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Theoretical Study of the Magnetic Properties of the Methyl Radical

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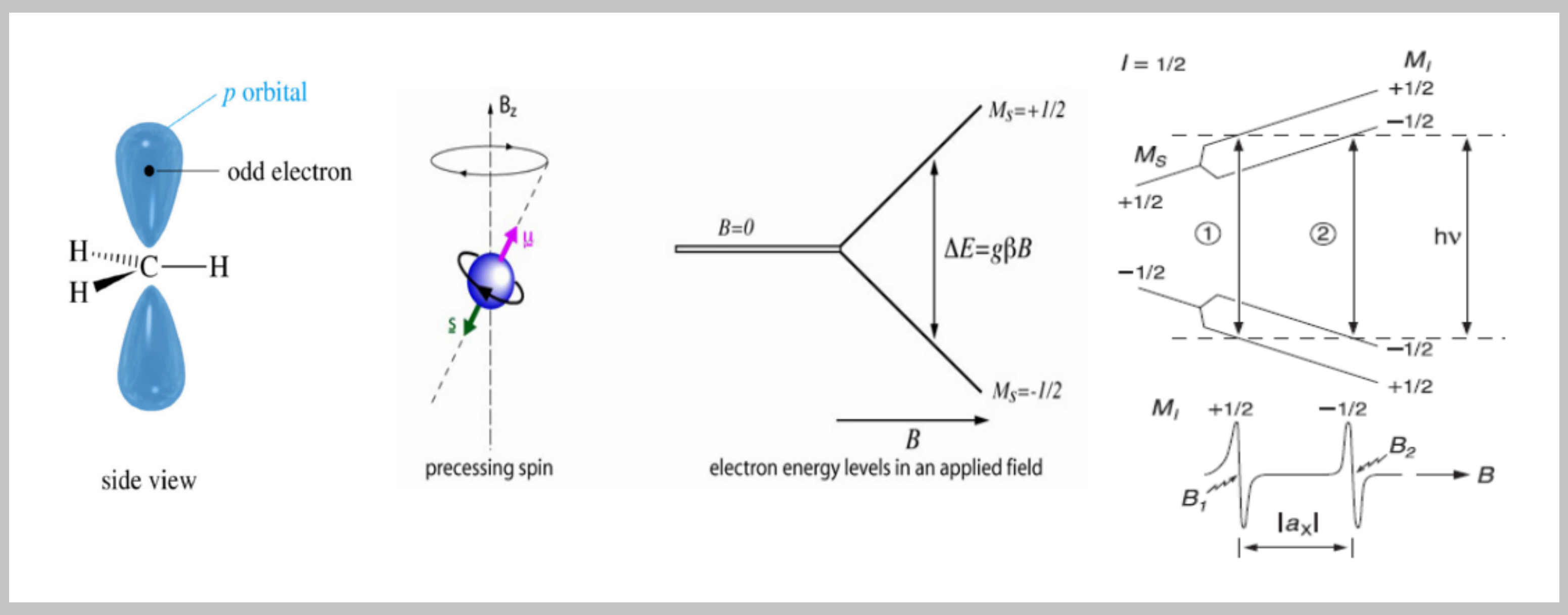
Introduction

Electronic contributions to molecular properties such as dipole moments, hyperfine constants, polarizabilities, etc. are often expected to be dominant so that they essentially determine the value of the property in question. Thus, theoretical values of properties reported in the literature are often purely electronic in that their calculation involves no ro-vibrational corrections and thermal averaging. However, there are many cases where the nuclear motion contributes significantly to the resulting property values; sometimes the nuclear contributions dominate over the electronic contributions. So, in general, it is necessary to consider the nuclear motion in order to obtain accurate theoretical predictions of molecular properties. The isotropic hyperfine coupling constants of the methyl radical CH_3 provides an example of this.

Hyperfine Interactions



http://www.st-andrews.ac.uk; http://wps.prenhall.com; See Ref. [1]

Ab initio Calculations

- The ab initio energies required for constructing the PES for the electronic ground state of CH_3 were calculated with the MOLPRO program package. Frozen-core calculations were carried out for 24000 symmetry-unique geometries at the ROHF-RCCSD(T)/aug-cc-pVTZ level of theory.
- For the coupling-constant surface, the geometry-dependent values of the isotropic hyperfine coupling constant (also known as Fermi contact term) were obtained at the same set of nuclear geometries used in the PES calculation.

Vibrational and Thermal Averaging

For an ensemble of molecules in thermal equilibrium at absolute temperature T, the thermal average of an operator $\hat{\mathbf{P}}$ is given by

$$\langle \hat{\mathbf{P}} \rangle_{\mathbf{T}} = \frac{1}{\mathbf{Q}} \sum_{\mathbf{i}} \mathbf{g_i} \, \mathbf{exp} \left(- \frac{\mathbf{E}^{(\mathbf{i})}_{\mathrm{rv}}}{\mathbf{kT}} \right) \langle \hat{\mathbf{P}} \rangle_{\mathbf{i}}$$

where $\mathbf{g_i}$ is the degeneracy of the ith state with the energy $\mathbf{E}^{(\mathbf{i})}_{\mathrm{rv}}$ relative to the ground state energy, $\mathbf{k}$ is the Boltzmann constant, $\mathbf{Q}$ is the internal partition function defined as

$$\mathbf{Q} = \sum_{\mathbf{i}} \mathbf{g_i} \, \mathbf{exp} \left(- \frac{\mathbf{E}^{(\mathbf{i})}_{\mathrm{rv}}}{\mathbf{kT}} \right)$$

and $\langle \mathbf{P} \rangle_{\mathbf{i}}$ is an expectation value of the operator $\hat{\mathbf{P}}$ in a rovibrational state $\mathbf{i}$

$$\langle \hat{\mathbf{P}} \rangle_{\mathbf{i}} = \langle \mathbf{\Phi}^{(\mathbf{i})}_{\mathrm{rv}} | \hat{\mathbf{P}} | \mathbf{\Phi}^{(\mathbf{i})}_{\mathrm{rv}} \rangle$$

The calculation of the quantities in the above equations requires the eigenvalues $\mathbf{E}^{(\mathbf{i})}_{\mathrm{rv}}$ and eigenvectors $\mathbf{\Phi}^{(\mathbf{i})}_{\mathrm{rv}}$ which are usually obtained variationally, that is, by matrix diagonalization [2].

Acknowledgments

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Results: Vibrational Energies and Contributions

- Calculated vibrational energies

Irrep	Cal.	Exp.	v_1 v_2 $v_3^{\ell_3}$ $v_4^{\ell_4}$
A_1'	601.1	606.5	$0\ 1\ 0^0\ 0^0$
E'	1389.0	1397.0	$0\ 0\ 0^0\ 1^1$
A_1'	3003.4	3004.4	$1\ 0\ 0^0\ 0^0$
E'	3159.5	3160.8	$0\ 0\ 1^1\ 0^0$

Table 1: Calculated vibrational energies (in cm^{-1}) for $^{12}CH_3$

- Carbon-13 isotropic HFCC in the methyl radical

Method/Basis set	$A^{\mathrm{iso}}_{\mathrm{eql}}$(G)	$A^{\mathrm{iso}}_{\mathrm{vib}}$(G)	$\Delta A^{\mathrm{iso}}_{\mathrm{vib}}$(G)	T(K)	Ref.
		other work			
QCISD(T)/TZVP	27.8	37.7	9.9(36%)	96	[3]
MCSCF/cc-pVTZus2st	27.7	37.3	9.6(35%)	0	[4]
B3LYP/Huz-IIIsu3	29.9	42.2	12.3(41%)	0	[5]
		our work			
CCSD(T)/aug-cc-pVTZ-J	25.8	37.1	11.3(44%)	96	
		Experiment			
Experiment	–	38.3	–	96	[6]

Table 2: Carbon isotropic HFCC in methyl radical CH_3 ($^2A''$)

Results: Out-of-Plane Bending Mode

Level	T_{vib}(cm^{-1})	$\langle A^{\mathrm{iso}}_{13C} \rangle$(G)
v_2		
1	596.2	52.8
2	1267.7	64.5
4	2749.6	76.0
8	6042.1	112.6
v_1		
1	3002.6	39.0
2	5960.1	41.4

Table 3: Vibrational term values T_{vib} (up to 6000 cm^{-1}) and vibrationally averaged HFCC values $\langle A^{\mathrm{iso}}_{13C} \rangle$ of the vibrational levels $\mathbf{v_2}\,\nu_2$ and $\mathbf{v_1}\,\nu_1$ of $^{13}CH_3$.

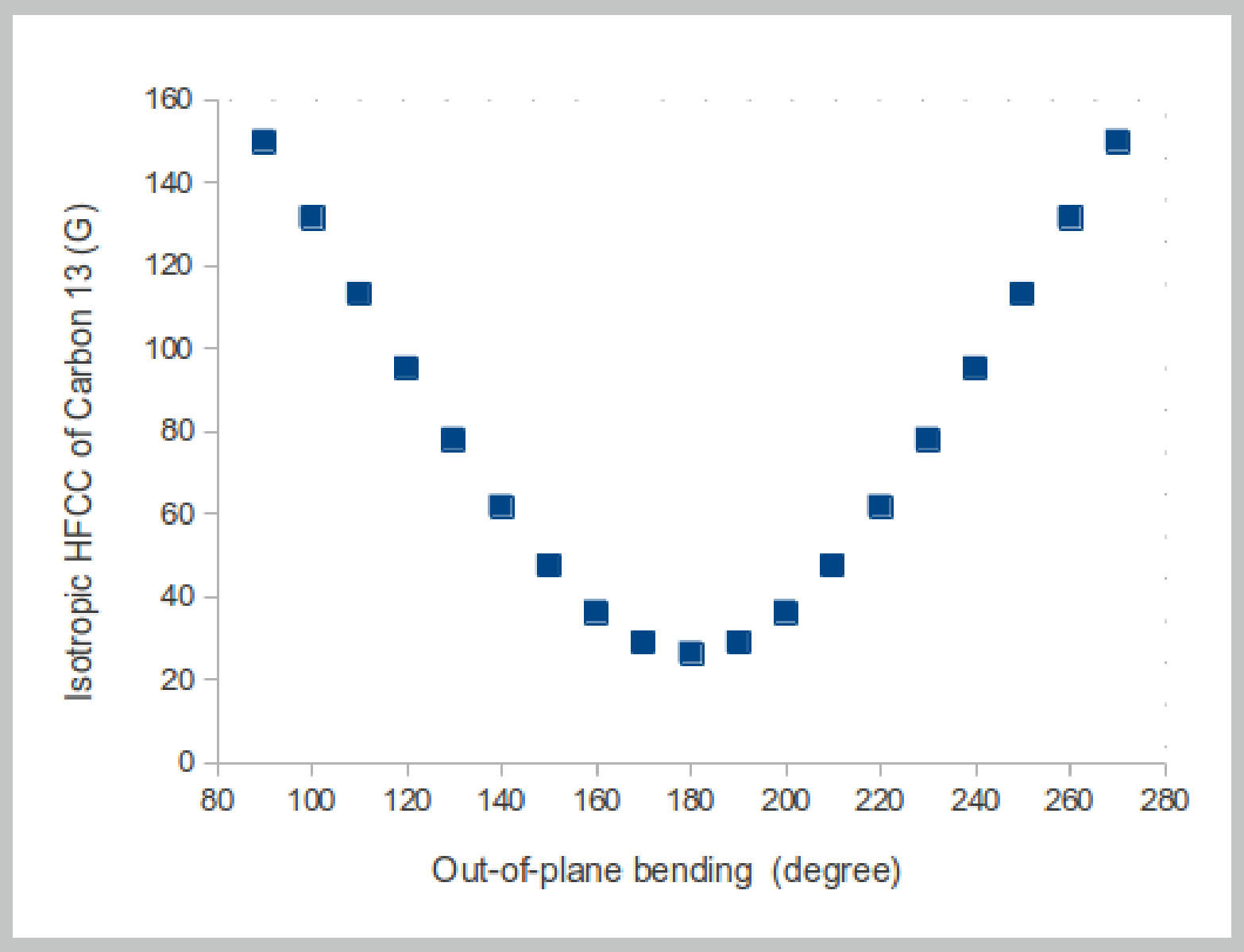

Figure 1: Carbon-13 isotropic HFCC v. out-of-plane bending mode in CH_3 at the CCSD(T)/EPR-III level of theory.

Conclusion

We conclude that with the high-level electronic structure methods and the variational treatment of the vibrational motion used in the present work, we are able to obtain a value of the carbon-atom isotropic HFCC of $^{13}CH_3$ in satisfactory agreement with the experimental value (Table II). In particular, we calculate realistically the large vibrational contribution to the HFCC which we find to be 44% of the equilibrium value. We find, in agreement with previous work, that the large contribution is associated with the out-of-plane bending motion and that thermal effects play a minor role.

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