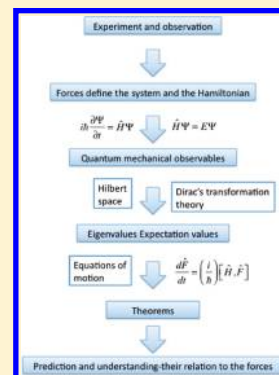


Worlds Apart in Chemistry: A Personal Tribute to J. C. Slater

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ABSTRACT: A reading of the book of Dirac's life entitled *The Strangest Man* is a most stirring experience, bringing one back to the beginnings of quantum mechanics where every attempt was made "to establish a basis for theoretical quantum mechanics founded exclusively on relationships between quantities which are in principle observable." The prime movers in this quest were Heisenberg and Dirac. One of Dirac's most important contributions in the passage from classical to quantum mechanics, a passage that consumed much of his early efforts, was unfortunately published in an obscure Russian journal where it remained largely unread until it was found by Feynman while a graduate student at Princeton. The paper posed the question, "what corresponds in the quantum theory to the Lagrangian method of classical mechanics?", a method that, as Dirac pointed out, is clearly superior in the simplicity of its structure to that of the classical Hamiltonian approach. Dirac's partial answer to this question provided the key to solving the problem of introducing the action integral into quantum mechanics that occupied Feynman's mind, leading to his formulation of the *path integral* technique. His contribution was followed two years later by Schwinger's independently derived statement of the *quantum action principle*, each contribution providing a complete formulation of quantum mechanics stated in terms of single principle. The present paper points out that the successful introduction of the action principle into quantum mechanics made possible by Dirac, enables one to proceed still further by extending Schwinger's quantum action principle to an open system, to an atom in a molecule. Thus the quantum theory of an atom in a molecule has its roots in the question posed by Dirac in 1933. The paper proposes a return to a greater use of the theorems of quantum mechanics in interpretive chemistry from that begun by Slater in 1933, a staunch advocate of theory following in the footsteps of observation.



1. PURPOSE

The purpose of this paper is to trace the evolution in the interpretation of chemical observations that carried one from the use of the theorems of physics tethered to observation to their present day replacement by models, some of which are neither related to observation nor derivable from the theorems of quantum mechanics. The development of the physics of an open system made possible by the extension of the action principle to an atom in a molecule has greatly extended the use of quantum mechanical theorems in the interpretation of chemical observations, prompting one to raise the possibility of interpretive chemistry being more directly related to the underlying quantum mechanics, to move from a world where the laws of physics are sometimes bypassed to one where they hold sway. One naturally begins this story with Slater's 1933 paper "The Virial and Molecular Structure" which marked the beginnings of our understanding of chemical bonding.¹ His approach to science has been aptly summarized by Mulliken:² "Slater constantly emphasizes and analyzes the interactions between experiment and theory, and between physical and chemical ideas and mathematical formulations."

2. EVOLUTION OF HAMILTONIAN INTO LAGRANGIAN MECHANICS

2.1. Rooting Quantum Mechanics in "Observables". Heisenberg made clear the necessity of escaping the confines of classical thinking as embodied in Bohr's atom, to establish quantum mechanics in the introductory sentence to his 1926

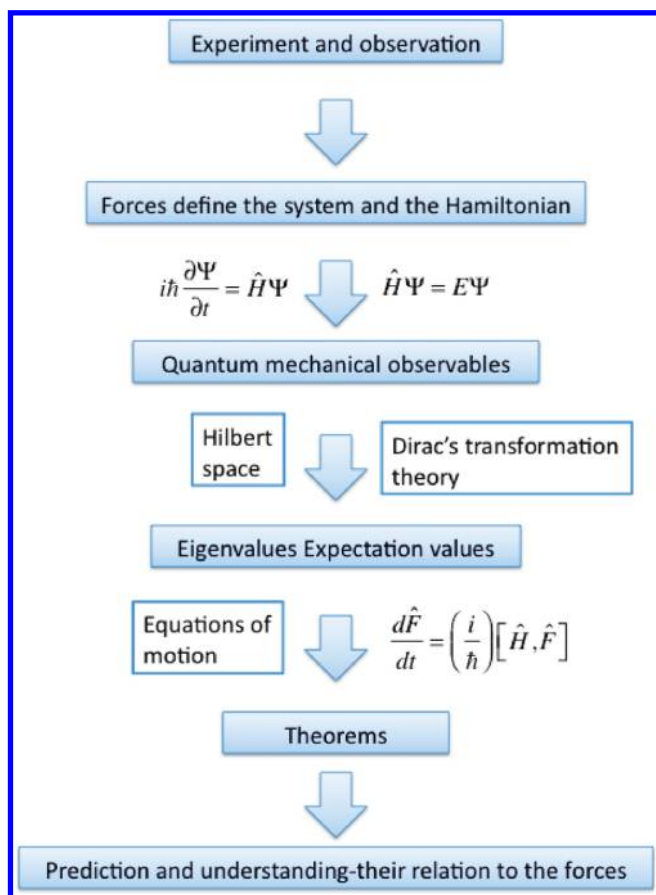
paper introducing his matrix formulation of quantum mechanics: "The present paper seeks to establish a basis for theoretical quantum mechanics founded exclusively on relationships between quantities which are in principle observable."^{3,4} His approach, expressed in terms of the equation of motion for the observables, emphasizes the ties that link theory to observation. This was the pervading drive of the group of young theoreticians that of course included Dirac, in establishing quantum mechanics, a story that is strikingly told in the book *The Strangest Man, The Hidden Life of Paul Dirac, Mystic of the Atom*.⁴ While Dirac had to introduce new, abstract mathematical ideas to express his development of quantum mechanics, he left no doubt that the goal of the theory was to understand and predict the observable properties of an atom. When he did offer support for any branch of philosophy, it was that presented by the "logical positivists", who held that a statement had meaning only if it could be verified by observation.

In the preface to the first edition of his book *Quantum Mechanics*,⁵ Dirac points out that he was faced with the choice of presenting the theory in its "symbolic form", which deals in an abstract way with the quantities of fundamental importance (the invariants, etc., of the transformations) as opposed to the method of coordinates or representations, which deals with sets of numbers corresponding to these quantities, a method commonly known under the headings

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Scheme 1^a

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of “Wave Mechanics” and “Matrix Mechanics”. These two different approaches are complementary to one another and have since evolved into today’s operational statement of quantum mechanics that is presented in Scheme 1.

2.2. Operational Structure of Quantum Mechanics. The underlying structure of quantum mechanics is illustrated in Scheme 1, one that stresses that all of physics, which certainly includes chemistry, originates in experiment followed by observation, observations that are then subjected to theoretical analysis. A system is defined by its forces, the forces determining the Hamiltonian in Schrödinger’s equation. The molecular Hamiltonian that is of interest here, is expressed in terms of the potential energy operators determined by the Coulombic forces between the electrons and nuclei, each system being identified by its unique nuclear-electron potential, the “external potential” of density functional theory. The resulting state vector or wave function is expressed as a linear superposition of base states spanning the Hilbert space. Dirac defines an observable to be a linear Hermitian operator expressible in terms of the dynamical (position and momentum) variables possessing a complete set of eigenfunctions, the base states that are employed in the representation of the state vector, a definition prompting the usage “Dirac observable”.⁵ A change in representation of the state vector from one set of base states that are eigenfunctions of one particular set of commuting observables, to another, is accomplished using Dirac’s transformation theory. There is a

Dirac observable associated with every property and it acts on a state vector to yield eigenvalues or expectation values that may or may not be measurable. *Each observable obeys a Heisenberg equation of motion and it is these equations that yield the theorems of quantum mechanics, examples being the virial theorem and the Ehrenfest and Feynman force theorems.* Through these theorems, one is able to predict and understand the properties of a system and relate the values of the observables to the forces that define the system.

2.3. From Dirac to the Physics of an Open System. In 1933 Dirac published a very important paper entitled “The Lagrangian in Quantum Mechanics”⁶ choosing to show his support for Soviet Physics by publishing the paper in a new Soviet journal where it remained essentially buried for a number of years. After outlining why the Lagrangian formulation of classical mechanics should be considered more fundamental than the approach based on Hamiltonian theory, Dirac went on to say “For these reasons it would seem desirable to take up the question of what corresponds in the quantum theory to the Lagrangian method of classical mechanics”. Thus Dirac sought the classical limit of the transformation function or transition amplitude $\langle q_{r2}, t_2 | q_{r1}, t_1 \rangle$ that connects two coordinate eigenstates at times t_1 and t_2 . He did this by the repeated use of his multiplicative law of transformation functions to obtain a limiting expression for the transformation function associated with the time displacement from t_1 to t_2 , showing it to be proportional to $\exp\{(i/\hbar)W\}$. W is the action integral, equal to $\int L dt$, taken between the limits t_1 and t_2 , and is interpreted as the sum over all individual coordinate-dependent terms in the Lagrangian L in the succession of values of t , an approach summarized in my book.⁷

Eight years later, Dirac’s limiting expression for the transformation function served as the starting point for Feynman’s development of the path integral technique, the story being told that Feynman over the course of a beer, while a graduate student at Princeton, inquired of a recent arrival from Schrödinger’s group in Berlin whether he knew of any application of the principle of least action in quantum mechanics.⁸ The visitor most certainly did and told Feynman of Dirac’s 1933 little known paper in the Soviet journal. The next day they found the article in the library and from it Feynman was able to deduce Schrödinger’s equation! The rest is history.

Feynman of course, considered all of the paths that connect the states at the initial and final times, each path having its own action W , and all values of $\exp\{(i/\hbar)W\}$ must be added together to obtain the total transition amplitude to yield Feynman’s *path integral*.⁹ Each contribution has the same modulus, but its phase is the classical action integral $(i/\hbar) \int L dt$ for the path.

$$\langle q_{r2}, t_2 | q_{r1}, t_1 \rangle = (1/N) \int \exp\{(i/\hbar) \int_{t_1}^{t_2} L dt\} \delta q_r(t) \quad (1)$$

The differential $\delta q_r(t)$ indicates that one must integrate over all paths connecting q_{r1} at t_1 and q_{r2} at t_2 .

Building on the same association, but starting from Dirac’s expression for a differential statement of the transformation function between times t_1 and t_2 , Schwinger obtained his statement of the *quantum action principle* which is a differential statement of Feynman’s path integral formulation as stated in eq 2¹⁰

$$\begin{aligned} \delta \langle q_{r2}, t_2 | q_{r1}, t_1 \rangle &= (i/\hbar) \langle q_{r2}, t_2 | \delta \hat{W}_{12} | q_{r1}, t_1 \rangle \\ &= (i/\hbar) \langle q_{r2}, t_2 | \delta \int_{t_1}^{t_2} \hat{L}[t] dt | q_{r1}, t_1 \rangle \quad (2) \end{aligned}$$

Equation 2 is expressed in terms of the action integral and Lagrange

function operators. The derivation of Schwinger's quantum action principle is developed in detail in my book.⁷

Both Feynman's and Schwinger's principles yield not only the equation of motion but also the commutation rules. To quote Schwinger, "It is the latter aspect (the mathematical scheme of linear operators and state vectors with its associated probability interpretation in Hilbert space) that we wish to develop, by substituting a single quantum dynamical principle for the conventional array of assumptions based on classical Hamiltonian dynamics and the correspondence principle."¹⁰

Thus the whole of quantum mechanics as outlined in Scheme 1, from Schrödinger's equation to the commutation relations, can be deduced from a single dynamical principle, the quantum action principle. The operational expression of this principle is obtained from an alternate differential expression for the variation of the transformation function that is characterized by the action of generators of infinitesimal unitary transformations $\hat{F}(t_1)$ and $\hat{F}(t_2)$ acting on the same eigenvectors, a comparison of the two expressions yielding the *principle of stationary action*

$$\delta\hat{W}_{12} = \hat{F}(t_2) - \hat{F}(t_1) \quad (3)$$

Schwinger's formulation is a marriage of Dirac's transformation theory and the action principle and thus it recovers Schrödinger's equation and Heisenberg's equation of motion for the observables, everything needed for the application of quantum mechanics. Infinitesimal unitary transformations, in addition to their role in the application of Dirac's transformation theory, are essential to the linking of classical and quantum mechanics, one of his primary goals, as is clear from Dirac's statement regarding infinitesimal contact and unitary transformations, "We have here the mathematical foundation of the analogy between the classical and quantum equations of motion, and can develop it to bring out the quantum analogues of all the main features of the classical theory of dynamics."

Remarkable as this is, Schwinger's new formulation does much more; it enables the extension of quantum mechanics as outlined in Scheme 1 to an open system.^{7,11–13} This is a necessary step in the generalization of quantum mechanics to an atom in a molecule, the atom necessarily being an open system, as it may exchange mass and momentum with its bonded neighbors. Schrödinger's equation is again obtained for the *total* system in the extension of his principle to an open system. The expectation values and associated equations of motion for each Dirac observable are defined for the open system, a bounded piece of the total system. It is the extension of Schwinger's principle to an open system that forms the basis for the quantum theory of atoms in molecules (QTAIM) by providing the quantum mechanical description of an atom in a molecule.¹³

Thus the basis for the development of the quantum mechanics of an open system was laid out by Dirac in his derivation of the limiting expression for the quantum analogue of the classical action for a single path linking the times t_1 and t_2 . It took just under twenty years for this suggestion to flower into the quantum mechanical expressions of Feynman and Schwinger and another thirty for its extension to an open system.

As important as the realization that the physics of an open system is grounded in the quantum action principle, is the finding that the boundary condition defining an open system is expressed in terms of the expectation value of a system's most important Dirac observable, the electron density operator as stated in terms of the Dirac delta function, $\hat{\rho}(r) = \delta(\hat{r} - r)$, thereby fulfilling the opening statement of intent given in Heisenberg's quotation, "to

establish a basis for theoretical quantum mechanics founded exclusively on relationships between quantities which are in principle observable." The quantum boundary condition is expressed in terms the gradient vector field of the electron density that uniquely partitions a system into spatial regions designated by Ω , satisfying the condition of exhibiting a local zero-flux in the gradient of the vector field through the surface $S(\Omega; \mathbf{r})$ bounding the open system,^{7,14}

$$\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0 \quad \text{for all points } \mathbf{r} \text{ on the surface } S(\Omega; \mathbf{r}) \quad (4)$$

The Heisenberg equation of motion for an open system obtained from the principle of least action is characterized by the presence of a flux in the associated current through its surface, the current along with the density, being the two quantities Schrödinger deemed essential for the understanding of the properties of matter. The Heisenberg equation of motion for an observable \hat{G} , generalized to any system Ω bounded by a "zero-flux" surface $S(\Omega; \mathbf{r})$, one that includes the total system, is given in eq 5, completing the outline of physics as presented in Scheme 1.

$$\begin{aligned} d\int\rho_G(\mathbf{r})/dt &= N/2\{(i/\hbar)\langle[\hat{H}, \hat{G}]\rangle_\Omega + cc\} \\ &- (1/2)\left\{\int dS(\mathbf{r}, \Omega) \mathbf{J}_G(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) + cc\right\} \\ &+ (1/2)\left\{\int dS(\mathbf{r}, \Omega) (\partial S/\partial t)\rho_G(\mathbf{r})\right\} \quad (5) \end{aligned}$$

It is expressed in terms of the associated electron and vector current densities $\rho_G(\mathbf{r})$ and $\mathbf{J}_G(\mathbf{r})$, the two physical properties that determine the properties of matter for an observable \hat{G} .⁷

One more important demonstration by Schwinger cements the extension of his principle given in eq 2 to an open system: his demonstration that the variation of the action and the generating operators of infinitesimal transformations must satisfy the additive law of composition, that is, $\delta\hat{W}_{13} = \delta\hat{W}_{12} + \delta\hat{W}_{23}$. This property ensures that the action integral operator may be expressed as a sum over the operators for all of the open systems (atoms) in a molecule, i.e., $\hat{W}_{12} = \sum_\Omega \delta\hat{W}[\Omega]_{12}$ to yield

$$\delta\langle q_2, t_2 | q_1, t_1 \rangle = (i/\hbar) \sum_\Omega \langle q_2, t_2 | \delta W[\Omega]_{12} | q_1, t_1 \rangle \quad (6)$$

where each open system is bounded by a surface of zero-flux in the gradient vector field of the electron density, eq 4.

3. BEGINNINGS OF QUANTUM CHEMISTRY

One could argue that quantum chemistry had its start with the paper by Heitler and London in 1927¹⁵ wherein they applied the wave equation derived the previous year by Schrödinger,¹⁶ to the hydrogen diatomic molecule and demonstrated that quantum mechanics could account for "covalent" bonding, as opposed to ionic bonding, which at the time was accounted for in terms of electrostatics. The Heitler–London (H–L) paper expressed the wave function for H_2 as a combination of two atomic-like terms: $a(1)b(2)$ assigning electrons 1 and 2 to atoms "a" and "b" and the term $a(2)b(1)$ where the electronic positions are exchanged between the atoms. This process was likened to quantum mechanical resonance (although H–L went to some lengths in their paper to counter this analogy) and the interpretation of bonding in terms of the wave function and "resonance" were to dominate theory from that moment to the present day, as

exemplified in the recent statement, “which showed that the bond energy in H_2 is due to resonance between the electrons as they exchange positions between the two atoms.”¹⁷

London noted in 1928 that the physical consequence of “resonance” was the accumulation of density between the nuclei, something that since then has been shown to be true for all wave functions that account for bonding and bonding cannot be uniquely linked to “resonance”.¹⁸ Schrödinger introduced the electron density $\rho(\mathbf{r})$, the vector current density $\mathbf{J}(\mathbf{r})$, and the equation of continuity, linking them in his fourth paper of 1926.¹⁹ Schrödinger, echoing the philosophy of Heisenberg and Dirac, strongly advocated that one relegate the use of the wave function to the determination of the observables $\rho(\mathbf{r})$ and $\mathbf{J}(\mathbf{r})$ and to avoid using ψ directly in the interpretation of physical observations. This advice was not followed and experimental chemistry is presently explained using empirical concepts, many of which do not relate directly to any measurable property or to quantum mechanical theorems. The use of the concept of “resonance”, for example, removes one from the realm of definable physical forces.

The fundamental role of the density in understanding chemical bonding was first pointed out by London in 1928 in a little-known companion paper to the one he coauthored with Heitler giving the quantum mechanical description of homopolar bonding.¹⁸ London gave contour diagrams of the density distributions associated with the antisymmetric and symmetric solutions to the Heitler–London (H–L) equations, his diagrams having been recently reproduced.²⁰ He obtained the densities by integrating $\psi^*\psi(\mathbf{r}_1, \mathbf{r}_2)$ over the coordinates of one of the electrons, employing the definition of the density $\rho(\mathbf{r})$ provided by Schrödinger in the preceding year. London’s paper presents the first calculated representations of the electron density. “... the density for the symmetric state shows the two atoms which are in a state of homo-polar binding. Here the two densities seem to draw closer and become one. *With the help of these figures, one can imagine how in complicated molecules the atoms which form a valence are connected by such a bridge of $\psi^*\psi$ -density, while all remaining atoms stay separate.*” His figure for the symmetric state clearly illustrates the buildup of density between the nuclei, an observation later commented on by Feynman:²¹ “It now becomes clear why the strongest and most important attractive forces arise when there is a concentration of charge between two nuclei.” *London was the first to define a bond path as a “bridge of density” and to postulate its physical significance in the understanding of bonding.* Unfortunately, this paper went unheeded (and remained so for 80 years) and instead the chemical community embraced the “mysterious wave function” and its associated “resonance”. It has in fact been stated by a proponent of this view that the bonding process is too complicated to be understood by the average chemist, the concept of a wave function being “too abstract and too elusive” for chemists to grasp!²²

4. RELATION OF CHEMICAL CONCEPTS TO THE THEOREMS OF QUANTUM MECHANICS

Slater introduced the use of theorems of quantum mechanics in the interpretation of chemical bonding in his famous paper entitled “The Virial and Molecular Structure” in 1933. We begin this section with a review of the original literature concerning the derivation of the theorems necessary for the interpretation of bonding. This section is necessary to correct the errors promulgated in the literature that attempt to downplay the pioneering role of Slater’s contributions.

Pauli’s 1933 book, later reprinted in 1958,^{23,24} gives derivations of the virial theorem, the Ehrenfest theorem and what became known as the Hellmann–Feynman theorem, crediting the original derivation of the virial theorem to Sommerfeld.²⁵ None of these theorems are employed by Pauli in discussions of chemical bonding. It is frequently stated incorrectly in the literature, as, for example, by Kutzelnigg,²⁶ that Hellmann gave a derivation of the virial theorem in 1933. He does not derive the virial theorem but instead begins with a statement of the theorem he ascribes to Fock.²⁷

Slater published an original derivation of the virial theorem in 1933.¹ His goal was to extend the virial theorem to describe the mechanics of a molecule displaced from its equilibrium geometry, thus requiring the presence of external or “impressed” forces to keep the nuclei fixed. He did this with the specific purpose of applying the theorem to a discussion of chemical bonding. The derivation begins with differentiation of Schrödinger’s equation with respect to an electronic coordinate x_i followed with multiplication by $x_i\psi^*$. The result can be rearranged to yield

$$\sum_i -(\hbar^2/8m) \sum_j [x_j[\psi^*(\partial^3\psi/\partial x_i^2 \partial x_j) - (\partial^2\psi^*/\partial x_i^2)(\partial\psi/\partial x_j)]] + [\sum_j x_j(\partial V/\partial x_j)]\psi^*\psi = 0 \quad (7)$$

This is followed by integration over coordinate space, wherein the first term is integrated by parts (the surface term so obtained vanishing on the boundary at infinity) to yield

$$-2T = \int d\tau \sum_j x_j (-\partial V/\partial x_j)\psi^*\psi = \mathcal{V} \quad (8)$$

Recalling that $F_j = (-\partial V/\partial x_j)$, the term on the right-hand side defines the virial of all the forces acting on the electrons, the virial \mathcal{V} . Slater applied this result to the formation of diatomic molecules from the separated atoms, using empirical potential energy functions to calculate the forces F_j acting on the nuclei for geometries removed from the equilibrium separation R_e , forces that were later identified with the Feynman force.²¹

Out of interest, Slater’s original derivation of the virial theorem served as the starting point for the first paper on the physics of an open system, one yielding the sufficient conditions for an atomic statement of the virial theorem.²⁸ This derivation was followed in 1975 by its variational derivation, using both the variational principle in a scaling of the electronic coordinates and the calculus of variations, for a system bounded by a zero-flux surface.²⁹ The variational derivation was obtained by an extension to a bounded system of Schrödinger’s original derivation of his “wave equation”.¹⁶ Schrödinger’s derivation is equivalent to the variation of a constrained action integral for an infinitesimal time interval³⁰ using the calculus of variations.

The virial theorem is the Heisenberg equation of motion for the Dirac observable $\mathbf{r} \cdot \mathbf{p}$, which has the dimensions of action. The potential energy defined in the molecular virial \mathcal{V} is given by the virial of the Ehrenfest forces exerted on the electron density, the Ehrenfest force theorem being the Heisenberg equation of motion for the Dirac observable $\mathbf{p} = -i\hbar\nabla$ and the force being determined by the time-rate-of-change of the momentum, as in classical theory. It is important that one understand that the molecular virial as defined in terms of the Ehrenfest force includes the virial of any external forces acting on the nuclei

In 1933 Slater ascribed the forces acting on the nuclei to the gradients of the potential energy surface, their identification as the Feynman electrostatic forces acting on the nuclei having to await the publication in 1939 of Feynman's paper "Forces in Molecules" submitted as a senior thesis under Professor Slater's tutelage.²¹ The original derivation of the theorem that later became known as the Hellmann–Feynman theorem was given by Pauli.

In 1933, Hellmann³¹ provided a derivation of the "Hellmann–Feynman" theorem before that published by Feynman. However, contrary to published statements, there is no discussion of the role of this theorem in chemical bonding, neither in the 1933 paper³¹ nor in the German or Russian versions of his book *Introduction to Quantum Chemistry*.^{32,33} This is to be contrasted with Feynman's 1939 paper establishing the electrostatic theorem that is devoted to the mechanics of bonding.²¹

Feynman's electrostatic theorem is the Heisenberg equation of motion for the Dirac observable $-i\hbar\nabla_{\alpha}$, the gradient operator referring to the coordinates of a nucleus α . Feynman's theorem demonstrates that bonding is a result of the accumulation of electron density between the nuclei exerting an attractive force sufficient to overcome the force of repulsion between them. It may be considered the cornerstone of the theory of chemical bonding. *It is this force and this force alone that determines whether a given nucleus experiences an attractive, a repulsive, or a vanishing force in any given geometry.* This statement of physics should be borne in mind when one encounters references to "Pauli or nonbonded repulsions".

The Ehrenfest force acting on the electron density and the Feynman forces acting on the nuclei are the only forces involved in the physics of chemical bonding, and they provide the tools that are needed to describe the forces acting in a molecule. The virial theorem provides a unified statement of these forces by relating them to the molecule's energy and its kinetic and potential contributions. The Feynman, Ehrenfest, and virial theorems play a dominant role in theories of chemical bonding, a topic central to conceptual chemistry. Slater's use of these theorems, begun in 1933, is used to illustrate the differences in the quantum mechanical and model based approaches to bonding.

4.1. Bonding as Understood in Terms of Quantum Mechanical Theorems. Slater gave his 1933 derivation of the virial theorem for the specific purpose of discussing the process of bonding, beginning with infinitely separated atoms. Slater's interpretation, which was later expanded upon in his book,³⁴ was the first attempt to account for chemical bonding using the theorems of quantum mechanics, as opposed to the use of the "resonance model" and other then current approaches based upon the Heitler–London wave function. He did so with the understanding that one must consider the contribution to the virial and hence to the kinetic and potential energies arising from the virial of the "Feynman forces" exerted on the nuclei.

Slater's molecular virial theorem written for a diatomic molecule may be expressed as

$$T = -E - R(dE/dR) = -E + RF(R) \quad (9)$$

The quantity $F(R) = -(dE/dR)$, is the Feynman force on a nucleus at separation R : One may recast eq 9 in terms of the changes in the energies relative to their values at infinite separation to give the relation between $\Delta E(R)$ and the kinetic energy $\Delta T(R)$

$$\Delta T(R) = -\Delta E(R) + RF(R) \quad (10)$$

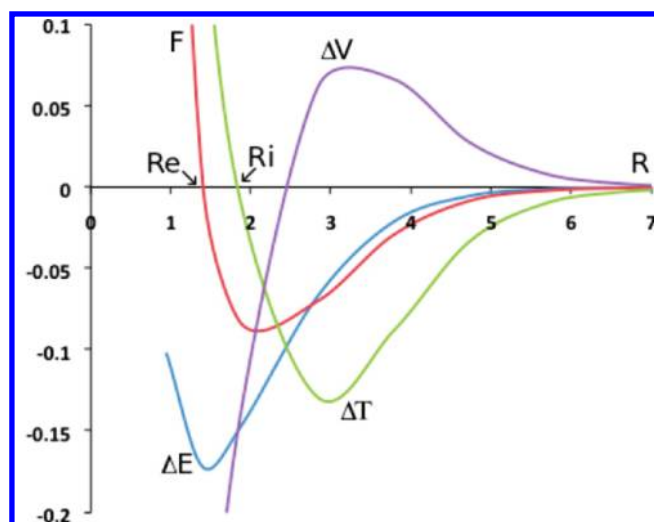


Figure 1. Feynman force $F = F(R)$ on a proton in ground state H_2 . The equilibrium separation is denoted by R_e and the inflection point in the $E(R)$ curve, where $F(R)$ is maximally attractive by R_i , which by chance, is close to the intersection of the axis with ΔT . Results from QCISD(full)/6-311++G(3pd), giving $R_e = 1.401$ (1.401) au and $D_e = 4.71$ (4.75) eV, experimental values in parentheses. Also shown is the variation in ΔE , ΔT , and ΔV with internuclear separation R for the ground state of the H_2 molecule in atomic units.

and the potential energy $\Delta V(R)$

$$\Delta V(R) = 2\Delta E(R) - RF(R) \quad (11)$$

Slater's use of the virial and Feynman theorems in the discussion of bonding is well-known and have been recently reviewed in detail.^{35,36} The behavior of $\Delta E(R)$, $\Delta T(R)$, $\Delta V(R)$, and $F(R)$ as a function of the internuclear separation R in a diatomic molecule are shown in Figure 1. This behavior of ΔT and ΔV was first established by Slater in his 1933 paper through the use of empirical molecular potential energy functions in conjunction with the virial theorem. It is important to understand that while the curves shown in Figure 1 are calculated for H_2 , their forms are universal, as shown for shared (covalent), polar, and van der Waals interactions.^{35,36}

What at first might be surprising to some in terms of the oft quoted statement of the virial theorem, that the kinetic energy must increase on bonding by an amount equal to the decrease in energy, is the apparent reversal in the stabilizing–destabilizing roles of the kinetic and potential energies displayed in Figure 1, with the potential energy initially increasing and the kinetic energy decreasing, as the atoms approach from infinity. This behavior is readily understandable by relating the changes in ΔT and ΔV through eqs 10 and 11, to the changes in the Feynman force on the nuclei $F(R)$, changes that are readily related to changes in the density displayed in the density difference maps $\Delta\rho(r)$ and their profiles along the internuclear axis, for the approach of two H atoms that are illustrated in Figures 2 and 3. These diagrams emphasize that the entire discussion of bonding can be presented in terms of quantum mechanical theorems and the "observable", i.e., measurable, electron density.^{37,38}

The virial of a force, the quantity $RF(R)$ in eqs 10 and 11, is negative and stabilizing when the Feynman force is attractive, $RF(R) < 0$. *It is only in the presence of an attractive force that ΔT and ΔV can change sign: $\Delta T < 0$ when $|RF(R)| > -\Delta E$ and $\Delta T = 0$ when $|RF(R)| = -\Delta E$; $\Delta V > 0$ when $-RF(R) > 2|\Delta E|$ and $\Delta V = 0$ when $2|\Delta E| = -RF(R)$.* Thus ΔV becomes negative before

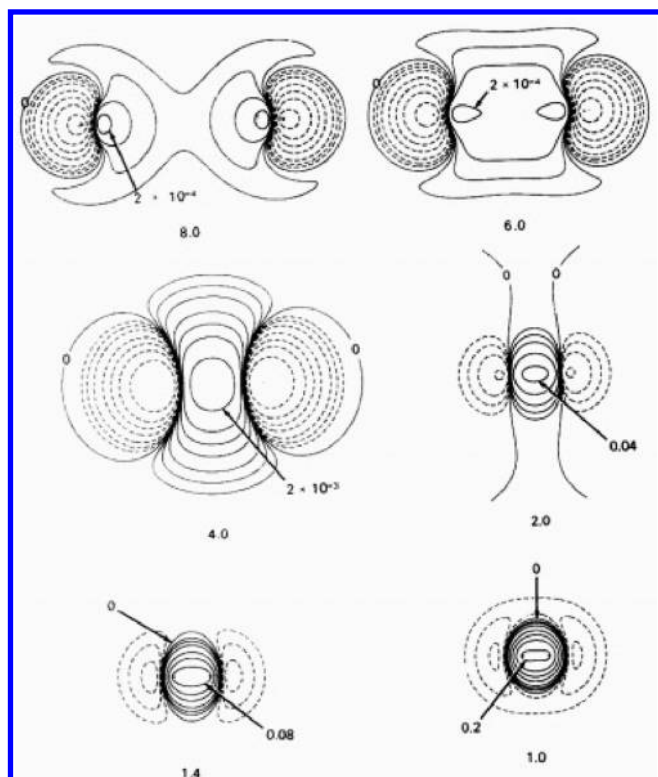


Figure 2. Density difference plots for the formation of ground state H_2 calculated from a correlated wave function. The internuclear separation is listed under each figure in au. The solid and dashed contours increase or decrease respectively from the zero contour in the order $\pm 2 \times 10^{-n}$, $\pm 4 \times 10^{-n}$, $\pm 8 \times 10^{-n}$ au for decreasing values of n . The maps for $R = 8, 6$, and 4 au begin with $n = 5$ and those for $2.0, 1.4$, and 1.0 au begin with $n = 3$. Note the inward polarization of the atomic densities at large separations as predicted by Feynman. At $R = 2$ au, the inflection point in the $E(R)$ curve, the boundary of the charge accumulation in the binding region passes through the nuclei and $F(R)$ is a maximum. For $R < 2$ au, density is increasingly placed in the antibinding regions. Reprinted with permission from: Bader, R. F. W. *An Introduction to the Electronic Structure of Atoms and Molecules*; Clarke Irwin & Co Ltd.: Toronto, Canada, 1970; available online at www.chemistry.mcmaster.ca/faculty/bader/aim/.

ΔT becomes positive. When the Feynman force is repulsive, $RF(R) > 0$ and $\Delta T > 0$ and $\Delta V < 0$.

The behavior in the range $\Delta T < 0$ and $\Delta V > 0$ is understandable in terms of the changes in the electron density that accompany the initial approach of the atoms as shown for $R = 8$ and 6 au in Figures 2 and 3. Electron density is removed from the immediate vicinities of both nuclei where $V(\mathbf{r})$ is maximally negative and $T(\mathbf{r})$ is maximally positive and accumulated in a diffuse distribution in the binding region resulting in the relaxation of the gradients in ρ and thus further reducing T . Thus V is increased, T is decreased, and the density accumulation in the binding region and its removal from the antibinding regions results in an attractive Feynman force on the nuclei. Each nucleus is attracted by its own *inwardly polarized density* and the resulting “boot strap” force is, as explained by Feynman, the origin of the initial $1/R^6$ long-range attraction between neutral atoms.

Thus the initial decrease in T is a result of the creation of attractive Feynman forces on the nuclei resulting from the accumulation of density in the internuclear region (Slater’s overlap density), the essential first step in bond formation and

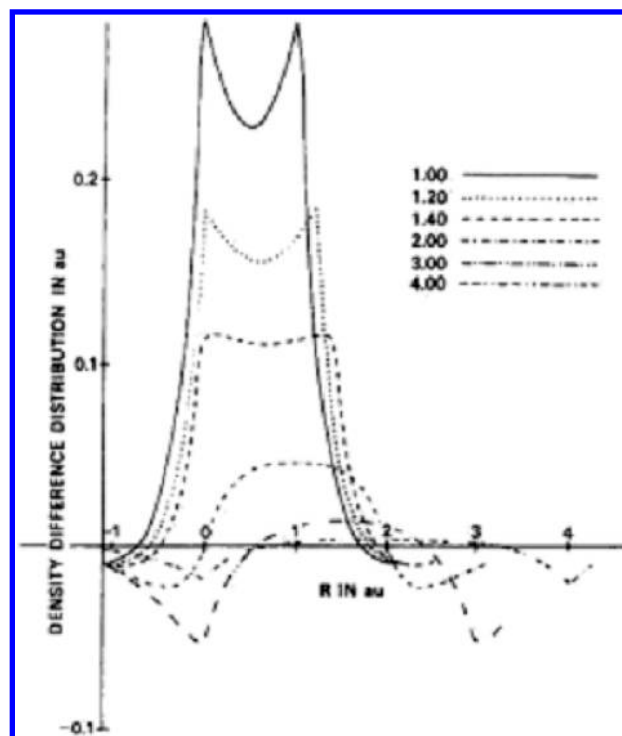


Figure 3. Profiles of the density difference plots for the formation of the hydrogen molecule along the internuclear axis. Note how the profiles emphasize the principal changes in the density: from its initial removal in the nuclear regions, to its ever increasing accumulation in the binding region, as well as at the nuclear positions. All of the changes depicted here result in attractive Feynman forces acting on the nuclei, as shown in Figure 1. No one viewing these changes in the density can possibly dispute Feynman’s electrostatic theorem, that bonding is a consequence of the accumulation of electron density in the internuclear region. It should be noted that the $\Delta\rho(\mathbf{r})$ maps for shared interactions for atoms past He differ from those for H_2 . They of course show an accumulation of density in the binding region, but the density in the regions of the nuclei undergoes a decrease rather than an increase.⁶¹ The increase in density at the protons plays a central role in the application of the “Hellmann model” to H_2 .^{26,42} The model is thus inapplicable beyond hydrogen. Reprinted with permission from: Bader, R. F. W. *An Introduction to the Electronic Structure of Atoms and Molecules*; Clarke Irwin & Co Ltd.: Toronto, Canada, 1970; available online at www.chemistry.mcmaster.ca/faculty/bader/aim/.

one that continues up to the equilibrium separation where $\Delta E = -\Delta T$. It is important to note that the decrease in T is found only when attractive Feynman forces act on the nuclei, and thus it does not occur at the equilibrium separation R_e .

One may combine the virial and Feynman theorems through the use of eqs 10 and 11 to obtain differential statements for $dT(R)$ and $dV(R)$ that are shown to be determined in their entirety by $F(R)$ and $dF(R)/dR$. These expressions yield constraints on the signs of the slopes $dT(R)/dR$ and $dV(R)/dR$, which are seen from Figure 1 to change sign with decreasing R . The derivation of these equations and their full discussion have been given previously.^{7,39} They demonstrate that the Feynman force and the kinetic and potential energies are all interdetermined by the virial theorem, noting in particular that the Feynman force $F(R)$ and its derivative $dF(R)/dR$, completely determine the behavior of both T and V over the entire range of internuclear separations, as first demonstrated by Slater in 1933 and illustrated in Figure 1. Figure 1 shows that the constraints imposed by $F(R)$ and $dF(R)/dR$ cause

ΔT to increase and ΔV to decrease before $R = R_c$ and thus ΔT begins its increase well before R_c . Ruedenberg and Schmidt⁴⁰ make an unfair criticism⁴¹ of Slater in relation to the demonstration that $F(R)$ and $dF(R)/dR$ completely determine the behavior of T , V , and E as a function of R .^{7,39} These same results demonstrate that a statement by Ruedenberg and Feinberg⁴³ to the contrary regarding the role of the Feynman theorem in this regard is wrong.

4.2. Models of Bonding Based upon Hellmann's Model. Slater's approach to bonding is counterbalanced by the work of those^{26,40,42–44} who make use of a model first proposed by Hellmann.^{32,33} Hellmann's book *Introduction to Quantum Chemistry* was first presented in a Russian translation of the German version. Hellmann was forced to flee Nazi Germany for Russia, where, unfortunately, he was later shot as a German spy. Hellmann's account, has been the subject of a careful reading of the Russian text, a translation that has previously been presented in detail.⁴⁵

This reading makes clear that Hellmann did not unequivocally support what became known as "Hellmann's model of bonding", one in which he ascribed bonding to a decrease in the kinetic energy, in direct violation of the virial theorem. The translation of the Russian text makes clear that any suggestion that Hellmann relegated the virial theorem to a secondary position relative to any of the models that he proposed are ill-founded. He used the electron in a box model to consider the approach of two identical atoms with a single valence electron each initially in its own box. In forming the molecule, the boxes are linked together and the electrostatic attraction of each valence electron with the field of the other atom gives attraction. From this point on, the contribution arising from the change in the potential energy of the electrons is ignored, a point that is later rectified with the statement in a discussion of the potential energy component of the particle in a box model: "We are no longer convinced that the actual cause of the bonding is the decrease in the kinetic energy, since a portion of the charge has a potential energy that can decrease upon the approach of the atoms", a conclusion that reflects his stated belief in the virial theorem.

The work of those who continue to follow and employ "Hellmann's model" has recently been the subject of a review.⁴⁵ They dispute the understanding that bonding is a result of the accumulation of electron density between the nuclei, a view summarized in the statement,⁴² "The ubiquitous statement that overlap accumulation of electrons in a bond leads to a lowering of the potential energy is based upon fallacious reasoning." A quotation from a recent paper summarizes the present interpretation of Hellmann's point of view: "Hellmann ... was convinced that covalent bonding resulted from a lowering of the kinetic energy due to the increase in volume available to the electron in the molecule, i.e., to delocalization",⁴⁰ statements in direct contradiction to Hellmann's final view of bonding as governed by the virial theorem. One school^{40,43} insists that an understanding of bonding must be based upon what is termed "variational reasoning".⁴⁶

Clearly, the proponents of "Hellmann's model" inhabit a world wherein the virial, Feynman, and Ehrenfest forces are violated. In a review of Hellmann's scientific contributions, Schwarz et al.⁴⁷ express surprise that there are still those who believe in Slater's and Feynman's view that "bond formation ... can arise only from the attraction between the positive nuclei and a growing negative charge in the bond region." In separating a molecule into atoms, one must overcome the electrostatic force of attraction of the nuclei for the electron density. There is no other force operative and hence it provides a both necessary and sufficient explanation of bonding. Schwarz et al. ignore the concept

of a force and its role in physics. Following Scheme 1, having once determined the wave function, one is in the real world of expectation values of observables. The observables of interest here are the ones yielding the theorems of Feynman and Ehrenfest and the virial theorem and, of course, the electron density. The density for a bound state is predicted to result in the accumulation of electron density in the internuclear region sufficient to overcome the forces of repulsion and lead to chemical bonding, the forces being determined by Feynman's theorem. QM has answered the question of how the electrostatic force yields bonding. The same force, when integrated over a change in internuclear separation, yields the corresponding change in energy, a quantity now related to changes in the density, as illustrated in Figure 2 and Figure 3 for the formation of the hydrogen molecule. When combined with the Ehrenfest and virial theorems, one has a complete physical description of chemical bonding.

Statements that a decrease in kinetic energy can lead to an increase in the stabilization of a system appear throughout the literature, a statement in direct violation of the virial theorem, because $\Delta T = -\Delta E$ for a displacement from one to another equilibrium geometry. It is, of course, possible for the kinetic energy to exhibit a decrease, but only when attractive Feynman forces act on the nuclei and contribute to the virial, as for example, during a chemical reaction when the system is moving on a downward slope of a potential energy surface and bond formation exceeds any bond breaking. The attractive force will attain a maximum value during this motion and then begin to decrease in magnitude, eventually vanishing in the equilibrium geometry of the product. The atomic statement of the virial theorem enables one to monitor the contribution of the attractive force to each atom's virial through the equation $\Delta T(\Omega) = -\Delta E(\Omega) + W(\Omega)$, where $W(\Omega)$ is the atomic contribution of the virial of the Feynman forces acting on the nucleus of atom Ω . This equation is, in effect, an atomic statement of the diatomic result that $\Delta T = -\Delta E + RF(R)$, eq 10, and may be interpreted in the same manner; ΔT decreasing when attractive forces act on the nucleus of the atom to yield a virial $W(\Omega) < 0$, which exceeds $-\Delta E(\Omega)$. With further motion along the reaction coordinate, E continues to decrease while the force diminishes as the equilibrium structure is approached. At some point, $-\Delta E$ exceeds $W(\Omega)$ and the kinetic energy begins to increase, attaining the value equal to $-\Delta E$ at the termination of the reaction. This behavior of the force and virial are the same as that shown in Figure 1 for the formation of a molecule. This example demonstrates that all of the theorems of quantum mechanics have an atomic counterpart, one that provides an atomic view of every chemical change.

In their discussion of the box model, in which they replace the "boxes" with orbitals, Schwarz et al.⁴⁷ proffer the oversimplified statement that the "electron clouds of the electrons can expand into the space of the neighbouring orbitals (in an apparent neglect of orbital overlap) leading to a reduction of the kinetic and total energy, which then results in chemical bonding." This view is to be contrasted with that of Slater. After properly accounting for the initial decrease in the kinetic energy at large separations, a result of attractive forces acting on the nuclei as portrayed in Figure 1 and accounted for by the virial and Feynman theorems, he notes that the kinetic energy begins to rise on closer approach because the electrons are forced into a smaller space as a result of the overlapping of the atomic orbitals, *the decrease in volume being proportional to the overlap integral S of the orbital model*. This argument sounds more plausible than Hellmann's claiming a doubling in available volume as two

“potential boxes” are joined together on bonding and in direct opposition to the view of Schwarz et al.⁴⁷ who state that *overlapping orbitals increase the volume available to the electrons*. This leads one to inquire “what happened to the orbital overlap integral?”, which is proportional to the decrease in volume as orbitals overlap. Slater’s argument sounds more plausible than one claiming an increase in available volume as potential “boxes” are joined together on bonding as in Hellmann’s model, and in direct opposition to the view of Schwarz et al. that *overlapping orbitals increase the volume available to the electrons*. One may obtain a direct answer to the change in volume encountered in passing from two isolated H atoms to the H₂ molecule by using the 0.001 au isodensity surface that determines the van der Waals volume.⁴⁸ The van der Waals volume of two isolated H atoms is 200 au compared to 119 au for the H₂ molecule. Thus formation of H₂ results in a nearly 2-fold decrease in volume as opposed to the doubling assumed by Hellmann.

Such criticisms are of no consequence to those who seek what is to them a fuller understanding of bonding. Bitter, Ruedenberg, and Schwarz for example, argue for the use of “Ruedenberg-type models employing fictitious non-quantum states in understanding bonding”, further stating that “all that can be said about bonding using the virial theorem is that the energy decreases and the kinetic energy undergoes an automatic concomitant increase.”⁴⁹ This point of view belies the discussion of bonding presented here in terms of the theorems of quantum mechanics known since the time of Slater’s 1933 paper.

5. CRITICISMS OF THE REAL WORLD APPROACH

A point that is emphasized in the quantum analysis of bonding is that all bonding (van der Waals, “nonbonded interactions”, metallic, covalent), followed by all degrees of polarity, down to the ionic limit, have a common physical origin as illustrated by the universality of the behavior of the energies and Feynman force illustrated in Figure 1.^{35,36} All bonding is the result of the accumulation of electron density in the binding region as required by Feynman’s electrostatic theorem. It is difficult to understand how one can dispute this physics in view of *the demonstration that bond paths—the lines of maximum electron density linking bonded atoms—recover all of the classical “bond” (i.e., textbook) structures of chemistry*,^{36,50} just as predicted by London in 1928.¹⁸ Just as important is the observation that there are no cases where a bond is predicted in the absence of a bond path. Even Slater emphasized that there is no fundamental distinction in the bonding mechanism operative in the measured extremes of van der Waals and covalent bonding.⁵¹ The response of those who oppose the role of Feynman’s electrostatic theorem in bonding, is to simply ignore the observational basis for the identification of a molecular structure with that defined by the linking of the bond paths.

This result of the universality of bonding is not shared by all, as illustrated by the statement, “At present it seems likely that the lowering of the kinetic energy pressure through electron sharing will remain a valid basic ingredient for nonionic covalent bonds in general, ...”⁵² Invoking the universality of bonding has led to misunderstandings of the theory, as exemplified recently: “It (QTAIM) maintains that *all* possible facets of bonding are considered, however, dismissing the chemically relevant differences between ionic, polar, covalent, H-bonding and van der Waals nonbonding and other interactions.”⁵³ These are the *very* examples whose characteristic signatures were displayed to demonstrate the

universal character of the virial, Feynman, and Ehrenfest theorems in atomic interactions.^{35,36,54–57} What distinguishes the bonding between the sets is not its physical origin, but rather the manner in which the density is distributed over the atomic basins; covalency being characterized by an equal sharing of the valence density, the ionic extreme by its localization within a single basin. The use of the properties of the density and energy related quantities at a bond critical point as bonding descriptors⁵⁸ is now the most widely employed method for the characterization of bonding obtained in experimental^{59,60} and theoretical densities.^{50,35,36,61} Its wide use is illustrated by its recent adoption by Shaik and co-workers in the classification of the different valence bond structures that participate in the so-called “charge-shift” model of chemical bonding.⁶² Of particular use in the topological classification scheme, is the local statement of the virial theorem that relates the Laplacian of the electron density to the competing contributions of the kinetic and electronic potential energy densities. The kinetic energy (as described in its positive definite form, denoted by G_b), in particular, plays a dominant role in these discussions, because its properties sharply distinguish the limiting forms of bonding. Thus shared interactions are found to have $G_b/\rho_b < 1$ and $\nabla^2\rho_b(\mathbf{r}) < 0$ while closed-shell interactions have $G_b/\rho_b \geq 1$ and $\nabla^2\rho_b(\mathbf{r}) > 0$. An excellent indication of the contrasting behavior of the kinetic energy in the bonded region between shared and closed-shell interactions is given by the ratio $T_{||}/T_{\perp}$ at the bond cp, the values for shared interactions in general being >10 while for closed-shell interactions it is in general <0.1 .⁶³

There are many published examples demonstrating that QTAIM and its consequences are not accepted by those who employ Morokuma’s energy decomposition analysis (EDA).⁶⁴ EDA, as do those employing Hellmann’s model, breaks a chemical change into a sequence of envisioned steps, one step in particular violating the Pauli exclusion principle (a point made by Morokuma). These criticisms have been responded to^{20,36,65} but one feels compelled to draw the attention of these critics to a cornerstone of the scientific method: one who questions a theory has two options; either disprove the theory or demonstrate that its predictions do not agree with experiment. Ignoring a theory or offering up unphysical criticisms do not suffice in science. It is fitting here to quote Slater: “A theoretical physicist in these days asks just one thing of his theories: if he uses them to calculate the outcome of an experiment, the theoretical predictions must agree, within limits, with the results of experiment. He does not ordinarily argue about philosophical implications of his theory.”⁶⁶

The ability of QTAIM to recover the experimental properties of atoms in molecules and the recovery of characteristic properties associated with a functional group has been verified many times and has served from the beginning as the source of its chemical relevance.^{7,67} The empirical theorem arising from these observations, that *the electron density of an atom in a molecule determines its additive contribution to all of the properties of the total system*,⁶⁸ is second only to the demonstration that the definition of an atom in a molecule is a consequence of the principle of least action. One unfamiliar with Schwinger’s principle may satisfy themselves with the quantum mechanical basis of the theory by following a heuristic proof that requires only knowledge of Schrödinger’s equation and the ability to integrate by parts.⁶⁹

6. EPILOGUE

I had the good fortune to attend Professor Slater’s lectures on quantum mechanics while a graduate student at MIT. These

lectures contributed to my decision to switch from experimental work in physical organic chemistry, under the guidance of Professor C. G. Swain, to theory, to better understand chemistry and its relation to physics, a topic close to Professor Slater's own interests. Consequently, upon graduation, I spent a year with Professor Longuet-Higgins in Cambridge. In later times, I had discussions of my work on the electron density and Feynman's theorem with Professor Slater and Professor Mulliken, sometimes together, at APS and other meetings. The electron density distributions were obtained from the laboratory of molecular structure and spectra (LMSS) of professors Mulliken and Roothaan. In 1968, Professor Slater attended a reception at my home as an Honorary Chairman of the third Canadian Theoretical Chemistry Conference.

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- (41) Ruedenberg and Schmidt⁴⁰ make an unfair comment Slater's discussion of bonding in their statement, "Slater, on the other hand, was aware that, at long ranges, the generalized virial theorem implied the incipient binding interactions to be due to a kinetic energy lowering, in disagreement with his interpretation." To suggest that Slater was unaware of any and all physical implications of his molecular virial theorem is inexcusable. Slater gives diagrams for and a full account of the variations in E , T , and V in his original 1933 paper and later gave a detailed discussion for H_2^+ and H_2 in his book that show precisely the same behavior as illustrated here in Figure 1 for H_2 . The statement by RS shows their misunderstanding of the virial theorem and its consequences as given by Slater. The long-range lowering in the kinetic energy is a consequence of the formation of an attractive Feynman force $F(R)$ and determined by the terms $F(R)$ and $R dF(R)/dR$ whose consequences for large values of R are shown in the $\Delta\rho$ maps for $R = 8$ and 6 au. This behavior has no bearing whatsoever on the situation found at the equilibrium separation discussed by RS, where $F(R)$ vanishes, accompanied by an increase in T and decrease in V to the values determined by the virial theorem as stated by Slater.
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- (46) Ruedenberg and co-workers^{40,43} have argued that one can get insight into the nature of chemical binding by imagining that as a molecule forms, it actually does, so to speak, try one wave function, then another before finding the most suitable one, an idea first presented in 1971 by Ruedenberg and Feinberg and referred here to as the "Ruedenberg's variational approach". One may indeed construct a trial function in a series of steps, adding further parameters and changing the functional form, testing each stage by determining the extent to which it lowers the energy, to finally arrive at a trial function that one deems satisfactory. This, however, is not "Ruedenberg's variational method". Ruedenberg instead wishes to investigate each member of a self-chosen set of trial functions up to the final exact solution for H_2^+ , ascribing physical meaning to each. One must note, however, that the choice of trial functions and their order of appearance are determined entirely by Ruedenberg, its individual steps being dictated neither by physics nor by observation, but by personal choice, as is the resulting analysis. One may note the similarity in the density difference map for $R = 6.0$ au in Figure 2, whose features are possible only in the presence of attractive Feynman forces, with that shown by Ruedenberg and Schmidt⁴⁰ for their imagined "sharing density", one of the steps in the variational approach that they propose to occur at R_e where the forces vanish.
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