Molecular line lists for scandium and titanium hydride using the Duo program

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Outline

1. Motivation
2. The DUO program
3. Scandium hydride (+TiH)
4. Summary
Motivation

- Exomol project: we want complete line lists of small molecules for astrophysics.
- For molecules with 2-5 main group atoms one can often get \textit{ab initio} an accuracy of \( \approx 1 \text{ cm}^{-1} \) for ro-vibrational spectrum.
- Interest also in transition metal diatomics (TMD): VO, FeH, CrH, NiH, \ldots.
- We developed the program DUO for treating open-shell diatomics.
Closed-shell: $^1\Sigma$ states

- Each electronic term treated separately.
- Energy levels given by 1D Schrödinger equations:

$$-rac{\hbar^2}{2\mu_v} \frac{d^2}{dr^2} \psi(r) + \left( V_n(r) + \frac{J(J+1)}{2\mu_r r^2} \right) \psi(r) = E_{n,v,J}\psi(r)$$

- It is normally possible to obtain PECs from experiment by direct-potential-fit techniques.
Open-shell molecules

- For non-$^{1}\Sigma$ terms the rotational part of the Hamiltonian becomes

\[
\hat{H}_R = \frac{1}{2\mu r^2} \left\{ (\hat{J}^2 - \hat{J}_z^2) + (\hat{S}^2 - \hat{S}_z^2) + (\hat{L}^2 - \hat{L}_z^2) \right. \\
+ (\hat{J}_+\hat{S}_- + \hat{J}_-\hat{S}_+) \\
- (\hat{J}_+\hat{L}_- + \hat{J}_-\hat{L}_+) \\
+ (\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+) \left\} \right.
\]

where (1) is the diagonal part, (2) is the S-uncoupling term, (3) is L-uncoupling and (4) the spin-electronic one.

- Spin-orbit also couples different terms.
The **Duo** program

- **Duo** deals with the coupled-surface case in a general way.
- Given of energy curves and couplings **Duo** computes energy levels and transition intensities.
- **Duo** can modify curves to fit experimental data.
- **Duo** can deal with *any* diatomic and is freely available!
The Duo program

Input, global options:
masses 1.0078250321 44.9559100
nstates 6
jrot 0

grid
  npoints 201
  range 1.00, 5.000
  type 0

end
The Duo program

Input, potential energy curves:

```
poten 2
name "B_1_Pi"
lambda 1
mult 1
units cm-1
units bohrs
type grid
values
2.00 59707.241
2.05 54376.745
2.10 49502.743
2.15 45044.928
...
```
Output, energy levels:

Eigenvalues for J = 0.0

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<th>J</th>
<th>N</th>
<th>Energy/cm</th>
<th>State</th>
<th>v</th>
<th>lambda</th>
<th>spin</th>
<th>sigma</th>
<th>omega</th>
<th>parity</th>
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Scandium hydride

- ScH is lightest TM molecule, 4 valence electrons $\Rightarrow$ ideal for electronic structure theory.
- Studied theoretically especially in the 1980s by Anglada et al.
We focus on the six lowest terms (only singlets known experimentally):
Scandium hydride

- PEC = valence + core + relativistic.
- We performed a very detailed study of accuracy for each component monitoring $T_e$, $r_e$, $\omega_e$, $D_e$, $\mu_e$ against “exact” FCI results.
Valence only summary

- CCSD(T) ⇒ $T_e$ to $\approx 60$ cm$^{-1}$, $\omega_e$ to $\approx 5$cm$^{-1}$.
- MRCI ⇒ $T_e$ to $\approx 30$ cm$^{-1}$, $\omega_e$ to $\approx 1.5$cm$^{-1}$.
- MRCI+$Q$ ⇒ $T_e$ to $\approx 60$ cm$^{-1}$, $\omega_e$ to $\approx 3.5$cm$^{-1}$.
- MRCI does very well in this test!
Core correlation and relativistic

- Outer-core $3s3p$ core correlation changes $\omega_e$ by 15-30 cm$^{-1}$, $T_e$ by $\approx 600$ cm$^{-1}$.
- Conclusion: MRCI spoilt by poor core correlation treatment: $T_e$ accurate only to $\approx 200$ cm$^{-1}$, $\omega_e$ to $\approx 5$.
- Relativistic effects affect $T_e$ by $\approx 600$ cm$^{-1}$.
There are 10 symmetry-independent coupling curves for the six terms, e.g. \( \langle 3\Sigma^+ | H_{SO} | 1\Pi \rangle \).

Matrix elements of \( \hat{L}_x \), \( \hat{L}_y \) and their squares appear in the L-uncoupling and spin-electronic terms.

All couplings rather insensitive to basis set and electron correlation used (CASSCF is okay).
## Comparison with experiment

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<thead>
<tr>
<th>$J$</th>
<th>$p$</th>
<th>energies</th>
<th>obs – calc</th>
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<td>obs ab initio refined ab initio refined</td>
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<tr>
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<td>$X^{1\Sigma^+}$, $v = 0$</td>
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## Comparison with experiment

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<th>$J = 10$</th>
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<td>$\mathbf{V}^1\Pi, \nu = 1$</td>
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</tbody>
</table>

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Scandium hydride
## Comparison with experiment

<table>
<thead>
<tr>
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<th>$\text{obs} - \text{calc}$</th>
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<tr>
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</tbody>
</table>

$A^1\Delta$, $\nu = 0$
Introduction

The DUO program

ScH

Summary

1500 K spectrum

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Scandium hydride
We predicted $D_0 = 18,290(60) \text{ cm}^{-1}$, disagrees by 2$\sigma$ with Kant and Moon’s 1981 experiment 16,600(700) cm$^{-1}$.

We predicted for $X^1\Sigma^+$ $\mu_e = 1.72(2)$ D, agrees with Le and Steimle experimental $\mu_e = 1.74(0.15)$ D.
TiH: Lowest states

Line list for lowest doublet and quartet states ready!
Summary

- **Duo** can be used to study diatomics in a general setting.
- Difficult to get good $T_e$, better electronic structure approaches needed.
- Even limited experimental data are invaluable.
- For some applications the completeness of theoretical line lists more important than accuracy.