# Ground States of Molecules. XXXI.[1] MINDO/3 Study of $CH_2$, $NH_2^+$, and $O_2$[2,3]

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**Abstract:** MINDO/3 calculations are reported for the three lowest states ($S_0$, $S_1$, $T_1$) of methylene ($CH_2$) and of the nitrenium ion ($NH_2^+$) and for the $^3\Sigma_g^-$, $^1\Sigma_g^+$, and $^1\Delta_g$ states of oxygen. The results for $CH_2$ are in better agreement with experiment than those from the most detailed ab initio calculations so far reported. The calculated energies and geometries of all three states of $O_2$ also agree well with experiment, the results again comparing favorably with those of ab initio calculations.

Methylene ($CH_2$) has aroused the interest of a number of theoreticians for several reasons.

First, this molecule is simple enough to allow rather sophisticated ab initio calculations in which allowance is made for electron correlation by using extensive configuration interaction (CI).

Secondly, while it has been shown experimentally[5] that $CH_2$ has a triplet ground state, widely varying estimates have been made of the singlet-triplet splitting. It is an obvious challenge to quantum chemists to see if their procedures correctly predict $CH_2$ to have a triplet ground state and to estimate the difference in energy between it and the lowest singlet.

Thirdly, according to simple MO theory, $CH_2$ should exist in two singlet states and a triplet state of not-too-dissimilar energies. It is of interest to try to predict the relative energies of the states as a function of the HCH bond angle.

Fourthly, the geometry of the lowest singlet state ($S_0$) has been established by spectroscopic measurements[6] and that of the triplet by ESR[5] and spectroscopic[7] studies. It is interesting to see if these geometries can be reproduced with MINDO/3.

A number of ab initio SCF calculations have been reported[8-17] for $CH_2$. These all agree in predicting the ground state to be a triplet. They also agree in predicting (correctly[6]) the lowest singlet state ($S_0$) to have a bond angle similar to that in $H_2O$, as one would also expect from simple MO arguments. The more sophisticated calculations[8,10,11,13-16] also agree in predicting the bond angle in triplet ($T_1$) $CH_2$ to be ca. 135°. Early spectroscopic studies[18] had indicated that triplet $CH_2$ is linear, or almost linear. However, ESR studies[5] showed this not to be the case, the bond angle being ca. 136°. A subsequent reexamination[7] of the spectroscopic data showed that they were in fact consistent with the bent structure.

Widely varying experimental estimates have been reported for the singlet-triplet ($S_0$-$T_1$) separation in $CH_2$. Early electron impact work[19] led to a value of 38 kcal/mol. However, it was not at all clear that the species in question had been correctly identified. Subsequent photochemical studies were believed to indicate a very small $S_0$-$T_1$ splitting (1-2[20] and 2.5[21] kcal/mol). The most recent experimental work has led to intermediate values (8[22] and 9[23] kcal/mol).

Little is as yet known of the nitrenium ion, $NH_2^+$, which is isoelectronic with $CH_2$, although derivatives of it have recently been shown to play a role as intermediates in chemical reactions.[24] It is interesting to try to predict how its properties will vary from those of $CH_2$. Three ab initio calculations for $NH_2^+$ have recently appeared.[25-27] All of these predict $NH_2^+$ to have a triplet ground state, like $CH_2$, but with a much larger $S_0$-$T_1$ separation (ca. 40 kcal/mol).

The last molecule considered here, $O_2$, has been studied in great detail, and its properties are well known experimentally.[28] Extensive SCF calculations have been reported, allowing estimates to be made[29] of the limiting Hartree-Fock values for the energies of the three lowest states ($^3\Sigma_g^-$, $^1\Delta_g$, $^1\Sigma_g^+$). Recently Schaeffer and Harris[30] have carried out a very detailed SCF-CI calculation, including 64 configurations.

We have studied the properties of these simple molecules using MINDO/3[31] for three reasons.

First, we thought it of interest to compare the results of our very simple procedure with those of ab initio SCF calculations for systems simple enough for refined ab initio calculations to have been feasible.

Secondly, we wanted to see if MINDO/3 could be extended satisfactorily to triplet states. Methylene and oxygen are among the very few molecules with triplet states that have been studied in detail.

Thirdly, assuming that MINDO/3 passed these tests satisfactorily, we thought it might provide chemically useful information concerning the properties of $NH_2^+$, for this has not yet been studied by ab initio methods of the same degree of elaboration as those used for $O_2$ and $CH_2$.

A preliminary account of some of our calculations for $CH_2$ and $O_2$ has already appeared.[3] Here we present the full results together with those for $NH_2^+$.

## Theoretical Procedure

According to the simple MO picture, four of the six valence electrons in $CH_2$ or $NH_2^+$ are used for CH or NH bonding. The remaining two electrons can then occupy the two unused valence AO's of C or N in three different ways. The lowest singlet ($S_0$) state has a closed shell structure with one of the two AO's doubly occupied. The remaining states have an electron in each of the AO's, with either antiparallel ($S_1$) or parallel ($T_1$) spin. The first of these can be treated by the standard closed shell MINDO/3 procedure.[31] In our approach, open shell systems (such as the $S_1$ and $T_1$ states of $CH_2$) are treated by the "half-electron" method.[32,33] This is included as an option in our MINDO/3 computer program.

The geometry of each species was found by minimizing the energy with respect to bond length ($r$) and (in $CH_2$, $NH_2^+$) bond angle ($\theta$). The energies of each of the three states of $CH_2$ and $NH_2^+$ were also calculated as a function of $\theta$ for $90° \leq \theta \leq 180°$, $r$ being optimized at each point.

As noted previously,[3] the energy of the $S_0$ state of $CH_2$ is not well represented by a single configuration treatment such as MINDO for large values of $\theta$. As $\theta \rightarrow 180°$, the HOMO and LUMO become degenerate, and the correla-

Table I. Calculated and Observed Properties of $CH_2$ in Various States

| State | Property | Experiment | MINDO/3 | MINDO/2[a] | Ab initio SCF | "Best" correlated ab initio SCF[b] |
|---|---|---|---|---|---|---|
| $S_0$ | $\Delta H_f$[c] | 101[d] | 100.2 | 95.8 | | |
| | $r_{CH}$, Å | 1.12[e] | 1.122 | 1.097[f] | 1.100[g], 1.133[h], 1.116[u] | 1.125 |
| | HCH angle, deg | 103.2[e] | 100.2 | 107 | 105.4[g], 104.4[h], 108[i], 105[j] 100[k], 105[l], 102.5[u] | 101.0 |
| $T_1$ | $\Delta H_f$[c] | 93.9 ± 0.7[m],<br>91.9 ± 1[n],<br>95.5[o] | 91.5 | 67.5 | | |
| | $r_{CH}$, Å | 1.078[p] | 1.078 | 1.062[f] | 1.069[g], 1.095[h], 1.096[q], 1.081[u] | |
| | HCH angle, deg | 136[p,r] | 134.1 | 142 | 132[g]. 133.3[h], 138[i], 132.5[j], 130[k], 135[l], 134.2[u] | |
| $S_1$ | $\Delta H_f$[c] | | 125.0 | 97.0 | | |
| | $r_{CH}$, Å | 1.05[p] | 1.078 | 1.050[f] | 1.092[h] | |
| | HCH angle, deg | 140 ± 15[p] | 141.7 | 180 | 143.8[h], 148[i], 180[j], 135[l] | |
| $S_0$, $T_1$ | $S_0-T_1$[s] | 8[t], 9[d] | 8.7 | 28.3 | 37[g], 22[h], 33[i], 25[j], 20.3[k], 11.5[l], 9.2 ± 3[u] | 11.0 ± 2 |

[a] Reference 35. [b] Reference 17. [c] Heat of formation (kcal/mol at 25°). [d] Reference 23. [e] Reference 6. [f] Corrected value; see reference 35. [g] Reference 10. [h] Reference 13. [i] Reference 8. [j] Reference 11. [k] Reference 15. [l] Reference 16. [m] V. K. Dibeler, M. Krauss, R. M. Reese, and F. N. Harllee, *J. Chem. Phys.*, 42, 3791 (1965). [n] W. A. Chupka and C. Lifshitz, *J. Chem. Phys.*, 48, 1109 (1968). [o] W. A. Chupka, J. Berkowitz, and K. M. A. Refaey, *J. Chem. Phys.*, **50**, 1938 (1969). [p] Reference 7. [q] Reference 9. [r] Reference 5. [s] Singlet–triplet ($S_0-T_1$) separation (kcal/mol). [t] Reference 22. [u] Reference 14.

tion energy increases correspondingly. The energy of the $S_0$ state is therefore overestimated relative to that of $S_1$. Thus whereas the two states become degenerate at $\theta$ = 180°, MINDO predicts $S_0$ to lie well above $S_1$. This difficulty is similar in nature to that encountered in bond-dissociation processes where the combined energy of the resulting pair of radicals is overestimated by a single configuration treatment.[34] The solution is the same in both cases, i.e., inclusion of CI with the lowest doubly excited configuration. Calculations for these states were therefore carried out both with and without such CI.

Similar problems arise in attempts to calculate the energies of the three lowest states of $O_2$. The corresponding configurations can be written in a straightforward manner if complex $\pi$ MO's are used; however, MINDO/3 uses only real MO's. In terms of real $\pi$ MO's $\pi_x$ and $\pi_y$, the various states can be shown to correspond to the following configurations or combinations of configurations:

$$^3\Sigma_g{}^- \frac{1}{(2)^{1/2}}|\pi_x\pi_y|;\ \frac{1}{(2)^{1/2}}|\bar{\pi}_x\bar{\pi}_y|;\ \frac{1}{2}\{|\pi_x\bar{\pi}_y| + |\bar{\pi}_x\pi_y|\} \tag{1}$$

$$^1\Delta_g \frac{1}{2}\{|\pi_x\bar{\pi}_x| - |\pi_y\bar{\pi}_y|\};\ \frac{1}{2}\{|\pi_x\bar{\pi}_y| - |\bar{\pi}_x\pi_y|\} \tag{2}$$

$$^1\Sigma_g{}^+ \frac{1}{2}\{|\pi_x\bar{\pi}_x| + |\pi_y\bar{\pi}_y|\} \tag{3}$$

Thus while the "half-electron" MINDO/3 procedure[32,33] should give a correct estimate of the energy of the triplet ($^3\Sigma_g{}^-$) ground state, it will *not* give a correct estimate for the $^1\Sigma_g{}^+$ state, because the singlet "half-electron" configuration corresponds to $|\pi_x\bar{\pi}_y|$ or $|\bar{\pi}_x\pi_y|$. The normal closed shell MINDO/3 treatment will likewise fail to give either singlet energy, the corresponding configuration being $|\pi_x\bar{\pi}_x|$ or $|\pi_y\bar{\pi}_y|$. In the latter case, however, the lowest "doubly excited" configuration will be $|\pi_y\bar{\pi}_y|$ or $|\pi_x\bar{\pi}_x|$, respectively. One can therefore find the energies of both singlet states simultaneously by including CI with the lowest doubly excited configuration, a standard option in the MINDO/3 program (cf. the calculations for near-linear $CH_2$ and $NH_2{}^+$ noted above). The 2 × 2 CI treatment gives the energies of both singlet states simultaneously (see eq 2 and 3).

## Results

Table I shows the MINDO/3 heats of formation ($\Delta H_f$) and geometries for the three lowest states of $CH_2$ together with experimental values and the results of ab initio calculations.[8-17] Since the latter give very poor estimates of heats of atomization and hence of derived values of $\Delta H_f$, these are not available. Instead, values for the $T_1$–$S_0$ separation are listed since this is a quantity both of experimental interest and accessible to ab initio methods.

Table II. MINDO/3 Formal Charges[a,b] in $CH_2$ and $NH_2{}^+$

| | Formal charges in $CH_2$ | | Formal charges in $NH_2{}^+$ | |
|---|---|---|---|---|
| State | H | C | H | N |
| $S_0$ | −0.0939 | 0.1878 | 0.1844 | 0.6311 |
| $S_0$ + CI | −0.0838 | 0.1675 | 0.1947 | 0.6105 |
| $S_1$ | 0.0837 | −0.1675 | 0.2888 | 0.4223 |
| $T_1$ | 0.0701 | −0.1402 | 0.2520 | 0.4961 |

[a] In units of the electronic charge. [b] The formal charge ($Q_m$) at atom $m$ is given by $Q_m = C_m - \Sigma_i{}^{(m)}q_i$ where $C_m$ is the core charge, $q_i$ is the total occupation of AO $i$, and the sum is over AO's of atom $m$.

Table II shows the calculated distributions of formal charges in the three states of $CH_2$.

Figure 1 shows the calculated variation in energy of each of the three states of $CH_2$ with bond angle $\theta$. Values for $S_0$ are shown with and without CI.

Table III shows the MINDO/3 heats of formation and geometries of the three states of $NH_2{}^+$, together with the $S_0$–$T_1$ separation and values from ab initio calculations.[25-27] No experimental values are as yet available. The calculated distributions of formal charge are listed in Table II, while Figure 2 shows the calculated variation in energy of each of the three states with bond angle $\theta$. Again, results for $S_0$ are given with and without CI.

Table IV compares the MINDO/3 and observed[28] properties of $O_2$ in its three lowest states, together with results from ab initio calculations.[29,30]

## Discussion

The geometries and relative energies of the various states of $CH_2$ have been calculated by a variety of ab initio procedures. It is gratifying to find (Table I) that MINDO/3 gives results that are apparently somewhat superior to even the most elaborate of these. Moreover MINDO/3 gives good estimates of heats of atomization, something that no ab initio SCF treatment can achieve at present even for so small a molecule as $CH_2$.

A particularly interesting problem is to determine the separation between the triplet ($T_1$) ground state and the

Table III. MINDO/3 and Ab Initio Results for $NH_2^+$ in Various States

| State | Property | MINDO/3 (with CI) | MINDO/3 (no CI) | Lee and Morokuma[a] | Hayes et al.[b] | Harrison and Eakers[c] |
|---|---|---|---|---|---|---|
| $S_0$ | $\Delta H_f$[d] | 283.6 | 289.8 | | | |
| | $r_{NH}$, A | 1.033 | 1.037 | 1.058 | 1.058 | 1.008 |
| | HNH angle, deg | 108.7 | 106.2 | 106[e], 115[f] | 120 | 122 |
| $T_1$ | $\Delta H_f$ | | 259.0 | | | |
| | $r_{NH}$, A | | 1.000 | 1.058 | 1.058 | 1.008 |
| | HNH angle, deg | | 140.4 | 146[e], 180[f] | 140 | 150 |
| $S_1$ | $\Delta H_f$ | | 295.0 | | | |
| | $r_{NH}$, A | | 0.996 | 1.058 | 1.058 | 1.008 |
| | HNH angle, deg | | 169.2 | 150[e], 180[f] | 180 | 180 |
| $S_0$, $T_1$ | $S_0-T_1$[g] | 24.6 | 30.8 | 45 | 36 | 45 |
| $S_0$, $S_1$ | $S_1-S_0$[h] | 11.4 | 5.2 | 8 | 4 | 4 |

[a] Reference 25. [b] Reference 26. [c] Reference 27. [d] Heat of formation (kcal/mol at 25°). [e] Results obtained using a minimum basis set of STO's. [f] Results using a double $\zeta$ basis set. [g] Singlet–triplet ($S_0-T_1$) separation (kcal/mol). [h] Singlet–singlet ($S_0-S_1$) separation (kcal/mol).

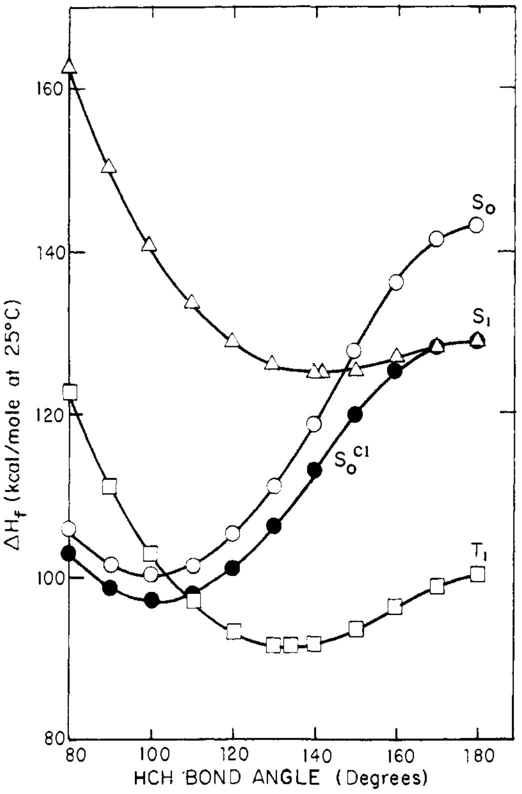

Figure 1. Plot of calculated (MINDO/3) heat of formation ($\Delta H_f$) vs. HCH bond angle for the $S_0$ (○), $S_1$ (△), and $T_1$ (□) states of $CH_2$. Values (●) are also given for $S_0$ including CI with the lowest doubly excited configuration.

Table IV. Calculated and Observed Properties of $O_2$

| Property | Method | $O_2$ ($^3\Sigma_g^-$) | $O_2$ ($^1\Delta_g$) | $O_2$ ($^1\Sigma_g^+$) |
|---|---|---|---|---|
| Heat of atomization, kcal/mol | MINDO/3 | 121.0 | 102.7 | 85.6 |
| | Observed[a] | 117.1 | 94.6 | 79.3 |
| | SCF[b] | 35.0 | 4.4 | −54.7 |
| | SCFCI[c] | 85.8 | 62.7 | 54.4 |
| Bond length, A | MINDO/3 | 1.206 | 1.206 | 1.206 |
| | Observed[a] | 1.21 | 1.22 | 1.23 |
| | SCFCI[c] | 1.30 | 1.33 | 1.34 |

[a] Herzberg, "Spectra of Diatomic Molecules", 2nd ed, McGraw-Hill, New York, N.Y., 1950. [b] A. C. Hurley, *Adv. Quantum Chem.*, 7, 315 (1973). [c] H. F. Schaeffer, III, and F. E. Harris, *J. Chem. Phys.*, 48, 4946 (1968).

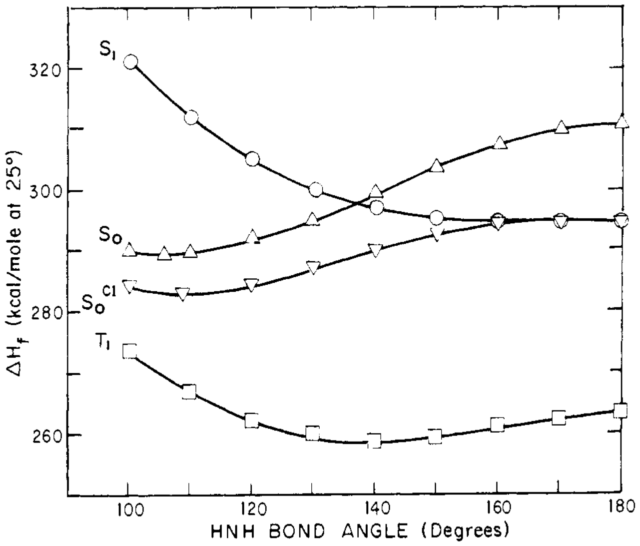

Figure 2. Plot of calculated (MINDO/3) heat of formation vs. HNH bond angle for the $S_0$ (△), $T_1$ (□), and $S_1$ (○) states of $NH_2^+$. Values (▽) for $S_0$ with inclusion of CI with the lowest doubly excited configuration are also shown.

lowest singlet ($S_0$). Earlier MINDO/2 calculations[35] had, like all but the most recent and most elaborate ab initio treatments, led to a $T_1$–$S_0$ separation that now seems almost certainly much too large. Note that MINDO/3 gives a value in complete agreement with the latest experimental estimates and the latest ab initio value.[14]

In estimating the $T_1$–$S_0$ separation, we used the energy calculated for $S_0$ without CI. It would be incorrect in this case to include CI, because MINDO/3 is parametrized without it. MINDO/3 consequently allows for electron correlation by appropriate modification of the electron repulsion integrals, as first suggested by Pariser and Parr.[36] Inclusion of CI in calculations for a normal closed shell molecule would then lead to an overallowance for electron correlation and consequently to a too negative heat of formation. CI should be included in MINDO/3 only when dealing with biradical-like systems, i.e., those in which the HOMO and LUMO are degenerate or almost degenerate. As pointed out above, this situation holds in linear $CH_2$ or $NH_2^+$ and in $O_2$.[37]

Figure 1 shows the calculated variations in energy of the three states of $CH_2$ as a function of the HCH angle $\theta$. Note that, when CI is included, the $S_0$ and $S_1$ states correctly become degenerate as $\theta \rightarrow 180°$. The variations in energy of the states with $\theta$ resemble qualitatively those predicted by ab initio methods. However MINDO/3, like MINDO/2, differs from them in predicting that the $S_0$ and $T_1$ states should cross as $\theta$ decreases. Indeed, MINDO/3 leads to an even larger value (104°) for the critical angle than did MINDO/2[35] (80°). This seems to suggest that cyclopropylidene may prove to have a singlet ground state.

Turning now to the results for $NH_2^+$ (Table III), here there are marked differences between the MINDO/3 results and those from the three published ab initio studies. Hayes et al.[26] and Harrison and Eakers[27] predicted the bond angle in $NH_2^+$ to be ca. 120°, while Lee and Morokuma[25] found the angle to change from 106 to 115° on increasing the size of their basis set. In the case of the triplet ($T_1$) state, Hayes et al.[26] and Harrison and Eakers[27] agree with MINDO/3 in predicting the bond angle to be similar to that in triplet $CH_2$, whereas Lee and Morokuma[25] found triplet $NH_2^+$ to be linear, using their larger basis set. All three ab initio calculations[25-27] agree in predicting a very high value for the $T_1$-$S_0$ separation. MINDO/3 agrees with them in predicting this to be greater than in the case of $CH_2$, but the MINDO/3 value is much less than the ab initio ones.

Since the ab initio calculations were carried out by procedures that gave much too large $T_1$-$S_0$ separations in $CH_2$, it seems likely that the MINDO/3 value for this, and probably also for the bond angles, is nearer to the truth.

The variations in energy of the three states of $NH_2^+$ with bond angle, predicted by MINDO/3 (Figure 2), agree qualitatively with those for $CH_2$. In this case, however, the $T_1$-$S_0$ separation at equilibrium is so large that the states do not cross at any reasonable value of the bond angle.

Note also that the effect of CI is greater in the $S_0$ state of $NH_2^+$ than $CH_2$, lowering it by 6.8 kcal/mol. The $T_1$-$S_0$ separation in Table III may therefore be a little large.

The calculated distributions of formal charge (Table II) present no unexpected features and agree quite well with those from the ab initio calculations. The Hartree-Fock method is believed to give good estimates of overall electron distributions (i.e., the first-order density matrix) even though the total energies are in error by ca. 1%.

The calculated energies of the three lowest states of $O_2$ (Table IV) again agree quite well with experiment, and the calculated separations between the states agree even better, i.e.,

$$\begin{aligned} {}^3\Sigma_g^- - {}^1\Delta_g &\text{ calcd, 17.8; obsd, 22 kcal/mol} \\ {}^3\Sigma_g^- - {}^1\Sigma_g^+ &\text{ calcd, 35.6; obsd, 38 kcal/mol} \end{aligned} \quad (4)$$

Table IV also shows the results of an SCF calculation that is believed[29] to approach the Hartree-Fock limit and of an SCF-CI calculation including 64 configurations.[30] The SCF results are clearly very unsatisfactory, giving very poor estimates of the separations of the three states and huge errors in the calculated heats of atomization. The ${}^1\Sigma_g^+$ state is even predicted to be dissociative. The SCF-CI calculation is much better, giving good estimates of the energies of the singlet state relative to the triplet ground state (${}^3\Sigma_g^- - {}^1\Delta_g$, 23.1, ${}^3\Sigma_g^- - {}^1\Sigma_g^+$, 31.4 kcal/mol, respectively; cf. eq 4) However, the calculated heats of atomization are all too small by ca. 30 kcal/mol and the calculated bond lengths too large by 0.1 Å. Clearly the MINDO/3 results are on balance much superior.

These three systems are all simple enough for very elaborate and detailed ab initio calculations to have been possible. In setting MINDO/3 against them, we are certainly playing an away match. It is therefore particularly gratifying that MINDO/3 has come so well out of the encounter, proving superior to the most detailed ab initio procedures that have as yet been used in this connection.

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## Appendix. The Validity of Calculations Using MINDO-Type Treatments

A referee has once again raised the standard objections to the use of MINDO/3 in connections such as this i.e.:

(1) Any semiempirical treatment is by nature no more than a "curve-fitting" approach which cannot be relied on outside the range of compounds used to determine the parameters in it.

(2) It is theoretically impossible for such a procedure to give satisfactory results for ions, using parameters derived from neutral molecules.

(3) Whenever cases are found where the procedure fails, the errors can be corrected by producing yet another set of parameters ("maybe MINDO/135" in the words of the present referee).

Since our replies to these criticisms in earlier papers of this series have apparently still passed unheeded, a further direct rebuttal seems appropriate.

I. It should be emphasized yet again that the first of these criticisms applies to *all* current methods, both ab initio and semiempirical, since none of them can treat the problems of structure and reactivity in any but a wholly empirical sense. The errors in the energies of organic molecules, calculated by the best available ab initio methods, are greater than the corresponding heats of atomization. Such a treatment cannot be used in an a priori sense to predict even the existence of molecules, let alone to estimate their properties. It may be that certain properties will in fact be well reproduced because of some cancellation of errors, but there is no good theoretical reason why this should be the case. Such applications are therefore by their nature wholly empirical and should in principle be limited to areas where the methods in question have been tested by comparison with experiment.

Calculations of molecular properties are, however, of little value if they merely reproduce experiment. The main purpose is to provide information in the twilight areas of chemistry where experimental data are currently unobtainable. The extrapolation of any empirical procedure into such regions clearly involves uncertainties. We must at least ensure that our procedure reproduces experiment in as many areas as possible where data are available. In particular, we should be able to reproduce the relative energies of a given collection of atoms in all the geometries accessible to experiment, i.e., the stable molecules denoted by minima in the corresponding potential surface and the plateau corresponding to isolated atoms. In other words, our procedure should reproduce heats of atomization, and these should be checked for molecules of as many different kinds as possible. It is also important that the errors should be reasonably constant for, if very large errors occur in any of the cases where experimental data are available, calculations for cases when such data are not available will be correspondingly uncertain.

MINDO/3 has been subjected[1,31] to extensive tests of this kind with apparent success. Calculations for several hundred molecules of many different types have given heats of atomization and geometries in reasonable agreement with experiment. While the average error in the former is larger than one would like (ca. 6 kcal/mol), it is at least reasonably uniform. Since the tests covered molecules of many kinds, including radicals, ions, radical ions, and even some "nonclassical" compounds, there seems to be good reason to believe that calculations for other species should give results of comparable accuracy.

It may be pointed out that no other procedure comes within sight of this level of performance. Even the most detailed ab initio SCF calculations, approaching the Hartree-Fock limit, give heats of atomization that can be in error by as much as −100 ($F_2$) or +100% ($N_2$). The situation is improved by inclusion of configuration interaction, but the errors still remain large (see Table IV). Calculations using minimum basis sets can also lead to very large errors in calculated heats of reaction.[39] These seem to be less if a basis set of double $\zeta$ type is used; however, such methods have been little tested because of the cost of the necessary calculations, and the limited results available suggest that the errors are in any case still at least as great as those given by MINDO/3.

Since the other current semiempirical methods (EH, CNDO, INDO) were parametrized to mimic the results of minimum basis set ab initio calculations, it is not surprising to find that they lead to even larger errors in calculated heats of atomization and heats of reaction.

II. As has already been pointed out above, MINDO/3 reproduces the properties of ions as well as it does those of neutral molecules, in spite of the fact that no ions were included in the basis set of species used in the parametrization. This uniform success is probably due to the procedure used to determine one-center parameters from atomic spectroscopic data (see part XVII[40]).

Even more surprising is the fact that MINDO/3 can apparently reproduce a large variety of ground-state properties, although it was parametrized only by reference to heats of atomization and molecular geometries. Such properties include molecular vibration frequencies and force constants, dipole moments, molecular electric polarizabilities, nuclear quadrupole coupling constants, ESCA chemical shifts, and the electronic band structure of polymers. Recently it has been found that MINDO/3 also gives satisfactory estimates of the lowest singlet and triplet excitation energies of molecules, although it was of course parametrized only with reference to ground states.

These results suggest that MINDO/3 must be much more than a mere "curve fitting" procedure, for such a procedure could not reproduce properties outside the range involved in the fitting procedure. One cannot, for example, use the Westheimer-Allinger molecular mechanics procedure to estimate properties of molecules other than their energies, geometries, and vibration frequencies. These considerations suggest that MINDO/3 must provide a much more profound account of molecular structure than any "curve fitting" procedure could possibly do.

We think this is probably due to the approach[39] we used in developing MINDO/3, i.e., considering the physical meaning of the various terms in the expression for the energy of a molecule and the best ways to incorporate their equivalent in MINDO/3. What we have in effect tried to do is to develop an analog of reality which will mimic in every detail the behavior of real molecules while still retaining the mathematical simplicity of the orbital approach.

A good parallel is provided by the concept of localized bonds, which has proved extremely useful in chemistry in spite of the fact that it cannot be justified in terms of rigorous quantum theory. This is because the localized bond model is not a representation of reality but rather an analog of it.[41] The relationship between the two is similar to that between the stresses and strains in the girders forming a bridge and the electric circuits set up by an engineer in an analog computer to mimic them. As a result of this relationship, he is able to use the analog computer to predict the behavior of the bridge before it is built; the localized bond model can be used likewise to predict the behavior of real chemical systems.

The orbital approximation can be regarded as a similar simplified analog of reality. It represents the situation that would arise in a universe parallel to ours in which there are no direct interelectronic repulsions, the electrons influencing each other indirectly by modifying the nuclear field. From this viewpoint, the Hartree-Fock approximation represents one possible analog of this kind in which the nuclear field is altered in a specific way. There is, however, no reason to suppose that this is the only way or even the best way. There may well be alternative modifications of the nuclear field that will lead to a much closer correspondence between our analog and the behavior of the "real" atoms and molecules in our own universe.

We could construct our analog by setting up assumed potential functions and solving the corresponding Schrödinger equation, using a variational approach as in the Roothaan-Hall SCF method. However, in this, the potential functions would appear only in the form of integrals involving them and the basis set functions. We could therefore equally well treat the integrals themselves as our parameters. This is essentially the approach we have followed in developing MINDO/3.

It might be argued on this basis that our approach is less meaningful than an ab initio one that aims directly at approximate solutions of the "real" Schrödinger equation. This would certainly be true if ab initio methods were more accurate or if we were concerned with problems where energies did not need to be known with high accuracy. In practice, as we have already pointed out, the possible errors in Hartree-Fock method are so large that it cannot be used to predict even the *existence* of molecules. It cannot therefore give information of any more fundamental chemical significance than can any other empirical procedure.

This point should be stressed because there is still a tendency to regard ab initio results as "real". A good example is provided by the familiar computer-drawn pictures of electron densities in molecules. It is of course a simple matter to derive similar plots from MINDO/3 eigenvectors, and the results are almost indistinguishable from the ab initio ones. Both are equally "real" or "unreal".

III. The third criticism, i.e., the danger of proliferation of parameters in semiempirical methods, is one we have in fact been particularly careful to avoid. Apart from a very preliminary version (MINDO/1), there have been just two main forms of MINDO together with a minor modification of MINDO/2 which we termed MINDO/2′. We have taken the view that parameters must not be changed until some new stable set has been reached, i.e., a set which leads to demonstrably superior results and which at the same time seems to have been developed to its limit. The development of MINDO/3 took 2 years and hundreds of hours of computer time. During this period, we had at least 100 sets of parameters that were clearly superior to MINDO/2; however, we did not release them, or even use them (apart from calculations designed to test them), because we thought that further improvement was still possible.

It seems particularly unwise for those working in the ab initio SCF field to raise this particular criticism in view of the chaotic state of affairs in their own domain. Literally dozens of different basis sets have been used in ab initio SCF calculations, and many calculations have been, and still are being, reported in which the basis set used is not even properly specified. While this makes it impossible to compare the results of different authors with one another, there is an even more serious problem. As Pople et al. have shown, the errors in calculated heats of reaction are very sensitive to the choice of basis set. Moreover the only detailed tests of ab initio SCF procedures are due to them and refer only to the basis sets they have used (STO-3G, 4-31G, etc.). The use of other basis sets in such connections therefore has no justification and can lead only to results of at best dubious chemical value.

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(37) It would of course be better in principle to parameterize MINDO/3 with inclusion of CI (with the lowest doubly excited configuration) throughout. Such a version of MINDO/2 has been reported.[34] At that time we were using a relatively inefficient geometry procedure (Simplex) which, however, worked equally well when CI was included. Our present geometry program,[38] based on the Davidon–Fletcher–Powell algorithm, is very much faster but requires a knowledge of the derivatives of the energy with respect to the geometrical variables. Such derivatives can be found very easily in a single-configuration MINDO/3 treatment but not if CI is included. Inclusion of CI throughout would therefore increase the computation time required out of all proportion to any possible gain. The effect of CI on the MINDO/3 energies of "normal" molecules is in any case small, nearly always in the range 1–3 kcal/mol.
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# Proximity and Bond Orientation Effects on Long-Range Proton–Fluorine Nuclear Spin–Spin Coupling Constants

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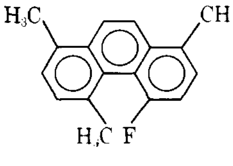
**Abstract:** A theoretical study is presented of the effects of H . . . F proximity and bond orientation on the long-range hydrogen-fluorine nuclear spin-spin coupling constants (LRHFC) in a variety of saturated and unsaturated fluoroorganic compounds. Calculated results for Fermi contact contributions are based on the finite perturbation theory (FPT) formulation for coupling constants in the semiempirical molecular orbital approximation of intermediate neglect of differential overlap (INDO). Calculated results are also given for intermolecular H–F coupling in several dimers since this makes it possible to vary the distances and orientations over ranges of distances and conformations which are not generally accessible for intramolecular coupling in individual molecules. In this way it is possible to demonstrate the complexity of the long-range coupling phenomenon, which is usually called "through-space", and which has been presumed to be dependent on only the internuclear separation. Indeed, large (usually negative) values of LRHFC are predicted when the nuclei are spatially close, but significant values can occur for other orientations. It is important to note that substantial *positive* values of LRHFC are obtained when the bond containing the hydrogen is directed *away* from the fluorine atom. This mechanism is shown to involve the orbitals on the fluorine and the carbon atom to which the hydrogen is bonded. In cases where one of the coupled nuclei can assume several orientations, the averaging of large values of opposite sign leads to small observed values. The calculated results are compared with the available experimental data and found to be in reasonable agreement for this level of approximate molecular orbital theory.

The importance of the effects of proximity of the atoms on long-range proton–fluorine coupling is clearly demonstrated[2a] by the 11.9-Hz value observed in the phenanthrene derivative **1**. Long-range H–F coupling (LRHFC) between the $CH_3$ and the F, which are separated by six bonds in **1**, would be much smaller in magnitude if the dominant mechanisms were $\sigma$–$\pi$ exchange and delocalization in



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