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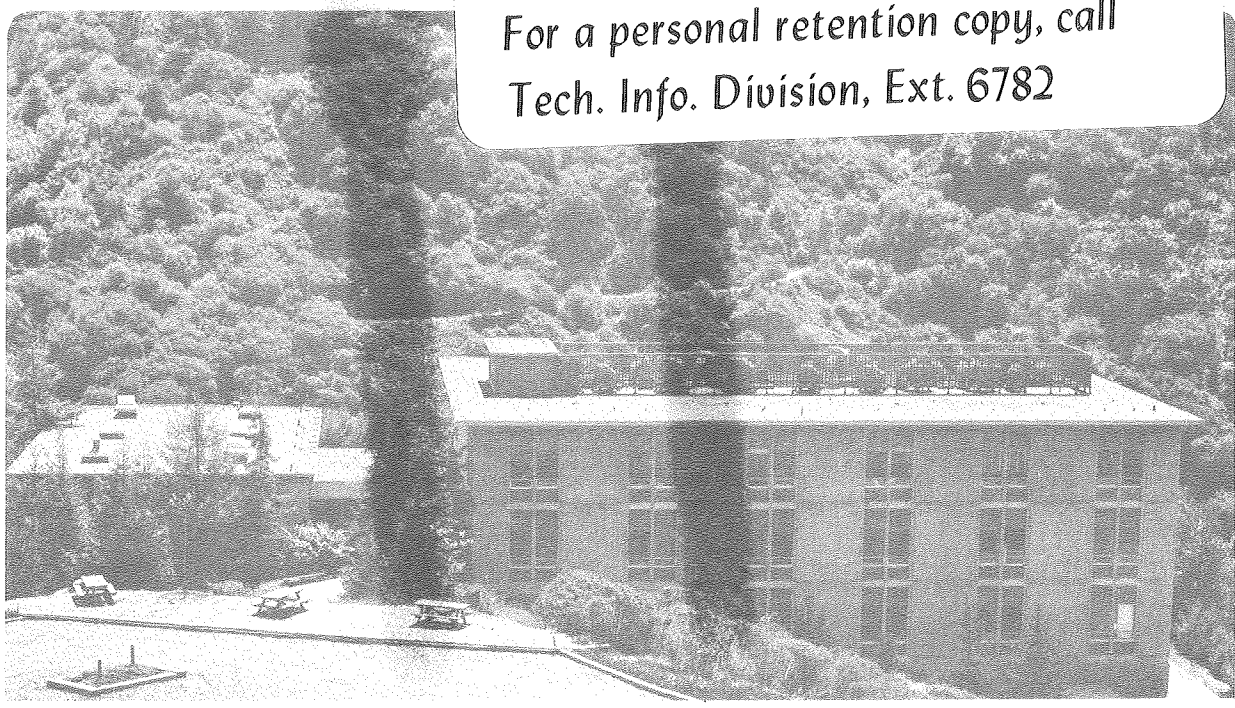
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VARIATIONAL TREATMENT OF MANY-BODY CORRELATION EFFECTS

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METHYLENE SINGLET-TRIPLET SEPARATION:
AN EXPLICIT VARIATIONAL TREATMENT OF MANY-BODY CORRELATION EFFECTS

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Abstract

The electronic structure of CH_2 has been addressed using theoretical techniques which allow for the variational inclusion of large classes of excitations differing by more than two electrons from the Hartree-Fock description. Specifically, a natural orbital transformation has been used to define orbitals for a full configuration interaction (CI) within the valence electron space. These full valence CI's include 56 configurations for $^1\text{A}_1$ methylene and 51 configurations for $^3\text{B}_1$ CH_2 . Subsequently all single and double excitations with respect to all configurations in the full valence are included in the final variation treatments, which involved 57,684 configurations ($^1\text{A}_1$) and 84,536 configurations ($^3\text{B}_1$).

The past decade has witnessed a number of experimental determinations¹⁻¹³ of the energy difference $\Delta E(S-T)$ between the lowest singlet and triplet electronic states of CH_2 . In the early 70's, controversy existed between values of ΔE clustering about 2 kcal^{1,2,5} and those clustering about 8 kcal.^{3,4} However this focus changed abruptly in 1976 with the publication by Zittel, Ellison, O'Neil, Herbst, Lineberger, and Reinhardt¹⁰ of the first direct (i.e., involving no thermochemical assumptions) measurement of $\Delta E(S-T)$. Their study of the photodetachment of CH_2^- yielded a much larger separation, $\Delta E = 19.5$ kcal. However, this result has very recently been challenged by the second direct determination, that of Hayden, Neumark, and Lee,¹⁴ who report $\Delta E \sim 9$ kcal from their molecular beam experiments.

Theoretical determinations of the methylene singlet-triplet separation have been relatively consistent over the past decade. In fact, almost all serious theoretical predictions have fallen in the range $T_e = 11 \pm 2$ kcal suggested in 1972 by Bender, Schaefer, Franceschetti, and Allen.¹⁵ Among the seven most definitive theoretical studies¹⁶⁻²² to date, the lowest total energies (i.e., "best" wave function in the variational sense) are those of Lucchese, Conrad, and Schaefer (LCS)²¹. However, LCS' treatment of many-body correlation effects²³ (i.e., configurations differing by more than two electrons from the Hartree-Fock reference configuration) was the most primitive of the six theoretical studies. Using a large basis set [designated C(11s 7p 3d/8s 7p 3d), H(6s 1p/4s 1p)], LCS carried out configuration interaction (CI) including all single and double excitations and found $\Delta E(S-T) = 13.8$ kcal. Many-body effects were

treated using Davidson's simple correlation for unlinked clusters,²⁴ and this yielded a final prediction of 11.4 kcal, in good agreement with the other definitive theoretical studies.^{16-20, 22}

The purpose of the present communication is to report an explicit and reasonably complete variational treatment of the effects of many-body effects on the methylene singlet-triplet separation ΔE . The primitive basis set chosen was the same as that of LCS,²¹ but contracted slightly less flexibly, to C(8s 5p 3d), H(4s 1p). This study was made possible by the newly-developed integer-based CI algorithm of Handy.²⁵ It was necessary to extend this method to the triplet case for the purposes of the present research.

Handy's algorithm uses an integer representation for both the CI vector and the two-electron integrals, both kept in the central memory throughout the calculation. These calculations were performed on a CDC 7600; the integrals were double-packed in the 60-bit wordlength. The number of two electron integrals was 237,289, and the accuracy to which they were held using the integer representation was 0.00000012, and therefore there was no loss of accuracy using this method (unlike the earlier calculations²⁵).

For singlet states, the CI program was written in terms of the following expansion functions

$$\begin{aligned} \Psi_{cd} &= \frac{1}{2} [A(1a_1^2 \phi_{c_1}^\alpha \phi_{c_2}^\alpha \phi_{c_3}^\alpha \phi_{d_1}^\beta \phi_{d_2}^\beta \phi_{d_3}^\beta) + A(1a_1^2 \phi_{d_1}^\alpha \phi_{d_2}^\alpha \phi_{d_3}^\alpha \phi_{c_1}^\beta \phi_{c_2}^\beta \phi_{c_3}^\beta)] \\ &= \frac{1}{2} [A(\phi_c^\alpha \phi_d^\beta) + A(\phi_d^\alpha \phi_c^\beta)] \quad \text{or} \\ \Psi_{cc} &= A(\phi_c^\alpha \phi_c^\beta) \end{aligned} \tag{1}$$

It was a straightforward matter to write a program which includes all

single and double excitations out of a full valence CI, using these expansion functions, when all the integrals are in central memory, although the length of the CI may be typically twice the length of the minimum possible space-spin configuration state function list. Further details may be found in Ref. 25.

To extend the program to triplet states, as required here, the expansion functions used were simply determinants

$$\begin{aligned} \Psi_{cd} &= A(1a_1^2 \phi_{c_1}^\alpha \phi_{c_2}^\alpha \phi_{c_3}^\alpha \phi_{c_4}^\alpha \phi_{d_1}^\beta \phi_{d_2}^\beta) \\ &= A(\phi_c^\alpha \phi_d^\beta) \end{aligned} \quad (2)$$

Using these functions, a program was written to include all single and double excitations out of a full valence CI; the resulting CI vector will be an exact triplet function. Because of the straightforward determinant representation, the program was simpler to write than the corresponding singlet program. Indeed, the program is operational for the determination of the lowest eigenvalue for every possible space-spin symmetry.

The above two advances mean that the integer-based CI method is now a very general method (providing the computer has a large enough central memory). The iterative procedure used to determine the lowest eigenvalue was, as previously, the standard Cooper-Nesbet method, which updates each CI coefficient, one at a time, and needs only one CI vector to be held in central memory. In these calculations convergence to 0.00001 hartree in the energy was achieved in 4 iterations.

The theoretical approach used here begins with what might be called a "full valence CI" in the sense of classical qualitative bonding theory.²⁶ The Hartree-Fock configurations for singlet and triplet methylene are

$$1a_1^2 2a_1^2 1b_2^2 3a_1^2 \quad (3)$$

and

$$1a_1^2 2a_1^2 1b_2^2 3a_1 1b_1 \quad (4)$$

However, the standard valence basis (or minimum basis, in somewhat more technical terms) also includes the $4a_1$ and $2b_2$ orbitals. Constraining the $1a_1$ orbital (essentially carbon $1s$) to be always doubly occupied, "full valence CI" includes all possible arrangements of the six valence electrons in the six valence orbitals ($2a_1$, $1b_2$, $3a_1$, $1b_1$, $4a_1$, and $2b_2$). For singlet methylene this full valence CI includes 56 1A_1 configurations, while for triplet methylene there are 51 3B_1 configurations in the full valence CI.

The increasingly standard treatment²³ of correlation effects in molecular systems is that used by LCS, namely CI including all single and double excitations relative to (3) for the singlet state or relative to (4) for the triplet state. With the $1a_1$ core orbital doubly-occupied this amounts to 3812 1A_1 and 4663 3B_1 configurations, and these results are seen in the Table, entry 2. As noted above, such a treatment takes no account of many-body correlation effects. In this research, we have included all single and double excitations relative to all configurations in the full valence CI. As entry 5 in the Table shows, such a CI treatment includes $(57,684 - 3,293) = 54,391$ higher (than double) excitations for the 1A_1 state and $(84,536 - 4,108) = 80,428$ higher excitations for the 3B_1 state. These higher excitations should include all of the most important valence shell triple, quadruple, quintuple, and sextuple excitations.

The procedure outlined in the paragraph above assumes that the first seven molecular orbitals are the most important in terms of the electronic

structure. In the present study this was guaranteed by using the natural orbitals obtained from the CISD wave functions detailed in entry 2 of the Table. The natural orbital occupation numbers prove this to be the case. For example, for singlet CH_2 , the largest occupation numbers are 2.000 ($1a_1$), 1.970 ($2a_1$), 1.962 ($1b_2$), 1.932 ($3a_1$), 0.045 ($1b_1$), 0.024 ($2b_2$), and 0.019 ($4a_1$). These are followed by the less important orbitals $5a_1$ (0.012), $6a_1$ (0.007), $3b_2$ (0.007), $1a_2$ (0.005), $2b_1$ (0.005), $7a_1$ (0.003), $4b_2$ (0.002), $8a_1$ (0.001), and $5b_2$ (0.001), with all other natural orbital occupation numbers being less than 0.0009.

The final entry in the Table reports a singlet-triplet energy difference of 10.5 kcal, or 0.3 kcal less than that obtained using the very much simpler Davidson's correction.²⁴ Considering possible sources of error, we contend that the exact value of T_e , assuming the Born-Oppenheimer approximation and the ordinary nonrelativistic Hamiltonian, falls in the range 10.5 ± 1.0 kcal.

The results of this paper may be compared with those of Roos and Siegbahn¹⁷ (10.9 kcal) and Bauschlicher and Shavitt²⁰ (10.6 kcal), who included all S+D excitations with respect to two configurations for the 1A_1 state and one configuration for the 3B_1 State. The previous study perhaps most closely related to this work is that of Harding and Goddard.¹⁹ Using the GVB procedure to solve for a valence space and virtual space, they included most of the important configurations through sextuple excitations and obtained a final ΔE of 10.6 kcal. Thus it appears that there is now nearly unanimous theoretical agreement concerning the value of the methylene singlet-triplet separation.

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Table. Summary of correlated wave functions for singlet and triplet methylene. All entries except the last employed molecular orbitals from single configuration SCF wave functions. The largest CI's employed natural orbitals from entry 2.

	Number of		Description of	Energy (hartrees)		ΔE (kcal)
	Configurations			Wave Function		
	Singlet	Triplet		Singlet	Triplet	
1.	1	1	Single Configuration SCF.	-38.89445	-38.93364	24.6
2.	3,812	4,663	All Single and Double (S+D) Excitations Relative to 1. $1a_1$ Orbital Always Doubly Occupied.	-39.04369	-39.06454	13.1
3.	3,293	4,108	Same as 2. but with the Three Highest SCF Virtual Orbitals Deleted from CI.	-39.04368	-39.06453	13.1
4.	3,293	4,108	Davidson Corrected 3.	-39.05395 ^a	-39.07124 ^a	10.8
5.	57,684	84,536	All S+D Excitations Relative to all configurations in the Full Valence CI. $1a_1$ Orbital Always Doubly Occupied and Three Least Important Natural Orbitals Deleted.	-39.05271	-39.06951	10.5

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^a Nonvariational results, i.e., not true upper bounds to total energies.

