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Formation of the chemical bond and orbital contraction

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Various criteria for orbital contraction, most of them independent of the variational principle and based rather on formal properties of the exact wave function, all indicate that the formation of the chemical bond in $H_2{}^+$ or H_2 is accompanied by orbital contraction. Partially basing his argument on previous work by Pettifor, Heine recently criticized Ruedenberg's analysis of the chemical bond, especially the concept of orbital contraction. We show this to be due to interpretative problems of the linear-combination-of-atomic-orbital (LCAO) concept. The consequences for LCAO band-structure calculations are discussed.

I. INTRODUCTION

A recent review by Heine[1] contains a chapter, "LCAO: From Under a Cloud to Out in the Sun," which sounds rather unfriendly towards quantum chemistry in general and to the famous Ruedenberg analysis of the chemical bond[2] in particular. Heine claims that "the contraction of the wave function . . . (upon formation of the covalent bond in $H_2{}^+$ or H_2) . . . is known to be spurious," referring to an older paper by Pettifor[3] where it was stated that "the bonding eigenfunction (of $H_2{}^+$) does *not* display the contractive behavior predicted by the variational LCAO wave function."

There is a difference between Pettifor[3] and Heine[1] inasmuch as Pettifor is critical only concerning the use of the concept of orbital contraction outside the linear-combination-of-atomic-orbital (LCAO) context, whereas Heine criticizes this concept even within the LCAO scheme (using, however, arguments from the non-LCAO work of Pettifor). We shall demonstrate that independently of the LCAO scheme and of the particular criterion chosen, there exists a contraction of the electronic charge associated with the formation of the chemical bond in $H_2{}^+$ or H_2, and that Heine's criticism is due to some misinterpretation of the LCAO scheme.

II. ORBITAL CONTRACTION AND DEFORMATION

In the simple LCAO approximation one describes a molecular orbital (MO) as a linear combination of atomic orbitals (AO's). For the $1\sigma_g$ and $1\sigma_u$ state of $H_2{}^+$ we may write

$$\psi(r)=N[\varphi_A(r)\pm\varphi_B(r)] , \quad (1)$$

where φ_A and φ_B are hydrogenlike orbitals,

$$\varphi_i(r)=N'\exp(-\alpha\,|\,R_i-r\,|\,),\quad i=A,B \quad (2)$$

and R_A and R_B are the positions of the nuclei A and B. In Secs. II to VIII we only consider the $1\sigma_g$ state.

This simple LCAO ansatz cannot be exact. It is, however, possible to write the exact wave function of $H_2{}^+$ as (1) in terms of two functions φ_A and φ_B [not of the form (2)], which are invariant with respect to symmetry operations that leave the nuclei invariant and which are exchanged by symmetry operations that exchange the nuclei. There is, in fact, not a single "primitive function" φ_A that "generates" the exact $\psi(r)$ according to (1) but rather an equivalence class of φ_A.[4] One can improve the φ_A in (1) from that given by (2) towards an "exact" primitive function, and in this way be guided by some criteria that the exact ψ should satisfy, the most common criterion—but not the only possible one—being the variation principle. The modifications of the φ_i given by (2) towards an exact primitive function are mainly of two types:

(1) *Contraction or expansion.* This can be achieved by changing the orbital exponent α in (2) from 1 to $\alpha>1$, or to $\alpha<1$, respectively. Alternatively and more generally, one can admix other basis functions with local angular momentum $l=0$ and different α's and/or different principal quan-

tum number.[5]

(2) *Angular deformation, polarization.* To take care of this, one has to admix basis functions with local angular momentum $l \neq 0$, mainly p-AO's.[6]

Table I shows the effect of the simplest types of contraction, of angular deformation, and of the two together on the energy of H_2^+ at $R = 2a_0$ (which is close to the equilibrium distance) with the deformation parameters determined by the variation principle.[7–9] Contraction (by changing α) is obviously more effective (with an energy lowering of 0.033 a.u.) than angular deformation (by adding a p-type AO)—energy lowering 0.012 a.u.—while the joint effect is nearly additive. Further angular deformation by addition of a d-type AO improves the energy by another 0.002 a.u., while the remaining difference of 0.0006 a.u. to the exact energy is recovered[9] if one accounts for more sophisticated radial deformation (inclusion of $2s$ and $3p$) as well as for angular deformation by adding AO's with $l = 3$ and $l = 4$. A unique decomposition of the energy according to l values is not possible in view of the basis overcompleteness problem (see also Refs. 6 and 9).

The LCAO approximation, especially with the inclusion of radial and angular deformation, is a very powerful tool in general. Therefore the definition of atomic-orbital contraction as given above is a useful one.

Heine[1] claims that the contraction, which is so effective for the energy, is an artifact of the variational approach, and that it is more physical to choose $\alpha = 1$ in Eqs. (1) and (2). However, we shall show that several other criteria, most of them independent of the variation principle, lead to an optimum $\alpha > 1$, and confirm that the formation of the chemical bond in H_2^+ is associated with orbital contraction.

TABLE I. Energies E (in hartree) and scaling factors α for LCAO wave functions of H_2^+ ($1\sigma_g$ state).

AO's	$-E(\alpha=1)$	$-E(\alpha=\alpha_{\text{opt}})$	α_{opt}	Remarks
$1s$	0.553 77	0.586 51	1.239	a,c
$1s,2p$	0.565 91	0.599 80	1.255	b,c,d
$1s,2p,3d$		0.602 02	1.246	e
Exact		0.602 62		f

[a] Reference 7.

[b] Reference 8.

[c] These values have been recalculated by us; they somewhat differ from those in the original references.

[d] Independent optimization (Ref. 9) of α for the $1s$ and $2p$-AO leads to $\alpha(1s) = 1.246$, $\alpha(2p) = 1.482$, and $-E = 0.600\,36$.

[e] Reference 9; the indicated value corresponds actually to independent optimization of the three α's, i.e., to $\alpha(1s) = 1.246$, $\alpha(2p) = 1.133$, and $\alpha(3d) = 1.319$; the energy with a single α should only be slightly higher.

[f] Reference 10.

If one has at one's disposition a wave function that is *not* obtained by the LCAO approach, e.g., that constructed by Pettifor[3] via a multiple-scattering technique or the virtually exact one[10] based on the separation of the Schrödinger equation in elliptic coordinates, then it is much easier to study the local properties of the *entire* MO rather than to analyze it in terms of its AO components.[4] However, one must then be very careful in drawing conclusions concerning the LCAO approach from such a local analysis. The main reason for this difficulty is that AO's overlap and that the MO near nucleus A is not only determined by the AO φ_A, but also by a contribution of φ_B which extends into the region of nucleus A. The erroneous conclusions of Heine and Pettifor are due to a confusion of local properties of the MO near the nuclei with properties of the AO's.

III. LONG-RANGE BEHAVIOR OF THE WAVE FUNCTION

Alrichs *et al.*[11] have shown that the exact electron density of the ground state of a molecule decays according to[12]

$$\sqrt{\rho(r)} \rightarrow c\,(1+r)^{(Q+1)/\sqrt{2\epsilon}-1} e^{-\sqrt{2\epsilon}r} , \tag{3}$$

where Q is the charge of the system, and ϵ the first ionization potential (IP). The exact IP's of H and H_2^+ (vertical at $R = 2a_0$) are 0.5 a.u. and 1.102 62 a.u., respectively, corresponding to the following asymptotic behavior of the wave function:

$$\begin{aligned} &\psi_H \sim \exp(-1.0r) , \\ &\psi_{H_2^+} \sim (1+r)^{0.347} \exp(-1.485r) , \end{aligned} \tag{4}$$

independent of the angle. Note that the virtually exact wave functions of Ref. 10 do satisfy (4).

As far as the long-range behavior of the wave function of H_2^+ is concerned, there is obviously a *contraction* as compared to the H atom. An LCAO function of type (1) and (2) simulates the asymptotic behavior of the exact wave function best if one chooses

$$\alpha = 1.485 . \tag{5}$$

IV. SHORT-RANGE BEHAVIOR OF THE WAVE FUNCTION

A. Density at the nucleus

In Table II the electron density at the nucleus for the H atom and for various descriptions of $H_2{}^+$ are collected. The classical superposition of two half H-atom densities raises the density already somewhat (since the wave function at the other nucleus also contributes). The interference terms in the LCAO wave function lower this density and one has to *contract the AO's* to arrive at the exact $H_2{}^+$ density. In order to reproduce the exact density with a simple LCAO function of Eqs. (1) and (2) one must choose

$$\alpha = 1.1795 \ . \tag{6}$$

B. Cusp condition

Equation (3) is an exact relation for the wave function at large distances. There exist still other properties of the exact wave function which can be derived in a precise formal manner. One of them is the cusp condition,[13] well known in quantum chemistry. Kato[13] has shown that the spherically averaged logarithmic derivative of the wave function at the position of a nucleus is given by its nuclear charge:

$$\overline{(\partial\psi/\partial r)}_{\vec{r}=\vec{R}_A} = -Z_A \psi(R_A) \ . \tag{7}$$

Trivially, the spherically symmetric component of a one-center expansion of a molecular orbital around either hydrogen atom therefore behaves as

$$\psi_0(\text{const})\exp(-1.0r)[1+O(r^2)] \tag{8}$$

TABLE II. Density at the nucleus in $e/(a_0)^3$ for $H_2{}^+$ at $R=2a_0$.

	$1\sigma_g$	$1\sigma_u$
Half a free H atom	0.1592	0.1592
Superimposed atoms with $\alpha=1$	0.1621	0.1621
Eqs. (1) and (2) with $\alpha=1$	0.1292	0.2877
Eqs. (1) and (2) with $\alpha=\alpha_D$[a]	0.2094	0.2056
"Exact" $H_2{}^+$ [Ref. 10(f)][b]	0.2094	0.2056

[a] $\alpha_D=1.1795$ for $1\sigma_g$; $\alpha_D=0.8643$ for $1\sigma_u$.

[b] Bates *et al.* [Ref. 10(f)] have tabulated wave functions that are not normalized to unity ($||\psi||^2=0.8378$ for $1\sigma_g$ and 1.7339 for $1\sigma_u$) but they have drawn contour maps for normalized wave functions; Pettifor (Ref. 3) has plotted their *unnormalized* wave functions.

and this behavior was indeed observed by Pettifor.[3] The averaged logarithmic derivative of the LCAO wave function is

$$d\ln\psi_{\text{LCAO}}/dr = -\alpha/(1+e^{-\alpha R}) \ .$$

At the internuclear distance $R=2a_0$ the LCAO wave functions fulfill criterion (7) for

$$\alpha = 1.109 \ , \tag{9}$$

which again demonstrates *orbital contraction.*

Parenthetically we note that Heine[1] as well as Pettifor[3] give incorrect expressions for $d\ln\psi_{\text{LCAO}}/dr$. The former sets it equal to $-\alpha$; the latter's equation (46) is equivalent to $-\alpha/(1+\alpha^{-1}e^{-\alpha R})$.

V. ELECTRON DENSITY AT THE BOND CENTER

Pettifor[3] defines the $l=0$ component ψ_0 of a one-center expansion of the $H_2{}^+$ MO around one nucleus, and then introduces the ratio $q=\psi_0$ (bond center)/$\psi_0(r=0)$ as a criterion for orbital contraction (Table III). This ratio is 0.442 for the LCAO ($-$MO) with $\alpha=1$. The ratio for the exact eigenfunction is lower: 0.384. Thus even Pettifor's criterion supports the idea of *orbital contraction* towards the nuclei. The latter q ratio is reproduced by a LCAO($-$MO) with

$$\alpha = 1.141 \ . \tag{10}$$

Strangely enough Pettifor compares the ratio $q_{\text{exact}}=0.384$ with that obtained for a single isolated hydrogen ground-state atom, which is $q_H=0.368$. Now it is apparent that, already upon classical superposition of two atomic charge distributions, the density increases more in the overlap region than it does near the nuclei, so that q increases. Thus, the inequality $q_{\text{exact}}>q_H$ exhibits the fact that the charge distribution of a molecule is more extended than that of a *single* atom. Only a considerable swelling of the single atom would bring its q ratio

TABLE III. q values (see text).

Free H atom ($\alpha=1$) $H_2{}^+$, LCAO with $\alpha=1.183$	0.368
Expanded H atom ($\alpha=0.957$) $H_2{}^+$, LCAO with $\alpha=1.141$ $H_2{}^+$, exact value	0.384
$H_2{}^+$, LCAO with $=1.0$	0.442

up to that of the molecule. Conversely only a considerable shrinkage of the constituent AO's φ_a, φ_b would bring the q ratio of ψ, as given by Eq. (1), down to the value of the isolated atom. In fact, a ψ with $\alpha=1.183$ would be needed to this end and this α happens to be larger than the aforementioned value $\alpha=1.141$. Pettifor's interpretation that this implies an "orbital expansion" only refers to the trivial fact that bonding molecular orbitals in molecules and solids are more extended than atomic orbitals in isolated atoms.

VI. VIRIAL THEOREM

At the molecular equilibrium distance, the exact wave function obeys the simple virial law

$$2\langle T\rangle=-\langle V\rangle \,. \tag{11}$$

This can be fulfilled by scaling α in the wave function (1) to the value

$$\alpha=1.239 \,, \tag{12}$$

which also minimizes the energy within the minimal basis-LCAO approach.[7]

The constructive interference of Ruedenberg,[2] or the contragadience of Goddard,[14] in the LCAO approximation results in a decrease of the kinetic energy. In order to restore the virial relation the LCAO wave function must be reorganized to increase $\langle T\rangle$ and to decrease $\langle V\rangle$. This can be achieved by localizing the electron density (contraction, with an increase of $\langle T\rangle$) in those parts of space where the valence electrons feel a very deep effective potential (thus decreasing $\langle V\rangle$). In the case of $H_2{}^+$ or H_2 this area is the vicinity of the nuclei. Consequently there will be a *contraction* of the LCAO(−MO) towards the nuclei. (In the case of nonhydrogen atoms, the situation is more involved,[15–17] among other things owing to the occupied core shells, and is easily understood within the pseudopotential concept.[17]

We see that the long-range behavior requires a strong contraction ($\alpha\approx1.5$), the behavior near the nucleus a rather weak contraction ($\alpha\approx1.1$ for the correct cusp, $\alpha\approx1.18$ for the correct density at the nucleus), while for the energy (and the right balance between kinetic and potential energy) which is mostly determined by the intermediate region, an intermediate contraction ($\alpha\approx1.25$) is best (see Table IV).[18]

VII. SIMULTANEOUS ORBITAL CONTRACTION AND DEFORMATION

We know from Table I and the discussion of Sec. II that the best α in the sense of the variation principle is nearly the same for a wave function without and with angular deformation. We have also determined the α for an $(1s/2p)$-LCAO wave function such that it reproduces the exact density at the nuclei, or the exact cusp relation. We have found, respectively,

$$\alpha=1.208,\quad \alpha=1.142 \tag{13}$$

to be compared with the variational optimum $\alpha=1.255$, while the long-range behavior still requires $\alpha=1.485$. We see that the optimum α according to the various criteria are now somewhat closer. For a sufficiently large AO expansion a single α should satisfy all criteria and this has to be the one which is correct for the long-range behavior (admixture of a function with a smaller α would spoil the behavior for large r). One sees, in fact, from Wasserman's results[9] that the variationally optimum α appears to converge to 1.5 for large AO basis sets.

The relatively small importance of orbital deformation in the LCAO description (as compared to the local one-center expansion[3]) is due to the fact that the bulk of the local asymmetry of the MO (the

TABLE IV. Optimum α values for various criteria in $H_2{}^+(1\sigma_g)$, $H_2{}^+(1\sigma_u)$, and $H_2(1\,{}^1\Sigma_g^+)$.

Criterion	Important for	$H_2{}^+(1\sigma_g)$ $R=2a_0$	$H_2{}^+(1\sigma_u)$ $R=2a_0$	$H_2(1\,{}^1\Sigma_g^+)$ $R=1.4a_0$
Cusp condition	Small r	1.109	0.797	1.189
Density at nucleus	Small r	1.180	0.864	1.198[a]
Variation principle	Intermediate r	1.239	0.901	1.190
Long-range behavior	Large r	1.485	1.156	1.100

[a] Corresponding to the density at the nucleus of $0.2300e/(a_0)^3$ from Ref. 22.

"lopsidedness" regarded as essential by Heine[1]) is achieved by the overlap of the AO's. In a local single-center expansion like that of Pettifor the local asymmetry can only be taken care of by substantial admixture of functions with $l > 0$, mainly p and d functions, such that these functions become much more important than in the LCAO framework.

VIII. OTHER EXPECTATION VALUES

The criteria discussed so far are by no means exhaustive. Another measure of orbital contraction is, e.g., the expectation value $\langle x^2 \rangle$, where x is a coordinate perpendicular to the bond axis. While $\langle x^2 \rangle = 1$ in the isolated atoms, it is only 0.6415 in $H_2{}^+$ which indicates *contraction* perpendicular to the bond.[19] The LCAO wave function reproduces this value for

$$\alpha = 1.300 . \tag{14}$$

A related quantity is the expectation value

$$T_x = -\frac{1}{2m}\left\langle \frac{\partial^2}{\partial x^2} \right\rangle$$

of the kinetic energy perpendicular to the bond. Ruedenberg *et al.*[2] pointed out that the increase in the kinetic energy required by the virial theorem takes mainly place *perpendicular* to the bond axis. T_x *increases* from 0.167 a.u. in the atom to 0.231 a.u. in $H_2{}^+$, indicating charge contraction towards the molecular axis. The *lowering* of the kinetic energy[20] shows up *in the direction of the bond* ($T_{\|} = 0.140$ a.u.). An LCAO wave function with

$$\alpha = 1.26 \tag{15}$$

approximately reproduces both components of the kinetic energy.

IX. ANTIBONDING $1\sigma_u$ STATE OF $H_2{}^+$ AND THE H_2 MOLECULE

While the formation of the bonding $1\sigma_g$ MO in $H_2{}^+$ is accompanied by AO contraction, an analogous AO expansion is found for the antibonding $1\sigma_u$ state. We consider this state at the equilibrium distance ($R = 2a_0$) of the $1\sigma_g$ state.

With $\alpha = 1$ one gets the energy $-0.160\,85$ a.u., whereas the minimum of the energy $-0.165\,81$ a.u. (to be compared with the exact energy[10(h)] of $-0.167\,53$ a.u.) is obtained for $\alpha = 0.9005$. The α values required for the correct long-range behavior, the correct density at the nucleus, and the correct cusp are collected and compared with those for the $1\sigma_g$ state in Table IV. Three of the four criteria imply orbital expansion, only the long-range behavior, which requires very strong contraction for the $1\sigma_g$ state, wants a slight contraction. As for the $1\sigma_g$ state, the highest exponent is needed for the long-range behavior and the lowest one for the cusp, while the best values for the energy and for the density at the nucleus are rather close.

Admixture of a p-AO does, unlike for the $1\sigma_g$ state, not lower the energy to any significant extent (only in the 7th decimal place). (It is similarly ineffective to use a Guillemin-Zener-type function,[2(d),21] which is very good for the $1\sigma_g$ state.)

One might suspect that the contraction in $H_2{}^+$ (mainly that needed for the long-range behavior) is not due to bonding but due to the net positive charge. That this net charge plays some role is confirmed by the $\alpha > 1$ value for the long-range behavior of the $1\sigma_u$ state. Nevertheless the results for the two-electron system H_2 in the bonding ground state are qualitatively similar to those for the $1\sigma_g$ state of $H_2{}^+$. The optimum α values, according to three criteria, for the H_2 ground state at its equilibrium distance are in the range 1.1 to 1.2 and certainly indicate AO contraction (see Table IV). Now the long-range behavior requires the least contraction (probably because there is no net charge as in $H_2{}^+$).

It is obvious that for a valid description of both the bonding and the antibonding MO of $H_2{}^+$ or H_2 AO's with rather different α are needed. However, the discussion of, for example, the band structure of solid metallic hydrogen in LCAO terms would become more complicated by the use of different AO's for the bottom and the top of the band. A compromise, though a poor one, would be to use the uncontracted AO with $\alpha = 1$. A better choice is suggested by quantum chemical experience, namely, to take at least two AO's per atom with different α (double-ζ basis). Noting that the derivative of a $1s$-AO with respect to α is a $2s$-AO, one may alternatively choose a $1s$ and a $2s$ function with $\alpha = 1$. One then gets the energies $-0.589\,16$ and $-0.166\,24$ a.u. for the $1\sigma_g$ and $1\sigma_u$ states, respectively, which are slightly lower than those obtained by optimizing α for either state individually.

X. CONCLUSION

If we compare the molecular wave function with the superposition of unmodified atomic densities or unmodified atomic orbitals (LCAO approach, cf. Heine[1]), then the formation of a chemical bond, especially in the case of hydrogen, is accompanied by charge and orbital contraction. This statement holds regardless of which criterion is chosen, although the very strong contraction needed for the correct long-range behavior in H_2^+ is partially due to the positive charge. The suggestion of Pettifor[3] to compare the molecular or crystal density with the density of a single atom does not yield any insight. Furthermore this comparison is of no consequence for the LCAO approach. Finally, it is inconsistent to take a criterion which is defined in the local *single* center expansion approach and then interpret the results in terms of the *multicenter* LCAO approach.

Since Heine has based his comments on orbital contraction or expansion on a study of the H_2^+ system, it has been legitimate for us to concentrate on the same system. One should, however, not forget that the hydrogen atom is unique in the sense that it does not possess occupied inner shells. So not all results of this study can be generalized to bonds between arbitrary atoms.

The formation of a bond usually increases the lowest ionization potential, such that the long-range behavior requires contraction of the valence AO's. This may not be very relevant for solid-state problems, except possibly for surface states. Contraction in the intermediate region in order to restore the virial relation does also generally take place, although the interplay between kinetic and potential energy is usually more complicated than in H_2^+ or H_2.

The spatial region near the nucleus is of special importance only for bonds to hydrogen. The discussion of Sec. IV cannot be generalized to atoms with occupied cores. The Pauli principle keeps the valence electrons outside the core, or in other words, core-valence orthogonality automatically restores the cusp condition for overlapping atoms quite accurately without any AO contraction or expansion. Therefore using a single unmodified set of AO's (or a so-called unscaled single-ζ set) is a reasonable approximation in semiquantitative calculations of the valence band of molecules or solids. Of course, significant improvement is obtained with basis sets more flexible in the valence shell. Especially for the 3*d* shell of transition metals, where there is no occupied core shell of the same symmetry, at least a double-ζ basis is inevitable, since atomic and molecular calculations show significant density differences within the 3*d* shell for different states.

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[5] One may try to separate those "radial" deformations that can be described by a simple "scaling," i.e., by a change of α, and those that correspond to "nonuniform scaling" which can be accounted for by admixture of other *s*-type AO's. This separation is, however, rather difficult (see also Ref. 6).

[6] The two types of deformation 1 and 2 are not even independent, since the two-center AO basis is overcomplete if it is chosen complete for either center. So the distinction between 1 and 2 is meaningful only for small basis sets that are sufficiently far from near linear dependence. (For a general discussion of this problem in a somewhat different context see Ref. 4.)

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[18] One can expect from the variational principle only that it accounts well for those parts of the wave function that contribute significantly to the energy. So the highest weight is given to that region of distances r from the nuclei (the "intermediate" region) where the electron is most likely. Then comes the (rather small) region near the nuclei, while the large-r region has negligible weight. The correct asymptotic behavior (3) is usually not obtained automatically.

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