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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
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.

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

$$ \langle \hat{P} \rangle_T = \frac{1}{Q} \sum_i g_i \exp \left( - \frac{E_i^{(0)}}{kT} \right) \langle \hat{P} \rangle_i $$

where $g_i$ is the degeneracy of the $i$th state with the energy $E_i^{(0)}$ relative to the ground state energy, $k$ is the Boltzmann constant, $Q$ is the internal partition function defined as

$$ Q = \sum_i g_i \exp \left( - \frac{E_i^{(0)}}{kT} \right) $$

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

$$ \langle \hat{P} \rangle_i = \langle \Phi \rangle_i | \hat{P} \rangle | \Phi \rangle_i $$

The calculation of the quantities in the above equations requires the eigenvalues $E_i^{(0)}$ and eigenvectors $\Phi_i^{(0)}$ which are usually obtained variationally, that is, by matrix diagonalization [2].

Acknowledgments
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Results: Vibrational Energies and Contributions
Calculated vibrational energies

<table>
<thead>
<tr>
<th>Irrep</th>
<th>Cal.</th>
<th>Exp.</th>
<th>$v_1$</th>
<th>$v_2$</th>
<th>$v_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A'</td>
<td>0</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>E</td>
<td>3.0</td>
<td>3.6</td>
<td>3.3</td>
<td>3.6</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Table 1: Calculated vibrational energies (in cm$^{-1}$) for CH$_3$

Carbon-13 isotropic HFCC in the methyl radical

<table>
<thead>
<tr>
<th>Method/Basis set</th>
<th>$A_{\text{iso}}^{(0)}$ (G)</th>
<th>$A_{\text{iso}}^{\text{vib}}$ (G)</th>
<th>$\Delta A_{\text{iso}}^{\text{vib}}$ (G)</th>
<th>$T$ (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>QCISD(T)/TZVP</td>
<td>27.8</td>
<td>37.7</td>
<td>9.9 (36%)</td>
<td>96</td>
<td>[3]</td>
</tr>
<tr>
<td>M062X/cc-pVTZs2st</td>
<td>27.7</td>
<td>37.3</td>
<td>9.6 (35%)</td>
<td>0</td>
<td>[4]</td>
</tr>
<tr>
<td>B3LYP/Huz-Illus3</td>
<td>31.9</td>
<td>42.2</td>
<td>12.3 (41%)</td>
<td>0</td>
<td>[5]</td>
</tr>
</tbody>
</table>

*other work*

Table 2: Carbon isotropic HFCC in methyl radical CH$_3$ ($^2\Sigma^+$)

Results: Out-of-Plane Bending Mode

<table>
<thead>
<tr>
<th>Level</th>
<th>$T_{\text{vib}}$ (cm$^{-1}$)</th>
<th>$A_{\text{iso}}^{\text{vib}}$ (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_2$</td>
<td>1</td>
<td>596.2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1267.7</td>
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<tr>
<td></td>
<td>4</td>
<td>2769.6</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>6042.1</td>
</tr>
<tr>
<td>$v_3$</td>
<td>1</td>
<td>3026.2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>5690.1</td>
</tr>
</tbody>
</table>

Table 3: Vibrational term values $T_{\text{vib}}$ (up to 6000 cm$^{-1}$) and vibrationally averaged HFCC values ($A_{\text{iso}}^{\text{vib}}$) of the vibrational levels $v_2$ and $v_3$.

Figure 1: Carbon-13 isotropic HFCC $v_2$ 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 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.

References