ab initio Computational Materials Science

Ralf Stoffel and Richard Dronskowski

Introduction to Quantum Mechanics: the Wave Function
Total Energy Calculations
Application to "Real-World" Problems
Temperature
Summary & Outlook

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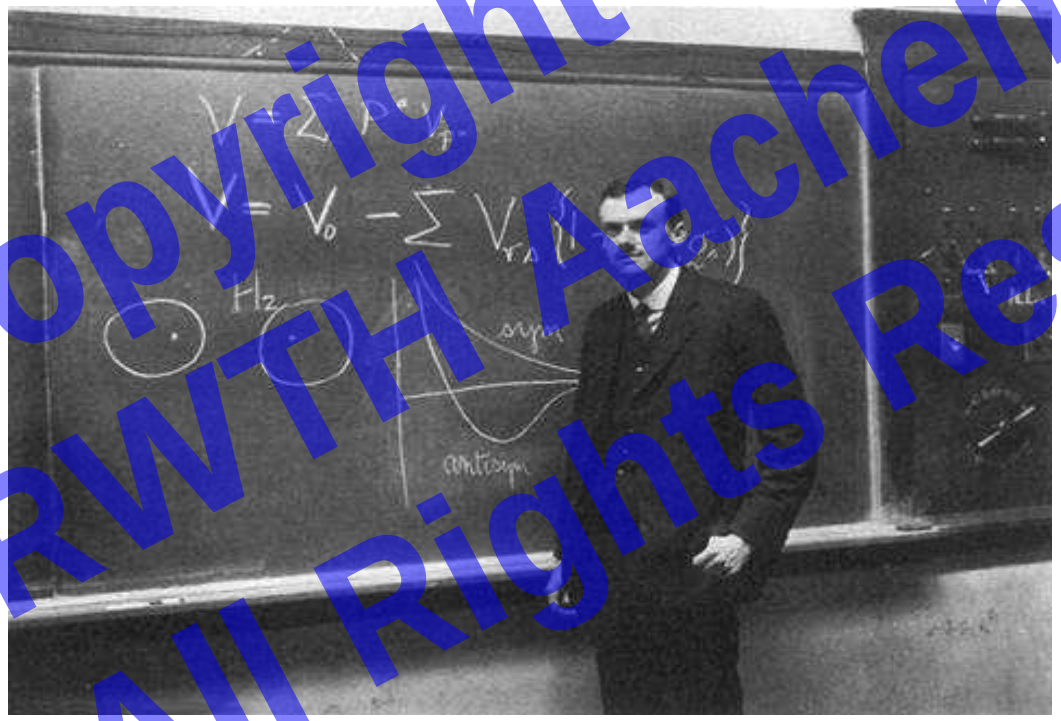
Where everything starts

"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.****"*



Paul Adrien Maurice Dirac (1929)

The Wave Function and Schrödinger´s Equation

$$\hat{H}\,\Psi = E\,\Psi$$

$\Psi = \Psi(R_i, r_i, t)$ **is** the entire atomic-like system

the wave function Ψ contains the **information in its entirety**, such as

- chemical constitution & configuration
- structures
- energies
- forces
- chemical bonding

and may be computed „from first principles“ (*ab initio*)

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Pioneers of Physics and Chemistry


Heitler


London


Bloch


Mulliken


Hoffmann


Slater


Pople


Parrinello


Schrödinger


Dirac


Fock


Hellmann


Pauling


Kohn

1926

2008

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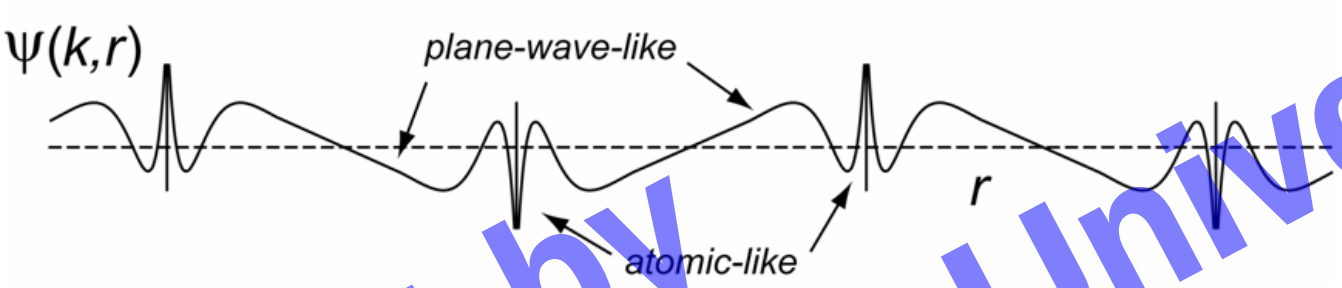
Reasons for Computational Materials Science



a reliable wave function (and its energy) gives access to

structural properties (lattice & spatial parameters)

electronic properties (band structures, densities-of-states, chemical bonding analysis, magnetism...)

thermodynamic properties (total energies, heats of formation, phonon dispersion → free energy, entropy, heat capacity)

Also: dynamic, optical, mechanical and other properties

Theoretical Calculation of Formation Enthalpy

$$\Delta G = \Delta H - T\Delta S \overset{\text{solid as a rock}}{\approx} \Delta H \approx \Delta E$$

density-functional (first-principles) total-energy calculations

E–V diagrams $\rightarrow$ $p = -\partial E/\partial V$ $\rightarrow$ $H = E + pV$

finally $\Delta H(p)$

➔ ***stability of solid compounds / different structure types***

➔ ***prediction of high-pressure phases***

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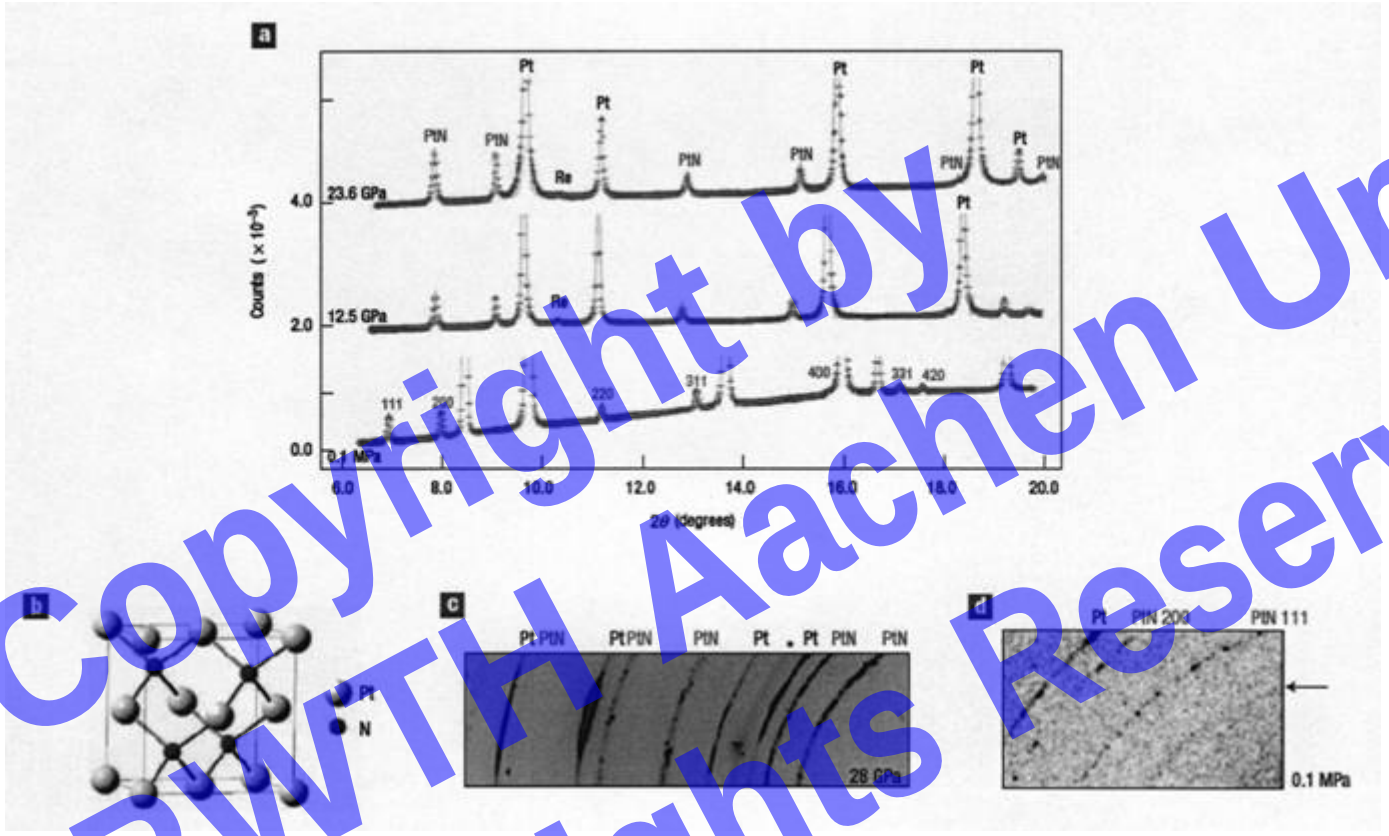
Platinum Nitride: "PtN"



from $Pt + N_2$
at $p > 45$ GPa
and $T > 2000$ K

X-ray data:
fcc unit cell with
$a = 4.8041$ Å,
[ZnS] type,
$B_0 = 372 \pm 5$ GPa

chemical analysis:
PtN_{1-x} with $x < 0.05$

E. Gregoryanz, C. Sanloup, M. Somayazulu,
J. Badro, G. Fiquet, H.-K. Mao, R. J. Hemley,
Nature Mater. **2004**, *3*, 294

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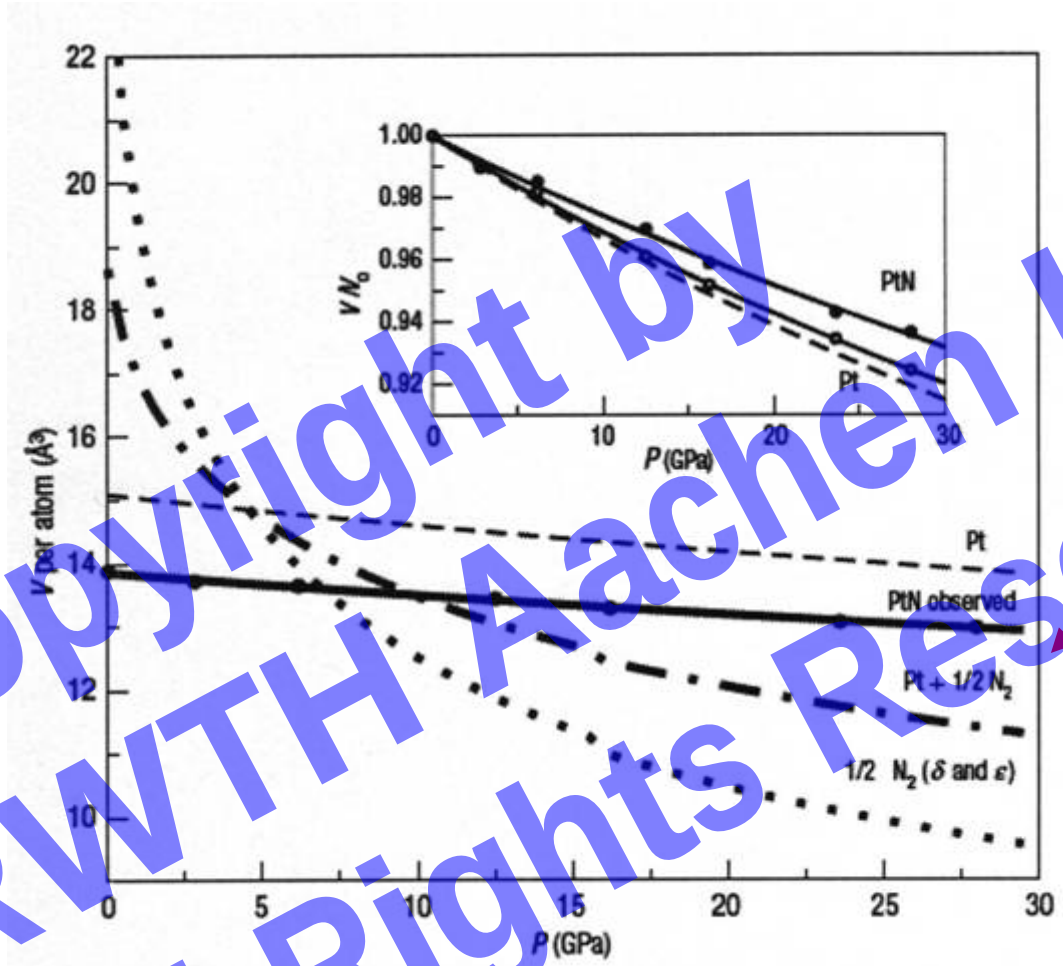
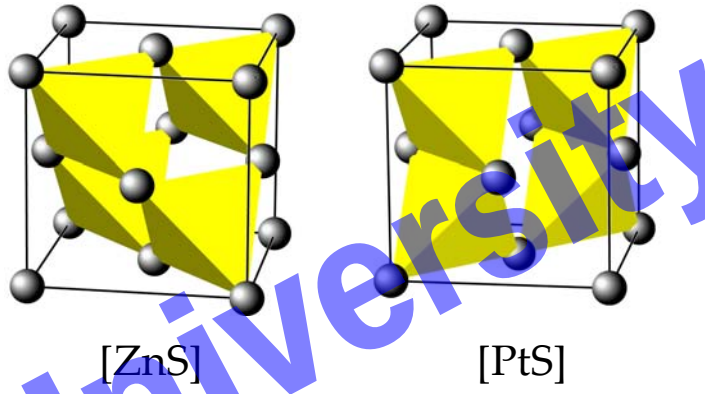
Platinum Nitride: the Obvious Discrepancy

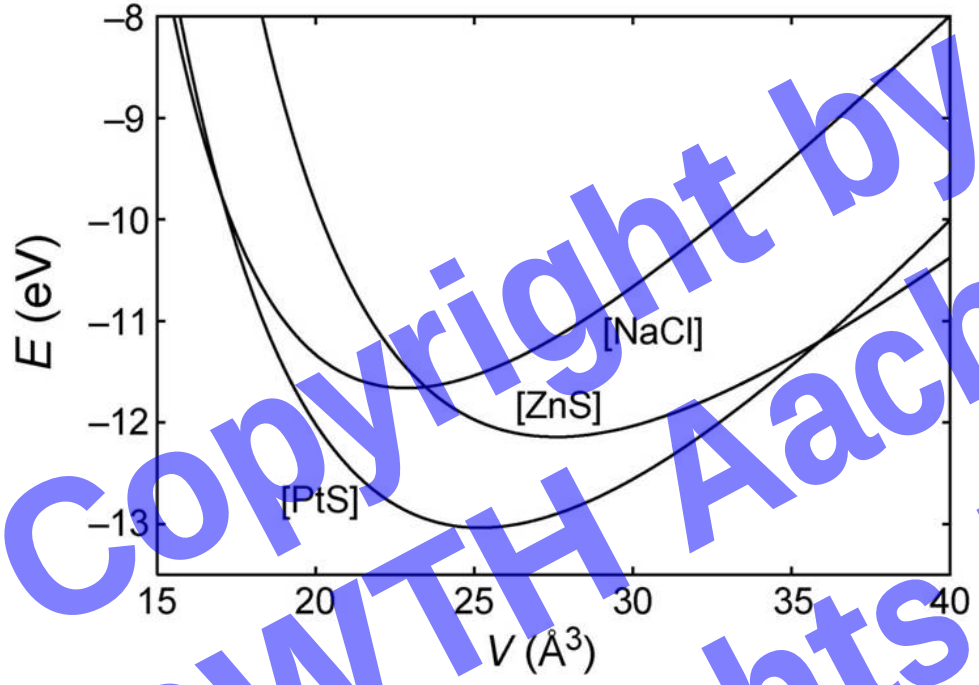


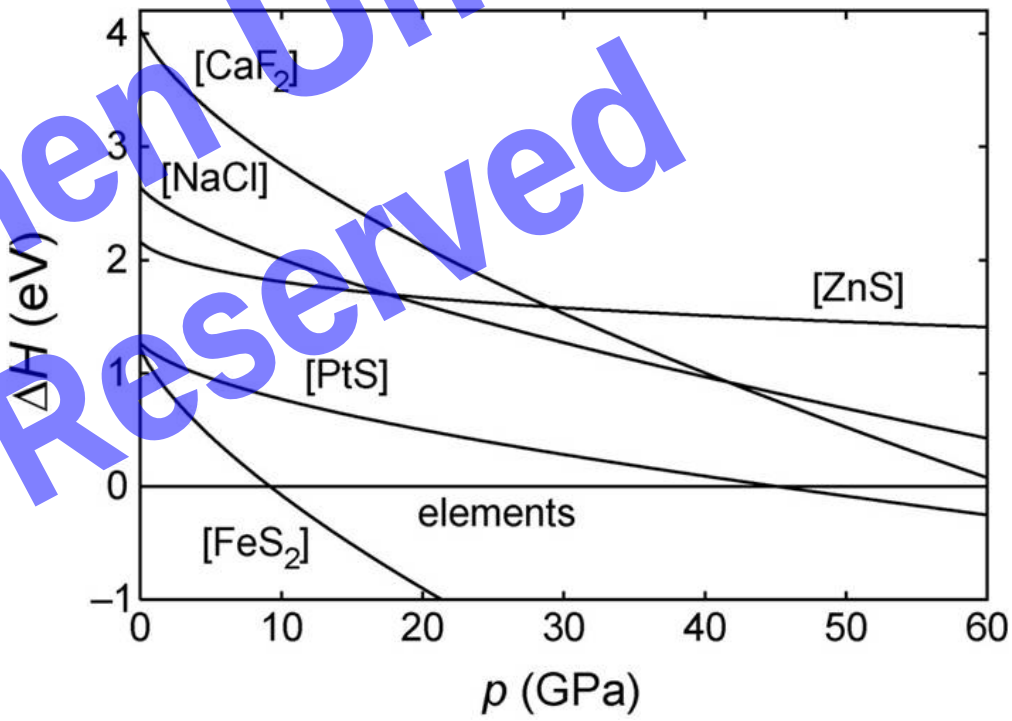
product phase is ***less*** *dense than the elements!*

Le Chatelier's principle violated

Platinum Nitride: E (V), H (p)



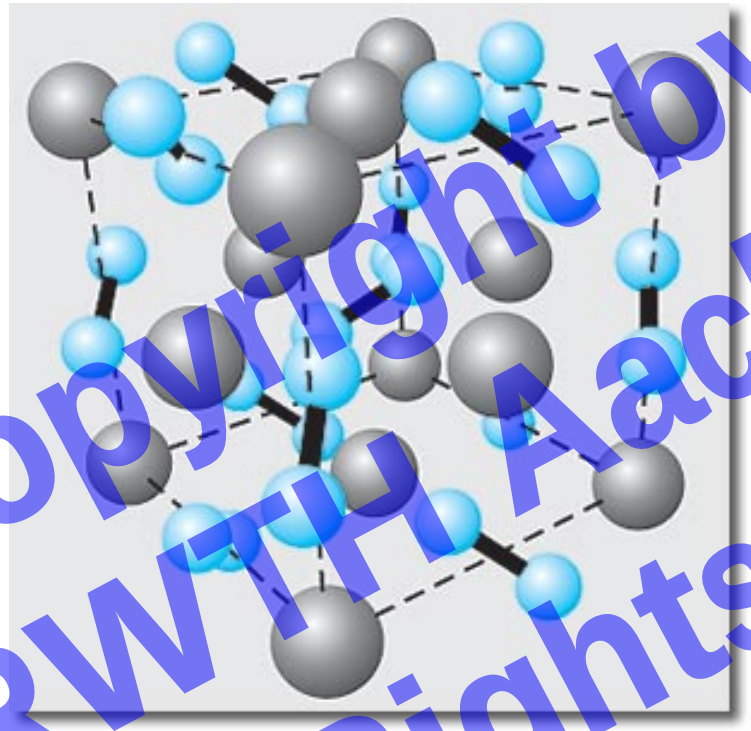




J. von Appen, R. Dronskowski,
Angew. Chem. Int. Ed. **2006**, *45*, 4365

“Platinum Nitride”: Experimental Realization

by repeating the 2004 experiments of Gregoryanz et al.:



composition: PtN_2, *not* PtN
pyrite [FeS_2] structure type
lattice parameter $a \approx 4.8$ Å
very large bulk modulus

…but they still call it a “nitride”

J. C. Crowhurst, A. F Goncharov, B. Sadigh, C. L. Evans, P. G. Morrall, J. L. Ferreira, A. J. Nelson
Science **2006**, *311*, 1275

ab initio Thermochemistry

Thermodynamic properties including temperature:

lattice vibrations (phonons) **→ Gibbs free energy**

$$G(T,p) = F(T,V) + pV$$

$$F(T,V) = E(V) + F_{ph}(T,V)$$

F_{ph} **(*T*,*V*):** ***phonon free energy***

$$F_{ph} = \frac{1}{2}\sum_{\vec{k},\nu}\hbar\omega\left(\vec{k},\nu\right) + k_B T \sum_{\vec{k},\nu}\ln\left[1-\exp\left(\frac{-\hbar\omega\left(\vec{k},\nu\right)}{k_B T}\right)\right]$$

we only need to know the ***phonon frequencies ω***

$\Rightarrow$ also **heat capacity** and **entropy**

How to obtain the phonon frequencies

1. Calculation of the forces F_α acting on the atoms when the other atoms are slightly ($u_\beta \approx 0.01$ Å) dislocated

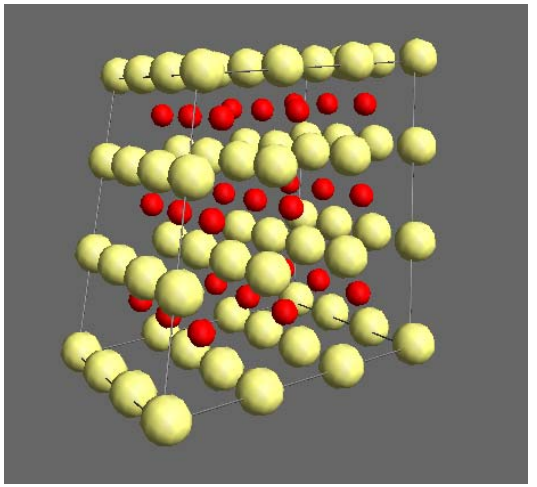
2. force constant matrix $\Phi_{\alpha\beta}$ $\quad \Phi_{\alpha\beta} = -\frac{F_\alpha}{u_\beta}$

3. dynamical matrix $D_{\alpha\beta}$ $\quad D_{\alpha\beta}(jj', \vec{k}) = \frac{1}{\sqrt{m_j m_{j'}}} \sum \Phi_{\alpha\beta} \exp\left[i\vec{k}\left(\vec{r} - \vec{r'}\right)\right]$

4. diagonalisation of $D_{\alpha\beta} \rightarrow \omega$

$$\left| D_{\alpha\beta}(jj') - \delta_{\alpha\beta}\delta_{jj'}\omega^2 \right| = 0$$

problem: supercells (> 50 atoms), high demand of computational time and memory (scaling $\approx N^{2\text{-}3}$)



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Project ELSA

Together with  and others:
Computational modelling and preparation of the
high temperature superconductor $YBa_2Cu_3O_{6+x}$

Our (quantum-chemical) part:

Prediction of thermochemical potentials where there is no experimental data available

First step: comparing properties of compounds with known thermochemical properties
(e.g. Cu, CuO, BaO, BaO_2…)

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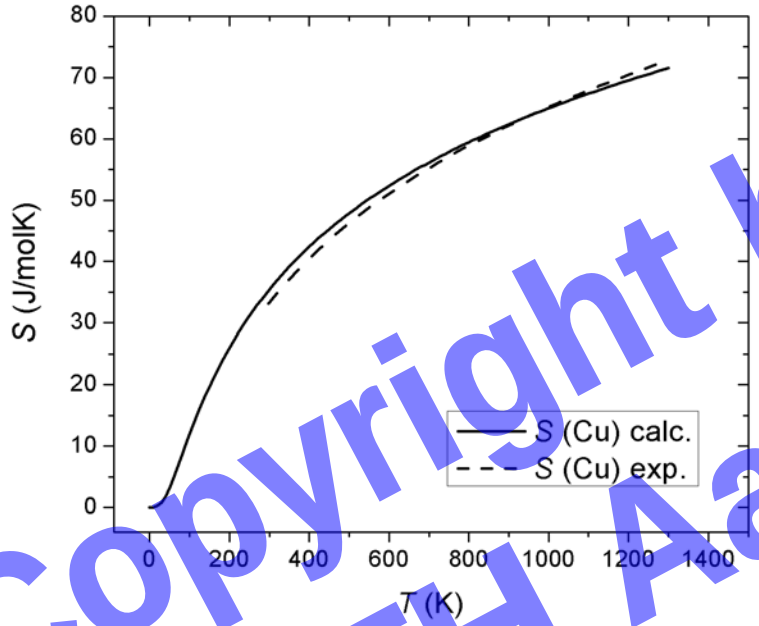
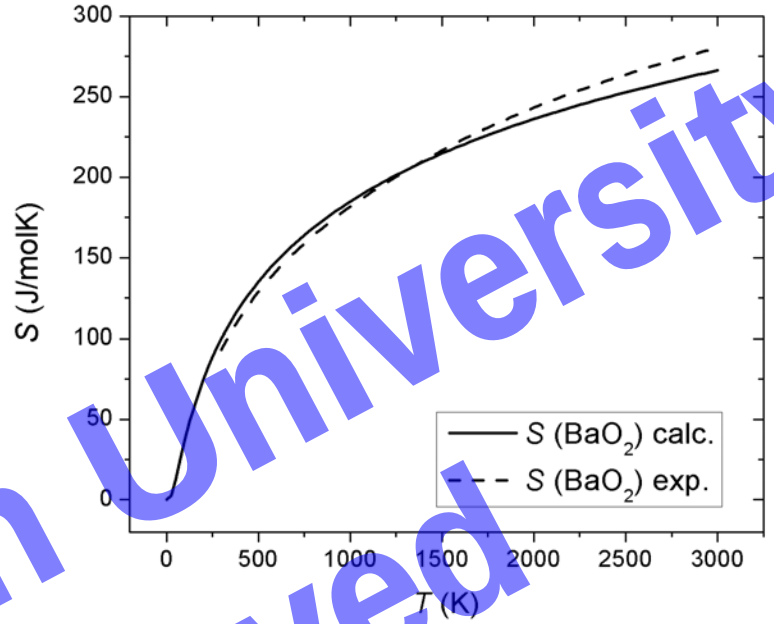
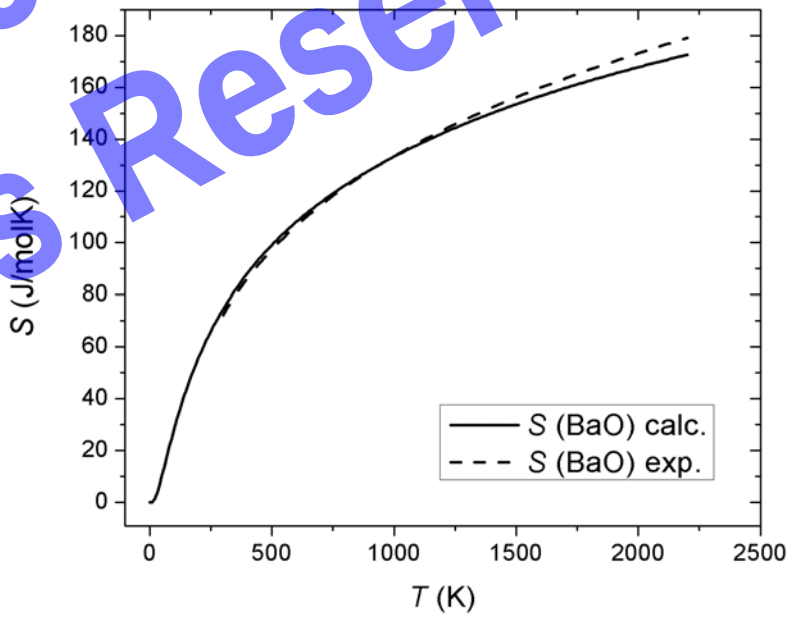
Entropy

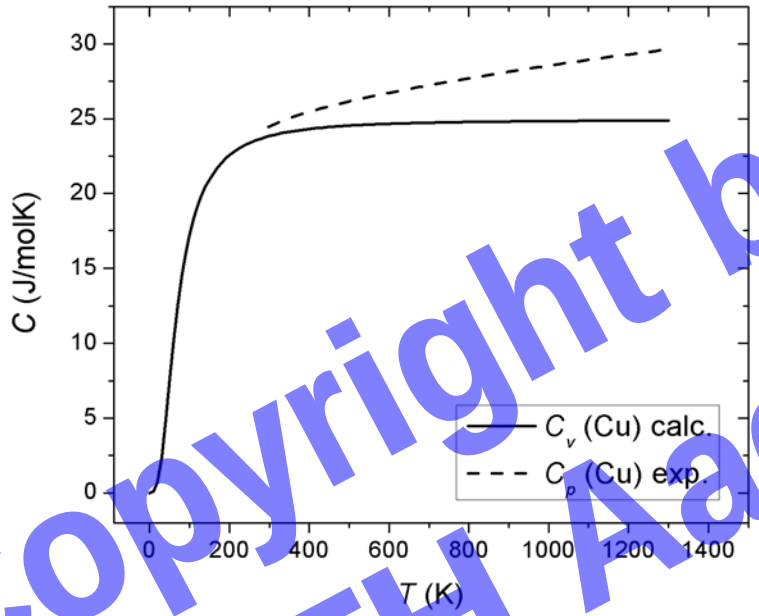


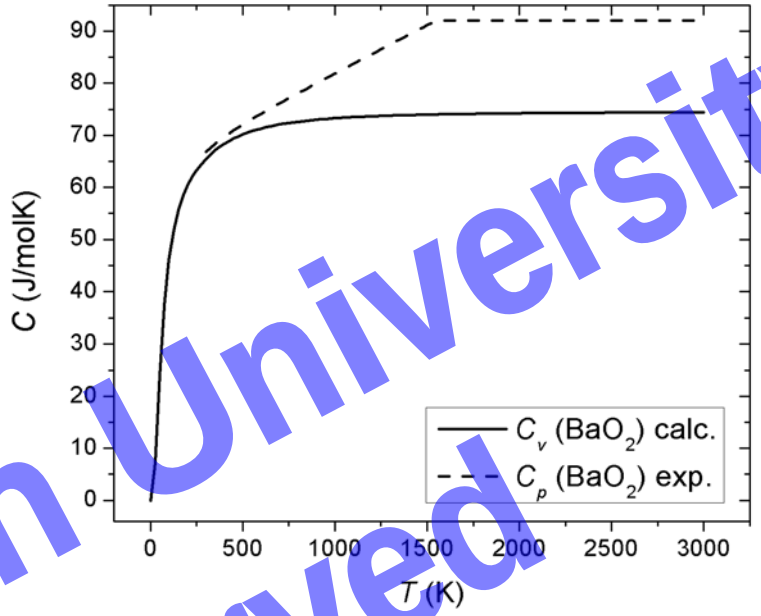


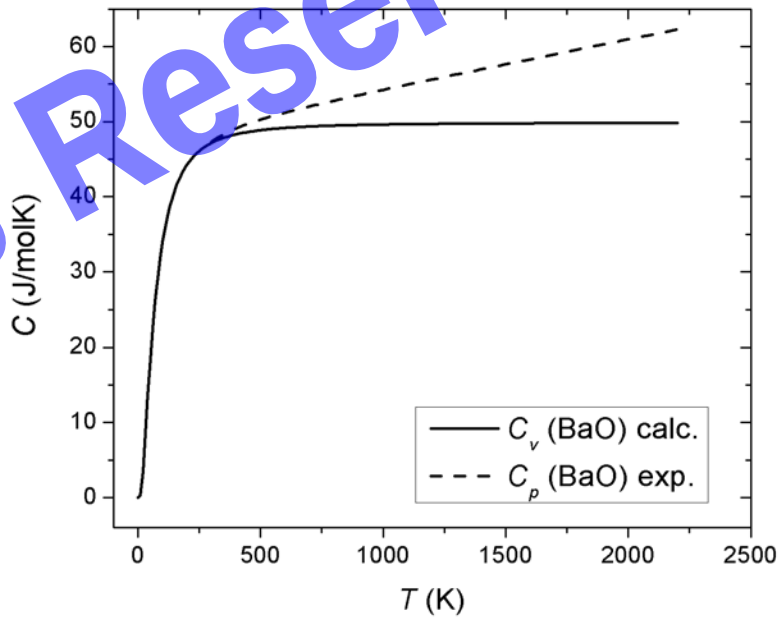


Good reproduction of experimental data, only small errors

Heat Capacity







Calculation of C_V not C_p

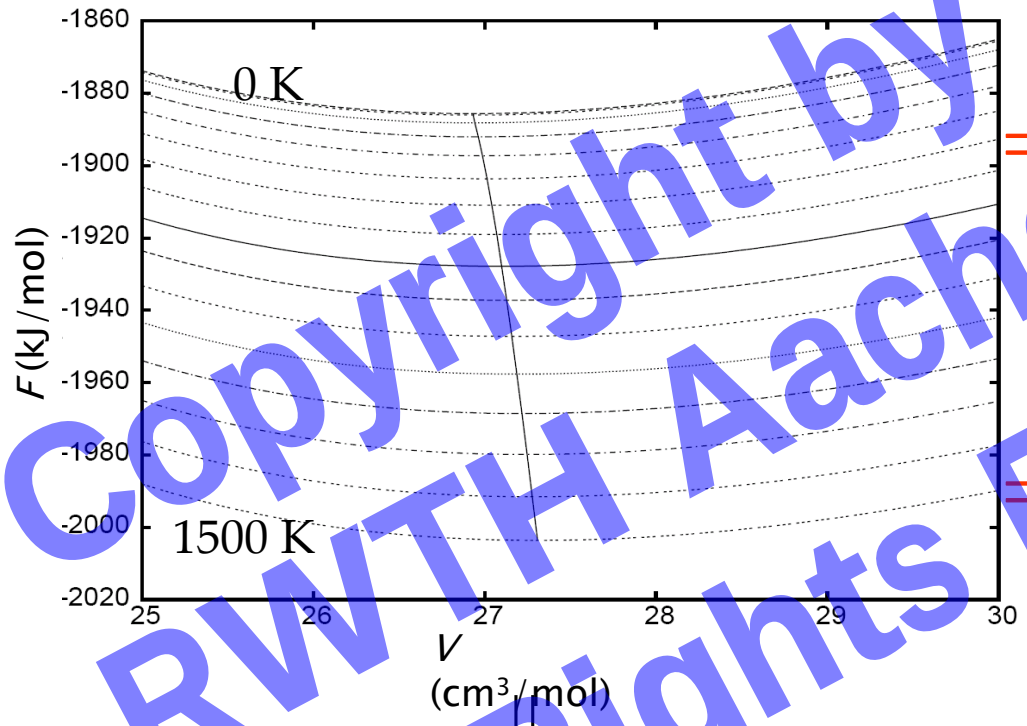
$\Rightarrow$ correction:

$C_p - C_V = \alpha^2 B_T V T \approx \text{const.} \cdot T$

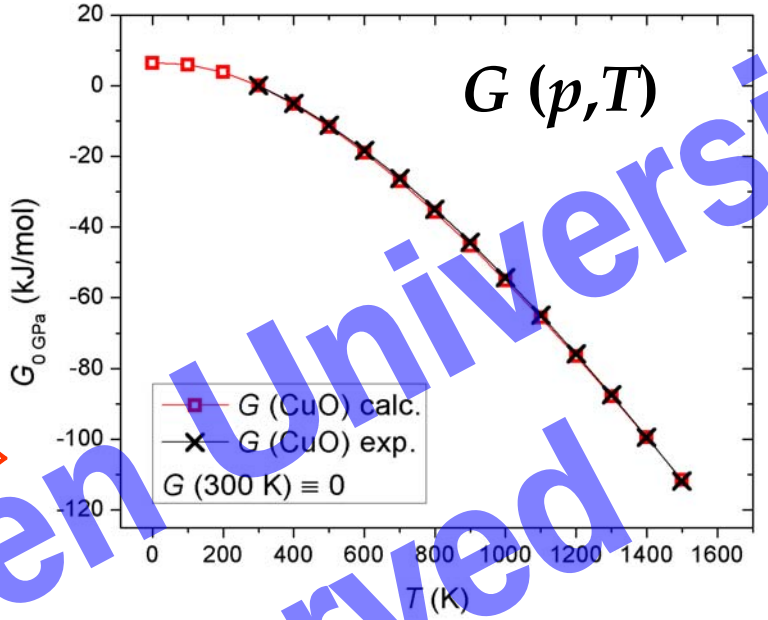
Free Energy

$F\,(T)$ at different V (96-110%)

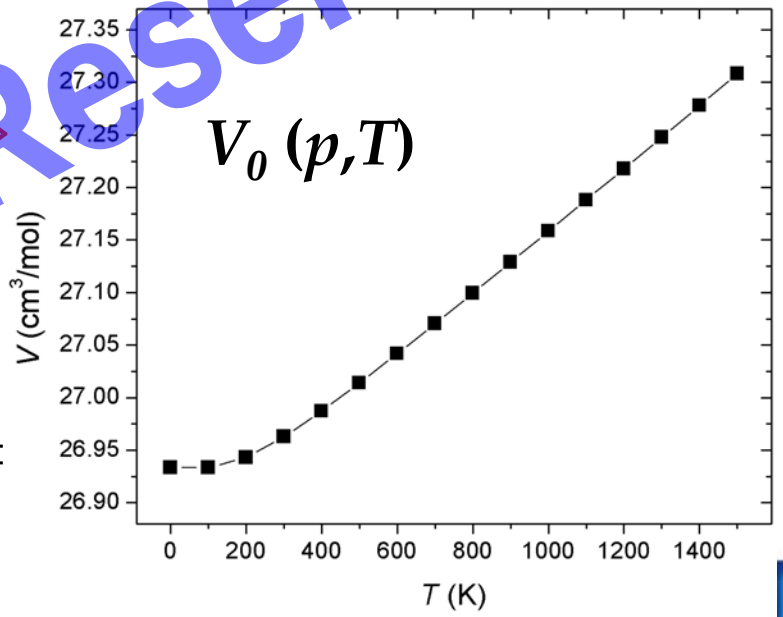
$\Rightarrow F\,(V)$ at different T



$\Rightarrow$



$\Rightarrow$



$\Downarrow B_T$ $\quad$ $\alpha \Leftarrow$

$$C_p = C_V + \alpha^2 B_T V T$$

Summary

- *ab initio* total energy calculations: access to $\Delta H\ (p)$ at 0 K

- lattice vibrations: T-dependent thermochemical properties,
  access to $G\ (p,T)$, S, C

- good estimation of *entropy* and *heat capacity* of compounds
  with known thermodynamical properties

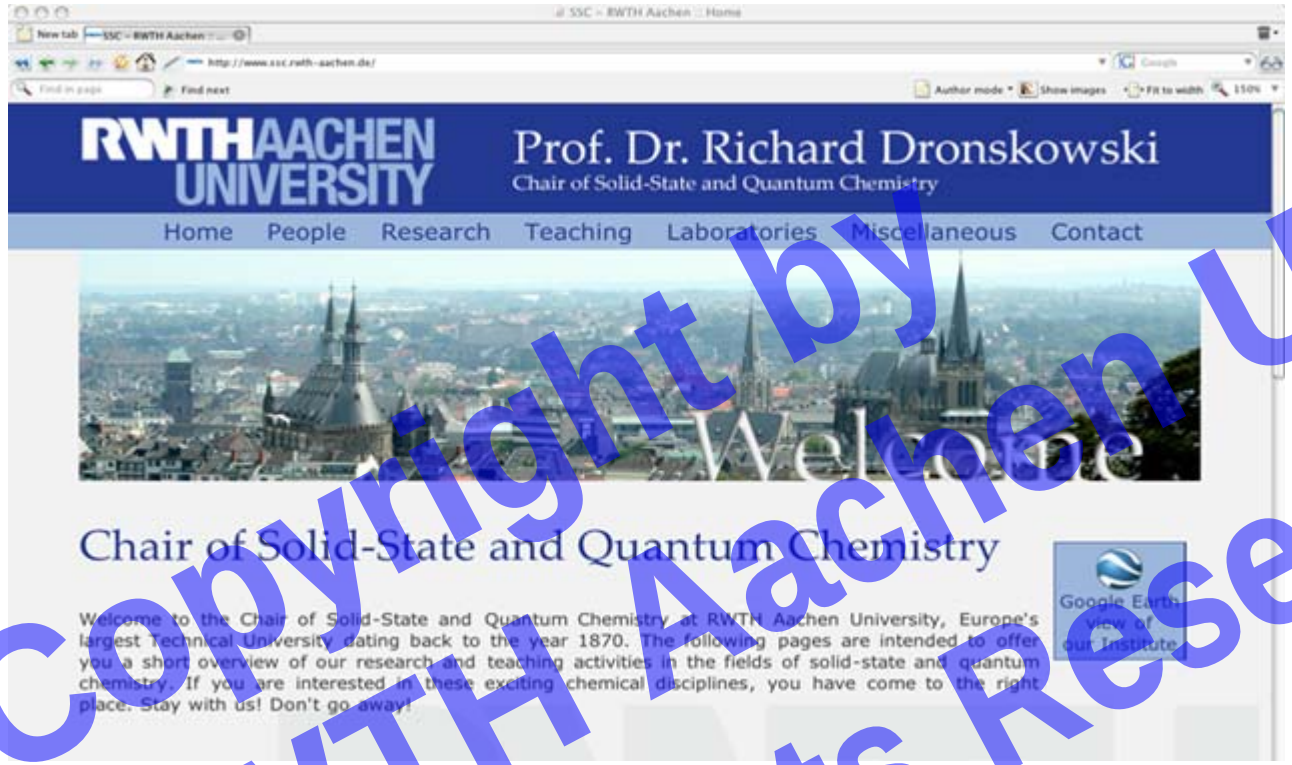
- next steps: properties of $YBa_2Cu_3O_{6+x}$

  handling of gaseous compounds (e.g. oxygen)?

  comparing of $\Delta G\ (p,T)$ with exp. data

  generate thermochemical data

For more information:



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