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

Permalink
https://escholarship.org/uc/item/1j75r332

Author
Saxe, Paul

Publication Date
2013-09-09
Submitted to the Journal of Physical Chemistry

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

Paul Saxe, Henry F. Schaefer III, and Nicholas C. Handy

September 1980

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks.
For a personal retention copy, call Tech. Info. Division, Ext. 6782

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
METHYLENE SINGLET-TRIPLET SEPARATION:
AN EXPLICIT VARIATIONAL TREATMENT OF MANY-BODY CORRELATION EFFECTS

Paul Saxe and Henry F. Schaefer III
Department of Chemistry and Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

and

Nicholas C. Handy
University Chemical Laboratory
Lensfield Road
Cambridge, England
Abstract

The electronic structure of CH₂ 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 ¹A₁ methylene and 51 configurations for ³B₁ CH₂. 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 (¹A₁) and 84,536 configurations (³B₁).
The past decade has witnessed a number of experimental determinations\textsuperscript{1-13} of the energy difference $\Delta E(S-T)$ between the lowest singlet and triplet electronic states of CH\textsubscript{2}. In the early 70's, controversy existed between values of $\Delta E$ clustering about 2 kcal\textsuperscript{1,2,5} and those clustering about 8 kcal\textsuperscript{3,4}. However this focus changed abruptly in 1976 with the publication by Zittel, Ellison, O'Neil, Herbst, Lineberger, and Reinhardt\textsuperscript{10} of the first direct (i.e., involving no thermochemical assumptions) measurement of $\Delta E(S-T)$. Their study of the photodetachment of CH\textsubscript{2}\textsuperscript{-} 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,\textsuperscript{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.\textsuperscript{15} Among the seven most definitive theoretical studies\textsuperscript{16-22} to date, the lowest total energies (i.e., "best" wave function in the variational sense) are those of Lucchese, Conrad, and Schaefer (LCS)\textsuperscript{21}. However, LCS' treatment of many-body correlation effects\textsuperscript{23} (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, and this yielded a final prediction of 11.4 kcal, in good agreement with the other definitive theoretical studies.

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 $\Delta E$. The primitive basis set chosen was the same as that of LCS, 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. 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 calculations).

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

$$\psi_{cd} = \frac{1}{2} \left[ A(la_1^2 \phi_c^\alpha \phi_c^\alpha \phi_c^\beta \phi_c^\beta) + A(la_1^2 \phi_d^\alpha \phi_d^\alpha \phi_d^\beta \phi_d^\beta) \right]$$

$$= \frac{1}{2} \left[ A(\phi_c^\alpha \phi_d^\beta) + A(\phi_d^\alpha \phi_c^\beta) \right]$$

or

$$\psi_{cc} = A(\phi_c^\alpha \phi_c^\alpha) + A(\phi_c^\beta \phi_c^\beta)$$

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

\[
\psi_{cd} = A(l_{a_1}^2 \phi_{c_1} \phi_{c_2} \phi_{c_3} \phi_{c_4} \phi_{d_1} \phi_{d_2})
\]

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.\textsuperscript{26} The Hartree-Fock configurations for singlet and triplet methylene are

\[
1a_1^2 2a_1^2 1b_2^2 3a_1^2
\]
and

\[ \begin{align*}
1a_1^2 & \quad 2a_1^2 & \quad 1b_2^2 & \quad 3a_1 & \quad 1b_1 \\
\end{align*} \]  

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 treatment 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 CH₂, the largest occupation numbers are 2.000 (1a₁), 1.970 (2a₁), 1.962 (1b₂), 1.932 (3a₁), 0.045 (1b₁), 0.024 (2b₂), and 0.019 (4a₁). These are followed by the less important orbitals 5a₁ (0.012), 6a₁ (0.007), 3b₂ (0.007), 1a₂ (0.005), 2b₁ (0.005), 7a₁ (0.003), 4b₂ (0.002), 8a₁ (0.001), and 5b₂ (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 $\Delta E$ of 10.6 kcal. Thus it appears that there is now nearly unanimous theoretical agreement concerning the value of the methylene singlet-triplet separation.
Acknowledgement

This research was supported by Director's Funds from the Lawrence Berkeley Laboratory, U.S. Department of Energy under contract Number W-7405-ENG-48. We thank Professor David A. Shirley for his support and Professor Y. T. Lee for helpful discussions and encouragement.
References


22. R. P. Saxon and B. Liu, presented at the First West Coast Theoretical Chemistry Conference, May, 1979, IBM Research Laboratory, San Jose, California.


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.

<table>
<thead>
<tr>
<th>Number of Configurations</th>
<th>Description of Wave Function</th>
<th>Energy (hartrees)</th>
<th>ΔE (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Singlet</td>
<td>Triplet</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-38.89445</td>
<td>-38.93364</td>
</tr>
<tr>
<td>2.</td>
<td>All Single and Double (S+D) Excitations Relative to 1. (1a_1) Orbital Always Doubly Occupied.</td>
<td>-39.04368</td>
<td>-39.06453</td>
</tr>
<tr>
<td>3.</td>
<td>Same as 2. but with the Three Highest SCF Virtual Orbitals Deleted from CI.</td>
<td>-39.05395(^a)</td>
<td>-39.07124(^a)</td>
</tr>
<tr>
<td>5.</td>
<td>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.</td>
<td>更要</td>
<td></td>
</tr>
</tbody>
</table>

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