

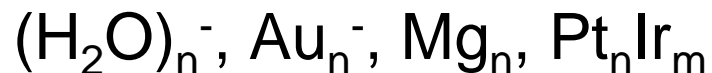
# Developing and Applying TURBOMOLE

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- I. Quantumchemical Methods: HF, MP2, DFT
- II. The RI Method - Efficient Calculation of J, K and MP2

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- III. Applications: Calculations of Clusters



# The Hartree-Fock Method

$$\text{Hamiltonian: } H = \underbrace{-\sum_A^N \sum_{\alpha}^n \frac{Z_{\alpha}}{|\mathbf{R}_A - \mathbf{r}_{\alpha}|} - \frac{1}{2} \sum_{\alpha}^n \nabla_{\alpha}^2}_{h_{\alpha}} + \sum_{\alpha}^n \sum_{\beta > \alpha}^n \frac{1}{|\mathbf{r}_{\beta} - \mathbf{r}_{\alpha}|}$$

**Variation Principle:**  $E = \langle \tilde{\Psi} | H | \tilde{\Psi} \rangle = \min$   $\tilde{\Psi} = \begin{vmatrix} \varphi_1(1) & \varphi_1(2) & \dots \\ \varphi_2(1) & \varphi_2(2) & \dots \\ \vdots & \vdots & \varphi_n(n) \end{vmatrix}$

→ HF equations:  $\underbrace{\left[ h(\alpha) + \sum_i (J_i(\alpha) - K_i(\alpha)) \right]}_{F(\alpha)} \varphi_i(\alpha) = \varepsilon_i(\alpha) \varphi_i(\alpha)$

**LCAO:**  $|p\rangle = \sum_{\mu} c_{p\mu} |\mu\rangle, |\mu\rangle = \dots e^{-\beta r^2} \rightarrow \mathbf{F}\mathbf{c} = \varepsilon\mathbf{S}\mathbf{c}$

→  $\Psi_{\text{HF}}$  (i.e.  $\mathbf{c}$ ) and  $E_{\text{HF}} = \langle \Psi_{\text{HF}} | H | \Psi_{\text{HF}} \rangle = \underbrace{D_{\nu\mu} h_{\nu\mu}}_{E_1} + \underbrace{(v\mu | \kappa\lambda) D_{\nu\mu} D_{\kappa\lambda}}_{E_J} - \frac{1}{2} \underbrace{(v\kappa | \mu\lambda) D_{\nu\mu} D_{\kappa\lambda}}_{E_K}$

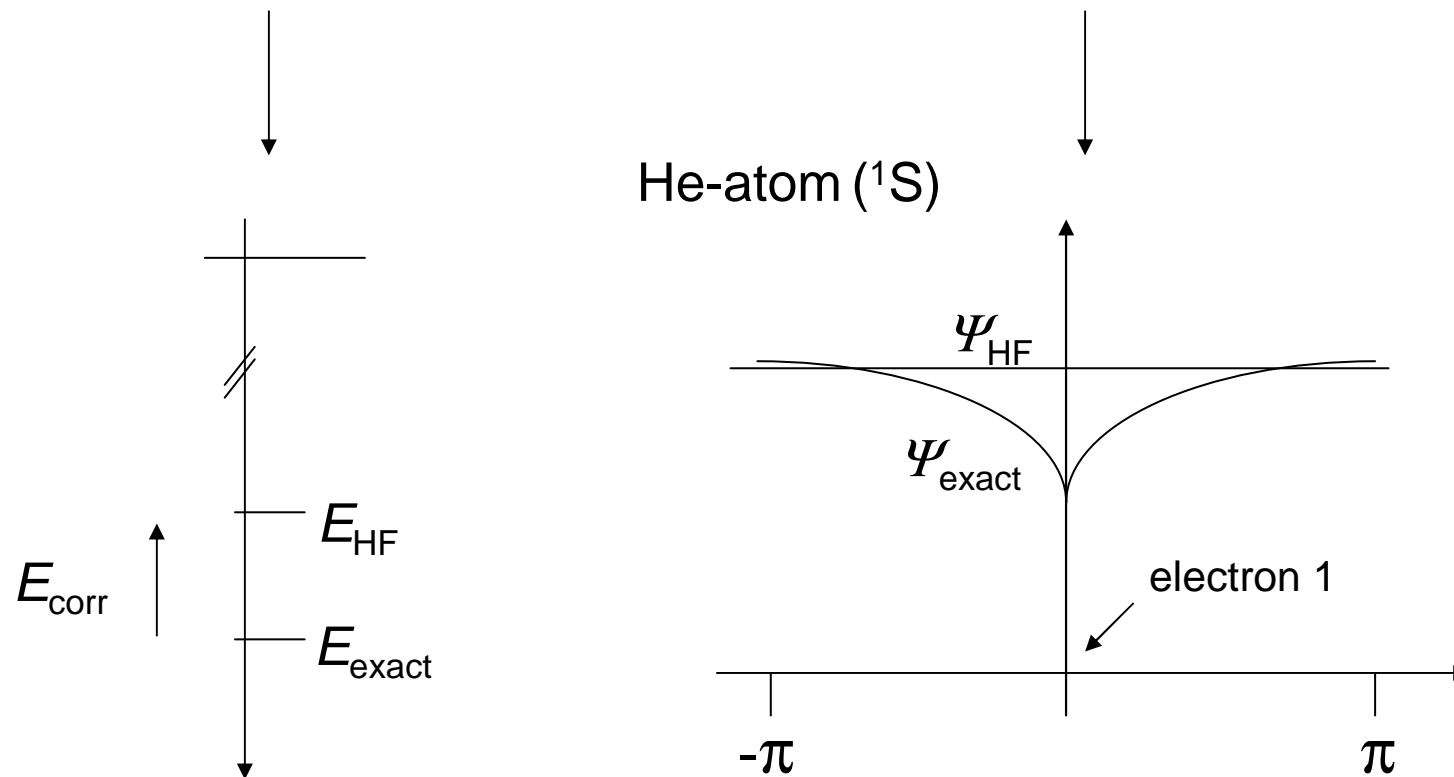
$$(v\mu | \kappa\lambda) = \int d\mathbf{r}_1 d\mathbf{r}_2 v(\mathbf{r}_1) \mu(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \kappa(\mathbf{r}_2) \lambda(\mathbf{r}_2), \quad D_{\nu\mu} = \sum_i n_i c_{\nu i} c_{\mu i}$$

## Applicability and Accuracy of HF

- main group compounds:  
equilibrium distances: few pm
- starting point for post-HF methods (at least if HF is not too bad)
- delocalised systems (e.g. (metal) clusters)
- appropriate basis sets: SV(P), check with TZVP

# Deficiencies of HF: Dynamic Electron Correlation

HF: variation principle  $\rightarrow$  mean field description



## Improvement I: Perturbation Theory (MP2)

$$E_{corr} = E_{exact} - E_{HF} \quad \rightarrow \quad \hat{V} = \hat{H}_{exact} - \hat{H}_{HF} = \sum_{\alpha < \beta} \frac{1}{r_{\alpha\beta}} - \sum_{\alpha} \{ \hat{J}(\alpha) - K(\alpha) \}$$

insert :  $\hat{H} = \hat{H}_{HF} - \lambda \hat{V}$  ,  $\Psi = \Psi_{HF} + \lambda \Psi_1 + \lambda^2 \Psi_2 + \dots$  in  $\hat{H} \Psi = E \Psi$

to get :  $E_0 + E_1 = E_{HF}$  ,  $E_2 = \langle \Psi_{HF} | V - E_1 | \Psi_1 \rangle$

Ansatz :  $\Psi_1 = \sum_{ia} t_i^a \Psi_{HF\ i}^a + t_{ij}^{ab} \Psi_{HF\ ij}^{ab} + \dots$

$$\rightarrow E_{MP2} = \sum_{iajb} t_{ij}^{ab} (ia | jb) \quad , \quad t_{ij}^{ab} = \sum_{iajb} \frac{2(ia | jb) - (ib | ja)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

+ excellent if HF is good; **fails, if HF fails**

+ most economic way to account for dispersive interactions

- appropriate bases: TZVPP, check by QZVPP, (SVP only qualitative)

- d<sup>10</sup> metals: QZVP, check by QZVPP

## Improvement II: Density Functional Theory

simple view:

$$\text{HF: } E = E_1 + E_J + E_x$$

$$\text{DFT: } E = E_1 + E_J + E_{\text{XC}}$$

$$E_{\text{XC}} = \int f(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \dots) d^3r = - \underbrace{k \int \rho(\mathbf{r})^{4/3} d^3r}_{\text{free electron gas}} + \dots$$

- $E_{\text{XC}}[\rho]$  exists, **no prescription to get exact one**
  - good for (metal) clusters: Becke-Perdew 86
- useful: almost universal, quite accurate, efficient
- **does not include dispersive interactions**
- appropriate bases: main groups: SVP, check with TZVP
  - transition metals: (SVP), TZVPP, check by QZVP

## Costs for HF, DFT and MP2

DFT:  $E = E_1 + E_J + E_{XC}$   $E_J = D_{\nu\mu} (\nu\mu | \kappa\lambda) D_{\kappa\lambda}$   $\rightarrow N^4$  Integrals  
 $N^4$  multiplications

HF:  $E = E_1 + E_J - E_K$   $E_K = \frac{1}{2} D_{\nu\mu} (\nu\kappa | \mu\lambda) D_{\kappa\lambda}$   $\rightarrow N^4$  Integrals  
 $N^4$  multiplications

MP2:  $E_{MP2} = \sum_{i,a,j,b} \frac{(ia | jb)[2(ia | jb) - (ib | ja)]}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$   $\rightarrow N^4$  Integrals (on disc)  
 $N^5$  multiplications  
 $(ia | jb) = \sum_{\nu,\mu,\kappa,\lambda} (\nu\mu | \kappa\lambda) C_{\nu i} C_{\mu a} C_{\kappa j} C_{\lambda b}$

Integrals:  $(\nu\mu | \kappa\lambda) = \int d\mathbf{r}_1 d\mathbf{r}_2 \nu(\mathbf{r}_1) \mu(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \kappa(\mathbf{r}_2) \lambda(\mathbf{r}_2)$

## II The RI Method

Goal: Avoid  $N^4$  integral evaluations  
and  $N^4$  integral storage (MP2)  
and  $N^5$  integral transformations (MP2).

J. L. Whitten; J. Chem. Phys. **58**, 4496 (1973)

B. I. Dunlap, J. W. D. Conolly, J. R. Sabin; J. Chem. Phys. **71**, 3396 (1979)

O. Vahtras, J. Almlöf, M.W. Feyereisen; Chem. Phys. Lett. **213**, 514 (1993)



## RI Approximation

central problem:  $(\nu\mu | \kappa\lambda) = \int d\mathbf{r}_1 d\mathbf{r}_2 \nu(\mathbf{r}_1)\mu(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \kappa(\mathbf{r}_2)\lambda(\mathbf{r}_2)$

approximate:  $\rho_{\nu\mu}(\mathbf{r}) = \nu(\mathbf{r})\mu(\mathbf{r}) \approx \tilde{\rho}_{\nu\mu}(\mathbf{r}) = \sum_P c_{\nu\mu}^P P(\mathbf{r})$

minimize:  $\int \{ \tilde{\rho}_{\nu\mu}(\mathbf{r}_1) - \rho_{\nu\mu}(\mathbf{r}_1) \} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \{ \tilde{\rho}_{\nu\mu}(\mathbf{r}_2) - \rho_{\nu\mu}(\mathbf{r}_2) \} d\mathbf{r}_1 d\mathbf{r}_2 = \min$

to get:  $c_{\nu\mu}^P = \sum_Q (\nu\mu | Q)(Q | P)^{-1}$

and finally:  $(\nu\mu | \kappa\lambda) \approx (\nu\mu | \kappa\lambda)_{RI} = \sum_P c_{\nu\mu}^P (P | \kappa\lambda) = \sum_{QP} (\nu\mu | Q) \underbrace{(Q | P)^{-1} (P | \kappa\lambda)}_{\text{"Resolution of the Identity"}}$

## Taking Advantage of RI: Coulomb Matrix

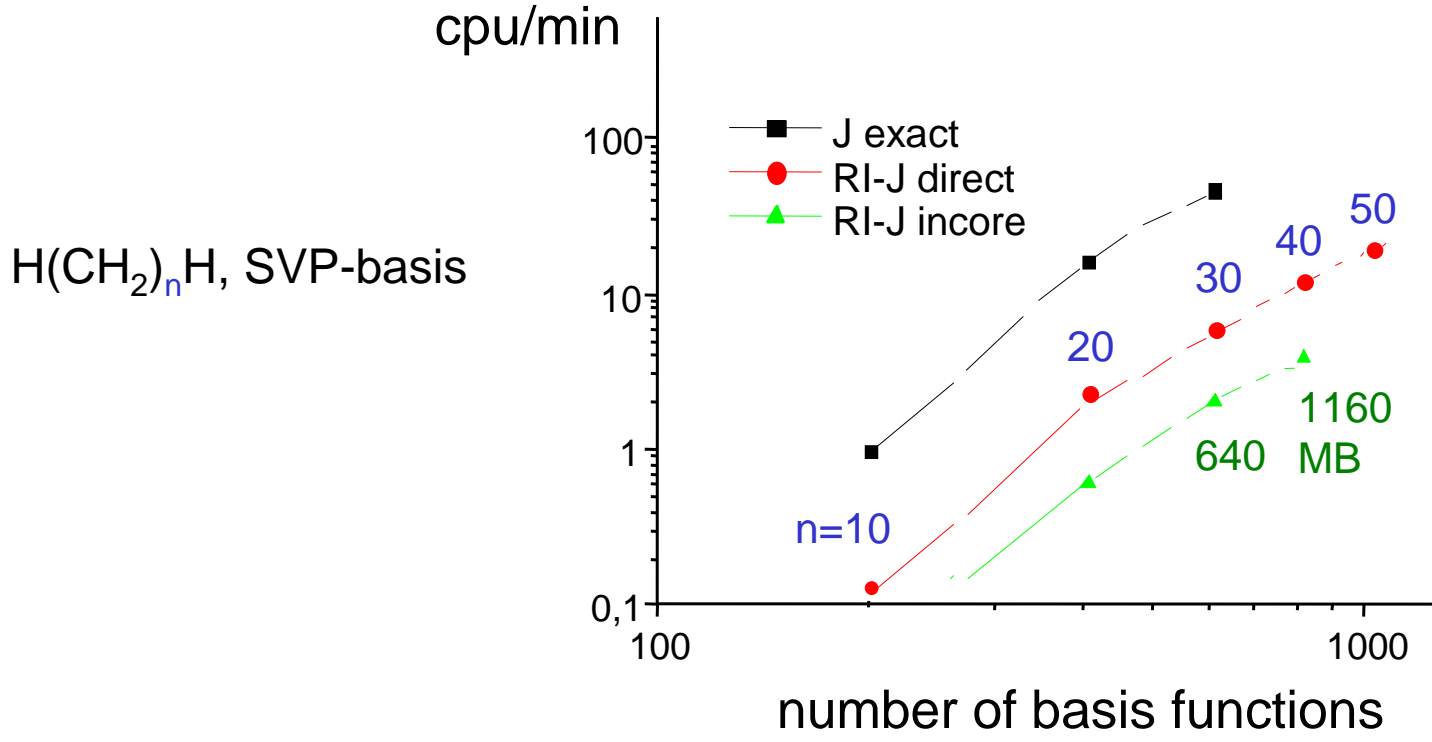
$$\begin{aligned}
 J_{\nu\mu} &= \sum_{\kappa\lambda} (\nu\mu | \kappa\lambda) D_{\kappa\lambda} \\
 J_{\nu\mu}^{RI} &= \sum_{\kappa\lambda} \sum_{P,Q} (\nu\mu | Q)(Q | P)^{-1} \underbrace{(P | \kappa\lambda)}_{N^2 N_x} D_{\kappa\lambda} \\
 &\quad \underbrace{\hspace{10em}}_{N^2 N_x} \\
 &\quad \underbrace{\hspace{15em}}_{N_x^2} \\
 &\quad \underbrace{\hspace{20em}}_{N^2 N_x}
 \end{aligned}$$

Integrals and multiplications:  $N^4 \rightarrow N^3$

Note:  $E(J,RI) = J_{\nu\mu}^{RI} D_{\nu\mu} \leq E(J,ex)$

K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs; Chem. Phys. Lett. **240**, 283 (1995).

# RI-J: Efficiency



## Taking Advantage of RI: Exchange Matrix

$$K_{\nu\mu} = \sum_{\kappa\lambda} (v\kappa | \mu\lambda) D_{\kappa\lambda} \quad , \quad D_{\kappa\lambda} = \sum_i c_{\kappa i} c_{\lambda i}$$

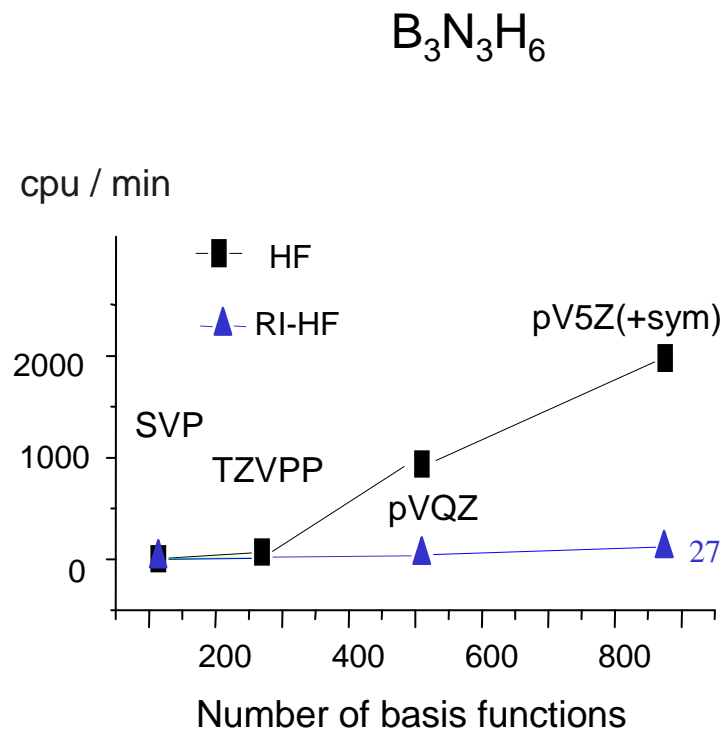
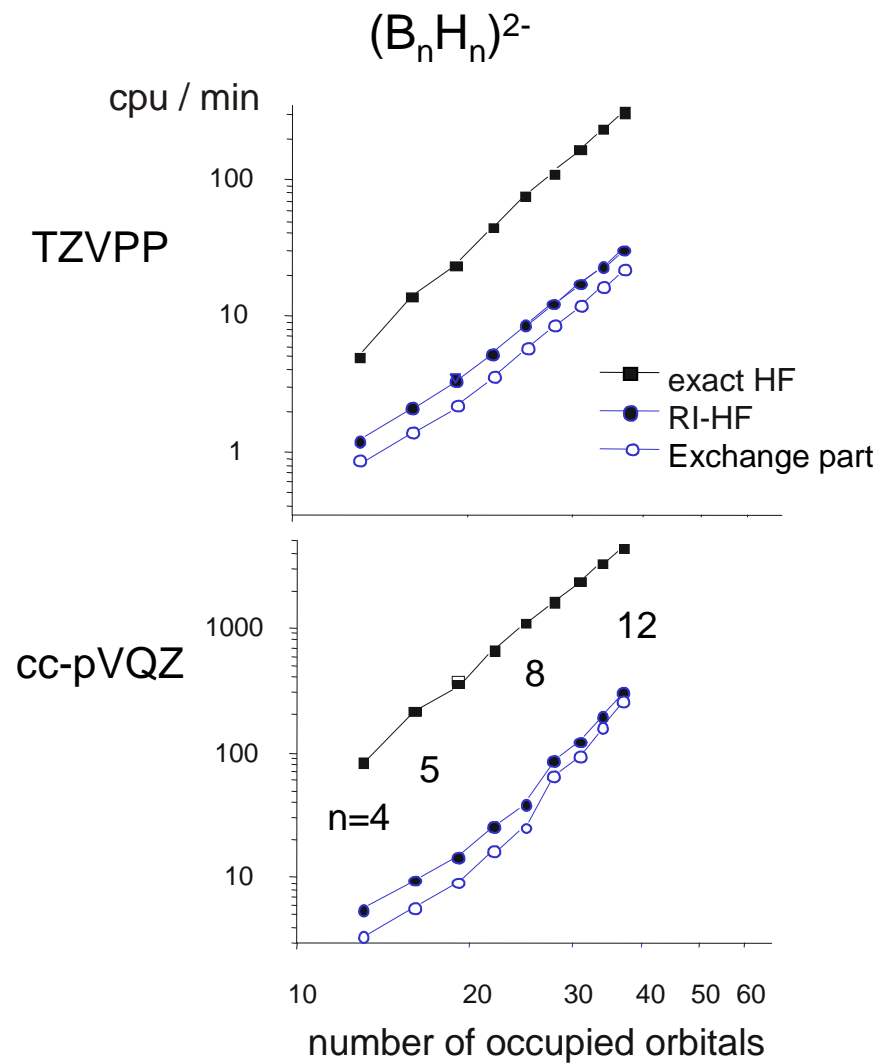
$$K_{\nu\mu}^{RI} = \sum_{\kappa\lambda} \sum_{P,Q,R,i} \underbrace{c_{\kappa i} (v\kappa | Q)}_{B_{i\nu}^P} (Q | P)^{-1/2} (P | R)^{-1/2} \underbrace{(R | \mu\lambda) c_{\lambda i}}_{B_{i\mu}^P}$$

Integrals:  $N^4 \rightarrow N^3$ , multiplications:  $N_{BF}^4 \rightarrow N_{BF}^2 N_X n_{occ}$

→ CPU times: conventional / RI  $\sim N_{BF}/n_{occ}$

Note:  $E(K,RI) = K_{\nu\mu}^{RI} D_{\nu\mu} \leq E(K,ex)$

# RI-K: Efficiency



## Taking Advantage of RI: MP2

$$E_{MP2} = \sum_{iajb} \frac{(ia | jb)[2(ia | jb) - (ib | ja)]}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

conventional:  $(ia | jb) = \sum_{\nu\mu\kappa\lambda} (\nu\mu | \kappa\lambda) c_{i\nu} c_{a\mu} c_{\kappa j} c_{\lambda b}$

$$RI : (ia | jb)_{RI} = \sum_{\substack{PQR \\ \nu\mu\kappa\lambda}} c_{i\nu} c_{a\mu} \underbrace{(\nu\mu | Q)(Q | P)^{-1/2}}_{B_{ia}^P} \underbrace{(P | R)^{-1/2}(R | \kappa\lambda)}_{B_{jb}^P} c_{\kappa j} c_{\lambda b}$$

Disc space:  $N^4 \rightarrow N^3$

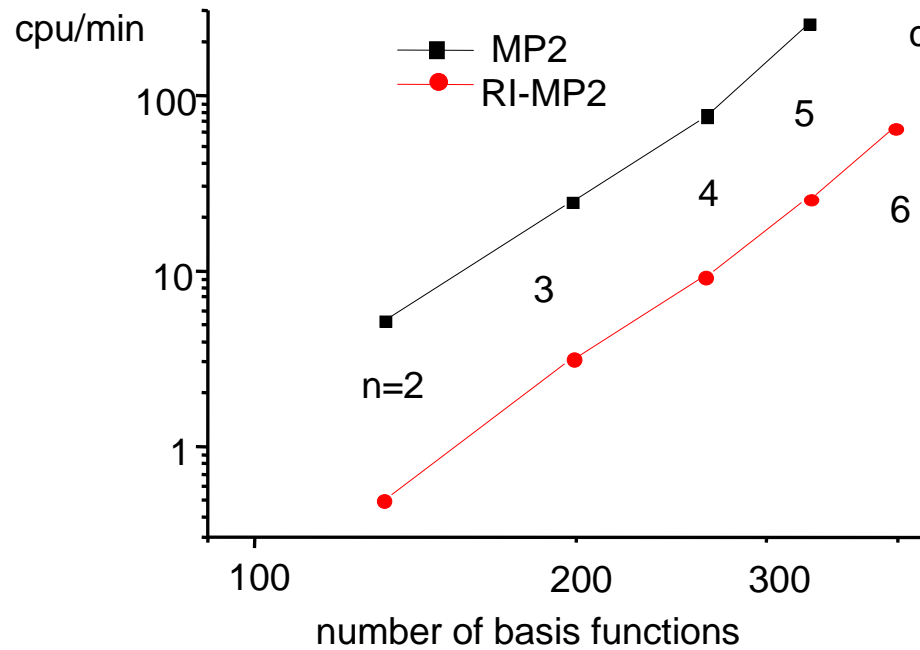
CPU times: conventional / RI  $\sim N_{BF}^4 n_{occ} / N_x n_{virt}^2 n_{occ}^2 \approx N_{BF} / n_{occ}$

Note:  $E(RI-MP2)$  is not variational.

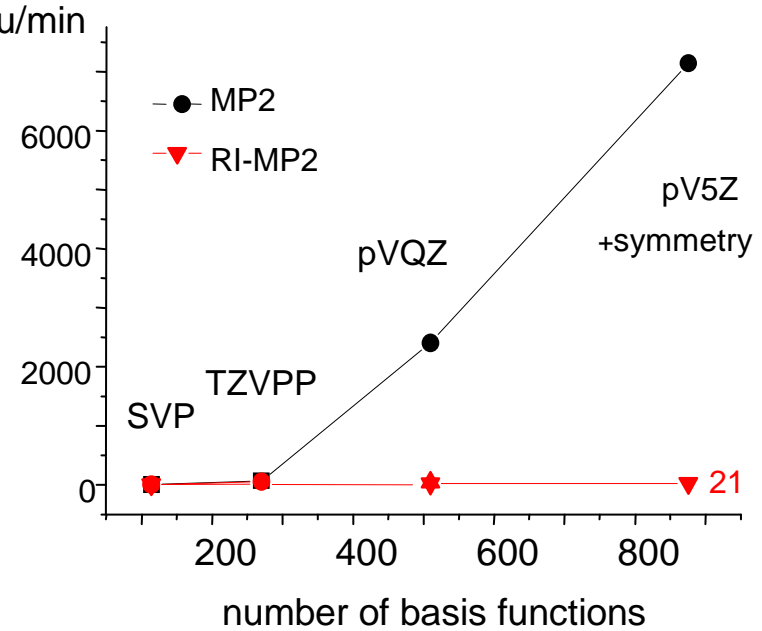
F. Weigend and M. Häser; Theor. Chim. Acc.; **97** 331 (1997).

# RI-MP2: Efficiency

$(\text{Cu}_2\text{S})_n$ , SVP basis



$\text{B}_3\text{N}_3\text{H}_6$



# RI-MP2 Gradients

1. Bilde  $(P|Q)^{-1/2}$
2. LOOP  $I$  ( $I$  ist eine Untermenge aktiver besetzter Orbitale)
  - berechne  $(\nu\mu|P)$
  - bilde  $B_{ip}^Q \leftarrow c_{\nu i} c_{\mu p} (\nu\mu | P)(P | Q)^{-1/2}$  speichere  $B_{ip}^P$
 ENDE LOOP  $I$
3. LOOP  $I$  ( $I$  ist eine Untermenge aktiver besetzter Orbitale)
  - LOOP  $J$  ( $J$  ist eine Untermenge aktiver besetzter Orbitale)
    - bilde  $(ia|jb) \leftarrow B_{ia}^Q B_{jb}^Q \quad (i \in I, j \in J)$
    - $t_{ij}^{ab} \leftarrow \{2(ia|jb) - (ib|ja)\} / (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)$
    - $Y_{ia}^P \leftarrow t_{ij}^{ab} B_{jb}^P$
    - $P_{bc} \leftarrow t_{ij}^{ab} (ia|jc) / (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_c)$
    - für " $\epsilon_i \approx \epsilon_j$ " :  $P_{ij} \leftarrow t_{ij}^{ab} (ia|kb) / (\epsilon_i + \epsilon_k - \epsilon_a - \epsilon_b)$
 ENDE LOOP  $J$ 
    - $L_{ap}'' \leftarrow Y_{ia}^P B_{ip}^P$
    - $\Gamma_{ia}^P \leftarrow Y_{ia}^Q (Q | P)^{-1/2}$
    - $\tilde{\gamma}_{PQ} \leftarrow \Gamma_{ia}^P B_{ia}^Q$
    - $\Gamma_{iv}^P \leftarrow \Gamma_{ia}^P c_{\nu a}$
    - speichere  $\Gamma_{iv}^P$  und  $\tilde{\gamma}_{PQ}$  auf Festplatte
 ENDE LOOP  $I$

4.  $\gamma_{PQ} \leftarrow \tilde{\gamma}_{PR} (R | Q)^{-1/2}$
- $E_{MP2}^{\xi} \leftarrow \gamma_{PQ} (P | Q)^{\xi}$
5. Loop  $\Xi$  (Untermenge von Basisfunktionen)
  - $E_{MP2}^{\xi} \leftarrow \Gamma_{iv}^P c_{\mu i} (\nu\mu | P)^{\xi} \quad (\nu \in \Xi)$
  - $L_{ip} \leftarrow (\nu\mu | P) \Gamma_{iv}^P c_{\mu p}$
 ENDE LOOP  $\Xi$
6. Berechne die übrigen Elemente von  $P_{ij}$  nach  $P_{ij} = (L_{ji} - L_{ij}) / 2(\epsilon_i - \epsilon_j)$ 
  - Setze zusammen:  $\tilde{\pi}_{pq} \leftarrow P_{ab} \oplus P_{ii} \oplus L_{if} / (\epsilon_i - \epsilon_f)$
  - und berechne  $A_{apqr} \tilde{\pi}_{qr}$  (AO-Basis)
  - Löse  $(\epsilon_a - \epsilon_l) Z_{al} + A_{albm} Z_{bm} = L_{al}'' - L_{la} - A_{lapq} \tilde{\pi}_{pq}$
7.  $\pi_{pq} \leftarrow \tilde{\pi}_{pq} \oplus Z_{al}$ 
  - $W_{pq} \leftarrow \frac{\epsilon_p + \epsilon_q}{2} \pi_{pq} \oplus \frac{1}{2} A_{lqrs} \pi_{rs} \oplus \frac{1}{2} L_{iq} \oplus \frac{1}{2} L_{aq}''$
8.  $E_{MP2}^{\xi} \leftarrow 2(\pi_{pq} + \delta_{ip} \delta_{iq}) h_{pq}^{(\xi)} - 2(W_{pq} + \delta_{ip} \delta_{iq} \epsilon_i) \tilde{S}_{pq}^{\xi}$
- $E_{MP2}^{\xi} \leftarrow 2(\pi_{pq} + \delta_{ip} \delta_{iq}) (\tilde{F}_{pq}^{(\xi)} - \tilde{S}_{pq}^{\xi})$

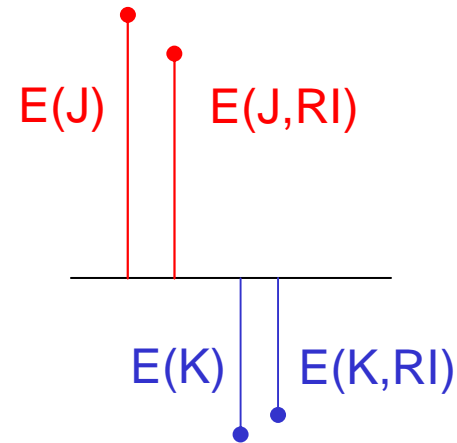


# Auxiliary Basis Sets

- Goal: RI errors 1 order of magnitude smaller than energy changes due to basis set changes
- use atom centred Gaussians, but different sets for J, K, and MP2
- optimization: **minimize at the atoms**

J, K:  $\Delta J = |E(J_{RI}) - E(J_{ex})|$ , same for K

MP2: 
$$\Delta I = \sum_{iajb} \frac{(\langle ij || ab \rangle - \langle ij || ab \rangle_{RI})^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$



We require: J,K:  $\Delta J, \Delta K < 20 \mu\text{H}$

MP2:  $|\Delta I|/|E_{MP2}| < 10^{-6}$ , and  $|E_{MP2} - E_{RIMP2}| < 20 \mu\text{H}$

size: J:  $N_x < 3N_{BF}$ , K, MP2:  $N_x < 4N_{BF}$

... and test at molecules...

# Some Details

J: 3-parameter even tempered set ( $\rightarrow$ jbasis)

K: Gradients for K(RI) with respect to exponents, relaxation ( $\rightarrow$ jkbas)

MP2: Gradients for  $\Delta I$ , relaxation ( $\rightarrow$ cbas)

Example: auxiliary basis sets for B-F (TZVPP):

	s	p	d	f	g
basis	62111	411	11	1	
jbasis (RI-DFT)	3111111	111	111	1	
jkbas (RI-HF)	1111111111	1111111	11111	11	1
cbas (RI-MP2)	11111111	111111	2111	111	1

# Accuracy: Tests at Small Molecules

RI-DFT:  $E(\text{electron-electron}) = -E(\text{XC}) + E(\text{J})$

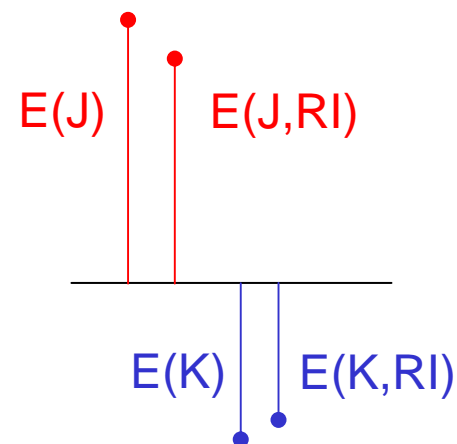
$$\Delta E(\text{J}) = E(\text{J}) - E(\text{J}, \text{RI})$$

RI-MP2:  $\Delta E = |E(\text{MP2}) - E(\text{MP2}, \text{RI})|$

RI-HF:  $E(\text{electron-electron}) = -E(\text{K}) + E(\text{J})$

$$\Delta E(\text{K}) = E(\text{K}, \text{RI}) - E(\text{K})$$

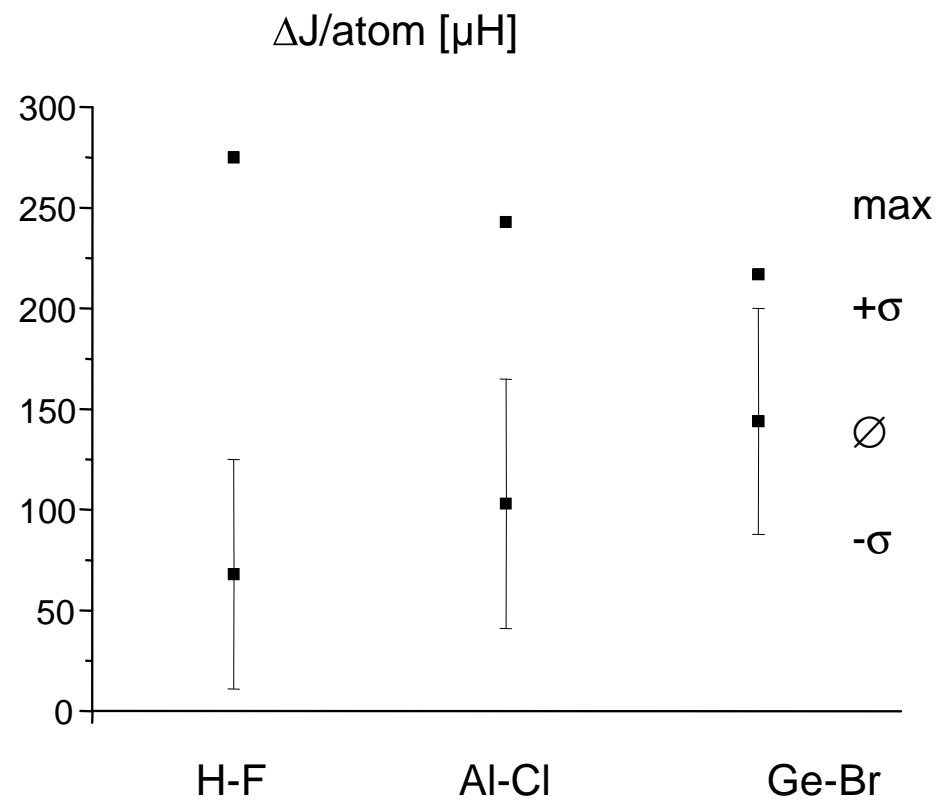
$\Delta E(\text{J})$ : as above, but with auxbasis also used for K



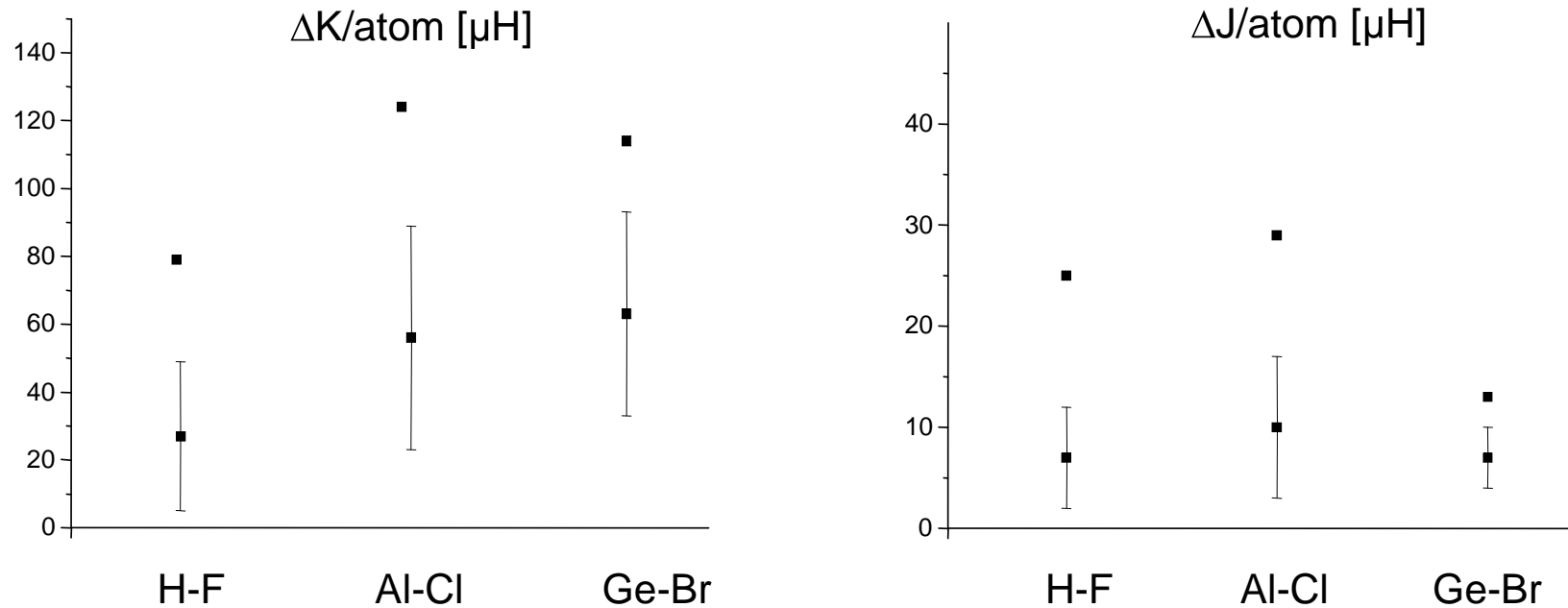
Ca. 100 molecules (H-Br):

Al<sub>2</sub>O<sub>3</sub> Al<sub>2</sub>S<sub>3</sub> AlCl<sub>3</sub> AlF<sub>3</sub> AlH<sub>3</sub> As<sub>4</sub> AsCl<sub>3</sub> AsCl<sub>6</sub><sup>-</sup> AsH<sub>3</sub> B<sub>2</sub>H<sub>6</sub> B<sub>3</sub>N<sub>3</sub>H<sub>6</sub> B<sub>4</sub>H<sub>4</sub> BF<sub>3</sub> BH<sub>3</sub>  
 BH<sub>3</sub>CO BH<sub>3</sub>NH<sub>3</sub> Br<sub>2</sub> BrCl BrO<sup>-</sup> BrO<sub>2</sub><sup>-</sup> BrO<sub>3</sub><sup>-</sup> BrO<sub>4</sub><sup>-</sup> C<sub>2</sub>H<sub>2</sub> C<sub>2</sub>H<sub>3</sub>N C<sub>2</sub>H<sub>4</sub> C<sub>2</sub>H<sub>6</sub> C<sub>4</sub>H<sub>4</sub> C<sub>6</sub>H<sub>6</sub>  
 CF<sub>4</sub> CH<sub>2</sub>O CH<sub>2</sub>O<sub>2</sub>CH<sub>3</sub>N CH<sub>3</sub>OH CH<sub>4</sub> CO CO<sub>2</sub> CS<sub>2</sub> Cl<sub>2</sub> ClF ClF<sub>3</sub> F<sub>2</sub> GaCl GaCl<sub>3</sub> GaFGaH<sub>3</sub>  
 GeCl<sub>4</sub> GeF<sub>4</sub> GeH<sub>4</sub> GeO GeO<sub>2</sub> H<sub>2</sub> H<sub>2</sub>CO<sub>3</sub> H<sub>2</sub>O H<sub>2</sub>O<sub>2</sub> H<sub>2</sub>SO<sub>4</sub> H<sub>3</sub>PO<sub>4</sub> HCN HCP HCl HF HNC  
 HNO HNO<sub>2</sub> HNO<sub>3</sub> HSH HSSH N<sub>2</sub> N<sub>2</sub>H<sub>2</sub> N<sub>2</sub>H<sub>4</sub> N<sub>4</sub> NF<sub>3</sub> NH<sub>3</sub> NH<sub>4</sub>F OF<sub>2</sub> P<sub>2</sub> PF<sub>3</sub> PF<sub>5</sub> PH<sub>3</sub> S<sub>2</sub>  
 S<sub>5</sub> SF<sub>2</sub> SF<sub>4</sub> SF<sub>6</sub> Se<sub>8</sub> SeH<sub>2</sub> SeO<sub>2</sub> SiCl<sub>4</sub> SiF<sub>4</sub> SiH<sub>4</sub> SiO<sub>2</sub> SiS<sub>2</sub>

## Errors of RI-J in DFT (TZVPP basis)

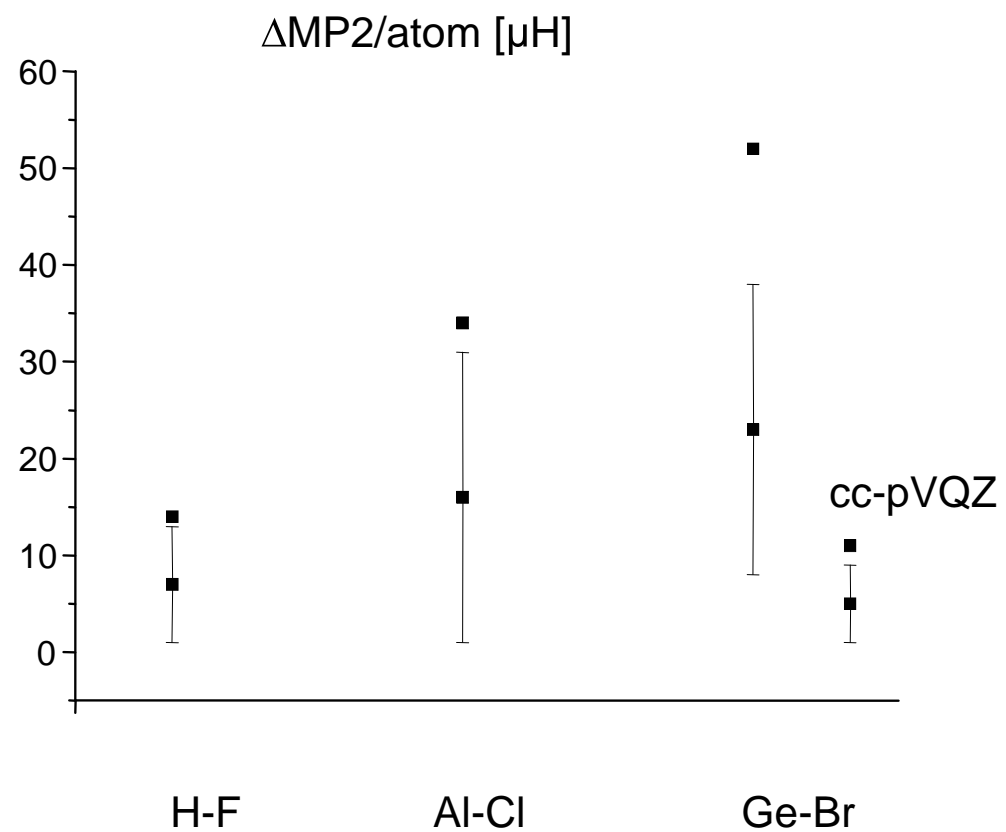


## Errors of RI-J and RI-K in HF (TZVPP basis)

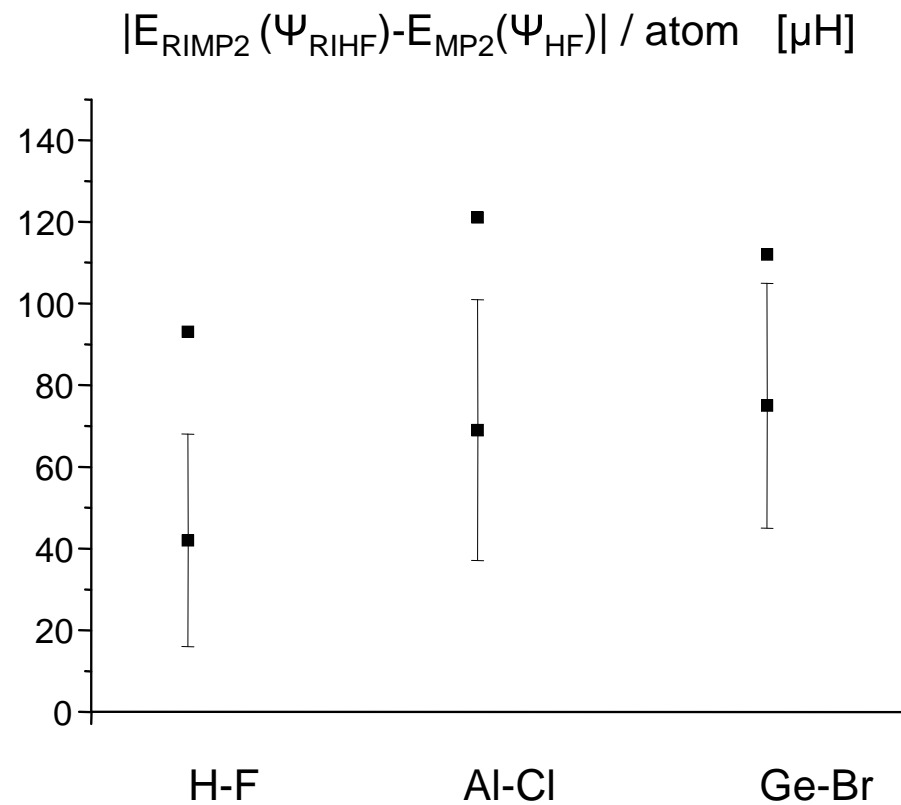


J and K both calculated with K-optimized auxiliary basis set

## Errors of RI-MP2 (TZVPP basis)



# RI-HF + RI-MP2 versus HF + MP2 (TZVPP basis)



# Errors in Properties for „Worst“ Cases

structure parameters:

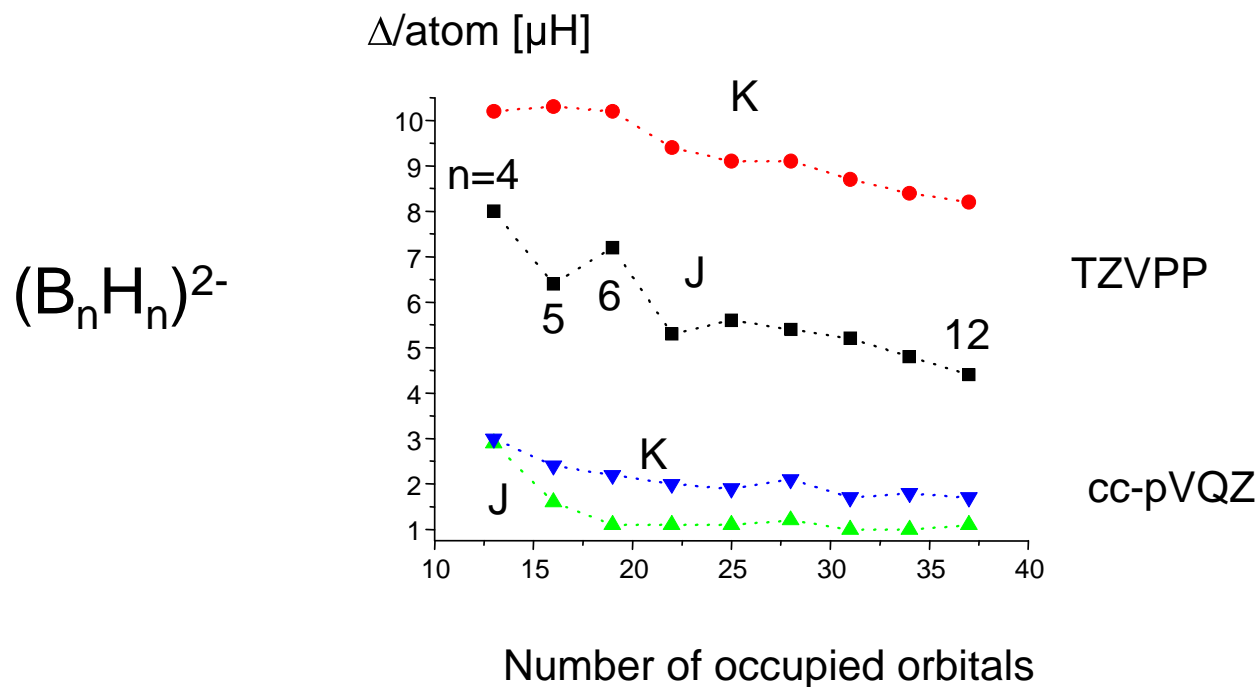
distances (bonds)            ca. 0.1 pm

angles:                        ca. 0.1 °

dipole moments:                ca. 0.01 Debye



# Size Dependency of Accuracy



- errors per atom slightly decrease with molecular size  
→ (partial) cancellation when calculating bond energies
- similar for MP2

# Summary: RI with Optimized Auxiliary Basis Sets

- **Efficiency** and **accuracy** of RI do **not** depend on a molecule's
  - geometric structure
  - electronic structure
  - composition
  - size (nearly)
- **Efficiency** (conventional/RI): RIDFT:  $\approx 10$ 
  - RI-HF(RIMP2):  $\sim N_{\text{BF}}/n_{\text{occ}}$ , TZVPP  $\approx 5(10)$
  - RIMP2: disc space  $N^4 \rightarrow N^3$
- **Accuracy:**
  - energy errors at least 1 o. M. smaller than energy changes due to changes of basis set
  - structure parameters nearly unaffected

# III Applications

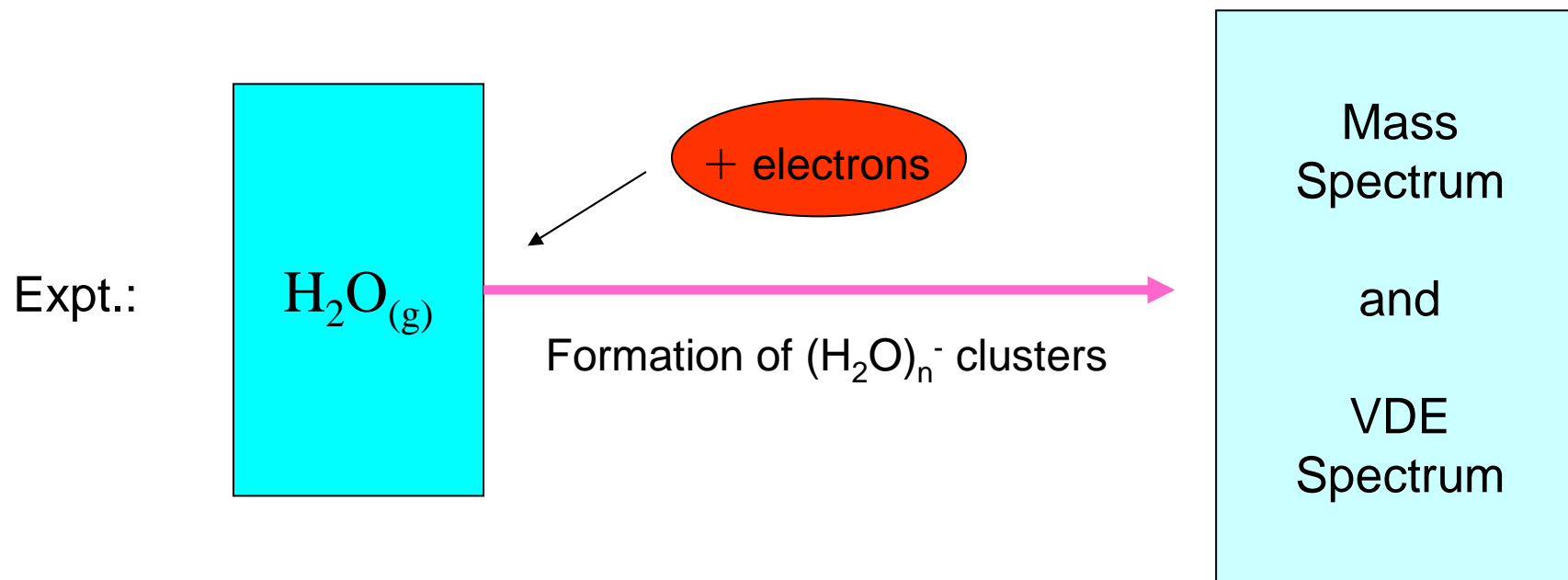
-Anions of Water Clusters

-Anions of Au Clusters

-Mg Clusters

-Mixed metal Clusters (Pt-Ir)

# Anions of Water Clusters



Theory:  $(\text{H}_2\text{O})_6^-$ :

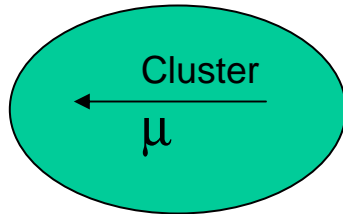
structure ?

bonding of the excess electron:

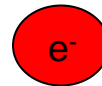
cage-like („solvated electron“) or dipole bound?

# Water Clusters: Quantumchemical Treatment

- optimization of many (ca. 40) isomers
- conditions to be fulfilled:
  1.  $VDE(QC) = E(X^-) - E(X) \approx VDE(Expt.)$
  2. Stability
- MP2 is best choice (bond energy of  $(H_2O)_2$  very close to experiment
- (possibly) dipole bound electron: floating basis

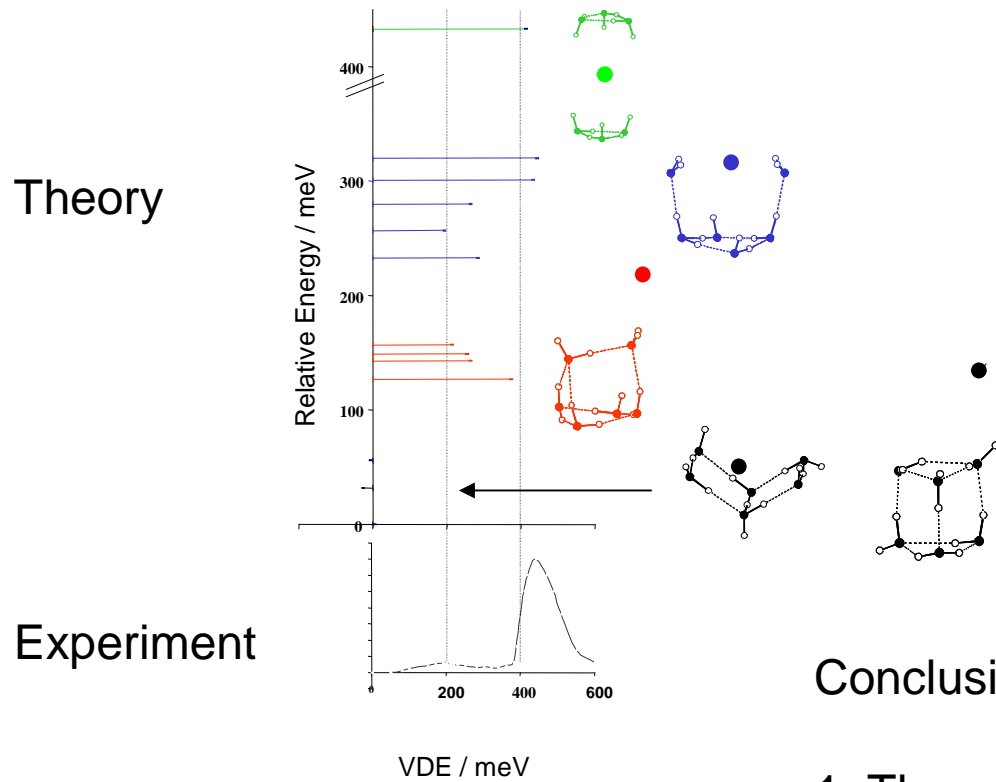


atoms  $\rightarrow$  basis functions



no atoms, no basis functions ??  $\rightarrow$  floating basis

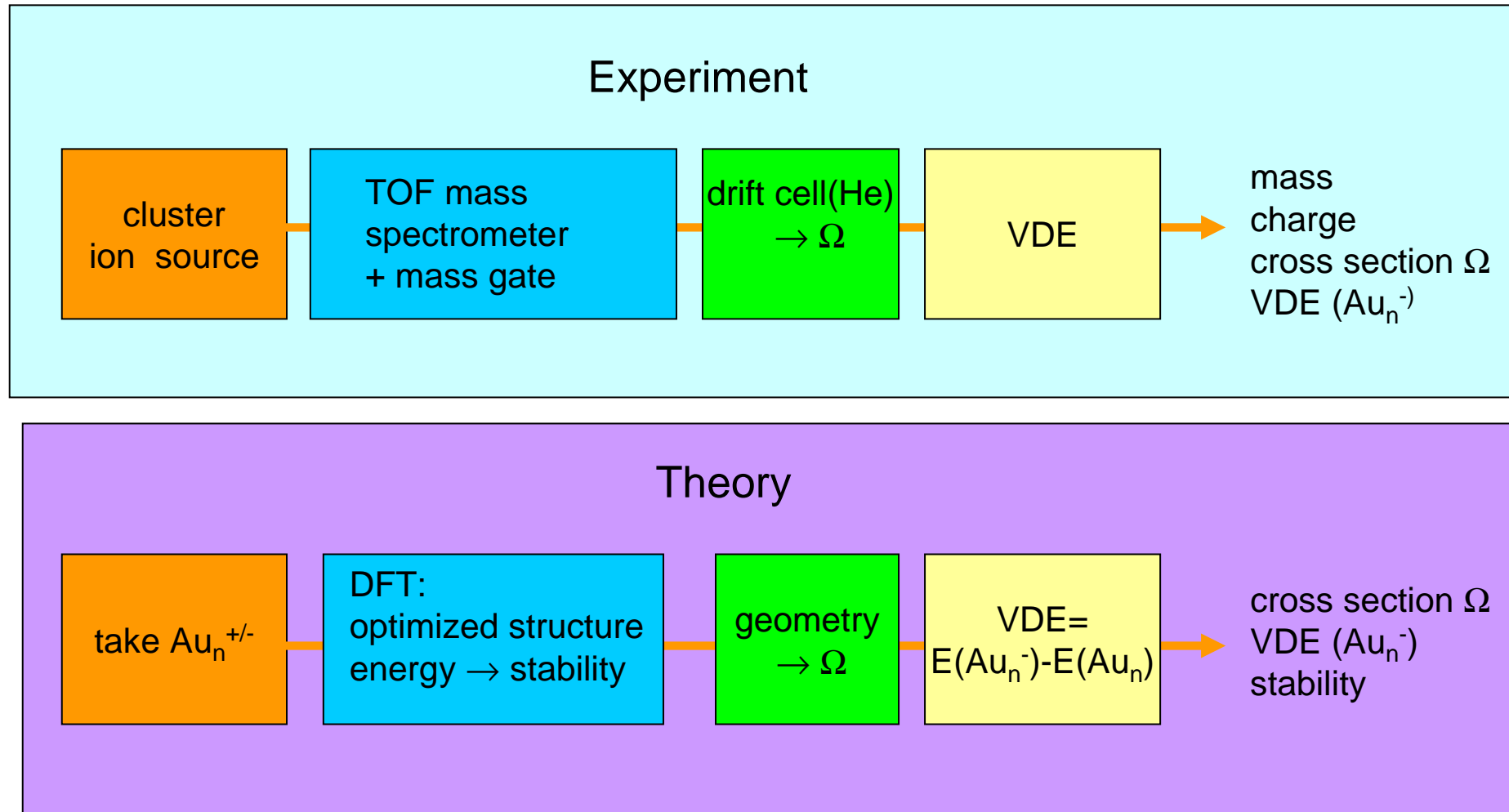
# Water Clusters: VDE Spectrum in Theory and Experiment



Conclusions:

1. The excess electron is dipole-bound.
2.  $(\text{H}_2\text{O})_6^-$  is metastable

# Combining Theory and Experiment: Ions of Gold Clusters



S. Gilb, P. Weis, F. Furche, R. Ahlrichs, M. Kappes, J Chem Phys, 116, 4094 (2002)

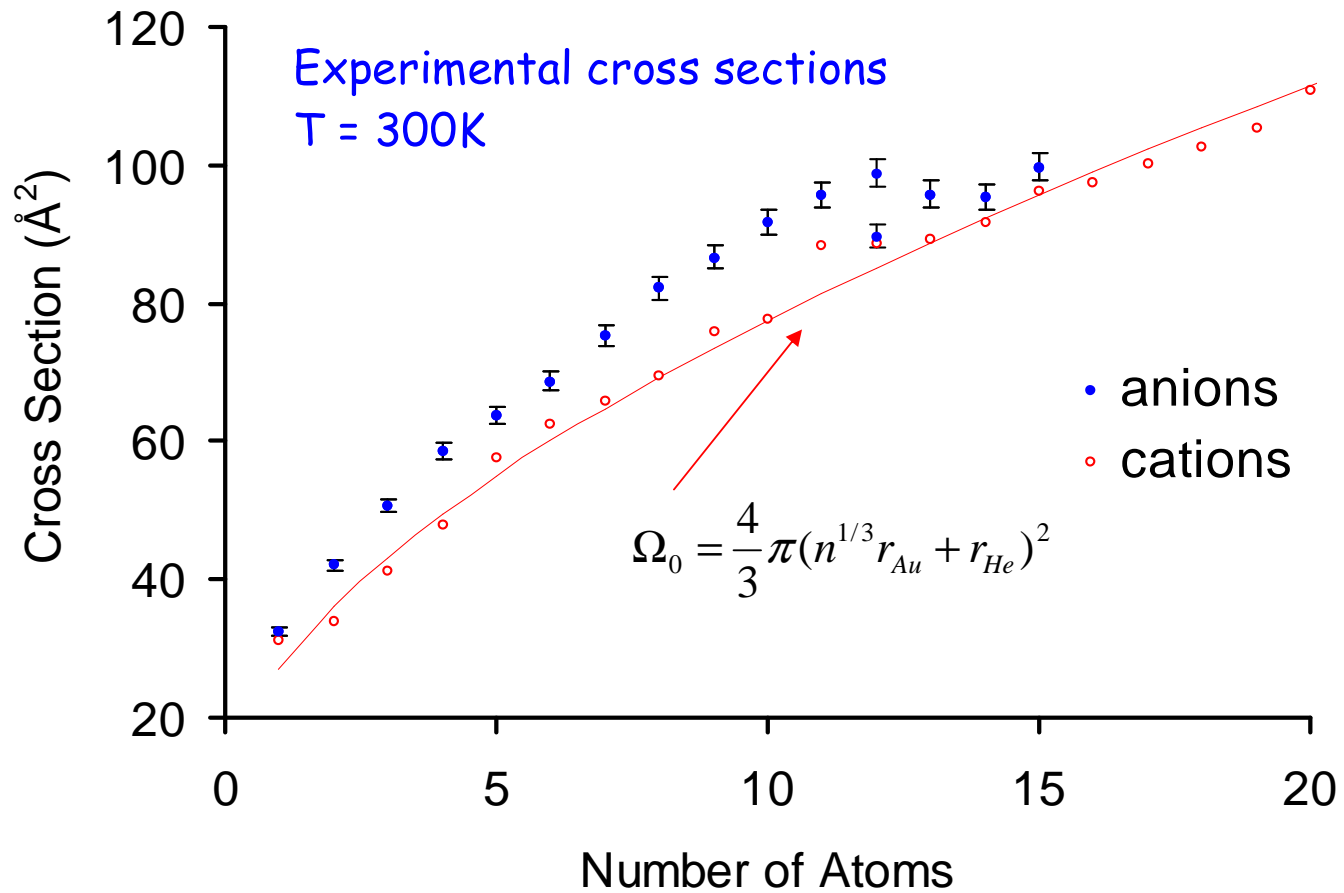
F. Furche, R. Ahlrichs, P. Weis, C. Jacob, S. Gilb, T. Bierweiler, M. Kappes, J Chem Phys, 117, 6982 (2002)

# Way of Proceeding

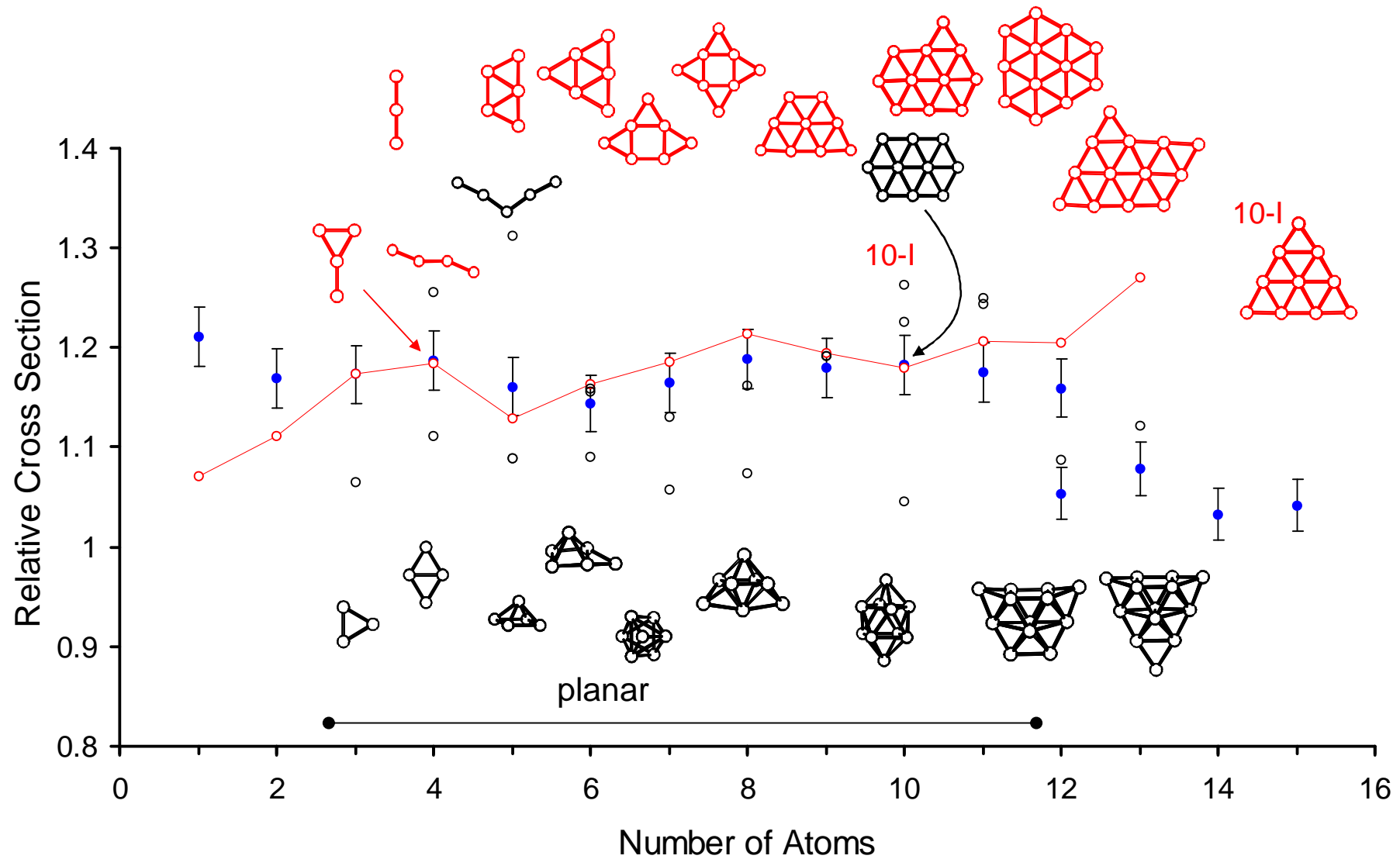
- optimization of overall more than 100 isomers
- check minimum by calculation of force constants
- regard only the few most stable isomers (for each n)
- comparison of cross section (and VDE)



# Gold Cluster Ions: Experimental Cross Sections



# Anions of Gold Clusters



# Clusters of Magnesium – a DFT Study

- Simple Concepts: Shells of Atoms and Electrons
- Small Clusters: Stability
- Larger Clusters: Stability and Electronic Structure

A. Köhn, F. Weigend and R. Ahlrichs, PCCP **3**, 711 (2001).

# Mg Clusters: Simple Concepts

Mg: Mg<sup>2+</sup>-core plus 3s<sup>2</sup> (+ empty 3p)

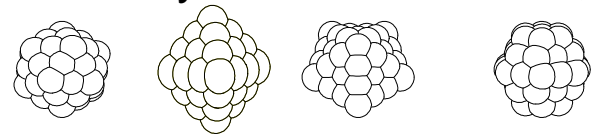
electronic shell model

Mg<sup>2+</sup> → uniform background  
→ harmonic oscillator

	Shell	n(e <sup>-</sup> )	sum	Mg <sub>n</sub>
—	4p3f2h1k	72	240	120
—	4s3d2g1i	56	168	84
—	3p2f1h	42	112	56
—	3s2d1g	30	70	35
—	2p1f	20	40	20
—	2s1d	12	20	10
—	1p	6	8	4
—	1s	2	2	1

atomic shell model

empty 3p: electron deficiency  
→ geometrically closed structures, e.g.



icosah	octa	cubocta	deca	tetra	„hcp“
				120	157
				84	103
	146			56	89
309	85		105	35	57
147	44	147	54	20	26
55	19	55	23	10	13
13	6	13	7	4	5

## Mg Clusters: DFT Treatments

Mg <sub>4</sub>	CCSD(T)	DFT(BP86)
r <sub>e</sub> /pm	310.3	309.4
D <sub>e</sub> /eV	1.14	1.22

→ DFT is o.k. (but take care for appropriate basis set!)

# Mg<sub>4</sub> : Effects of Electron Correlation

1. Hartree Fock (mean field)

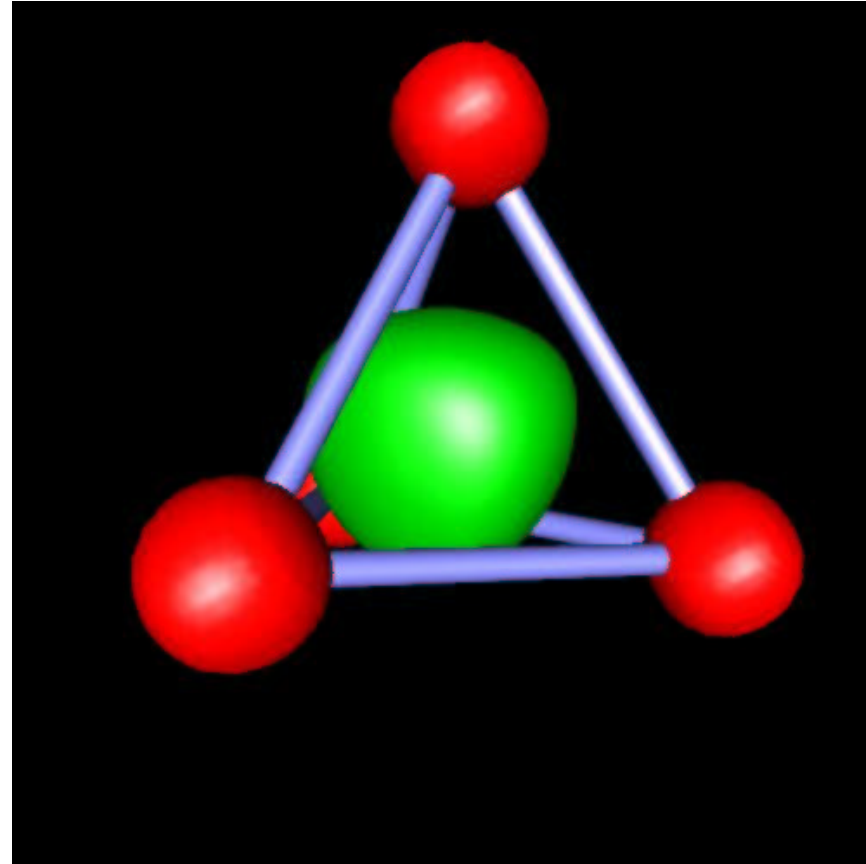
2. MP2 perturbation theory

$$(V=H_{\text{exact}}-H_{\text{HF}})$$

→ perturbed wave function  $\Psi_{\text{MP2}}$

→ changes in electron density due to electron correlation:  $\rho_{\text{MP2}} = |\Psi_{\text{MP2}}|^2$ :

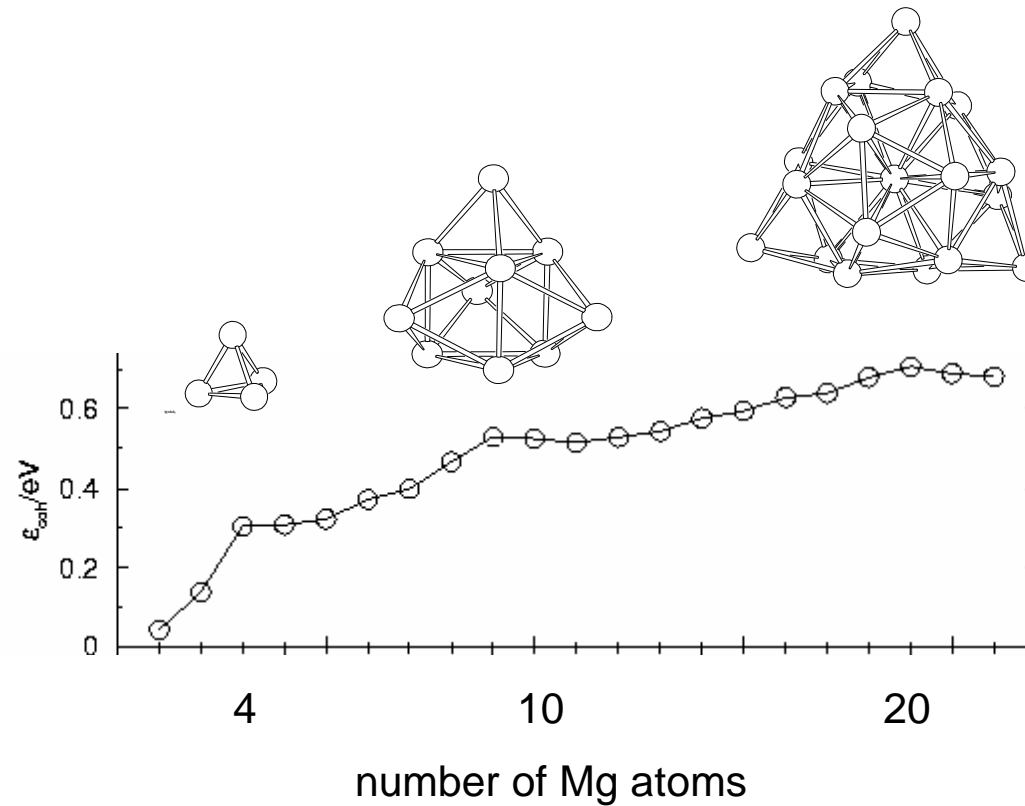
**lower** density near the nuclei, **higher** density in the middle of the tetrahedron



# Stability of Small Clusters $Mg_n$ ( $n < 23$ )

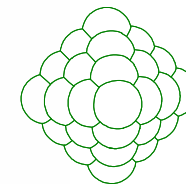
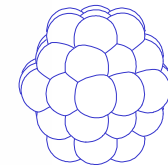
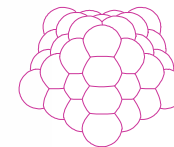
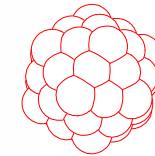
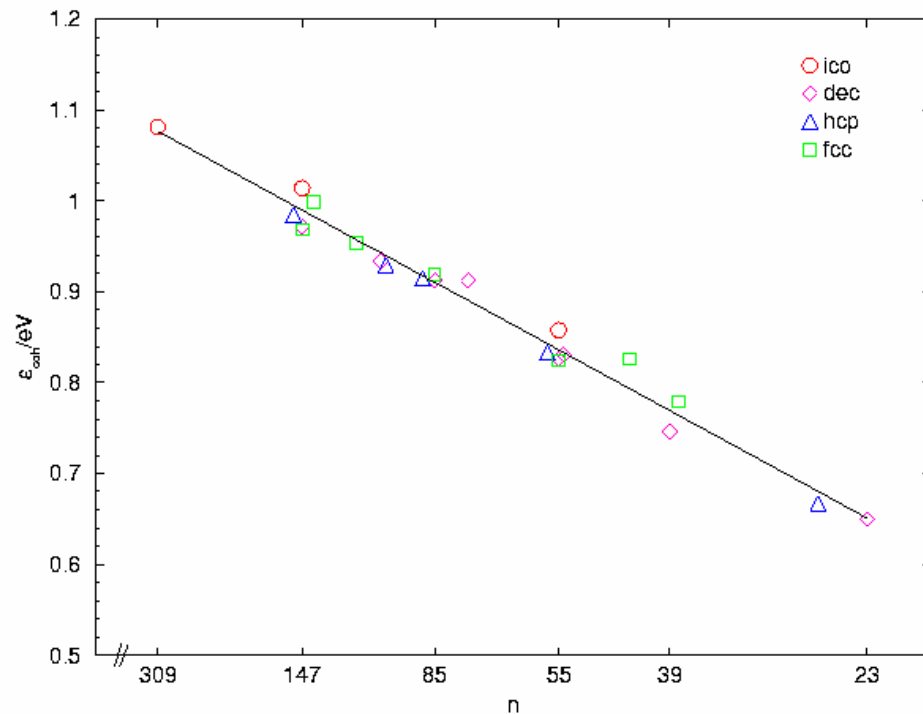
1. simulated annealing  $\rightarrow$  local minima
2. check by calculation of IR frequencies

$$\epsilon_{coh} = E_{at}(Mg_n) / n$$



# Cohesive Energies of Large Mg Clusters

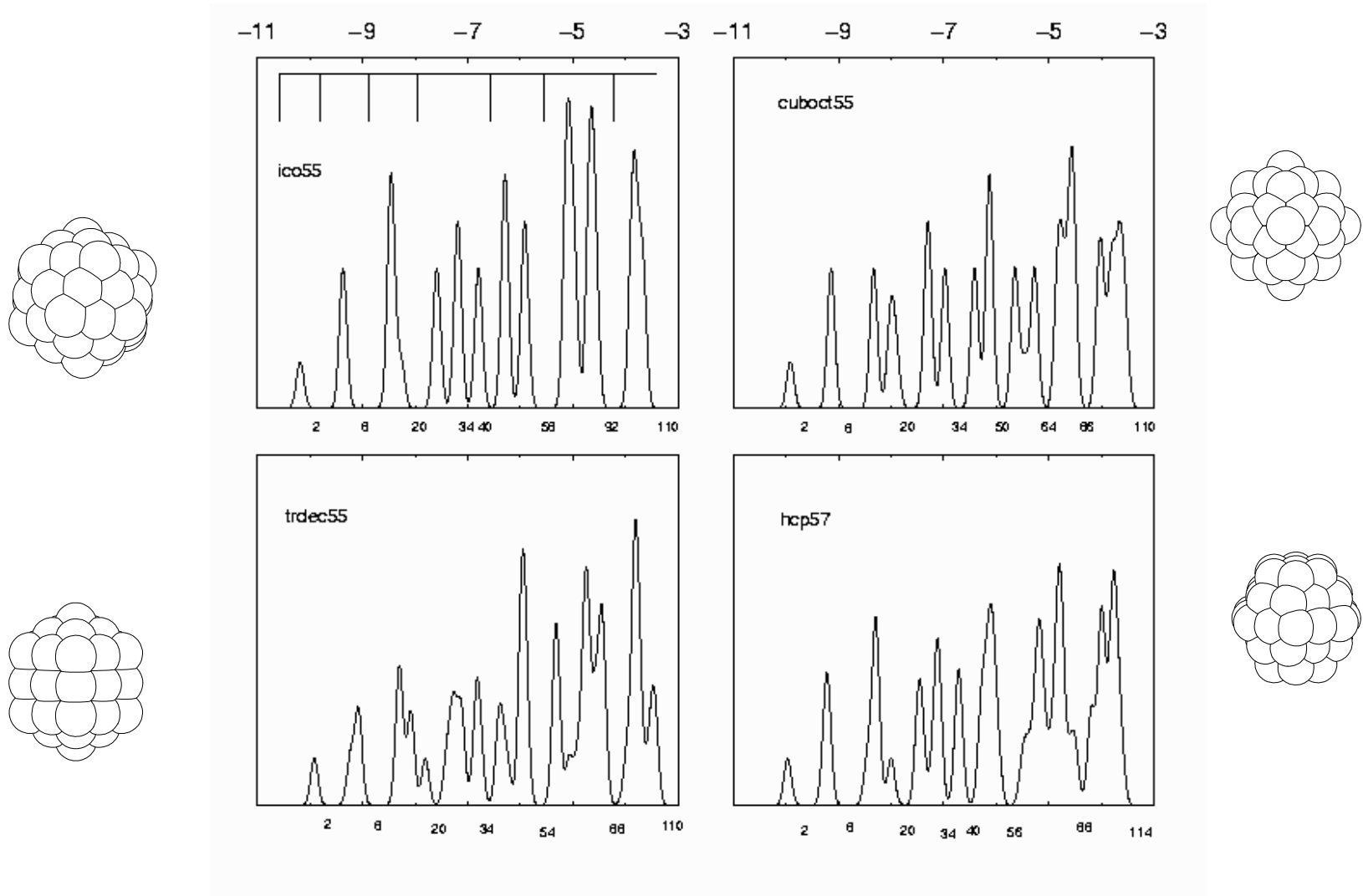
$$\mathcal{E}_{coh} = \mathcal{E}_{coh,bulk} + a_{surface}n^{-1/3} + a_{edge}n^{-2/3} + a_{corner}n^{-1}$$



- no clear pictures, but rather preference of icosahedra than hcp
- extrapolation to bulk: 1.38 eV (Expt.:1.51 eV, bulk DFT: 1.43)



# Validity of the Shell Model: DOS

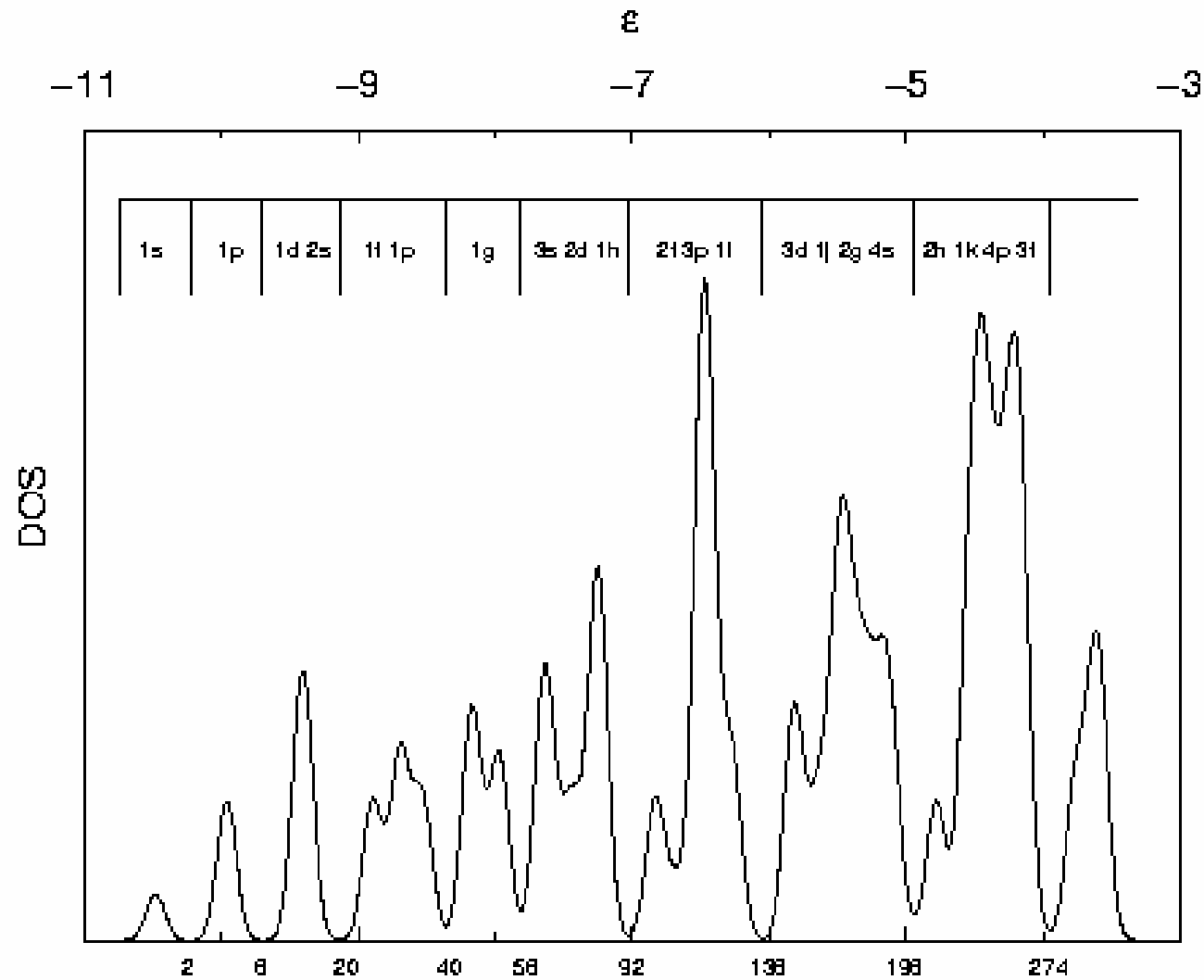


Magic electron numbers: 2, 8, 20, 40, 70, 112

# Shell Model: Anharmonic Distortions and Subshells

harmonic			distorted			DFT				
Shell	$n(e^-)$	sum			$n(e^-)$	sum	ico	cuboct	trdec	hcp
3p2f1h	42	112		3p	6	112				
				2f	14	106	X	(86)	(88)	(88)
				1h	22	92				
3s2d1g	30	70		3s	2	70		(64)		
				2d	10	68		50		
				1g	18	58	X		(54)	(56)
2p1f	20	40		2p	6	40				X
			1f	14	34	X	X	X	X	
2s1d	12	20	2s	2	20					
			1d	10	18	X	X	X	X	
1p	6	8	1p	6	8					
						X	X	X	X	
1s	2	2	1s	2	2					
						X	X	X	X	

# Mg<sub>147</sub>(I<sub>h</sub>): Shell Model and DOS



# Binary Metal Clusters: $\text{Pt}_{13-n}\text{Ir}_n$ as an Example

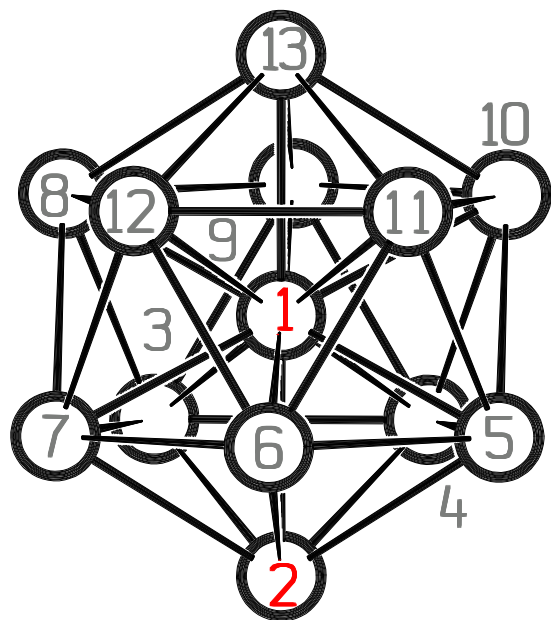
Problem: N-atomic cluster:  $2^N$  possible distributions for metal A and B

- Strategy:
1. Start with homoatomic clusters, find minima
  2. First consider symmetric cases, substitute only one or a few atoms
  3. Try to find (and understand) building principles
  4. Apply them to predict distribution in general cases, i.e.  
no (or low) symmetry, multiple substitutions
  5. Calculate ,best candidates‘

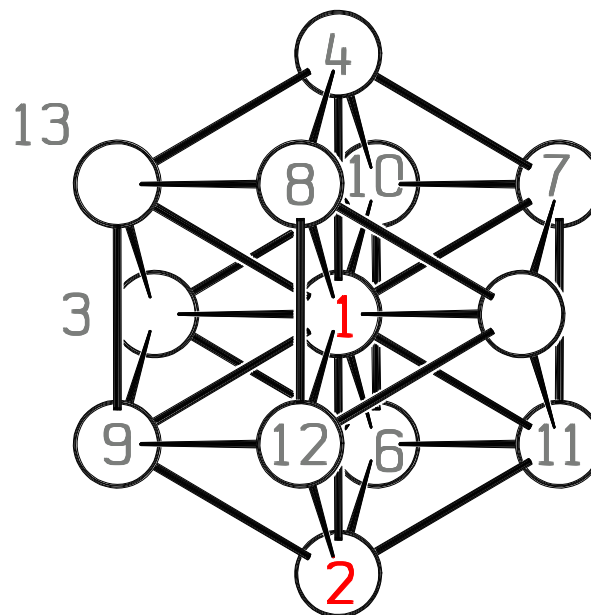
Method: DFT(BP86), TZVPP basis sets

Claudia Schrod, Florian Weigend...

# Pt<sub>13</sub> and Ir<sub>13</sub>: High Symmetries, Homoatomic Cases



I<sub>h</sub>



O<sub>h</sub>

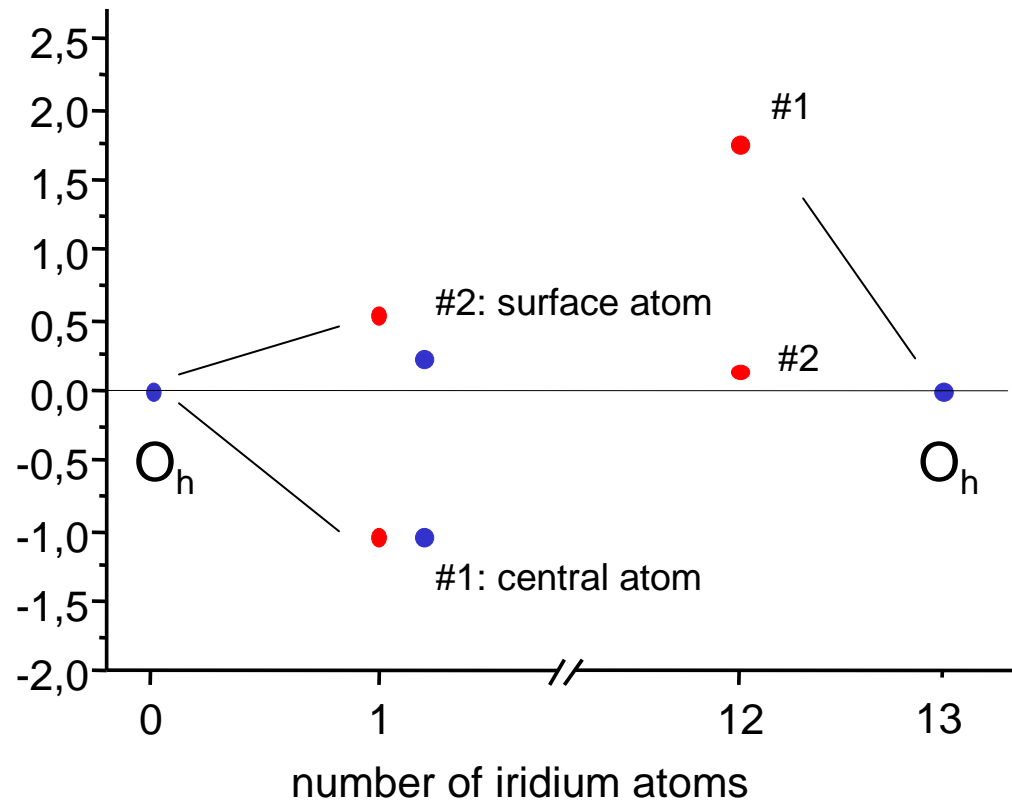
Pt and Ir: O<sub>h</sub> more stable than I<sub>h</sub> by ca. 0.4 eV

# $\text{Ir}_n\text{Pt}_{13-n}$ : High Symmetry, Substitution of One Atom

$$\Delta E = E(\text{Ir}_n\text{Pt}_{13-n}) - \frac{1}{13} [nE(\text{Ir}_{13}) + (13-n)E(\text{Pt}_{13})]$$

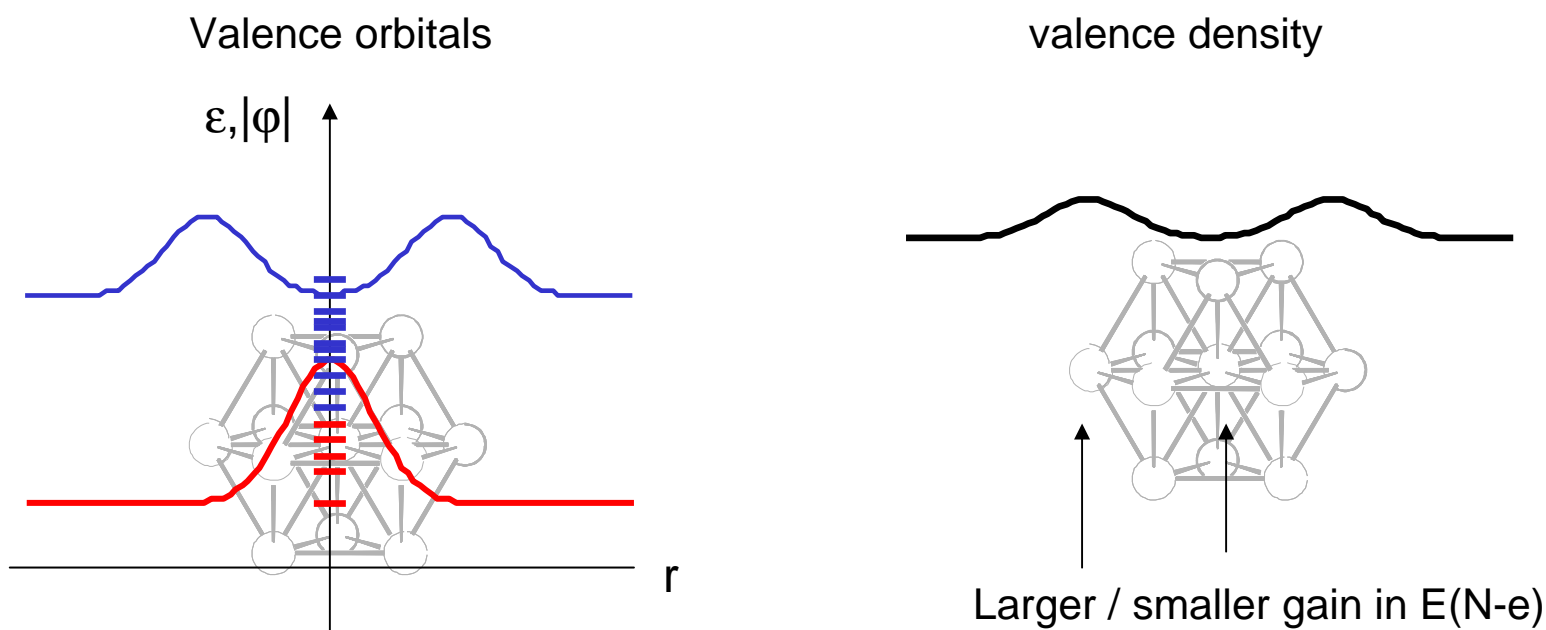
- Single point calculation for geometry of  $\text{Pt}_{13}$
- In optimised geometry

- very similar for  $\text{I}_h$



# How to Make Plausible

- Start from  $\text{Pt}_{13}$ :  $E = E(\text{N-N}) - E(\text{N-e}) + E(\text{e-e}) + E(\text{e,kin})$
- replace one Pt atom by Ir ( $Z \rightarrow Z-1$ ), do not change MOs and occupations
  - A) Lower N-N repulsion, but B) also lower N-e attraction
  - different size of cancellation of A) and B) for different sites
  - different change of energy for different sites



(electron deficiency, e.g.  $\text{Al}_{12}\text{Si}$ : central position for Si preferred by ca. 0.7 eV)

# Single Substitutions: Extrapolation from Homoatomic Case

- Start from Pt<sub>13</sub>:  $E = E_{\text{NN}} - E_{\text{Ne}} + E_{\text{ee}} + E_{\text{e,kin}}$
- consider a specific site: change  $Z \rightarrow Z + \delta Z$  leads to change  $\delta E$

$$\delta E = [E_{\text{NN}}(Z + \delta Z) - E_{\text{NN}}(Z)] - \left\langle \Psi \left| \sum_{\alpha} \frac{\delta Z}{R_{I\alpha}} \right| \Psi \right\rangle$$
$$\rightarrow \Delta E = \frac{\delta E}{\delta Z} * \Delta Z$$

- calculate  $\Delta E$  for different sites, compare with uniform distribution of  $\Delta Z/13$  at all sites  
→ Relative energies for Ir occupying all positions



# Pt<sub>13-n</sub>Ir<sub>n</sub> : Accuracy of Extrapolation

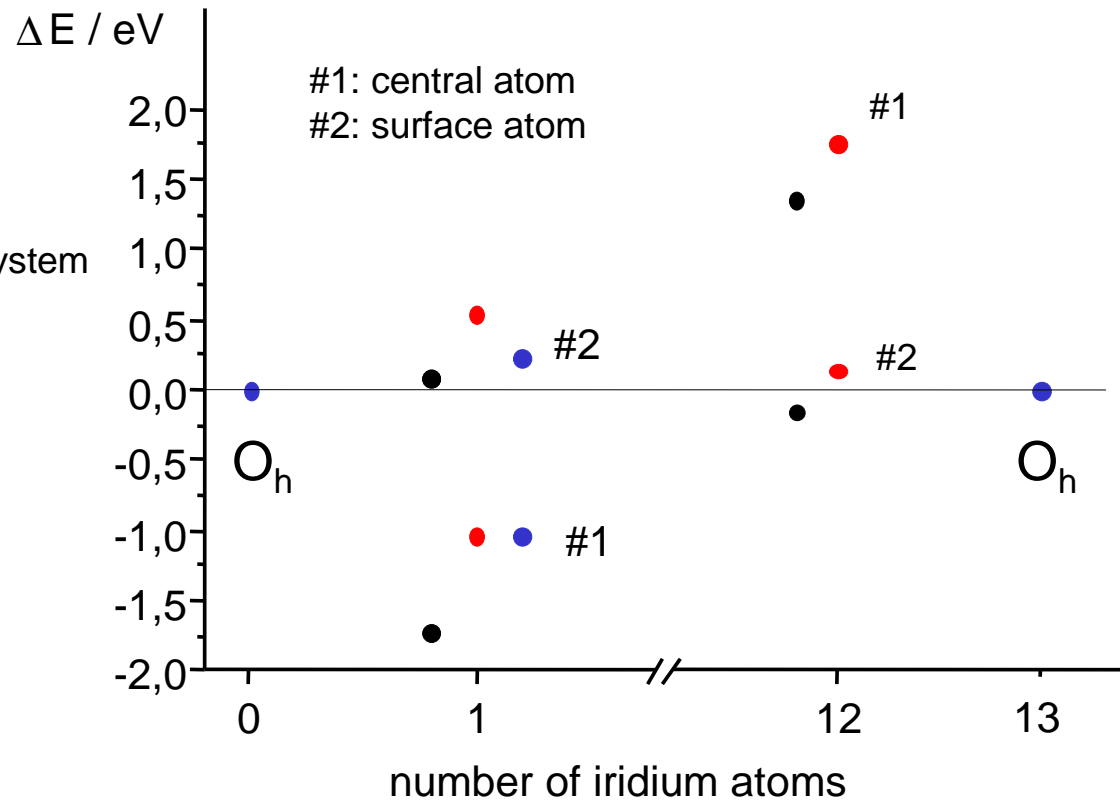
- Extrapolation from homoatomic system

$$\Delta E_i = \frac{\partial E(\text{M}_{13})}{\partial Z_i} \Delta Z_i$$

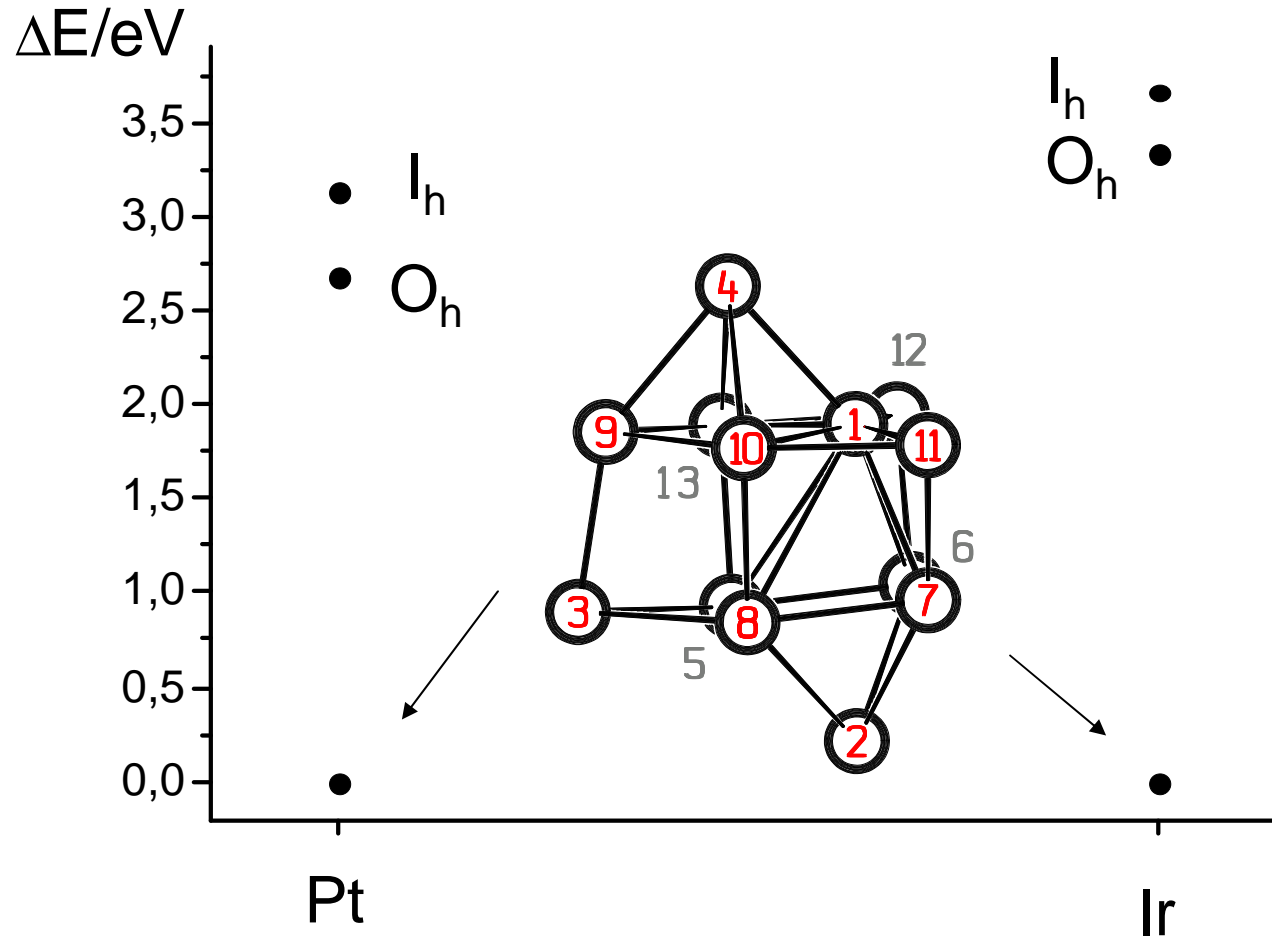
- Single point calculation for geometry of Pt<sub>13</sub>

- In optimised geometry

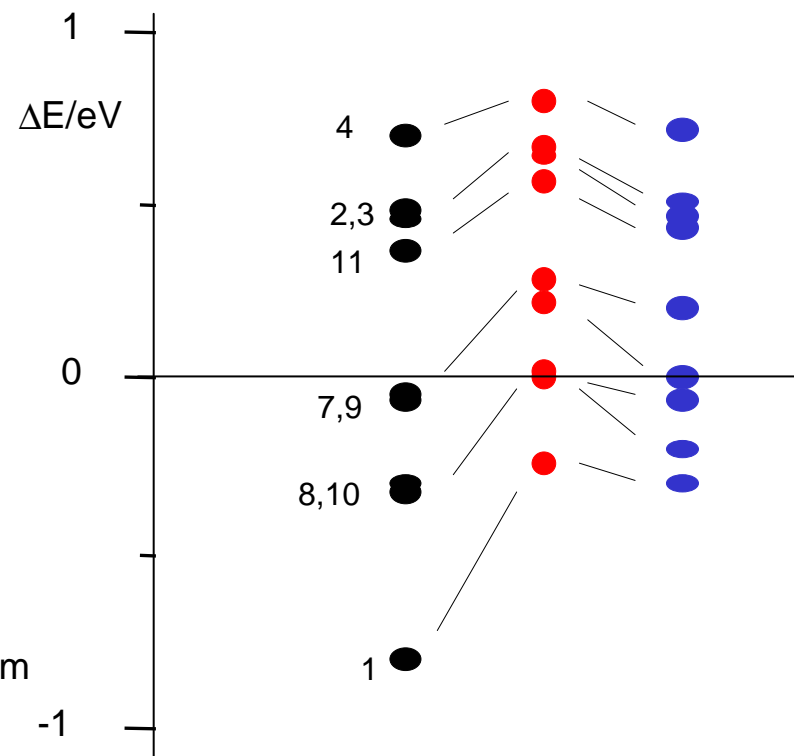
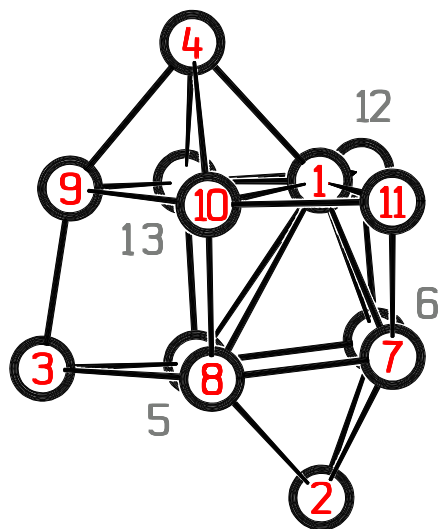
$$\Delta E = E(\text{Ir}_n \text{Pt}_{13-n}) - \frac{1}{13} [nE(\text{Ir}_{13}) + (13-n)E(\text{Pt}_{13})]$$



# Pt<sub>13</sub> and Ir<sub>13</sub> : More Stable Isomer(s)



# Pt<sub>13-n</sub>Ir<sub>n</sub>: Low Symmetry, Substitution of One Atom



- Extrapolation from homoatomic system

$$\Delta E = \frac{\partial E(\text{M13})}{\partial Z_i} \Delta Z_i$$

- Single point calculation for geometry of Pt<sub>13</sub>

- In optimised geometry

$$\Delta E = E(\text{Ir}_n \text{Pt}_{13-n}) - \frac{1}{13} [nE(\text{Ir}_{13}) + (13-n)E(\text{Pt}_{13})]$$

# Extrapolation From Homoatomic Case: Multiple Substitutions

- substitution of M atoms at positions I in an N-atomic system:
- $\delta Z_I$ : additional charge  $\delta Z$  added at all positions I

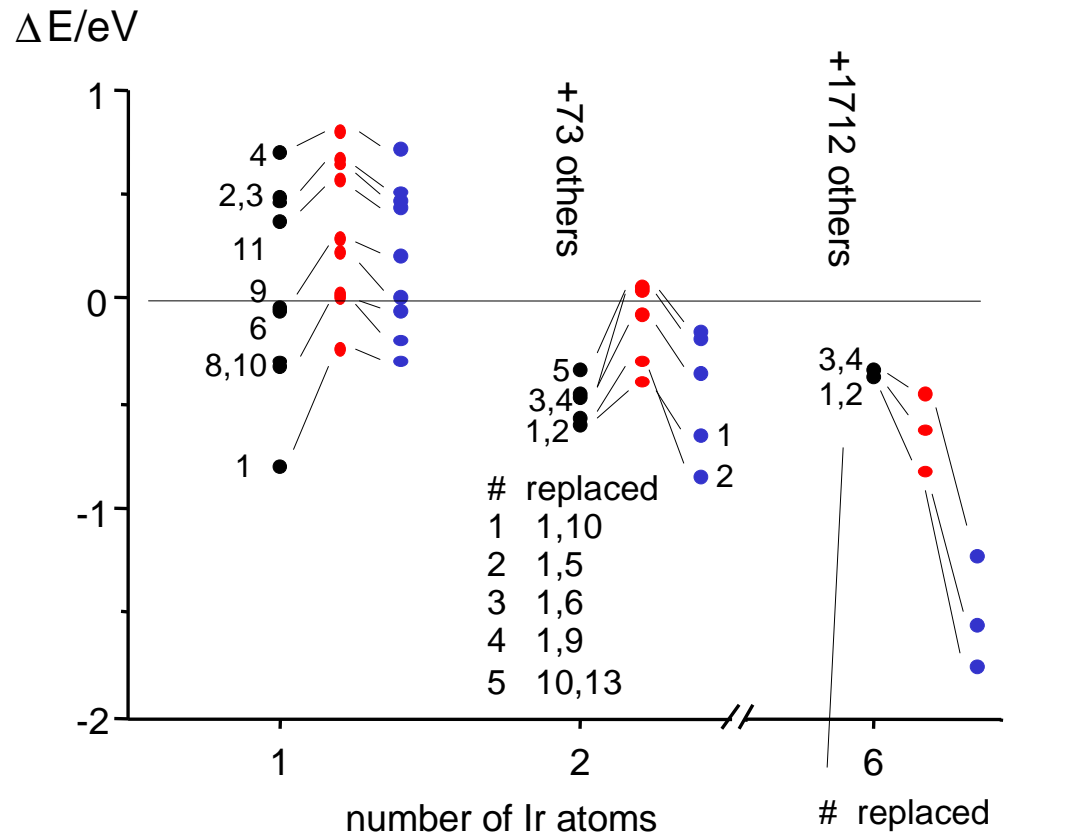
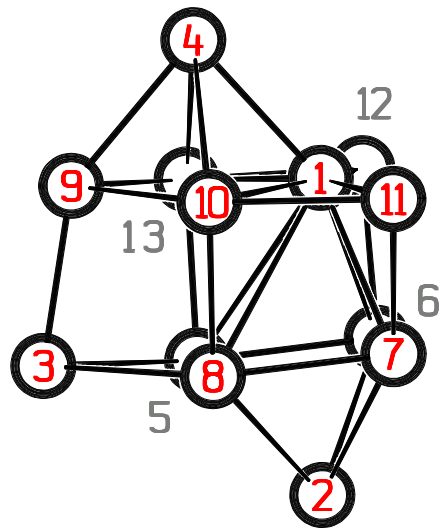
$$\Delta E = \underbrace{\frac{E_{NN}(Z_I + \delta Z_I) - E_{NN}(Z_I)}{\delta Z}}_{\Delta E_{NN}} * \frac{\Delta Z}{M} - \sum_I \underbrace{\frac{\delta E_{Ne}}{\delta Z_I}}_{\Delta E_{Ne}} * \frac{\Delta Z_I}{M}, \quad \frac{\delta E_{Ne}}{\delta Z_I} = \frac{\left\langle \Psi \left| \sum_{\alpha} \frac{\delta Z_I}{R_{I\alpha}} \right| \Psi \right\rangle}{\delta Z}$$

- all ( $2^N$ ) substitutions:

1. Only once:  $\partial E_{Ne} / \partial Z_i$ ,
2.  $2^N$  times:  $\Delta E_{NN}$ ,  $\Delta E_{Ne}$  from  $\partial E_{Ne} / \partial Z_i$   
 → extrapolated values for all distributions

3. Final DFT calculation only for „best“ candidates

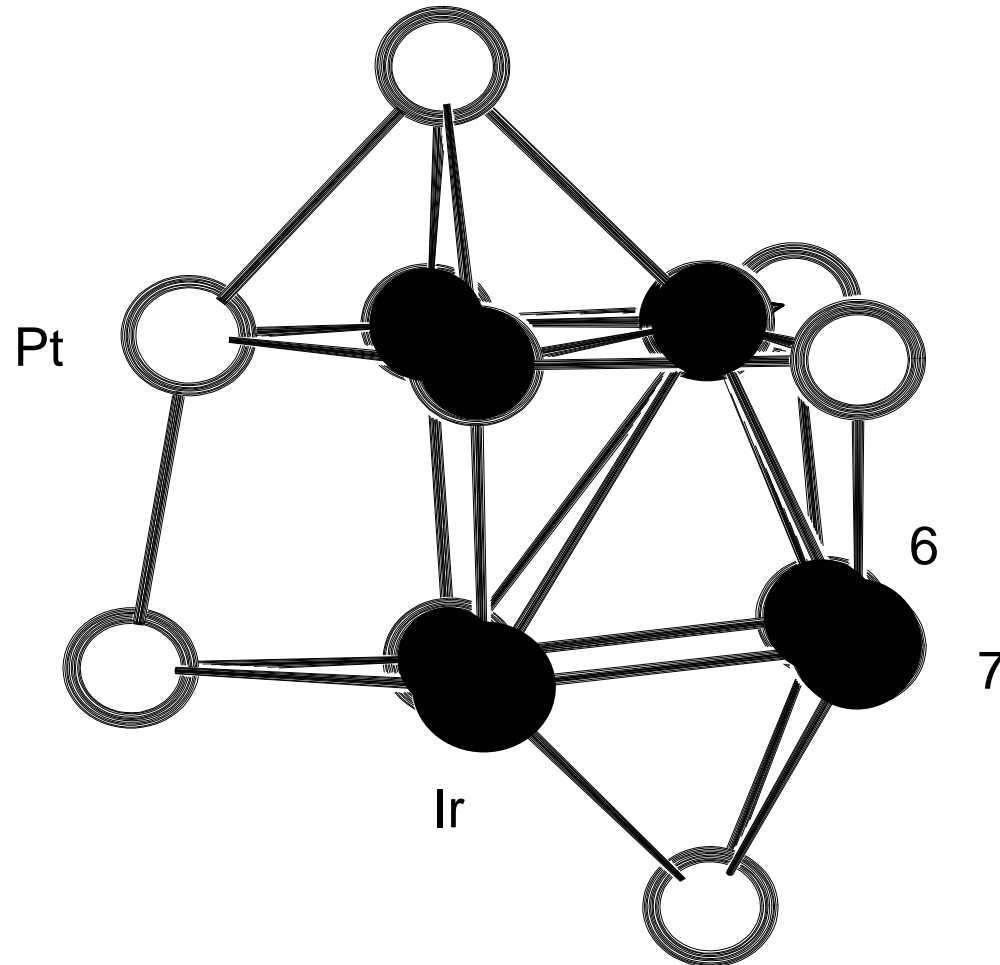
# Pt<sub>13-n</sub>Ir<sub>n</sub>: Low Symmetry, Multiple Substitutions



- From perturbation theory
- Single point calculation for geometry of Pt<sub>13</sub>
- In optimised geometry

- | # replaced | 1             | 2 | 3 | 4 |
|------------|---------------|---|---|---|
| 1          | 1,5,6,8,10,13 |   |   |   |
| 2          | 1,5,8-10,13   |   |   |   |
| 3          | 1,5-7,10,13   |   |   |   |
| 4          | 1,5,6,9,10,13 |   |   |   |

# $\text{Pt}_{13-n}\text{Ir}_n$ : The Most Stable of $2^{13}$ Isomers



$\text{Pt}_6\text{Ir}_7$ :  $\Delta E=1.8$  eV

+ very similar energies for  $\text{Pt}_7\text{Ir}_6$  (6: Pt) and  $\text{Pt}_8\text{Ir}_5$  (6,7: Pt)

# Summary: Applications

- Calculation of stabilities by DFT and HF+MP2.  
→ prediction of stable isomers
- Comparison of calculated and measured data  
→ geometric structure
- Verification of (simple) models by calculations