

Theory of chemical reactions of vibronically excited $\text{H}_2(B^1\Sigma_u^+)$. II. Noble gas dihydrides

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The recently discovered chemically bound excited state of HeH_2 from large MRD-CI calculations can be explained in terms of the highly ionic character of the $\text{H}_2B^1\Sigma_u^+$ excited state at $R = 4.0$ a.u. and the resulting binding between it and the polarized He via electrostatic and overlap (with the diffuse "H⁻" center) effects. Based on this explanation, a theory for chemical reactions of normally nonreactive systems is proposed. These reactions may occur when one of the reacting molecules is excited vibronically to a state of maximum ionicity. The $\text{H}_2B^1\Sigma_u^+$ state presents a convenient test case. State-specific, open shell SCF calculations have been carried out for the $\text{He} + \text{H}_2^*$, $\text{Ne} + \text{H}_2^*$, and $\text{Ar} + \text{H}_2^*$ systems. The results for $\text{He} + \text{H}_2^*$ agree with the MRD-CI calculations and demonstrate that electron correlation is reasonably constant over the potential energy surface. NeH_2^* and ArH_2^* molecules are predicted for the first time to bind chemically in an excited $^1A'$ state at geometries similar to HeH_2^* and close to a crossing with the unbound ground state into which they can decay radiatively or via nonadiabatic coupling. Our results suggest that, in accordance with the previous observations by Fink *et al.* [J. Chem. Phys. **56**, 900 (1972)] of quenching of fluorescence of the $\text{H}_2B^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ transition in a $\text{He} + \text{H}_2^*$ system, quenching should be observed in $\text{Ne} + \text{H}_2^*$ and $\text{Ar} + \text{H}_2^*$ systems, but this time for higher vibrational numbers.

I. INTRODUCTION

It is well known that the potential energy surfaces describing the collisions between noble gases and the H_2 molecule in their closed shell ground state is repulsive. Systems involving similar closed shell species (e.g., $\text{He} + \text{HF}$, $\text{H}_2 + \text{H}_2$, $\text{H}_2 + \text{CH}_4$, etc.) are also nonbonding chemically. Their energy surfaces are characterized only by van der Waals minima. Much sophisticated theoretical and experimental work has been published on the electronic structure and dynamics of such systems (e.g., Refs. 1-6 and references therein).

In this paper we suggest that systems such as the above can form, in certain cases, chemically bound excited states which can break up by radiative transitions to the repulsive ground state or by nonadiabatic couplings. These excited states open the possibility for new spectroscopic observations, photochemical reactions and studies of chemical dynamics. The systems of interest here are the noble gas dihydrides whose ground repulsive energy surface has been and continues to be^{1,6} a subject of research. We present the first results showing bound NeH_2 and ArH_2 molecules in an excited state, $^1A'$, formed from the reaction of $\text{H}_2B^1\Sigma_u^+$ with the 1S ground state of the noble gases. In the accompanying paper,⁷ a prediction of a bound excited state of H_4 in an *a priori* chosen geometry is made, in further confirmation of the proposed theory.

The impetus for this proposal has come from the recent results of large configuration-interaction calculations,⁸ using the MRD-CI approach and programs,^{9,10} which showed for the first time that the system $\text{H}_2(^1\Sigma_u^+) + \text{He}(^1S)$ has a

bound excited state near an avoided crossing with the ground state of the same symmetry. It is bound by 1.5 eV in a geometry in which the H-H distance is $4.0a_0$, the He center of H_2 distance is $1.5a_0$, and the angle between the He-H₂ and the H-H axis is 45° . These calculations were carried out with the intention of obtaining a well-described excited potential energy surface for dynamical studies, by extending the calculations of Römelt *et al.*⁵ to more geometrical points. In view of the previous literature and calculations⁵ which emphasized the van der Waals nature of this system, the minimum of 1.5 eV was unexpected.

This finding gave rise to the question as to its origin in terms of general chemical features. A plausible explanation was based on the fact that the $\text{H}_2B^1\Sigma_u^+$ state is ionic at intermediate distances.¹¹ As He approaches H_2^* , the H-H bond stretches close to maximum ionicity producing a multipole field which captures the slightly polarized He at a geometry which favors energy reduction through small overlap between "H⁻" and He and large Coulomb interactions between "H⁺" and He.

Supporting evidence for this bonding model comes from the calculated H-H and the smaller of the He-H internuclear distances of the $(\text{HeH}_2)^*$ molecule. These are $4.0a_0$ and $1.41a_0$ respectively. Kołos and Wolniewicz¹¹ have reported that the maximum ionicity of the $\text{H}_2B^1\Sigma_u^+$ state is at $4.0a_0$. Similarly, the HeH^+ molecule has an equilibrium distance of $1.44a_0$.¹²

In the next sections we demonstrate the implementation of this idea on the $(\text{He, Ne, and Ar}) + \text{H}_2^*$ surfaces, whose geometries near the bound minimum are chosen *a priori* and whose energy surfaces are computed from state-

specific, open shell SCF calculations.

Based on the aforementioned facts and analysis, it is reasonable to theorize the existence of bound excited states of the species NeH₂, ArH₂, or (H₂)₂, or of similar polyatomic compounds involving on the one hand vibronically excited states in geometries of high ionicity and on the other "non-reactive" closed shell ground states.

II. THEORY AND APPLICATION TO NOBLE GAS DIHYDRIDES

The first prediction of a bound HeH₂^{*} molecule was based on results of extensive calculations which include electron correlation.⁸ For NeH₂ and ArH₂, there are no specific proposals in the literature for their existence in bound states. These systems are of medium size. Configuration-interaction calculations^{5,7-9} on their ground or excited state potential energy surfaces would be very costly, time consuming, and perhaps incomplete without any theoretical guidance about the expected symmetry and nuclear geometry.

In this paper we make the proposal which, in line with the results of Ref. 8, states that many known nonreactive (H₂ + closed shell ground state) systems can actually undergo chemical binding when H₂ is excited to the B¹Σ_u⁺ state which, in a vibrationally excited level, becomes highly ionic. Similar situations are expected to hold for other molecules. For example, we have calculated a strongly bound excited state of H₄ for an *a priori* chosen geometry.⁷ It is based on the character of such maximum ionicity excited states (MIES) that predictions can be made of the existence of bound excited states in compound systems and of their approximate geometries. The conceptualization of this type of binding is based on three building blocks:

(a) The "positive ion complex." That is that part of the molecule which includes the H⁺ center. In the present case, the relevant element is the MH⁺ (M = He, Ne, Ar,...) internuclear distance.¹²

(b) The "geometry of maximum ionicity." In the case of H₂ B¹Σ_u⁺, this occurs at R = 4.0a₀.¹¹

(c) The overlap and the volume (steric) effects of the molecule added to the MIES. Here, the relative size of the noble gases imply an enlargement of internuclear distances as we go from HeH₂ to NeH₂ to ArH₂.

Having adopted an excited state for the system (H₂ B¹Σ_u⁺ + molecule) and a particular geometry as the possible configuration corresponding to a bound minimum in the energy hypersurface, the question of its numerical verification arises. Instead of resorting to large scale computations,^{5,8,10} which would be almost forbidding for a small computer, we have applied the notion of *state-specific* Hartree-Fock calculations for excited states,¹³ which allows a clearer and consistent recognition of the importance of electron correlation. Thus, the electronic structure of the H₂ B¹Σ_u⁺ state as well as that of the noble gases suggests that, to a good approximation, electron correlation should subtract out in going from the separated M + H₂^{*} system to the equilibrium geometry of the expected bound MH₂^{*}, the bonding being essentially electrostatic with no pairing of electrons either along the H-H or along the M-H bond. This understanding points to the reliability of an *excited state op-*

timized, open shell SCF calculation for predicting the salient features of the energy surface and of the binding.

State specific calculations of open-shell singlet excited states which have a lower closed shell ground state present two theoretical difficulties:

(1) The question of the proper construction and solution of the SCF equations.

(2) The question of the "variational collapse" to an energy below the exact one and the alteration of the character of the wave function due to orbital mixing of the lower state.

In principle, the second problem requires the diagonalization of at least a 2 × 2 matrix which includes the ground and the first excited singlet configurations. For example, the variational collapse of the He 1s2s ¹S Hartree-Fock state is corrected by a multiconfigurational HF (1s2s + 1s²) calculation.¹³

In the case of the MH₂ (M = He, Ne, Ar) molecules, convergence to solutions for the ground and excited states was achieved by maximizing the character of the H₂ ground or excited state orbitals in the optimized vectors.

Conceptually this is similar to a procedure for obtaining SCF and correlated solutions of highly excited states without the inclusion of lower states of the same symmetry.¹⁴ The program which was used has been written by Hunt (modified by Surrat) and is based on the orthogonality constrained basis set expansion (OCBSE) method of Hunt *et al.*¹⁵

The way we carried out the calculations is the following: First we computed SCF functions for the H₂ ¹Σ_g⁺ ground state and the H₂^{*} B¹Σ_u⁺ excited state (see Fig. 1). Then we initialized the MH₂ ground and excited state ¹A' calculations by constructing molecular orbitals corresponding to the H₂ ¹Σ_g⁺ and ¹Σ_u⁺ SCF orbitals. Iterations were done by maximizing the *overlap* between the orbitals of two consecutive solutions.

The convergence and the resulting character of the functions was consistent. Furthermore, comparison of our optimized state specific HeH₂^{*} results with our accurate MRD-CI results⁸ shows no variational collapse and good

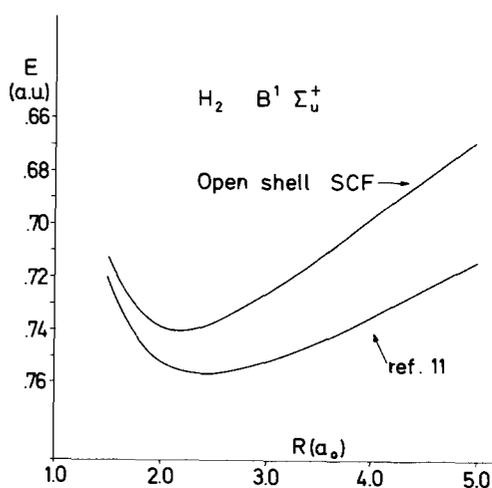


FIG. 1. Comparison between the present open-shell SCF calculations for the H₂B¹Σ_u⁺ potential and the accurate ones of Kolos and Wolniewicz (Ref. 11).

TABLE I. Comparison between the present open-shell SCF results for the binding energy (in mhartree) of the ¹A' excited state of HeH₂ and those from the MRD-CI calculations of Ref. 8. For fixed R (= 1.5a₀) and ϑ (= 4.0a₀) (see Table III).

ϑ (deg)	MRD-CI (Ref. 8)	Open-shell SCF (this work)
20°	265.4	248.1
40	- 43.8	- 29.7
45	- 55.8	- 33.6
50	...	- 20.0
60	- 33.1	- 11.6

orthogonality to the ground state—separately optimized—SCF ¹A' function.

The basis sets for H and He, Ne, and Ar were taken from the literature.¹⁶ However, in order to describe the excited state better, we used uncontracted diffuse s and p functions while an additional d function with exponent 0.05 was used for Ar.

The geometry search was guided by our MRD-CI results⁸ on HeH₂^{*} and the previous analysis. Having discarded the standard (e.g., Refs. 5, 6, and 17) geometries of collinear and perpendicular approach to the H₂ molecule around its equilibrium distance, we concentrated on geometries where the H-H distance ranged from 3.8a₀ to 5.8a₀, the distance R of M from the center of the bond was initialized by considering the MH⁺ distance¹² and the angle between M and the center of the bond was initialized at 45°.

III. RESULTS

Our essential results are summarized in Tables I-III and in Figs. 1-4.

Tables I and II present a comparison between the present state-specific SCF calculations of the binding energy of the HeH₂^{*} ¹A' state and the previous ones⁸ which include electron correlation. Out of the many which were calculated, only a few relevant geometries are presented. As anticipated, the open shell SCF calculations yield similar results and the same essential information, i.e., that the He + H₂(B¹Σ_u⁺) system can bind chemically at a geometry which is in accordance with the criteria of the previous section.

Similar calculations have yielded the first results sup-

TABLE II. Comparison between the present open-shell SCF results for the binding energy (in mhartree) of the ¹A' excited state of HeH₂ and those from the MRD-CI calculations of Ref. 8. For fixed R (= 1.5a₀) and ϑ (= 45°).

r(a ₀)	MRD-CI (Ref. 8)	Open-shell SCF (this work)
1.4	...	188.7
2.4	98.8	139.9
3.0	23.7	13.8
3.5	- 35.2	- 27.2
3.8	...	- 30.6
4.0	- 55.8	- 33.6
4.2	...	- 34.6
4.5	- 44.9	- 10.5
5.0	- 25.8	0.5
6.0	19.1	20.9

TABLE III. Geometries of minimum energy of the ¹A' excited state of the noble gas dihydrides, according to the present state-specific SCF calculations. A detailed search of the hypersurface was outside the scope of this study (see the text).

	r(a.u.)	R (a.u.)	ϑ (deg)	SCF Binding energy (eV) (with respect to M(¹ S) + H ₂ (B ¹ Σ _u ⁺))
M = He	4.2	1.4	45	1.1
Ne	4.4	2.1	50	1.1
Ar	4.8	2.6	55	1.0

porting our prediction of a bound ¹A' excited state for the NeH₂^{*} and ArH₂^{*} systems at a geometry near a crossing with the repulsive ground ¹A' state.

We point out that, whereas for the ground repulsive state the total energy varies monotonically with the nuclear repulsion energy, for the excited state this is not the case. As the geometry approaches that of minimum energy, the overlap effects are such that they cause a lowering of the total energy (and binding) independently of the nuclear repulsion energy.

The geometries of minimum energy of the open-shell SCF calculations are presented in Table III. Needless to say, the "exact" geometries need not coincide with those of Table III. However, we expect that the salient features of binding and triangular geometry are correct.

Figure 1 compares our open-shell SCF calculations of

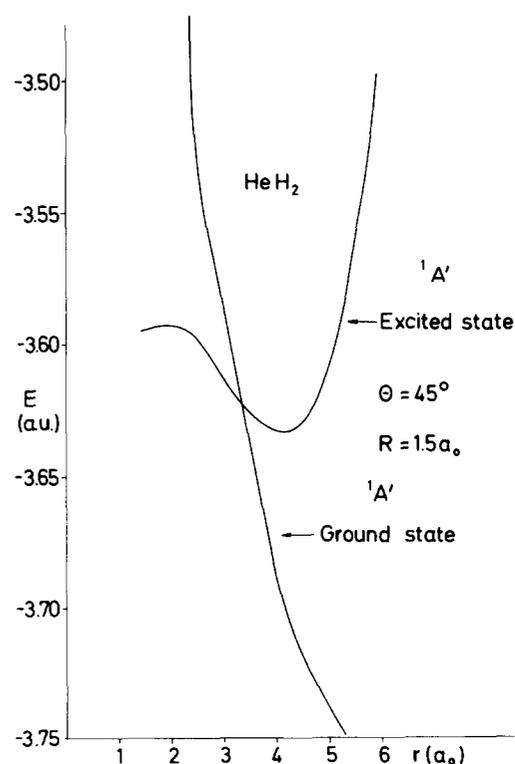


FIG. 2. Diabatic potential energy surfaces for the ground and first excited ¹A' states of HeH₂, as a function of the H-H internuclear distance r, from geometry optimized closed and open-shell SCF calculations. The excited state curve goes through the minimum (Table III).

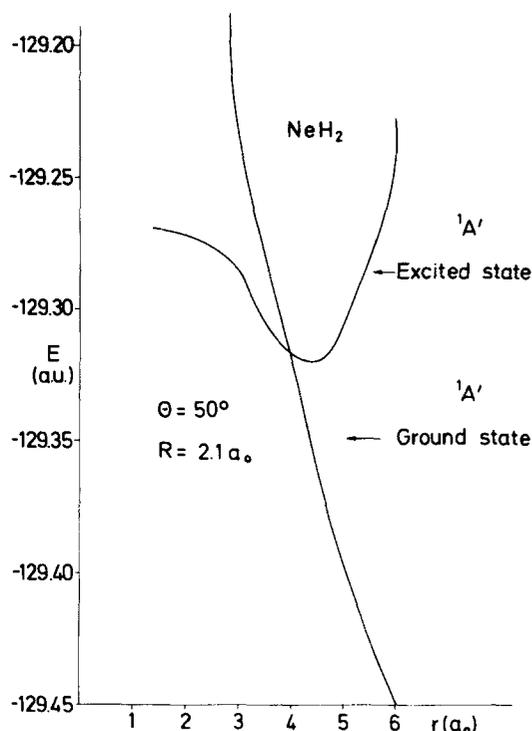


FIG. 3. Diabatic potential energy surfaces for the ground and first excited ${}^1A'$ states of ArH_2 , as a function of the H-H internuclear distance r , from geometry optimized closed and open-shell SCF calculations. The excited state curve goes through the minimum (Table III).

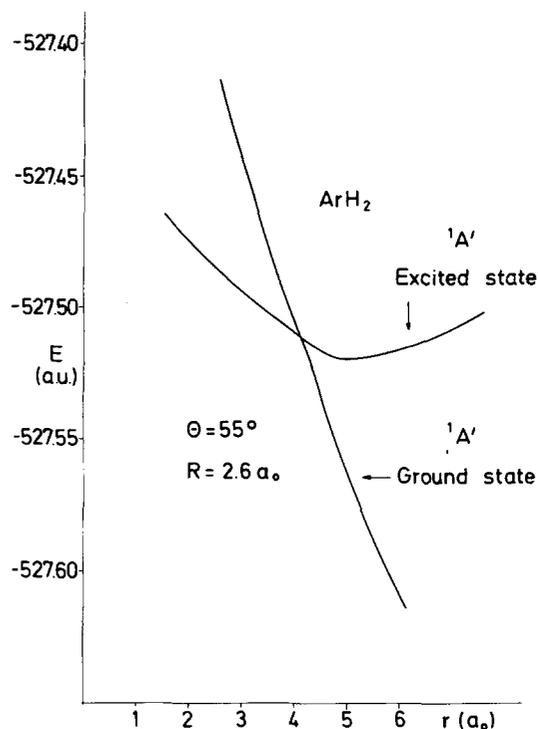


FIG. 4. Diabatic potential energy surfaces for the ground and first excited ${}^1A'$ states of NeH_2 , as a function of the H-H internuclear distance r , from geometry optimized closed and open-shell SCF calculations. The excited state curve goes through the minimum (Table III).

the $\text{H}_2 B^1\Sigma_u^+$ energy surface with the accurate ones of Kołos and Wolniewicz.¹¹ This calculation tested our program and the expectation that, for this state and similar ionic ones, state specific electron correlation effects on the binding and the shape of the potential energy surface for small internuclear distances (and other properties such as the quadrupole moment) are small.

Figures 2–4 depict the diabatic SCF curves, obtained from two separate calculations on the ground and the first excited singlet, as a function of the H-H internuclear distance r and for fixed ϑ and R (see Table III). When configuration–interaction is introduced, the attractive curve is conserved and an avoided crossing appears.⁸ This proximity of the ground and excited state surfaces in HeH_2 has led Farantos *et al.*⁸ to a plausible explanation of the quenching of the $\text{HD } B^1\Sigma_u^+(v'=3) \rightarrow X^1\Sigma_g^+$ fluorescence in the presence of He, observed by Fink *et al.*¹⁸ Our bonding predictions present a critical test of the chemical physics of this energy transfer process: Laser experiments of vibrationally excited $B^1\Sigma_u^+$ colliding with Ne and Ar should also show quenching of $B^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ fluorescence, only that this time this should occur at higher vibrational numbers.

IV. CONCLUSION

When H_2 is excited vibronically to the $B^1\Sigma_u^+$ state, it can react chemically with the closed shell singlet states of the noble gases. This conclusion is based on the results of the large CI calculations on HeH_2^8 and on the analysis and open

shell SCF calculations of this paper. The SCF binding energies are of the order of 1.0 eV at geometries depicted in Table III. In future work, the Landau–Zener model as well as semiclassical collision theory will be applied to predict essential information about the dynamics.⁸

The bonding occurring in HeH_2^* , NeH_2^* , and ArH_2^* has been explained in general electrostatic and overlap terms and a theoretical model was advanced, whereby predictions of stable geometries of excited states of normally nonreactive systems can be made. Thus, it appears that the noble gas dihydrides are only a subset of a class of polyatomic compounds which may have a bound singlet excited state above a repulsive ground state. This class can be defined as involving the chemical binding of a molecular MIES (maximum ionicity excited state) with another atom or molecule, in an overall geometry approximately predicted by the rules of Sec. II.

The proximity of the avoided crossings between the repulsive lower state and the bound excited state,¹⁹ suggests the possibility of a number of stereospecific chemical reactions involving H_2 .

In the accompanying paper⁷ we apply this theory to the four center reaction $\text{H}_2 + \text{H}_2^*$, which can serve as a prototype for a large class of organic photochemical pericyclic $2S + 2S$ processes.²⁰ A strongly bound excited H_4 molecule is predicted at a geometry of trigonal pyramid.

Note added in proof. Using the analysis presented here and in Ref. 7, Nicolaides, Petsalakis, and Theodorakopoulos have now predicted and computed at a large CI level the existence and the geometries of chemically bound singlet excited states in $(\text{H}_2)_3$ and $(\text{H}_2)_5$ clusters.

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