constituents. Two atoms that share a zero-flux interatomic surface in equilibrium are bonded to one another.[40,42,43] The presence of the bond path is but a useful way of depicting and summarizing which pairs of atoms share an interatomic surface. That this shorthand notation mimics the way in which the same information is conveyed by the structures that evolved from experimental chemistry is surely one of the most powerful of all the physical vindications of the zero-flux boundary condition.

QTAIM demonstrates the unity of QM—a single theory embraces all that can be measured—from the total system, molecule, or crystal to the atoms of which they are composed.

Appendix

From the Open System Commutator, Eq 7, to the Surface Integral, Eq 9. The symbol "·" in eq 8 denotes the scalar product of two vectors, one being the gradient vector

$$\nabla = \mathbf{i}\partial/\partial x + \mathbf{j}\partial/\partial y + \mathbf{k}\partial/\partial z$$

where **i**, **j**, and **k** denote unit, orthogonal vectors; $\mathbf{i}\cdot\mathbf{i} = \mathbf{j}\cdot\mathbf{j} = \mathbf{k}\cdot\mathbf{k} = 1$. Carrying out the differentiation indicated in eq 8 yields

$$(-\hbar^2/2m)\{\nabla\psi^*\cdot\nabla(\hat{A}\psi) + \psi^*\nabla^2(\hat{A}\psi) - \nabla^2\psi^*(\hat{A}\psi) - \nabla\psi^*\cdot\nabla(\hat{A}\psi)\}$$

The first and final terms cancel, yielding

$$(-\hbar^2/2m)\{\psi^*\nabla^2(\hat{A}\psi) - \nabla^2\psi^*(\hat{A}\psi)\}$$

which indeed equals the difference obtained when the operator $\hat{T} = -(\hbar^2/2m)\nabla^2$ acts on the terms ψ^* and $\hat{A}\psi$ in eq 7. One may obtain the final surface term in eq 9 directly from eq 7 by using Green's theorem which states

$$\int\{\phi\nabla^2\varphi - \varphi\nabla^2\phi\} = \oint\{\phi\nabla\varphi - \varphi\nabla\phi\}\cdot\mathbf{n} \qquad \text{with} \quad \phi = \psi^* \text{ and } \varphi = \hat{A}\psi$$

Extension to the Many-Electron Case. The only step that may require comment on the extension to the many-electron case concerns eq 8. In the many -electron case, the RHS of eq 8 becomes eq A-1, where the summation is over the kinetic

$$(-\hbar^2/2m)\sum_i\int_\Omega \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\tau'\ \nabla(\mathbf{r}_i)\cdot\{\psi^*\nabla(\mathbf{r}_i)(\hat{A}(\mathbf{r}_1)\psi) - \nabla(\mathbf{r}_i)\ \psi^*(\hat{A}(\mathbf{r}_1)\psi)\} \quad (\text{A-1})$$

energy operators of all N electrons, including $\mathbf{r}_1$. A coordinate $\mathbf{r}_\mathrm{i}$ that is integrated over all space is differentiated from the coordinate $\mathbf{r}_1$ that is integrated over the open system Ω. Applying Gauss' theorem to a term in the sum for $\mathbf{r}_\mathrm{i} \neq \mathbf{r}_1$, the symbol $\mathrm{d}\tau''$ denoting the removal of coordinate $\mathbf{r}_\mathrm{i}$ from the integration over all space, yields eq A-2. Each such term

$$(-\hbar^2/2m)\int_\Omega \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\tau'' \oint \mathrm{d}S(\mathbf{r}_i)\ \{\psi^*\nabla(\mathbf{r}_i)(\hat{A}(\mathbf{r}_1)\psi) - \nabla(\mathbf{r}_i)\ \psi^*(\hat{A}(\mathbf{r}_1)\psi)\}\cdot\mathbf{n}(\mathbf{r}_i) \quad (\text{A-2})$$

vanishes because the surface term reduces to a term proportional to the flux in the current $\mathbf{j}(\mathbf{r}_\mathrm{i})$ in the surface at infinity, eq A-3. The only term that survives is obtained when the surface term

$$(-\hbar^2/2m)\int_\Omega \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\tau'' \oint \mathrm{d}S(\mathbf{r}_i)\ \{\hat{A}(\mathbf{r}_1)[\psi^*\nabla(\mathbf{r}_i)\psi - \psi\nabla(\mathbf{r}_i)\psi^*]\}\cdot\mathbf{n}(\mathbf{r}_i) \quad (\text{A-3})$$

applies to the coordinate $\mathbf{r}_1$ defining the surface of Ω, as given in eq A-4, which, upon comparison with eq 18 of the text, is

$$(-\hbar^2/2m)\oint \mathrm{d}S(\mathbf{r}_1;\Omega) \int \mathrm{d}\tau'\ \{\psi^*\nabla(\mathbf{r}_1)(\hat{A}(\mathbf{r}_1)\psi) - \nabla(\mathbf{r}_1)\ \psi^*(\hat{A}(\mathbf{r}_1)\psi)\}\cdot\mathbf{n}(\mathbf{r}_1) \quad (\text{A-4})$$

the term that yields the flux in the current $\mathbf{j}_\mathrm{A}$ in eq 19.

References and Notes

(1) Dalton, J. *New System of Chemical Philosophy*, facsimile ed.; Dawson: London, Manchester, 1808.

(2) Schrödinger, E. *Ann. D. Phys.* **1926**, *79*, 361.

(3) Bader, R. F. W.; Srebrenik, S.; Nguyen Dang, T. T. *J. Chem. Phys.* **1978**, *68*, 3680−3591.

(4) Bader, R. F. W. *Phys. Rev.* **1994**, *B 49*, 13348−13356.

(5) Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem.* **1981**, *14*, 63−124.

(6) Schwinger, J. *Phys. Rev.* **1951**, *82*, 914−927.

(7) Heisenberg, W. *Z. Phys.* **1926**, *38*, 411.

(8) One of the conceptual advantages of deriving the theory of an atom in a molecule from Schwinger's principle is that it yields both Schrödinger's equation and the Heisenberg equation of motion in a single unified approach, by combining the action principle with Dirac's transformation theory.

(9) Bader, R. F. W.; Cheeseman, J. R.; Laidig, K. E.; Breneman, C.; Wiberg, K. B. *J. Am. Chem. Soc.* **1990**, *112*, 6530−6536.

(10) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 1001−1012.

(11) Cremer, D.; Kraka, E.; Slee, T. S.; Bader, R. F. W.; Lau, C. D. H.; Nguyen-Dang, T. T.; MacDougall, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 5069−5075.

(12) Cremer, D.; Childs, R. F.; Kraka, E. In *The Chemistry of the Cyclopropyl Group*; John Wiley & Sons Ltd: New York, NY 1995; *Vol. 2*, pp 339−409.

(13) Bader, R. F. W. Atoms in Molecules. In *Encyclopedia of Computational Chemistry*; John Wiley and Sons: Chichester, U.K., 1998; Vol. 1.

(14) Keith, T. A.; Bader, R. F. W. *Can. J. Chem.* **1996**, *74*, 185−200.

(15) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2329.

(16) Cortés-Guzmán, F.; Bader, R. F. W. *Coord. Chem. Rev.* **2005**, *249*, 633−662.

(17) Bader, R. F. W.; Matta, C. F.; Cortés-Guzmán, F. *Organometallics* **2004**, *23*, 6253−6263.

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

(19) A reader unfamiliar with Gauss' or divergence theorem is referred to my book[18] or to volume II of Feynman's Lectures on Physics[20] for a readable account.

(20) Feynman, R. P.; Leighton, R. B.; Sands, M. *The Feynman Lectures on Physics. Vol II*; Addison-Wesley Publishing Co. Inc.: Reading, MA, 1964.

(21) Schrödinger, E. *Ann. D. Phys.* **1926**, *81*, 109.

(22) Indeed, the first variational derivation of the theory of atoms in molecules was obtained by generalizing Schrödinger's derivation of his wave equation to a system with finite boundaries, a generalization show to be possible only if the atom was bounded by a surface of zero flux in the gradient vector field of the electron density.[23]

(23) Srebrenik, S.; Bader, R. F. W. *J. Chem. Phys.* **1975**, *63*, 3945−3961.

(24) Schrödinger, E. *Ann. D. Phys.* **1927**, *82*, 265.

(25) Bader, R. F. W.; De-Cai, F. *J. Chem. Theory Comp.* **2005**, *1*, 403−414.

(26) Bader, R. F. W.; Beddall, P. M. *J. Chem. Phys.* **1972**, *56*, 3320−3329.

(27) Bader, R. F. W.; Nguyen-Dang, T. T.; Tal, Y. *Rep. Prog. Phys.* **1981**, *44*, 893−948.

(28) Any trajectory traced out by the gradient of the density satisfies the zero-flux condition at every point with the exception of those that terminate at a nuclear position where the density exhibits a cusp and its gradient is not defined.[29] The only trajectories that define a two-dimensional manifold and satisfy the zero-flux condition at every point are those that terminate at a bond critical point where the gradient vector of the density vanishes.

(29) Bader, R. F. W. *Theor. Chem. Acc.* **2002**, *107*, 381−382.

(30) In a nonequilibrium geometry, the atomic statement of the virial theorem is again in accord with the statement for the total molecule, the kinetic energy now containing a component from the atom's share of the virial of the Feynman forces acting on the nuclei, the quantity $W(\Omega)$[31], to yield $-T(\Omega) = T(\Omega) + V(\Omega) + W(\Omega) = E(\Omega) + W(\Omega)$. Thus the energy of an atom in a molecule is always defined and, like all atomic properties, is additive.

(31) Keith, T. A. In *Quantum Theory of Atoms in Molecules From Solid State to DNA and Drug Design*; Matta, C. F., Boyd, R. J., Eds.; Wiley-VCH: Weinheim, Germany, 2007; pp 61−94.

(32) Libit, L.; Hoffmann, R. *J. Am. Chem. Soc.* **974**, *96*, 1370−1383.

(33) Matta, C. F.; Bader, R. F. W. *J. Phys. Chem. A* **2006**, *110*, 6365−6371.

(34) *The Quantum Theory of Atoms in Molecules: Fom Solid State to DNA and Drug Design*; Matta, C. F., Boyd, R. J., Eds.; Wiley-VCH: Weinheim, Germany, 2007.

(35) Bethe, H. Obituary. *New York Times* **2005**, March 18.

(36) Bader, R. F. W. *Monatsh. Chem.* **2005**, *136*, 819−854.

(37) Bader, R. F. W.; Stephens, M. E. *J. Am. Chem. Soc.* **1975**, *97*, 7391−7399.

(38) Fradera, X.; Austen, M. A.; Bader, R. F. W. *J. Phys. Chem. A* **1999**, *103*, 304−314.

(39) Bader, R. F. W.; Heard, G. L. *J. Chem. Phys.* **1999**, *111*, 8789−8798.

(40) Bader, R. F. W. *J. Phys. Chem. A* **1998**, *102*, 7314−7323.

(41) Anderson, J.; Ayers, P. W. Submitted for publication.

(42) Hernández-Trujillo, J.; Cortés-Guzmán, F.; Fang, D. C.; Bader, R. F. W. *Faraday Discuss.* **2007**, *135*, 79−95.

(43) Bader, R. F. W.; Hernández-Trujillo, J.; Cortés-Guzmán, F. *J. Comput. Chem.* **2007**, *28*, 4−14.