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Theories of binding in H_2^+

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Summary. A common, traditional potential energy expression for the theoretical binding energy in the simplest LCAO treatment of H_2^+ (i.e. using 1*s* eigenfunctions of the atoms) is derived in the context of Ruedenberg's theory, by virtue of a cancellation between the interference kinetic energy and an identifiable positive part of the interference potential energy arising from charge moving away from "dative" protons. Thus, although electron sharing raises the total potential energy, its net contribution to the binding energy may be equated to the negative part of the interference potential energy which is due to charge moving towards "opposite" protons. It is shown that this potential energy expression remains approximately valid when the atomic orbitals are optimally scaled. For contracted orbitals, the cancellation within the interference energy is not exact, and the explanation of contraction through the variation principle is less transparent from a potential energy viewpoint than it is in Ruedenberg's analysis. However, when the orbitals are both contracted and polarised the cancellation is closer to being exact, and the minimisation of the total energy is achieved through competition between the term representing the atomic promotion and deformation energy on the one hand, and the usual potential energy expression on the other.

Key words: H_2^+, binding energy of – Interference charge density – Variational reasoning

1 Introduction

At the fundamental level there is only one theory of binding in H_2^+, and that corresponds to an exact solution of the Schroedinger equation. However there is within quantum chemistry a tradition which looks for explanation at a different level, in terms of physical models or analogies which will qualitatively but reliably reproduce the results of the Schroedinger equation for H_2^+ (and other prototypes) and anticipate such results for more complicated molecules. It is at this level that there has been more than one interpretation of binding in H_2^+ and some need of a resolution of their apparently conflicting claims.

From the earliest applications of quantum mechanics to H_2^+ and H_2 until about thirty years ago there was apparently no problem concerning the qualitative understanding of chemical binding. The historic idea of sharing electrons between atoms had received quantum mechanical expression in the form of overlap between atomic wavefunctions. It was known that for stable molecules this overlap produced an accumulation of charge between the nuclei; and that a theorem, the virial theorem, required potential energy in a molecule to be lower than in its separate atoms. Hence arose the widespread view that "the accumulation of charge between the nuclei reduces potential energy". There appears to be no single original source for this view, although it was adopted by very many textbooks. The strength of electron sharing was sometimes attributed to the overlap charge density, sometimes to the overlap integral.

In a series of papers beginning in 1962 [1] and culminating in three papers [2–4] between 1970 and 1975, Ruedenberg and his school mounted an important criticism of the traditional theory of binding. Ruedenberg contended, as had Hellmann [5] before him, that the constructive overlap between atomic wavefunctions reduces kinetic energy, not potential energy. Ruedenberg then argued that this reduction of kinetic energy causes (through the variational principle) the wavefunction to contract, with a resulting lowering in potential energy and a raising of kinetic energy. The lowering of potential energy is essentially atomic in character, and is exceeded by the rise in kinetic energy associated with the same parts of the charge density. Kinetic energy has a dual role in Ruedenberg's theory. It opposes the shrinkage of the atomic densities, but this opposition is weakened through electron sharing, leading to lower potential energy than is found in the isolated atom.

Textbooks, especially at the elementary level, have been slow to adapt their treatments of binding to include the role of kinetic energy. This may have been due to criticism by Bader [6, 7] from the standpoint of the virial theorem. However by 1978 Ruedenberg's theory had been endorsed by Mulliken [8] and by Kutzelnigg [9]. The role of kinetic energy has also been acknowledged by Atkins [10]. Daudel [11] has remarked: "Ruedenberg has shown that the usual presentation is not convenient". On the other hand, Levine [12] considers the question as not yet settled.

As a result of Ruedenberg's work there is a general recognition of the fact that binding cannot be understood without considering both kinetic and potential energy. However this raises the question: why was the traditional theory able to account for the binding energy in terms of potential energy integrals only? Is this result an artefact of a poor wavefunction and, if not, how can it be reconciled with Ruedenberg's theory? The present work is an attempt to find answers to these questions. Because Ruedenberg's ideas are so important to our own analysis, a brief commentary on these ideas will be given first.

2 Ruedenberg's Theory

Without loss of generality, the ground state of the H_2^+ molecule may be represented by the normalised sum of atomic orbitals a and b, i.e.

$$\psi = (a + b)/(2 + 2S)^{1/2}, \tag{1}$$

where

$$S = \langle a | b \rangle \tag{1a}$$

It is well known that by taking sufficiently flexible functions a and b the ψ function may become, through the variation method, an exact solution to the electronic Schroedinger equation. In this section we shall be content with the simple form of ψ first proposed [13] by Finkelstein and Horowitz (FH) where

$$a = (\zeta^3/\pi)^{1/2} \exp(-\zeta r_a), \tag{1b}$$

and

$$b = (\zeta^3/\pi)^{1/2} \exp(-\zeta r_b). \tag{1c}$$

The only variational parameter in the FH wavefunction is the orbital exponent ζ, for which accurate values have been provided by Kim et al. [14] and also by Feinberg et al. [2]. Thus we consider orbital contraction (increasing ζ) but not orbital polarisation at this stage.

The charge density, ρ, can be expanded as follows:

$$\rho = \psi^2 = (a^2 + b^2 + 2ab)/2(1 + S) \tag{2}$$

Ruedenberg's theory now focuses upon the difference between the molecular charge density, ρ, and the "quasi-classical" charge density, ρ^{qc}, which would be found if atomic densities and not atomic wavefunctions were additive, i.e.

$$\rho = \rho^{qc} + \rho^{i}, \tag{3}$$

where

$$\rho^{qc} = (a^2 + b^2)/2 \tag{3a}$$

and

$$\rho^{i} = [2(ab) - S(a^2 + b^2)]/(2 + 2S). \tag{3b}$$

The term ρ^i is called the interference density. This is the quantity which Ruedenberg identifies with electron sharing and which, he contends, shows the essentially quantum mechanical nature of the problem. The interference density describes the *shift* of electronic charge from the atomic regions into the bond. It is positive in the region between the protons where the overlap charge density dominates; but ρ^i has significant negative "tails" in the vicinity of the protons.

The expectation value of the total energy

$$E = \langle\psi|H|\psi\rangle = [\langle a|H|a\rangle + 2\langle a|H|b\rangle + \langle b|H|b\rangle]/(2 + 2S) \tag{4}$$

may be partitioned into "atomic", "quasi-classical" and "interference" contributions, E^a, E^{qc} and E^i, just as ρ was partitioned into ρ^{qc} and ρ^i, i.e.

$$E = E^a + E^{qc} + E^i, \tag{5}$$

where

$$E^a + E^{qc} = [\langle a|H|a\rangle + \langle b|H|b\rangle]/2 \tag{5a}$$

and

$$E^i = [2\langle a|H|b\rangle - S\langle a|H|a\rangle - S\langle b|H|b\rangle]/(2 + 2S). \tag{5b}$$

In comparing Eqs. (5a) and (5b) with (3a) and (3b) it is apparent that the matrix element $\langle a|H|b\rangle$ has been associated with the density fragment ab, and $\langle a|H|a\rangle$ is associated with a^2. Now, as far as the potential energy operator V is concerned, these associations are straightforward because $\langle\psi|V|\psi\rangle$ is the same as $\int V\rho\,d\tau$; and therefore, if ρ is divided into fragments then a corresponding division is possible for the total potential energy integral. However, for the kinetic energy operator $\hat{T}$, the same reasoning does not apply, because $\langle\psi|\hat{T}|\psi\rangle$ is not the same as $\int\hat{T}\rho\,d\tau$. Ruedenberg [5] has given a formal connection in terms of a density matrix. We shall relate here this division of E to the expectation value of a novel intermediate wavefunction.

We wish to calculate the energy ($E^{a} + E^{qc}$) from a wavefunction ψ' which will give the charge distribution ρ^{qc}, i.e.

$$|\psi'|^2 = (a^2 + b^2)/2. \tag{6}$$

One solution to this equation is

$$\psi' = (a + \mathrm{i}b)/\sqrt{2}. \tag{7}$$

It is now easy to see that, in fact,

$$E^{a} + E^{qc} = \langle\psi'|H|\psi'\rangle \tag{8}$$

is in agreement with (5a) and that

$$E^{i} = \langle\psi|H|\psi\rangle - \langle\psi'|H|\psi'\rangle \tag{8a}$$

is in agreement with (5b). The form of ψ' is physically reasonable: one would expect that the linear combination of atomic orbitals with phase difference $\pi/2$ would be a non-bonding state, since the combination ($a + b$) with phase difference zero is a binding state and the combination ($a - b$) with phase difference π is antibinding. This is confirmed by actual calculations which show that ($E^{a} + E^{qc}$) is equal to the energy of a hydrogen atom at a distance R from a bare proton, or two "half atoms" at a distance R apart, with no repulsion between the "half electrons".

Since

$$\langle a|H|a\rangle = \langle b|H|b\rangle, \tag{9}$$

we find

$$E^{a} + E^{qc} = \langle a|H|a\rangle \tag{10}$$

$$= \langle a| - \tfrac{1}{2}\nabla^2 - 1/r_a - 1/r_b + 1/R|a\rangle. \tag{10a}$$

E^{a} and E^{qc} are defined by

$$\mathrm{E}^{a} = \langle a| - \nabla^2/2 - 1/r_a|a\rangle = 0.5\zeta^2 - \zeta \tag{10b}$$

$$= -0.5 + (\zeta - 1)^2/2$$

and

$$E^{qc} = \langle a|1/R - 1/r_b|a\rangle = 1/R - \int(a^2/r_b)\mathrm{d}\tau \tag{10c}$$

At large internuclear distances, where $\zeta = 1$ and $1/R$ cancels the Coulombic integral, and E^{a} has the value -0.500 (all energies are in atomic units). Both E^{a} and E^{qc} increase monotonically as R decreases and the optimum value of ζ increases until, at $R = 2.0a_0$, when $\zeta = 1.2387$, the value of ($E^{a} + E^{qc}$) lies above the energy of the dissociation products by about half of the theoretical binding energy.

Since E^{i} is the difference between $\langle\psi|H|\psi\rangle$ and $\langle\psi'|H|\psi'\rangle$, it can be said to be the driving force, variationally speaking, behind the wavefunction rearrangement $\psi' \rightarrow \psi$, i.e. it is the "cause" of binding. The question is: which part of E^{i}, the kinetic or the potential, makes E^{i} negative? Ruedenberg showed that it is the interference kinetic energy T^{i}, and that the interference potential energy V^{i} is positive and smaller than $|T^{i}|$. This is an important point, because we shall show later there is another way to look at E^{i}. Ruedenberg's analysis of E^{i} is

$$E^{i} = T^{i} + V^{i}, \tag{11}$$

where

$$T^{\mathrm{i}} = [2\langle a|\hat{T}|b\rangle - S\langle a|\hat{T}|a\rangle - S\langle b|\hat{T}|b\rangle]/(2 + 2S), \tag{11a}$$

$$V^{\mathrm{i}} = [2\langle a|V|b\rangle - S\langle a|V|a\rangle - S\langle b|V|b\rangle]/(2 + 2S), \tag{11b}$$

and

$$V = -1/r_{\mathrm{a}} - 1/r_{\mathrm{b}}. \tag{11c}$$

The quantity T^{i} is negative for all internuclear distances, it has a value of -0.180 at $R = 2a_0$ and goes through a minimum near to $R = 1a_0$. The V^{i} term is positive at all internuclear distances, it has a value of 0.054 at $R = 2a_0$ and goes through a maximum near $R = 2a_0$. The sign of T^{i} reflects the fact that the transfer of charge density into the internuclear region has reduced the gradient of the density at all points along the internuclear axis, thereby reducing the bond-parallel component of the kinetic energy. The sign of V^{i} reflects the fact that charge has been moved from a region near to the protons where V is low to a region where V is higher. Both T^{i} and V^{i} are zero for the united atom and for the separated atoms. The magnitudes of both T^{i} and V^{i} are enhanced by orbital contraction (i.e. increasing ζ from 1.0) for all distances below about $R = 4a_0$, and this is in spite of the fact that the overlap integral between the contracted orbitals is smaller. (As Ruedenberg remarked, the idea that large overlap integrals favour binding does not apply to scale variation).

In view of the fact that similar ideas will be used in connection with a potential energy interpretation, we recapitulate the binding process and the role of E^{i} in it. The wavefunction rearrangement can be thought of as a three stage process (eventually four stages, when polarisation of atomic orbitals is also included). This process can be described by the following scheme, where the superscript zero indicates $\zeta = 1$ and normalising constants have been omitted for convenience:

$$a^0 \rightarrow (a^0 + ib^0) \rightarrow (a^0 + b^0) \rightarrow (a + b).$$

The initial state of the system, a^0, describes a normal hydrogen atom in a state of repulsion with a bare proton at a distance R. In the first step a state is formed with the same kinetic and potential energies as the initial state but with a symmetric distribution of charge. Although this step involves no energy change it has an important effect on the interpretation of what follows, because the electron has lost any identification with a particular nucleus. In the second step a bonding state $(a^0 + b^0)$ is formed through the lowering of energy which accompanies the introduction of new terms in charge density, namely ρ^{i}. This step is "driven" by the E^{i} term. The final stage is the scale variation of the atomic orbitals which leads to a lower total energy and to a redistribution between kinetic and potential energy reestablishing the virial relation. Here again it can be argued that it is the interference energy, and T^{i} in particular, which determines variationally whether ζ increases or decreases from 1.

A glance at Eqs. (10) shows that $(E^{\mathrm{a}} + E^{\mathrm{qc}})$ will behave under scale variation very much like $(0.5\,\zeta^2 - \zeta)$, because (i) for a wide range of internuclear distances the effect of ζ variation upon the Coulombic integral, $\int (a^2/r_{\mathrm{b}})\,\mathrm{d}\tau$, is quite small compared with the effect of ζ variation on the monatomic terms, and (ii) E^{a} behaves like the energy of an isolated hydrogen atom on scale variation i.e. it goes up whether ζ decreases or increases from 1. It follows that the total energy E will be reduced by the scale variation which reduces E^{i}; and since $|T^{\mathrm{i}}|$ is the larger and more ζ-sensitive part of E^{i}, it will usually be the determinant of the way ζ changes.

At $R = 2a_0$ orbital contraction reduces E^{i}, while within E^{a} a decrease in the monatomic potential energy from -1 to $-\zeta$ is more than cancelled by a rise in kinetic energy from $1/2$ to $\zeta^2/2$. The optimum value of ζ corresponds to the point of balance between decreasing E^{i} and increasing E^{a}. At this point, the virial relationship

$$2\bar{T} + \bar{V} = 0 \tag{12}$$

is fulfilled. ($\bar{T}$ is the total kinetic energy, and $\bar{V}$ is the total potential energy including $1/R$). Ruedenberg has called the behaviour of kinetic energy near $R = 2a_0$ paradoxical in the sense that an initial lowering of kinetic energy through sharing leads to a state of higher $\bar{T}$ and lower $\bar{V}$ through contraction. It is sometimes said that "the orbitals contract because T^{i} is negative". This is true in the region of the equilibrium internuclear distance, where the virial relation indicates the directions in which $\bar{T}$ and $\bar{V}$ must change. But over the whole range of R it is the way that T^{i} changes with ζ which determines whether the orbitals expand or contract. For $R = 6a_0$, for example, T^{i} is reduced by a slight expansion of the orbitals and optimal ζ is 0.995. As Ruedenberg noted, there is nothing paradoxical about the role of kinetic energy here or indeed for any R greater than $3a_0$, because the total kinetic energy is lower than in the hydrogen atom.

Ruedenberg's theory was criticised by Bader [6] on the grounds that the "reference" atomic orbitals change during the contraction step from being true hydrogen ground states to promoted states a and b in which the virial relationship (for the atom) is violated. Prior to contraction it was the molecular wavefunction $(a^0 + b^0)$ which did not conform to the virial relation. Thus negative contributions to the kinetic energy appear to be important for binding either when the molecular wavefunction gives an inappropriately low molecular kinetic energy, or when the "reference" atomic state gives an inappropriately high atomic kinetic energy. This criticism is not persuasive.

There are two criticisms involved here. The first is an objection to the use of virtual molecular states in which the distribution between kinetic and potential energy violates the virial relation. This would seem to be an excessive restriction to place on a method of understanding binding through the variation principle, a principle which actually explains the virial relation. The second point concerns the way in which the various contributions to the total energy are grouped together for cancellation. Bader seems to dislike the combination of the monatomic terms into a promoted atom energy because this is positive (relative to the normal atom energy) and may serve to exaggerate the significance of the negative contributions to the total binding energy. Yet the promotion energy can be expressed as the difference between two expectation values, and its magnitude is small compared with magnitudes of the kinetic and potential energies which comprise it.

The general question as to which terms may validly be cancelled or combined is important because there is more than one way in which combinations can be made. It is fairly clear that one should not combine energy terms derived from ρ^{qc} with terms from ρ^{i}, because then the resulting term will not be identifiable with an expectation value or a difference in expectation values, according to a recipe such as Eq. (8) or Eq. (8a). Also, the terms derived from ρ^{qc}, the promoted atom energy and the quasi-classical electrostatic energy, have distinct physical meanings and should be kept apart. However, we shall see that for the terms derived from ρ^{i} there is an interesting combination which is different from Ruedenberg's.

Bader's other main criticism [7] was that orbital contraction (through increase in ζ) in hydrogen is exceptionally large. In molecules where the atomic orbital exponents have not changed very much from free atom values, the increase in kinetic energy required by the virial theorem must be achieved by promotion of electrons from one atomic orbital to another. It may be that in cases like these something like the usual potential energy theory may be more appropriate. It is interesting to note that the most detailed examination of Ruedenberg's theory on larger molecules, by Goddard et al. [15], concentrated on simple hydrides.

Ruedenberg's advocacy of the variational principle as a method of understanding binding was very important and our approach will be strongly influenced by it. Nevertheless, the deficiencies of a variational wavefunction of given general form are not the same for all types of molecules; and therefore the processes which are imagined to correct those deficiencies may not be equally valid for types of molecule. It may be that Ruedenberg's theory and the dual role of kinetic energy is a particularly suitable explanation of binding when hydrogen is involved.

3 The connection between Ruedenberg's theory and the conventional (Potential Energy) approach

Ruedenberg's theory focuses on the difference between the molecular and the sum of atomic charge densities, and leads to an expression for the binding energy involving several terms each of which is an expectation value or is a difference between two expectation values. In this way deformations of the wavefunction may be interpreted variationally. The potential energy (PE) treatment of H_2^+ which antedates Ruedenberg's analysis, by contrast, focuses on the difference between the molecular and atomic Hamiltonians. The "extra" terms in the molecular Hamiltonian are potential energy operators and these terms seem to suggest sharing of electrons between atomic sub-systems; but they do not necessarily guarantee binding. Moreover, for the "simple" LCAO wavefunction (i.e. when $a = a^0, b = b^0$) the PE approach leads to an expression for the binding energy which does not appear to be a difference between two expectation values. We shall therefore try to derive the usual PE expression within the context of Ruedenberg's theory, and thereby bring it in line with variational reasoning.

The essential element of our analysis is a decomposition of the interference density into two unambiguously defined parts, ρ_A^i and ρ_B^i, as follows:

$$\rho^i = \rho_A^i + \rho_B^i, \tag{13}$$

where

$$\rho_A^i = (ab - Sa^2)/(2 + 2S) \tag{13a}$$

and

$$\rho_B^i = (ab - Sb^2)/(2 + 2S) \tag{13b}$$

The two fragments, ρ_A^i and ρ_B^i, can be thought of as pieces of charge density which were associated, in the non-bonding state, with the "half" atoms A and B respectively, and which have moved into the internuclear region as a result of orbital interference. These two fragments are not, of course, geometrically separate; they are interpenetrating.

It is now possible to recognise two different contributions to V^i: a large positive part, V_{away}^i, which is the sum of interactions between each fragment and its "parental" proton; and a negative part, V_{toward}^i, which is the sum of the interactions between each fragment and its "opposite" proton:

$$V^{\mathrm{i}}_{\mathrm{away}} = -\int(\rho^{\mathrm{i}}_{\mathrm{A}}/r_{\mathrm{a}})\,\mathrm{d}\tau - \int(\rho^{\mathrm{i}}_{\mathrm{B}}/r_{\mathrm{b}})\,\mathrm{d}\tau\,, \tag{14}$$

$$V^{\mathrm{i}}_{\mathrm{toward}} = -\int(\rho^{\mathrm{i}}_{\mathrm{A}}/r_{\mathrm{b}})\,\mathrm{d}\tau - \int(\rho^{\mathrm{i}}_{\mathrm{B}}/r_{\mathrm{a}})\,\mathrm{d}\tau\,, \tag{15}$$

The total interference potential energy, as given by Eqs. (11b) and (11c), may now be expressed as

$$V^{\mathrm{i}} = -\int\rho^{\mathrm{i}}(r_{\mathrm{a}}^{-1} + r_{\mathrm{b}}^{-1})\,\mathrm{d}\tau = V^{\mathrm{i}}_{\mathrm{away}} + V^{\mathrm{i}}_{\mathrm{toward}}\,. \tag{16}$$

It is noteworthy that although $V^{\mathrm{i}}_{\mathrm{away}}$ and $V^{\mathrm{i}}_{\mathrm{toward}}$ are identifiable parts of the potential energy, neither corresponds to a difference in expectation values, unlike V^{i}. Because the molecule is homonuclear, both $V^{\mathrm{i}}_{\mathrm{away}}$ and $V^{\mathrm{i}}_{\mathrm{toward}}$ can be expressed as twice the contribution from $\rho^{\mathrm{i}}_{\mathrm{A}}$ only, so that

$$V^{\mathrm{i}}_{\mathrm{away}} = \langle a| - 1/r_{\mathrm{a}}|b - Sa\rangle/(1+S)\,, \tag{17}$$

$$V^{\mathrm{i}}_{\mathrm{toward}} = \langle a| - 1/r_{\mathrm{b}}|b - Sa\rangle/(1+S)\,. \tag{18}$$

Again, because the molecule is homonuclear, it is evident from Eq. (11a) that T^{i} may be formulated as

$$T^{\mathrm{i}} = \langle a| - \nabla^2/2|b - Sa\rangle/(1+S)\,. \tag{19}$$

Returning now to Ruedenberg's expression for the total energy (5), and reexpressing E^{i} with the help of Eqs. (11), (16) and (19), we find

$$E = E^{\mathrm{a}} + E^{\mathrm{qc}} + T^{\mathrm{i}} + V^{\mathrm{i}}_{\mathrm{away}} + V^{\mathrm{i}}_{\mathrm{toward}}\,. \tag{20}$$

Consider first the simple theory with $\zeta = 1$, $a = a^0$ and $b = b^0$. A remarkable cancellation occurs between T^{i} and $V^{\mathrm{i}}_{\mathrm{away}}$. From Eqs. (17) and (19) one obtains

$$T^{\mathrm{i}} + V^{\mathrm{i}}_{\mathrm{away}} = \langle a^0|\,\nabla^2/2 - 1/r_{\mathrm{a}}|b^0 - Sa^0\rangle/(1+S)\,. \tag{21}$$

But a^0 is an eigenfunction of the free atom Hamiltonian:

$$(-\nabla^2/2 - 1/r_{\mathrm{a}})a^0 = -0.5a^0\,, \tag{22}$$

so that

$$T^{\mathrm{i}} + V^{\mathrm{i}}_{\mathrm{away}} = -0.5\langle a^0|b^0 - Sa^0\rangle/(1+S) = 0 \tag{23}$$

Since, furthermore, E^{a} is -0.5 when ζ is 1, the total energy expression (20) becomes

$$E = -0.5 + E^{\mathrm{qc}} + V^{\mathrm{i}}_{\mathrm{toward}}\,. \tag{24}$$

By substituting for E^{qc} from Eq. (10c) and for $V^{\mathrm{i}}_{\mathrm{toward}}$ from Eq. (18), it is easy to see that Eq. (24) is the same as the expression for the binding energy as presented in countless textbooks, i.e.

$$-(\text{binding energy}) = E + 0.5 = \langle a^0|1/R - 1/r_{\mathrm{b}}|a^0 + b^0\rangle/(1+S)\,. \tag{24a}$$

The derivation of Eq. (24) through the cancellation of T^{i} with $V^{\mathrm{i}}_{\mathrm{away}}$ suggests a choice of ways in which to visualise the role of the interference density. Either one can regard the transfer of charges $\rho^{\mathrm{i}}_{\mathrm{A}}$ and $\rho^{\mathrm{i}}_{\mathrm{B}}$ into the bond as producing an increase in the total potential energy which is exceeded by the decrease in kinetic energy; or one can say that the transfer of these charges produces an increase in potential energy with respect to "dative" protons which exactly compensates for the decrease in kinetic energy, so that the net result is a decrease in the potential energy resulting from the approach of the charges towards the "opposite" protons. The latter point of view is neat, in that $V^{\mathrm{i}}_{\mathrm{toward}}$ is then approximately the binding energy itself at $R = 2a_0$ (E^{qc} being small for spherical orbitals). On the other hand, $V^{\mathrm{i}}_{\mathrm{toward}}$ does not have the form of an expectation value difference and, moreover, is only equal to an expectation value difference when the cancellation between $V^{\mathrm{i}}_{\mathrm{away}}$ and T^{i} is exact.

It is interesting to see why the usual textbook derivation of Eq. (24a) does not uncover the fact that the transfer of charge away from each proton produces a decrease in kinetic energy and a compensating increase in potential energy. The expectation value of the total energy is given by

$$E = \langle a + b|H|a + b\rangle/(2 + 2S). \tag{25}$$

At some point in the usual derivation advantage is taken of the symmetry of the wavefunction and of H and this implicitly reformulates the expectation value [Eq. (25)] as

$$E = \langle a|H|a + b\rangle/(1 + S) \tag{26}$$

$$= \langle a| - \nabla^2/2 - 1/r_{\mathrm{a}} - 1/r_{\mathrm{b}} + 1/R|a + b\rangle/(1 + S) \tag{26a}$$

$$\begin{aligned} &= \langle a| - \nabla^2/2 - 1/r_{\mathrm{a}}|a + b\rangle/(1 + S) \\ &\quad + \langle a|1/R - 1/r_{\mathrm{b}}|a + b\rangle/(1 + S). \end{aligned} \tag{26b}$$

The substitutions $a = a^0$ and $b = b^0$, together with the eigenvalue equation (18), then yield

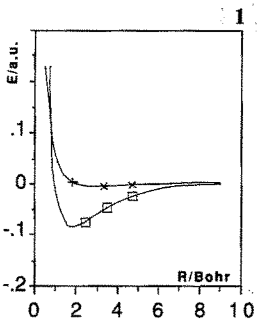
$$E = -0.5\langle a^0|a^0 + b^0\rangle/(1 + S) + \langle a^0|1/R - 1/r_{\mathrm{b}}|a^0 + b^0\rangle/(1 + S), \tag{27}$$

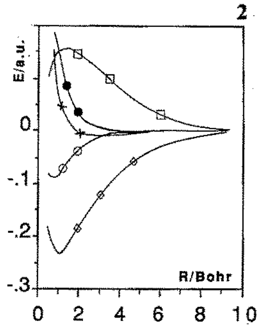
which is clearly the same as the familiar result (24a). The first term in Eq. (26b) is actually the same as $(E^{\mathrm{a}} + T^{\mathrm{i}} + V^{\mathrm{i}}_{\mathrm{away}})$ and it also contains the expectation value of the kinetic energy; but its contributions to the binding energy are concealed by the use of the free atom eigenvalue equation. The contribution of the kinetic energy is even harder to see when Eq. (26) is derived from the molecular eigenvalue equation, rather than from the expectation value (25). This derivation, which would be valid only if $(a + b)$ were the exact wavefunction, has been given in general form by Richardson and Pack [16] and leads to a formula for energy differences which might be called the 'Integral Hellmann–Feynman theorem with an atom-in-molecule reference state'.

All the derivations of Eqs. (24) and (24a) are quite sound at $R = 5a_0$, where $\zeta = 1.00$ is optimal and the simple MO wavefunction is the same as the FH wavefunction and quite close to the exact wavefunction. At shorter internuclear distances the simple MO wavefunction gives the wrong distribution between total kinetic and potential energies, due to lack of orbital scaling. Can one therefore expect that Eq. (24) and the picture of binding suggested by its derivation will retain some validity at internuclear distances where $\zeta > 1$ and where the atomic orbitals are not eigenfunctions of free atom Hamiltonians? The answer, surprisingly, is yes; because if one returns to (20) and recalculates all the integrals from appropriately scaled atomic orbitals then $(E^{\mathrm{a}} + T^{\mathrm{i}} + V^{\mathrm{i}}_{\mathrm{away}})$ is still found to remain constant and remarkably close to -0.500 for all R from $1.5a_0$ to ∞, as shown in Fig. 1. In this range of R the deviations from -0.500 are negative, but amount to little more than 10% of the theoretical binding energy for any given R. For distances less than $1.5a_0$ the value of $(E^{\mathrm{a}} + T^{\mathrm{i}} + V^{\mathrm{i}}_{\mathrm{away}})$ rises steeply.

At $R = 2a_0$ one finds

$$E^{\mathrm{a}} + T^{\mathrm{i}} + V^{\mathrm{i}}_{\mathrm{away}} = -0.506 \tag{28a}$$





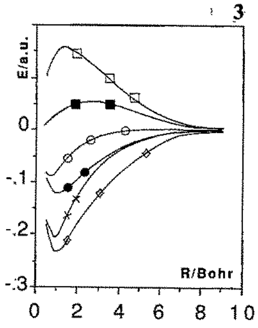


Fig. 1. $(E^{\mathrm{qc}} + V^{\mathrm{i}}_{\mathrm{toward}})$ and $(E^{\mathrm{a}} + T^{\mathrm{i}} + V^{\mathrm{i}}_{\mathrm{away}} + 0.5)$ for FH wavefunction: □ $E^{\mathrm{qc}} + V^{\mathrm{i}}_{\mathrm{toward}}$; × $E^{\mathrm{a}} + T^{\mathrm{i}} + V^{\mathrm{i}}_{\mathrm{away}} + 0.5$

Fig. 2. Analysis of $(E^{\mathrm{a}} + T^{\mathrm{i}} + V^{\mathrm{i}}_{\mathrm{away}} + 0.5)$ for FH wavefunction: × $E^{\mathrm{a}} + T^{\mathrm{i}} + V^{\mathrm{i}}_{\mathrm{away}} + 0.5$; ● $E^{\mathrm{a}} + 0.5$; ○ $T^{\mathrm{i}} + V^{\mathrm{i}}_{\mathrm{away}}$; ◇ T^{i}; □ $V^{\mathrm{i}}_{\mathrm{away}}$

Fig. 3. Analysis of the interference energy for FH wavefunction: × E^{i}; ■ V^{i}; □ $V^{\mathrm{i}}_{\mathrm{away}}$; ● $V^{\mathrm{i}}_{\mathrm{toward}}$; ◇ T^{i}; ○ $T^{\mathrm{i}} + V^{\mathrm{i}}_{\mathrm{away}}$

and

$$E^{\mathrm{qc}} + V^{\mathrm{i}}_{\mathrm{toward}} = -0.081. \tag{28b}$$

Thus, *the binding energy* $[(0.5 + E^{\mathrm{a}} + T^{\mathrm{i}} + V^{\mathrm{i}}_{\mathrm{away}}) + (E^{\mathrm{qc}} + V^{\mathrm{i}}_{\mathrm{toward}})]$ *is dominated by the potential energy expression* $(E^{\mathrm{qc}} + V^{\mathrm{i}}_{\mathrm{toward}})$ *whether the orbitals are scaled or not.* The improvement in the theoretical binding energy which results from scaling can thus be principally associated with the decrease in $(E^{\mathrm{qc}} + V^{\mathrm{i}}_{\mathrm{toward}})$ from -0.0537 (for $\zeta = 1$) to -0.0806 (for the optimal value $\zeta =$ of 1.2387). The value of $(0.5 + E^{\mathrm{a}} + T^{\mathrm{i}} + V^{\mathrm{i}}_{\mathrm{away}})$ decreases from 0 to -0.006 which represents only 7% of the theoretical binding energy of -0.087.

Why does scaling have such a small effect on $(E^{\mathrm{a}} + T^{\mathrm{i}} + V^{\mathrm{i}}_{\mathrm{away}})$? Explicit evaluation shows that, *for the FH wavefunction*, one has the formal mathematical identity $T^{\mathrm{i}} = -\zeta V^{\mathrm{i}}_{\mathrm{away}}$, so that

$$T^{\mathrm{i}} + V^{\mathrm{i}}_{\mathrm{away}} = -V^{\mathrm{i}}_{\mathrm{away}} \quad (\zeta - 1), \tag{28c}$$

with $V^{\mathrm{i}}_{\mathrm{away}} > 0$. Thus, even when $\zeta > 1$, the residual term $(T^{\mathrm{i}} + V^{\mathrm{i}}_{\mathrm{away}})$ is small. In addition, it is largely cancelled by the increase in E^{a}, i.e. by the promotion energy resulting from scaling. The decomposition of $(E^{\mathrm{a}} + T^{\mathrm{i}} + V^{\mathrm{i}}_{\mathrm{away}} + 0.5)$ in terms of its contributions is displayed in Fig. 2 as a function of the internuclear distance.

The approximate cancellation of T^{i} with $V^{\mathrm{i}}_{\mathrm{away}}$ for appropriately scaled wavefunctions means that the picture of binding suggested by the simplest MO wavefunction can be qualitatively retained for the FH wavefunction. Once again one can take the view that the negative, bond forming part of E^{i} is $V^{\mathrm{i}}_{\mathrm{toward}}$, as an alternative to Ruedenberg's view that it is T^{i}. The PE viewpoint focuses on the negative contribution to E^{i} arising because $\langle a|1/r_{\mathrm{b}}|b\rangle$ is greater than $S\langle a|1/r_{\mathrm{b}}|a\rangle$, whereas the kinetic energy viewpoint focuses on the negative contribution to E^{i} arising because $\langle a| -\nabla^2/2|b\rangle$ is smaller than $S\langle a| -\nabla^2/2|a\rangle$. As with the simple MO wavefunction, $V^{\mathrm{i}}_{\mathrm{toward}}$ is approximately equal to the binding energy at $R = 2a_0$; whereas T^{i} has a magnitude of about twice the theoretical binding energy at that distance (see Fig. 3). At internuclear distances less than $R = 2a_0$, the quantity $(T^i + V^i_{away})$ is not small: it drops steeply and goes through a minimum at about $R = 0.8a_0$ as shown in Fig. 3.

Can the PE viewpoint be related to a variational interpretation of orbital scaling in H_2^+? Referring to Eq. (20), one finds that, at most internuclear distances, scaling changes $(E^{qc} + V^i_{toward})$ in the same direction as the total energy. For R greater than $5a_0$ a slight expansion of the orbitals lowers $(E^{qc} + V^i_{toward})$ and raises $(E^a + T^i + V^i_{away})$. When R is less than $2.5a_0$, a contraction in the orbitals lowers both V^i_{toward} and E^{qc}, and produces a rise in E^a which, for $\zeta > 1.1$, overcomes the drop in $(T^i + V^i_{away})$. There is however a considerable range, namely $5a_0 > R > 3a_0$, where V^i_{toward} is raised by orbital contraction and where the small decrease in E^{qc} is insufficient to make $(E^{qc} + V^i_{toward})$ lower overall. In this region the optimal value of ζ is established largely by competition between the rise in E^a and the drop in $(T^i + V^i_{away})$. Over the whole range of R the more elegant explanation of scaling is Ruedenberg's viewpoint, emphasising the role of T^i.

4 The inclusion of polarisation

The case for the usefulness of the PE point of view is somewhat strengthened when the analyses of section 2 are applied to the wavefunction originally proposed [17] by Guillemin and Zener (GZ). This function can be regarded as being as close to an exact solution of the Schroedinger equation as our purposes require. The GZ wavefunction has the same form as Eq. (1)

$$\psi = (\alpha + \beta)/(2 + 2S)^{1/2}, \tag{29}$$

with

$$S = \langle \alpha | \beta \rangle \tag{29a}$$

but now the atomic wavefunctions are given by

$$\alpha = \gamma \exp[-(\zeta_1 r_a - \zeta_2 r_b)], \qquad \beta = \gamma \exp[-(\zeta_2 r_a - \zeta_1 r_b)], \tag{29}$$

where γ is a normalisation constant. These wavefunctions behave like 1 s orbitals polarised towards each other. The wavefunction ψ reduces to the FH form when $\zeta_2 = 0$. Increasing ζ_2/ζ_1 results in increasing polarisation which transfers charge from outside the protons into the internuclear region. Once again Kim et al. [14] have provided optimum value of ζ_1 and ζ_2 for a range of R. All the quantities computed for the FH wavefunction (T^i, V^i_{away}, V^i_{toward}, E^{qc}) were recomputed for the GZ case by simply replacing a by α and b by β in the appropriate equations. The total binding energy is $(0.5 + E^\alpha + E^{qc} + E^i)$ where E^α is defined by

$$E^\alpha = \langle \alpha | -1/2\nabla^2 - 1/r_a | \alpha \rangle. \tag{30}$$

First we look at the quantity $(E^{qc} + V^i_{toward})$ which was approximately the same as the theoretical binding energy for the FH wavefunction. It is now equal to about 150% of the binding energy at $R = 2a_0$ for the GZ wavefunction. At each R the value of $(E^{qc} + V^i_{toward})$ lies below the corresponding FH value by a factor of between 2 and 3. The rest of the total energy, $(E^\alpha + T^i + V^i_{away})$, now increases monotonically with decreasing R. This is shown in Fig. 4.

The behaviour of $(E^\alpha + T^i + V^i_{away})$ for the GZ wavefunction is analysed in Fig. 5. It appears that polarisation has increased V^i_{away} and decreased $|T^i|$, so that $V^i_{away} > |T^i|$ for all $R \geqslant 1.4a_0$, but never by more than 0.015. The cancellation

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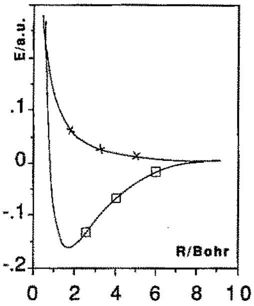

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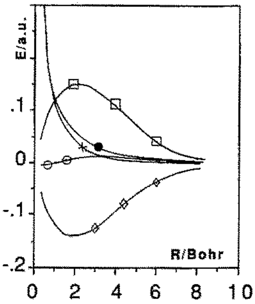

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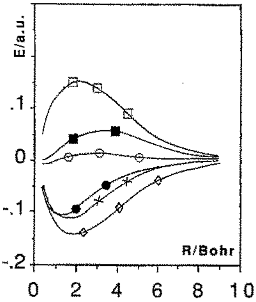

Fig. 4. $(E^{qc} + V^{i}_{\text{toward}})$ and $(E^{\alpha} + T^{i} + V^{i}_{\text{away}} + 0.5)$ for GZ wavefunction: □ $E^{qc} + V^{i}_{\text{toward}}$; × $E^{\alpha} + T^{i} + V^{i}_{\text{away}} + 0.5$

Fig. 5. Analysis of $(E^{\alpha} + T^{i} + V^{i}_{\text{away}} + 0.5)$ for GZ wavefunction: × $E^{\alpha} + T^{i} + V^{i}_{\text{away}} + 0.5$; ● $E^{\alpha} + 0.5$; ○ $T^{i} + V^{i}_{\text{away}}$; ◇ T^{i}; □ V^{i}_{away}

Fig. 6. Analysis of the interference energy for GZ wavefunction: × E^{i}; ■ V^{i}; □ V^{i}_{away}; ● V^{i}_{toward}; ◇ T^{i}; ○ $T^{i} + V^{i}_{\text{away}}$

between T^{i} and V^{i}_{away} is generally much better than it was for the FH wavefunction. Near to $R = 2a_0$ the value of $(E^{\alpha} + T^{i} + V^{i}_{\text{away}})$ is -0.448 which is quite close to E^{α} (-0.459); while $(E^{qc} + V^{i}_{\text{toward}})$ is -0.154. There is an echo here of one of quantum chemistry's old ideas – that energy $(E^{\alpha} + 0.5)$ "traded away" in forming a promoted state is "recovered with profit" in forming a covalent bond.

The analysis of the interference energy in Fig. 6 shows how accurately E^{i} may be equated to V^{i}_{toward}. Indeed, V^{i}_{toward} appears to be a robust quantity which mimics the binding energy itself while the wavefunction is improved from the FH wavefunction (Fig. 3), to the GZ wavefunction (Fig. 6). The value of V^{i}_{toward} at $R = 2a_0$ is very close to the theoretical binding energy for each wavefunction while the minimum value of V^{i}_{toward} occurs at $R = 2a_0$ for the simple MO, at $R \sim 1.1a_0$ for the FH wavefunction and at $R = 1.4a_0$ for the GZ wavefunction. The residual quantity $(T^{i}_{\text{away}} + V^{i}_{\text{away}})$ varies more wildly from zero (simple MO) to -0.035 (FH) to 0.011 (GZ).

When one looks at the polarisation step

$$a + b \rightarrow \alpha + \beta .$$

from a variational point of view, it is found (at $R = 2$) that decrease in energy takes place in the E^{qc} term, from 0.012 for the FH function to -0.051 for GZ. This arises from the change in the Coulombic integral,

$$\int (a^2/r_b)\,d\tau \rightarrow \int (\alpha^2/r_b)\,d\tau .$$

In the same step, the interference energy E^{i} actually increased from -0.127 to -0.093. There is a change in the promotion energy meanwhile from 0.029 to 0.041. These results are understandable on physical grounds. Polarisation transfers charge from outside the nuclei into the bond. This increases the magnitude of the Coulombic integral; but it also 'compensates' the nuclear regions for charge lost in electron sharing, thereby making T^{i} and E^{i} less negative. The fact that E^{qc} and E^{i} change in opposite directions during the polarisation step is a further reason for keeping E^{qc} and terms derived from E^{i} apart in our variational thinking; although V^{i}_{toward} does change in the same direction as E^{qc} in the polarisation step. At $R = 2a_0$ one finds that V^{i}_{toward} changes from -0.085 (FH wavefunction) to -0.104 (GZ wavefunction). The "traditional" potential energy expression, let it be said again, is a combination of E^{qc} and V^{i}_{toward}.

If contraction and polarisation are combined into a single step, i.e.

$$a^0 + b^0 \rightarrow \alpha + \beta,$$

the change in E^{qc} (from 0.027 in the simple MO to -0.051 in GZ) is still greater than the corresponding change in E^{i} (from -0.081 to -0.093). However, it should be noted that the magnitude of E^{i}, i.e. the contribution to the binding energy from electron sharing, is greater than the quasi-classical electrostatic term for all the wavefunctions considered.

5 Concluding remarks

Our calculations have explained what seemed to be a puzzle in the "simple" LCAO theory of H_2^+: that the total potential energy is higher than the value found in the free atom, but the binding energy can be expressed entirely in terms of potential energy integrals. The explanation lies in a cancellation between T^{i} and V^{i}_{away} which leaves the theoretical binding energy being represented approximately by (minus) V^{i}_{toward}. This result remains approximately valid even when the wavefunction is properly scaled, and when it is polarised. At the same time, by placing this traditional potential energy expression within the context of Ruedenberg's theory we have placed the traditional picture in the context of variational reasoning.

Has this work in any way modified the role to be given to kinetic energy in binding? Clearly both kinetic and potential energy must be considered in order to understand binding, and a convenient cancellation of terms in the total energy does not eliminate the physical roles of those terms, at the very least because cancellations are not unique. For example at great internuclear separation, the cancellation within E^{i} is nearly exact and the binding energy is accurately given by V^{i}_{toward}. Nonetheless, it is the reduction in kinetic energy which makes the total energy lower than in the isolated atom at these distances. However, near the equilibrium distance, the kinetic energy plays a dual role and, in circumstances where the cancellation between T^{i} and V^{i}_{away} is close to being exact, it may be conceptually simpler to explain the deformation of the wavefunction under the variation principle without T^{i}. These circumstances do not obtain with the FH wavefunction, but may be found for the GZ wavefunction. We do not know which of these two situations is the more typical of covalent binding in other molecules.

Covalent binding arises from the delocalisation of charge due to electron sharing; and delocalisation is essentially a quantum mechanical phenomenon. The problem has always been to explain why the charge distribution in a molecule takes the form it does, using reasoning which is consistent with quantum mechanics. The holistic nature of quantum mechanics is more evident for the kinetic energy than it is for the potential energy: but for that very reason it is also appealing to emphasise the role of potential energy if the charge density is to be analysed into parts. The construct V^{i}_{toward} could prove of considerable value for a qualitative understanding of charge distributions in molecules, if certain other contributions to the variational total energy can be justifiably assumed to cancel out. This use of V^{i}_{toward} would be on a quite different basis from the use of the Integral Hellmann

Feynman theorem, a method which formally excludes kinetic energy but which cannot explain the charge distribution in as much as it is not a variational approach.

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