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Review Article

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Methylene: a turning point in the history of quantum chemistry and an enduring paradigm

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Abstract: Prior to 1970, no successful ab initio electronic structure predictions were made that challenged experiment for polyatomic molecules. For diatomics, the work of Ernest Davidson stands out, in 1960 explaining that two spectroscopically known but misunderstood electronic states of H_2 were in fact part of the very same potential energy curve. Another diatomic example was the startling 1968 overturn by Kolos and Wolniewicz of the “known” experimental dissociation energy of H_2. Moving to polyatomics, the research in 1970 concerning the structure of triplet methylene captured the imagination of many chemists, and the 1982 success of theory for the singlet-triplet separation of methylene confirmed for many the great usefulness of ab initio theory. In the second half of this paper, the utility of methods based on single Slater determinant reference wavefunctions for both singlet and triplet methylene is demonstrated. In particular, we examine how the optimized geometries and harmonic vibrational frequencies of triplet and singlet CH_2 evolve with systematic improvements in basis set size and valence electron correlation treatment. To accurately pinpoint the geometric structures and singlet-triplet splitting of methylene, we perform comprehensive focal point analyses (FPA) that push the level of theory to new heights, leveraging core-valence basis sets up to sextuple-zeta quality and all-electron coupled-cluster methods through CCSDTQ(P) appended with relativistic (MVD1) and non-Born-Oppenheimer (DBOC) corrections. Our final FPA prediction for the singlet-triplet splitting is 9.01 kcal mol^{-1}, in complete agreement with the best empirical estimate of 9.00 ± 0.01 kcal mol^{-1}. The corresponding optimized FPA geometries are $[r_e(\text{H–C}), \theta_e(\text{H–C–H})] = (1.1063\ \text{Å}, 102.35°)$ for $\tilde{a}^1A_1$ CH_2 and $(1.0756\ \text{Å}, 133.94°)$ for $\tilde{X}^3B_1$ CH_2, in close agreement with the best existing experimental and theoretical structures but with a little finer precision. Our outcomes not only affirm the validity of the contemporary single-reference coupled-cluster theory pushed to high order but also provide definitive resolutions for a paradigmatic molecule that has long been emblematic of the challenges and triumphs that have shaped a century of quantum chemistry.

Keywords: Electronic structures; quantum chemistry; quantum science and technology.

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Historical perspectives

Prior to 1970, chemists often considered ab initio quantum chemistry to be elegant and beautiful, but not able to make reliable predictions of chemical interest. Until that date, an often-cited failure of ab initio methods was the methylene molecule CH_2. The pioneering 1960 research[1] of Frank Boys (Cambridge University) predicted the bond angle of triplet methylene to be 129°. However, in his 1961 endowed lecture at Cornell University, future Nobelist Gerhard Herzberg concluded the triplet ground state to be linear. Herzberg's somewhat belittling remark[2] was that "our experimental values are distinctly different from these (Boys) but not excessively so, when the approximate nature of the calculations is considered." The CH_2 attack on ab initio quantum mechanical methods continued with Christopher Longuet-Higgins, Chair Professor at Cambridge. Using semi-empirical methods (combining theory with experimental constraints), Longuet-Higgins[3] reproduced Herzberg's linear geometry for CH_2. Longuet-Higgins' assessment was even more pointed than that of Herzberg: "It may be that future theoretical progress will require elaborate variational calculations such as those of Foster and Boys on CH_2, but until the results of such machine experiments can be interpreted physically, there would seem to be a place for more empirical theories such as that which we now describe."

Even within the theoretical community, during the 1960s there seemed to be acceptance of the "fact" that the Foster and Boys prediction of bent CH_2 was in error. Future Nobelist John Pople (later a close friend of HFS) reported with G. A. Segal some better semi-empirical computations on CH_2,[4] predicting, like Boys, a bent structure (in this case 141°) for the triplet ground state. Unfortunately, these authors accepted Herzberg's linear CH_2 structure and rationalized what they thought was their incorrect theoretical prediction. They stated, "This is a situation where the CNDO approximation is least satisfactory" because it "neglects the one-center exchange integral." Pople and Segal concluded, "This triplet stabilization is probably a maximum in the linear form, and its inclusion would very likely modify the calculated bond angle."

Although other sources would confirm the great theoretical "disaster" for CH_2, one more will suffice here. In 1969, Jim Harrison and Lee Allen (both excellent theorists) reported the best ab initio CH_2 computations to date.[5] Like Frank Boys, Harrison and Allen predicted triplet CH_2 to be bent, this time with a bond angle of 138°. However, Harrison and Allen were also intimidated by the Herzberg experiments: "We certainly wish the present results to be regarded with conservatism, and there is certainly room for a greatly improved theoretical treatment." Focusing on a possible weakness in their methodology, Harrison and Allen added, "Because of the very flat potential curves of the $^3B_1$ and $^1B_1$ states, the predicted equilibrium angles of 138 and 148°, respectively, could be changed significantly with minor changes in the atomic bases."

During the summer 1968 Gordon Conference on Theoretical Chemistry, HFS met a uniquely gifted young theorist, Charlie Bender. Charlie had been a PhD student with Ernest Davidson at the University of Washington and would accept a position at the University Computing Company in Palo Alto, next to Stanford University, where HFS had carried out doctoral studies. Before HFS began at Berkeley as an Assistant Professor, a collaboration with Bender was agreed upon. Knowing the terrible reputation of theory with respect to the CH_2 structure, methylene was attacked with new theoretical methods. During the first year of HFS on the Berkeley faculty, a controversial paper on the CH_2 problem was submitted, concluding the molecule to have a bond angle of 135°. The paper was not at all apologetic, stating, "On the basis of the present and previous ab initio calculations and the stated experimental uncertainties, we conclude that the CH_2 ground state is nonlinear with a geometry close to $r = 1.096$ Å, $\theta = 135.1°$."[6] Five years later, the distinguished organic chemists George Hammond and Peter Gaspar[7] stated in their review, "In 1970 Bender and Schaefer reported by far the most elaborate calculation carried out to date on methylene, or indeed almost any molecule." For the moment, Charlie Bender and HFS were near the peak of theoretical developments in computational quantum chemistry. Very fortunately for HFS (assistant professorships in chemistry at Berkeley were more often than not terminated after a few years), the controversial prediction of bent triplet methylene was quickly confirmed experimentally by Ed Wasserman (Bell Labs) and by Bob Bernheim and Phil Skell at Penn State.[8,9] A fuller description of events following can be found elsewhere.[10]

The second shoe of the methylene controversy took much longer to fall. The energy separation (T_0) between the ground triplet ($^3B_1$) and lowest singlet ($^1A_1$) state of methylene is important for organic chemistry because the reactions of singlet carbenes (CR_2 or CRR') with olafins tend to be stereospecific while those of triplet carbenes are not. By the year 1972, there was a wide range of experimental T_0 values from 2 to 10 kcal mol^{-1}. In that year, Hay, Hunt, and Goddard[11] used their newly developed and very promising generalized valence bond (GVB) method with a double-zeta basis to predict a CH_2 singlet-triplet separation (T_e) of 11.5 kcal mol^{-1}. Very shortly thereafter, Bender and HFS with Donald Franceschetti and Lee Allen from Princeton addressed the same problem.[12] The two papers[11,12] thank each other for private communications. The Berkeley-Princeton collaboration[12] used a large triple-zeta basis set and a more complete description of electron correlation. It was concluded, rather daringly, that the true CH_2 singlet-triplet separation was 11 ± 2 kcal mol^{-1}. These proposed error bars pointed a big target on the proverbial backs of the authors.

All seemed satisfactory for the Cal Tech and Berkeley theoretical predictions of the singlet-triplet splitting of methylene until 1976. In that year, the first *direct* experimental measurement was reported by Carl Lineberger and coworkers[13] at Boulder. Lineberger was already recognized both as a brilliant experimental physical chemist and a friend to all in the community. Via the laser photodetachment of the CH_2^- anion, Lineberger concluded that T_0 was 19.5 ± 0.7 kcal mol^{-1}. This meant that all the previous experimental estimates (2–10 kcal mol^{-1}) were wrong, as were the Cal Tech and Berkeley theoretical results. Most observers quickly accepted the validity of the conclusions of the Boulder group, and the theorists were subjected to a certain amount of humiliation,[10] which need not be recapitulated here. One exception not yet in print is the statement by legendary statistical mechanician Berni Alder at his April 14, 1981 seminar to the Chemistry Department at Berkeley: "If they can't even get CH_2 right, what hope is there for quantum chemistry?"

Six painful years after the Carl Lineberger experiment, the great quantum chemistry "disaster" was overturned. In 1982, Yuan Lee and his group (including now-prominent Dan Neumark) reported the second direct experimental measurement of the CH_2 singlet-triplet energy separation.[14] Their result was 8.5 ± 0.8 kcal mol^{-1}, in agreement with the Berkeley-Princeton result of 11 ± 2 kcal mol^{-1} from ten years earlier. And thus the reliability of state-of-the-art ab initio quantum chemistry was secured. There were battles yet to come,[10] but the momentum was permanently shifted.

Since the early 1980s, extensive experimental[15–27] and theoretical efforts[28–46] have focused on further elucidating the structure and spectroscopic properties of methylene and related species, as nicely summarized in Refs. 28 and 36. Most relevant to the current work, a series of papers on triplet methylene by Bunker et al.[31,32] and Jensen et al.[30] (1982–1986) fit a large body of microwave, infrared, and photodetachment spectroscopic data using nonrigid bender Hamiltonians, resulting in (r_e, θ_e) = (1.0766 ± 0.0014 Å, 134.037 ± 0.045°) for $\tilde{X}^3B_1$ CH_2. A subsequent 1988 paper by Jensen and Bunker[33] employed the Morse oscillator-rigid bender internal dynamics (MORBID) Hamiltonian to fit all rotation-vibration data for triplet CH_2, leading to the benchmark empirical singlet-triplet splitting of 8.998 kcal mol^{-1}. This compares excellently to the 2003 ab initio T_0 result of 8.972 kcal mol^{-1} computed by Császár and coworkers[36] using a valence focal point method, augmented with corrections resulting from core correlation, relativity, and DBOC. For the $\tilde{a}^1A_1$ CH_2 state in 1989, Petek and coworkers[26] determined equilibrium rotational constants and thus the equilibrium structure (r_e = 1.107 ± 0.002 Å, θ_e = 102.4 ± 0.4°) from infrared flash-kinetic spectroscopy. More recently in 2024, Egorov and coworkers[28,29] constructed ab initio potential energy surfaces (PES) for both $\tilde{X}^3B_1$ and $\tilde{a}^1A_1$ methylene, culminating in comprehensive rovibrational line lists. Each PES was built from all-electron CCSD(T)/aug-cc-pCV*XZ* (X = T, Q, 5, 6) results and included DBOC and scalar relativistic corrections as well as high-order correlation adjustments, namely CCSDT and CCSDT(Q) with cc-pVQZ, CCSDTQ with cc-pVTZ, and CCSDTQP with cc-pVDZ. The final values for (r_e, θ_e) for the triplet and singlet states are (1.0756 Å, 133.92°) and (1.1064 Å, 102.31°), respectively, in excellent agreement with the best empirical results cited above,[26,32] but significantly more precise in the triplet case.

Theoretical approach

The single-configuration Hartree-Fock method is inadequate for the lowest singlet state of CH_2, especially near linear geometries where the $\tilde{a}^1A_1$ and open-shell singlet $\tilde{A}^1B_1$ states coalesce into a doubly-degenerate $^1\Delta$ manifold.

As early as 1971, the coefficients for the two most important configurations of the $\tilde{a}^1A_1$ electronic wavefunction in the region of the bent equilibrium geometry were found[45] in a natural orbital representation to be

$$0.962 \qquad 1a_1^2\,2a_1^2\,1b_2^2\,3a_1^2$$

$$0.194 \qquad 1a_1^2\,2a_1^2\,1b_2^2\,1b_1^2$$

Thus, the Hartree-Fock configuration $\ldots 3a_1^2$ represents 92.5 % of the wavefunction, while the second configuration $\ldots 1b_1^2$ represents 3.8 % of the wavefunction in a natural orbital representation. Although 3.8 % of the wavefunction might be considered not terribly important, it is enough to make single-configuration Hartree-Fock comparisons of the $\tilde{X}^3B_1$ and $\tilde{a}^1A_1$ states of CH_2 very inaccurate. For example, our computations near the complete basis limit show the Hartree-Fock singlet-triplet separation for CH_2 to be 25 kcal mol^{-1}, far above the best experimental value[33,46] of 9.0 kcal mol^{-1}. At present, coupled-cluster theory is the most reliable electronic structure methodology for the description of molecular systems well-described by a single configuration.[47,48] Single-reference coupled-cluster theory will approach the exact solution to the Schrödinger equation if carried to high enough excitation levels. In the present research, we investigate how far the coupled-cluster methodology needs to be pushed to pinpoint the methylene singlet-triplet separation.

Single-point energies, optimized geometries, and harmonic vibrational frequencies for singlet and triplet methylene were computed using a systematic progression of electronic wavefunction methods, starting with Hartree-Fock theory[49,50] and second-order Møller-Plesset (MP2)[51] perturbation theory, and then followed by coupled-cluster methods[52,53] proceeding from single and double excitations (CCSD) to full single, double, triple, and quadruple excitations (CCSDTQ).[54–56] Perturbative triple CCSD(T) and quadruple CCSDT(Q) excitation methods[57,58] were also employed owing to their popularity and effectiveness. Finally, an additional perturbative pentuple excitation CCSDTQ(P)[59,60] energy correction was applied to rigorously approach the full configuration interaction (FCI) limit.

The correlation-consistent polarized-valence orbital basis sets of Dunning[61–64] were used throughout this research, namely cc-pVXZ (X = D, T, Q, 5), along with the related core-valence basis sets cc-pCVXZ (X = D, T, Q, 5, 6). Thus, definitive conclusions regarding basis set dependence were reached. All computations with CCSD(T) and lower levels were performed using the CFOUR package,[65,66] while those of CCSDT and higher levels through CCSDTQ(P) were obtained with the MRCC program[67,68] interfaced with Psi4[69] and its OPTKING geometry optimization program when applicable.

A composite focal point analysis (FPA) scheme[70,71] was employed to rigorously approach the ab initio limit of the singlet-triplet energy splitting of CH_2 as well as the $\tilde{X}^3B_1$ and $\tilde{a}^1A_1$ equilibrium geometries. Our methodology mirrors that used highly successfully in our recent publication[72] on fulminic acid (HCNO) and HCN. Single-point energies through CCSD(T) used a ROHF reference, whereas higher-order corrections (CCSDT and beyond) used UHF. To reach the complete basis set (CBS) limit, extrapolations of the Hartree-Fock total energies (E_{HF}) and the all-electron MP2, CCSD, and CCSD(T) correlation energies (E_{corr}) were performed according to the following equations:[73,74]

$$E_{\mathrm{HF}}(X) = E_{\mathrm{HF,CBS}} + be^{-cX} \tag{1}$$

$$E_{\mathrm{corr}}(X) = E_{\mathrm{corr,CBS}} + bX^{-3} \tag{2}$$

where X is the cardinal number of the correlation-consistent basis set series. The E_{HF} extrapolations used cc-pCV(Q,5,6)Z total energies, while E_{corr} extrapolations were based on all-electron (AE) cc-pCV(5,6)Z results. Within the FPA scheme, higher-order correlation increments (δ) were computed as follows:

$$\delta[\mathrm{CCSDT(Q)}] = E_{\mathrm{corr}}(\mathrm{CCSDT(Q)/cc\text{-}pCVQZ}) - E_{\mathrm{corr}}(\mathrm{CCSDT/cc\text{-}pCVQZ}) \tag{3}$$

$$\delta[\mathrm{CCSDTQ}] = E_{\mathrm{corr}}(\mathrm{CCSDTQ/cc\text{-}pCVQZ}) - E_{\mathrm{corr}}(\mathrm{CCSDT(Q)/cc\text{-}pCVQZ}) \tag{4}$$

$$\delta[\mathrm{CCSDTQ(P)}] = E_{\mathrm{corr}}(\mathrm{CCSDTQ(P)/cc\text{-}pCVTZ}) - E_{\mathrm{corr}}(\mathrm{CCSDTQ/cc\text{-}pCVTZ}) \tag{5}$$

Two auxiliary corrections (Δ), namely the scalar relativistic one-electron mass-velocity and Darwin terms (MVD1)[75–77] and the diagonal Born-Oppenheimer (DBOC) correction,[43] were computed at the AE-CCSD(T)/cc-pCV5Z and AE-CCSD/cc-pCVQZ levels of theory, respectively. Thus, the final FPA energy is evaluated according to the following expression:

$$\begin{aligned} E_{\text{FPA}} &= E_{\text{HF, CBS}} + E_{\text{corr, CBS}}[\text{CCSDT}] + \delta[\text{CCSDT(Q)}] + \delta[\text{CCSDTQ}] \\ &\quad + \delta[\text{CCSDTQ(P)}] + \Delta(\text{MVD1}) + \Delta(\text{DBOC}) \end{aligned} \tag{6}$$

Results and discussion

Survey of the valence correlation series

Tables 1 and 2 detail our valence correlation results for the $\tilde{X}^3B_1$ and $\tilde{a}^1A_1$ states of methylene. The data include optimized bond distances (r_e) and bond angles (θ_e), total energies, harmonic vibrational frequencies (ω_i), and the singlet-triplet splitting (T_e). The intent of these tables is to elucidate the requirements for a precise theoretical description of methylene. Because the structure of methylene has historically been such a contentious issue, it is particularly worthwhile to assess whether frozen-core correlation methods with finite basis sets can accurately converge on the true equilibrium geometries of the singlet and triplet states.

For θ_e of the $\tilde{X}^3B_1$ state, Hartree-Fock theory gives 131.45° with the DZ basis set but quickly converges thereafter to a CBS limit of 131.84°. The MP2 bond angles are somewhat more sensitive to basis set, with (DZ, TZ, QZ, 5Z) results of (131.74, 132.79, 132.99, 133.05)°. The CCSD and CCSD(T) bond angles also increase with basis set size, although with somewhat quicker convergence than for MP2. For CCSD, θ_e incrementally increases from 132.24° (DZ) to 133.61° (5Z), whereas the corresponding CCSD(T) results match those of CCSD to within 0.1°. Full treatment of triples excitations (CCSDT) past CCSD(T) changes the bond angle by 0.03° in the case of DZ and 0.01° or less along the rest of the basis set series. In moving from CCSDT to CCSDT(Q), the (DZ, TZ, QZ, 5Z) bond angles are shifted by only (+0.01, −0.02, +0.01, +0.01)°. Further treatment of correlation with CCSDTQ does not yield any deviations more than 0.03° from the corresponding CCSDT(Q) angles. For all methods employed, θ_e exhibits strong basis set dependence and is consistently widened in traversing the basis set series. For example, the (DZ → TZ, TZ → QZ, QZ → 5Z) increments in the bond angle for CCSDT are (+1.29, +0.19, +0.04)°. Thus, extending the coupled-cluster series beyond connected triple excitations has very little impact on θ_e, while basis set effects are persistent. The [CCSD(T), CCSDT, CCSDT(Q)] results with the largest basis set employed (cc-pV5Z) are (0.34, 0.33, 0.32)° smaller than the empirical result. Such valence correlation treatments thus fail to precisely nail down the bond angle of triplet methylene.

The bond distance (r_e) of the $\tilde{X}^3B_1$ state decreases from DZ to TZ by (0.0108, 0.0165, 0.0175) Å for (HF, MP2, CCSD) and this increment settles to 0.0172 Å for CCSD(T) and beyond. Afterwards, the TZ → QZ shift for all methods is approximately −0.001 Å, with that of the QZ → 5Z shift being −0.0004 Å or less. As found for the bond angle, higher-order correlation methods hardly change the CCSDT results, with shifts no more than 0.0001 Å. The CCSD(T)/cc-pV5Z $r_e = 1.0769$ Å is merely 0.0003 Å longer than the empirical result. CCSDT/cc-pV5Z slightly worsens r_e, rendering this value 0.0005 Å too long, and the CCSDT(Q) bond distance with the same basis set is 0.0006 Å too long. Thus, the bond distances in Table 1 are essentially converged to the valence FCI limit by CCSDT(Q) and demonstrate good agreement with the empirical benchmark, but this comparison is specious because CBS extrapolation, core correlation, and auxiliary terms have not yet been considered.

For $\tilde{a}^1A_1$ methylene, the [HF, MP2, CCSD, CCSD(T)] bond angles once again systematically increase with increasing cardinality of basis set: the overall DZ → 5Z changes are (+1.05, +1.37, +1.47, +1.46)° with the largest contributor of these overall shifts being the initial DZ → TZ adjustments of (+0.83, +0.97, +1.09, +1.07)°. Interestingly, the HF/cc-pVDZ θ_e happens to be within 0.35° of the empirical result, but more robust basis sets increase and worsen the bond angle predictions to an error of +1.4° in the case of 5Z. In contrast, MP2 follows the desired trend of higher quality basis sets producing incrementally more accurate outcomes. With MP2/cc-pVDZ, θ_e is 1.5°

Table 1: Triplet CH_2 ($\tilde{X}^3B_1$) optimized bond distances (r_e, Å) and bond angles (θ_e, °), total energies (E_{tot}, E_h), and harmonic vibrational frequencies (ω_i, cm^{-1}).

	r_e(H–C)	θ_e(H–C–H)	E_{tot}	ω_1 (a_1)	ω_2 (a_1)	ω_3 (b_2)
UHF						
cc-pVDZ	1.0808	131.45	−38.92684	3281	1199	3497
cc-pVTZ	1.0700	131.83	−38.93786	3262	1201	3472
cc-pVQZ	1.0693	131.84	−38.94035	3265	1203	3473
cc-pV5Z	1.0692	131.84	−38.94097	3266	1203	3474
MP2						
cc-pVDZ	1.0902	131.74	−39.01978	3202	1159	3437
cc-pVTZ	1.0737	132.79	−39.05548	3203	1143	3437
cc-pVQZ	1.0722	132.99	−39.06602	3208	1137	3444
cc-pV5Z	1.0718	133.05	−39.06963	3209	1135	3446
CCSD						
cc-pVDZ	1.0947	132.24	−39.04005	3152	1129	3376
cc-pVTZ	1.0772	133.42	−39.07446	3155	1112	3380
cc-pVQZ	1.0759	133.57	−39.08348	3161	1106	3387
cc-pV5Z	1.0755	133.61	−39.08608	3162	1105	3388
CCSD(T)						
cc-pVDZ	1.0956	132.22	−39.04182	3139	1126	3365
cc-pVTZ	1.0784	133.48	−39.07785	3140	1105	3366
cc-pVQZ	1.0772	133.66	−39.08733	3144	1097	3372
cc-pV5Z	1.0769	133.70	−39.09008	3145	1092	3374
CCSDT						
cc-pVDZ	1.0959	132.19	−39.04220	3135	1126	3362
cc-pVTZ	1.0787	133.48	−39.07834	3136	1105	3363
cc-pVQZ	1.0775	133.66	−39.08780	3141	1097	3369
cc-pV5Z	1.0771	133.71	−39.09052	3141	1094	–
CCSDT(Q)						
cc-pVDZ	1.0960	132.20	−39.04228	3135	1125	3361
cc-pVTZ	1.0788	133.46	−39.07841	3135	1104	3362
cc-pVQZ	1.0775	133.67	−39.08790	3140	1096	3368
cc-pV5Z	1.0772	133.72	−39.09061	3140	1093	–
CCSDTQ						
cc-pVDZ	1.0960	132.20	−39.04229	3134	1125	3361
cc-pVTZ	1.0788	133.49	−39.07842	3135	1104	3362
Empirical[32]	1.0766(14)	134.037(45)	–	–	–	–

too small, whereas MP2 with a QZ and 5Z basis improves this discrepancy to merely 0.3° and 0.2°, respectively. The CCSD and CCSD(T) angles with the same basis set differ by no more than 0.02°; in the case of CCSD(T), θ_e goes from 100.54° (DZ) to 102.00° (5Z). The [CCSD(T), CCSDT] θ_e values for (TZ, QZ, 5Z) are smaller than the empirical result by [(0.79, 0.51, 0.40), (0.60, 0.30, 0.21)]°, showing significant changes with both full inclusion of triple excitations and basis set augmentation. Higher-order θ_e results do not differ from CCSDT by more than 0.03°. As is the case for the $\tilde{X}^3B_1$ bond angle, the best valence correlation treatment in Table 2 remains approximately 0.2° away from the empirical result, and thus a precise theoretical θ_e requires a more rigorous treatment.

Table 2: Singlet ($\tilde{a}^1A_1$) CH_2 optimized bond distances (r_e, Å) and bond angles θ_e, °), total energies (E_{tot}, E_h), harmonic vibrational frequencies (ω_i, cm^{-1}), and singlet-triplet splitting (T_e, kcal mol^{-1}).

	r_e(H–C)	θ_e(H–C–H)	E_{tot}	ω_1 (a_1)	ω_2 (a_1)	ω_3 (b_2)	T_e
RHF							
cc-pVDZ	1.1071	102.74	−38.88110	3108	1497	3176	28.70
cc-pVTZ	1.0957	103.57	−38.89255	3092	1496	3155	28.44
cc-pVQZ	1.0946	103.72	−38.89536	3098	1492	3161	28.23
cc-pV5Z	1.0944	103.79	−38.89610	3100	1490	3164	28.16
MP2							
cc-pVDZ	1.1217	100.85	−38.99144	2984	1429	3067	17.78
cc-pVTZ	1.1044	101.82	−39.03100	2990	1430	3067	15.36
cc-pVQZ	1.1025	102.09	−39.04330	2999	1425	3079	14.25
cc-pV5Z	1.1020	102.22	−39.04769	3002	1422	3082	13.77
CCSD							
cc-pVDZ	1.1279	100.54	−39.01964	2913	1418	2987	12.81
cc-pVTZ	1.1090	101.63	−39.05657	2930	1422	2999	11.23
cc-pVQZ	1.1070	101.90	−39.06657	2942	1419	3012	10.62
cc-pV5Z	1.1065	102.01	−39.06951	2945	1418	3016	10.40
CCSD(T)							
cc-pVDZ	1.1291	100.54	−39.02258	2897	1406	2975	12.07
cc-pVTZ	1.1105	101.61	−39.06138	2912	1407	2983	10.34
cc-pVQZ	1.1086	101.89	−39.07191	2922	1403	2996	9.68
cc-pV5Z	1.1081	102.00	−39.07504	2925	1401	2999	9.44
CCSDT							
cc-pVDZ	1.1288	100.67	−39.02330	2898	1399	2978	11.86
cc-pVTZ	1.1102	101.80	−39.06219	2913	1398	2985	10.13
cc-pVQZ	1.1084	102.10	−39.07270	2923	1394	2998	9.48
cc-pV5Z	1.1080	102.19	−39.07579	2925	1393	–	9.24
CCSDT(Q)							
cc-pVDZ	1.1289	100.67	−39.02345	2898	1398	2977	11.81
cc-pVTZ	1.1103	101.82	−39.06238	2912	1396	2985	10.06
cc-pVQZ	1.1085	102.12	−39.07291	2922	1392	2998	9.40
cc-pV5Z	1.1080	102.22	−39.07601	2924	1390	–	9.16
CCSDTQ							
cc-pVDZ	1.1289	100.69	−39.02348	2898	1398	2977	11.80
cc-pVTZ	1.1104	101.82	−39.06241	2911	1396	2984	10.05
Empirical[a]	1.107(2)	102.4(4)	–	–	–	–	9.37

[a] Equilibrium geometry taken from Ref. 26. The T_e value arises by adding the ZPE correction[37] of 0.37 kcal mol^{-1} to the empirical T_0 result[33] of 9.00 ± 0.01 kcal mol^{-1}.

For HF through CCSD(T), the bond distance is consistently shortened with increasing basis set size, with reduction in magnitude for each increment. For example, the (DZ → TZ, TZ → QZ, QZ → 5Z) shifts for CCSD(T) are (−0.0186, −0.0019, −0.0005) Å. These same CCSD(T) bond distances are longer than the empirical result by (0.0221, 0.0035, 0.0016, 0.0011) Å for (DZ, TZ, QZ, 5Z). In the same basis set series, the CCSDT r_e deviations from the empirical benchmark are +(0.0218, 0.0032, 0.0014, 0.0010) Å, demonstrating only minor shifts from CCSD(T). Higher-order increments beyond CCSDT amount to less than 0.0001 Å. The key conclusion from Tables 1 and 2 is that the valence correlation series predict (θ_e, r_e) to within (0.3°, 0.0003 Å) and (0.2°, 0.001 Å) of the empirical benchmarks for the $\tilde{X}^3B_1$ and $\tilde{a}^1A_1$ states of methylene, respectively, but pinpointing the geometries of these species requires more rigorous theoretical methods.

Perhaps the most salient issue in our theoretical treatment of methylene is the determination of its singlet-triplet energy gap, which serves as a stringent test for state-of-the-art electronic structure methods. Table 2 reports T_e results for the valence correlation series. As mentioned above, the HF predictions are far-removed from the benchmark (T_e = 9.37 kcal mol^{-1}) and are quite insensitive to basis set, ranging from 28.7 to 28.2 kcal mol^{-1} with the DZ to 5Z basis sets. In contrast, the corresponding MP2 results show marked improvements: T_e (DZ, 5Z) = (17.8, 13.8) kcal mol^{-1}. This MP2 range is narrowed at CCSD and CCSD(T) to the quite reasonable values (12.8, 10.4) and (12.1, 9.4) kcal mol^{-1}, respectively. Consistent with observations for the equilibrium geometries, basis set effects are paramount to achieving accurate predictions. The T_e (DZ → TZ, TZ → QZ, QZ → 5Z) shifts amount to (1.7, 0.7, 0.2) kcal mol^{-1} in both the CCSD(T) and CCSDT cases. Ascension to CCSDT(Q) and beyond affects T_e by less than 0.1 kcal mol^{-1}. Császár and coworkers[36] note that core electron correlation effects on T_e are substantial, approximately 0.3 kcal mol^{-1}, meaning that consideration of core correlation impacts T_e more than higher-order correlation increments. Moreover, in a landmark 1986 paper, Handy, Yamaguchi, and Schaefer[43] found that the DBOC contribution to T_e is 0.11 kcal mol^{-1}. Thus, none of the valence correlation results in Tables 1 and 2 can be considered definitive without inclusion of auxiliary corrections and basis set extrapolation. In particular, the agreement of CCSD(T)/cc-pV5Z and CCSDT(Q)/cc-pVQZ with the empirical benchmark to better than 0.1 kcal mol^{-1} is a consequence of error cancellation.

Definitive focal point analyses

Tables 3 shows our FPA optimized geometries of the $\tilde{X}^3B_1$ and $\tilde{a}^1A_1$ states of methylene using all-electron correlation methods and basis set extrapolation appended with scalar relativistic and DBOC effects. We also push the coupled-cluster series to include perturbative pentuple excitations [CCSDTQ(P)]. When applying this composite FPA methodology to the HCN molecule,[72] all bond distances agree with reliable empirical benchmarks within 0.0002 Å. For $\tilde{X}^3B_1$ and $\tilde{a}^1A_1$ methylene, the AE-CCSD(T)/CBS values are (r_e, θ_e) = (1.0752 Å, 133.90°) and (1.1060 Å, 102.20°), respectively. These CBS extrapolations differ from the corresponding explicit AE-CCSD(T)/cc-pCV6Z results by no more than 0.0001 Å and 0.03°. Pushing to AE-CCSDT/CBS and AE-CCSDT(Q)/CBS changes r_e of the triplet state by +0.0002 and −0.0001 Å, respectively, and θ_e is widened by 0.01° with each sequential step. The AE-CCSDTQ/CBS and AE-CCSDTQ(P)/CBS optimized geometric parameters are the same as those of AE-CCSDT(Q)/CBS to the reported accuracy. The singlet methylene r_e shifts are the same magnitude of those of the triplet state but in the opposite direction: the AE-CCSD(T)/CBS r_e of 1.1060 Å is shifted (−0.0002, +0.0001) Å in going to [AE-CCSDT/CBS, AE-CCSDT(Q)/CBS] with no appreciable changes thereafter. The θ_e shift from AE-CCSD(T) to AE-CCSDT is more pronounced at 0.22°, but the next increment is only 0.03° as the bond angle settles to 102.45°. Starting with the AE-CCSDTQ(P)/CBS geometries, inclusion of scalar relativistic effects merely reduces r_e by 0.0001 Å for the $\tilde{X}^3B_1$ state and narrows θ_e by 0.02° for the $\tilde{a}^1A_1$ state, while leaving the other parameters unaltered to the precision given. The $\tilde{X}^3B_1$ methylene (r_e, θ_e) results are only slightly perturbed with further inclusion of DBOC, as the adjustments from the AE-CCSDTQ(P)/CBS + MVD1 geometry are (+0.0002 Å, +0.02°). However, the $\tilde{a}^1A_1$ state demonstrates more noticeable changes: DBOC addition to the AE-CCSDTQ(P)/CBS + MVD1 results changes (r_e, θ_e) by (+0.0004 Å, −0.08°).

The final AE-CCSDTQ(P)/CBS + MVD1 + DBOC (r_e, θ_e) for the $\tilde{X}^3B_1$ and $\tilde{a}^1A_1$ states of methylene are (1.0756 Å, 133.94°) and (1.1063 Å, 102.35°), respectively. Our r_e result for $\tilde{X}^3B_1$ methylene matches the very recent high-level computations of Egorov et al.[28,29] to the precision in Table 3, whereas our θ_e is 0.02° larger. A bit more discrepancy is witnessed for the $\tilde{a}^1A_1$ state, as our results differ from those of Ref. 29 by 0.0001 Å and 0.04°. There are a few differences in the methodology of Egorov and coworkers[28,29] compared to ours including: no CBS extrapolation for $\tilde{X}^3B_1$ CH_2 and a different extrapolation procedure for $\tilde{a}^1A_1$; use of the Douglas-Kroll-Hess (DKH4) approach for relativistic corrections; higher-order coupled-cluster corrections from frozen-core rather than all-electron computations; and DBOC evaluation from FC-CCSD/cc-pVTZ rather than AE-CCSD/cc-pCVQZ. While none of these

Table 3: Triplet ($\tilde{X}^3B_1$) and singlet ($\tilde{a}^1A_1$) methylene optimized bond distances (r_e, Å) and bond angles (θ, °) from rigorous FPA procedures.

Level of theory	**$\tilde{X}^3B_1$ CH_2**		**$\tilde{a}^1A_1$ CH_2**	
	r_e(H–C)	**θ_e(H–C–H)**	**r_e(H–C)**	**θ_e(H–C–H)**
AE-CCSD(T)/cc-pCV6Z	1.0752	133.88	1.1061	102.17
AE-CCSD(T)/CBS	1.0752	133.90	1.1060	102.20
AE-CCSDT/CBS	1.0754	133.91	1.1058	102.42
AE-CCSDT(Q)/CBS	1.0755	133.92	1.1059	102.45
AE-CCSDTQ/CBS	1.0755	133.92	1.1059	102.45
AE-CCSDTQ(P)/CBS	1.0755	133.92	1.1059	102.45
AE-CCSDTQ(P)/CBS + MVD1	1.0754	133.92	1.1059	102.43
AE-CCSDTQ(P)/CBS + MVD1 + DBOC	1.0756	133.94	1.1063	102.35
Egorov et al. (ab initio)[28,29]	1.0756	133.92	1.1064	102.31
Empirical[26,32]	1.0766(14)	134.037(45)	1.107(2)	102.3(4)

differences constitute a significant concern, our new results in Table 3 should be considered slightly more rigorous and preferable.

The empirical benchmark for $\tilde{X}^3B_1$ methylene is taken from a 1986 paper by Bunker and coworkers[32] whereby 152 rotation and rotation-bending energy levels were determined from a large volume of microwave, infrared, and photodetachment spectroscopic data (0–4500 cm^{-1}) for CH_2 and two isotopologues. This data was then fit using two different nonrigid bender Hamiltonians, both of which were obtained using second-order perturbation theory to average over the two stretching vibrations. The equilibrium geometry and shape of the potential surface was then adjusted until the fit of the energy level separations to the experimental data was optimized. Our r_e result for $\tilde{X}^3B_1$ methylene is 0.0010 Å shorter than that of Bunker and coworkers[32] but within the reported uncertainty of ± 0.0014 Å. The θ_e presented here is 0.097° smaller than the empirical benchmark, in good agreement albeit outside the reported error bound of ± 0.045°. For the $\tilde{a}^1A_1$ state, the empirical benchmark is taken from a 1989 paper by Petek and coworkers,[26] who measured the symmetric- and antisymmetric-stretch infrared spectra of this state from 2600 to 3050 cm^{-1} by flash-kinetic spectroscopy. After removing data that were predicted to be triplet-perturbed, the remaining lines for the fundamental bands were fit to a Watson Hamiltonian including Coriolis coupling between the aforementioned vibrational states. This endeavor resulted in high-resolution rotational constants of fundamental vibrational levels, from which equilibrium rotational constants were surmised and hence an equilibrium structure for $\tilde{a}^1A_1$ methylene was obtained. Our reported r_e of 1.1064 Å is aligned with the empirical benchmark of 1.107 ± 0.002 Å, and the θ_e of 102.35° in this work is in near-perfect agreement with the empirical 102.3 ± 0.4°. We deem our best theoretical (r_e, θ_e) results to not only be in full accord with experiment but actually more accurate and precise. The successes witnessed here for the historically controversial methylene structure constitute a genuine triumph for modern quantum chemical methods.

In Table 4, we present all-electron FPA results for T_e with two-dimensional extrapolation to both the orbital basis set (CBS) and electron correlation (FCI) limits. Trends in Table 4 are similar to those witnessed in Table 2. At 24.7 kcal mol^{-1}, the single-configuration HF/CBS estimate for T_e significantly overshoots the converged NET/CBS result by a prodigious 15.4 kcal mol^{-1}. Inclusion of electron correlation at the MP2 level leads to substantial recovery from the deficiencies inherent to HF: T_e is reduced by a sizeable 10.9 kcal mol^{-1} at the MP2/CBS level, although it is still 4.5 kcal mol^{-1} above the NET/CBS target. Within the MP2/cc-pCVXZ (X = D, T, Q, 5, 6) series, T_e is reduced by over 3 kcal mol^{-1}, with values of (17.3, 15.4, 14.5, 14.1, 14.0) kcal mol^{-1} corresponding to each successive cardinal number. Moreover, an additional reduction of 0.23 kcal mol^{-1} is achieved by CBS extrapolation, demonstrating the deficiencies of even the best explicit computations.

We now turn to the coupled-cluster electron correlation series to tighten the CH_2 singlet-triplet splitting further. At the CBS limit, CCSD corrects the MP2 result by 3.1 kcal mol^{-1}, arriving at a T_e result of 10.6 kcal mol^{-1}. The energy gap is significantly reduced by another 1 kcal mol^{-1} with inclusion of perturbative triples: T_e[CCSD(T)/CBS] = 9.6 kcal mol^{-1}. Basis set effects with CCSD are strong but less pronounced than with MP2. For CCSD, the (DZ, TZ, QZ, 5Z, 6Z) core-

Table 4: Singlet-triplet energy splitting (T_e, kcal mol^{-1}) of CH_2.[a]

	T_e(HF)	δ[MP2]	δ[Ȼ]	δ[Ȼ(T)]	δ[ȻT]	δ[ȻT(Q)]	δ[ȻTQ]	δ[ȻTQ(P)]	NET
cc-pCVDZ (AE)	25.32	−8.02	−4.51	−0.76	−0.22	−0.05	−0.01	−0.001	11.73
cc-pCVTZ (AE)	24.97	−9.56	−3.94	−0.94	−0.23	−0.08	−0.02	0.001	10.20
cc-pCVQZ (AE)	24.76	−10.21	−3.56	−0.99	−0.24	−0.09	−0.01	[0.001]	[9.66]
cc-pCV5Z (AE)	24.70	−10.53	−3.35	−1.01	[−0.24]	[−0.09]	[−0.01]	[0.001]	[9.46]
cc-pCV6Z (AE)	24.67	−10.71	−3.25	−1.02	[−0.24]	[−0.09]	[−0.01]	[0.001]	[9.37]
CBS	[24.66]	[−10.94]	[−3.10]	[−1.03]	[−0.24]	[−0.09]	[−0.01]	[0.001]	[9.26]

$$T_e = T_e(\text{NET/CBS}) + \Delta\text{MVD1} + \Delta\text{DBOC} = 9.26 - 0.06 + 0.17 = 9.37\ \text{kcal mol}^{-1}$$

$$T_0 = T_e + \Delta\text{ZPE}^{b} = 9.37 - 0.37 = \mathbf{9.01\ kcal\ mol^{-1}}$$

[a] AE-CCSD(T)/cc-pCV5Z reference geometries: [r_e(H–C), θ_e(H–C–H)] for singlet and triplet methylene are (1.1062 Å, 102.15°) and (1.0753 Å, 133.87°), respectively. Ȼ is shorthand for CCSD. The symbol δ denotes increments in T_e with respect to the preceding level of theory in the electron correlation series, beginning with HF and MP2 and followed by CCSD through CCSDTQ(P). Brackets signify results from CBS extrapolations [eqs (1) and (2)] or additivity assumptions. The sum across each row yields the NET column entry, which approximates the FCI result with the corresponding basis set. AE refers to all-electron. Triplet CH_2 results were computed with an ROHF reference through CCSD(T), switching to a UHF reference starting with CCSDT. [b] The zero-point energies (ZPE) of the $(\tilde{X}\,^3B_1, \tilde{a}\,^1A_1)$ states of CH_2 are reported[37] as (10.67 ± 0.03, 10.31 ± 0.04) kcal mol^{-1}.

valence basis set series produces T_e values of (12.8, 11.5, 11.0, 10.8, 10.7) kcal mol^{-1}. With ascension to CCSD(T), the incremented CCSD → CCSD(T) corrections δ[Ȼ(T)] are less sensitive to basis set than with either MP2 or CCSD. In particular, δ[Ȼ(T)] = (−0.76, −0.94, −0.99, −1.01, −1.02) kcal mol^{-1} for (DZ, TZ, QZ, 5Z, 6Z), demonstrating the merit of the essential FPA assumption that high-order correlation increments are less sensitive to basis set than lower-order ones.

As we proceed further up the coupled-cluster hierarchy, the critical question is whether high-order and auxiliary corrections can close the approximately 0.2 kcal mol^{-1} discrepancy between the CCSD(T)/CBS T_e result and the empirical benchmark of 9.37 kcal mol^{-1}. There is further modest improvement in the T_e predictions with the full CCSDT method as the gap is narrowed by 0.24 kcal mol^{-1} at the CBS limit. The CCSDT(Q) and full CCSDTQ methods predict T_e to within 0.1 kcal mol^{-1} of the CCSDT results, cumulatively reducing T_e by another 0.1 kcal mol^{-1}. The FPA layout here shows once again that the higher-order correlation contributions become progressively less sensitive to basis set. With a final push toward the FCI limit, AE-CCSDTQ(P)/cc-pCV*X*Z (X = D, T) values impact T_e by a miniscule (−0.001, +0.001) kcal mol^{-1}, respectively. Thus, the dual extrapolation presented in Table 4 yields a strongly converged T_e(NET/CBS) = 9.26 kcal mol^{-1}.

For an application this exacting, it is essential to assess the effects of auxiliary corrections on the singlet-triplet splitting. Upon incorporation of first-order scalar relativistic effects (MVD1), T_e is further lowered by 0.06 kcal mol^{-1}. However, the diagonal Born-Oppenheimer correction (DBOC) raises this result by 0.17 kcal mol^{-1}. Furthermore, comparison to the empirical T_0 value necessitates a zero-point energy (ZPE) correction. Toward this end, a ΔZPE of 0.37 ± 0.05 kcal mol^{-1} is ascertained from Furtenbacher and coworkers[37] on the basis of rigorous variational vibrational computations, superseding various earlier results[33–35,44] for this quantity. This ΔZPE renders our final singlet-triplet splitting energy as T_0 = 9.01 kcal mol^{-1}, virtually indistinguishable from the best empirical T_0 value[33] of 9.00 ± 0.01 kcal mol^{-1}. Our FPA computations thus yield a resounding resolution to decades of historical controversy.

Conclusions

As we mark the centenary of quantum mechanics, Paul A. M. Dirac's famous 1929 declaration still echoes: "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble."[78] Driven by this vision, theoretical chemistry has made monumental strides in the decades since, with methylene standing as a paradigmatic molecule that has served as a litmus test for both the success and reputation of the field. We have reviewed the remarkable changes (specifically in 1970 and 1982) in the attitudes of non-theoretical chemists toward ab initio computational quantum chemistry. The corollary to these changed attitudes is that today, quantum chemical methods are used in a large fraction of papers published in the best journals in chemistry. In the second half of this report, we witness triumphs of modern quantum chemistry in pinpointing the equilibrium geometry of methylene. The final results for the optimized structures of the $\tilde{a}^1A_1$ and $\tilde{X}^3B_1$ states of CH_2 are in complete accord with the empirical benchmarks, and we deem our values to actually be more accurate and precise. Moreover, our final FPA T_0 result of 9.01 kcal mol^{-1} achieves near-perfect agreement with the best empirical result of 9.00 ± 0.01 kcal mol^{-1}. These conclusions serve as a compelling example of the extraordinary progress theoretical chemistry has made toward realizing the vision articulated by Dirac nearly a century ago.

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