

# Correlation energy difference models for first and second row hydrides\*

P. F. Zittel<sup>†</sup> and W. C. Lineberger<sup>‡</sup>

Department of Chemistry, University of Colorado, Boulder, Colorado 80309  
and Joint Institute for Laboratory Astrophysics, University of Colorado and National Bureau of Standards,  
Boulder, Colorado 80309  
(Received 30 April 1976)

Experimental measurements of electron affinities and intercombination splittings for first- and second-row diatomic hydrides are used with accurate, near Hartree-Fock calculations to determine the change in electron correlation energy ( $\delta E_{\text{corr}}$ ) on negative ion formation and intercombination excitation. Values of  $\delta E_{\text{corr}}$  for the diatomic processes are found to be nearly identical to  $\delta E_{\text{corr}}$  for the analogous united atom and separated atom processes. The results are interpreted in terms of the similarity between the  $\pi$  molecular orbitals of the diatomic and the  $p$  orbitals of the atomic species. The analysis is extended to some triatomic dihydrides for which the relevant experimental and theoretical data are available.

## I. INTRODUCTION

Recent photodetachment experiments<sup>1-7</sup> have provided very accurate determinations of the electron affinities (EA) of most of the first- and second-row diatomic hydrides and of some triatomic dihydrides. Several intercombination energy differences between different low-lying electronic states of these neutrals and negative ions have also been accurately measured. These results, coupled with accurate molecular SCF calculations<sup>8-16</sup> on neutrals and negative ions, make it possible to examine the role of electron correlation energy in negative ion formation and in intercombination splittings between low-lying electronic states.

Models have been proposed for estimating electron correlation energy changes upon addition of an electron to a neutral molecule and for intercombination excitation processes. Cade<sup>8,12</sup> has proposed that correlation energy changes in diatomic hydride processes can be approximated by the correlation energy changes in the analogous united atom (UA), or possibly separated atom (SA), processes. This assumption, coupled with accurate SCF calculations, has led to predictions of electron affinities<sup>8</sup> and intercombination energy differences<sup>12</sup> for first- and second-row diatomic hydrides. Accurate experimental determinations of these EA's and intercombination splittings, together with near Hartree-Fock calculations, make it possible to determine these correlation energy changes "experimentally," and hence to assess the validity of such approximations.

In a few triatomic dihydrides ( $\text{CH}_2$ ,  $\text{NH}_2$ ,  $\text{SiH}_2$ ), where experiments and accurate SCF calculations are available, we are again able to evaluate correlation energy changes for negative ion formation and intercombination excitations. These data enable us to assess the accuracy of separated atom (SA) and united atom (UA) approximations to correlation energy differences. These models will have useful predictive abilities as further near Hartree-Fock molecular calculations are performed.

## II. EXPERIMENTAL AND THEORETICAL BACKGROUND

The total energy of an atom or nonrotating molecule, neglecting spin-orbit interactions, can be written as

the sum of three terms

$$E_{\text{tot}} = E_{\text{SCF}} + E_{\text{corr}} + E_{\text{rel}},$$

where  $E_{\text{SCF}}$  is the large basis set limit of a single-configuration, nonrelativistic, Hartree-Fock calculation;  $E_{\text{rel}}$  is the relativistic energy; and  $E_{\text{corr}}$  is the electron correlation energy, which reflects the failure of the single-configuration SCF procedure to completely describe the nonrelativistic energy. For negative ion formation (e. g.,  $\tilde{X}^3\Sigma^-\text{NH} - \tilde{X}^2\Pi\text{NH}^-$ ), or intercombination excitation (e. g.,  $\tilde{X}^3\Sigma^-\text{NH} - \tilde{a}^1\Delta\text{NH}$ ), one measures the energy difference between final and initial states

$$\delta E_{\text{expt1}} = \delta E_{\text{SCF}} + \delta E_{\text{corr}} + \delta E_{\text{rel}}. \quad (1)$$

In the case of negative ion formation  $\delta E_{\text{expt1}} = -EA$ , and for intercombination excitation  $\delta E_{\text{expt1}}$  is the experimental intercombination energy difference. For electron attachment and intercombination excitation,  $\delta E_{\text{rel}}$  is insignificant<sup>8,12</sup> ( $< 0.001$  hartree, where 1 hartree = 27.2117 eV) compared to the other terms in Eq. (1), so that Eq. (1) reduces to

$$\delta E_{\text{expt1}} = \delta E_{\text{SCF}} + \delta E_{\text{corr}}. \quad (2)$$

For many cases of interest,  $\delta E_{\text{SCF}}$  has been accurately calculated, and one is able to determine directly the value of  $\delta E_{\text{corr}}$  for the electron attachment, or intercombination excitation, process.

## III. NEGATIVE ION FORMATION

### A. Determination of $\delta E_{\text{corr}}$

We have used Eq. (2) with recent experimental measurements of EA and accurate SCF calculations to determine  $\delta E_{\text{corr}}$  for electron addition to most first- and second-row diatomic hydrides. The SCF energies for relevant neutral and ion states are taken from Cade's calculations<sup>8,9</sup> and are estimated to be within 0.001 hartree of the Hartree-Fock limit. The experimental electron affinities correspond to transitions between zero-point vibrational levels, not between potential minima as in the case for the SCF calculations. The correction to the experimental EA's for changes in vibrational zero-point energy is small ( $< 0.015$  eV) and is made in the few cases where it is significant. Since the SCF calculations do not include the

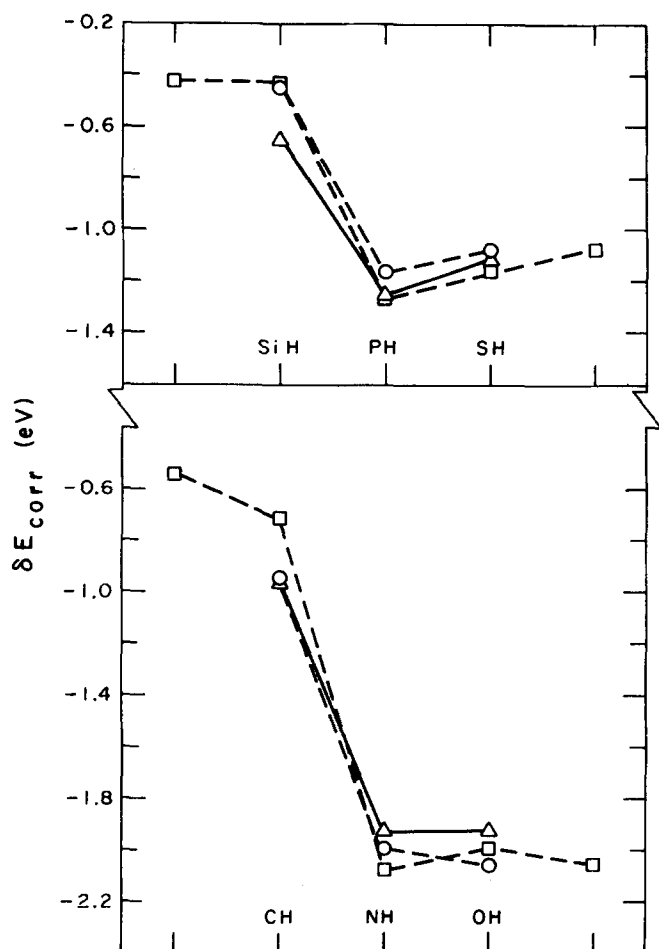


FIG. 1. Electron correlation energy change,  $\delta E_{\text{corr}} = E_{\text{corr}}(\text{ion}) - E_{\text{corr}}(\text{neutral})$ , accompanying the formation of the negative ions from the first- and second-row diatomic hydrides. The results are plotted for the diatomic hydride ( $-\Delta-$ ), corresponding united atom ( $--\square--$ ), and corresponding separated atom ( $\cdots\circ\cdots$ ). For example, the points plotted for OH refer to  $\text{OH}({}^2\Pi) \rightarrow \text{OH}^{-}({}^1\Sigma^+)$  ( $-\Delta-$ ),  $\text{F}({}^2P) \rightarrow \text{F}^{-}({}^1S)$  ( $--\square--$ ), and  $\text{O}({}^3P) \rightarrow \text{O}^{-}({}^2P)$  ( $\cdots\circ\cdots$ ).

spin-orbit coupling, the experimental EA's are also modified to correspond to the energy difference between term centers of gravity. This correction is also small ( $< 0.015$  eV). The resulting values for  $\delta E_{\text{corr}}$  are listed in Table I and are probably accurate to  $\sim 0.05$  eV. The results are also plotted ( $-\Delta-$ ) in Fig. 1.

## B. United atom model

Cade and Huo<sup>17</sup> have demonstrated that the change in electron correlation energy which accompanies the formation of the united atom (UA) from a first- or second-row diatomic hydride (AH) is not a strong function of the atom A within a given row. The argument is extended to imply that  $\delta E_{\text{corr}}$  for the UA formation process is not a strong function of the number of electrons on AH (i. e., is about the same for AH and  $\text{AH}^-$ ). With this assumption one surmises that  $\delta E_{\text{corr}}$  for the negative ion formation process,  $\text{AH} \rightarrow \text{AH}^-$ , is about the same as  $\delta E_{\text{corr}}$  for the atomic process,  $\text{UA}(\text{AH}) \rightarrow \text{UA}(\text{AH}^-)$ .

Very accurate SCF calculations for the relevant neutral and negative ion united atoms, as well as excellent measurements of EA for the atoms, are available.<sup>18,19</sup> Only EA(N) has not been measured, apparently because  $\text{N}^-$  is not stable. We have used Hotop and Lineberger's<sup>19</sup> estimated value of  $\text{EA}(\text{N}) = (-0.07 \pm 0.08)$  eV in the following analysis. As they are for the diatomic hydrides, the atomic EA's are slightly modified to correspond to energy differences between term centers of gravity. Table I lists the values of  $\delta E_{\text{corr}}$  for the UA electron attachment processes which correlate with the diatomic hydride processes. The results are also plotted ( $--\square--$ ) on Fig. 1.

Some question arises as to which state of N should be used as the UA state of  $\text{CH}(\tilde{X}^2\Pi)$ . Both  $\text{N}({}^2P)$  and  $\text{N}({}^2D)$  give rise to  ${}^2\Pi$  states of CH, and since  $E({}^2D) < E({}^2P)$ , the  $\text{N}({}^2D)$  state is the proper adiabatic limit for  $\tilde{X}^2\Pi$  CH. However, in terms of describing electron correlation energy, the  $\text{N}({}^2P)$  state may be a better model for  $\text{CH}(\tilde{X}^2\Pi)$ .  $\text{N}(2s^22p^3)$  and  $\text{CH}(2\sigma^23\sigma^2\pi^1)$  have double-valence-excited configurations,  $\text{N}(2p^5, {}^2P)$  and  $\text{CH}(3\sigma^2\pi^3, {}^2\Pi)$ , which can mix with the  $\text{N}(2s^22p^3, {}^2P)$  and  $\text{CH}(2\sigma^23\sigma^2\pi^1, \tilde{X}^2\Pi)$  configurations, respectively, contributing significantly to  $E_{\text{corr}}$  in both cases. No double-valence-excited configuration of symmetry  ${}^2D$  exists for N, and one might expect a smaller correlation energy for  $\text{N}({}^2D)$  than for  $\text{N}({}^2P)$ . (Indeed one finds<sup>18,20</sup>  $|E_{\text{corr}}(\text{N}, {}^2P)| - |E_{\text{corr}}(\text{N}, {}^2D)| \approx 0.65$  eV.) If one intends

TABLE I. Electron correlation energy change (eV) for diatomic hydride negative ion formation (1 eV  $\approx$  23.06 kcal/mole).

System	$\delta E_{\text{exptl}}^a$ (eV)	$\delta E_{\text{SCF}}^b$ (eV)	$\delta E_{\text{corr}}$ (eV)
AH $\text{CH}(\tilde{X}^2\Pi_u) \rightarrow \text{CH}^{-}(\tilde{X}^3\Sigma^-)$	-1.25	-0.28	-0.97
UA $\text{N}({}^2D) \rightarrow \text{N}^{-}({}^2P)$	-2.31	-0.70	-1.61
UA <sup>c</sup> $\text{N}({}^2P) \rightarrow \text{N}^{-}({}^2P)$	-3.51	-2.55	-0.96
SA $\text{C}({}^3P) \rightarrow \text{C}^{-}({}^4S)$	-1.27	-0.55	-0.72
AH $\text{NH}(\tilde{X}^3\Sigma^-) \rightarrow \text{NH}^{-}(\tilde{X}^2\Pi_i)$	-0.38	+1.55	-1.93
UA $\text{O}({}^3P) \rightarrow \text{O}^{-}({}^2P)$	-1.46	+0.54	-2.00
SA $\text{N}({}^4S) \rightarrow \text{N}^{-}({}^2P)$	+0.07 <sup>d</sup>	+2.15	-2.08
AH $\text{OH}(\tilde{X}^2\Pi_i) \rightarrow \text{OH}^{-}(\tilde{X}^1\Sigma^+)$	-1.83	+0.10	-1.93
UA $\text{F}({}^2P) \rightarrow \text{F}^{-}({}^1S)$	-3.42	-1.36	-2.06
SA $\text{O}({}^3P) \rightarrow \text{O}^{-}({}^2P)$	-1.46	+0.54	-2.00
AH $\text{SiH}(\tilde{X}^2\Pi_u) \rightarrow \text{SiH}^{-}(\tilde{X}^3\Sigma^-)$	-1.29	-0.64	-0.65
UA $\text{P}({}^2D) \rightarrow \text{P}^{-}({}^3P)$	-2.14	-1.36	-0.78
UA <sup>c</sup> $\text{P}({}^2P) \rightarrow \text{P}^{-}({}^3P)$	-3.05	-2.60	-0.45
SA $\text{Si}({}^3P) \rightarrow \text{Si}^{-}({}^4S)$	-1.40	-0.96	-0.44
AH $\text{PH}(\tilde{X}^3\Sigma^-) \rightarrow \text{PH}^{-}(\tilde{X}^2\Pi_i)$	-1.02	+0.23	-1.25
UA $\text{S}({}^3P) \rightarrow \text{S}^{-}({}^2P)$	-2.08	-0.91	-1.17
SA $\text{P}({}^4S) \rightarrow \text{P}^{-}({}^3P)$	-0.73	+0.54	-1.27
AH $\text{SH}(\tilde{X}^2\Pi_i) \rightarrow \text{SH}^{-}(\tilde{X}^1\Sigma^+)$	-2.33	-1.21	-1.12
UA $\text{Cl}({}^2P) \rightarrow \text{Cl}^{-}({}^1S)$	-3.65	-2.57	-1.08
SA $\text{S}({}^3P) \rightarrow \text{S}^{-}({}^2P)$	-2.08	-0.91	-1.17

<sup>a</sup>Since the calculated values of  $\delta E_{\text{SCF}}$  do not include spin-orbit coupling,  $\delta E_{\text{exptl}}$  is modified to correspond to the energy difference between term centers of gravity. A small correction for the change in zero-point vibrational energy is also made. Data are from Refs. 1-5, 19, and 20.

<sup>b</sup>References 8, 9, and 18.

<sup>c</sup>Alternate choice for UA limit is explained in text.

<sup>d</sup>Value of  $-\text{EA}(\text{N})$  is extrapolated result given in Ref. 19.

to compare the adequacy of the one-configuration SCF calculation for  $\text{CH}(\tilde{X}^2\Pi)$  to the adequacy of the one-configuration SCF calculation for the UA state of N, the  $\text{N}(^2P)$  state is a better choice than the  $\text{N}(^2D)$  state. The value of  $\delta E_{\text{corr}}$  is listed in Table I for both UA processes. The value of  $\delta E_{\text{corr}}$  resulting from the  $\text{N}(^2P)$  united atom limit for  $\text{CH}(\tilde{X}^2\Pi)$  is plotted in Fig. 1 and agrees very well with  $\delta E_{\text{corr}}$  for the diatomic hydride. The value of  $\delta E_{\text{corr}}$  obtained with the  $\text{N}(^2D)$  united atom limit is smaller by  $-0.65$  eV and in poorer agreement. These arguments apply analogously to the  $\tilde{X}^2\Pi$  SiH state and the  $\text{P}(^2D, ^2P)$  united atom limits.  $\delta E_{\text{corr}}$  for the  $\text{P}(^2P)$  limit is plotted in Fig. 1 and agrees with the diatomic result about as well as does  $\delta E_{\text{corr}}$  for the  $\text{P}(^2D)$  limit, which is smaller by  $-0.33$  eV.

Before discussing the similarity of the UA and diatomic results and examining the dependence of  $\delta E_{\text{corr}}$  on the nature of atom A, the analogous separated atom electron attachment processes will be considered.

### C. Separated atom model

The electron attachment processes for the diatomic hydrides considered here involve the addition of an electron to a  $1\pi$  (or  $2\pi$ ) molecular orbital. It has been demonstrated that the  $\pi$  orbital for these hydrides is not strongly bonding and is essentially an atomic  $p$  orbital, centered on the heavy atom. The small differences<sup>1-4</sup> in equilibrium internuclear separation and vibrational frequency between neutral and negative ion molecules confirm the nonbonding nature of the  $\pi$  orbital, and a recent determination<sup>21</sup> of the hyperfine coupling constant for  $\tilde{a}^1\Delta$  PH has led to the conclusion that the PH  $2\pi$  orbital is essentially a phosphorous  $3p$  atomic orbital. In addition, the electron affinities of the diatomic hydrides are in each case comparable to the electron affinities of the separated heavy atom. These facts suggest that the separated atom, A, may be a good model for estimating electron correlation energy changes for the diatomic, AH.

The SA states of  $\text{A}(\text{A}^-)$  which correlate with the diatomic,  $\text{AH}(\text{AH}^-)$ , are listed in Table I with the values of  $\delta E_{\text{corr}}$  calculated with Eq. (2). The results are also plotted (---□---) in Fig. 1.

### D. Discussion of diatomic results

As Fig. 1 shows, the change in electron correlation energy associated with negative ion formation from a first- or second-row diatomic hydride is nearly identical to the change associated with the analogous united atom, or separated atom, process. The strong correspondence is attributed to the basically atomic nature of the attached  $\pi$  electron and to the concurrent small geometry change between neutral and negative ion molecules. The small geometry change suggests that the occupied molecular orbitals which are not involved in the electron attachment process are quite similar for neutral and ion. Thus, the dominant contribution to  $\delta E_{\text{corr}}$  comes from the addition of correlation energy between the attached electron and the residual electrons and not from correlation changes among the re-

sidual electrons.

Figure 1 indicates that there is a significant difference ( $\sim 0.8$  eV) in the values of  $\delta E_{\text{corr}}$  for formation of  $\text{NH}^-$  and  $\text{OH}^-$  compared to the value for  $\text{CH}^-$ . The same is true for the analogous second-row hydrides and analogous united and separated atoms. The configurations of NH and OH are  $(\dots \pi^2)$  and  $(\dots \pi^3)$ , respectively, and electron attachment places an electron into an already singly occupied component of the doubly degenerate  $\pi$  orbital. The correlation energy between the electrons of a doubly occupied orbital should be significant, and a large value for  $\delta E_{\text{corr}}$  upon forming a doubly occupied orbital is expected. The configuration of CH is  $(\dots \pi^1)$ . Adding an electron does not produce a doubly occupied orbital, and  $\delta E_{\text{corr}}$  should not be as large as it is for the former case. The arguments for the UA and SA cases are analogous, as well as for the isovalent second-row diatomics and atoms. The values<sup>18,19</sup> of  $\delta E_{\text{corr}}$  for the additional negative ion formation processes,  $\text{F}(^2P) - \text{F}^-(^1S)$ ,  $\text{B}(^2P) - \text{B}^-(^3P)$  and the analogous second-row atoms, have been included on the SA curve in Fig. 1 to indicate that the preceding argument extends to the other  $s^2p^n$  atoms. ( $\text{Be}^-$  and  $\text{Mg}^-$  with configuration  $s^2p$  are not stable, and an accurate  $\delta E_{\text{corr}}$  is not available for those electron attachment processes.)

### E. Extension to triatomic dihydrides

The comparison of  $\delta E_{\text{corr}}$  for diatomic hydride electron attachment processes to  $\delta E_{\text{corr}}$  for the analogous atomic processes may reasonably be extended to triatomic dihydrides ( $\text{AH}_2$ ), in which the additional electron enters a molecular orbital which is essentially an atomic orbital centered on atom A. Among the first- and second-row triatomics, the experimental EA and near Hartree-Fock energies of neutral and negative ion are available only for  $\text{NH}_2$ . The attachment process is  $\text{NH}_2(^2B_1) \rightarrow \text{NH}_2(^1A_1)$  with  $\text{EA} = 0.78$  eV.<sup>1</sup> The additional electron enters an already singly occupied  $b_1$  molecular orbital, which is essentially a nitrogen  $2p$  orbital out of the plane of the molecule. The geometries of neutral and ion are nearly identical, according to experiment<sup>1</sup> and calculation,<sup>10,11</sup> in agreement with the picture of the  $b_1$  orbital as essentially nonbonding. The SCF energies of neutral ( $-55.5757$  hartree)<sup>10</sup> and ion ( $-55.5210$  hartree)<sup>11</sup> have been calculated and are estimated to be  $< 0.02$  hartree above the Hartree-Fock limit. Equation (2) gives  $\delta E_{\text{corr}} = (-2.27 \pm 0.54)$  eV for the attachment process, where the error limits include the errors both in  $\text{EA}(\text{NH}_2)$  and  $\delta E_{\text{SCF}}$ . The result compares well with  $\delta E_{\text{corr}}$  for the SA process [ $\text{N}(^4S) - \text{N}^-(^3P)$ ,  $\delta E_{\text{corr}} = -2.08$  eV], and for the UA process [ $\text{F}(^2P) - \text{F}^-(^1S)$ ,  $\delta E_{\text{corr}} = -2.06$  eV].

It would be interesting to extend this comparison to the negative ion formation processes,  $\text{CH}_2(^1A_1) \rightarrow \text{CH}_2(^2B_1)$  and  $\text{SiH}_2(^1A_1) \rightarrow \text{SiH}_2(^2B_1)$ . These attachment processes involve the addition of an electron to an unoccupied  $b_1$  molecular orbital with little change in molecular geometry<sup>6</sup> and should correspond to SA and UA processes about as well as does the  $\text{NH}_2$  result. In both cases the attachment energy is known,<sup>3,6</sup> and accurate SCF calculations are available<sup>15</sup> for the neutral  $^1A_1$  state.

TABLE II. Electron correlation energy change (eV) for diatomic hydride intercombination excitation (1 eV  $\approx$  23.06 kcal/mole).

System	$\delta E_{\text{expt1}}$ <sup>a</sup> (eV)	$\delta E_{\text{SCF}}$ <sup>b</sup> (eV)	$\delta E_{\text{corr}}$ (eV)
AH NH( $\bar{X}^3\Sigma^- \rightarrow \bar{a}^1\Delta$ )	1.56	1.83	-0.27
UA O( $^3P \rightarrow ^1D$ )	1.96	2.18	-0.22
SA N( $^4S \rightarrow ^2D$ )	2.38	2.85	-0.47
AH NH( $\bar{a}^1\Delta \rightarrow \bar{b}^1\Sigma^+$ )	1.05	1.74	-0.69
UA O( $^1D \rightarrow ^1S$ )	2.22	3.22	-1.00
SA N( $^2D \rightarrow ^2P$ )	1.19	1.85	-0.66
AH PH( $\bar{X}^3\Sigma^- \rightarrow \bar{a}^1\Delta$ )	0.95	1.25	-0.30
UA S( $^3P \rightarrow ^1D$ )	1.12	1.45	-0.33
SA P( $^4S \rightarrow ^2D$ )	1.41	1.90	-0.49
AH CH( $\bar{X}^2\Pi \rightarrow \bar{a}^4\Sigma^-$ )	0.72	-0.28	1.00
UA N( $^2D \rightarrow ^4S$ )	-2.38	-2.85	0.47
UA <sup>c</sup> N( $^2P \rightarrow ^4S$ )	-3.58	-4.70	1.12
SA C( $^6P \rightarrow ^3P$ )	0	0	0

<sup>a</sup>Since the calculated values of  $\delta E_{\text{SCF}}$  do not include spin-orbit coupling,  $\delta E_{\text{expt1}}$  is modified to correspond to the energy difference between term centers of gravity. A small correction for the change in zero-point vibrational energy is also made. Experimental results are from Refs. 2, 4, 7, 20, and 24.

<sup>b</sup>References 12-14 and 18.

<sup>c</sup>Alternate choice for UA limit is explained in text.

Unfortunately, SCF calculations have not been made for the negative ion states.

It would also be interesting to extend this kind of comparison to the ( $^2A_2'$ SiH<sub>3</sub> -  $^1A_1'$ SiH<sub>3</sub>) and ( $^2A_2'$ CH<sub>3</sub> -  $^1A_1'$ CH<sub>3</sub>) electron attachment processes to determine whether the  $a_2'$  molecular orbital may be treated like an atomic  $p_z$  orbital. In both cases, the  $a_2'$  orbital apparently has bonding character, and geometry changes may accompany the attachment process.<sup>22,23</sup> Unfortunately, the SCF calculations for SiH<sub>3</sub> and SiH<sub>3</sub><sup>-</sup> are probably not sufficiently accurate, and EA(CH<sub>3</sub>) has not been determined.

## IV. INTERCOMBINATION SPLITTING RESULTS

### A. Diatomic hydrides

Recent measurements of intercombination energy splittings in NH<sup>7,24</sup> and PH,<sup>4</sup> coupled with accurate SCF calculations<sup>12,13</sup> for the relevant electronic states, make it possible to directly evaluate the difference in electron correlation energy between different electronic states of the same ground electronic configuration. Table II lists the experimental energy splittings, SCF splittings, and electron correlation energy differences calculated with Eq. (2) for states of NH and PH.

The low lying  $^3\Sigma^-$ ,  $^1\Delta$ , and  $^1\Sigma^+$  states of PH and NH arise from the  $\pi^2$  ground electronic configuration and have nearly identical equilibrium internuclear separations for a particular molecule. Since the diatomic hydride  $\pi$  orbitals are essentially the heavy atom  $p$  orbitals, one might expect the difference in correlation energy between the states to be similar to the difference between analogous states of the united, or possibly separated atoms. Cade<sup>12</sup> has suggested that the corre-

lation energy change accompanying the formation of the UA from the diatomic is independent of the electronic state of a particular configuration of the diatomic, and this assumption implies that  $\delta E_{\text{corr}}(\text{AH}) \approx \delta E_{\text{corr}}(\text{UA})$  for the analogous intercombination splittings. The values of  $\delta E_{\text{corr}}$  for the analogous UA and SA splittings are presented in Table II.

The  $\bar{a}^4\Sigma^-$  state of CH requires the excitation of a  $3\sigma$  bonding electron into a  $1\pi$  orbital and in this respect is different from the preceding cases. The equilibrium internuclear separations of ground and excited states are, however, nearly identical, according to calculations<sup>13,14</sup> and experiment.<sup>2</sup> The choice of the appropriate UA limit for  $\bar{X}^2\Pi$  CH is slightly ambiguous. The proper adiabatic limit is, of course, N( $^2D$ ). The alternate choice of N( $^2P$ ) for the UA limit was explained in Sec. IIIB and is considered because N( $^2P$ ) and  $\bar{X}^2\Pi$  CH are equivalent in terms of the number of double-valence-excited configurations which can contribute to  $E_{\text{corr}}$ . Values of  $\delta E_{\text{corr}}$  for both UA limits are listed in Table II, and the value for the N( $^2P$ ) limit agrees best with  $\delta E_{\text{corr}}(\text{AH})$ , as it did for the negative ion formation process (Sec. IIIC).

As Table II indicates, the values of  $\delta E_{\text{corr}}$  for the united atom intercombination splittings are quite close to the diatomic hydride results and generally in better agreement than the SA results. The one exception is NH( $\bar{a}^1\Delta \rightarrow \bar{b}^1\Sigma^+$ ). The reason for the poor agreement in this case is not qualitatively obvious. An SCF energy for NH( $\bar{b}^1\Sigma^+$ ) which is lower by 0.010 hartree would bring diatomic and UA results into agreement.

### B. Extension to triatomic dihydrides

We have extended this comparison to splittings between the low-lying electronic states of CH<sub>2</sub> and SiH<sub>2</sub>. Accurate SCF calculations for the  $^3B_1$  and  $^1A_1$  states of CH<sub>2</sub> and SiH<sub>2</sub> have been made,<sup>15</sup> and the energy splittings have now been measured.<sup>3,6</sup> The resulting values of  $\delta E_{\text{corr}}$  for the singlet-triplet intercombination splittings appear in Table III. Less accurate SCF calculations are available<sup>16</sup> for the  $^1B_1$  state of CH<sub>2</sub>, and we have determined the value of  $\delta E_{\text{SCF}}(^3B_1\text{CH}_2 - ^1B_1\text{CH}_2)$  using the  $^1B_1$  and  $^3B_1$  results of this calculation for the sake of consistency. The experimental ( $^3B_1 - ^1B_1$ ) energy splitting is the sum of the separately measured ( $^3B_1 - ^1A_1$ )<sup>6</sup> and ( $^1A_1 - ^1B_1$ )<sup>25</sup> splittings. The resulting value for  $\delta E_{\text{corr}}(^3B_1\text{CH}_2 - ^1B_1\text{CH}_2)$  appears in Table III.

Table III also contains the values of  $\delta E_{\text{corr}}$  for the splittings in the united atoms O and S, analogous to the CH<sub>2</sub> and SiH<sub>2</sub> splittings. The agreement between triatomic and UA values is good in spite of the fact that the ( $^3B_1 - ^1A_1$ ) excitation involves a bonding  $a_1$  molecular orbital which is not completely analogous to an atomic  $p$  orbital. The excitation also involves a significant geometry change,<sup>6</sup> although the dependence of  $E_{\text{corr}}$  on bond angle may not be strong for these molecules.<sup>26</sup>

## V. CONCLUSION

We have found that the united atom model for estimating electron correlation energy changes is an ex-

TABLE III. Electron correlation energy differences (eV) for triatomic intercombination splittings (1 eV  $\cong$  23.06 kcal/mole).

System	$\delta E_{\text{exptl}}^a$ (eV)	$\delta E_{\text{SCF}}^b$ (eV)	$\delta E_{\text{corr}}$ (eV)
AH <sub>2</sub> CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> → <sup>1</sup> A <sub>1</sub> )	0.84	1.08	-0.24
UA O( <sup>3</sup> P → <sup>1</sup> D)	1.96	2.18	-0.22
AH <sub>2</sub> CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> → <sup>1</sup> B <sub>1</sub> )	1.71	1.86	-0.15
UA O( <sup>3</sup> P → <sup>1</sup> D)	1.96	2.18	-0.22
AH <sub>2</sub> SiH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> → <sup>3</sup> B <sub>1</sub> )	$\leq$ 0.60	0.23	$\leq$ 0.37
UA S( <sup>1</sup> D → <sup>3</sup> P)	-1.12	-1.45	0.33

<sup>a</sup>Modified to correspond to energy differences between term centers-of-gravity. Results from Refs. 3, 6, and 25.

<sup>b</sup>References 15 and 16.

cellent approximation for the following processes:

(1) Negative ion formation from the first- and second-row diatomic hydrides.

(2) Intercombination excitations of the first- and second-row diatomic hydrides.

(3) Negative ion formation and intercombination excitation for some first- and second-row triatomic dihydrides, where the processes involve atomiclike molecular orbitals.

In case (1) the separated atom model is equally good, but in cases (2) and (3) it is less accurate and more ambiguous to apply.

As more experimental and theoretical data become available, these models should be tested for other triatomic and tetraatomic hydrides. Particularly for diatomic hydrides, these models for  $\delta E_{\text{corr}}$ , together with accurate SCF calculations, should be useful for predicting electron affinities and intercombination splittings which have not yet been measured.

#### ACKNOWLEDGMENT

We are very grateful to Dr. S. V. O'Neil for numerous helpful discussions.

\*Supported by the National Science Foundation through Grants MPS72-05169 and MPS75-01565.

<sup>†</sup>Present address: Chemistry and Physics Laboratory, The Aerospace Corp., P. O. Box 92957, Los Angeles, CA 90009.

<sup>‡</sup>Camille and Henry Dreyfus Teacher-Scholar.

<sup>1</sup>R. J. Celotta, R. A. Bennett, and J. L. Hall, *J. Chem. Phys.* **60**, 1740 (1974).

<sup>2</sup>A. Kasdan, E. Herbst, and W. C. Lineberger, *Chem. Phys. Lett.* **31**, 78 (1975).

<sup>3</sup>A. Kasdan, E. Herbst, and W. C. Lineberger, *J. Chem. Phys.* **62**, 541 (1975).

<sup>4</sup>P. F. Zittel and W. C. Lineberger, *J. Chem. Phys.* **65**, 1236 (1976).

<sup>5</sup>B. Steiner, *J. Chem. Phys.* **49**, 5097 (1968).

<sup>6</sup>P. F. Zittel, G. B. Ellison, S. V. O'Neil, E. Herbst, W. C. Lineberger, and W. P. Reinhardt, *J. Am. Chem. Soc.* **98**, 3731 (1976).

<sup>7</sup>P. C. Engelking and W. C. Lineberger, *J. Chem. Phys.* (in press).

<sup>8</sup>P. E. Cade, *Proc. Phys. Soc. London* **91**, 842 (1967); P. E. Cade, *J. Chem. Phys.* **47**, 2390 (1967).

<sup>9</sup>P. E. Cade and W. M. Huo, *At. Data Nucl. Data Tables* **12**, 415 (1973).

<sup>10</sup>C. F. Bender and H. F. Schaefer III, *J. Chem. Phys.* **55**, 4798 (1971).

<sup>11</sup>M. A. Robb and I. G. Csizmadia, *Int. J. Quantum. Chem.* **5**, 605 (1971).

<sup>12</sup>P. E. Cade, *Can. J. Phys.* **46**, 1989 (1968).

<sup>13</sup>W. M. Huo, *J. Chem. Phys.* **49**, 1482 (1968).

<sup>14</sup>G. C. Lie, J. Hinze, and B. Liu, *J. Chem. Phys.* **57**, 625 (1972).

<sup>15</sup>J. H. Meadows and H. F. Schaefer III, *J. Am. Chem. Soc.* **98**, 4383 (1976).

<sup>16</sup>S. V. O'Neil, H. F. Schaefer III, and C. F. Bender, *J. Chem. Phys.* **55**, 162 (1971).

<sup>17</sup>P. E. Cade and W. M. Huo, *J. Chem. Phys.* **47**, 614 and 649 (1967).

<sup>18</sup>E. Clementi, *Tables of Atomic Functions* (IBM Corp., San Jose, 1965); E. Clementi and C. Roetti, *At. Data Nucl. Data Tables* **14**, 117 (1974).

<sup>19</sup>H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data* **4**, 539 (1975).

<sup>20</sup>C. E. Moore, *Natl. Bur. Stand. (U.S.) Circ.* **467**, Vol. 1 (1948).

<sup>21</sup>P. B. Davies, D. K. Russell, and B. A. Thrush, *Chem. Phys. Lett.* **36**, 280 (1975).

<sup>22</sup>F. Driessler, R. Alrichs, V. Staemmler, and W. Kutzelnigg, *Theor. Chim. Acta* **30**, 315 (1973).

<sup>23</sup>B. Wirsam, *Chem. Phys. Lett.* **18**, 578 (1973).

<sup>24</sup>A. Gilles, J. Masanet, and C. Vermeil, *Chem. Phys. Lett.* **25**, 346 (1974).

<sup>25</sup>G. Herzberg and J. W. C. Johns, *Proc. R. Soc. London Ser. A* **295**, 707 (1966).

<sup>26</sup>V. Staemmler, *Theor. Chim. Acta.* **31**, 49 (1973).