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Physical Understanding through Variational Reasoning: Electron Sharing and Covalent Bonding†

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Energy changes of stationary states resulting from geometric parameter changes in the Hamiltonian can be understood by variational reasoning in terms of the physical attributes of the kinetic and the potential energy functionals. In atoms as well as molecules, the energy minimization determines the ground state as the optimal compromise between the potential pull of the nuclear attractions and the localization-resisting kinetic pressure of the electron cloud. This variational competition is analyzed for the exact ab initio ground-state wave function of the hydrogen molecule ion to elucidate the formation of the bond. Its electronic wave function is shown to differ from the ground-state wave function of the hydrogen atom by polarization, sharing, and contraction, and the corresponding contributions to the binding energy are examined in detail. All told, the critical feature is that a molecular orbital, contracting (in the variational context) toward two nuclei simultaneously, can lower its potential energy while maintaining a certain degree of delocalization. As a consequence, its *kinetic* energy functional has a lower value than that of an orbital contracting toward a single nucleus equally closely. By contrast, the *potential* energy functional is lowered equally effectively whether the orbital contracts toward one nucleus or simultaneously toward two nuclei. Because of this weaker kinetic energy pressure, the electrostatic potential pull of the nuclei in the molecule is able to attach the orbital more tightly to each of the nuclei than the pull of the single nucleus in the atom is able to do. The role of the virial theorem is clarified. Generalizations to other molecules are discussed.

1. Introduction

1.1. Differences in Energetic Stability. The physical explanation of differences in energetic stabilities must be counted among the important expectations that experimental chemists have of quantum chemists, and many models have indeed been developed to rationalize energy differences under various conditions. The object of the present study is to clearly formulate a rigorous theoretical foundation for all such explanations and to suggest that it will be fruitful to clarify the relations that specific models have to the fundamental analysis. Because of the complexity of most chemical situations, it is of course no simple matter to establish such connections. However, using modern computational power to this end should help to narrow the gap between quantitative quantum chemical number crunching and the experimentalists' qualitative intuition.

In the first half of the present study, we address the following general question: What does one mean, indeed what can one mean, by a "physical understanding" of differences between ground-state energies of molecular systems? We shall develop an approach to this problem that is squarely based on the variation principle, which in our opinion furnishes the only rigorous basis that is viable in general. In the second half of the study, this variational reasoning will then be used to elucidate the relationship between covalent bonding and electron sharing.

1.2. Covalent Bonding and Electron Sharing. Berzelius proposed the first modern theory of chemical binding by conjecturing that atoms are always bonded by what later came to be termed ionic interactions. His thinking was undoubtedly influenced by the contemporary discoveries during the first decade of the 19th century, namely, Volta's discovery of the electric battery, Davy's and Berzelius's discovery of electrolysis, and Dalton's conception of the atomic model. Within a few decades, however, Dumas, Liebig, Wöhler, and others isolated and synthesized many nonpolar organic compounds and thereby demonstrated the existence of what we now call covalent bonds. By 1860, when the first international chemical congress convened in Karlsruhe, it became recognized that hydrogen and the gases in the upper right corner of the periodic table form covalently bonded homonuclear diatomic molecules, as Avogadro (1811) and Ampère (1814) had proposed half a century earlier.[1] This insight proved crucial for the definitive establishment of atomic weights and chemical stoichiometries and the development of the periodic table shortly thereafter. On the other hand, however, these covalent attractions presented a puzzle and a challenge in the quest for a *physical understanding* of chemical binding. It led for instance to speculations about modifications of the electrical forces that would result in short-range attractions,[2] and it contributed to the long-lasting chasm between organic chemists and physicists.

The discoveries of the electron by Thomson (1897) and of the atomic nuclei by Rutherford (1911) confirmed the electrical nature of the forces within atoms and molecules. Since, by virtue of Earnshaw's theorem of electrostatics,[3] any stable state of such point charges necessarily requires moving particles, the kinetic energy played an essential part in Bohr's planetary model (1913). It also played a key role in Schrödinger's subsequent wave mechanics (1926) inasmuch as the wave character of the electronic distribution, which is the basis for energy quantization, is due to the fundamental difference between quantum mechan-

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ics and classical mechanics in the treatment of the kinetic energy. We shall see that it also plays an essential role in covalent bonding.

Stimulated by the discovery that the light electrons were mobile within atoms and that their motions followed new laws, G. N. Lewis[4] proposed in 1916 that a covalent bond is the result of an electron pair being *shared* between two atoms. This conjecture was validated in 1927 by Heitler and London's calculation of the first quantum mechanical wave function for the hydrogen molecule,[5] and since then, all quantum chemical calculations have confirmed the importance of electron sharing for covalent bonding.

A further clarification came however from the calculations by Burreau,[6] Pauling,[7] Finkelstein and Horowitz,[8] Guillemin and Zener,[9] and Hylleraas[10] for the hydrogen molecule ion which showed that it is in fact the sharing of a *single* electron that establishes a covalent bond. This result implied that the two-electron bond is essentially the cumulative result of the effects of each electron being shared individually between the atoms (tempered, of course, by the effect of interelectronic repulsions). Thus, the question became why the sharing of *one* electron between atoms leads to covalent bonding in quantum mechanics.

1.3. Present Approach. To develop a physical understanding of the connection between electron sharing and covalent binding on the basis of variational reasoning, we shall examine the hydrogen molecule ion because, in this system, electron sharing is solely responsible for the covalent bond. In all other molecules, the potential energy functional is more complex and embodies additional interactions that complicate the binding process, such as quasi-classical Coulombic attractions, an increase or decrease of electron correlations, and Pauli exclusion effects, which account, e.g., for ionic and correlation bonding.[11] All of these are essentially absent in the hydrogen molecule ion so that electron sharing can be examined on its own merits. The H_2^+ ion is of course quite unique. Nonetheless, the accurate in-depth understanding of this simple case produces relevant insights that cannot be bypassed on the way to a valid understanding of more complicated situations. Rozendahl and Baerends have indeed shown that essential inferences regarding the kinetic energy deduced from the analysis of H_2^+ remain valid in more complex covalent bonds.[12]

To be conclusive, the present exposition is based on a thorough variational analysis of an *essentially exact* wave function of H_2^+ at the theoretical equilibrium distance. It was calculated in terms of an uncontracted (14s, 6p, 3d, 2f, 1g) basis set of 26 σ-type spherical Gaussian atomic orbitals on each atom, which was optimized for the present purpose.[13] The equilibrium distance found differs from the exact value[14] by 7×10^{-6} bohr. The energy found for H_2^+ lies 0.55 μhartree above the exact result.[14] The energy found for the H atom in this basis lies 0.1 μhartree above the exact value of 0.5 hartree. The virial ratio $|\langle\psi|V|\psi\rangle/\langle\psi|\mathbf{T}|\psi\rangle|$ is 2.0000037 and 2.0000003 for H_2^+ and H, respectively.

Our conclusions will substantially confirm inferences from considerably simpler analyses of much simpler wave functions that had been advanced by one of the authors and his co-workers over four decades ago[15-19] and that had been further developed by Kutzelnigg[20] and Goddard[21] shortly thereafter. These views were subsequently also espoused in books by Fukui,[22] Mulliken,[23] Kutzelnigg,[24,25] Steiner,[26] and Klapötke et al.[27] and accepted by others.[28]

Notwithstanding the writings of these authors, serious misconceptions regarding this subject have persisted to remain widespread, notably but by no means only in the didactic literature. We therefore start by bringing into focus the basic physical principles that are relevant for valid and cogent causative reasoning on these matters and then proceed to identify the physical elements that are pertinent for the role of electron sharing in covalent binding. The hope is that the careful exposition will encourage a reassessment of the wisdom of perpetuating ad-hoc or even erroneous conjectures on this fundamental chemical phenomenon.

2. Physical Understanding of Electronic Ground States by Means of the Variation Principle

2.1. A Historical Controversy. In 1933, two seemingly incompatible views were advanced to gain a physical understanding of the bonds in H_2 and H_2^+, both combining quantitative information with qualitative intuition. Hellmann,[29] with a perceptive grasp of the above-mentioned relevance of the kinetic energy for the existence of quantum mechanical ground states, was convinced that covalent bonding resulted from a lowering of the kinetic energy due to the increase in the volume available to the electron in the molecule, i.e., to delocalization. Slater[30] on the other hand observed that, by virtue of the rigorous virial theorem, it is in fact the potential energy that decreases upon bond formation whereas the kinetic energy increases. Noting that, due to orbital overlap, electron sharing generates an accumulation of electronic charge between the nuclei, he surmised that the attraction of this *accumulated* charge by *both* nuclei is the cause of the potential energy lowering that establishes the covalent bond. Hellmann was aware of the virial theorem and of the challenge it presented for his interpretation. Although he could not resolve this conflict, he remained convinced that his intuition was correct, in particular since it seemed to be supported by the Heitler–London calculation[5] of H_2. 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.

This dichotomy of interpretation continued to exist for several decades, and in the 1950s, one of the present authors was exposed to both sides while being introduced to quantum chemistry as a postdoctoral fellow at the University of Chicago. John R. Platt[31] was a firm believer in Hellmann's view as were many solid-state physicists.[32] Robert S. Mulliken highly respected the work of J. C. Slater as well as C. A. Coulson, who had essentially accepted Slater's reasoning,[33] but he had kept an open mind on this question at that time.

In fact, the transition from classical to quantum mechanics had essentially changed the meaning of the question *why?* and of its possible answers. Statements on chemical binding are essentially comparative statements on molecular electronic ground-state energies for different fixed atomic arrangements. The existence of a ground state is a quantum mechanical phenomenon, unknown in classical mechanics. Thus, understanding the origin of chemical binding is contingent upon understanding the factors that determine the magnitude of the electronic ground-state energy of a given molecular system at a given nuclear geometry. Here, we base ourselves on the physical concept of the potential energy surface whose firm theoretical foundation is the validity of the Born–Oppenheimer separation.

While the ground-state energy is a physical observable, the problem at hand is not the discussion of physical measurements, nor does it have to do with forces relevant in time-dependent molecular dynamics. Rather, the problem is to identify the reasons why the stationary states of the time-independent

Schrödinger equation have specific quantitative eigenvalues and eigenfunction shapes under specific conditions. The first basic question is therefore whether it is in fact at all possible to cast a cogent mathematical analysis of *these* reasons in a form that allows for a physical interpretation.

2.2. Physical Understanding on the Basis of a Variational Analysis. It is manifestly desirable to attack the problem of physical understanding from a position that is rigorous as well as universal. For the bound states of the time-independent Schrödinger equation of the electrons in a molecule, such a rigorous and universal point of departure is offered by the variation principle, which is just as fundamental as the Schrödinger equation, since the latter is in fact the associated Euler equation of variational calculus. To use *variational reasoning* to gain an understanding of the factors that determine the magnitudes of ground-state energies essentially means to *estimate conceptually* the various terms in the energy functionals that enter the *quantitative* (e.g., computational) minimization process. If one can conceptually assess how the magnitudes of the contributions to $\langle\psi|\mathscr{H}|\psi\rangle$ depend on the shape of ψ, then one can explain the quantitative result of the variational minimization.

Such conceptual assessments are in fact possible because the terms in the *energy functional* $\langle\psi|\mathscr{H}|\psi\rangle$ can be estimated using the same physical interpretations regardless of whether ψ is an eigenfunction of $\mathscr{H}$. This is straightforward for the terms in the *potential* energy functional, since all of its parts have electrostatic forms whose quantitative dependence on ψ is familiar from classical theory. The quantitative dependence of the *kinetic* energy functional on ψ, on the other hand, can be readily assessed by using for it the alternative form[34]

$$\langle\psi|\boldsymbol{T}|\psi\rangle = +{}^{1}/_{2}\sum_{k}\int \mathrm{d}q(\nabla_{k}\psi)^{2} \tag{2.1}$$

where the sum over k goes over all electrons, dq covers all coordinates of all electrons, the wave function is assumed to be normalized, and atomic units are used. By means of this expression, which is a sum of positive contributions, the examination of the changes in the gradient of ψ can yield an estimation of corresponding changes in $\langle\psi|\boldsymbol{T}|\psi\rangle$. A well-known consequence is, for instance, the uncertainty-principle-type relation between the average localization and the average kinetic energy of ψ. By conceptually assessing the kinetic and potential energy functional values in this manner on the basis of their physical interpretations, variational predictions can be made regarding specific ground-state energy values.

While it is true that, among the various comparison energy values examined in such an analysis, only the minimal one is the physically observed stationary energy of the system, it is also true that the "virtual" comparison energy values are in principle physically observable energy expectation values as well. It is in this sense that variational reasoning regarding the energy functional furnishes a physical understanding of quantum mechanical stationary energies.

The present authors are not aware of any other quantitative approach of equal rigor, power, and generality to this problem. Indeed, a close examination of traditional rationalizations regarding various specific types of chemical bonding reveals that nearly all of them appeal de facto in one way or another to variational reasoning, even if the relationship is not always explicitly traced. Variational premises provide, for instance, the underpinning for the widely used concept of "resonance stabilization" through the superposition of appropriate valence bond structures.

Frequently, however, such explanations ignore that both the kinetic and the potential energy functionals should always be accounted for with equal care. It is in fact just this omission by both authors that was the source of the disagreement between the early interpretations of Hellmann and Slater mentioned at the beginning of section 2.1.

2.3. Variational Competition between the Kinetic and Potential Energy Functionals. As is common in quantum chemistry, the term "variation principle" has been used somewhat loosely in section 2.2. The rigorous mathematical variation principle is actually more restricted in scope. Namely, it states only that the first variation of the energy functional, i.e., $\delta[\langle\psi|\mathscr{H}|\psi\rangle/\langle\psi|\psi\rangle]$, vanishes for all variations $\delta\psi$ if and only if ψ is an eigenfunction of the Hamilton operator $\mathscr{H}$. This rigorous variation principle makes no statement regarding whether there exists a lowest eigenvalue, i.e., a ground state.[35] That, however, is just the question of interest in the present context.

In fact, the existence of ground states is the consequence of a specific property of molecular electronic Hamiltonians, namely, that they are all *bounded from below*. It is because of this feature, in conjunction with the rigorous variation principle and certain regularity requirements, that the energy functional of such an operator has a lower bound and that it reaches this bound for an eigenfunction, which is then the ground state.

Why are molecular Hamiltonians bounded from below? This is because of the physics intrinsic to these Hamiltonians, namely, that they are the sum of a kinetic operator $\boldsymbol{T}$ and a potential operator $\boldsymbol{V}$ and that the kinetic energy functional $\langle\psi|\boldsymbol{T}|\psi\rangle$ and the potential energy functional $\langle\psi|\boldsymbol{V}|\psi\rangle$ of the electronic energy *respond antagonistically* when the wave function changes in such a manner that the electron distribution approaches the fixed nuclei more closely: On one hand, because of the attraction between electrons and nuclei, the negative potential integral $\langle\psi|\boldsymbol{V}|\psi\rangle$ tends toward *minus infinity* as ψ concentrates closer and closer around the nuclei in a molecule. On the other hand, it follows from eq 2.1, in conjunction with the normalization of ψ, that the positive kinetic integral $\langle\psi|\boldsymbol{T}|\psi\rangle$ tends toward *plus infinity* as ψ concentrates more and more closely around any nucleus. A common physical interpretation of this behavior is that the uncertainty relation forces an increase in the absolute values of the momentum components in response to spatial localization. There exists therefore a variational tug-of-war between what we may call the "variational electrostatic potential pull" and the "variationally resisting kinetic pressure" when the electron cloud tries to attach itself more closely to the nuclei. Specifically, moreover, when ψ contracts toward any nucleus, $\langle\psi|\boldsymbol{V}|\psi\rangle$ decreases proportional to the average inverse distance from that nucleus whereas $\langle\psi|\boldsymbol{T}|\psi\rangle$ increases proportional to the square of this inverse distance. Therefore, a compromise, where the total energy functional is a minimum, can and will be reached in this competition.

The result of the variational minimization is thus a wave function ψ_o that lowers the term $\langle\psi|\boldsymbol{V}|\psi\rangle$ as much as possible while concomitantly increasing the term $\langle\psi|\boldsymbol{T}|\psi\rangle$ as little as possible. The optimal compromise in this variational competition determines the shape of ψ_o and the value of $E_\mathrm{o} = \langle\psi_o|\mathscr{H}|\psi_o\rangle$. The physical interpretation of the variational process is therefore that the nuclear electronic attractions continue to pull a variational wave function in some form together around the fixed nuclei in a molecule until the variational kinetic energy pressure resists further localization and enforces a bound from below. This competition also occurs when the potential energy contains electronic repulsions as long as they do not destabilize the system altogether.

Parenthetically, it may be mentioned that the kind of reasoning pursued in the present study can manifestly be generalized to excited states.

2.4. Optimal Ratio of the Kinetic Energy to the Potential Energy. The specific dependence of the kinetic and potential energy expectation values on the average distance from any nucleus, which is a characteristic of all molecular electronic Hamiltonians involving only Coulombic interactions, as mentioned in section 2.3, has a further important consequence regarding the variation process. Namely, for isolated atoms as well as for molecules at equilibrium as well as at transition-state geometries, the variational minimum ψ_o of the electronic energy functional is characterized by the equality

$$E_o = \langle\psi_o|\mathscr{H}|\psi_o\rangle = {}^1/_2\langle\psi_o|\boldsymbol{V}|\psi_o\rangle = -\langle\psi_o|\boldsymbol{T}|\psi_o\rangle \quad (2.2)$$

which is known as the virial theorem.

While this relation is often derived from the Schrödinger equation,[29,30] i.e., only for the eigenfunctions of $\mathscr{H}$, it is relevant in the present context that there exists a connection to the variation principle. As Löwdin[36] has shown, eq 2.2 is a consequence of applying the variation principle to certain parameters that govern the concentration of a wave function around the nuclei, such as notably the orbital exponents in atom-centered LCAO expansions. It should be added that the theorem is also satisfied when the atomic orbital basis of a calculation is chosen large enough so that the LCAO expansions of the molecular orbitals can mimic orbital exponent optimizations with sufficient accuracy. Mulliken[23] has used the terms “shrinking toward” and “swelling away from” the nuclei to describe such molecular orbital variations in general.

In the present variational analysis, the virial theorem is a very useful tool because it furnishes an understanding of the effect of orbital shrinking and swelling on the optimization process which allows prediction of some of its results. In particular, if a given trial function yields $T < -V/2$, then its kinetic energy is still low enough so that the total energy can be variationally lowered by wavefunction adjustments that concentrate more density *into* localized regions of low potential energy. On the other hand, if the trial function yields $T > -V/2$, then the total energy can be variationally lowered by adjustments that *remove* density from such regions.

It should be kept in mind, though, that there exist limitations regarding the use of the virial theorem, notably: (1) the theorem is a necessary but not a sufficient condition for the variational minimum. (2) In the presence of inner core electrons, the application of the virial theorem will be more complicated since it applies to core *plus* valence electrons and not to valence electrons alone. (3) The simple form (eq 2.2) of the theorem holds only at those points on potential energy surfaces where the gradient vanishes, e.g., minima, maxima, and transition states.[29,30] The last two points will be further commented upon in section 8.3.

3. Comparing Ground-State Energies of Related Systems

A binding energy analysis requires the comparison of two or more systems that differ in the values of certain parameters in the Hamiltonian. To exhibit and clarify some basic issues regarding such comparisons, we first examine the parameter dependence of the ground state for a simple system.

3.1. Parameter Dependence of the Variational Competition. Even the physical understanding of the value of the most elementary quantity of molecular physics, viz., the ionization potential of the hydrogen atom, requires an appreciation of the variational competition between the kinetic and potential energy functionals.

Consider a negative particle of mass m with the charge of an electron moving in the field of a single infinitely heavy positive particle with charge Z. Its Schrödinger equation, in atomic units, is

$$(-1/2m)\nabla^2\phi + (-Z/r)\phi = E\phi \quad (3.1)$$

For $m = 1$, $Z = 1$ we have the hydrogen atom, $m = 273$ would correspond to the π-muon, and $Z = 6$ would represent the carbon nucleus. The ground-state wave function has the form

$$\phi = (\zeta^3/\pi)^{1/2}\exp(-\zeta r) \quad (3.2)$$

whose energy functional

$$\langle\phi|\mathscr{H}|\phi\rangle = H(\zeta) = T(\zeta) + V(\zeta) \quad (3.3)$$

has the kinetic and potential parts

$$\langle\phi|\boldsymbol{T}|\phi\rangle = T(\zeta) = \zeta^2/2m, \quad \langle\phi|\boldsymbol{V}|\varphi\rangle = V(\zeta) = -Z\zeta \quad (3.4)$$

The actual solution can be obtained by (i) inserting the function in eq 3.2 into the Schrödinger equation (3.1), (ii) minimizing the energy functional in eq 3.3 with respect to ζ, or (iii) inserting the kinetic and potential energy functionals into the virial identity in eq 2.2. Thereby, one obtains the values

$$\zeta = \zeta_o = mZ, \quad E_o = -{}^1/_2 mZ^2 \quad (3.5)$$

To gain a physical understanding of the value E_o, we examine the variational competition between the kinetic and potential energy functionals in eq 3.3 in detail.

Figure 1 exhibits the variation of $T(\zeta)$, $V(\zeta)$, and $H(\zeta)$ with ζ for three cases, viz., $m = 1$ with $Z = 1$, $Z < 1$, and $Z > 1$, corresponding to an electron in the field of different nuclei. Note that, actually, the value of $-V(\zeta)/2$ is plotted (green). In all cases, the positive kinetic term (red) dominates in the region of strong orbital shrinkage (i.e., for large ζ) so that the total energy (blue) increases to positive infinity. The negative potential term (green) dominates in the region of large orbital expansion (i.e., for small ζ) so that the total energy $H(\zeta)$ is negative and eventually goes to zero. By construction, the intersection of the red and the green lines marks the ζ values where, in each case, the virial theorem is satisfied. Manifestly, in each case this ζ value is also the one where the minimum of $H(\zeta)$ occurs.

Thus, Figure 1 illustrates the physical analysis of the variational minimization discussed in sections 2.2, 2.3, and 2.4, namely, that the variational nuclear attraction pulls the electronic wave function toward the nucleus until the variational kinetic

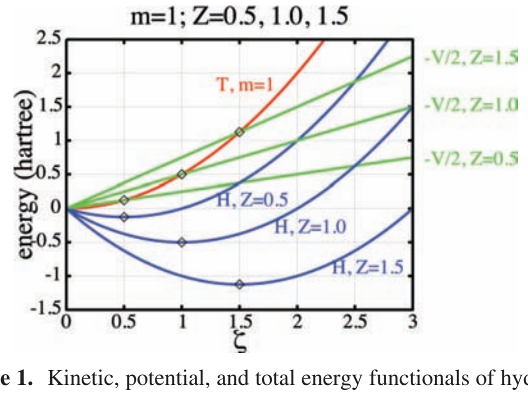

Figure 1. Kinetic, potential, and total energy functionals of hydrogen atom analogues of eqs 3.1−3.5 as functions of the orbital exponent ζ: kinetic functional T (red) for $m = 1$ and potential functionals $-V/2$ (green) and total energy functionals H (blue) for $Z = 0.5$, 1.0, and 1.5. The tilted squares indicate the minima of H and the corresponding virial intersections $T = -V/2$.

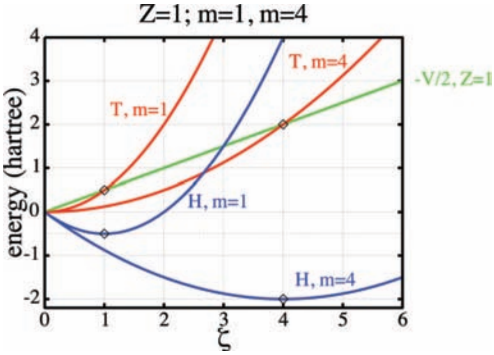

Figure 2. Kinetic, potential, and total energy functionals of hydrogen atom analogues of eqs 3.1−3.5 as functions of the orbital exponent ζ: potential functional $-V/2$ (green) for $Z = 1$and kinetic functionals T (red) and total energy functionals H (blue) for $m = 1$ and 4. The tilted squares indicate the minima of H and the corresponding virial intersections $T = -V/2$.

energy pressure resists further localization and, furthermore, that this optimal compromise can be predicted by the virial theorem.

For $m = 1$, $Z = 1$, the intersection of T and $-^1/_2V$ occurs for $\zeta = 1$ and the total energy is −0.5 hartree. For $Z > 1$, i.e., a stronger nuclear attraction, the intersection moves to a larger ζ value ($\zeta_o = Z$), the orbital contracts, and the total energy $H(\zeta_o) = -^1/_2Z^2$ is lowered. For a weaker nuclear attraction, i.e., $Z < 1$, the opposite happens. Thus, increasing (decreasing) the nuclear attraction binds the electron more (less) tightly, in agreement with classical electrostatic intuition.

A different comparison is illustrated by Figure 2. It exhibits plots similar to those of Figure 1, but for the two cases $m = 1$, $Z = 1$ and $m = 4$, $Z = 1$, here the potential functional is the same, but the kinetic functionals differ; namely, the change from $m = 1$ to $m = 4$ lowers the kinetic functional for every argument value ζ, since the mass m appears in the denominator of $T(\zeta)$. The change from $m = 1$ to $m = 4$ therefore shifts the "virial intersection" of $T(\zeta)$ and $-V(\zeta)/2$ from $\zeta = 1$ to $\zeta = 4$, and this shift leads to a lowering of the energy minimum by a factor of 4.

In this case, the orbital shrinkage and the energy lowering in the context of the variational competition have therefore a reason different from that in Figure 1. Here, the stabilization occurs because the variational kinetic energy pressure, which resists localization, is weakened (by the increase in m) so that a greater contraction by the potential pull is variationally allowed and leads to a greater energy lowering. We thus have the superficially paradoxical situation that the *weakening* of the variational kinetic energy pressure *for each* ζ leads to an *increase* in the kinetic energy of the *optimal* value of $\zeta = \zeta_o$. This is just one example of a contragradient relaxation response that occurs also in other areas of physics when a variation principle is operative.[17,37]

3.2. Two Possible Origins of Ground-State Energy Shifts. The discussed comparisons demonstrate that the difference in the ground-state energies of two related systems can be a consequence of differences in the physical characteristics of their kinetic energy functionals (i.e., the value of m in eq 3.1), in their potential energy functionals (i.e., the value of Z in eq 3.1), or in both functionals. The case of Figure 2 demonstrates moreover that, even if system A is lower in energy than system B by virtue of having a larger mass, i.e., as a consequence of a difference in the structure of the kinetic energy functional, nonetheless system A has a higher kinetic energy and a lower potential energy than system B. It is thus not possible to identify the origin of the greater stability of A by simply comparing the kinetic and potential components of the actual energy eigenvalues of the two systems.

This observation furthermore reveals that the virial theorem furnishes no clue whatsoever regarding the origin of the energy difference between two systems. Consider, for instance, two systems, A and B, that have a Hamiltonian corresponding to eq 3.1. If one knows that A has a lower ground-state energy than B, then one can deduce from the virial theorem that A has a lower potential energy and a higher kinetic energy than B in the ground state. Nonetheless, if one does not know the values of m and Z, then one has no way of telling whether the energy difference is a consequence of the two systems differing in the variational behavior of their *kinetic* energy functionals or their *potential* energy functionals. Equation 3.5 shows that the difference could be due to a change in m or Z.

There persists a widespread physical-chemical lore that the virial theorem has implications regarding the physical reasons for one system having a lower total energy than another, namely, that this is *always* a consequence of a difference in the characteristics of the electrostatic *potential* energy functionals of the systems. The preceding discussion illustrates that this is patently not so. The virial theorem provides no information regarding those structural changes in the kinetic and the potential energy functionals that are responsible for changes in the energy eigenvalues. Only independent physical analyses of the kinetic as well as the potential functionals can reveal the specific characteristics of the variational kinetic pressure and the variational nuclear pull in specific systems that determine changes in the ground-state energy values. Without such an analysis, the virial theorem per se cannot reveal any reasons for shifts in energy eigenvalues upon changes in the physical parameters of a system. Once the energy functional is given, the virial theorem is a useful tool inasmuch as it offers a shortcut toward identifying variational minima with respect to orbital shrinking toward and orbital swelling away from the nuclei.

3.3. Analysis of Ground-State Energy Shifts by Energy Resolution. In less simple systems, the causative connection between the parameters in the Hamiltonian and its eigenvalues is not as transparent as in the case discussed in section 3.1. This is so, for instance, in the case of chemical binding, where the parameter is the internuclear distance. Moreover, as we have seen in section 3.2, it is not possible to identify the origin of the greater stability of one system over another by simply comparing the kinetic and potential components of their energy eigenvalues. However, we shall now show that there exists an alternative way of variationally analyzing ground-state energy shifts, namely, by examining the kinetic and potential functionals for appropriately chosen wave functions that are *intermediate* between the eigenfunctions of the compared systems. We shall illustrate this approach by comparing two systems of the type previously considered in section 3.1, but the approach can be manifestly generalized.

Let systems 1 and 2 both be defined by a Hamiltonian of the type given by eq 3.1, viz.

$$\mathcal{H}_1 \text{ given by } m = 1, Z = 1 \qquad \mathcal{H}_2 \text{ given by } m = 4, Z = 0.7$$

According to eqs 3.2 and 3.5, one finds

$$E_1 = -0.5, \zeta_1 = 1 \quad \text{and} \quad E_2 = -0.98, \zeta_2 = 2.8$$

so that system 2 is more stable than system 1 and the corresponding ground-state wave function $\phi_2(\zeta_2)$ is more contracted than the ground-state wave function $\phi_1(\zeta_1)$. Equation 3.5 leaves no doubt that both the energy lowering and the orbital contraction result from the increase in the mass m (from 1 to 4) in spite of the slight decrease in the nuclear charge Z (from 1 to 0.7). Hence, system 2 is the more stable one because its resisting kinetic pressure is weaker, even though its weaker potential pull would tend to make it less stable. We shall now show how one can arrive at this insight without any knowledge of the values of m and Z merely by examining various values of certain energy functionals.

To this end, we choose ϕ_1, the ground state of $\mathscr{H}_1$, as an *initial guess* for the ground state of the Hamiltonian $\mathscr{H}_2$. We thus consider the energy lowering from system 1 to system 2 as the result of the following two sequential steps:

$$E_1 = \langle \phi_1 | \mathscr{H}_1 | \phi_1 \rangle \rightarrow \langle \phi_1 | \mathscr{H}_2 | \phi_1 \rangle \rightarrow \langle \phi_2 | \mathscr{H}_2 | \phi_2 \rangle = E_2 \quad (3.6)$$

In the first step, the wave function ϕ_1 is transferred unchanged from system 1 to system 2 ("transfer step"). In the second step, the variational minimization of system 2 changes the wave function to its ground state ϕ_2 ("variation step"). The corresponding energies are

(energies in hartree)	$\langle \phi \| \boldsymbol{T} \| \phi \rangle$	$\langle \phi \| \boldsymbol{V} \| \phi \rangle$	$\langle \phi \| \mathscr{H} \| \phi \rangle$	$-V/2T$
ϕ_1 with $\mathscr{H}_1$	**0.5**	−1	−0.5	1
ϕ_1 with $\mathscr{H}_2$	0.125	−0.7	−0.575	2.8
ϕ_2 with $\mathscr{H}_2$	0.98	−1.96	−**0.98**	1

The last column lists the values of the virial ratio $|V/2T|$.

If one is given only the energy data in this table while being ignorant of the values of m and Z, one can now reason as follows with respect to the energy lowering from $E_1 = -0.5$ hartree to $E_2 = -0.98$ hartree.

Since the wave function ϕ_1 remains unchanged in the transfer step, it must be the change in the *kinetic operator* $\boldsymbol{T}$ that leads to a *lowering of the kinetic functional* by 0.375 in this step. Similarly, it must be the change in the *potential operator* $\boldsymbol{V}$ that leads to an *increase in the potential energy functional* by 0.3. The decrease in the total energy functional by 0.075 in the transfer step is thus due to a change in the kinetic operator, i.e., to a weakening of the resisting kinetic energy pressure when $\boldsymbol{T}_1$ is changed into $\boldsymbol{T}_2$ in the transfer step.

At this intermediate stage, the virial ratio has however become 2.8, which is far from the value 1 that it has to be for the ground state of $\mathscr{H}_2$. Thus, ϕ_1 cannot be this ground state. Indeed, since we have $E_2 < E_1$ and since the virial theorem holds for both systems, we must have

$$\langle \phi_2 | \boldsymbol{T}_2 | \phi_2 \rangle > \langle \phi_1 | \boldsymbol{T}_1 | \phi_1 \rangle = 0.5$$

$$\langle \phi_2 | \boldsymbol{V}_2 | \phi_2 \rangle < \langle \phi_1 | \boldsymbol{V}_1 | \phi_1 \rangle = -1$$

The variational minimization will therefore lower the energy further and simultaneously reestablish the virial ratio.

Specifically, since the transfer step led to a value of T that is too small relative to $|V/2|$, the variation step will lower the energy functional through a lowering of the potential functional with a concomitant (but smaller) increase of the kinetic functional, unit T becomes equal $|V/2|$. For the system at hand, such changes in the energy functional can only be brought about by an orbital contraction from ϕ_1 to ϕ_2.

The energetic reasoning therefore shows that the weakening of the kinetic energy pressure in the transfer step (i) *directly* lowers the energy functional and (ii) by creating a virial theorem violation, *induces* a further energy lowering through orbital contraction in the variation step. Knowing that the Hamiltonians of both systems have the general form of eq 3.1, one can then *infer* from the energy analysis that the energetic stabilization in going from system 1 to system 2 must be the consequence of an increase in the mass of the orbiting particle.

4. Variational Analysis of Bond Formation in H_2^+

4.1. Connecting the Atomic and the Molecular Energy Functionals. We shall now pursue the same line of stepwise reasoning that we applied in section 3.3 to elucidate the difference between the ground-state energy of the hydrogen atom and the ground-state energy of the hydrogen molecule ion at its equilibrium distance. Thus, we consider this energy lowering as the result of the following two sequential steps:

$$E(H) = \langle 1s_A | \mathscr{H}_A | 1s_A \rangle \rightarrow \langle 1s_A | \mathscr{H} | 1s_A \rangle \rightarrow \langle \psi | \mathscr{H} | \psi \rangle = E(H_2^+) \quad (4.1)$$

where $1s_A$ is the ground state of the atom, ψ is the ground state of the molecule, and

$$\mathscr{H}_A = \boldsymbol{T} - r_A^{-1} \quad \text{and} \quad \mathscr{H} = \boldsymbol{T} - r_A^{-1} - r_B^{-1} + R^{-1} \quad (4.2)$$

are the Hamiltonians of the atom and the molecule, respectively, with R being the internuclear equilibrium distance. In the first step, the $1s_A$ orbital is transferred unchanged from the atom to the molecule (transfer step) so that it provides an initial guess for the wave function of the molecule at the equilibrium distance. The second step, in which $1s_A$ changes into ψ, represents a variational minimization (variation step) within the molecule. Correspondingly, the bond-forming energy lowering

$$E_B = E(H_2^+) - E(H) = \langle \psi | \mathscr{H} | \psi \rangle - \langle 1s_A | \mathscr{H}_A | 1s_A \rangle \quad (4.3)$$

can be expressed as the sum of a transfer term and a variation term:

$$E_B = \underbrace{[\langle 1s_A | \mathscr{H} | 1s_A \rangle - \langle 1s_A | \mathscr{H}_A | 1s_A \rangle]}_{\text{transfer term}} + \underbrace{[\langle \psi | \mathscr{H} | \psi \rangle - \langle 1s_A | \mathscr{H} | 1s_A \rangle]}_{\text{variation term}} \quad (4.4)$$

where we have added and subtracted the term $\langle 1s_A | \mathscr{H} | 1s_A \rangle$, i.e., the *molecular* energy functional calculated using the *atomic* ground state $1s_A$ as an initial guess.

The first bracket in eq 4.4 represents the transfer step and establishes a relation between a specific energy functional of the atom and a specific energy functional of the molecule. It can be written as

$$[\langle 1s_A | \mathscr{H} | 1s_A \rangle - \langle 1s_A | \mathscr{H}_A | 1s_A \rangle] = \langle 1s_A | \mathscr{H} - \mathscr{H}_A | 1s_A \rangle \quad (4.5)$$

and since $\mathscr{H}$ and $\mathscr{H}_A$ contain the same kinetic energy term, it represents the change in the *potential* energy of atom A (nucleus plus electron) when a proton is moved from infinity to the equilibrium distance $R = 1.9972$ bohr of H_2^+ while leaving the electronic wave function $1s_A$ unchanged. By virtue of eq 4.2, this term becomes

$$\langle 1s_A | \mathscr{H} - \mathscr{H}_A | 1s_A \rangle = \langle 1s_A | R^{-1} - r_B^{-1} | 1s_A \rangle$$
$$= R^{-1} - \int dx\, dy\, dz\, (1s_A)^2 / r_B = E_{QC} \quad (4.6)$$

and therefore represents the Coulombic electrostatic energy between a proton at B and the atom A (i.e., nucleus plus ground-state electron density at A). We call it the *zeroth-order quasi-classical energy* and denote it by E_{QC}.

Since $1s_A$ is spherically symmetric around A, Newton's theorem of potential theory applies to the integral on the right-hand side, which therefore becomes

$$\int dx\, dy\, dz\, (1s_A)^2 / r_B = R^{-1} \int^* dx\, dy\, dz\, (1s_A)^2 \quad (4.6a)$$

where the integral $\int^* dx\, dy\, dz$ covers only the inside of the sphere with radius $R = 1.9972$ bohr around nucleus A. This

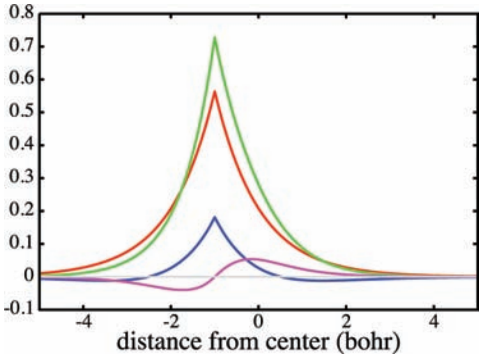

Figure 3. Orbital plots along the internuclear axis exhibiting the decomposition given by eq 4.10 for the quasi-atomic orbital ψ_A (green) in terms of its projection 0.970546 $1s_A$ (red), its contraction deformation 0.2055013 δs_A (blue), and its polarization deformation 0.1257342 δp_A (purple). All orbital amplitudes are in bohr$^{-3/2}$.

sphere contains 94.48% of the charge of the hydrogen ($1s_A$) orbital so that the insertion of eq 4.6a into eq 4.6 yields

$$E_{QC} = (1 - 0.94480)/1.9972 = +27.64 \text{ mh (mh = millihartrees)} \quad (4.7)$$

Thus, while the presence of the second nucleus lowers the electrostatic potential energy of the electron in the orbital at $1s_A$ by close to 0.5 hartree, this increase in electron–nuclear attraction is overcompensated by the concomitant increase in the repulsion between the two nuclei.

Having thus gained a physical understanding of the potential energy difference (eq 4.5), which accounts for the magnitude of the first term in eq 4.4, i.e, the transfer step, the task of achieving a physical understanding of the binding energy E_B is now narrowed down to the analysis of the change of the molecular energy functional $\langle\phi|\mathcal{H}|\phi\rangle$ when ϕ is morphed from $1s_A$ into ψ, i.e., the variation step that *lowers* the energy through the second term in eq 4.4. This task manifestly requires a detailed understanding of the structure of the molecular wave function ψ.

4.2. Connecting the Molecular and Atomic Wave Functions. Can the *molecular* ground-state orbital ψ in any way be related to $1s_A$, the *atomic* ground-state orbital? A closer examination of the near-exact ground-state orbital ψ of the hydrogen molecule ion, referenced in section 1.3, reveals that it can in fact be expressed as a superposition of two normalized orbitals, ψ_A and ψ_B, that are only slight deformations of the corresponding exact ground-state orbitals $1s_A$ and $1s_B$ of the free hydrogen atoms A and B, respectively. Indeed, if one writes ψ as the superposition

$$\psi = (\psi_A + \psi_B)/[2 + 2\langle\psi_A|\psi_B\rangle]^{1/2} \quad (4.8)$$

where ψ_A contains only the 26 basis AOs on atom A and ψ_B contains only the 26 basis AOs on atom B mentioned in section 1.3, then the normalized constituent orbitals ψ_A and ψ_B have the overlap integrals

$$\langle\psi_A|1s_A\rangle = \langle\psi_B|1s_B\rangle = 0.970546 \quad (4.9)$$

with the respective free-atom orbitals $1s_A$ and $1s_B$. We therefore call ψ_A and ψ_B *quasi-atomic orbitals*. They are mirror images of each other. There are reasons to believe that ψ_A and ψ_B as constructed here are close approximations to a basis-set-independent decomposition of ψ.

However, even though 94% of the quasi-atomic orbital consists of the atomic 1s orbitals, omitting the 6% deviations will decrease the resulting binding energy by about 50%, a typical case where, in R. S. Mulliken's words, "a little bit goes a long way". It is therefore important to understand the character of the deformation that changes $1s_A$ into ψ_A. It is exhibited by expressing ψ_A as the following superposition:[13]

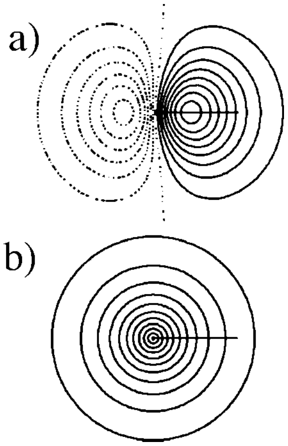

Figure 4. (a) Contour plot of the normalized polarizing deformation δp_A (see eq 4.10) in a plane containing the internuclear axis. (b) Contour plot of the 1s orbital. The contour increment is 0.05 bohr$^{-3/2}$. Positive contours are shown as solid lines. Nodes and negative contours are shown as dotted–dashed lines. The solid straight lines connect the nuclei.

$$\psi_A = 0.9705463\ 1s_A + 0.2055013\ \delta s_A + 0.1257342\ \delta p_A \quad (4.10)$$

where

δs_A = a normalized superposition of the 14 s orbitals on A

= a spherically deformation that is orthogonal to $1s_A$

δp_A = a normalized superposition of the 12 $p\sigma$, $d\sigma$, $f\sigma$, $g\sigma$ orbitals on A

= an angular deformation, orthogonal to $1s_A$ and δs_A

Figure 3 illustrates the decomposition of ψ_A in terms of the three components on the right-hand side of eq 4.10. Plotted along the internuclear axis are: 0.97055 $1s_A$ in red, 0.20550 δs_A in blue, 0.12573 δp_A in purple, and ψ_A in green. It is apparent that the admixture of δs_A leads to a *contraction* of the $1s_A$ orbital and that the admixture of δp_A leads to a *polarization* of the spherical orbital in the direction of the proton B. From the orthogonality of the three terms in eq 4.10, it follows that

$$1 = 0.9419601 + 0.0422308 + 0.0158091 \quad (4.11)$$

which shows that the quasi-atomic orbital ψ_A consists of 94% of the free-atom $1s_A$ orbital and that the 6% deformation is 73% spherical and 27% nonspherical in character.

The three-dimensional polarizing character of the angular deformation δp_A is apparent from its contours in a plane containing the internuclear axis, which are displayed in Figure 4 together with the contours of the $1s_A$ orbital. The deformation δp_A is seen to have a predominantly p-type shape, but with its spatial extension being only that of the 1s orbital.

The *contraction* deformation, on the other hand, which results from admixing the spherical deformation δs_A, is closely related to the type of intra-atomic contraction that has been discussed in detail in section 3.1. That becomes apparent by expressing the *spherical component* of ψ_A in eq 4.10 as

$$0.97055\ 1s_A + 0.20550\ \delta s_A = 0.99206\ \psi^s_A \quad (4.12a)$$

where the orbital

$$\psi^{s}{}_{A} = 0.978310\ 1s_A + 0.207145\ \delta s_A \tag{4.12b}$$

is normalized. This normalized spherical orbital is found to be essentially identical with a contracted hydrogen 1s orbital, as evidenced by the overlap integral

$$\langle \psi^{s}{}_{A} | 1s^{*}{}_{A} \rangle = 0.999562 \tag{4.13}$$

where $1s^*_A$ is the contracted 1s orbital of eq 3.2 with $\zeta = \zeta^* = 1.2654$. This value of ζ^* maximizes the overlap of $1s^*$ with $\psi^s{}_A$. Thus, 99.96% of the spherical deformation of ψ_A represents a 1s-type contraction.[38]

It will prove instructive to consider the contraction from $1s_A$ to $\psi^s{}_A$ of eq 4.12b as a *continuous* orbital sequence described by

$$\phi^{s}{}_{A}(t) = (1 - t^2)^{1/2}(1s_A) + t(\delta s_A) \tag{4.14}$$

so that

$$1s_A \rightarrow \phi^{s}{}_{A}(t) \rightarrow \psi^{s}{}_{A} \quad \text{as} \quad 0 \rightarrow t \rightarrow t^* = 0.207145 \tag{4.14a}$$

Each of these intermediate orbitals $\phi^s{}_A(t)$ can then also be associated with an orbital exponent $\zeta(t)$ of a contracted 1s-type orbital, namely, the one that has maximum overlap with $\phi^s{}_A(t)$. Manifestly, these intermediate orbital exponents vary as follows:

$$1 \rightarrow \zeta(t) \rightarrow \zeta^* = 1.2654 \quad \text{as} \quad 0 \rightarrow t \rightarrow t^* = 0.207145 \tag{4.14b}$$

and by virtue of eq 4.13, all the intermediate overlap integrals lie between 1 and 0.999562. These orbital exponents $\zeta(t)$ can therefore be used to characterize the gradual contraction of eq 4.14 by relating it to the gradual contraction in the atomic case that was discussed in detail in section 3.1.

It is apparent that the described structure of the exact wave function ψ is the reason for the success of the very early intuitive wave functions that approximated ψ as a superposition of scaled 1s and $2p\sigma$ atomic orbitals.[39,40]

4.3. Morphing the Atomic $1s_A$ Orbital into the Molecular Orbital ψ. In view of the decomposition of ψ exhibited in section 4.2, morphing the *atomic* ground-state orbital $1s_A$ into the *molecular* ground-state orbital ψ, which constitutes the variation step, implies three changes: polarizing and contracting the atomic orbitals $1s_A$ and $1s_B$ and superposing them according to eq 4.8, i.e., "sharing". We therefore resolve the orbital change $1s_A \rightarrow \psi$ into the following three sequential steps: polarization, sharing, and contraction. It can be shown[13] that the characteristics of the quantitative energy changes associated with the three steps do not depend drastically upon the sequence in which they are performed. The sequence chosen here has the virtue of didactic simplicity. The three orbital changes are defined as follows:

$$\text{polarization: } 1s_A \rightarrow ps_A = 0.992064\ 1s_A + 0.1257342\ \delta p_A \tag{4.15a}$$

$$\text{sharing: } ps_A \rightarrow \psi_p = (ps_A + ps_B)/[2 + 2\langle ps_A | ps_B \rangle]^{1/2} \tag{4.15b}$$

$$\text{contraction: } \psi_p \rightarrow \psi = (\psi_A + \psi_B)/[2 + 2\langle \psi_A | \psi_B \rangle]^{1/2} \tag{4.15c}$$

The polarized atomic orbital ps_A in eq 4.15a is obtained from the expansion of ψ_A (eq 4.10) by omitting the contraction term δs_A and adjusting the coefficient of $1s_A$ so that ps_A is normalized. Thus, the first step merely describes a polarization of the atomic $1s_A$ orbital. The second step creates the normalized superposition of the polarized ps orbitals on atoms A and B, and it therefore generates electron sharing. In the third step, the polarized orbitals ps_A and ps_B on centers A and B simultaneously contract to the quasi-atomic constituents ψ_A and ψ_B, respectively, thus creating the normalized molecular ground-state wave function ψ.

It is a simple matter to visualize the last step, i.e., the contraction of ψ_p (eq 4.15b) into ψ (eq 4.15c), as a *gradual* process because the polarized atomic orbital ps_A of eq 4.15a and the quasi-atomic orbital ψ_A of eq 4.10 can both be expressed in terms of the contractive spherical atomic orbital sequence $\phi^s{}_A(t)$ that was introduced in eq 4.14 in section 4.2. Indeed, one readily deduces from eq 4.14a that

$$ps_A = 0.992064\ \phi^{s}{}_{A}(t = 0) + 0.1257342\ \delta p_A \tag{4.16}$$

and

$$\psi_A = 0.992064\ \phi^{s}{}_{A}(t = t^*) + 0.1257342\ \delta p_A \tag{4.17}$$

so that the contraction step can be described by the continuous variation of the parameter t in $\phi^s{}_A(t)$ from 0 to $t^* = 0.207145$. The same holds for $\phi^s{}_B(t)$.

In section 4.2 we had furthermore shown (see eq 4.14b) that the parameter t in $\phi^s{}_A(t)$ determines an orbital exponent $\zeta(t)$ that relates the contraction of $\phi^s{}_A(t)$ to the type of *spherical atomic orbital contraction* discussed in section 3.1, and the same holds for $\phi^s{}_B(t)$. The *gradual molecular orbital contraction* $\{\psi_p \rightarrow \psi\}$ corresponding to eq 4.15c can therefore also be monitored by following this atomic orbital exponent $\zeta(t)$. This characterization of the contraction will prove useful in section 7.2.

4.4. Resolution of the Energy Lowering in the Variation Step in Terms of Polarization, Sharing, and Contraction. In correspondence with the described resolution of the *orbital* change $1s_A \rightarrow \psi$, we shall analyze the lowering of the *molecular energy functional* $\langle \phi | \mathscr{H} \phi \rangle$ in the variation step, i.e., the second term in eq 4.4, by resolving this energy change into the following sum:

$$[\langle \psi | \mathscr{H} \psi \rangle - \langle 1s_A | \mathscr{H} 1s_A \rangle] = E_{PO} + E_{SH} + E_{CO} \tag{4.18}$$

where

$$E_{PO} = \langle ps_A | \mathscr{H} ps_A \rangle - \langle 1s_A | \mathscr{H} 1s_A \rangle = \text{polarization energy} \tag{4.19a}$$

$$E_{SH} = \langle \psi_p | \mathscr{H} \psi_p \rangle - \langle ps_A | \mathscr{H} ps_A \rangle = \text{sharing energy} \tag{4.19b}$$

$$E_{CO} = \langle \psi | \mathscr{H} \psi \rangle - \langle \psi_p | \mathscr{H} \psi_p \rangle = \text{contraction energy} \tag{4.19c}$$

By virtue of the resolution (eq 4.18) and the definition of the quasi-classical energy (eqs 4.5 and 4.6), the total binding energy of eqs 4.3 and 4.4 is then given by the sum

$$E_B = E(H_2{}^+) - E(H) = E_{QC} + E_{PO} + E_{SH} + E_{CO} \tag{4.20}$$

At this point, it is useful to recall from section 2.4 that the virial theorem is valid for the atom as well as for the molecule at the equilibrium geometry. Hence, it is also valid for the binding energy E_B difference, so that

$$E_B = {}^1/_2 V_B = -T_B \tag{4.21}$$

$$V_{QC} + V_{PO} + V_{SH} + V_{CO} = -2(T_{QC} + T_{PO} + T_{SH} + T_{CO}) \tag{4.21a}$$

where V and T denote the corresponding potential and kinetic energies. Thus, since E_B is negative, the kinetic energy always increases and the potential energy always decreases when the molecule is formed.

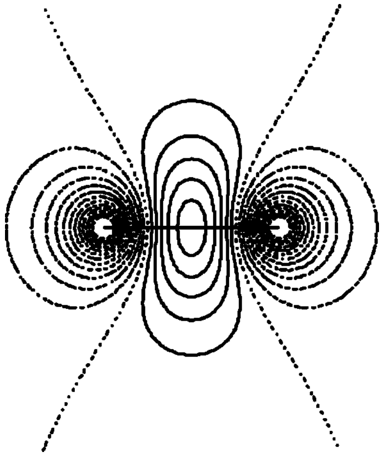

Figure 5. Contours of the interference density $\psi_p^2 - (ps_A + ps_B)/2$ occurring in eq 6.4. The contour increment is 0.002 bohr^{-3}. Positive contours are shown as solid lines. Nodes and negative contours are shown as dotted−dashed lines.

The following sections examine why each of the three terms of the variation step, given in eq 4.18, lowers the energy functional.

5. Energy Functional Lowering through Atomic Orbital Polarization

The first step in the sequence of eqs 4.19a−4.19c, eq 4.19a, represents the change of the molecular energy functional when the orbital $1s_A$ is polarized according to eq 4.15a. Consider the kinetic and potential components of this polarization energy:

$$E_{PO} = T_{PO} + V_{PO} \tag{5.1}$$

It is apparent from Figure 3 that the result of the polarization is a *skewing* of the $1s_A$ orbital toward the nucleus B. This skewing increases the attraction of the orbital on A to the proton B and lowers the potential part of the energy functional so that $V_{PO} < 0$. On the other hand, Figure 4 shows that the polarization is accomplished by the admixture of an orbital that has a node, while approximately maintaining the spatial extension of the 1s orbital. Such an admixture has a higher kinetic energy than the 1s orbital, and hence, polarization will increase the kinetic part of the energy functional so that $T_{PO} > 0$. The quantitative values are as follows:

$$V_{PO} = -45.44 \text{ mh}, \quad T_{PO} = 10.01 \text{ mh}, \quad E_{PO} = -35.43 \text{ mh} \tag{5.2}$$

The contribution V_{PO} represents an *inter*-atomic effect, whereas the contribution T_{PO} represents an *intra*-atomic effect.

If one combines the polarization energy with the quasi-classical energy discussed in section 4.1 and given by eq 4.7, one finds

$$E_{QC} + E_{PO} = 27.64 - 35.43 = -7.79 \text{ mh} \tag{5.3}$$

Thus, polarization alone leads only to a very weak binding, viz., about 8% of the total binding energy of about 103 mh.

6. Energy Functional Lowering through Electron Sharing

The second step in the sequence of eqs 4.19a−4.19c, viz. eq 4.19b, yields the change of the molecular energy functional when the polarized atomic orbital ps_A is replaced by the superposition of the polarized orbitals ps_A and ps_B on the two atoms. It thus embodies the energetic result of electron sharing. Decomposing the sharing energy into its kinetic and potential parts

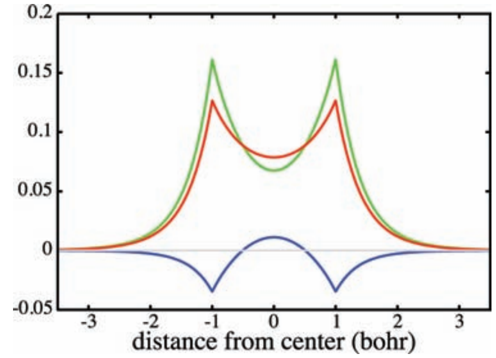

Figure 6. Molecular density ψ_p^2 (red), atomic density average $(ps_A + ps_B)/2$ (green), and interference density $\psi_p^2 - (ps_A + ps_B)/2$ (blue), plotted along the internuclear axis. Densities are given in bohr^{-3}.

$$E_{SH} = T_{SH} + V_{SH} \tag{6.1}$$

one finds the quantitative values

$$V_{SH} = 33.62 \text{ mh}, \quad T_{SH} = -97.25 \text{ mh}, \quad E_{SH} = -63.63 \text{ mh} \tag{6.2}$$

which shows that electron sharing lowers the energy functional considerably more than the atomic polarization.

More importantly, in contrast to the polarization energy, the sharing energy lowering is the result of a *lowering of its kinetic part* ($T_{SH} < 0$). The *potential part* actually *raises* the energy ($V_{SH} > 0$), but by a much smaller amount.

6.1. Electron Sharing Raises the Potential Energy Functional. That electron sharing *increases* the potential energy has the following reason. From the definition (eq 4.19b) of the sharing energy, one finds for its potential part

$$V_{SH} = \langle \psi_p | \mathbf{V} | \psi_p \rangle - \langle ps_A | \mathbf{V} | ps_A \rangle \tag{6.3}$$

where $\mathbf{V}$ is the potential part of the Hamiltonian $\mathscr{H}$ defined in eq 4.2. Since $\mathbf{V}$ is symmetric in A and B, we can rewrite this potential sharing energy in the symmetrized form (note that R^{-1} cancels out)

$$\begin{aligned} V_{SH} &= \langle \psi_p | \mathbf{V} | \psi_p \rangle - {}^1\!/_2[\langle ps_A | \mathbf{V} | ps_A \rangle + \langle ps_B | \mathbf{V} | ps_B \rangle] \\ &= -\int \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z\, (r_A^{-1} + r_B^{-1})[\psi_p^2 - {}^1\!/_2(ps_A + ps_B)] \end{aligned} \tag{6.4}$$

Since the density difference in the brackets in the integral is the difference between the square of the sum of two amplitudes and the sum of the squares of the amplitudes, it describes a wave-theoretical interference, and we therefore call it the *interference density*.

The contours of the interference density in a plane containing the bond axis are displayed in Figure 5. They show that it represents a *charge shift* from the regions near the nuclei into the region between the nuclei, i.e., a *charge accumulation in the bond* at the expense of *charge depletion near the nuclei*. The origin of this charge shift is apparent from Figure 6, which exhibits plots along the internuclear axis for the interference density (blue) as well as for its two components, viz., the density of the shared orbital (green) and the average of the constituent atomic densities (red). It illustrates how the normalized superposition of the ps_A amplitudes generates constructive interference in the bond region and destructive interference in the atomic regions.

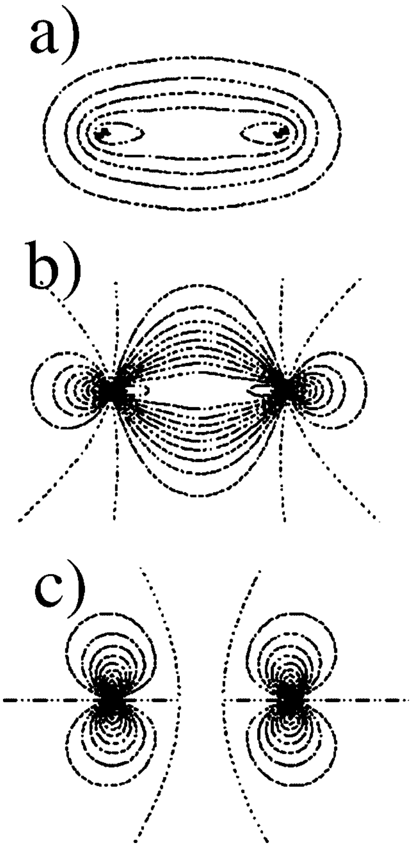

Figure 7. (a) Contours of the kinetic interference density, i.e., the entire integrand of the integral on the right-hand side of eq 6.6. (b) Contours of the contributions of the z component to the countours in (a). (c) Contribution of the sum of the x and y components to the countours in (a). All closed contours are negative; the open contours are zero. The contour increment is 0.005 hartree/bohr^3.

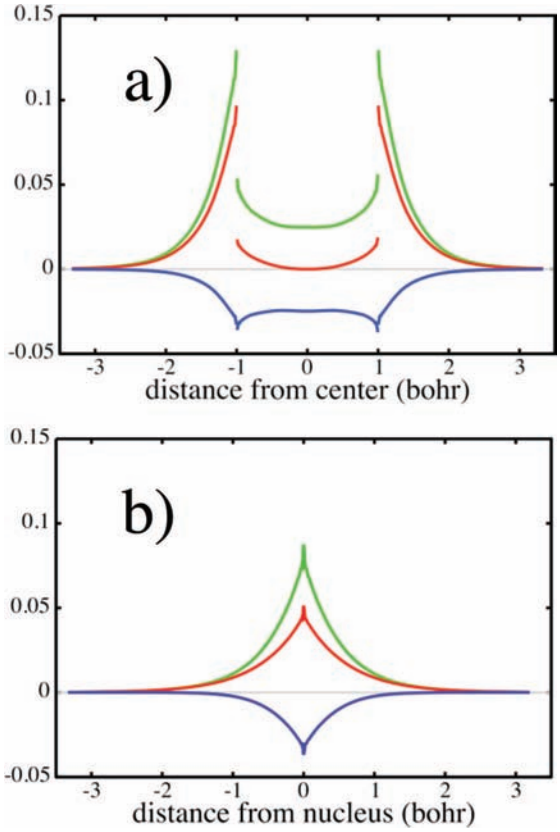

Figure 8. Plots along (a) the internuclear axis and (b) an axis perpendicular to the bond axis and passing through one of the nuclei for the total kinetic interference density (blue) of Figure 7a and its two parts, viz., the molecular squared gradient $^1/_2(\nabla\psi_p)^2$ (red) and the average of the squared gradients of the atoms $[^1/_2(\nabla ps_A)^2 + {}^1/_2(\nabla ps_B)^2]/2$ (green). Kinetic densities are in hartrees/bohr^3.

This shift of charge manifestly *raises* the potential energy expectation value because the potential $(-r_A^{-1} - r_B^{-1})$ in the integrand of eq 6.4 is less negative in the bond region than near the nuclei. The frequently repeated conjecture (see section 2.1) that charge accumulation in the bond through electron sharing per se lowers the potential energy is thus *not* borne out by the quantitative examination.

6.2. Electron Sharing Lowers the Kinetic Energy Functional. Why does electron sharing between atomic orbitals lower the kinetic energy? From the definition (eq 4.19b) of the sharing energy, one finds for its kinetic part

$$T_{SH} = \langle\psi_p|\boldsymbol{T}|\psi_p\rangle - \langle ps_A|\boldsymbol{T}|ps_A\rangle \qquad (6.5)$$

The simplest explanation for this difference being negative is that changing the wave function from ps_A to ψ_p essentially represents a *delocalization* of the electronic wave function. Orbital delocalizations typically lower orbital kinetic energies, as is exemplified by the lowering of the kinetic energy of a free particle in a box when the length of the box is increased. This is because the maintenance of normalization when an orbital spreads over a larger region requires an overall attenuation of the orbital and, hence, also of its gradient (provided that no additional node is introduced), which will lower the kinetic energy according to eq 2.1. This effect is related to the uncertainty principle between position and momentum.[29,31,32]

This general reasoning is confirmed by a more detailed examination. To this end, we symmetrize expression 6.5 without changing its value, as we did for the potential energy in eq 6.4. This yields

$$T_{SH} = \langle\psi_p|\boldsymbol{T}|\psi_p\rangle - {}^1/_2[\langle ps_A|\boldsymbol{T}|ps_A\rangle + \langle ps_B|\boldsymbol{T}|ps_B\rangle]$$
$$= \int dx\, dy\, dz\, \{({}^1/_2\, \nabla\, \psi_p)^2 - [{}^1/_2(\nabla ps_A)^2 + {}^1/_2(\nabla ps_B)^2]/2\} \qquad (6.6)$$

Let us call the integrand in the integral the *kinetic interference density*. Figure 7 shows contours of the kinetic interference density in a plane containing the bond axis. Panel a displays the contours of the total kinetic interference density, panel b displays the contours of the bond parallel contribution, and panel c displays the sum of the two bond-perpendicular contributions. All contours in Figure 7 are parts of rotationally symmetric contour surfaces. It is seen that all contributions are *negative everywhere*, the largest contributions coming from the bond-parallel component $^1/_2(\partial\psi_p/\partial z)^2 - [^1/_2(ps_A/\partial z)^2 + {}^1/_2(\partial ps_B/\partial z)^2]/2$.

The origin of the negative kinetic interference density is apparent from Figure 8, which shows plots of the kinetic interference density (blue) as well as of its two parts $^1/_2(\nabla\psi_p)^2$ (red) and $[^1/_2(\nabla ps_A)^2 + {}^1/_2(\nabla ps_{AB})^2]/2$ (green) along the internuclear axis. These plots exhibit that the delocalization of the orbital from one to two centers indeed attenuates the gradient of the wave function everywhere, and this is also in agreement with the shapes of the corresponding densities in Figure 6. The attenuation is particularly strong for the bond-parallel (z) component in the bond region due to the vanishing of $\partial\psi_p/\partial z$ on the bond-bisecting central plane, as shown by the red curve touching the axis in Figure 6a.

7. Energy Functional Lowering through Orbital Contraction

7.1. Electron Sharing Induces Orbital Contraction. Inserting the values found for the quasi-classical energy E_{QC} (eq 4.7), the polarization energy E_{PO} (eq 5.2) and the sharing energy E_{SH} (eq 6.2) into expression 4.20 of the binding energy E_B, we obtain

$$E_B = E_{QC} + E_{PO} + E_{SH} + E_{CO} = -71.42\text{ mh} + E_{CO} \qquad (7.1a)$$

Thus, the molecular wave function that incorporates only polarization and sharing between the two centers already yields binding. The corresponding kinetic and potential components of E_B, viz.

$$T_B = T_{QC} + T_{PO} + T_{SH} + T_{CO}$$

$$= 0 + 10.01 - 97.25 + T_{CO} = -87.24\text{ mh} + T_{CO} \qquad (7.1b)$$

$$V_B = V_{QC} + V_{PO} + V_{SH} + V_{CO}$$

$$= 27.64 - 45.44 + 33.62 + V_{CO} = 15.82\text{ mh} + V_{CO} \qquad (7.1c)$$

show moreover that this binding is due to the lowering of the *kinetic* energy coming from electron sharing.

However, the binding energy E_B generated by the *actual* molecular wave function ψ must be the sum of a *negative potential* contribution and a *positive kinetic* contribution. This follows from the virial theorem as noted at the end of section 4.4. Thus, the orbital ψ_p, consisting of shared polarized atomic orbitals, cannot be the actual molecular ground state, and therefore, the final wave function change from ψ_p to ψ, namely, the contraction step formulated in eqs 4.15c and 4.19c, must (i) lower the energy further and (ii) reestablish the virial ratio. In fact, the energy contributions of this contraction step are

$$V_{CO} = -221.08\text{ mh}, \quad T_{CO} = +189.87\text{ mh}, \quad E_{CO} = -31.21\text{ mh} \qquad (7.2)$$

After insertion of these contributions into eq 7.1a, the binding energy satisfies indeed the virial relationship. This is exhibited in Table 1, which lists the complete breakdown in terms of all discussed contributions.

Looking at the whole picture, one sees that electron sharing lowers the energy in two ways: First, it lowers the energy functional *directly* through the decrease of its kinetic part. Second, it thereby creates a virial theorem violation that *induces* a further energy-lowering modification of the wave function, which reestablishes the virial relationship. It is therefore responsible for −94.84 mh out of the total of −102.63 mh.

A remarkable detail regarding the final kinetic energy increase upon bond formation is exhibited in Table 2, which lists its Cartesian breakdown. It shows that the overall increase is entirely embodied in the increase of the bond-perpendicular x and y components. For the bond-parallel z component of the kinetic energy, on the other hand, the increase due to contraction does not overcome the lowering due to sharing. The negative value of this component is the survivor of the strong bond-parallel kinetic energy lowering that results from the delocalization in this direction.

7.2. Orbital Contraction Plays the Same Variational Role in the Molecule as It Does in the Atom. To gain a physical understanding of the origin of the energy changes occurring in the contraction step, we compare the just discussed analysis of the binding energy with the earlier analysis of the *atomic* energy changes in section 3.3. There exists a fundamental similarity. In both cases, (i) an intermediate wave function lowers the value of the energy functional relative to its initial value through a *decrease in the kinetic contribution*, and this creates a violation of the virial theorem, and (ii) the energy is then lowered further, and the virial relationship is reestablished through a *wave function contraction*. To be sure, there are differences in both the kinetic and potential parts: (i) The kinetic energy lowering of the intermediate wave function is caused by an increase in the mass of the moving particle in the atomic case, but by sharing the electron cloud between the two centers in the molecular case. (ii) The potential energy lowering is the result of a wave function contraction toward one center in the atomic case, but simultaneously toward two centers in the molecular case. Nonetheless, the same variational competition is at work in the contraction steps occurring in the molecule ion and in the atom. In both cases, the violation of the virial theorem indicates that the optimal balance between the potential nuclear pull and the kinetic pressure has not been reached for the intermediate wave function: specifically, since $-V > 2T$, the potential pull is still stronger than the resisting energy pressure at this stage. The potential energy pull from the nuclear attraction is therefore able to contract the orbital further toward one nucleus or two nuclei until the resisting kinetic energy pressure has risen to the virial value $T = -V/2$, at which point the total energy functional has its minimum.

TABLE 1: Breakdown of the Binding Energy of H_2^+ in Terms of Quasi-Classical, Polarization, Sharing, and Contraction Contributions

energy, mh		T	V	E
quasi-classical	E_{QC}	0	27.64	27.64
polarization	E_{PO}	10.01	−45.44	−35.43
sharing	E_{SH}	−97.25	33.62	−63.63
contraction	E_{CO}	189.87	−221.08	−31.21
binding	E_B	**102.63**	**−205.26**	**−102.63**

TABLE 2: Cartesian Breakdown of the Kinetic Energy Increase from H to H_2^+: Kinetic Energy of H_2^+ minus Kinetic Energy of H (mh)

x component	y component	z component	total
64.32	64.32	−26.01	102.63

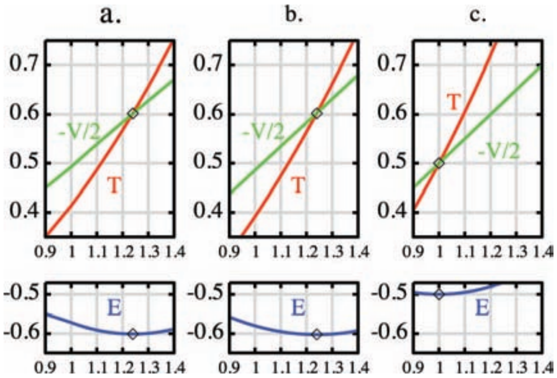

Figure 9. Comparison of variational competition in H_2^+ and H: variation of the kinetic (red), potential (green), and total (blue) energy functionals for various contractions as functions of the contraction parameter ζ. (a) Contraction for H_2^+ as described in section 4.3 starting with eq 4.17. (b) Contraction for the atomic analogue with $m = 1.27537$, $Z = 0.97199$. (c) Contraction for the H atom ($m = 1$, $Z = 1$). Abscissas = ζ. Ordinates are in hartrees.

The similarity between the two cases can be exhibited explicitly by following the contraction from the uncontracted (polarized + shared) molecular wave function ψ_p to the contracted actual molecular wave function ψ by means of the continuous deformation that has been described at the end of section 4.3. As was shown there, this continuous contraction of the molecular orbital can be characterized and monitored by an orbital exponent ζ that has a meaning very similar to that used in the atomic case discussed in section 3.1.

Figure 9a exhibits the continuous changes of the kinetic, potential, and total energies plotted versus the just mentioned orbital-exponent analogue ζ, as the wave function gradually contracts from ψ_p to ψ. For comparison, Figure 9b exhibits the corresponding energy plots of the hydrogen atom analogue defined in section 3.1 by eqs 3.3 and 3.4 for mass $m = 1.276$ and charge $Z = 0.972$. (Note that, as was done in Figures 1 and 2 in section 3.1, the value of $-V/2$ is plotted rather than V.) The graphs for the molecular and atomic cases in parts a and b, respectively, of Figure 9 are seen to resemble each other extremely closely, notwithstanding the fact that increasing ζ describes a contraction toward one nucleus in Figure 9b whereas it describes a simultaneous contraction toward two nuclei in Figure 9a. To exhibit the contrast to the hydrogen atom, Figure 9c shows the corresponding plots for that case, where $m = 1$ and $Z = 1$.

This similarity suggests that the potential and kinetic energy changes associated with contraction in the molecule have their origin predominantly in the interaction of the spherical component $\psi^s{}_A$ with nucleus A and that of the spherical component $\psi^s{}_B$ with nucleus B. This conclusion is indeed in agreement with more detailed calculations.[41] The nature of the variational competition between the kinetic pressure and the potential pull is thus essentially the same in the molecular and atomic cases. We conclude that, in the molecule, orbital contraction plays the same role in the context of the variational competition between the kinetic and potential energy functionals as it does in the atomic case discussed in section 3.

8. Conclusions

8.1. Variational Analysis as a Basis for Physical Understanding.

Bond formation is caused by changes in the electronic energy of stationary states that result from changes in the geometric parameters in the Hamiltonian.

Such energy changes can be understood by *variational reasoning* in terms of the physical attributes of the kinetic and potential energy functionals. In atoms as well as in molecules at a fixed nuclear geometry, the variational energy minimization determines the ground state by seeking the optimal compromise between the potential pull of the nuclear attractions and the localization-resisting kinetic pressure of the electron cloud. The former attempts to lower the energy functional by shrinking the electronic wave function toward the nuclei; the latter counteracts such shrinkage by raising the value of the energy functional. For atoms as well as for molecules at equilibrium geometries and transition states, the optimal compromise between these two antagonists in the variational competition occurs when the kinetic energy functional has risen to the "virial value" $T = -{}^1/_2V$.

8.2. Electron Sharing and Covalent Bonding in the Hydrogen Molecule Ion.

Since $H_2{}^+$ has a lower energy than H, it follows that the virial value $T = |V/2| = |E|$ of $H_2{}^+$ at its equilibrium geometry is larger than that of the H atom. In the context of the competition between T and V, which occurs when the respective orbitals shrink variationally, this difference implies that, by the time the kinetic energy has risen to the virial value, the potential energy V in the molecule has sunk to a lower value than that in the atom. In other words, the molecular kinetic energy functional "lags behind" the atomic kinetic energy functional in its ability to check the potential energy functional lowering through shrinkage toward the nuclei. Understanding the reason for this difference is the critical issue. The results of the preceding sections lead to the following qualitative picture that exhibits how the variational process in $H_2{}^+$ differs from that in in the H atom.

Imagine that, in each system, we start with a very diffuse spherical orbital as an initial guess. In each system, the variational energy lowering will then result in a contraction of this initial orbital because the electrostatic nuclear pull prevails at large distances from the nuclei. In the *atom*, this variational contraction will be toward one nucleus and end up with the spherical wave function (see section 3.1)

$$1s = \pi^{-1/2} \exp(-r) \tag{8.1}$$

In the *molecule*, on the other hand, the variational contraction will aim simultaneously toward both nuclei. Imagine this orbital shrinkage to occur in two steps. The contraction in the first step leads to the intermediate orbital given by eq 4.15b, viz.

$$\psi_p = (ps_A + ps_B) \times \text{Normalization} \tag{8.2}$$

where ps_A and ps_B are the polarized 1s orbitals on the two atoms, as defined by eq 4.15a. The second contractive step leads then from this orbital to the actual ground-state orbital of $H_2{}^+$, given by eq 4.15c, viz.

$$\psi = (\psi_A + \psi_B) \times \text{Normalization} \tag{8.3}$$

As is apparent from Table 1, the *potential* energy of the *intermediate* wave function (eq 8.2) in the molecule is close to that of the 1s orbital in the atom (in fact it is about 15 mh higher; see eq 7.1c). This is because (i) each of the two halves of the electron cloud of the intermediate molecular wave function (eq 8.2) is on average about as close to its respective nucleus as the entire (1s) electron cloud is to its nucleus in the atom and (ii) the attraction of the left half of the electron to the right nucleus plus the attraction of the right half of the electron to the left nucleus cancels almost exactly against the repulsion between the nuclei.[42]

Thus, the potential energy can be lowered by shrinkage with approximately equal effectiveness *regardless* of whether the electron cloud contracts toward one nucleus or simultaneously toward both nuclei.

By contrast, the *kinetic* energy responds very differently to variational shrinkage. As seen from Table 1, the kinetic energy of the intermediate wave function (eq 8.2) is almost 90 mh *lower* than that of the 1s wave function in the atom (see eq 7.1b). This is because an *inherent delocalization* is *maintained* when the molecular orbital simultaneously shrinks toward both nuclei and this delocalization has an attenuating effect on the expectation value ${}^1/_2\int dq\,(\nabla\psi)^2$, when compared with that of an equally close approach of the spherical orbital toward a single nucleus.

Thus, for every degree of shrinkage, as characterized for instance by the exponent parameter ζ in Figure 9, the molecular *kinetic* energy value is significantly lower than the atomic value, whereas the *potential* energies of the two systems differ relatively little. Because of this weakening (compared to the atom) of the molecular resisting kinetic pressure for a given contraction around the nuclei, and hence a given potential pull, this potential pull is able to shrink the orbital in the molecule more tightly than it can in the atom before the kinetic energy rises to the virial value $|V/2|$. As a result, the molecular

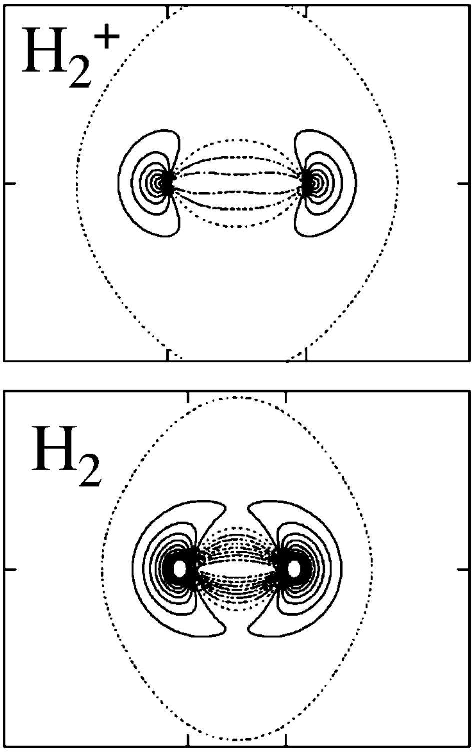

Figure 10. Contours of the kinetic energy density differences of (a) eq 8.4 and (b) eq 8.5. Positive contours are shown as solid lines. Nodes and negative contours are shown as dotted–dashed lines. The contour increment is 0.01 hartree/bohr^3. The bond-parallel panel length is 3.5 Å. Nuclear positions are indicated by tick marks.

variational minimum occurs for a lower potential energy and hence a lower total energy (and of course a higher kinetic energy) than in the atom.

The covalent bond in H_2^+ is therefore due to the weakening of the kinetic energy functional in the context of the variational competition. This weakening is caused by the delocalization of the electron over two centers and this is just what is meant by "sharing". In short:

> ***Covalent bonding occurs when electron delocalization through electron sharing softens the outward kinetic pressure and thereby allows the electron wave to exploit attractive local potential regions more effectively within the framework of the variational competition.***

In the H_2^+ ion, the more attractive regions are near the nuclei and *not*, as is commonly conjectured, in the bond center (see the last paragraph of section 6.1). Hellmann's intuition (see section 2.1) was therefore on target even if he did not place the problem into the variational context and did not make the connection between kinetic energy attenuation, orbital contraction, and the virial theorem.

It might seem odd that, even though electron sharing generates bonding through a modification of the kinetic energy functional, the ground-state kinetic energy *increases* upon bonding. The resolution of this superficial paradox is that the modification of the kinetic energy functional determines the actual ground-state energy *indirectly*, namely, through a modification of the variational process: Figure 9 illustrates how the overall lowering of the kinetic energy functional curve leads to an *increase* in the kinetic energy for the optimized energy minimum. As mentioned before, "relaxations" that undo initially introduced changes are well-known to occur also in other physical contexts[17,37] when a variation principle is operative.

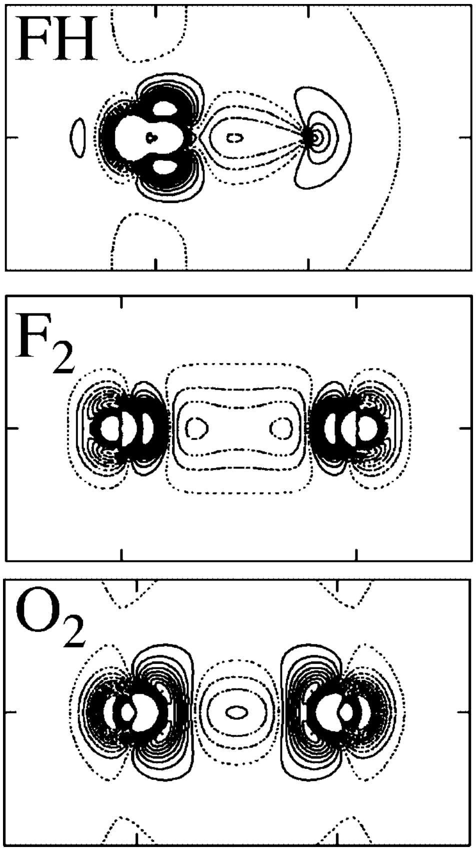

Figure 11. Contours of the kinetic energy density differences of eq 8.6 for the molecules FH, F_2, and O_2. Positive contours are shown as solid lines. Nodes and negative contours are shown as dotted–dashed lines. The contour increment is 0.05 hartree/bohr^3. The bond-parallel panel length is 2.8 Å. Nuclear positions are indicated by tick marks.

8.3. Chemical Binding in Other Molecules. While the variation principle and the virial theorem remain valid in molecules with many electrons, the variational process and its interpretation become nonetheless more complex in these systems than in the hydrogen molecule ion.[43]

For various reasons, the quasi-classical Coulombic interactions can become attractive. Already in the hydrogen molecule, they are somewhat attractive because the nuclear–electronic attractions outweigh the sum of the nuclear and the electron–electron repulsions. Nonetheless, the kinetic consequences of electron sharing found in H_2^+ predominate also in H_2.[44] However, in bonds involving electrons of the L and M shells, *strong* quasi-classical attractions have been documented.[45] Furthermore, the near-degeneracy between atomic orbitals of different angular momenta facilitates orbital polarization in these systems. In heteroatomic bonds partial charge transfer can occur. On the other hand, the Pauli exclusion principle, a consequence of the many-electron antisymmetry requirement, generates repulsive energy contributions from doubly occupied orbitals, notably, but not only, from inner shells and lone pairs. Orthogonality of the valence orbitals of one atom to closed shells of other atoms introduces interatomic repulsions. Major energy contributions can furthermore come from changes in the interelectronic repulsions upon bond formation, including changes in the correlation energy. The latter contribute for instance half of the binding energy in the F_2 molecule, and the weak bonds in "van der Waals molecules" are entirely due to electron correlations since they generate the dispersion forces.

The application of the virial theorem becomes more intricate when, in the presence of core orbitals, valence electrons are described as moving under the influence of "effective" potentials. For such effective potentials, the simple virial theorem does not hold and the overall orbital shrinkage is not as simple as it is for bonded hydrogen atoms.[46] This subject deserves further exploration. In this context, it may also be recalled that the virial theorem in the simple form used above holds only at those points on potential energy surfaces where the gradient vanishes (minima, maxima, transition states), but not at other points.[29,30] On other parts of reaction paths, one has to develop the variational reasoning without assistance from the virial relation regarding the variational minimum. This is possible,[16] but more laborious.

Even with all these complications, certain aspects of the kinetic energy carry over from the H_2^+ ion to other molecules, as can be inferred from the following simple comparisons. Figure 10a exhibits contours of the difference

$$^1/_2(\nabla\psi)^2 - 0.5[^1/_2(\nabla 1s_A)^2 + {}^1/_2(\nabla 1s_B)^2] \qquad (8.4)$$

It differs from the kinetic interference density after the integral sign in eq 6.6 by ψ being the *actual* wave function of H_2^+ and $1s_A$ and $1s_B$ being the *actual* hydrogen atom wave functions. The negative contours in the bond region are manifestly related to the fact, discussed in the last paragraph of section 7.1, that the bond-parallel component of the kinetic energy change upon bond formation is negative (even though the total kinetic energy change is positive). Figure 10b displays the analogous contours for the kinetic energy of the hydrogen molecule, namely

$$\sum_k n_k {}^1/_2(\nabla\phi_k)^2 - [^1/_2(\nabla 1s_A)^2 + {}^1/_2(\nabla 1s_B)^2] \qquad (8.5)$$

where ϕ_k and n_k are the 140 natural orbitals and their occupation numbers of H_2, obtained from a CI wave function calculated with an uncontracted, exponent-optimized 14s,6p,3d,2f,1g basis. Its energy lies 0.2 mh above the exact value of Kolos and Nakatsuji.[47] The similarity in the contour maps is manifest.

Furthermore, Figure 11 shows the corresponding contour maps for the total kinetic MCSCF energies of the molecules FH, F_2, and O_2, i.e., the differences

$$\sum_k n_{AB,k} {}^1/_2(\nabla_k \phi_{AB,k})^2 - \sum_k n_{A,k} {}^1/_2(\nabla_{A,k})^2 - \sum_k n_{B,k} {}^1/_2(\nabla\phi_{B,k})^2 \qquad (8.6)$$

where $\phi_{AB,k}$ are the natural orbitals of the molecular full valence MCSCF wave functions and $\phi_{A,k}$ and $\phi_{B,k}$ are the atomic ROHF orbitals of the two atoms, respectively, while $n_{X,k}$ are the respective occupation numbers.[48] All maps exhibit negative contours for this difference in the bond region similar to those of H_2^+ and H_2 in Figure 10.

One might be tempted to infer from Figures 10 and 11 that it is the kinetic energy lowering shown in the bond region that allows for a contraction toward the nuclei from the regions perpendicular to and outside the bond and that this accounts for the lower total energy. In this regard, the conclusions of section 3.2 should however be kept in mind, namely, that the cause of energy stabilization can be a change in the kinetic energy functional and, yet, it may be that this sole cause cannot be recognized by examining the total change in the actual wave function, i.e., without examining intermediate wave functions.

That there exists a general connection between electron sharing and kinetic energy is also implied by the Rozendahl and Baerends's analysis[12] of the electron momentum densities in first-row homonuclear diatomic molecules.

It thus appears that the *softening* of the kinetic pressure in the energy functional due to the delocalization caused by electron sharing is a universal ingredient of covalent binding and, presumably, distinguishes it from ionic and correlation binding.[43]

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(39) In the Finkelstein−Horowitz approximation (see ref 8), the orbital ψ_A is a single 1s orbital, whose orbital exponent $\zeta = 1.237$ is obtained by energy minimization. It is very similar to the value $\zeta^* = 1.2654$, quoted after eq 4.13, which is obtained by overlap maximization.

(40) Dickinson introduced the polarizing scaled p orbital: Dickinson, B. N. *J. Chem. Phys.* **1933**, *1*, 317. He found that the optimal 2ps orbital had the exponential factor $\exp(-\zeta^* r)$, with ζ^* equal to that of the 1s* orbital in eq 4.13. Thus, the polarizing orbital was contracted to the size of the contracted 1s* orbital.

(41) See refs 16 and 17.

(42) A detailed discussion of this point is given in ref 17. This cancellation may also be relevant in a broader context, e.g., in the discussion of Walsh's rules. See: Buenker, R. J.; Peyerimhoff, S. D. *Chem. Rev.* **1974**, *74*, 127.

(43) See ref 11e, p 127.

(44) See ref 15.

(45) See ref 11d.

(46) See ref 11a.

(47) Kolos, W. *J. Chem. Phys.* **1994**, *101*, 1330. Nakatsuji, H. *Phys. Rev. Lett.* **2004**, *93*, 030403.

(48) Jensen's "PC3" basis sets were used for fluorine and oxygen. They contain the following numbers of contracted orbitals: 6s, 5p, 4d, 2f, 1g. See: Jensen, F. *J. Chem. Phys.* **2001**, *115*, 9113.

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