Comparison of INDO and *Ab Initio* Methods for Correlated Wave Functions of the Ground and Excited States of Methylene and Ethylene[1a]

W. R. Wadt[1b] and W. A. Goddard III*

Contribution No. 4868 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109. Received April 1, 1974

Abstract: The usefulness of the INDO integral approximation for correlated wave functions was tested by carrying out GVB calculations on (1) the three lowest states of methylene as a function of bond angle and (2) the three lowest states of ethylene as a function of the dihedral twist angle. The methylene potential curves obtained with INDO were in good agreement (0.2 eV errors) with *ab initio* results, while the ethylene curves were very poor (2 to 4 eV errors). Comparison with *ab initio* calculations revealed two major problems in the INDO method: (1) the use of empirical values from atomic spectra for the one-center exchange integrals and (2) the use of only one resonance or β parameter per atom.

In recent years, great progress has been made in developing sufficiently rapid *ab initio* techniques, so that high-quality calculations can be performed on moderate size molecules, e.g., O_3,[2a,b] CO_2,[2c] C_4H_6,[3] C_6H_6,[4] and simple reactive surfaces.[5] Nevertheless, *ab initio* techniques are still too slow to treat the reactive surfaces and electronic states of larger molecules at the numerous geometries required to delineate reaction or energy transfer mechanisms. As a result, it would appear necessary to use semiempirical techniques for studying the chemical dynamics of large molecules.

Numerous *ab initio* investigations[6] have shown the simple wave functions obtained from Hartree–Fock calculations to lead to improper descriptions of electronic excitation energies and of processes involving bond dissociation (or formation). In studying reactions, the basic form of the wave function should be inherently capable of correctly describing the reactive potential surface and, hence, a properly correlated wave function should be used.

Since approximate integral methods have generally been based on and used with Hartree–Fock (HF) wave functions, it is quite possible that the semiempirical parameterizations are inappropriate for correlated wave functions. We have tested this by comparing the results of *ab initio* and approximate integral methods for correlated wave functions. Specifically, the INDO approximate integral method[7] was used, since it is parameterized to fit *ab initio* Hartree–Fock calculations (rather than experiment) and, hence, is more likely to involve parameters that would also be appropriate for correlated wave functions.

Recently, we compared the results of extensive configuration interaction calculations on the excited states of ozone using INDO and *ab initio* integrals.[8] There were significant errors (20–30%) in the vertical excitation energies, but more important was the result that INDO is strongly biased toward short bond lengths and small bond angles. In fact, the triangular state of ozone was calculated to be 6–7 eV below the true open ground state!

Ab initio studies of ozone have shown the crucial importance of correlated wave functions for obtaining even qualitatively correct results. For example, HF wave functions lead to a triplet ground state, while experiment and configuration interaction calculations both indicate that ozone has a singlet ground state.[2b] Consequently, ozone is a very stiff test on the efficacy of approximate methods. Herein we test the use of INDO for describing the potential surfaces of the first three states of methylene as a function of bond angle and the first three states of ethylene as a function of dihedral twist angle. These systems provide the simplest prototypes for n → π* and π → π* transitions.

Ab initio calculations on methylene[9] and ethylene[10] have shown that the generalized valence bond (GVB) method[11] leads to a good description of the potential surfaces. Consequently, we will use the GVB type of correlated wave function for these comparisons.

(1) (a) Partially supported by grants (GP-15423 and GP-40783X) from the National Science Foundation; (b) NSF Predoctoral Fellow 1970–1974.

(2) (a) P. J. Hay and W. A. Goddard III, *Chem. Phys. Lett.*, **14**, 46 (1972); P. J. Hay, T. H. Dunning, Jr., and W. A. Goddard III, *ibid.*, **23**, 457 (1973); (b) W. A. Goddard III, P. J. Hay, and T. H. Dunning, Jr., *J. Amer. Chem. Soc.*, to be submitted for publication; (c) N. W. Winter, C. F. Bender, and W. A. Goddard III, *Chem. Phys. Lett.*, **20**, 489 (1973).

(3) (a) T. H. Dunning, Jr., R. P. Hosteny, and I. Shavitt, *J. Amer. Chem. Soc.*, **95**, 5067 (1973); (b) G. B. Levin and W. A. Goddard III, to be submitted for publication.

(4) (a) W. C. Ermler and C. W. Kern, *J. Chem. Phys.*, **58**, 3458 (1973); (b) P. J. Hay and I. Shavitt, *Chem. Phys. Lett.*, **22**, 33 (1973).

(5) (a) C. F. Bender, P. K. Pearson, S. V. O'Neill, and H. F. Schaefer III, *J. Chem. Phys.*, **56**, 4626 (1972); (b) S. V. O'Neill, P. K. Pearson, and H. F. Schaefer III, *ibid.*, **58**, 1126 (1973); (c) P. K. Pearson, W. J. Hunt, C. F. Bender, and H. F. Schaefer III, *ibid.*, **58**, 5358 (1973); (d) C. W. Wilson, Jr., and W. A. Goddard III, *J. Chem. Phys.*, **56**, 5913 (1972); (e) S. Shih, R. J. Buenker, S. D. Peyerimhoff, and C. J. Michejda, *J. Amer. Chem. Soc.*, **94**, 7620 (1972).

(6) H. F. Schaefer III, "The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results," Addison-Wesley, Reading, Mass., 1972.

(7) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

(8) W. R. Wadt and W. A. Goddard III, *J. Amer. Chem. Soc.*, **96**, 1689 (1974).

(9) P. J. Hay, W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, **13**, 30 (1972).

(10) (a) W. J. Hunt, W. A. Goddard III, and T. H. Dunning, Jr., to be submitted for publication; (b) W. J. Hunt, Ph.D. Thesis, California Institute of Technology, 1971; (c) W. Kaldor and I. Shavitt, *J. Chem. Phys.*, **48**, 191 (1968), reported MBS configuration interaction calculations which were equivalent to the simplest GVB description of ethylene.

(11) P. J. Hay, W. J. Hunt, and W. A. Goddard III, *J. Amer. Chem. Soc.*, **94**, 8293 (1972).

Table I. Methylene Energies (eV), $R_{CH} = 2.1a_0$

		INDO		Ab initio[a]		
		HF	GVB(1)	HF	GVB–CI	Exptl
Excitation energies	$^3B_1 \rightarrow {}^1A_1(0,0)$	0.57	0.32	1.03	0.50	$<1.0^b$
	$^1A_1 \rightarrow {}^1B_1(0,0)$	1.05	1.30	0.75	1.40	1.34^c
	$^1A_1 \rightarrow {}^1B_1(vert)$	1.81	2.06	1.32	1.88	2.06^d
	$^3B_1 \rightarrow {}^1B_1(135°)$	1.62	1.62		1.90	
	$^3B_1 \rightarrow {}^1B_1(180°)$	1.14	1.14		1.80	
Inversion barriers	$^3B_1$	0.62	0.62		0.40	
	$^1A_1$	1.73	1.41		1.69	
	$^1B_1$	0.13	0.13		0.28	
Calcd bond angles,^{e}	$^3B_1$	129	129		128	136^f
deg	$^1A_1$	107	106		103	102.4^g
	$^1B_1$	144	144		134	$\sim140^h$

^{a} Employed a double ζ basis set with d functions on carbon.[9] ^{b} Estimated upper limit (footnote h). ^{c} Lowest observed transitions (footnote h). Extrapolation of isotope shifts indicated a 0.88 eV adiabatic excitation energy (footnote g). ^{d} Obtained assuming the vertical transition to correspond to the middle of the observed $^1B_1$ (0ν0) ← $^1A_1$ (000) spectrum and adding 0.08 eV to correct for the zero-point energy of the $^1A_1$ state (footnote h). ^{e} The bond angles were determined using cubic splines with the points $\angle HCH = 90, 105, 135, 180, 225, 255,$ and 270°. More extensive geometry optimization of ab initio CI calculations (S. V. O'Neill, H. F. Schaefer III, and C. F. Bender, *J. Chem. Phys.*, **55**, 162 (1971)) using a DZ basis leads to the following bond angles: ($^3B_1$) 133°, ($^1A_1$) 104°, and ($^1B_1$) 144°. ^{f} E. Wasserman, W. A. Yager, and V. Kuck, *J. Amer. Chem. Soc.*, **92**, 749 (1970). ^{g} G. Herzberg, "Electronic Structure of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966. ^{h} G. Herzberg and J. W. C. Johns, *Proc. Roy. Soc., Ser. A*, **295**, 107 (1966).

Methylene

Pople and Beveridge[12] reported INDO HF potential curves for the ground and lowest excited states of methylene ($^3B_1$ and $^1A_1$, respectively), using a fixed CH bond distance. Their results are compared with *ab initio* HF and GVB–CI calculations[9] in Table I. Somewhat surprisingly, the INDO HF numbers are in better agreement with the *ab initio* GVB–CI calculations than with the *ab initio* HF calculations, which the INDO integral approximation was parameterized to reproduce. Therefore, one might suspect that using INDO with an appropriately correlated wave function would lead to worse agreement with the *ab initio* GVB–CI results. We will see below that this is indeed the case.

In the HF description of methylene the $^3B_1$ and $^1A_1$ states are described as

$$^3B_1: \quad (3a_1)(1b_1)$$
$$^1A_1: \quad (3a_1)^2 \qquad (1)$$

where we have ignored the

$$(1a_1)^2(2a_1)^2(1b_2)^2 \qquad (2)$$

configuration common to both states. The CI calculations show that the correlation energy of the $^1A_1$ state is much larger than that of the $^3B_1$ state, so that HF calculations lead to an adiabatic excitation energy of 1.03 eV whereas the CI calculations lead to 0.50 eV.[9] The simplest wave function treating the $^3B_1$ and $^1A_1$ states consistently is the GVB(1) wave function[13] in which the paired orbital of (1) is described as

$$\Psi^{GVB} = \phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2) =$$
$$\sqrt{1 - \lambda^2}\phi_{3a_1}(1)\phi_{3a_1}(2) - \lambda\phi_{1b_1}(1)\phi_{1b_1}(2) \qquad (3)$$

rather than as

$$\Psi^{HF} = \phi_{3a_1}(1)\phi_{3a_1}(2) \qquad (4)$$

(12) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

(13) We are able to obtain consistent descriptions of the methylene states with the simplest GVB wave function, in which all the pairs but one are doubly occupied, for two reasons. First, the remaining pairs involve the C 1s core orbital or the CH bond orbitals, so that introducing a GVB pair description does not lead to a large effect.[11] Second, and more important, the correlation energy of these pairs is nearly the same in both states ($^3B_1$, $^1A_1$) and does not change much as the molecule is bent.
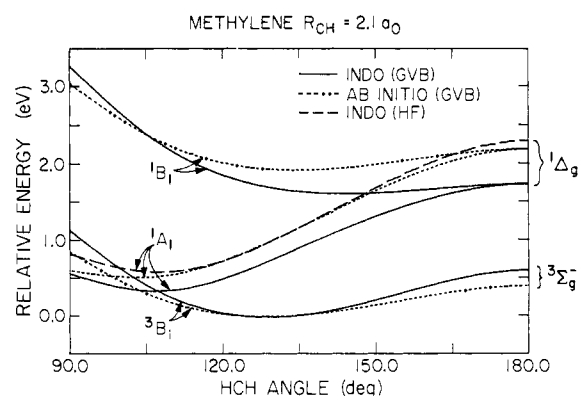
METHYLENE $R_{CH} = 2.1 a_0$

Figure 1. Comparison of *ab initio* and INDO potential energy curves for the low-lying states of methylene as a function of HCH angle ($R_{CH} = 2.1a_0 = 1.11$ Å).

(In the GVB method the orbitals of (2) and (3) are solved for self-consistently.) Since the nonbonding orbitals of the $^3B_1$ state are not paired, the HF and GVB(1) descriptions of this state are the same.[13] The higher lying $^1B_1$ state is also described consistently with a GVB(1) wave function and so will be included in our calculations.

The potential curves as a function of HCH bond angle (using a bond length of 2.1 Å) are shown in Figure 1. The *ab initio* results of Figure 1 are based on an extensive basis set (double ζ plus d polarization functions).[9] Use of the HF wave function with INDO leads to slightly better agreement with *ab initio* calculations than does the GVB–INDO wave function, indicating some fortunate cancellation of errors. As shown in Table I, GVB–INDO does lead to significant errors in the rotational barriers for the $^3B_1$ (too large by 50%) and $^1B_1$ (too small by 50%) states. The flatness of the $^1B_1$ INDO potential curve is also manifest in a significantly larger equilibrium bond angle (144° for INDO *vs.* 134° for *ab initio*). Nevertheless, the overall shape of the GVB–INDO potential surfaces is good, differing by ~0.2 eV from the *ab initio* results.

The worst error in the INDO calculations is the description of the separation between the $^3B_1$ and $^1B_1$ states, especially for large bond angles. For linear

methylene the $^3B_1$–$^1B_1$ energy separation is just $2K_{xy}$ where K_{xy} is the exchange integral between p_x and p_y orbitals on the carbon (taking z as the HCH axis). In the INDO approximation, K_{xy} is set equal to the Slater–Condon parameter

$$(3/25)F^2 = 0.57 \text{ eV}$$

which was obtained by fitting the atomic spectrum. The nonempirical value of K_{xy} for Slater 2p orbitals is 0.98 eV. For carbon the atomic ^3P–^1D splitting (1.26 eV) used to fit the Slater–Condon parameter, $(3/25)F^2$, is small relative to the comparable molecular singlet–triplet splitting ($\sim$1.80 eV), which is more in line with the nonempirical value for the exchange integral. Using the nonempirical value for K_{xy} instead of the empirical result would improve the approximate integral potential curves, indicating that empirical evaluation of approximate integrals need not be beneficial.

For linear methylene the $^1B_1$ and $^1A_1$ states coalesce into the $^1\Delta_g$ state, so that the $^1A_1$–$^3B_1$ and $^1B_1$–$^3B_1$ splitting energies are the same. The open shell HF wave functions for the $^1\Delta_g$ state are

$$^1\Delta_g = \begin{cases} 2^{-1/2}(xy + yx) \\ 2^{-1/2}(x^2 - y^2) \end{cases}$$

ignoring the doubly occupied core part of the wave function. However, Pople and Beveridge[12] employed a *closed* shell HF wave function for the $^1A_1$ state at 180°, *i.e.*

$$^1A_1 = x^2 \text{ or } y^2$$

This amounts to mixing in equal portions of the higher energy $^1\Sigma_g{}^+$ state

$$^1\Sigma_g{}^+ = 2^{-1/2}(x^2 + y^2)$$

The energy of the closed shell $^1A_1$ wave function is higher by just K_{xy} relative to the energy of the correct open shell wave function. As a result, Pople and Beveridge obtained a $^1A_1$–$^3B_1$ splitting energy of 1.71 eV for linear CH_2, which is in much better agreement with the *ab initio* CI value of 1.80 eV.

Ethylene

Few results of INDO calculations have been reported on the excited states of hydrocarbons with isolated or conjugated ethylenic groups. The explanation for the paucity of calculations is that the INDO approximation treats ethylenic $\pi \rightarrow \pi^*$ transitions very poorly, as will be shown for ethylene.

The MO description for the π system of ground state (denoted as N) ethylene is

$$N(^1A_{1g}): \quad (\pi)^2$$

while for the $\pi \rightarrow \pi^*$ excited states (denoted as T and V) it is

$$T(^3B_{1u}): \quad (\pi)(\pi^*)$$

$$V(^1B_{1u}): \quad (\pi)(\pi^*)$$

To obtain a comparable description of these three states we allow the N state to be described by a GVB pair

$$\phi_{a\pi}(1)\phi_{b\pi}(2) + \phi_{b\pi}(1)\phi_{a\pi}(2)$$

(solving for all orbitals self-consistently) so that each state has two singly occupied orbitals.

Calculations on the three states of ethylene were carried out as a function of the dihedral twist angle. The results are shown in Table II and compared with

Table II. Energies for Ethylene (eV) Using the GVB(1) Wave Function[a]

			Ab initio		
		INDO	MBS[b]	DZ[c]	Exptl[d]
Vertical	$N(^1A_{1g})$	0.0	0.0	0.0	0.0
excitation	$T(^3B_{1u})$	8.48	4.70	4.24	4.4
energies	$V(^1B_{1u})$	15.25	13.28	9.99	7.65
Rotational	N state	5.23		2.91	2.82
barriers	T state	3.27		1.39	
	V state	7.27		1.84	
Adiabatic	$T \leftarrow N$	5.23		2.85	
excitation	$V \leftarrow N$	7.98		6.42	
energies					
N–T separation at $\theta = 90°$		0.0		0.06	

[a] The experimental ground state geometry of ethylene (footnote *d*) with $R_{CH} = 1.086$ Å, $R_{CC} = 1.338$ Å, and $\angle HCH = 117.4°$ was used for the planar states, while the CC bond was lengthened to $R_{CC} = 1.41$ Å for the perpendicular states ($\theta = 90°$). [b] This work using a MBS of Slater orbitals with Slater exponents. [c] Reference 10b used $R_{CC} = 1.35$ Å for the planar states. [d] A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).

ab initio calculations. All the INDO energy separations involving the N, T, and V states are too large by 2–4 eV! *Ab initio* calculations have shown that the V state involves a very diffuse π^* orbital,[14] and, hence, a method such as INDO based on a minimal basis would be expected to yield poor results (with a minimal basis, *ab initio* calculations lead to a V $\leftarrow$ N excitation energy too high by 5.5 eV). However, even minimal basis *ab initio* calculations lead to a T $\leftarrow$ N excitation energy within 0.25 eV of the experimental value, whereas the INDO value is too high by a factor of 2.

Using a HF wave function for the planar N state would have raised the energy of the ground state by $\sim$1 eV,[10] leading to an apparent improvement in the $\pi\pi^*$ excitation energies. This results from a fortuitous partial cancellation of INDO errors with correlation effects. However, use of the closed shell HF wave function for describing the rotational barrier of ethylene would have increased the barrier from the bad value of 5.3 eV obtained with GVB–INDO to a far worse value of 7.27 eV for HF–INDO, 2.6 times the correct value of 2.8 eV. This indicates that one should not rely on fortuitous cancellations; one should base approximations on suitably correlated wave functions in order to obtain reliable approximations.

Naively, one might believe that introduction of configuration interaction (CI) will always help overcome the deficiencies of an approximate method. However, INDO calculations on ozone showed that CI actually led to *worse* excitation energies.[8] For ethylene, we performed a full CI in the space spanned by the four GVB orbitals obtained by splitting the π and CC σ bonding orbitals in the planar N state. The vertical excitation energies to the T and V states were hardly changed by the CI.

The origin of the error in the excitation energies may be readily found by breaking down the excitation energy

(14) (a) T. H. Dunning, Jr., W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, **4**, 147 (1969); (b) C. F. Bender, T. H. Dunning, Jr., H. F. Schaefer III, W. A. Goddard III, and W. J. Hunt, *ibid.*, **15**, 171 (1972).

into one- and two-electron contributions. INDO provides a relatively good approximation for the two-electron part, differing from the exact value by 0.35 eV. However, the one-electron part of the $\pi \rightarrow \pi^*$ excitation energy (for both N $\rightarrow$ T and N $\rightarrow$ V), which may be written as (having transformed to orthogonal atomic orbitals)

$$\langle \pi | t + v + (2J - K)_\sigma | \pi \rangle - \langle \pi^* | t + v +$$
$$(2J - K)_\sigma | \pi^* \rangle = 2 \langle 2p_x{}^l | t + v + (2J - K)_\sigma | 2p_x{}^r \rangle$$

is off by 3.43 eV. In INDO, the one-electron part is just $2\beta_{xx} = 2\beta_c{}^0 S_{xx}$ or -11.38 eV compared to the exact value of -7.95 eV. Thus, the large excitation energies in INDO arise from the use of a β parameter that is too large for the π orbitals. The problem is that in INDO there is only one β per atom, instead of a separate β for each set of orbital interactions, e.g., s–s, s–p_σ, p_σ–p_σ, and p_π–p_π. Using a single β is fine for relatively isotropic systems, e.g., alkanes, but not for anisotropic systems, e.g., alkenes. Del Bene and Jaffe[15] encountered this problem in using CNDO/2 to describe the excited states of aromatic molecules. They reparameterized CNDO using two β's per atom (β_σ and β_π) and obtained reasonable results for excitation energies to singlet excited states of various π-electron systems.

The use of a single isotropic β in INDO favors π orbitals relative to σ orbitals. For example, with INDO the highest occupied orbital of ground state ethylene is not $1b_{3u}(\pi)$ but $1b_{3g}(\sigma)$ and Koopmans' theorem ionization potentials for the π orbitals in ground state methylene and ethylene are high by 3 and 4.5 eV, respectively. One would expect that INDO would treat n $\rightarrow \pi^*$ and $\sigma \rightarrow \pi^*$ transition energies better than $\pi \rightarrow \pi^*$, since n and σ orbitals are treated more correctly than π orbitals.[16,17] Tables I and III show that this is indeed

Table III. $\sigma \rightarrow \pi^*$ Vertical Excitation Energies (eV) for Ethylene

	INDO–GVB(1)	*Ab initio*[a] DZ–CI
2 $^1B_{1g}$	11.6	9.89
2 $^3B_{1g}$	11.4	9.52
3 $^1B_{2g}$	13.6	11.34
3 $^3B_{2g}$	13.2	10.79

[a] R. J. Buenker, S. D. Peyerimhoff, and W. E. Kammer, *J. Chem. Phys.*, **55**, 814 (1971).

the case. The ethylene $\sigma \rightarrow \pi^*$ vertical excitations are high by 2 eV or less, which is nearly half the error present in the $\pi \rightarrow \pi^*$ energies. Recalling that the use of HF wave functions for both the ground and excited states effectively raises the energy of the former by 1 eV, it is clear how INDO HF calculations have in the past produced reasonable vertical excitation energies for some n $\rightarrow \pi^*$ and $\sigma \rightarrow \pi^*$ transitions.[17] Such agreements should not lead one to put too much confidence in INDO results.

(15) J. Del Bene and H. H. Jaffe, *J. Chem. Phys.*, **48**, 1807, 4050 (1968).

(16) Segal[17] previously used the INDO method to describe the low-lying excited states for various small molecules. He also found that the $\pi \rightarrow \pi^*$ transitions were treated much worse than $\sigma \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$, and $\sigma \rightarrow \sigma^*$ transitions. However, only transitions to $^1\pi\pi^*$ states, which require diffuse functions for proper description, were examined. Segal realized that the gross errors were not just due to the INDO method but no comparison was made to the available *ab initio* results,[10,14a] which would have indicated problems in the INDO approximation itself.

(17) G. A. Segal, *J. Chem. Phys.*, **53**, 360 (1970).

Conclusion

The calculations reported here were intended to test the validity of the INDO integral approximation for correlated wave functions. On the surface the results were mixed. Using INDO with simple GVB(1) wave functions led to HCH bending potential curves (for the three lowest states of methylene) that were in good agreement ($\sim$0.2 eV) with *ab initio* calculations. Similar INDO–GVB(1) calculations on the rotation barriers for the three lowest states of ethylene produced errors of 2 to 4 eV relative to *ab initio* results. However, in both cases the INDO approximation frequently led to worse discrepancies when properly correlated wave functions were employed in lieu of closed shell HF wave functions. The errors inherent in the INDO method were often partially canceled by correlation effects not properly taken into account by a closed shell HF wave function. Moreover, the discrepancies encountered in the INDO treatment of ethylene indicate that the failures of the integral approximation are not limited to systems for which HF fails to give a qualitatively correct description, e.g., ozone. In other words, although INDO was parameterized to reproduce MBS HF results, it is not reliable even for calculating HF wave functions for simple systems such as ethylene.

Comparison of the approximate calculations with *ab initio* results for methylene and ethylene uncovered two major trouble spots in the INDO method. The use of empirical rather than nonempirical values for the one-center exchange integrals led to a small $^3B_1$–$^1B_1$ splitting energy in methylene. This result points out the problem of empiricising approximate methods. One must be careful when fitting parameters to experiment that (i) the system is representative of a broad class of interesting systems and (ii) the experimental result is inherently describable; i.e., an *ab initio* calculation with the same wave function and basis set would give a good result. The first condition was not met in this case as the atomic singlet–triplet splitting was much smaller than the comparable molecular splittings. An example of violating the second condition would be to adjust parameters in the INDO approximation so as to reproduce the experimental N $\rightarrow$ V vertical excitation energy, which cannot be properly described with a MBS. This principle was violated, for example, in developing the PPP approximation.[18]

The large vertical excitation energies and rotational barriers for the N, T, and V states in INDO arise from using one β parameter per atom. As a result, the β's for π orbitals are too large, while those for σ orbitals are slightly too small.

We investigated ways of solving this problem and came up with the following modification of INDO. For each diatomic pair, one takes the integrals over a valence set of Slater atomic orbitals and transforms them to orthogonal atomic orbitals. The transformed integrals, which correspond to $\beta_{\mu\nu} = \langle \mu | t + v | \nu \rangle$, are determined. By doing this at various internuclear separations, one can obtain the distance dependence of $\beta_{\mu\nu}$, which turns out to be nearly exponential. Exponential fits to the nonempirical $\beta_{\mu\nu}$ integrals are used to replace the INDO values for these integrals. We have found that for ethylene and benzene the introduction of the nonempirical β's leads to reasonable

(18) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466 (1953).

$\pi \rightarrow \pi^*$ transition energies for the $\pi\pi^*$ states that are well described by a minimal basis set.[19] To obtain good vertical excitation energies to diffuse excited states, such as the V state in ethylene, one must modify the integral approximation to allow more flexible basis sets.

For an approximate integral method to be useful in describing interesting chemical processes, it must provide good results in conjunction with correlated wave functions. Since the available approximations have

(19) W. R. Wadt and W. A. Goddard III, unpublished results.

been based on the HF wave function and are not always reliable, even when used with HF wave functions, the results with correlated wave functions cannot be expected to be very good. This appears to be the case. It is clear that new approximate integral methods must be developed in the context of suitably correlated wave functions. If the initial wave function cannot correctly describe the system, how can the integral approximations be expected to be properly balanced? We are presently developing and analyzing integral approximations with correlated wave functions.

Electrostatic Force Theory for a Molecule and Interacting Molecules. IV. Long-Range Forces between Two Atoms

Hiroshi Nakatsuji*[1a] and Toshikatsu Koga[1b]

Contribution from the Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan, and the Belfer Graduate School of Science, Yeshiva University, New York, New York 10033. Received April 20, 1974

Abstract: The electrostatic force (ESF) theory which was shown previously to be useful for *molecular structures* and *chemical reactions* is here applied to *long-range forces*, using the same laboratory fixed coordinate system. In the ESF theory, the basic concepts are common to all of these important phenomena. The origins of the long-range forces between two well-separated atoms are shown to be the atomic dipole (AD) and the extended gross-charge (EGC) forces. For the long-range forces between two neutral S-state atoms, only the AD force is responsible for the leading terms. If one of the interacting atoms is a bare nucleus, the long-range force can be obtained only from the EGC force. In a perturbative treatment, the nth order corrections to the AD and EGC forces are obtained from the nth order and $(n-1)$th order corrections to the electron density, respectively. These long-range AD and EGC forces are calculated for two simple systems: the H(1s)–H$^+$ and H(1s)–H(2p) systems. Both of the AD and EGC forces are shown to be very important. Excellent agreements are obtained between the energetic and force treatments in the final *numerical* values. However, the theoretical origins and the interpretations of the long-range *forces* are quite *different* from those of the *energetic* theories. The differences between these standpoints are discussed in some detail. The necessity of the "higher order" wave function for the calculation of the Hellmann–Feynman force does not mean the "complexity" of the results. The results preserve the *conceptual simplicity* of the ESF theory.

R ecently, there seems to be some renewed interests on the use of the electrostatic Hellmann–Feynman theorem[2,3] for many chemically important phenomena.[4-7] One motive common to these studies lies in the conceptual simplicity of the theorem written in a laboratory fixed coordinate system as

$$\mathbf{F}_A = -\langle \Psi | \partial \mathcal{H}/\partial \mathbf{R}_A | \Psi \rangle$$
$$= Z_A \left\{ \int \rho(\mathbf{r}_1)\mathbf{r}_{A1}/r_{A1}{}^3 d\mathbf{r}_1 - \sum_{B(\neq A)} Z_B \mathbf{R}_{AB}/R_{AB}{}^3 \right\} \quad (1)$$

(1) (a) Until January 1975, Department of Chemistry, University of North Carolina, Chapel Hill, N. C. 27514, and after that ref 1b; (b) Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan.

(2) H. Hellmann, "Einführung in die Quantenchemie," Deuticke, Vienna, 1937, p 285.

(3) R. P. Feynman, *Phys. Rev.*, **56**, 340 (1939).

(4) B. M. Deb, *Rev. Mod. Phys.*, **45**, 22 (1973), and the references cited therein.

(5) R. F. W. Bader, W. H. Henneker, and P. E. Cade, *J. Chem. Phys.*, **46**, 3341 (1967), and the succeeding papers.

(6) A. B. Anderson, N. C. Handy, and R. G. Parr, *J. Chem. Phys.*, **50**, 3634 (1969); A. B. Anderson and R. G. Parr, *ibid.*, **53**, 3375 (1970), and the succeeding papers.

(7) (a) H. Nakatsuji, *J. Amer. Chem. Soc.*, **95**, 345, 354, 2084 (1973), which are referred to in the text as papers I, II, and III; (b) H. Nakatsuji, T. Kuwata, and A. Yoshida, *ibid.*, **95**, 6894 (1973); (c) H. Nakatsuji, *ibid.*, **96**, 24, 30 (1974).

where the notations are the same as those in the previous reports.[7] Namely, the force acting on a nucleus A of a system is given through the classical electrostatics for the interactions among charged nuclei and the electron cloud, if a reasonably good[8] electron density is obtained by quantum-mechanical calculations.

For the long-range interactions, Feynman[3] stated in his original report a conjecture that the van der Waals forces would be due to the simultaneous inward polarizations of the electron clouds of the interacting atoms, the extent of the polarization being proportional to $1/R^7$. After this report, no calculations had been done for 27 years until Frost[9] applied this theorem to the long-range interactions of the H(1s)–H$^+$ and H(1s)–H(1s) systems. However, his numerical results were unsatisfactory when he used the approximate wave functions for the calculations. It is well known that

(8) (a) A. C. Hurley, *Proc. Roy. Soc., Ser. A*, **226**, 170, 179, 193 (1954); "Molecular Orbitals in Chemistry, Physics, and Biology," P.-O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 161; (b) L. Salem and E. B. Wilson, Jr., *J. Chem. Phys.*, **36**, 3421 (1962).

(9) A. A. Frost, University of Wisconsin Theoretical Chemistry Report, WIS-TCI-204, Dec 1966.