

An **effective-Hamiltonian** approach to  $\text{CH}_5^+$ ,  
using ideas from **atomic spectroscopy**  
in Condon & Shortley's 1935 book

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# Physical Model

The molecular quantum mechanics of  $\text{CH}_5^+$  are mapped onto the atomic quantum mechanics of  $\text{C}^+$ .

1. The **C atom in  $\text{CH}_5^+$**   $\rightarrow$  the **nucleus in  $\text{C}^+$** .  
It represents a heavy-particle source of a central field.
2. The **5 protons in  $\text{CH}_5^+$**   $\rightarrow$  the 5 **electrons in  $\text{C}^+$** .
3. **Valence electrons in  $\text{CH}_5^+$**   $\approx$  a negatively charged “soup” (ignore e-soup in vib-rot Hamiltonians)  $\rightarrow$  free space in  $\text{C}^+$
4. The **CH diatomic molecule**  $\rightarrow$  the **H atom**.  
The 1-proton molecule  $\rightarrow$  the 1-electron atom.

$$\text{CH: } r_p \theta_p \phi_p l_p \rightarrow \text{H: } r_e \theta_e \phi_e S_e$$
$$|v, j, m_j, m_l\rangle \rightarrow |n, l, m_l, m_s\rangle$$

A big change in the 1-particle problem is caused by the difference in the radial equation = difference in  $V_{CF}$

$$V_{CF} (\text{CH}) = (1/2)k(r - r_0)^2 \rightarrow V_{CF} (\text{H}) = -e^2/r$$

- (i)  $\rightarrow +\infty$  at  $r = 0$   $\rightarrow -\infty$  at  $r = 0$
- (ii) has  $r_{eq}$  value has no  $r_{eq}$  value

(i) decouples  $j$  from  $v$ .

$$|v, j, m_j, m_l\rangle \rightarrow |n, l, m_l, m_s\rangle$$

$$0 \leq j \text{ for all } v \quad 0 \leq l \leq n-1$$

$$1s, 1p, 1d \dots \quad 1s$$

$$2s, 2p, 2d \dots \quad 2s, 2p$$

$$3s, 3p, 3d \dots \quad 3s, 3p, 3d$$

(i) & (ii) cause a change in the 1-particle “orbital energies”

$$E = (v+1/2)h\sqrt{(k/m) + bj(j+1)} \rightarrow E = -R/n^2$$

( $k \approx 5$  mdyne/Å gives  $v_{CH} \approx 2900$  cm<sup>-1</sup>,  $b = 14.5$  cm<sup>-1</sup>  $\approx B(\text{CH})$ ).

Now switch from 1-electron atom to 5-electron atom C+  
We need to introduce H-H repulsion terms.

H-H “bending” potentials in CH<sub>5</sub><sup>+</sup> (involving 5θ<sub>*i*</sub>, 5φ<sub>*i*</sub>) →  
electron-electron repulsion in C<sup>+</sup> (repulsion parameter *g*)

$$V_{HH} = g \sum_{i>j=1}^5 1/r_{ij}$$

Now we have the two parameters that are needed to define two limiting cases. The free-rotor limit has (*b* >> *g*) and the high-barrier limit has (*g* >> *b*), where *b* = the rotational constant and *g* = the H-H repulsion parameter.

Interesting to follow levels from one limiting case to the other, because 7 LAM rotations in free-rotor limit must turn into 7 SAV bending vibrations in high-barrier limit. (3 of the 10 LAM rotations remain rotations for *g* >> *b*.)

C&S 5-electron basis set = product of 1-electron functions

$$|n_1, l_1, m_{l1}, m_{s1}\rangle |n_2, l_2, m_{l2}, m_{s2}\rangle |n_3, l_3, m_{l3}, m_{s3}\rangle |n_4, l_4, m_{l4}, m_{s4}\rangle |n_5, l_5, m_{l5}, m_{s5}\rangle$$



$$|v_1, j_1, m_{j1}, m_{l1}\rangle |v_2, j_2, m_{j2}, m_{l2}\rangle |v_3, j_3, m_{j3}, m_{l3}\rangle |v_4, j_4, m_{j4}, m_{l4}\rangle |v_5, j_5, m_{j5}, m_{l5}\rangle$$

C&S give explicit equations for calculating matrix elements of their one-electron operators:  $F = \sum_i f_i$  (our  $V_{CF}$  = central field) and two-electron operators:  $G = \sum_{i>j} g_{ij}$  (our  $V_{HH}$  = repulsion) in this basis set, after it is antisymmetrized using  $\mathcal{A}$  to satisfy the Pauli exclusion principle.

It appears that we can use C&S  $\mathcal{A}$ ,  $F$ ,  $G$  formalism with only minor changes for  $\text{CH}_5^+$  (but there is no time to discuss these very interesting theoretical details in this talk).

## Another effect of the difference in radial equation is massive configuration interaction in $\text{CH}_5^+$

Configuration interaction is usually a small effect in atoms, since configurations are usually well separated in energy. But in  $\text{CH}_5^+$ , many configurations of the same parity are degenerate, **so configuration interaction will be a dominant effect in  $\text{CH}_5^+$** . Consider one example (atomic R-S notation has a molecular meaning here).

Energy	Configuraton	Russell-Saunders Terms	$2l+1J$	
18b	$s^2d^3$	$4(\text{P}, \text{F})$	$2(\text{P}, 2\text{D}, \text{F}, \text{G}, \text{H})$	
18b	$sp^3f$	$6\text{F}$	$4(\text{P}, 2\text{D}, 4\text{F}, 2\text{G}, \text{H})$	$2(2\text{P}, 4\text{D}, 5\text{F}, 4\text{G}, 2\text{H})$

A program is being written to cope with this  
= present (early) stage of the project.

There is a big problem with this model for  $\text{CH}_5^+$ .  
Free-rotor limit is OK. High-barrier limit is NO GOOD.

The  $1/r_{ij}$  2-body repulsion term gives  $D_{3h}$  equilibrium structures and  $C_{4v}$  transition states  $\neq$  **ab initio**. Other 2-body terms also give  $D_{3h}$  equilibrium geometries.

Can we devise 3-body (or 4-,5-body) terms that give the  $\text{H}_2\text{—CH}_3^+$  equilibrium structure? Even if we can, C&S do not consider 3,4,5-body electron-electron interaction matrix elements, so a completely new theoretical development will be necessary.

N.B.  $\text{PF}_5$  has  $D_{3h}$  equilibrium structure, but no observable tunneling splittings.



$L \cdot S$  spin-orbit interaction in  $C^+ \rightarrow$   
nuclear-Spin-overall-Rotation in  $CH_5^+$  = very small.

$$V_{SR} = C \sum_{i=1}^5 J_i \cdot I_i$$

Setting  $C = 0$  means only Russell-Saunders atomic thinking is needed;  $j$ - $j$  coupling will never occur !

# Notation for two rotational configurations in $\text{CH}_5^+$

Energy Configuraton Russell-Saunders Terms =  $^{2I+1}J$

$6b$   $1s^2 1p^3$   $4S^\circ 2P^\circ 2D^\circ$

$10b$   $1s^2 1p^2 1d$   $4(\text{PDF}) 2(\text{S}, 2\text{P}, 2\text{D}, 2\text{F}, \text{G})$

Program is written to count R-S terms for any configuration.  
How do we give this atomic notation molecular meaning?

$1s^2 1p^2 1d$  means: No C-H stretches excited. There are  
2 protons with  $j=0$ , 2 protons with  $j=1$ , 1 proton with  $j=2$

$E = 6b \approx 87 \text{ cm}^{-1}$ ,  $E = 10b \approx 145 \text{ cm}^{-1}$ , since  $B(\text{CH}) = 14.5 \text{ cm}^{-1}$

$I = \sum_i I_i$  = total nuclear spin of the 5 protons in  $\text{CH}_5^+$

$J = \sum_i j_i$  = total rotational angular momentum  $J$  of  $\text{CH}_5^+$

$^\circ$  means odd parity under Permutation-Inversion  $E^*$  in  $\text{CH}_5^+$