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# Note on Open Shell Restricted SCF Calculations for Rotation Barriers about C–C Double Bonds: Ethylene and Allene

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It is shown that *ab initio* open-shell SCF calculations yield acceptable results for rotation barriers about double bonds in contrast to more conventional closed-shell SCF calculations. Using basis sets of double zeta + polarization quality the SCF values for the rotation barriers of ethylene and allene are obtained to be 48 and 50 kcal/mole, respectively. An IEPA estimate of the influence of electron correlation leads to values of 64 and 52 kcal/mole, respectively, which are in reasonable agreement with the experimental values.

**Key words:** Rotation barriers about C–C double bonds – Ethylene – Allene

## 1. Introduction

It has been observed that *ab initio* SCF calculations (i.e. closed-shell Hartree-Fock (RHF) calculations) are very successful in predicting inversion barriers and rotation barriers about C–C single bonds, but fail completely for rotation barriers about C–C double bonds. Typical *ab initio* SCF values for the rotation barrier of ethylene, for example, are 129 kcal/mole [1] or 126 kcal/mole [2] which are almost twice as high as the experimental value of 65 kcal/mole [3]. Similarly, for allene the SCF result of 82.1 kcal/mole [2] has to be compared to an experimental value close to 47 kcal/mole [4]. (In the latter paper references to numerous previous calculations of the rotation barrier of allene may be found, the results of which range between 27 and 92 kcal/mole.)

On the other hand, semiempirical SCF calculations seem to be much more reliable: With MINDO/2 Dewar and Kohn [5] obtained values of 53.5 and 36.7 kcal/mole for the rotation barriers of ethylene and allene, respectively. Using the MINDO/3 parametrization, the agreement with experiment is even better, the results are 63.9 and 46.9 kcal/mole, respectively [6].

In order to correct the wrong *ab initio* SCF rotation barriers about C–C double bonds most authors proposed to include electron correlation by means of configuration interaction (CI). In fact, a 2 × 2 CI using virtual SCF orbitals reduces the rotation barrier of ethylene to 83 kcal/mole [1, 2], and a more complete CI [7, 20] or a "double configuration SCF" (DC-SCF) [8] combined with a reoptimization of the C–C distance for the rotated molecule yield values between 63 and 64 kcal/mole, i.e. values of almost chemical accuracy.

In this note we want to show that it is not necessary to apply the powerful, but very time consuming CI method in order to obtain acceptable values for rotation barriers even about C–C double bonds. Obviously, the reason for the poor closed-shell SCF results is that the singlet ground state of molecules like ethylene, allene etc. has closed-shell structure at its equilibrium geometry, but open-shell structure in the rotated configuration (twisted ethylene, planar allene etc.). A balanced description therefore requires the use of an open-shell (restricted) SCF method for the rotated geometry in addition to the closed-shell treatment for the equilibrium geometry. One then expects to get rotation barriers which are in the order of 10 kcal/mole too small since the correlation energy difference between a doubly occupied orbital and two singly occupied ones is about 10 kcal/mole [9].

In Sect. 2 of this paper we present a brief description of our restricted open-shell SCF method for singlet states with two singly occupied orbitals. Sect. 3 contains SCF results for the rotation barriers of ethylene and allene and an estimate of the correlation correction to them.

## 2. Open-Shell SCF Procedure and Orbital Basis Set

The open-shell SCF method which we have used for singlet states containing two singly occupied orbitals is an extension of McWeeny's single-operator method [10] for the "simple" case (i.e. the case where all singly occupied orbitals have the same spin quantum number) and can be briefly described as follows.

The one-particle Hilbert space connected with the two-determinantal SCF wavefunction

$$\Phi_0 = \frac{1}{\sqrt{2}} \{ |\varphi_1 \bar{\varphi}_1 \cdots \varphi_n \bar{\varphi}_n \varphi_a \bar{\varphi}_b| - |\varphi_1 \bar{\varphi}_1 \cdots \varphi_n \bar{\varphi}_n \bar{\varphi}_a \varphi_b| \}$$

can be subdivided into four parts: The subspaces of doubly occupied orbitals ($D$), virtual orbitals ($V$), and the singly occupied orbitals, $\varphi_a(A)$ and $\varphi_b(B)$.

To make the energy expectation value of $\Phi_0$ stationary with respect to variations of the occupied orbitals is equivalent to fulfilling Brillouin conditions for the following types of rotations: $D \leftrightarrow V$, $D \leftrightarrow A$, $D \leftrightarrow B$, $A \leftrightarrow V$, $B \leftrightarrow V$, ($A \leftrightarrow B$). We exclude this last rotation since it changes the form of the wavefunction $\Phi_0$ and limit ourselves to the case where $\varphi_a$ and $\varphi_b$ belong to different symmetry species. These Brillouin conditions can be combined with appropriate projection operators to construct one open-shell Fock-operator $F^{os}$, the eigenfunctions of which are the canonical HF orbitals (compare [10] for the "simple" open-shell case). Using the abbreviations

$$F_c = h + \sum_j n_j (J_j - \tfrac{1}{2} K_j)$$

$$F_{0a} = F_c + \tfrac{3}{2} K_b - \tfrac{1}{2} K_a$$

$$F_{0b} = F_c + \tfrac{3}{2} K_a - \tfrac{1}{2} K_b$$

where $h$ is the one-particle operator and $n_j$ the occupation number of the orbital $j$, $F^{\mathrm{os}}$ can be written in block form as (only the lower triangle is given):

$$F^{\mathrm{os}} = \frac{1}{3} \left[ \begin{array}{cccc|c} D & A & B & V & \\ 5F_c - F_{0a} - F_{0b} & & & & D \\ 2F_c - F_{0a} & 3F_c & & & A \\ 2F_c - F_{0b} & 0 & 3F_c & & B \\ F_c & F_{0a} & F_{0b} & F_c + F_{0a} + F_{0b} & V \end{array} \right]$$

Since it is only necessary that the nondiagonal blocks of $F^{\mathrm{os}}$ vanish in order to fulfill the Brillouin conditions we can a) change the diagonal blocks by adding arbitrary submatrices – which of course changes the orbital energies and transforms the canonical orbitals among each other – and b) change the relative weights of the nondiagonal blocks with respect to the diagonal ones. The latter possibility is used for convergence acceleration since it corresponds to a change in the two by two rotation angles [11].

We should mention that our operator $F^{\mathrm{os}}$ is only a special case of the more general operator as given by Hirao *et al.* [12] and Davidson *et al.* [24]. Our procedure is computationally rather simple and can use the same acceleration scheme as implemented in our closed-shell SCF program [13]. Generally, not more than 8–15 iterations are necessary up to self-consistency, but of course each iteration is three times slower than one closed-shell iteration since three different two-electron operators have to be constructed in each iteration: $\sum n_j (J_j - \frac{1}{2} K_j)$, $K_a$, and $K_b$.

Throughout this paper Gaussian lobe functions are used as orbital basis set. The construction of *p*- and *d*-functions follows the rules given in Ref. [14]. All calculations are performed using an 8*s*, 4*p* Huzinaga basis set [15] for the carbon atom and a 4*s* Huzinaga set [16] for the H atoms, both contracted to double zeta quality. In some cases a set of *d*-functions with an orbital exponent of 0.7 had been added for the carbon atoms.

## 3. Results and Discussion

In the Tables 1 and 2 our results for the rotation barriers of ethylene and allene are contained. For the equilibrium configurations experimental geometries were taken [17, 18]; for the rotated configurations only the C–C distances were optimized; reoptimization of the C–H bond lengths and HCH angles is of minor influence on the barriers. In the case of twisted ethylene we also investigated deviations from planarity at the C atoms. Similarly to $CH_3$[19] we found that each C atom prefers a

**Table 1.** Rotation barrier of ethylene

| | | Planar ($D_{2h}$) | Twisted ($D_{2d}$) | $\Delta E$(kcal/mole) |
|---|---|---|---|---|
| | $R_{CC}$ | 1.335 Å | 1.47 Å[a] | |
| | $R_{CH}$ | 1.09 Å | 1.09 Å | |
| | $\theta_{HCH}$ | 117.4° | 120°/118°[b] | |
| SCF | $2\zeta$ | −77.99426 a.u. | −77.92153 a.u. | 45.7 |
| | $2\zeta+d_c$ | −78.01866 a.u. | −77.94189 a.u. | 48.2 |
| SCF+ $\pi^2 \to \pi^{*2}$ | $2\zeta$ | −78.02281 a.u. | −77.92153 a.u. | 63.6 |
| | $2\zeta+d_c$ | −78.04416 a.u. | −77.94189 a.u. | 64.2 |

[a] Optimized.

[b] Slightly different HCH angles to guarantee that the singly occupied orbitals belong to different symmetry species.

planar configuration with $sp^2$ hybridization, but the force constant for the out-of-plane vibration is very small. For allene no deviations from linearity were investigated.

To guarantee that the two singly occupied orbitals in the twisted ethylene belong to different symmetry species we reduced its symmetry from $D_{2d}$ to $C_{2v}$ by taking slightly different HCH angles. This affects the barrier by less than 0.5 kcal/mole. In the planar allene such a procedure is not necessary since the two singly occupied orbitals are non-degenerate and belong to different symmetry species: the lower one is the nonbonding $\pi$-orbital on the outer C atoms ($a_2$), the higher one is a nonbonding $p_y$-orbital localized mainly on the inner C atom ($b_2$). The calculated SCF rotation barriers of the two molecules as given in the Tables 1 and 2 obviously are much better than those obtained in the conventional closed shell SCF scheme (as mentioned in the introduction). The result for ethylene is about 15 kcal/mole below the experimental value, in the case of allene it is really very close to the value measured by Roth *et al.* [4] for substituted allenes. The influence of $d_c$-functions is rather small increasing the barrier in either case by only 2 kcal/mole on SCF level.

The quite pronounced difference in the reliability of our SCF results for the two rotation barriers can be understood by looking at the role of electron correlation: In ethylene, one bonding electron pair ($1\pi_u^2$) is broken during rotation about the C–C bond and two nonbonding $p$-orbitals localized on the two C atoms become singly occupied. This has two main effects: a) Due to the weakening of the C–C bond its bond length increases from 1.335 Å to 1.47 Å, and b) the correlation energy is decreased since generally an electron pair has a larger correlation energy than two singly occupied orbitals (compare e.g. Ref. [9]). In allene, on the other hand, the remaining $\pi$-electron pair can extend over the whole C–C–C chain after rotation; the gain in the allyl resonance energy (13–14 kcal/mole [4]) compensates the loss in correlation energy and is the reason for the only slight increase of the C–C bond length from 1.31 Å to 1.35 Å. Thus, it is reasonable to expect a different accuracy for the SCF results of the two rotation barriers.

The main difference in the correlation energies of the two configurations in ethylene originates from the $\pi^2 \to \pi^{*2}$ double substitution which contributes 0.02855 a.u. or

Table 2. Rotation barrier of allene

| | | Orthogonal ($D_{2d}$) | Planar ($D_{2h}$) | $\Delta E$(kcal/mole) |
|---|---|---|---|---|
| | $R_{CC}$ | 1.31 Å | 1.35 Å[a] | |
| | $R_{CH}$ | 1.09 Å | 1.09 Å | |
| | $\theta_{HCH}$ | 118° | 118° | |
| SCF | $2\zeta$ | $-115.80778$ a.u. | $-115.73152$ a.u. | 47.9 |
| | $2\zeta + d_c$ | $-115.84514$ a.u. | $-115.76578$ a.u. | 49.8 |
| SCF + IEPA ($\pi$) | $2\zeta$ | $-115.86997$ a.u. | $-115.78269$ a.u.[b] | 54.8 |
| | | | $-115.7871$ a.u.[c] | 52.0 |

[a] Optimized.

[b] Correlation energy of the $\pi$-electrons of the corresponding triplet state included.

[c] Corrected for the dynamic spin polarization of the singlet state.

0.02550 a.u. (without and with $d_c$-functions, respectively) to the correlation energy in equilibrium geometry, but is completely absent in the rotated configuration. This contribution changes the rotation barrier to 63.6 or 64.2 kcal/mole. Though it is hardly justified to assume that all other contributions to the correlation energy are the same for the two configurations (e.g. the one for the $\sigma_{cc}$ bonding pair should change considerably) the agreement of our estimate with Wood's DC-SCF calculation [8] as well as with experiment [3] shows that we have accounted for the most important effect.

An estimate of the correlation contribution to the rotation barrier in allene is more difficult and can be obtained as follows: First, IEPA calculations [21] are performed for the $\pi$-electrons both in the closed shell non-planar equilibrium geometry and in the triplet state of the planar configuration [22]. The correlation energies obtained with the double zeta basis set are $-0.06219$ a.u. (singlet, $D_{2d}$) and $-0.05117$ a.u. (triplet, $D_{2h}$). Assuming that the open shell singlet and triplet states have the same correlation energy the barrier is raised by 0.01102 a.u. to 54.8 kcal/mole. But actually, the correlation energies of the open shell singlet and triplet states differ in the contribution of the "dynamic spin polarization" [23] which favors the singlet by 0.0044 a.u. This lowers the rotation barrier to 52 kcal/mole, to be compared to the experimental value of 47 kcal/mole [4].

## 4. Conclusions

In this paper we have shown that the application of open-shell *ab initio* SCF methods leads to acceptable results for rotation barriers about C–C double bonds. Their errors are comparable to other cases in which energy differences between closed- and open-shell states for a fixed number of electrons have to be considered: Generally, the correlation energy of the closed-shell state is by 10–15 kcal/mole larger than that of the open-shell state. The SCF rotation barriers, therefore, are expected to be that much too small.

Our calculations show that this argument holds in the case of ethylene, but that in allene the gain of the allyl resonance energy during rotation compensates this effect.

In view of these results it is slightly surprising that the MINDO/3 calculations of Dewar and coworkers [6] for the two rotation barriers agree so excellently with experiment, particularly if one remembers that in the MINDO/3 calculations also the rotated configuration is treated as a closed-shell state. Thus, the MINDO/3 calculations give a wrong description of the state, i.e. a wrong wavefunction, even if the rotation barrier is very accurate.

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*Note added in proof.* Following a suggestion by Prof. J. A. Pople and Prof. P. von R. Schleyer (private communication) we performed some additional calculations in order to check whether deviations from linearity at the central C atom in allene have an influence on its rotation barrier. The result was exactly what we expected from the analogy with methylene [9]: In SCF approximation both the triplet and the open-shell singlet with the ... $\pi p_y$ configuration are bent with an angle close to 140° and an energy which is about 8 kcal/mole below that in the linear geometry. Inclusion of electron correlation is expected to lower this value considerably, as it is the case for methylene [9]. Therefore, bending of the C–C–C chain will decrease our value of 52 kcal/mole for the rotation barrier of allene by a few kcal/mole and will bring it in much better agreement with experiment. The two closed-shell singlet states, however, are very strongly affected by bending, but for all angles they are much higher in energy than the open-shell singlet.

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