

THE VALENCE BOND AUFBAU PRINCIPLE FOR MOLECULAR EXCITED STATES*

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A modified Aufbau principle for the excited states of molecules is presented. This principle is based on generalized valence bond orbitals (with spatial projection) rather than the traditional molecular orbitals. The excited orbital is modeled after the series of one-electron *heteronuclear* diatomic molecules. These ideas are illustrated for the case of the excited $1,3\Sigma^+$ states of H_2 .

1. Introduction

The nature of molecular excited states was pivotally clarified by the development of the concepts of molecular orbitals and orbital correlation diagrams, and in particular by the work of Hund and Mulliken [1, 2]. In specific, consider the orbital correlation diagram for H_2 , which has the form shown in fig. 1a (based on the states of H_2^+). From this diagram we expect the low-lying Σ states of H_2 to be described as follows (in order of increasing energy):

$$(1\sigma_g)^2 \rightarrow 1^1\Sigma_g^+,$$

$$1\sigma_g 1\sigma_u \rightarrow 1^3\Sigma_u^+, 1^1\Sigma_u^+,$$

$$1\sigma_g 2\sigma_g \rightarrow 1^3\Sigma_g^+, 2^1\Sigma_g^+,$$

where the states to be derived from each configuration are listed on the right. One is gratified to find that this ordering of the states is correct — although there remain some disappointing aspects with the description. Even with self-consistent (Hartree–Fock) calculations of the optimum orbitals as a

function of internuclear distance (R), the wavefunction based on the configuration $(1\sigma_g)^2$ leads to a very poor description of the ground state of H_2 at large R (at $R = \infty$ the error is 7.74 eV) [3]. More seriously, many excited configurations are predicted to correlate with the wrong separated atom limits. For example, at large R the $1\sigma_g$ and $1\sigma_u$ orbitals of H_2^+ have the form

$$1\sigma_g = 1s_L + 1s_R,$$

$$1\sigma_u = 1s_L - 1s_R$$

(ignoring normalization), where $1s_L$ and $1s_R$ are H 1s orbitals on the left and right, respectively. Thus the $3\Sigma_u^+$ and $1\Sigma_u^+$ states constructed from configurations $1\sigma_g 1\sigma_u$ would be expected to dissociate into hydrogen atoms, each in the ground state. However, the only two-electron states that can be constructed from two ground state H atoms are the $1\Sigma_g^+$ and $3\Sigma_u^+$ states. In fact the lowest $1\Sigma_u^+$ state dissociates to one H atom in the 1s state and one H atom in an $n = 2$ state (2s or 2p).

The types of difficulties and inconsistencies mentioned above occur quite generally and become even more troublesome for larger molecules. It would be desirable to improve upon the orbital correlation diagram (OCD) concept in order to remove these difficulties, yet we would want to retain the conceptual simplicity of the OCD that has made it of such great

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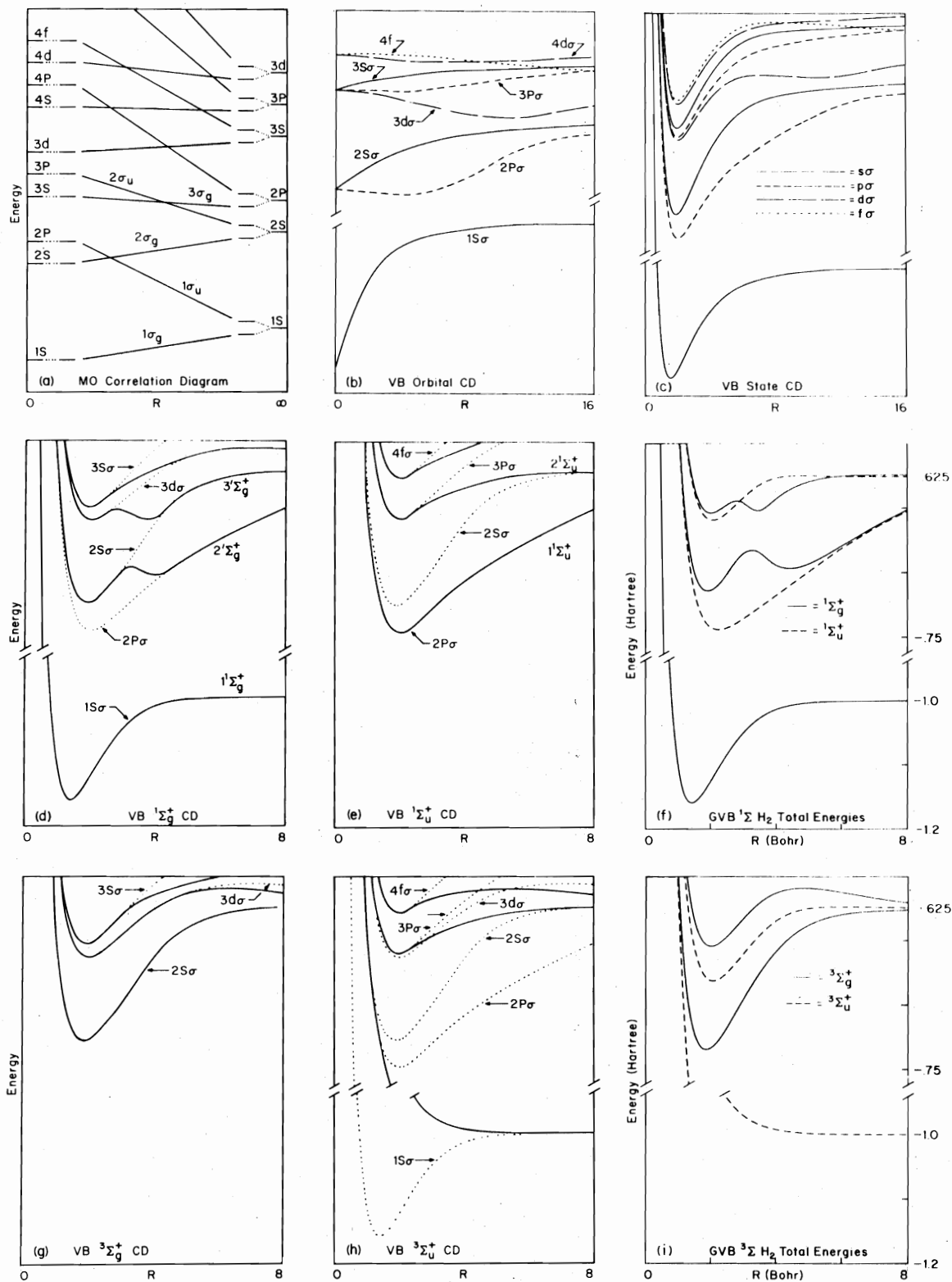


Fig. 1. Caption see next page.

utility. In this paper we discuss an alternative type of orbital correlation diagram based on orbitals obtained from generalized-valence-bond type wavefunctions and illustrate this approach for the case of the H_2 molecule.

2. The form of the wavefunctions

A basic aspect of the OCD concept is the correlation of the molecular states with their united-atom and separated-atom limits. Since we want to ensure that our description behaves correctly at large R , we will first examine the known limiting forms for $R = \infty$. The lowest states must involve a hydrogen 1s orbital on the left and right, which yields the spatial wavefunctions^{*,**}

$$1s_L 1s_R + 1s_R 1s_L, \quad (1a)$$

$$1s_L 1s_R - 1s_R 1s_L, \quad (1b)$$

leading to $^1\Sigma_g^+$ and $^3\Sigma_u^+$ symmetries respectively when combined with a spin function and antisymmetrized.

We will denote these states as:

$$^1\Sigma_g^+ \begin{bmatrix} 1s_L & 1s_R \end{bmatrix}, \quad (2a)$$

$$^3\Sigma_u^+ \begin{bmatrix} 1s_L \\ 1s_R \end{bmatrix}, \quad (2b)$$

* We need deal with only the spatial wavefunctions since direct spin interactions are neglected (they are quite small for H_2). However, because of the Pauli principle a permutationally symmetric spatial wavefunction such as (1a) must correspond to a singlet state and an antisymmetric wavefunction such as (1b) must correspond to a triplet state.

** Here $1s_L$ and $1s_R$ denote hydrogen 1s orbitals (at $R = \infty$) on the left and right, respectively; the orbital position in a product denotes the electron number [e.g., $\phi_a \phi_b$ implies $\phi_a(1) \phi_b(2)$].

where orbitals in the same row are understood to be symmetrically combined [as in (1a)] and orbitals in the same column are understood to be antisymmetrically combined [as in (1b)]. At large R the other states of the system must involve excited states of the atoms, the lowest of which would be one H atom in the 1s state and one in an $n = 2$ state (2s or 2p). In general we use two orbitals, ϕ_a and ϕ_b (say $\phi_a = 1s_L$, $\phi_b = 2s_R$) and obtain the following four two-electron wavefunctions

$$^1\Sigma_g^+ \begin{bmatrix} \phi_{aL} & \phi_{bR} \end{bmatrix}_g \equiv \begin{bmatrix} \phi_{aL} & \phi_{bR} \end{bmatrix} + \begin{bmatrix} \phi_{aR} & \phi_{bL} \end{bmatrix}, \quad (3a)$$

$$^1\Sigma_u^+ \begin{bmatrix} \phi_{aL} & \phi_{bR} \end{bmatrix}_u \equiv \begin{bmatrix} \phi_{aL} & \phi_{bR} \end{bmatrix} - \begin{bmatrix} \phi_{aR} & \phi_{bL} \end{bmatrix}, \quad (3b)$$

$$^3\Sigma_g^+ \begin{bmatrix} \phi_{aL} \\ \phi_{bR} \end{bmatrix}_g \equiv \begin{bmatrix} \phi_{aL} \\ \phi_{bR} \end{bmatrix} + \begin{bmatrix} \phi_{aR} \\ \phi_{bL} \end{bmatrix}, \quad (3c)$$

$$^3\Sigma_u^+ \begin{bmatrix} \phi_{aL} \\ \phi_{bR} \end{bmatrix}_u \equiv \begin{bmatrix} \phi_{aL} \\ \phi_{bR} \end{bmatrix} - \begin{bmatrix} \phi_{aR} \\ \phi_{bL} \end{bmatrix}. \quad (3d)$$

With one H atom excited, the excitation can be either on the left or the right, leading to the two terms in each of the wavefunctions (3). The same procedure applies to the higher excited states.

The wavefunctions in (2) and (3) were constructed using atomic orbitals and are the exact molecular states for $R = \infty$. For definite R the exact wavefunctions can no longer be written in such simple forms; however, we will consider approximate wavefunctions at finite R where the form of the wavefunction is taken as in (2) or (3) but in which the orbitals (ϕ_a and ϕ_b) are solved for variationally rather than taken as atomic orbitals. This process of self-consistent evaluation of the orbitals is analogous to that involved in the Hartree-Fock method, except that the wavefunction in (2) or (3) is not a simple Slater determinant. Since the wavefunction of (2) has the form of a valence bond wavefunction, the method of self-consistent optimization of the or-

Fig. 1. (a) Standard MO correlation diagram (based on H_2^+). (b) Scaled LiH^{+3} electronic energies from ref. [11]. (c) Scaled LiH^{+3} electronic energies added to H_2^+ ground state total energy. (d) Valence bond (VB) correlation diagram for $^1\Sigma_g^+$. (e) VB correlation diagram for $^1\Sigma_u^+$. (f) Ab initio GVB energies for $^1\Sigma_{g,u}^+$. (g) VB correlation diagram for $^3\Sigma_g^+$. (h) VB correlation diagram for $^3\Sigma_u^+$. (i) Ab initio GVB energies for $^3\Sigma_{g,u}^+$.

bitals is referred to as *generalized valence bond* (GVB) [4,5] *,**.

3. The orbitals

Self-consistent calculations were carried out for the optimum orbitals of the form (3) for the lowest two states of each of the symmetries $1\Sigma_u^+$, $3\Sigma_g^+$, and $3\Sigma_u^+$ and the lowest three states of $1\Sigma_g^+$ symmetry. In each case there is one orbital, ϕ_a , resembling a hydrogen 1s orbital on the left. This orbital appears relatively unchanged as we proceed from state to state and does not change much even as R is varied. On the other hand, as shown in fig. 2, the other orbital (ϕ_b) differs markedly from state to state and in some cases changes significantly as R is varied.

Thus the various low-lying excited states of H_2 may be described as in (3) where $\phi_a \sim 1s_L$. That is, these states may all be considered as single excitations

* Coulson and Fischer [6] first noticed that the Weinbaum wavefunction could be written in the form (1a) with semi-localized orbitals and Hurley et al. [7] suggested variationally optimizing the natural orbitals of such wavefunctions. Similar suggestions were also made by Löwdin [8] and early variational calculations on the $1\ 1\Sigma_g^+$ state of H_2 were reported by Davidson and Jones [9] and in refs. [4]. An alternative scheme for handling general spin and permutational symmetry through use of the group operators G_i^{γ} and optimization of the orbital products was developed and applied by Goddard [4] and referred to as the GI method. The modifications necessary for spatial projections were mentioned and the resulting equations were referred to as extended GI (projected GI would have been a better term). These equations were derived in detail by Gallup [5] (who refers to the resulting wavefunctions as projected Hartree products) and applied to the $1\ 1\Sigma_g^+$ state of H_2 .

An essential conclusion from our work is that a sufficiently general form must be chosen for the wavefunction so that no restrictions need be artificially placed on the orbitals to obtain the proper spatial or permutational many-electron symmetry. Such restrictions should be used for a particular state only when the resulting effects have been demonstrated to be negligible.

** Note that the orbitals of (3) and (4) are solved for *after* spatial projection. For the calculations reported herein, the variational equations are set up so as to converge quadratically (a modified Newton-Raphson approach) and are solved using a basis set expansion. A basis of 32 gaussian functions (10s, 6p) was used. Further details will be presented elsewhere.

(of ϕ_b) from a ground state

$$\begin{bmatrix} \phi_a & \phi_b \end{bmatrix}_g = \begin{bmatrix} 1s_L & 1s_R \end{bmatrix}_g.$$

This suggests that in constructing an orbital correlation diagram for H_2 , we may concentrate on the form expected for ϕ_b .

In the self-consistent field procedure, we solve for ϕ_b by solving an integro-differential equation that can be written in the form [4]

$$H_b \phi_{kb} = \epsilon_{kb} \phi_{kb}, \quad (4)$$

where H_b is a one-electron operator involving an effective field due to ϕ_a . As indicated in (3) there are four basic couplings of the orbitals for Σ states; hence, given a specific ϕ_a , there are four equations of the form (4). Each of these equations leads to a whole spectrum of optimum ϕ_b orbitals, appropriate for that coupling. Each of these one-electron states corresponds to an excited state of H_2 . For large R the solutions of (4) must reduce to hydrogen atomic functions, and in this limit we expect a similar ϕ_b for four different two-electron states [cf. eq. (3)].

Since ϕ_a is primarily concentrated near the left proton, we would expect ϕ_a to effectively shield the left proton from ϕ_b . Thus the field seen by ϕ_b could be qualitatively viewed as a nearly unshielded proton on the right and a nearly shielded proton on the left (say, an effective charge of $Z_{\text{eff}} \approx 1/5$). Then the spectrum of states, $\{\phi_b\}$, and the dependence of each state on R would be expected to resemble that of a one-electron diatomic molecule with charges $Z_L = Z_{\text{eff}}$ and $Z_R = 1$. That is, our model for establishing the shapes of the potential energy curves will be a one-electron *heteronuclear* diatomic molecule.

4. Correlation diagrams

Based on calculations in the literature [10, 11] of such one-electron diatomics as HeH^{+2} and LiH^{+3} , we expect the energy level diagram for one-electron moving in the field ($Z_{\text{eff}}, 1$) to appear as shown in fig. 1b (where united-atom notation has been used). It is to be noticed that some curves show marked bonding effects, while others are nearly flat. For ex-

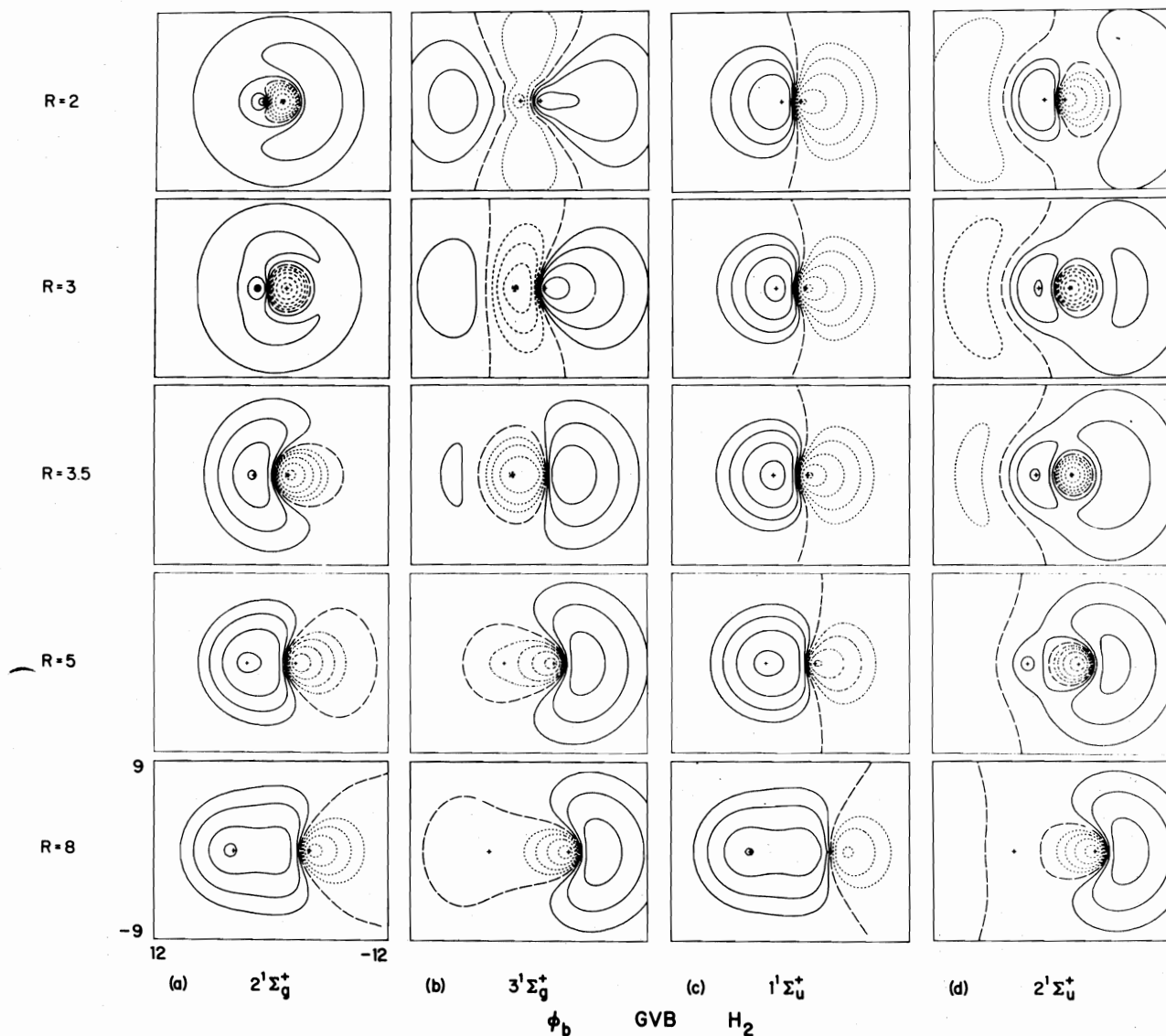


Fig. 2. The GVB orbitals for some excited singlet states of H_2 . Only the ϕ_b orbital is shown [cf. eq. (3)] since the ϕ_a orbital is nearly the same for each state. The contours plotted (in au) are 0, ± 0.01 , ± 0.02 , ± 0.04 , ± 0.08 , etc. All plots are 18×24 bohr with the nuclei designated by a + symbol.

ample, the 1σ state, which is a $1s$ orbital at very large and very small R , contributes strongly to bonding for $R < 2a_0$.

The $2p\sigma$, $3d\sigma$, $4f\sigma$, etc., states generally lead to bonding and a minimum at large R . This can be understood by noting that the overall size and shape of the various orbitals (i.e., states) of the molecule depend

only slightly on the internuclear distance, and that each of $n\sigma$ orbitals with $l = n - 1$ has two principal concentrations of charge density along the internuclear axis. The minimum energy then occurs for R comparable to the distance between these lobes of charge density. On this basis we expect the maximum bonding (for a total effective charge of 1) in the

above $n\sigma$ orbitals (with $l = n - 1$) to occur for $R \approx 2n(n-1)$, i.e., $R \approx 4a_0$ for $2p\sigma$, $R \approx 12a_0$ for $3d\sigma$, and $R \approx 24a_0$ for $4f\sigma$.

Qualitatively accurate energy curves can be obtained for the states of H_2 by adding the energy curve expected for ϕ_b to that of H_2^+ (due to ϕ_a), leading to fig. 1c, but we have yet to include any dependence upon spin or spatial symmetry. For example, consider the $2^1\Sigma_g^+$ state, which from fig. 1c would be expected to be

$$\boxed{1s\sigma \quad 2p\sigma}_g \quad (5)$$

If ϕ_b retains the $2p\sigma$ character all the way to $R = 0$, then the united atom wavefunction $\phi_{1s}\phi_{2p}$ would have u spatial symmetry, and the projected wavefunction (5) would vanish. Thus, we know that the self-consistent orbital ϕ_b must change character before $R = 0$. For small R the character of ϕ_b is expected to be $2s\sigma$; which is the lowest excited state in fig. 1b, c that allows $1^1\Sigma_g^+$ symmetry for $R = 0$. The change of character should occur mostly around 3 to $4a_0$; that is, the region in which the $n = 2$, ϕ_b orbital begins to overlap significantly with the $1s$ orbital on the other center.

The $2p\sigma$ orbital is strongly bonding at large R ; so the energy of the $2^1\Sigma_g^+$ state should drop rapidly as R is decreased to $\approx 4a_0$. For smaller R the $2p\sigma$ character in ϕ_b is replaced by $2s\sigma$ character, leading to an increase in energy. Finally, for smaller R (≈ 2.5 to $2a_0$). The ϕ_a orbital contributes to the binding (as in H_2^+) leading to a second energy minimum around $2a_0$ (as in H_2^+). The net result of these effects should be a double minimum in the energy curve for the $2^1\Sigma_g^+$ state as indicated in fig. 1d. This double minimum is well known [12-14] (first predicted theoretically by Davidson in 1961).

Fig. 2a shows the ϕ_b orbital for the $2^1\Sigma_g^+$ state obtained from the herein reported ab initio GVB calculations. We see that the orbital changes continuously from $2p\sigma$ -like at large R to $2s\sigma$ -like at small R , with the principal changes occurring around 3 to $4a_0$. The ab initio GVB energies are shown in fig. 1f, in which can be seen the expected double minimum.

Consider next the $1^1\Sigma_u^+$ state, expected from fig.

1c to resemble

$$\boxed{1s\sigma \quad 2p\sigma}_u \quad (6)$$

Since the orbitals in (6) permit the proper u symmetry for $R = 0$, the ϕ_b orbital for $1^1\Sigma_u^+$ should retain its $2p\sigma$ character even to $R = 0$ (that it does is shown by the GVB orbitals in fig. 2c). We expect bonding due to ϕ_a (favoring $R = 2a_0$) and bonding due to $\phi_b = 2p\sigma$ (favoring $R = 4a_0$). Thus this state should exhibit a somewhat larger R_e than does H_2^+ (it does, $R_e = 2.43$ as compared with $R_e = 2.0a_0$ for H_2^+ and the other excited states of H_2) and should lead to significantly more stability than H_2^+ (it does, $D_e = 3.6$ eV as compared with $D_e = 2.8$ eV for H_2^+). [See figs. 1e and 1f for the predicted and ab initio energy curves.]

In general, to determine the effects of symmetry restrictions, we will examine the form of the wavefunction [(2) and (3)] for $R = 0$ (united atom) and allow only those states with the proper symmetry. The allowed united atom limits are:

$$1^1\Sigma_g: 1s\sigma, 2s\sigma, 3d\sigma, 3s\sigma, \dots,$$

$$1^1\Sigma_u: 2p\sigma, 3p\sigma, 4f\sigma, 4p\sigma, \dots,$$

$$3^1\Sigma_g: 2s\sigma, 3d\sigma, 3s\sigma, 4d\sigma, \dots,$$

$$3^1\Sigma_u: 2p\sigma, 3p\sigma, 4f\sigma, 4p\sigma, \dots$$

Incorporating these limits into the basic energy level diagram of fig. 1c results in the final energy level diagrams given in figs. 1d, e, g, h. For comparison the calculated energy curves are given in fig. 1f, i. The above simple rules lead to qualitatively correct energy levels for the lower states, and we expect this to be true also for the higher states.

Interesting features in the higher states include: a double minimum in the $3^1\Sigma_g^+$ state (previously predicted by Davidson, 1961, ref. [12]), an energy minimum at large R ($\approx 12a_0$) for (at least singlet) states involving $3d\sigma$ character, and an energy maximum at smaller R as the $3d\sigma$ loses its bonding effect (cf., figs. 1b, c). As a result the $4^1\Sigma_g^+$ and $3^1\Sigma_u^+$

are expected to have multiple minima and the $2^3\Sigma_g^+$ and $3^3\Sigma_u^+$ states to each have a hump. Other multiple minima are expected for higher excited states.

5. Summary

We have found from an examination of the orbitals of the one-electron heteronuclear diatomics and of GVB wavefunctions of H_2 , a conceptual scheme for the qualitative discussion of the wavefunctions and energies of excited states. For an N -electron molecule the GVB equations for orbital ϕ_N involves an effective field due to the other $N - 1$ electrons and the spectrum of eigenfunctions of this effective field yield a good approximation to each of the various excited states of the molecule. Thus the OCD based on GVB is only for the last orbital of the system; the Aufbau principle describes the result of the inclusion of this last orbital. This contrasts with the MO OCD where we start with the bare nuclear framework and add electrons to orbitals until all N electrons are used up.

The MO OCD is quite convenient for considering the electronic symmetries of states near the R_e of the ground state. An advantage of the GVB OCD is that the behavior of various excited states can be considered for even large changes in the internuclear distance. In addition we found above that the GVB OCD leads to good predictions of the form of the energy curves of the states of H_2 . For larger systems the MO OCD and Aufbau principle led to qualitative use-

ful predictions. At least as much is to be expected from the GVB OCD and Aufbau principle.

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