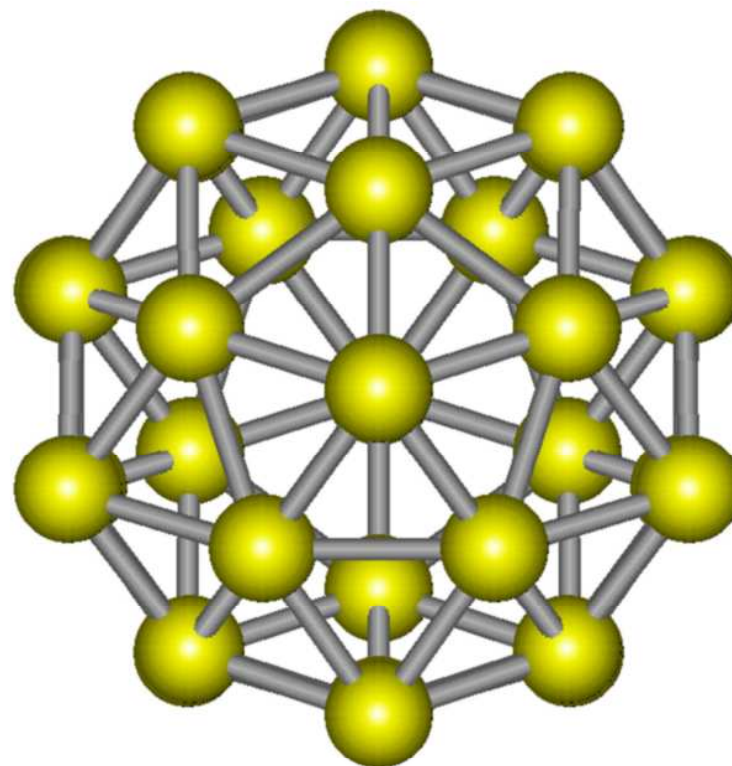


Au₃₂: a 24-carat golden fullerene

Mikael Johansson, Dage Sundholm, Juha Vaara

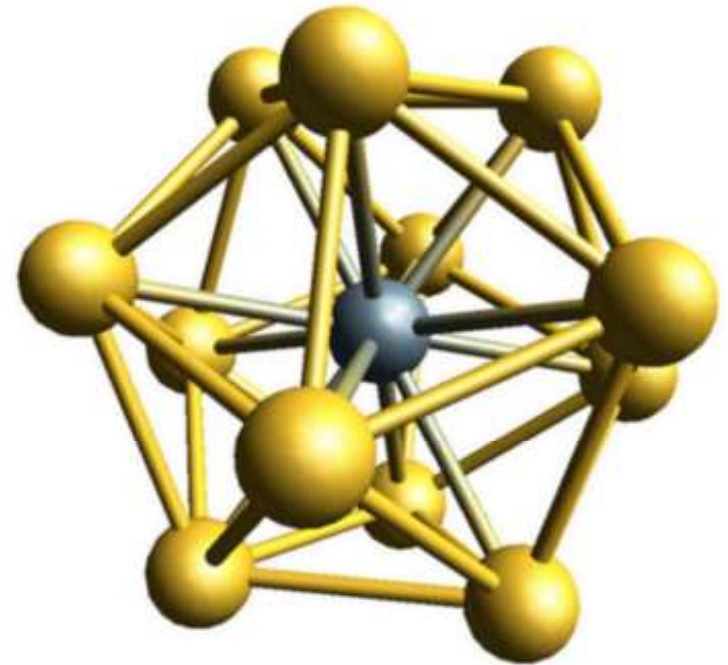
mikael.johansson@helsinki.fi

University of Helsinki,
Department of Chemistry



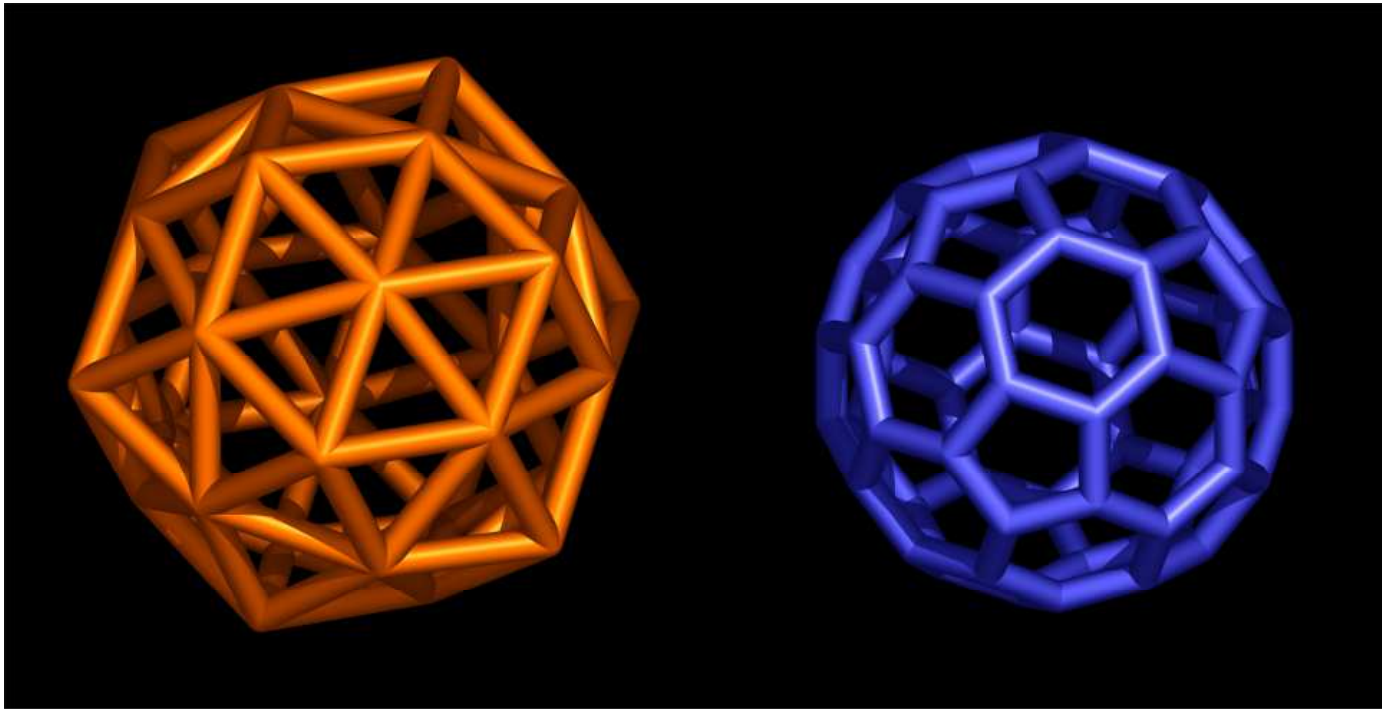
- Recently, the interest towards golden structures has soared
- Many new areas of application have been discovered for gold nanoparticles

- A good example is **WAu₁₂**, the existence of which was first predicted by Pyykkö and Runeberg, and later synthesised by Wang and co-workers:



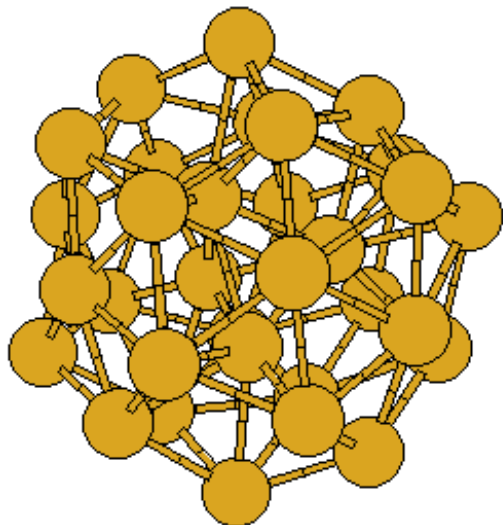
- WAu₁₂ was the first cluster to be dubbed a "**golden fullerene**"

- By using the "arch fullerene" C_{60} as a template Au_{32} was born
- Au_{32} is structurally very similar to C_{60} , having the vertices and planes interchanged, *i.e.*, Au at the centre of each 5 and 6-ring
- Both are spherical, of icosahedral I_h symmetry, hollow, and of comparable size:

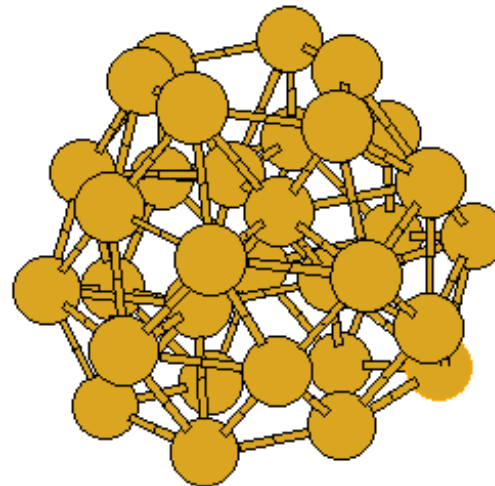


- A rigorous **density functional** study of the stability was performed
- Functionals used: **BP86**, pure and popular
PBE0, hybrid, theoretically purish
- Programs used: **TURBOMOLE 5.6**
a modified **deMon**
- The energetics of Au₃₂, the fullerene, was compared to a number of compact, lump-like structures
- In the litt., 2 lumps have been proposed as global minima:

*C*₂:



*D*₂:



- Energy difference in favour of I_h with the **VQZPP** basis (8s7p6d3f) / [7s4p4d3f] + Stuttgart 60 electron ECP:

	C_2	D_2
BP86	150	182 kJ/mol
PBE0	79	123

- **A quite large basis set is required in the study!**
- $\Delta\Delta E$ between TZVPP(2f) and VQZPP is still 10–20 kJ/mol.
- **DFT is, however, suboptimal** for evaluating the aurophilic attraction, and has been found to slightly overstabilise planar gold
- Therefore, it cannot be concluded that I_h is the *true* global minimum.

- Even so, I_h -Au₃₂ seems a chemically **robust** molecule (VQZPP basis):

	Au₃₂		C₆₀	
	BP86	PBE0	BP86	PBE0
$\Delta E_{\text{HOMO-LUMO}}$ (eV)	1.7	2.5	1.6	3.0
frontier orbital config.	$(t_{2u})^6(g_u)^8(g_g)^0$		$(g_g)^8(h_u)^{10}(t_{1u})^0$	
vibrational freqs. (cm ⁻¹)				
lowest	30	37	257	273
highest	145	147	1560	1674

Au₃₂ is stabilised by two effects:

1. Relativity

2. Spherical aromaticity

- Annulene aromaticity follows the well-known Hückel $4N+2$ rule
- In 2000, a new form of aromaticity for I_h -fullerenes was proposed:
- **Spherical aromaticity** follows the $2(N+1)^2$ rule

COMMUNICATIONS

Spherical Aromaticity in I_h Symmetrical Fullerenes: The $2(N+1)^2$ Rule**

Andreas Hirsch,* Zhongfang Chen, and Haijun Jiao

*Dedicated to Professor Fred Wudl
on the occasion of his 60th birthday*

- Assuming the 32 6s electrons of Au in Au_{32} to take part in the aromaticity, the SA rule is fulfilled with $N=3$.

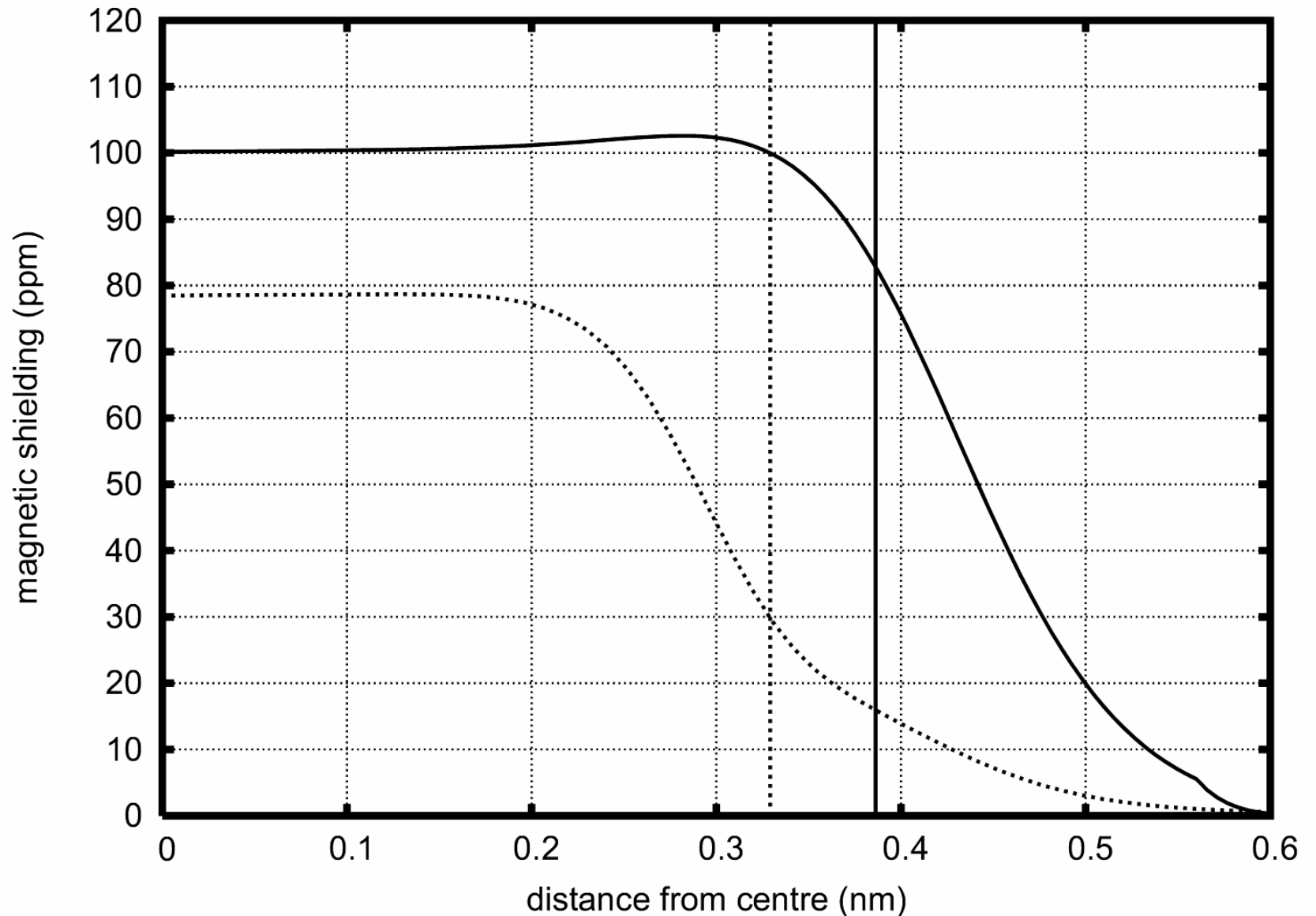
- SA in fullerenes leads to a **high diamagnetic shielding inside the cage**:

Table 2. Calculated and experimental endohedral ^3He chemical shifts and symmetries of $\text{He}@C_{60}$ species with different degrees of π -electron filling.

Species	Symmetry	$\delta(^3\text{He})_{\text{calcd}}^{[b]}$	$\delta(^3\text{He})_{\text{expt}}$
C_{60}^{10+} (closed $l = 4$ shell)	$I_h^{[a]}$	-81.4	–
C_{60}	$I_h^{[c]}$	-8.0	$-6.3^{[1]}$
C_{60}^{6-}	$I_h^{[a]}$	-55.6	$-48.7^{[8]}$

[a] Weak bond length alternation between the [6,6] and [5,6] bonds of 0.03 \AA for C_{60}^{10+} and 0.02 \AA for C_{60}^{6-} (B3LYP/6-31G*). [b] GIAO-SCF/3-21G//B3LYP/6-31G*.^[18] [c] Strong bond length alternation between [6,6] and [5,6] bonds of 0.06 \AA (B3LYP/6-31G*).

- Au_{32} and the C_{60}^{10+} cation behave like **miniature magnetic Faraday cages**:



- The spherical aromaticity seems **crucial** for the stability
- The **ions of Au₃₂** are much less stable compared to the lump like structures
- Preliminary PBE0 calculations (and experiments) indicate the **anion Au₃₂⁻** to actually prefer lumpiness already at DFT level!

Vertical EA (PBE0/VQZPP//TZVPP(2f))

I_h	C_2	Δ		Vertical IP			
247	343	96 kJ/mol		I_h	C_2	Δ	
				674	637	37 kJ/mol	

- For more, see: M.P. Johansson, D. Sundholm and J. Vaara, "Au₃₂: A 24-Carat Golden Fullerene", *Angew. Chem. Int. Ed.* **43** (2004) 2678–2681.

Alphabetical Thanks

Pekka Manninen, Michael Patzschke, Pekka Pyykkö

CSC – Scientific Computing Ltd. provided ample CPU-time

The Magnus Ehrnrooth Foundation and Waldemar von Frenckells
Stiftelse is acknowledged for financial support