Theor Chim Acta (1985) 68: 69-86

THEORETICA CHIMICA ACTA

Chemical binding and electron correlation in diatomic molecules as described by the FORS model and the FORS-IACC model

Michael W. Schmidt*, **M. T. Brenda Lam****, **Stephen T. Elbert, Klaus Ruedenberg**

Ames Laboratory USDOE and Department of Chemistry Iowa State University, Ames, IA 50011, USA

(Received February 1, 1985)

Using the model of the Full Optimized Reaction Space including the Intra-Atomic Correlation Correction, binding energies and other electronic properties have been calculated for several states of a number of diatomic molecules. In most cases this theoretical approach yields results agreeing with experimental values to within 0.2 eV. The investigation covers the molecules BH, CH, NH, OH, FH, N_2, O_2, F_2.

Key words: Electron correlation — Atoms in molecules — FORS/CASSGF — Diatomic molecules — Dissociation curves — Spectra — Dipole moments

1. Introduction

In preceding papers the basic principles and the mathematical formulations of the FORS model [1] and the FORS IACC model [2] for molecular calculations were outlined. While the former is expected to recover non-dynamical degeneracy-type correlation energy changes, the latter is expected to recover certain dynamical correlation energy changes that occur along paths of chemical reactions. The FORS model, as used here, represents the best wavefunction that is possible when *all configurations or valence bond structures in the full valence space are taken into account and when, in addition, all orbitals are fully optimized* in the molecule. The FORS IACC model determines corrections to this wavefunction and its energy that are obtained by a method which represents a further development of

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* *Present address*: Department of Chemistry, North Dakota State University, Fargo, ND, 58105

** *Present address*: Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4 the "Atoms-in-Molecule" and the "Intra-Atomic-Correlation-Correction" approaches of Moffit and Hurley [3].

During the formation of diatomic molecules there occur extensive rearrangements of the electronic structures of the combining atoms and, for this reason, the theoretical reproduction of diatomic dissociation curves presents one of the more severe tests of any electronic structure theory's ability to predict quantitatively energy changes that occur during chemical reactions. Moreover, extensive and accurate experimental information is available for diatomic molecules[4], so that the actual performance of any theory can be assessed without any ambiguity.

In the present investigation we report the results of applying the aforementioned two models to the calculation of binding energies and dissociation curves for a number of states in a series of diatomic molecules. Considering the conceptual and operational simplicity of these models, their quantitative performance is gratifying.

2. Basis sets

In order to test the effectiveness of the proposed models in a credible fashion, it is essential that any errors associated with the limitation of the basis set be

Table 1. Basis sets and basis set errors in SCF calculations of atoms and diatomic molecules

Molecule	Atomic basis set[a]	Atomic error[b] (mh)	Polarization function[c]	Molecular error[d] (mh)
		Homonuclear molecules		
H_2	$10s3p1d/5s3p1d$	0.005	$\zeta_p = 0.3, 1.3, 5.4$ $\zeta_d = 1.96$	0.015
H_2	$6s2p/3s2p$	0.16	$\zeta_p = 0.4, 1.6$	0.54
Li_2	$12s3p1d/6s3p1d$	0.16	$\zeta_p = 0.0678, 0.264, 1.03$ $\zeta_d = 0.275$	0.3
B_2	$14s7p2d/4s3p2d$	0.16	$\zeta_d = 0.145, 0.913$	3.5
C_2	$14s7p2d/4s3p2d$	0.32	$\zeta_d = 0.2, 1.0$	4.7
N_2	$14s7p2d/5s3p2d$	0.57	$\zeta_d = 0.2, 1.0$	7.5
O_2	$14s7p2d/4s3p2d$	0.98	$\zeta_d = 0.5, 1.6$	7.9
F2	$14s7p2d/4s3p2d$	1.57	$\zeta_d = 0.5, 1.6$	6.0

Molecular error in heteronuclear molecules (mh)

NO[e,f]	5.9	CN[e]	4.0	NH[g]	2.27
CO[e]	6.3	BH[g]	0.48	OH[g]	2.06
BO[e]	−1.1	CH[g]	0.78	FH[g]	3.66

[a] Even-tempered gaussian basis of Reference [5]

[b] Error of SCF calculation with respect to the exact Hartree-Fock limit for the ground states. See Reference [5]

[c] See Reference [6]

[d] Error of SCF calculation with respect to SCF calculation with extensive exponential basis set for molecular ground states.

[e] Basis set as above

[f] Basis set for NO is $14s7p2d/5s3p2d$ for both atoms

[g] Basis set on hydrogen for all hydrides cited is the $6s2p/3s2p$ set

smaller than those errors for which the model is to be held responsible. For this reason, very large atomic basis sets were employed in the present calculations, typically a 14*s*, 7*p*, 2*d* eventempered gaussian primitive set [5] contracted in Raffenetti-fashion [6] to a 5*s*, 3*p*, 2*d* basis, which corresponds to a basis of "triple zeta plus double polarization" or better quality. In Table 1 there are listed the basis sets for the various atoms and their performance in atomic and molecular SCF calculations. The intra-atomic error increases from 0.1 millihartree in Li to 1.6 millihartree in F. It is safe to assume that with this accuracy, basis set superposition errors leading to fortuitously good binding energies will be negligible. The moledular errors increase from 0.3 millihartree in Li_2 to about 8 millihartree in O_2. They are due to omission of *f* polarization orbitals and, perhaps, to insufficient optimization of *d*-orbitals.

3. FORS calculations

The calculations reported here pertain to the ground states of diatomic molecules at their experimental equilibrium distances. The theoretical minimum of SCF calculations often occurs at slightly smaller distances, whereas FORS calculations often yield slightly elongated bonds. In either case, the calculated dissociation energies would increase only insignificantly by geometry optimization.

All atoms, except hydrogen, contribute two doubly filled core orbitals, namely the 1s AO's, and four reactive CGO's (configuration generating orbitals)

Table 2. Characterization of full reaction space of ground state of some diatomic molecules

Molecule	Symmetry	Equilibrium distance (bohr)	No. of SAAPs[a]	States of separated atoms
		Homonuclear molecules		
H_2	$^1\Sigma_g^+$	1.4	2	$^2S+^2S$
Li_2	$^1\Sigma_g^+$	5.07	8	$^2S+^2S$
B_2	$^3\Sigma_g^-$	3.0905	136	$^2P+^2P$
C_2	$^1\Sigma_g^+$	2.3897	264	$^3P+^3P$
N_2	$^1\Sigma_g^+$	2.068	176	$^4S+^4S$
O_2	$^3\Sigma_g^-$	2.2817	44	$^3P+^3P$
F_2	$^1\Sigma_g^+$	2.68	8	$^2P+^2P$
		Heteronuclear molecules		
CN	$^2\Sigma^+$	2.2144	616	$^3P+^4S$
BO	$^2\Sigma^+$	2.2977	616	$^2P+^3P$
CO	$^1\Sigma^+$	2.132	316	$^3P+^3P$
NO	$^2\Pi$	2.1747	252	$^4S+^3P$
		Hydrides		
BH	$^1\Sigma^+$	2.3289	19	$^2P+^2S$
CH	$^2\Pi$	2.1163	18	$^3P+^2S$
NH	$^3\Sigma^-$	2.0	9	$^4S+^2S$
OH	$^2\Pi$	1.8324	10	$^3P+^2S$
FH	$^1\Sigma^+$	1.7325	8	$^2P+^2S$

[a] In terms of symmetry adapted molecular orbitals

namely 2*s*, 2*px*, 2*py*, 2*pz*. The number of configurations obtained by allowing for all possible couplings between the CGO's in a molecule, i.e. the dimension of the full valence space, depends upon the number of electrons. It is largest when there are about as many electrons as there are orbitals.

In Table 2 there are listed various data for the molecules considered which are pertinent to the reported calculations, namely the symmetry of the molecular ground-state, the symmetries of the ground states of the separated atoms, the internuclear equilibrium distances and the dimension of the full reaction space. The numbers listed for this dimension are actually the number of spin-adapted antisymmetrized products (SAAP's) which constitute the practical basis of our calculational procedure. It is possible to form certain linear combinations with *fixed* coefficients of these SAAP's with incompletely filled π-shells, yielding configuration state functions (CSF's) which belong to the appropriate irreducible representations of $C_{\infty v}$ or $D_{\infty h}$. The number of such configuration state functions with independently variable coefficients is often smaller than the number of SAAP's listed.

The calculations were performed with the ALIS system for molecular calculations [7a]. The generation of the Full Reaction Space is accomplished by a program

Table 3. Total energies from SCF and FORS calculations

	Energies (in hartrees)			
	Molecule		Atom	
Molecule	SCF	FORS	SCF	FORS
		Homonuclear molecules		
H_2[a]	−1.1336	−1.1521	−0.5	−0.5
H_2[b]	−1.1331	−1.1514	−0.4998	−0.4998
Li_2	−14.8712	−14.9006	−7.4326	−7.4326
B_2	−49.0874	−49.2180	−24.5289	−24.5601
C_2	−75.4015	−75.6373	−37.6883	−37.7056
N_2	−108.9853	−109.1345	−54.4004	−54.4004
O_2	−149.6575	−149.7627	−74.8084	−74.8084
F_2	−198.7641	−198.8444	−99.4078	−99.4078
		Heteronuclear molecules		
CN	−92.2192	−92.3708	see above	
BO	−99.5566	−99.6782	see above	
CO	−112.7829	−112.9144	see above	
NO	−129.2894	−129.4055	see above	
		Hydrides		
BH	−25.1309	−25.1858	see above	
CH	−38.2786	−38.3135	see above	
NH	−54.9756	−55.0026	see above	
OH	−75.4188	−75.4432	see above	
FH	−100.0666	−100.0909	see above	

[a] Basis set is 10*s*3*p*1*d*/5*s*3*p*1*d*

[b] Basis set is 6*s*2*p*/3*s*2*p*

called SAAP which is described elsewhere [7b]. The resulting quantitative data are listed in Table 3, namely the SCF and FORS energies for the molecules and the separated atoms. The atomic FORS energies differ from the SCF energies in boron and carbon, because the ground states of these two atoms involve FORS configuration interactions: s^2p and p^3 in B, s^2p^2 and p^4 in C.

From the data in Table 3 one deduces the binding energies listed in Table 4. An appropriate measure of the effectiveness of the FORS model is the fraction of the correlation contribution to the binding energy which is recovered by the model, as defined by

$$\{\Delta E(\text{FORS})-\Delta E(\text{SCF})\}/\{\Delta E(\text{exp})-\Delta E(\text{SCF})\},$$

where $\Delta E = E(\text{molecule}) - E(\text{separated atoms})$ is the binding energy. It is seen that the FORS model recovers between 70% and 95% of the correlation error. By and large, the model is more effective when the number of valence electrons is smaller than the number of valence orbitals. In absolute values the remaining error lies between 5 and 30 kcal/mole. This is larger than the 2-5 kcal error attributable to basis set deficiencies and it is still larger than the accuracy desired

Table 4. Dissociation energies from FORS calculations

Molecule	SCF (eV)	FORS (eV)	exp[a] (eV)	Correlation recovered (%)	Error of FORS approximation (Kcal/mole)
Homonuclear molecules					
H_2[b]	3.635	4.14	4.748	45	14.1
H_2[c]	3.629	4.13	4.748	45	14.3
Li_2	0.16	0.96	1.068	88	2.5
B_2	0.81	2.64	3.08	81	10.1
C_2	0.68	6.14	6.32	97	4.1
N_2	5.02	9.06	9.905	83	19.5
O_2	1.12	3.98	5.213	70	28.4
F_2	−1.40	0.78	1.658	71	20.2
Heteronuclear molecules					
CN	3.55	7.21	7.89	84	15.7
BO	5.97	8.42	8.40	101	−0.5
CO	7.79	10.89	11.226	90	7.7
NO	2.19	5.35	6.615	71	29.2
Hydrides					
BH	2.78	3.42	3.57	81	3.5
CH	2.46	2.95	3.63	41	15.7
NH	2.06	2.79	3.85	41	24.4
OH	3.01	3.67	4.62	41	21.9
FH	4.33	4.99	6.12	37	26.1

[a] D_0^0(NH) from Piper [11a]; atomic data from Moore [11b]; all other molecular data from Huber and Herzberg [4]

[b] Basis set is *10s3p1d/5s3p1d*

[c] Basis set is *6s2p/3s2p*

Table 5. Dipole moments (in Debye)

Molecule	SCF	FORS	exp[a]
CN (C^+N^-)	2.30	1.62	1.45
BO (B^+O^-)	3.00	2.34	—
CO (C^-O^+)	−0.26	0.30	0.122
NO (N^-O^+)	−0.31	0.24	0.159

[a] Experimental values from Reference [4]

for many chemical predictions. It should be noted, however, that dissociation of diatomics involves extreme changes in electron correlations. In many reactions between larger molecules the changes in electron correlation are much less severe and the FORS model can then be expected to yield energy differences accurate to a few kcal/mole.

The present calculations do allow a *prediction* regarding the BO molecule which has received little experimental or theoretical attention. So far its bond energy has not been well determined experimentally; published values range from 7.4 to 9.2 eV. Since in all cases, except BO, the FORS model recovers 70–95% of the binding energy correlation error, and since it recovers 84% in the isoelectronic CN molecule, it seems most likely that a similar result is also valid for BO. Assuming that (85 ± 10)% is in fact recovered for this molecule, this would lead to a bond energy prediction of (8.85 ± 0.3) eV which is considerably larger than the recently reported thermodynamical value of 8.44 ± 0.12 eV [4].

In Table 5 there are listed the dipole moments achieved by the FORS wavefunctions. In all cases the FORS values are improvements over the SCF values. A large source of the remaining error may be the failure to average over the vibrations of the atoms [8]. The dipole moment of BO has not been measured so far. Its prediction in Table 5 is probably accurate to ±0.3 Debye.

4. FORS IACC calculations

4.1. Method

The FORS IACC methodology is described in detail in Ref. [2]. The *first* step consists in forming, from the optimized configuration generating MO's, a basis of "*localized* FORS MO's", which have the character of "*molecule-adapted atomic valence orbitals*" spanning the same FORS orbital space. From these orbitals one can then construct "*molecule-adapted (deformed) atomic state functions*" and, from them, *antisymmetrized products of molecule-adapted atomic state functions of the two atoms*, N-electron functions which are called "*composite functions*" (CF's). These CF's form an alternate configurational basis for the Full Reaction Space. The *second* step is then to determine the transformation matrix which *expresses the* SAAP'*s generated from the localized* FORS MO'*s in terms of the* CF'*s generated from the same orbitals.* Once this connection has been established, the hamiltonian matrix in the Full Reaction Space can be recalculated *including the intra-atomic correlation correction* (IACC) and, from this corrected matrix, an improved energy and improved wavefunction are found. The corrections are such that, except for basis set inadequacies, *exact* energies result for the separated atoms.

For homonuclear diatomic molecules, the number of SAAP's *generated from the localized* FORS MO'*s* (needed to span the Full Reaction Space) is greater than the number of SAAP's *generated from the natural* FORS MO'*s*, because of the absence of $g-u$ symmetry. The number of *composite functions* required to span the Full Reaction Space is in general still larger, as discussed in detail in reference [2]. For the molecules which have been investigated, specifics are given in Table 6. Listed are the symmetries and equilibrium distances of various states, the symmetries of the separated species, the number of localized-MO-generated SAAP's and the number of CF's required to span the Full Reaction Space.

The calculations were performed using the ALIS system [7a] augmented by a program (TMAT) to generate the aforementioned transformation matrix and a program (IACC) to determine the corrected hamiltonian matrix.

4.2. *Calculations at equilibrium distances*

The energy results of the FORS IACC calculations for the systems mentioned in Table 6 at their equilibrium distances are presented in Table 7. For the sake of comparison, the results from SCF and FORS calculations are also included. As

Table 6. Specifics of various states of some diatomic molecules

Molecule	State and Symmetry	No. of SAAPs[a]	No. of CFs	Equilibrium distance (bohr)	Symmetry of Dissociated species
Homonuclear molecules					
H_2	$X^1\Sigma_g^+$	3	4	1.4	$^2S+^2S$
N_2	$X^1\Sigma_g^+$	328	584	2.068	$^4S+^4S$
O_2	$X^3\Sigma_g^-$	96	118	2.2817	$^3P+^3P$
F_2	$X^1\Sigma_g^+$	16	22	2.68	$^2P+^2P$
Hydrides					
BH	$X^1\Sigma^+$	19	25	2.3289	$^2P+^2S$
CH	$X^2\Pi$	18	22	2.1163	$^3P+^2S$
	$a^4\Sigma^-$	10	11	2.0470	$^3P+^2S$
	$A^2\Delta$	16	22	2.0823	$^1D+^2S$
	$B^2\Sigma^-$	17	22	2.2080	$^3P+^2S$
	$C^2\Sigma^+$	22	24	2.1057	$^1D+^2S$
NH	$X^3\Sigma^-$	12	14	2.0	$^4S+^2S$
	$a^1\Delta$	12	21	2.0	$^2D+^2S$
	$b^1\Sigma^+$	19	25	2.0	$^2P+^2S$
OH	$X^2\Pi$	10	12	1.8324	$^3P+^2S$
FH	$X^1\Sigma^+$	8	10	1.7325	$^2P+^2S$

[a] SAAPs in terms of Projected Localized FORS MOs (= Molecule adapted valence AOs)

Table 7. Energies from SCF, FORS and FORS IACC calculations

Molecule	State and Symmetry	At Equilibrium distance energies (in hartree) SCF	FORS	IACC	ΔE[a] (mh)	Separated atoms energies (in hartree) SCF	FORS	IACC
				Homonuclear molecules				
H_2	$X^1\Sigma_g^+$	−1.1336	−1.1521	−1.1679	0.25	−0.9996	−0.9996	−0.9996
N_2	$X^1\Sigma_g^+$	−108.9853	−109.1345	−109.6660	6.33	−108.8008	−108.8008	−109.2304
O_2	$X^3\Sigma_g^-$	−149.6575	−149.7627	−150.4133	1.26	−149.6168	−149.6168	−150.2286
F_2	$X^1\Sigma_g^+$	−198.7640	−198.8443	−199.6673	0.95	−198.8156	−198.8156	−199.6246
				Hydrides				
BH	$X^1\Sigma^+$	−25.1309	−25.1858	−25.3081	0.46	−25.0287	−25.0599	−25.1589
CH	$X^2\Pi$	−38.2786	−38.3135	−38.4921	0.76	−38.1881	−38.2055	−38.3580
	$a^4\Sigma^-$	−38.2892	−38.3073	−38.4580	1.68	−38.1881	−38.2055	−38.3580
	$A^2\Delta$	−38.1794	−38.1962	−38.3871	0.59	−38.1308	−38.1476	−38.3121
	$B^2\Sigma^-$	−38.1574	−38.2030	−38.3904	1.58	−38.1881	−38.2055	−38.3580
	$C^2\Sigma^+$	−38.1272	−38.1615	−38.3488	1.06	−38.1308	−38.1476	−38.3121
NH	$X^3\Sigma^-$	−54.9756	−55.0025	−55.2501	1.16	−54.9002	−54.9002	−55.1150
	$a^1\Delta$	−54.9087	−54.9298	−55.1939	0.92	−54.7953	−54.7953	−55.0281
	$b^1\Sigma^+$	−54.8442	−54.8977	−55.1559	1.36	−54.7271	−54.7620	−54.9838
OH	$X^2\Pi$	−75.4188	−75.4432	−75.7901	0.95	−75.3082	−75.3082	−75.6141
FH	$X^1\Sigma^+$	−100.0666	−100.0909	−100.5490	1.38	−98.9076	−98.9076	−99.3121

[a] $\Delta E = E(\mathrm{FOPC}) - E(\mathrm{IACC})$. FOPC = First order perturbation correction

discussed in Ref. [2], it is possible to obtain approximations to the FORS-IACC energies from FORS wavefunctions by first order perturbation theory. These approximate energies lie in all cases above those obtained by diagonalizing the corrected hamiltonian matrix. The deviations of the first order energies from the exact ones are also listed.

The dissociation energies obtained from these calculations, together with the experimental values and those resulting from SCF and FORS calculations are listed in Table 8. With the exception of the ground states of N_2 and BH and the

Table 8. Dissociation energies from SCF, FORS and FORS IACC calculations

Molecule	State and Symmetry	exp[b]	D_e (eV) SCF	D_e (eV) FORS	D_e (eV) IACC	Error[a] (eV) SCF	Error[a] (eV) FORS	Error[a] (eV) IACC
			Homonuclear molecules					
H_2	$X^1\Sigma_g^+$	4.75	3.64	4.15	4.58	1.11	0.6	0.17
N_2	$X^1\Sigma_g^+$	9.91	5.02	9.08	11.86	4.89	0.83	−1.95
O_2	$X^3\Sigma_g^+$	5.21	1.11	3.97	5.03	4.1	1.24	0.18
F_2	$X^1\Sigma_g^+$	1.66	−1.40	0.78	1.16	3.06	0.88	0.50
			Hydrides					
BH	$X^1\Sigma^+$	3.57	2.78	3.43	4.06	0.79	0.14	−0.49
CH	$X^2\Pi$	3.63	2.46	2.94	3.65	1.17	0.69	−0.02
	$a^4\Sigma^-$	2.91	2.75	2.77	2.72	0.16	0.14	0.19
	$A^2\Delta$	2.03	1.32	1.78	2.04	0.71	0.25	−0.01
	$B^2\Sigma^-$	0.41	−0.84	−0.07	0.88	1.25	0.48	−0.47
	$C^2\Sigma^+$	0.96	−0.10	0.38	1.00	1.06	0.58	−0.04
NH	$X^3\Sigma^-$	3.85	2.06	2.78	3.68	1.79	1.07	0.17
	$a^1\Delta$	4.67	3.08	3.66	4.51	1.59	1.01	0.16
	$b^1\Sigma^+$	4.80	3.18	3.69	4.68	1.62	1.11	0.12
OH	$X^2\Pi$	4.62	3.01	3.67	4.79	1.61	0.95	−0.17
FH	$X^1\Sigma^+$	6.12	4.33	4.99	6.45	1.79	1.12	−0.33

[a] Error = D_e(calc) − D_e(exp)

[b] D^0(NH) from Piper [11a]; atomic data from Moore [11b]; all other molecular data from Huber and Herzberg [4] in eV

Table 9. Excitation energies of diatomic molecules from SCF, FORS and FORS IACC calculations (T_e)

Transition (eV)	SCF	FORS	FORS IACC	exp[a]
CH $X^2\Pi \rightarrow a^4\Sigma^-$	−0.29	0.18	0.98	0.72[b]
$\rightarrow A^2\Delta$	2.70	3.20	2.90	2.86
$\rightarrow B^2\Sigma^-$	3.30	3.02	2.81	3.16
$\rightarrow C^2\Sigma^+$	4.12	4.15	3.95	3.93
NH $X^3\Sigma^- \rightarrow a^1\Delta$	1.83	1.97	1.52	1.57
$\rightarrow b^1\Sigma^+$	3.58	2.84	2.49	2.63

[a] From Huber and Herzberg [4], see however footnote b

[b] From electron detachment experiment by C. Lineberger and coworkers [12]. T_0 = 0.742 eV, zeropoint energy change = −0.018 eV

Table 10. Dipole Moments (in Debye)

Molecule	State	SCF	FORS	IACC	exp[a]
BH	$^1\Sigma^+$	1.756	1.315	1.473	1.27
CH	$X^2\Pi$	1.589	1.582	1.415	1.46
	$a^4\Sigma^-$	0.537	0.517	0.702	—
	$A^2\Delta$	0.923	0.839	0.876	—
	$B^2\Sigma^-$	1.572	1.450	1.484	—
	$C^2\Sigma^+$	0.939	0.928	0.955	—
NH	$X^3\Sigma^-$	1.629	1.536	1.728	—
	$a^1\Delta$	1.660	1.547	1.723	1.49
	$b^1\Sigma^+$	1.689	1.461	1.661	—
OH	$^2\Pi$	1.793	1.668	1.811	1.54–1.72
FH	$^1\Sigma^+$	1.946	1.803	1.852	1.69–1.83

a Experimental values from Ref. [4]

$B^2\Sigma^-$ excited state of CH, the theoretical results improve consistently when proceeding from the SCF to the FORS and the FORS-IACC model. The same holds for the molecular excitation energies of CH and NH which are listed in Table 9. An analysis of the origin of the failures in N_2, BH and CH should prove constructive for a better understanding of the correlation error and an appropriate improvement of the model.

The FORS IACC approach also yields corrected wavefunctions in the FORS configuration space. Whether or not these represent improvements over the FORS wavefunctions can be tested by calculating molecular properties. The dipole moments predicted by the SCF, the FORS and the FORS IACC models are lisated in Table 10. As regards this particular property, there seems to be no significant difference between the performance of the two models.

4.3. Calculation of dissociation curves

In the case of the molecule CH, the FORS IACC approach was used to follow the entire dissociation process for the ground state $X^2\Pi$ and the four low lying excited states $a^4\Sigma$, $B^2\Sigma^-$, $A^2\Delta$, $C^2\Sigma^+$, which result when one electron is moved from the σ bonding orbital to one of the low π-orbitals. Figures 1 and 2 display the dissociation curves derived with a fitting program (DIAPOT [9]) from FORS and FORS IACC calculations, together with estimated experimental curves. The latter were obtained using data from the calculations of Lie, Hinze, and Liu [13] and slightly correcting them (by less than 2%) to yield the experimental values at the equilibrium distance and at infinite separation through the empirical adjustments

$$\underset{\text{estim exp}}{E}(R) = E_{\text{LHL}}(R) + E_{\text{exp}}(R=\infty) - E_{\text{LHL}}(R=\infty)$$
$$+\{D_e(\text{LHL}) - D_e(\text{exp})\}\exp[-(r-R_e)^2].$$

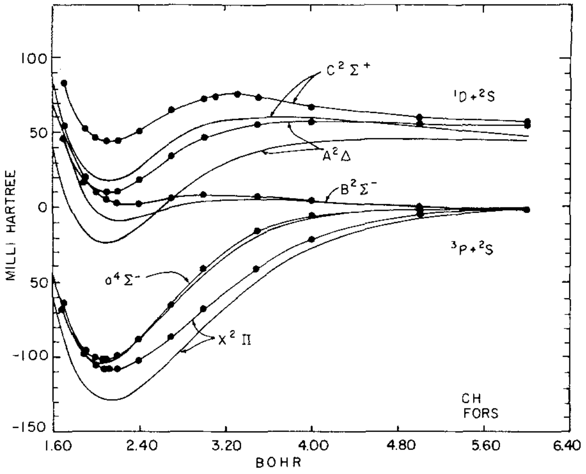

Fig. 1. Dissociation curves of the lowest five states of the CH molecule. Solid lines: Estimated experimental curves (see text). Solid lines with dots: FORS calculations. Dots indicate evaluated points

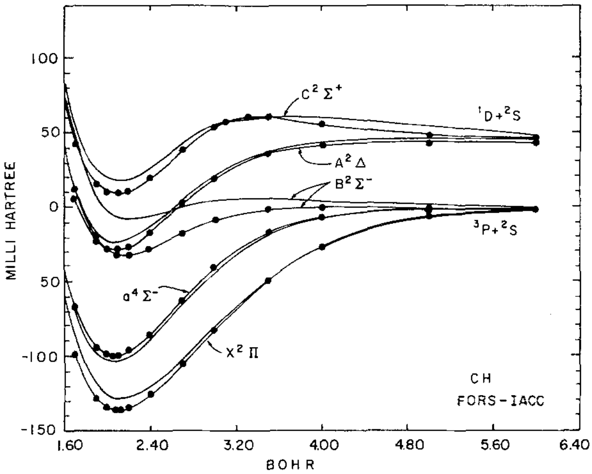

Fig. 2. Dissociation curves of the lowest five states of the CH molecule. Solid lines: Estimated experimental curves. Solid lines with dots: FORS-IACC calculations. Dots indicate evaluated points

With the exception of the previously mentioned $B^2\Sigma^-$ state, the improvements achieved by the Intra-Atomic Correlation Correction is self-evident. A Dunham analysis [9, 10] of these curves yields the results listed in Table 11.

4.4. Molecular wave-functions as superpositions of antisymmetrized products of deformed atomic states

As was mentioned in Section 4.1, and as has been elaborated in detail in reference [2], the FORS IACC approach is based on *expressing molecular wavefunctions in*

Table 11. Spectroscopic Constants for Five States of CH

	R_e (bohr)	D_e (eV)	B_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	α_e (cm^{-1})
			$X^2\Pi$			
FORS	2.142	2.949	14.11	2695	63	0.595
FORS IACC	2.094	3.695	14.76	2923	61	0.571
Lie et al.[a]	2.113	3.506	14.50	2886	82	0.589
experiment[b]	2.116	3.64	14.46	2859	63	0.534
			$a^4\Sigma^-$			
FORS	2.063	2.726	15.20	3031	28	0.485
FORS IACC	2.053	2.677	15.24	3168	75	0.438
Lie et al.[a]	2.053	2.836	15.36	3146	72	0.553
experiment[b]	2.050	2.92[c]	15.40	3145	72	0.55
			$A^2\Delta$			
FORS	2.093	1.259	14.78	2864	111	0.738
FORS IACC	2.070	1.980	15.11	3103	100	0.541
Lie et al.[a]	2.083	1.900	14.98	2970	99	0.697
experiment[b]	2.082	2.01	14.93	2931	97	0.697
			$B^2\Sigma^-$			
FORS	2.301	0.05	12.22	1951	342	1.305
FORS IACC	2.164	0.85	13.82	2581	226	1.177
Lie et al.[a]	2.216	0.24	13.51	2142	223	1.933
experiment[b]	2.263	0.39	12.65	2251	230	—
			$C^2\Sigma^+$			
FORS	2.103	0.377	14.63	2752	93	0.737
FORS IACC	2.083	1.007	14.92	2916	70	0.947
Lie et al.[a]	2.100	0.783	14.76	2888	107	0.771
experiment[b]	2.106	0.94	14.60	2840	126	0.718

[a] G. C. Lie, J. Hinze, and B. Liu [13]
[b] K. P. Huber and G. Herzberg [4]
[c] From excitation energy on Table 9

terms of composite functions of atomic states (CF's). These are antisymmetrized products of deformed atomic state functions. In CH there are three kinds. Composite functions of type CH:

$$\tilde{\mathscr{A}}\{|C, s^n p^{4-n}, {}^{2S+1}L(M_L, M_S)\rangle|H, {}^2S(m_s)\rangle\}, \tag{1}$$

composite functions of the type C^+H^-:

$$\tilde{\mathscr{A}}\{|C^+, s^n p^{3-n}, {}^{2S+1}L(M_L, M_S)\rangle|H^-, {}^1S(0)\rangle\}, \tag{2}$$

and composite functions of the type C^-H^+:

$$|C^-, s^n p^{5-n}, {}^{2S+1}L(M_L, M_S)\rangle. \tag{3}$$

Here the first factors denote antisymmetric state functions of C, C^+ and C^-, and the second factors denote the corresponding state functions of H and H^-. The symbol $\tilde{\mathscr{A}}$ is the coset antisymmetrizer which establishes antisymmetrization between the electrons of carbon and those of hydrogen. The value of $M_L + m_L =$

M_L and that of $(M_S + m_S)$ must be equal to the respective *molecular* angular momentum components.

Although *qualitative discussions* of relationships between diatomic and atomic states are neither new nor uncommon in various spectroscopic contexts [14], no *quantitative analysis* of this kind has been presented to date, because there

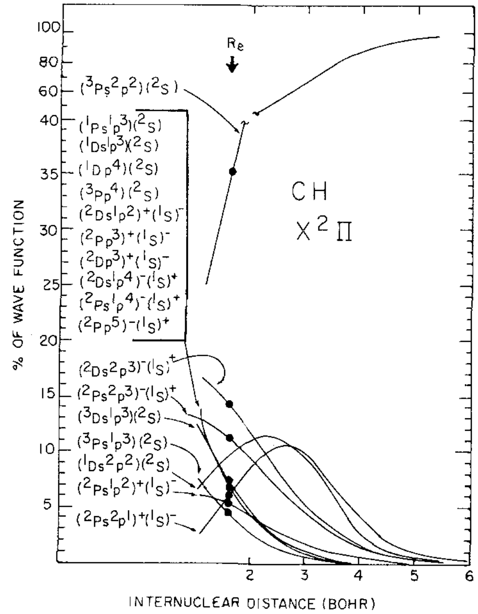

Fig. 3. Decomposition of $X^2\Pi$ state of CH in terms of composite functions (antisymmetrized products of deformed atomic states of C and H) as a function of the internuclear distance. R_e = equilibrium distance. For definitions of the composite functions, see Eq. (1), (2), (3). See text for the bracketed set of states. The ordinate scale changes at 40%

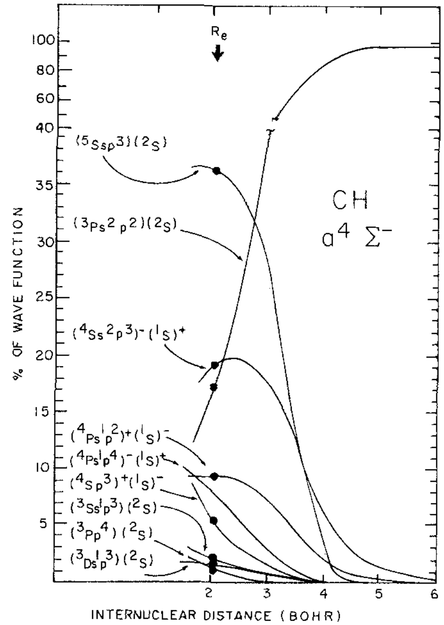

Fig. 4. Decomposition of the $a^4\Sigma^-$ state of CH in terms of composite functions (antisymmetrized products of deformed atomic states of C and H) as a function of the internuclear distance. R_e = equilibrium distance. For definitions of the composite functions, see Eqs. (1), (2), (3). The ordinate scale changes at 40%

existed no quantitative formulation for such decompositions of molecular wavefunctions before the development of the FORS model and of orthogonal composite functions within this framework. It is therefore of interest to examine the deformed-atomic-state decompositions of the FORS IACC wavefunctions of the calculated five molecular states as functions of the internuclear distance.

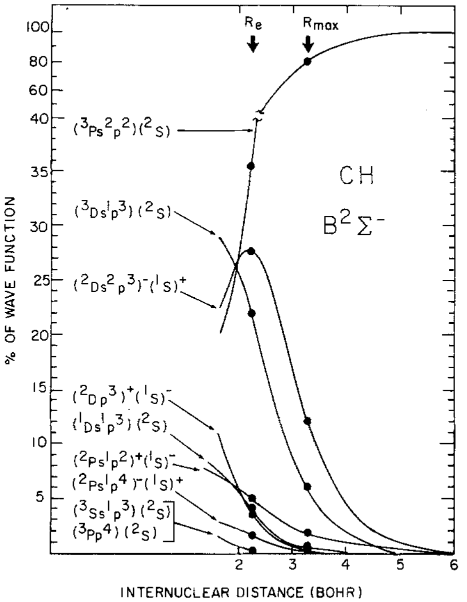

Fig. 5. Decomposition of the $B^2\Sigma^-$ state of CH in terms of composite functions (antisymmetrized products of deformed atomic states of C and H) as a function of the internuclear distance. R_e = equilibrium distance. $R_{\max}$ = distance where the curve has a maximum. For definitions of the composite functions, see Eqs. (1), (2), (3). See text for the bracketed set of states. The ordinate scale changes at 40%

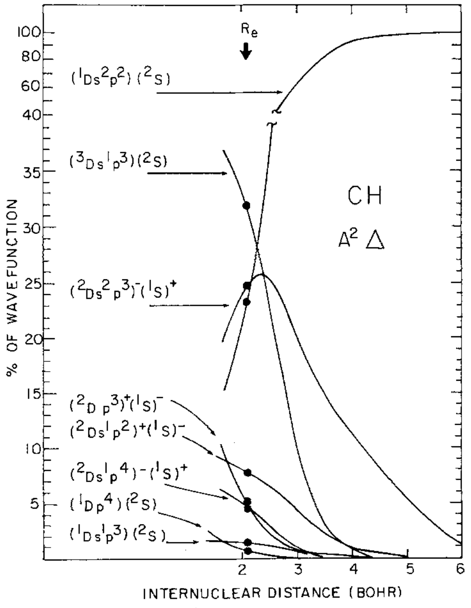

Fig. 6. Decomposition of the $A^2\Delta$ state of CH in terms of composite functions (antisymmetrized products of deformed atomic states of C and H) as a function of the internuclear distance. R_e = equilibrium distance. For definitions of the composite functions, see Eq. (1), (2), (3). The ordinate scale changes at 40%

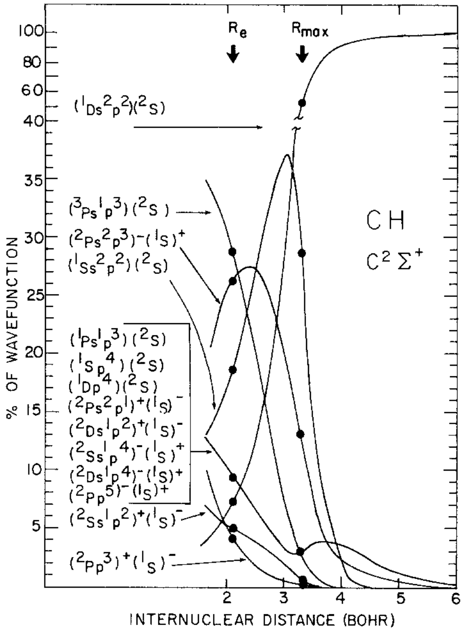

Fig. 7. Decomposition of the $C^2\Sigma^+$ state of CH in terms of composite functions (antisymmetrized products of deformed atomic states of C and H) as a function of the internuclear distance. R_e = equilibrium distance. R_{max} = distance where the curve has a maximum. For definitions of the composite functions, see Eqs. (1), (2), (3). See text for bracketed set of states. The ordinate scale changes at 40%

These decompositions are displayed in Fig. 3-7. Plotted are the *squares* of the coefficients (which add up to unity) of the various composite functions. Where several (M_L, M_S, m_S) components *of the same atomic term* occur in the expansion of the molecular wavefunction, the sum of the squares of their coefficients is plotted. The symbols labelling the curves are related to the definitions (1), (2), (3) given above in an obvious manner. [For example, $\mathscr{A}\{|C, s^2p^2, {}^3P\rangle|H, {}^2S\rangle\}$ is denoted by $({}^3Ps^2p^2)({}^2S)$]. In Fig. 3, 5, 7, there are several contributions which are quite small. In these cases only the sum of their contributions is plotted and the corresponding curves are labelled by brackets containing all contributing states.

Figures 3-7 yield a number of insights.

First, it can be seen that the dominant composite function (CF) at the equilibrium distance is the dissociative CF for the X and B states. However, for the a, A and C states the dissociative CF is not the predominant contributor to the wavefunction at the equilibrium distance; in fact it contributes only seven percent to the wavefunction for the C states at its equilibrium distance.

Second, the CF decomposition plots are instructive regarding the electric dipole moments. Lie, Hinze, and Liu [13] (LHL) have calculated the dipole moment functions for all the valence states of CH. *At the equilibrium distances*, all five states have negative dipole moments, corresponding to C^-H^+. Our figures show that, at the equilibrium distances, all five states have at least one very important C^-H^+ charged CF contributor, in addition to important neutral CF's. The LHL dipole moment functions show furthermore that the a, A, and B states have *negative* dipoles at *all R*, while the X and C states have *long range positive* dipoles. The CF decomposition explains this as well because, at R values greater than 3.5 bohr, the X and C states have as their most important charged contributor a C^+H^- CF. (For the C state this is the $(^2Ps^2p^1)^+(^1S)^-$ term, which is 2.5% of the wavefunction at $R = 4$ bohr).

A third feature which can be explained by the CF decomposition is the occurrence of the long range maxima in the B and C states. Lie et al. [13] attribute the hump in the B state to an avoided crossing between the repulsive $(^3P)(^2S)$ and the attractive $(^2)^-(^1S)^+$ CF's. This is born out by the CF decomposition shown in Fig. 6, where the neutral CF decreases and the charged CF increases in importance as the bond forms. Note however that the neutral CF remains the dominant contributor at R_e, and is very dominant at the potential maximum. Lie et al also state that the potential hump in the C state is due to the avoided crossing of the repulsive $(^1D)(^2S)$ and the attractive $(^2P)^-(^1S)^+$ CF's. Figure 7 confirms indeed that this particular neutral CF decreases rapidly in importance, whereas this charged CF rises rapidly in importance as the bond distance decreases. Note however also that the repulsive $(^1S)(^2S)$ CF has a large weight as well in the wavefunction for R values between 2.5 and 4. This additional repulsive contributor causes the hump in the C state to be larger than that for the B state.

Finally, an inference can be made from Figs. 3 and 4 regarding a suggestion by Bauschlicher and Shavitt [15]. They suggest consideration of the following two series of molecular electronic states:

	C	CH	CH_2
$^3Ps^2p^2$	$E(\text{rel}) = -0.0135$ hartree	$^2\Pi$	$^1A_1$
$^5Ss^1p^3$	$E(\text{rel}) = -0.0111$ hartree	$^4\Sigma^-$	$^3B_1$

The relativistic corrections [16] shown for the carbon atom imply that the relativistic correction to the carbon ^5S–^3P *splitting* reduces this splitting by about 1.5 kcal/mol. (This relativisitc correction is larger than one normally expects for carbon, because one of the states involve a singly occupied 2s level.) Feller and Davidson [17] have suggested that, if this relativistic correction carries over to methylene, the theoretical methylene singlet–triplet nonrelativistic splittings of 10–12 kcal/mol would be in better agreement with the recent experimental findings near 8 kcal/mol.

The analyses of the CH wavefunctions shown in Figs. 3 and 4 provide a qualitative and quantitative test of the above hypostheses. Figure 3 shows that the ground state ($X^2\Pi$) of CH is dominated by the ^3P state of carbon, and that the most important constituent in the $a^4\Sigma^-$ state is indeed the ^5S state of carbon, even though this state dissociates to the ^3P ground state of carbon. Thus the two sequences presented above are qualitatively confirmed. However the indicated states of carbon, although being the most important contributors, comprise only about 35% of the wavefunction at the equilibrium distances. A perturbation theory estimate of the relativistic correction to each of the CH state is given by

$$\Delta E_{\text{rel}} = \Sigma c_i^2 \Delta E_i(\text{rel}),$$

where c_i^2 is the percent contribution of each CF to the total wavefunction. The relativistic correction to the doublet ground state found in this way is −0.0127 hartree, and the correction to the quartet state is −0.0120 hartree. Thus the relativistic corrections decrease the quartet-doublet splitting in the CH radical by only 0.5 kcal/mol. This correction is much smaller than the 1.5 kcal/mol correction for the analogous carbon atom splitting. Unless the relativistic correction increases considerably in going from CH to CH_2, relativistic effects seem unable to quantitatively account for the 2–4 kcal/mol discrepancy between current nonrelativistic calculations and experiments on the methylene radical. Qualitatively however, the relativistic corrections for both C and CH act to reduce the computed nonrelativistic splittings. The suggestion by Feller and Davidson may still be viable because it is possible that direct computation of the molecular relativistic corrections in CH could differ from the perturbative incorporation of atomic relativistic corrections outlined here for CH.

5. Conclusion

Molecular electronic wavefunctions obtained through the FORS approach furnish physical insights that would be difficult to come by other means. When augmented by the Intra-Atomic Correlation Correction, the method usually yields quite accurate values for the variation of the energy with deformations of the molecular geometry. Moreover, these results are obtained with a modest computational effort.

Some problems remain to be addressed before routine applications are possible. It will be necessary to clarify the reasons why, in a few cases, the Intra-Atomic Correlation Correction has yielded unsatisfactory results. It will be necessary to develop rules for deleting in advance ineffective configurations when molecules become large enough for the full reaction space to encompass excessive numbers of configurations. Finally, for those systems where the composite functions embody multiply ionic states of atoms, suitable values must be found for the corresponding atomic correction terms. It is our belief that useful solutions to these problems exist.

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