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K. Balasubramanian, Paul Saxe, Phillip A. Christiansen, Kenneth S. Pitzer, and Henry F. Schaefer III

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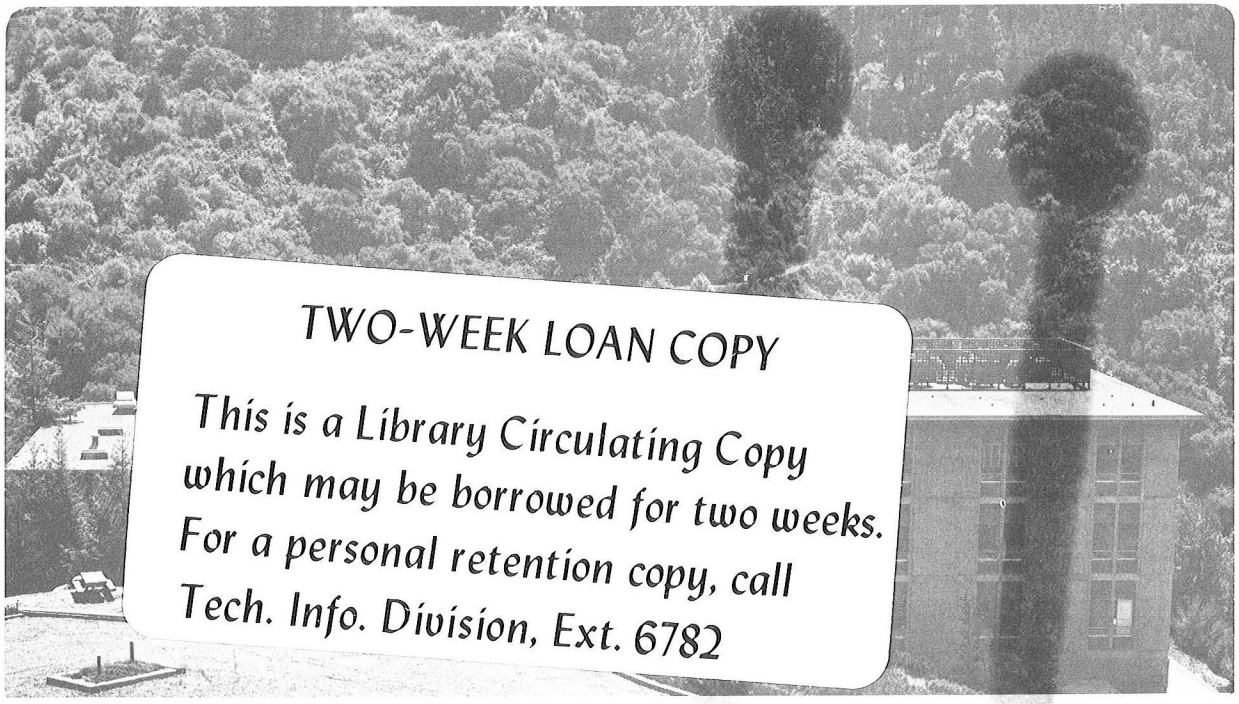

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Relativistic Contributions to the Singlet-Triplet Separation in Methylene

K. Balasubramanian, Paul Saxe, Phillip A. Christiansen, Kenneth S. Pitzer

and

Henry F. Schaefer III

Department of Chemistry
and
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Abstract

Relativistic corrections to the $^1A_1 - {}^3B_1$ energy separation in methylene are obtained by treating the major relativistic terms in the Breit-Pauli Hamiltonian not only as a first order perturbation but also a part of a total Hamiltonian which allows calculations at both SCF and CI levels. The correction obtained for the singlet - triplet separation is 24 cm^{-1} with first order perturbation calculations and 35 cm^{-1} when the relativistic terms are treated variationally. The correction for the $^3P - {}^5S$ separation of carbon is 95 cm^{-1}. The relativistic correction thus obtained for the singlet-triplet separation in methylene ($\sim$35 cm^{-1}) is too small to explain the difference between the theory and experiment.

1. Introduction

In recent years several authors have investigated the $^1A_1$-$^3B_1$ separation in methylene from both experimental [1-7] and theoretical standpoints [8-19]. Recent experimental values for this separation range from 6 to 19.5 kcal/mole. The latter value obtained by Zittel et al. [6] is quite precise (± 0.7 kcal/mole), but questions have been raised about alternate interpretations [15] of the data yielding a substantially lower value near 9 kcal/mole. An investigation using a molecular beam of CH_2CO just completed by Hayden et al. [7] yields 8.2 ± 0.5 kcal/mole. The results of several theoretical calculations [8-19] including configuration interaction (CI) are close to 11 kcal/mole; most recently a calculation [19] with a very large basis set and very extensive CI yields 10.5 ± 1.5 kcal/mole. Thus there is still a discrepancy between the experimental and calculated values after allowing for uncertainties in each case. However an additional uncertainty is due to the fact that the zero point vibrational energies of singlet and triplet CH_2 are not reliably known.

In the past a possible source of this discrepancy between the theory and experiment was thought to be relativistic corrections, essentially from the carbon atom [20-23]. Feller and Davidson [20] used Desclaux's [24] average configurational Dirac-Hartree-Fock atomic calculations and proposed a relativistic correction to the singlet-triplet separation in methylene of 1.5 kcal/mole (525 cm^{-1}), assuming the electronic configuration of the carbon atom to be s^2p^2 and sp^3 in the $^1A_1$ and $^3B_1$ states, respectively. Wood and Pyper [21] questioned this estimate and then carried out [22] relativistic and non-relativistic atomic calculations (by the Dirac-Fock method with the velocity of light set to a very large value in the non-relativistic case) and deduced a relativistic correction of 120 cm^{-1} rather than 525 cm^{-1}. More recently, Davidson et al. [23] calculated the

relativistic correction to the singlet-triplet separation of methylene directly by treating the major relativistic terms of the Breit-Pauli Hamiltonian as a first order perturbation. They concluded that the relativistic correction in this approximation is only 0.07 millihartrees ($\sim$15 cm^{-1}) and also showed that the assumption of s^2p^2 and sp^3 hybridization for singlet and triplet CH_2 is incorrect.

The relativistic terms contained in the Breit-Pauli Hamiltonian are corrections to the non-relativistic Hamiltonian to first order in α^2, where α is the fine structure constant. Thus these terms are usually used for the first order perturbation calculations. However, as noted by Cowan and Griffin [25], the use of these terms as a part of a total Hamiltonian does give results that are in good agreement with full Dirac-Fock calculations provided the behavior close to the nucleus is restricted appropriately; this aspect is discussed in the next section. In this communication we treat the relativistic terms in the Breit-Pauli Hamiltonian not only as a first order perturbation but also as part of a total Hamiltonian which allows calculations at both SCF and CI levels. To our knowledge these are the first strictly ab initio all-electron correlated wavefunctions for polyatomics reported to date using a relativistic Hamiltonian.

2. Theory

The calculations presented here were carried out with the Breit-Pauli Hamiltonian [26] including the following terms, given in atomic units.

$$H_0 = \frac{1}{2} \sum_i p_i^2 + V$$

$$H_1 = -\frac{\alpha^2}{8} \sum_i p_i^4$$

$$H_2 = \frac{\alpha^2}{8} \sum_i \nabla^2 V_i$$

$$H_3 = -\frac{8\pi\alpha^2}{3} \sum_{i<j} \sum [\underset{\sim}{s}_i \cdot \underset{\sim}{s}_j \, \delta^3(r_{ij}) + \frac{1}{r_{ij}^3} \{\underset{\sim}{s}_i \cdot \underset{\sim}{s}_j - 3(\underset{\sim}{s}_i \cdot \underset{\sim}{r}_{ij} \times (\underset{\sim}{s}_j \cdot \underset{\sim}{r}_{ij})\}]$$

with

$$V = \sum_i V_i, \; V_i = -\frac{Z}{r_i} + \sum_{j<i} (1/r_{ij}), \; \nabla^2 \left(\frac{1}{r}\right) = -4\pi\delta^3(r),$$

and α is the fine structure contant. H_0 is the nonrelativistic Hamiltonian, H_1 is the mass velocity correction, H_2 is the Darwin correction and H_3 is the interaction between the spin magnetic dipole moments of two electrons. The second term in H_3 vanishes for the singlet states. For other states it makes finite but negligible contributions for light atoms. Hence this term was neglected in our calculations. The expectation value of $\underset{\sim}{s}_i \cdot \underset{\sim}{s}_j$ is given by

$$\overline{2\underset{\sim}{s}_i \cdot \underset{\sim}{s}_j} = S(S+1) - 3/2$$

where S is the total spin quantum number.

We report two sets of calculations. In the first set H_1, H_2 and H_3 were treated as first order perturbations to the non-relativistic treatment, while in the second set these terms were incorporated in the total Hamiltonian which facilitates relativistic corrections at both SCF and CI levels. Our SCF calculations were carried out with a (11s7p3d/8s5p3d) Gaussian basis set for carbon and (6s1p/4s1p) for the hydrogen atom.

Further, CI calculations were carried out which included 4663 configurations for the triplet and 3812 configurations for the singlet states. These configurations were generated by single and double excitations from the relativistic singlet and triplet SCF states.

For the SCF calculations an important complication arises due to the divergence of the mass velocity term of the Breit-Pauli Hamiltonian in the region close to the atomic origin. This problem has been noted by several authors [25,27]. It arises as a result of the series expansion in terms of α^2 of the relativistic kinetic energy operator. Cowan and Griffin [25] avoid this divergence in their numerical SCF calculations by fitting the wavefunction close to the point nucleus by a two-term series expansion. For Gaussian basis sets the total Breit-Pauli relativistic kinetic energy contribution for s functions with exponents of the order of $1/\alpha^2$ or larger becomes negative, resulting in unrealistic wavefunctions and energies if corrections above first order in α^2 are included. Nevertheless, this problem can be avoided if such high exponent s functions are heavily contracted with functions having much smaller exponents, using coefficients from non-relativistic SCF calculations. This effectively limits the relativistic kinetic energy correction to first order in the vicinity of the nucleus.

3. Results and Discussions

The non-relativistic and relativistic SCF and CI energies of the singlet and triplet states are shown in Table I in atomic units. Table II contains the relativistic correction to the singlet-triplet separation in millihartrees (also in cm^{-1} and kcal/mole) calculated with first order perturbation, SCF and CI treatments. For a comparison we also carried out relativistic SCF calculations of the ^3P and ^5S states of the carbon

atom with the Hamiltonian and basis sets described in Section 2. We obtained the relativistic SCF correction for the $^3P - ^5S$ separation to be 95 cm^{-1}, which is in reasonable agreement with 120 cm^{-1} obtained by Wood and Pyper [22] with Dirac-Fock calculations. From Table II, it can be inferred that all these calculations predict a small relativistic correction to the singlet-triplet separation in methylene. The relativistic correction for this separation is 24 cm^{-1} obtained from first order perturbation, while the relativistic CI treatment predict 35 cm^{-1}. We obtain the Mulliken population on the carbon atom for the singlet and triplet states of methylene to be $s^{1.3}\ p^{2.9}$ and $s^{1.5}\ p^{2.6}$ using our basis set, with the precise difference in the s populations being 0.256. Thus the assumption made in earlier papers that the carbon atom is s^2p^2 and sp^3 in the singlet and triplet states of methylene is not correct. This was pointed out earlier by Davidson, Feller and Phillips [23] who obtained a difference of 0.3 between their s population on the carbon atom of the singlet and triplet states. If we assume the relativistic correction to the singlet-triplet separation to be essentially due to change in the s population of carbon and multiply Wood and Pyper's correction by an appropriate factor which corresponds to this change in s population we obtain 30 cm^{-1}. This is in close agreement with our calculations.

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Table I. Relativistic and Non-relativistic SCF and CI Energies in Atomic Units using the Breit-Pauli Hamiltonian

State	$E^{(a)}_{SCF,NR}$	$E^{(b)}_{SCF,R}$	$E^{(c)}_{CI,NR:SCF,NR}$	$E^{(d)}_{CI,R:SCF,NR}$	$E^{(e)}_{CI,R:SCF,R}$
$^3B_1$	-38.9336	-38.9453	-39.0645	-39.0751	-39.0763
$^1A_1$	-38.8945	-38.9063	-39.0437	-39.0544	-39.0556

(a) Non-relativistic self-consistent field.

(b) Relativistic self-consistent field.

(c) Non-relativistic configuration interaction with non-relativistic self-consistent field.

(d) Relativistic configuration interaction with non-relativistic self-consistent field.

(e) Relativistic configuration interaction with relativistic self-consistent field.

Table II. Relativistic Corrections to the $^1A_1 - {}^3B_1$ Separation of Methylene using the Breit-Pauli Hamiltonian

Method	Relativistic Contribution in milliHartree	in kcal/mole	in cm^{-1}
First Order Perturbation	0.107	.067	24
Relativistic Self-Consistent Field	0.151	.095	33
Relativistic Configuration interaction with relativistic self-consistent field	0.159	.100	35
Relativistic Configuration Interaction with non-relativistic self-consistent field	0.132	.083	30