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Relativistic Electronic Structure Theory for SHE

Talk

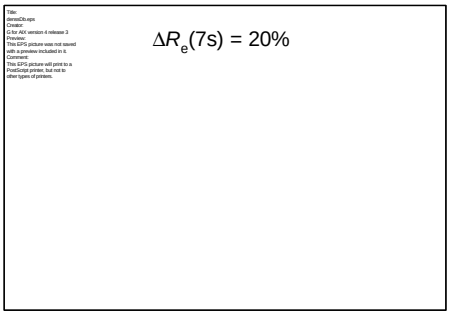
Relativistic effects

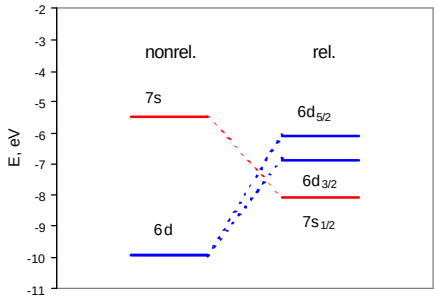
$$m = m_0 / \sqrt{(1-(v/c)^2}$$

$$a_0 = 4pe_0\hbar^2 / me^2$$

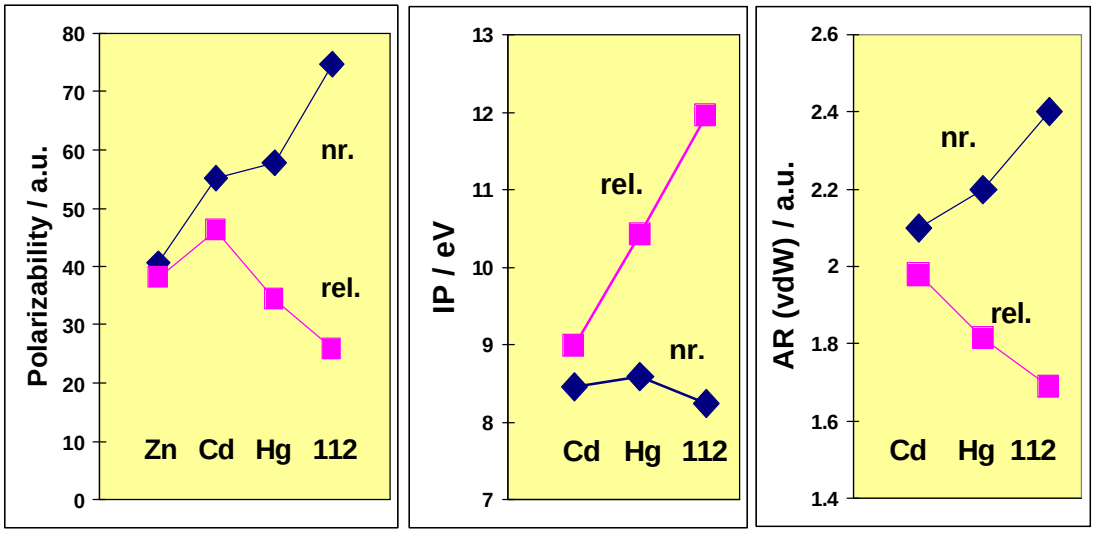
scale as ~ Z^2

- contraction and stabilization of s and $p_{1/2}$ orbitals
- expansion and destabilzation of d and f orbitals
- SO splitting of p, d, f orbitals
  $j = l \pm s$

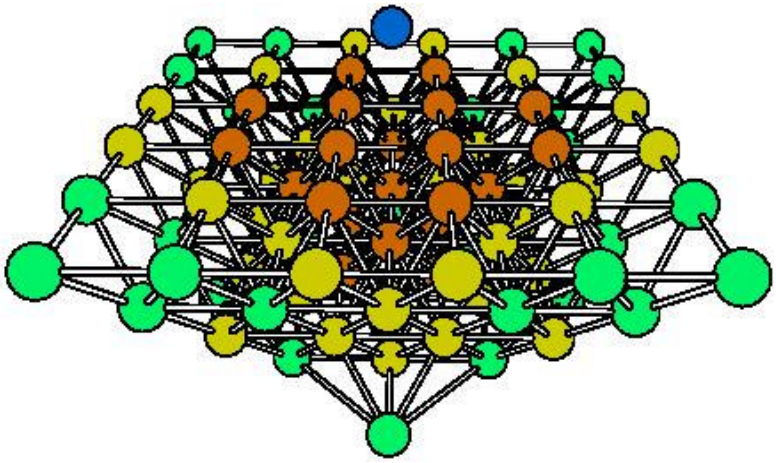




Relativistic Effects on Atomic Properties of Group-12 Elements



Ad-atom on the embedded gold cluster



Relativistic Quantum-Chemical Methods and Systems

Dirac-Fock method

Dirac operator

$$h_D = c\boldsymbol{a}_i r_i + (b - 1)c^2 + V(\vec{r})$$

4-c wave-functions: $f_{nkm} = \begin{bmatrix} j \\ \vec{j} \end{bmatrix} = \begin{Bmatrix} \frac{P_{nk}(r)}{r} \mathrm{Y}_{km}(\vec{r}, x) \\ i\frac{Q_{nk}(r)}{r} \mathrm{Y}_{-km}(\vec{r}, x) \end{Bmatrix}$

Dirac-Coulomb-Breit

$$h = \sum_i h_D(i) + \frac{1}{2}\sum_{i,j}\left\{\frac{1}{\vec{r}_{i,j}} + h_B(i,j)\right\}$$

$$h_B(i,j) = -1/2[(a_i a_j)r_{ij}^{-1} + (a_i \boldsymbol{r}_{ij})(a_j \boldsymbol{r}_{ij})r_{ij}^{-3}]$$

Electron correlation: CI, MP2, CCSD(T)

Systems	Examples	Properties
Atoms	till Z=122	el. conf., IP (0.01 eV)
MCDF	Rf - Hs	IP, IR, *E*°

Molecules	113H,114H_2, 118H_4	D_e, R_e, k

Relativistic Density-Functional Theory Method (DFT-RGGA)

Single-particle equations

$$\left\{\hat{t} + V^N + V^C + \frac{dE^{ex}[r,\vec{m}]}{dr} - m_B b\vec{\Sigma}\frac{dE^{xc}[r,\vec{m}]}{d\vec{m}}\right\} f_i = e_i f_i$$

$$i = 1, ..., N.$$

$\hat{t} = a\mathbf{p} + b$ - Dirac kinetic-energy operator

Electronic and magnetization densities

$$r(\vec{r}) = \sum_i n_i f_i^+(\vec{r}) f_i(\vec{r}) \qquad \vec{m}(\vec{r}) = -m_B \sum_{i=1}^{M} n_i f_i^+(\vec{r}) b\vec{\Sigma} f_i(\vec{r})$$

Systems: chemically interesting
(trends/rel. effects./exp. predictions)

Systems	Examples	Properties
Molecules	$RfCl_4$, $DbOCl_3$, SgO_2Cl_2, BhO_3Cl, HsO_4	D_e, R_e, ν; ΔH_{ads}, T_{ads}
Cluster/solid	Hg-Au_n, 112-Au_n	ΔH_{ads}, T_{ads}
Aqueous	$RfCl_6^{2-}$, $DbOCl_5^{2-}$, $SgOF_5^-$, etc.	*c.f.* (K_i), K_d

Predictions of the Adsorption Temperature for the Heaviest Elements

For a comparative study: $K_A(T_A) = K_B(T_B)$

$$e^{-\Delta E_A / RT_A} \frac{Q_A^s}{Q_A^g} = e^{-\Delta E_B / RT_B} \frac{Q_B^s}{Q_B^g}$$

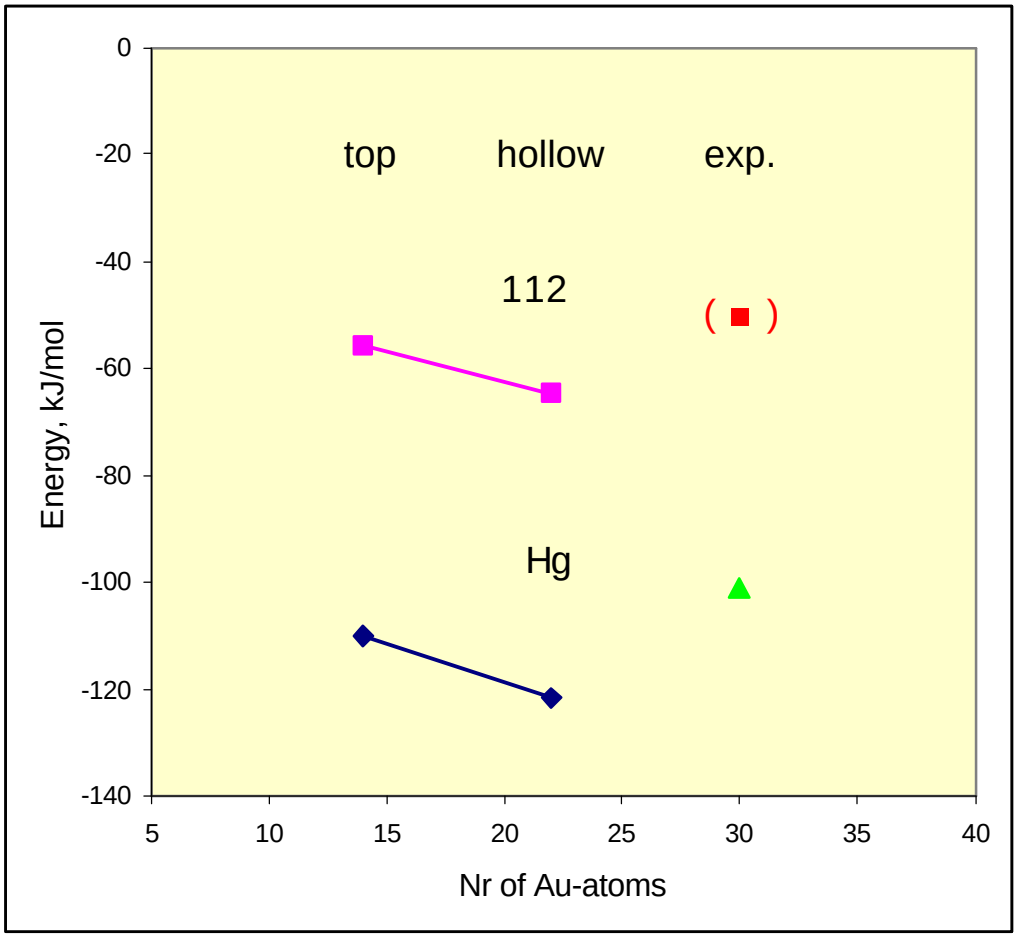
Model of localized adsorption

$$e^{-\Delta E_A / RT_A} \left(\frac{pIR_A^2}{d^2} - 1 \right) \frac{T_A^{3/2}}{n_A^3 r_A^3 m_A^{3/2}} = e^{-\Delta E_B / RT_B} \left(\frac{pIR_B^2}{d^2} - 1 \right) \frac{T_B^{3/2}}{n_B^3 r_B^3 m_B^{3/2}}$$

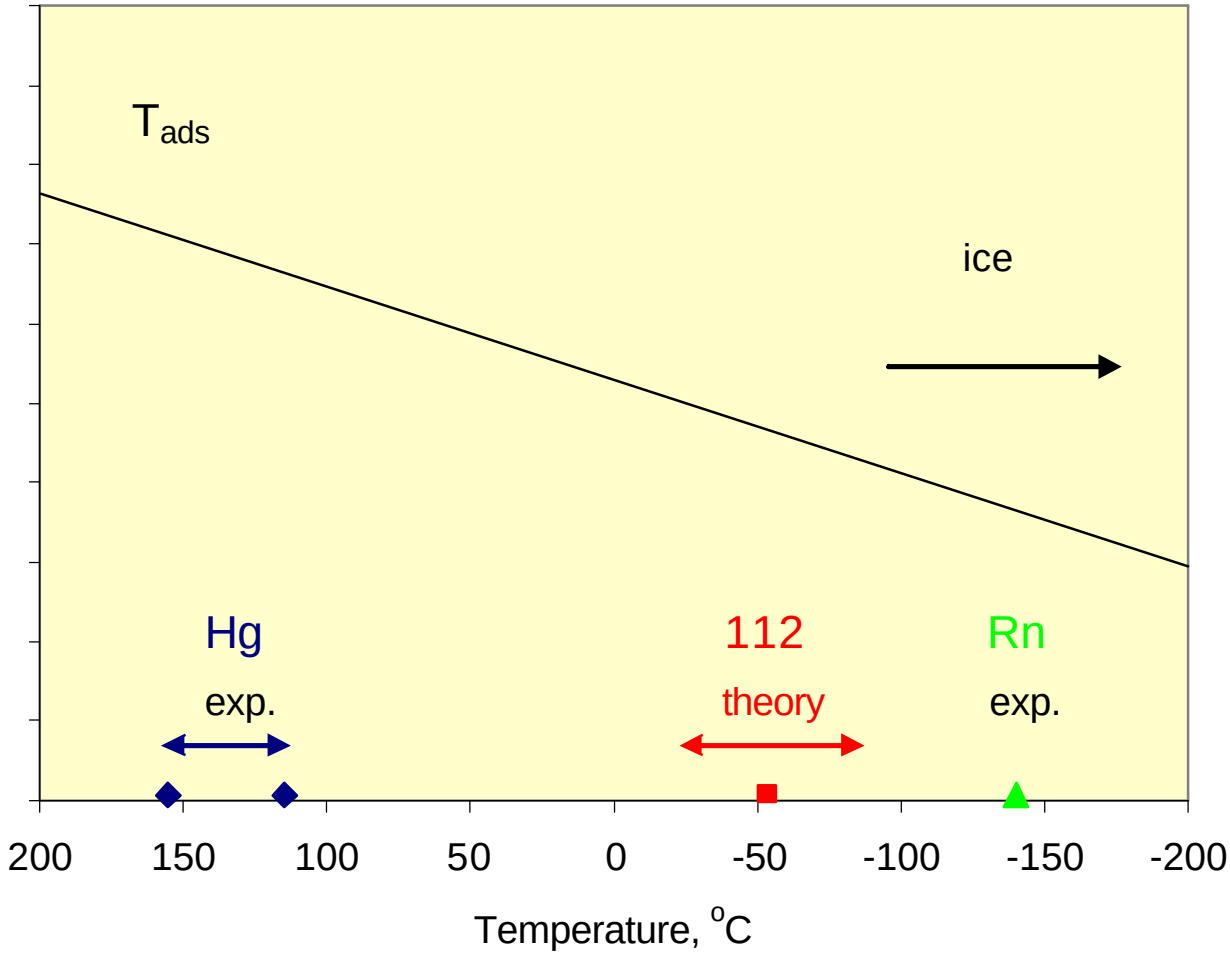
Properties of Hg and element 112

Property	Hg	112
r_{max} (6s/7s), Å	1.217	1.113
IR, Å	1.36	1.41
m, g/at	186	283
$\nu_{0,}$ s^{-1}	$2.99 \cdot 10^{12}$	$2.21 \cdot 10^{12}$
ΔH_{ads}, kJ/mol	121.6 (101 – exp.)	64.6
T_{ads}, K	428 (exp.)	T_{ads}(Hg) - 200

Calculated Adsorption Energy of Hg and Element 112 on Gold Clusters of Different Size



Adsorption Temperature of Hg, Rn, and Element 112 on Gold Surface


T ads
ice
Hg
exp.
112
theory
Rn
exp.
200
150
100
50
0
-50
-100
-150
-200
Temperature, °C