



HAL
open science

Stability, structure and dynamics of doped helium clusters from accurate quantum simulations

Marius Lewerenz

► **To cite this version:**

Marius Lewerenz. Stability, structure and dynamics of doped helium clusters from accurate quantum simulations. 2013. hal-00832982

HAL Id: hal-00832982

<https://hal.science/hal-00832982v1>

Submitted on 11 Jun 2013

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

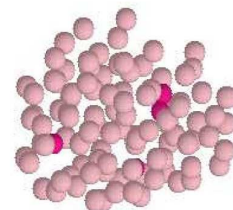
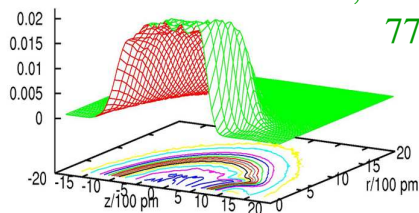
L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Stability, structure and dynamics of doped helium clusters from accurate quantum simulations

Marius Lewerenz

Laboratoire de Modélisation et Simulation Multi Echelle
FRE 3160 CNRS

Université Paris Est (Marne la Vallée)
5, Blvd. Descartes, Champs sur Marne
77454 Marne la Vallée Cedex 2



Acknowledgments

Paris-Est:

Mohamed Elhiyani, Ph. D student, Mg@He_n

Jiang Ji, Masters student, $\text{Mg}^+@He_n$, $\text{Ar}^+@He_n$

Prague:

Prof. Petr Slavíček, $\text{Pb}^{4+}@He_n$

Nottingham:

Prof. Tim Wright

Adrian Gardner, Ph. D student, Mg^+He

What makes helium clusters interesting?

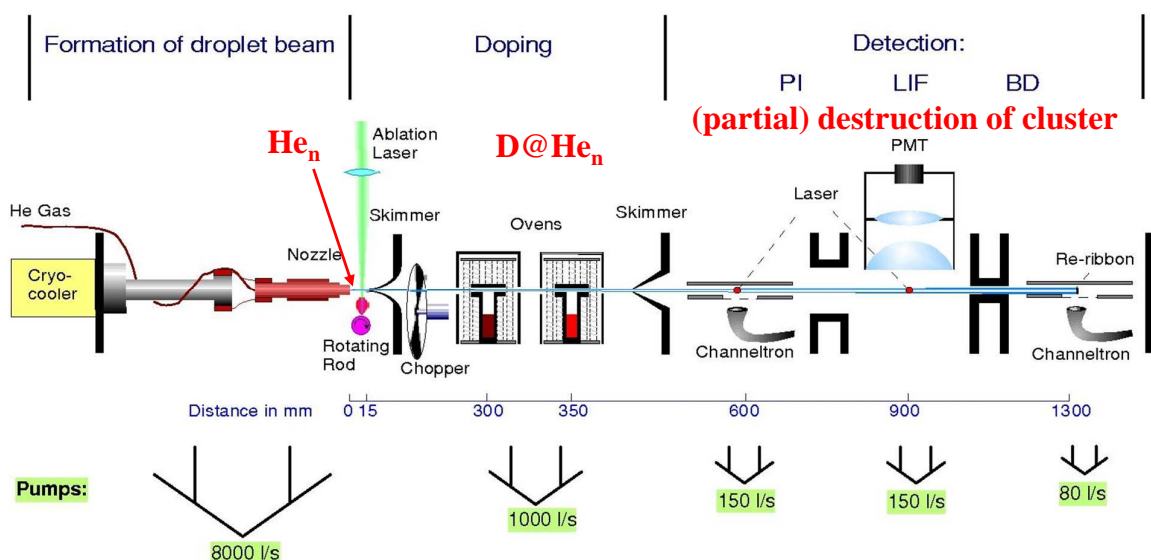
- Helium-helium interaction is of **weak van der Waals** type, closed shell atoms of very low polarisability, $D_e \approx 7.6 \text{ cm}^{-1}$
 - Helium atoms have a relatively small mass.
 - Large zero point energy effects (D_0 for $\text{He}_2 \approx 0.001 \text{ cm}^{-1}$).
 - Helium clusters are a quantum liquid.
 - Quantum statistical effects: **bosonic** ^4He , fermionic ^3He .
 - **Superfluidity** in bulk liquid ^4He below 2.17 K, in ^3He at mK level
 - **A very special solvent: Is there a new chemistry?**
-
- Implantation of dopants through (multiple) inelastic collisions.
 - Weak interactions with dopant.
 - Binding energy and position of dopants depend on quantum effects.

Delicate balance between potential and quantum kinetic energy

Plenty of interesting experiments and not that much theory!

A typical helium droplet experiment

(ask the local experts for details)



Recent applications of helium clusters

- Matrix spectroscopy with minimal perturbations: **OCS, (HF)_n, biomolecules at 0.4 K, radicals**
- Reaction dynamics at very low temperatures: **Ba + N₂O → BaO + N₂**
- Preparation of reactive intermediates: **HF ⋯ CH₃, HCN ⋯ CH₃ etc.**
- Preparation of high spin metal polymers: **Na₃, K₃, Rb₃ etc.**
- Assembly of cold clusters: **Ag_n, Mg_n**
- Thermodynamically unstable isomers: **linear (HCN)_n**
- Nanomodels for molecule-surface interactions: **HCN⋯Mg₃ etc.**

- Container for soft ionisation for analytical mass spectrometry?
- Energy dissipation by coupling to the bath?
- Confinement medium for cluster ignition and Coulomb explosion.
- Spacer for interatomic Coulombic decay (ICD).

**Where does a dopant D go after hitting the helium cluster?
Which factors control association of several dopants?**

Modelling doped helium clusters (D@He_n)

- We need an accurate potential model:
High level **electronic structure including relativistic effects**,
inject results into additive or non additive many body models.
- Stationary state properties (energies, structures):
We need a reliable quantum many body method with
uniform accuracy over a large range of n:
Quantum Monte Carlo: random walks in imaginary time
- What about real time dynamics?
How do dopants recombine inside helium clusters?
What is the effect of the helium bath on dissociating molecules or
clusters?
Dynamics of a many-body quantum system is a hard problem:
We have to invent some smart approximations → ZPAD

Diffusion quantum Monte Carlo (DMC)

- Isomorphism between **time dependent Schrödinger equation** and a **multi dimensional diffusion equation** (Fermi, Ulam)
- Exact solution except for statistical errors

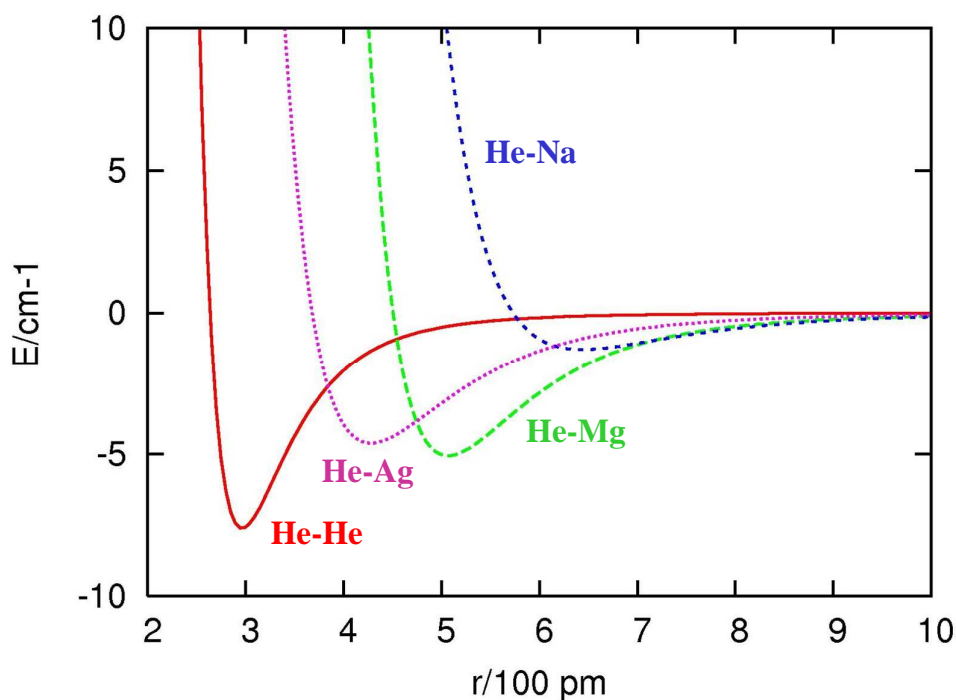
$$i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t} = \left\{ -\frac{\hbar^2}{2} \sum_{j=1}^n \frac{1}{m_j} \nabla_j^2 + \{V(\vec{r}) - E_{ref}\} \right\} \Psi(\vec{r}, t)$$

$$\frac{\partial C(\vec{r}, t)}{\partial t} = \left\{ \sum_{j=1}^n D_j \nabla_j^2 - k(\vec{r}) \right\} C(\vec{r}, t) .$$

Solution by propagation of an ensemble of random walkers in imaginary time
Cartesian coordinates, precision $\sigma_E/E = 10^{-6} - 10^{-3}$

Pair potentials involving helium and metals

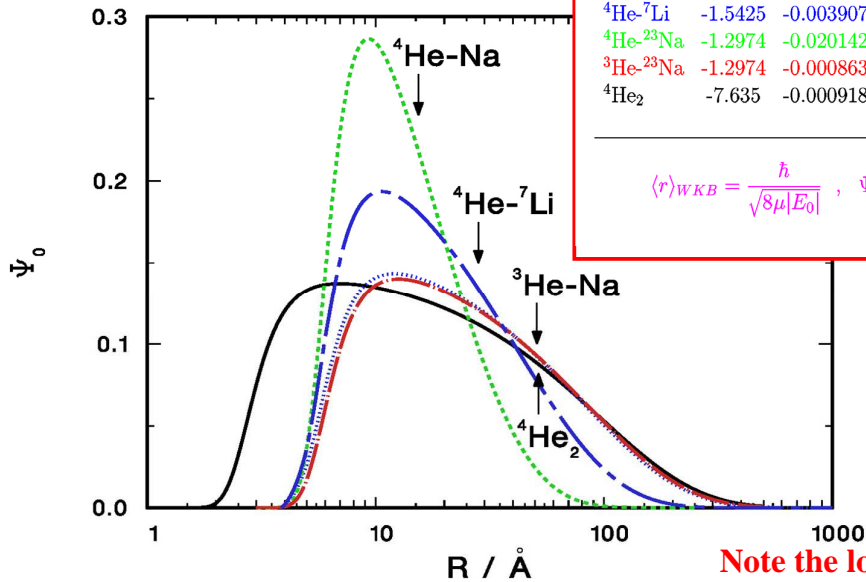
Shallower well than **He-He** and larger equilibrium distance for **He-M**



Alkali-helium dimers

Variational calculations with large basis sets of Laguerre functions, PRL 1999

All alkali-helium dimers appear to possess a single bound state but are yet unobserved



	V_{min}	E_0	r_{min}	$\langle r \rangle$	$\langle r \rangle_{WKB}$	$\langle T \rangle$
${}^4\text{He}-{}^6\text{Li}$	-1.5425	-0.001053	6.16	48.53	40.80	0.033457
${}^4\text{He}-{}^7\text{Li}$	-1.5425	-0.003907	6.16	28.15	20.56	0.063601
${}^4\text{He}-{}^{23}\text{Na}$	-1.2974	-0.020142	6.43	15.41	7.83	0.125440
${}^3\text{He}-{}^{23}\text{Na}$	-1.2974	-0.000863	6.43	50.85	42.79	0.027745
${}^4\text{He}_2$	-7.635	-0.000918	2.97	51.68	47.89	0.069649

$\langle r \rangle_{WKB} = \frac{\hbar}{\sqrt{8\mu|E_0|}}$, $\Psi = \exp(ikr)$, $k \approx \frac{\sqrt{2\mu E_0}}{\hbar}$

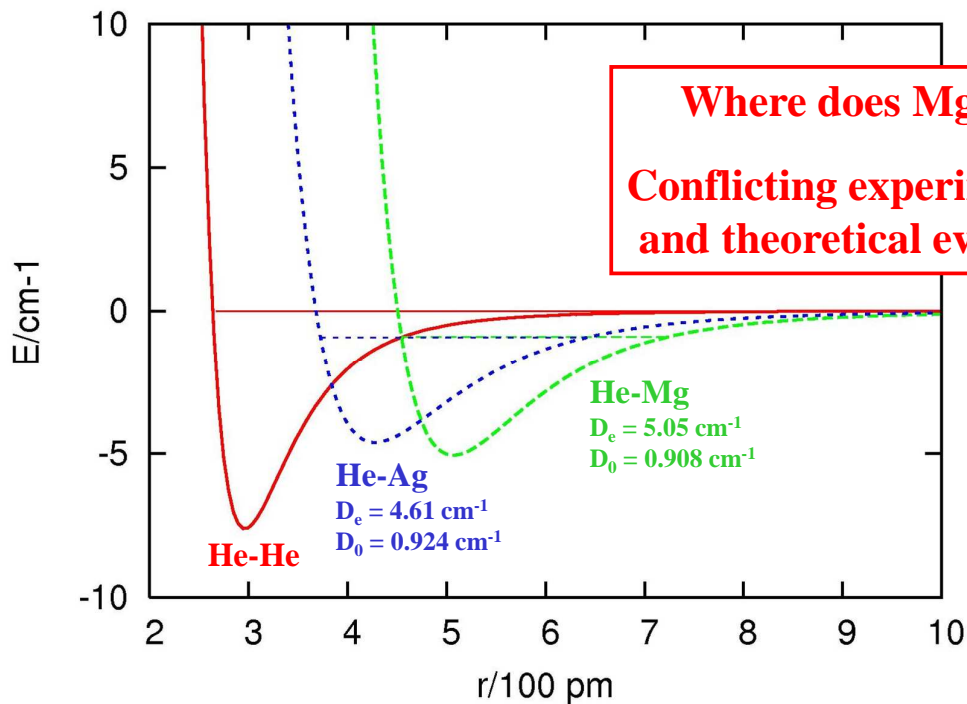
Predicted to be extremely weakly bound and diffuse

Relevance for BEC?

Note the log scale!

Comparison between silver and magnesium

Silver is known to penetrate into helium clusters and to form Ag_n clusters



Where does Mg go?
Conflicting experimental and theoretical evidence

He-He
 $D_e = 4.61 \text{ cm}^{-1}$
 $D_0 = 0.924 \text{ cm}^{-1}$

He-Ag
 $D_e = 4.61 \text{ cm}^{-1}$
 $D_0 = 0.924 \text{ cm}^{-1}$

He-Mg
 $D_e = 5.05 \text{ cm}^{-1}$
 $D_0 = 0.908 \text{ cm}^{-1}$

Incomplete aggregation of Mg atoms inside helium clusters?

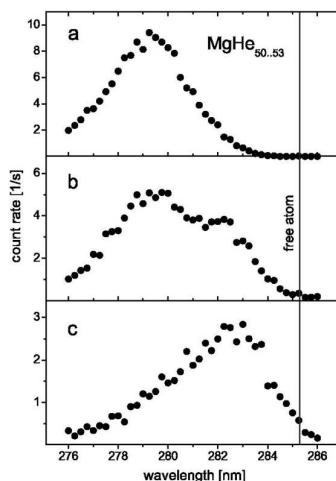


FIG. 2. R2PI spectra of magnesium doped helium droplets consisting of 6000 atoms detected on the Mg monomer mass channel [15] at different doping conditions. With fewer than one Mg atom on average [panel (a)] the spectrum shows a single maximum centered at 279 nm. At a higher doping with two Mg atoms per droplet, an additional structure at 282.5 nm appears [panel (b)]. Increasing the mean number of Mg atoms to 4 [panel (c)] the peak at 279 nm vanishes and the absorption around 282.5 nm becomes dominant.

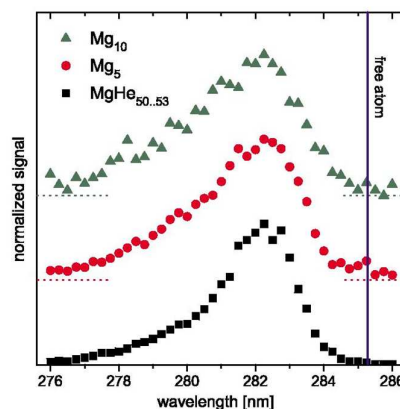
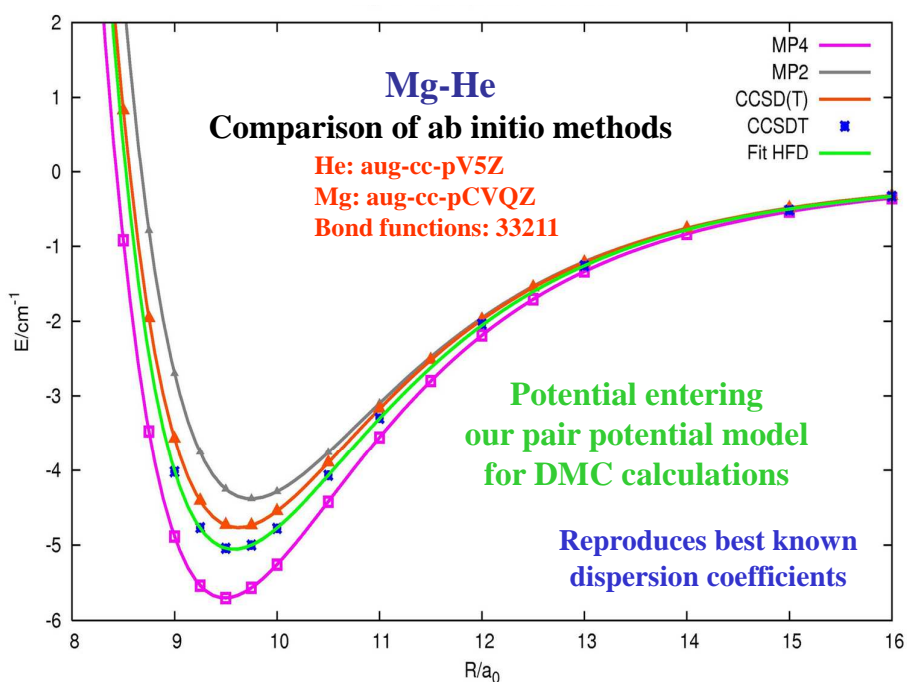


FIG. 3. (Color online) R2PI spectra of helium droplets consisting of 40 000 atoms doped with an average of 8 Mg atoms for different mass channels. The high similarity to the monomer spectrum recorded at the same conditions implies that all species originate from the same atomic precursor.

Przystawik et al.
Phys. Rev. A 78, 021202(R) (2008)

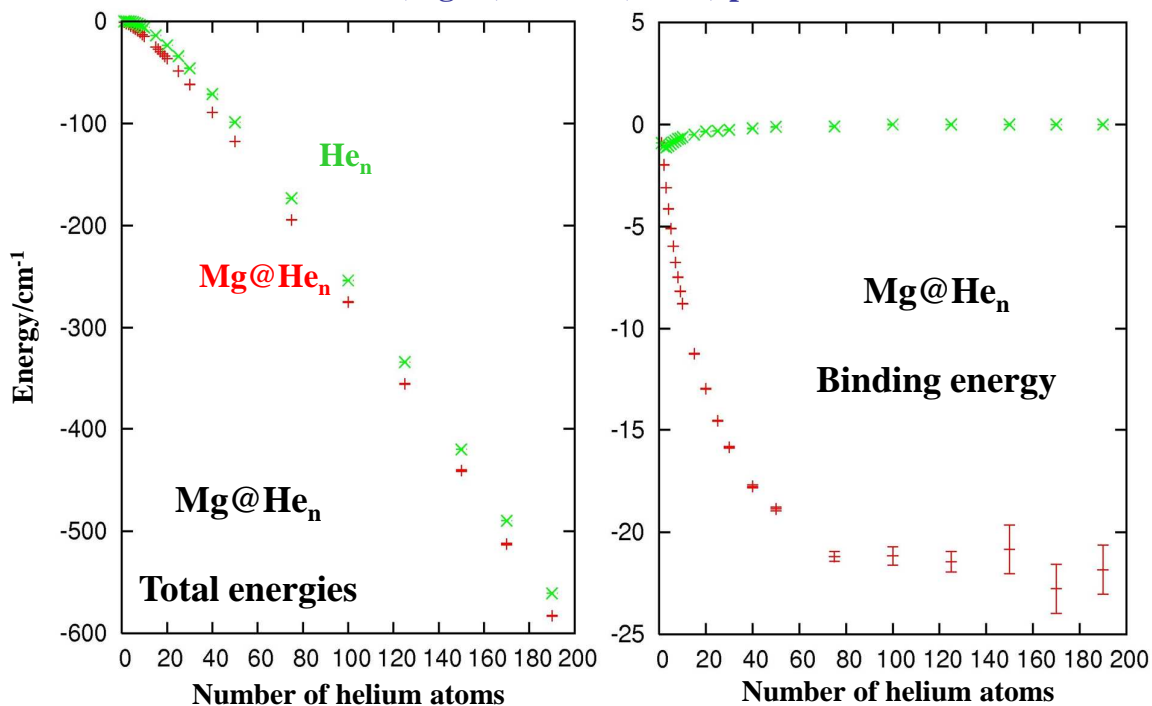
Mg-He $1\Sigma^+$ electronic ground state calculations

Best explicitly calculated CCSDT potential essentially confirms Hinde's 2003 extrapolation



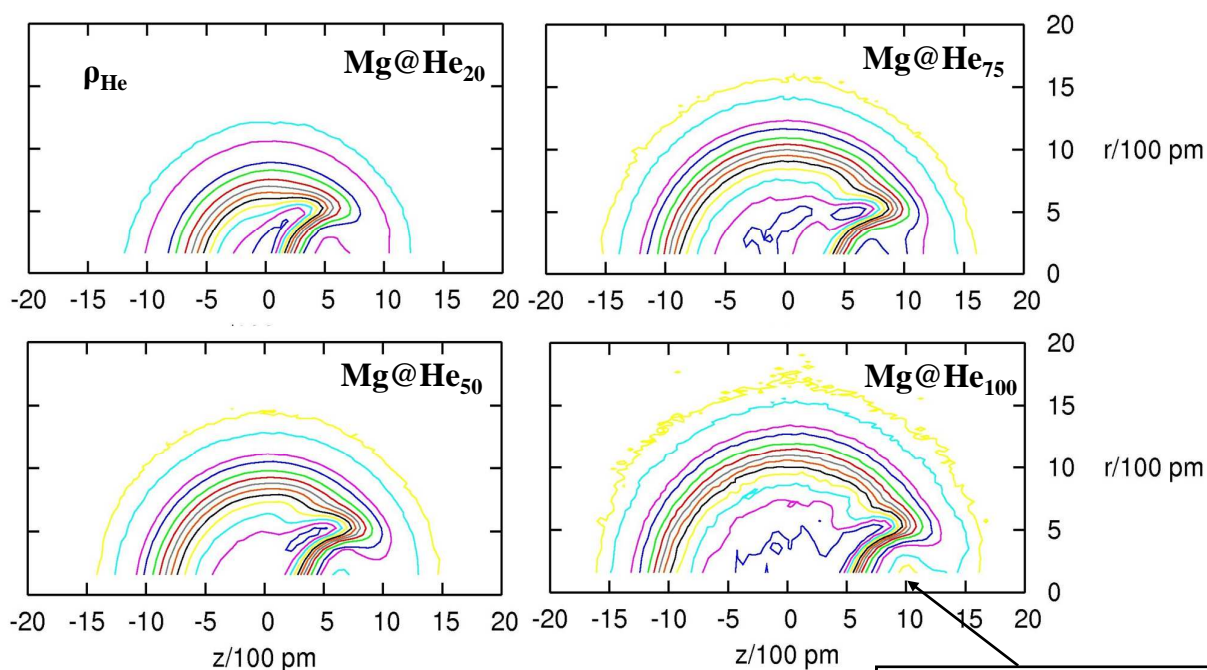
DMC results: total and binding energies

CCSDT(MgHe)+HFDB(HeHe) potential



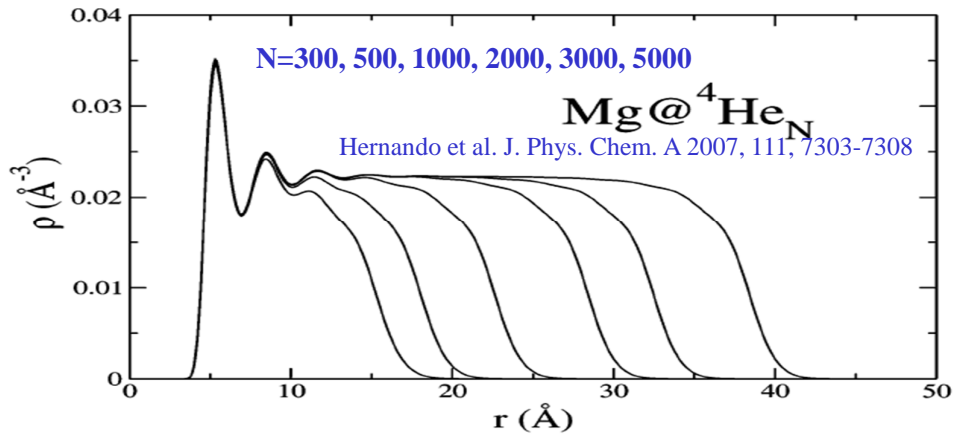
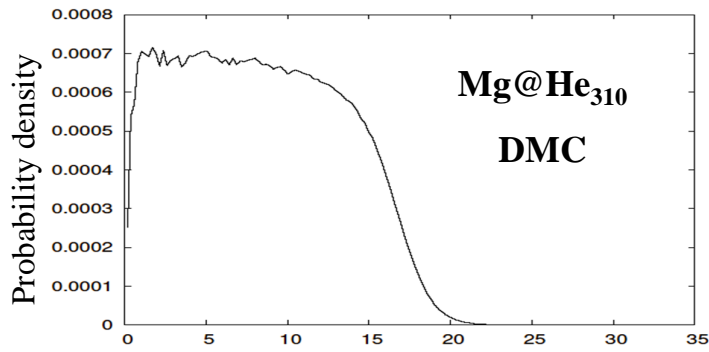
DMC: He density contours in cylinder coordinates

(descendent weighting)



Hole in He density: Mg

Radial helium density profiles for Mg@He_n

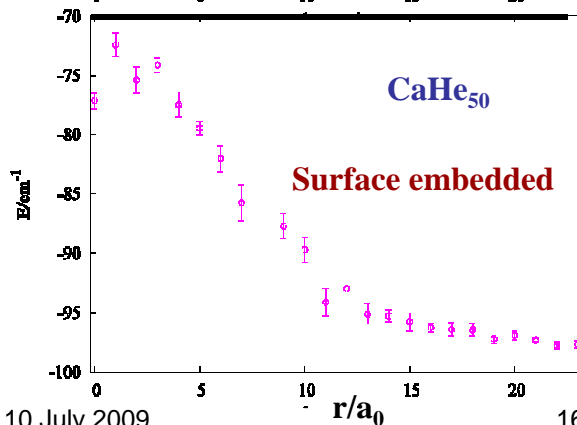
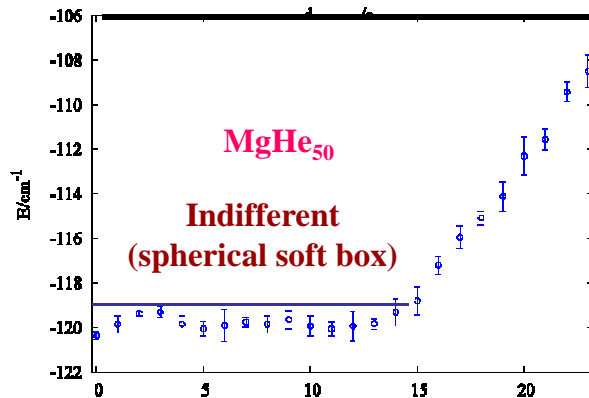
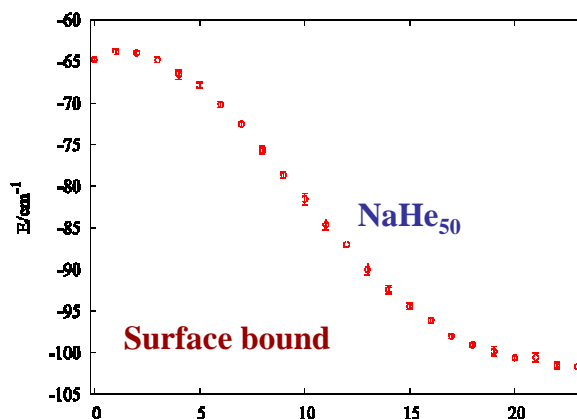
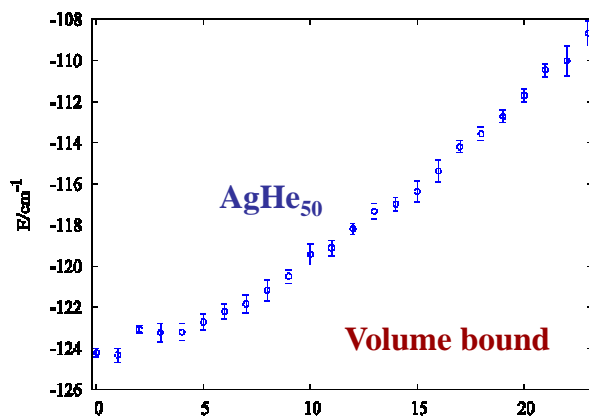


Marius Lewerenz

U. Leicester, 10 July 2009

15

DMC calculation with radial constraint



Marius Lewerenz

U. Leicester, 10 July 2009

16

Quantum gel of neon atoms in liquid helium

DFT, J. Eloranta, Phys. Rev. B 77, 134301 (2008)

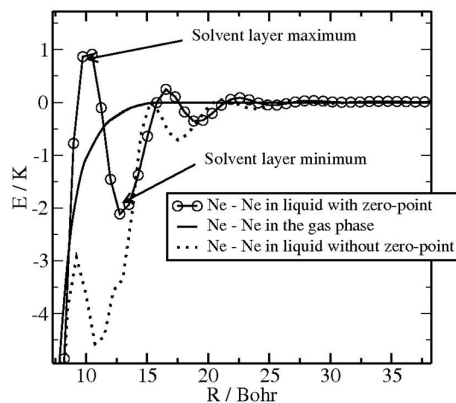


FIG. 1. Ne-Ne pair potentials in the gas phase (solid line) and in superfluid ^4He (circles with zero point; dotted without zero point) as a function of atomic distance are shown.

**Check this for Mg with DMC
(distance constraint Mg-Mg)
and the ZPAD method (diffusion rate etc.)**

Marius Lewerenz

U. Leicester, 10 July 2009

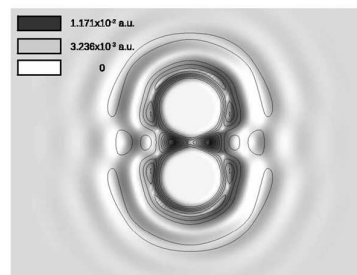
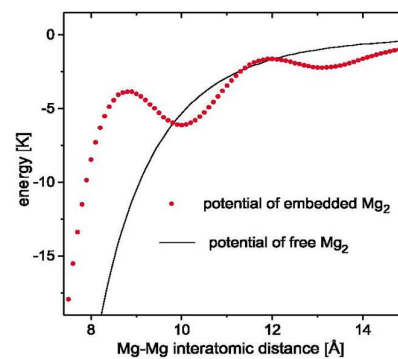
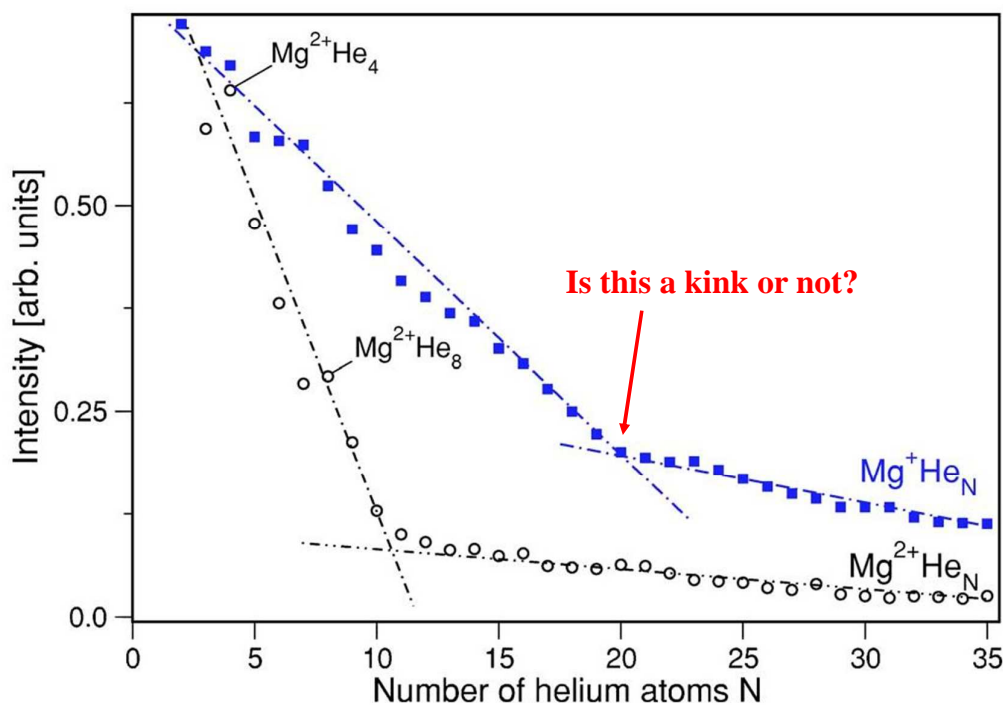


FIG. 3. 2D contour plot of superfluid helium density at the solvent layer minimum geometry for Ne-Ne. Note that a ring of solid helium exists around the neck of the molecular axis. The data shown in Fig. 2 correspond to a one-dimensional cut along the axis.



Mg^{q+}He_n mass spectra after fs pulse ionisation

Döppner et al. 2007



Marius Lewerenz

U. Leicester, 10 July 2009

18

DMC calculations for Mg^+He_n

Isotropic interaction, moderate non-additivity:

$^2\Sigma^+$ ground state potential for $\text{Mg}^+ (3s^1)$ - He interaction
(RCCSD(T)/core correlation/infinite basis extrapolation)
from **T. G. Wright, A. Gardner (unpublished)**.

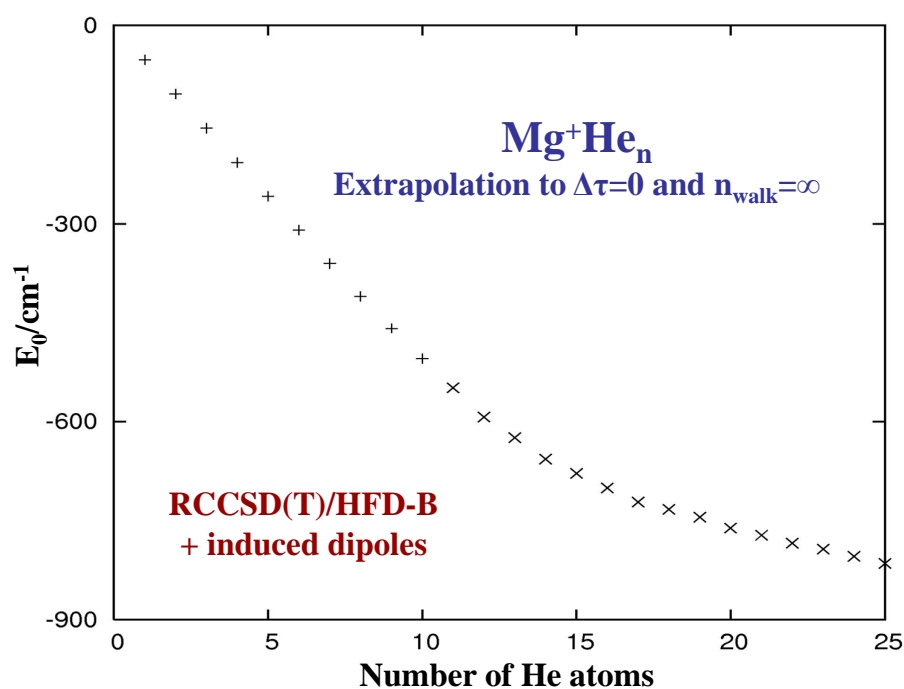
Ab initio points fitted to **HFD-style analytical form** with
fixed C_4 coefficient computed from $\alpha_{\text{He}} = 1.41 \text{ a}_0^3$.

Standard van der Waals He-He potential.

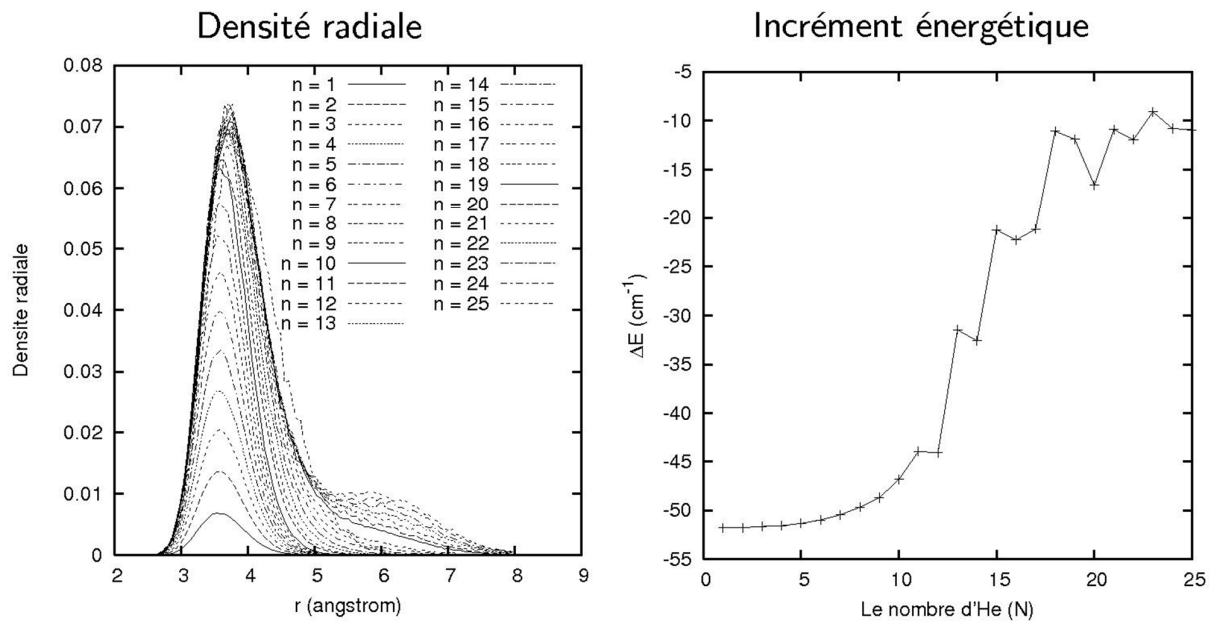
Additional interaction between **induced dipoles** on He atoms.

Optimised trial wave functions with correct permutational
symmetry.

DMC ground state energies for Mg^+He_n



DMC radial density and energy for Mg^+He_n



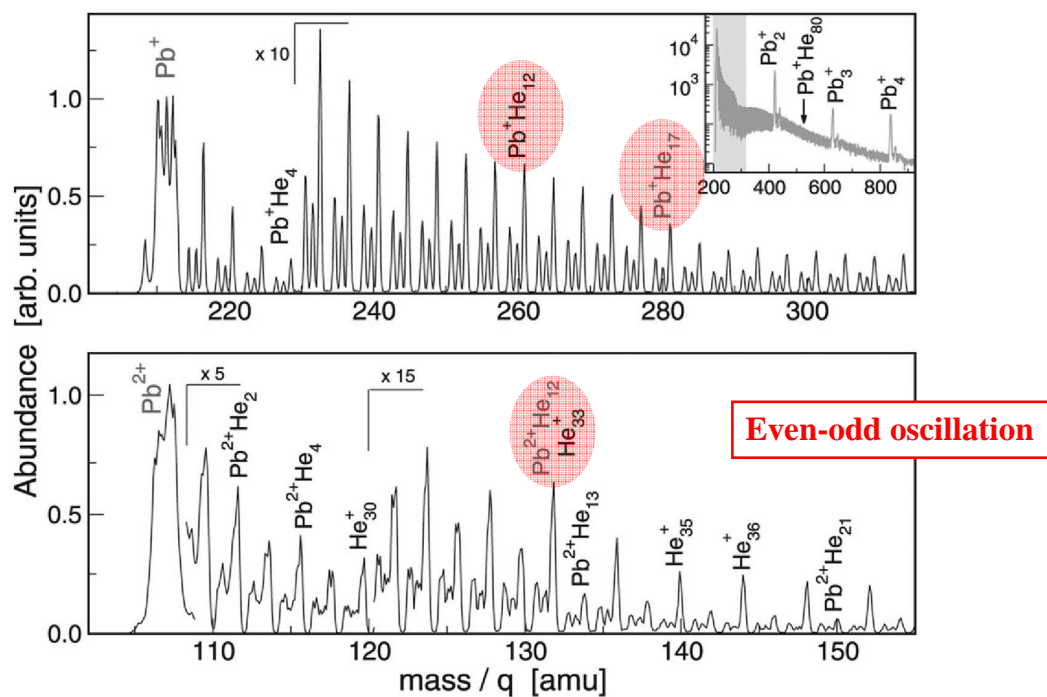
Marius Lewerenz

U. Leicester, 10 July 2009

21

$\text{Pb}^{q+}\text{He}_n$ mass spectra after fs pulse ionisation

Döppner et al. 2007



Marius Lewerenz

U. Leicester, 10 July 2009

22

Coordination in the Gas Phase

The Search for the Species with the Highest Coordination Number**

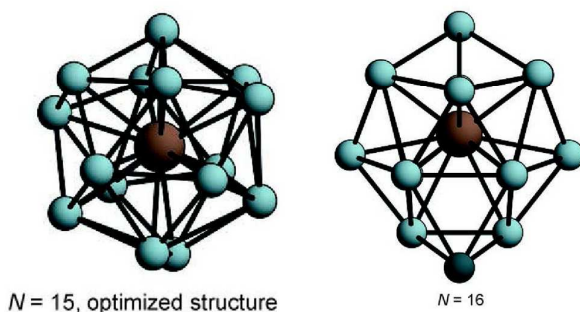
Andreas Hermann, Matthias Lein, and Peter Schwerdtfeger*

The question of the highest possible coordination number for an atom is addressed as this is related to the Gregory–Newton problem of kissing hard spheres.^[1] Using first-principles quantum chemical simulations we show that the interaction of Pb^{2+} with He atoms results in remarkably stable PbHe_{15}^{2+} with 15 atoms in the first coordination sphere forming a Frank–Kasper polyhedron.^[2] The Pb–He distances do not change significantly by subsequent filling of the first coordination shell as one expects for a hard-sphere model. Such high coordination numbers have been proposed only in liquid simulations so far.^[3]

The problem of how many spheres (N_{max} , called the kissing number or Newton number) of a given radius R can be

conjunction with coordination numbers higher than 12 stabilized by the surrounding matrix.^[2]

Herein we take a different approach. We look for a single molecule MX_N in the gas phase of high coordination number N which can be experimentally verified. We choose a large positively charged central atom, $\text{M} = \text{Pb}^{2+}$, and a very small ligand, $\text{X} = \text{He}$. Both atoms have reasonably small polarizabilities ($\alpha_{\text{He}} = 1.38 \text{ au}^{[10]}$ and $\alpha_{\text{Pb}^{2+}} = 14.1 \text{ au}^{[11]}$), and therefore fit the hard-sphere model quite well. The ionization potential of Pb^+ (15.03 eV) is much smaller than that of He (24.58 eV).^[12] Hence, Pb^{2+} –He does not undergo a Coulomb explosion and there is no (or minimal) charge transfer from He to Pb^{2+} . Hence the Pb^{2+} –He interaction $V(R)$ is mainly of



N = 15, optimized structure

N = 16

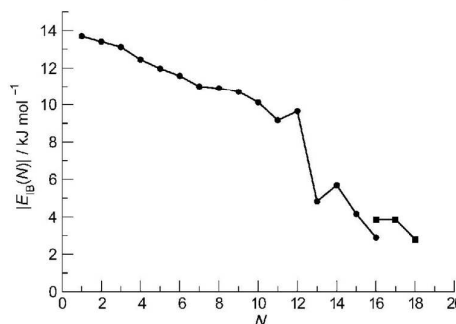


Figure 4. E_B for PbHe_N^{2+} . Circles: minima of one-shell structures; squares: minima of two-shell structures.

Marius Lewerenz

U. Leicester, 10 July 2009

23

DMC calculations for $\text{Pb}^q + \text{He}_n$ **$\text{Pb}^{2+}\text{He}_n$:**

Isotropic Pb^{2+} - He interaction (Pb^{2+} s^2 valence shell, Pb^{2+} -He $X^1\Sigma^+$).

Induced dipoles on He, He-dipoles induce a noticeable dipole on Pb^{2+} :

Non additive many body potential model checked against ab initio.

 Pb^+He_n :

Anisotropy due to Pb^+ s^2p valence shell $\rightarrow X^2\Pi$ and $A^2\Sigma^+$ states for Pb^+He .

Strong **spin-orbit interaction** in Pb^+ ($\Delta = 14081 \text{ cm}^{-1}$):

Non additive many body potential model including induced dipoles on He with additional spin-orbit mixing included using atomic Δ_{Pb^+}

(complex 6 x 6 matrix to diagonalise in each DMC step).

CCSD(T) calculations with Stuttgart pseudopotentials for both systems in collaboration with Petr Slavíček.

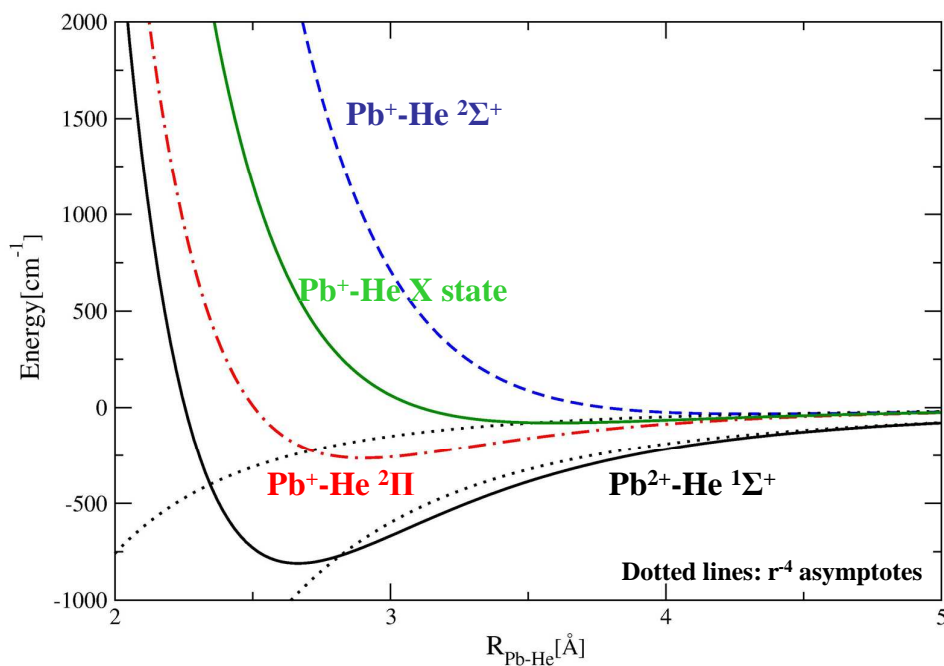
> 10^9 DMC samples, large ensemble sizes to suppress ensemble size bias

Marius Lewerenz

U. Leicester, 10 July 2009

24

Pair interaction potentials for Pb^q+He_n

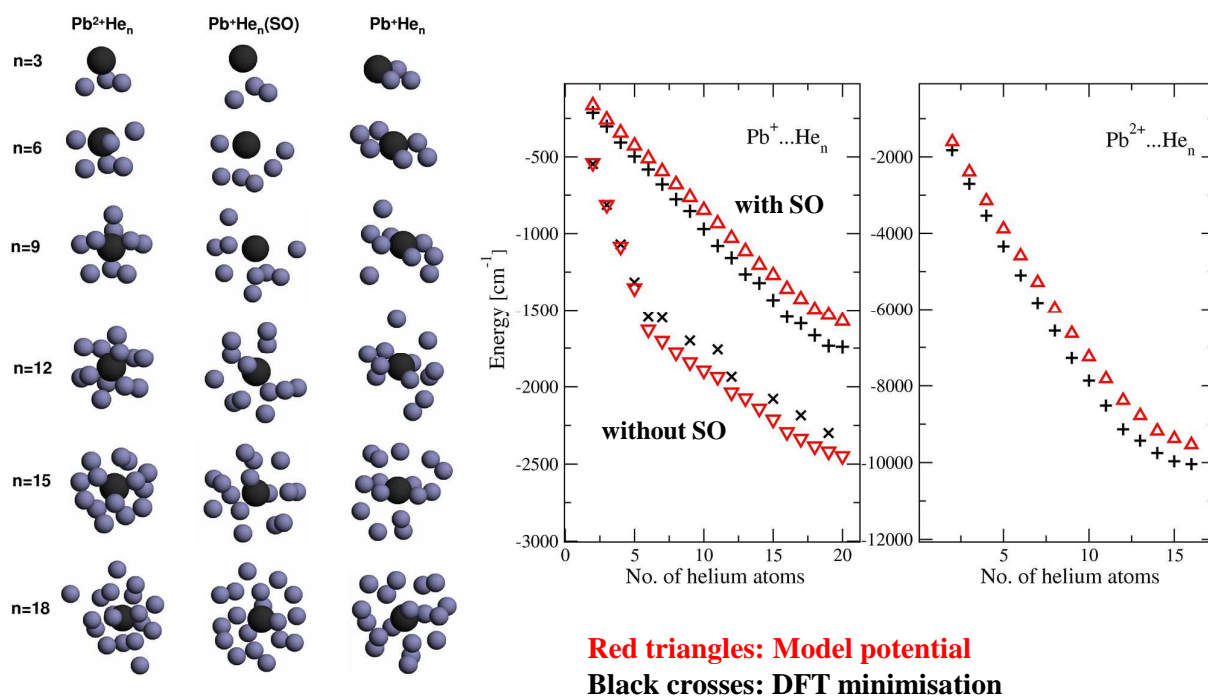


Marius Lewerenz

U. Leicester, 10 July 2009

25

Minimum energy structures for Pb^q+He_n

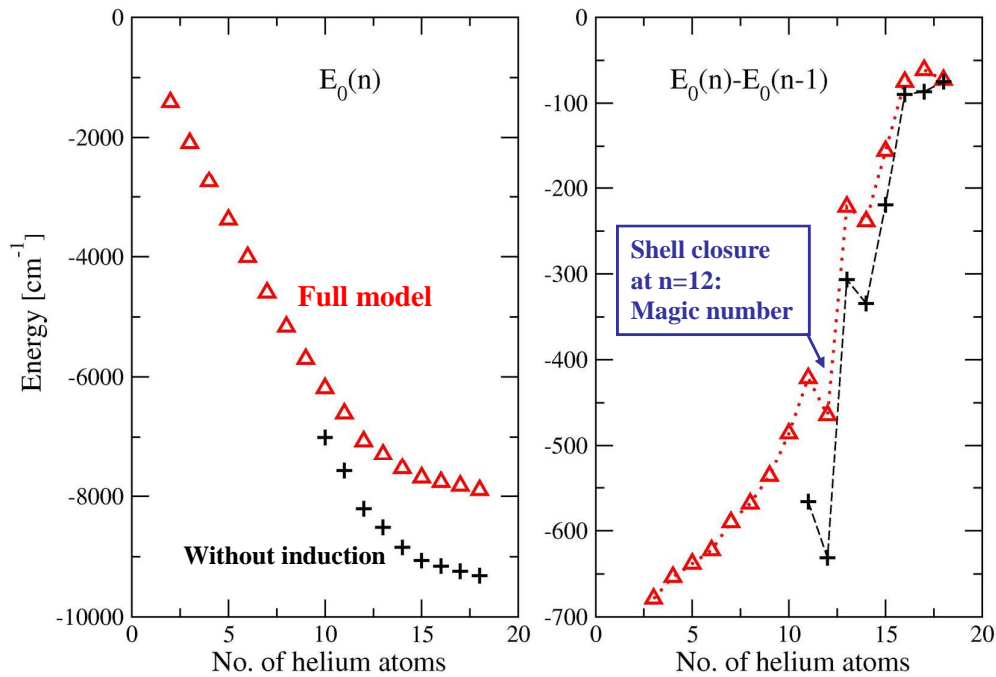


Marius Lewerenz

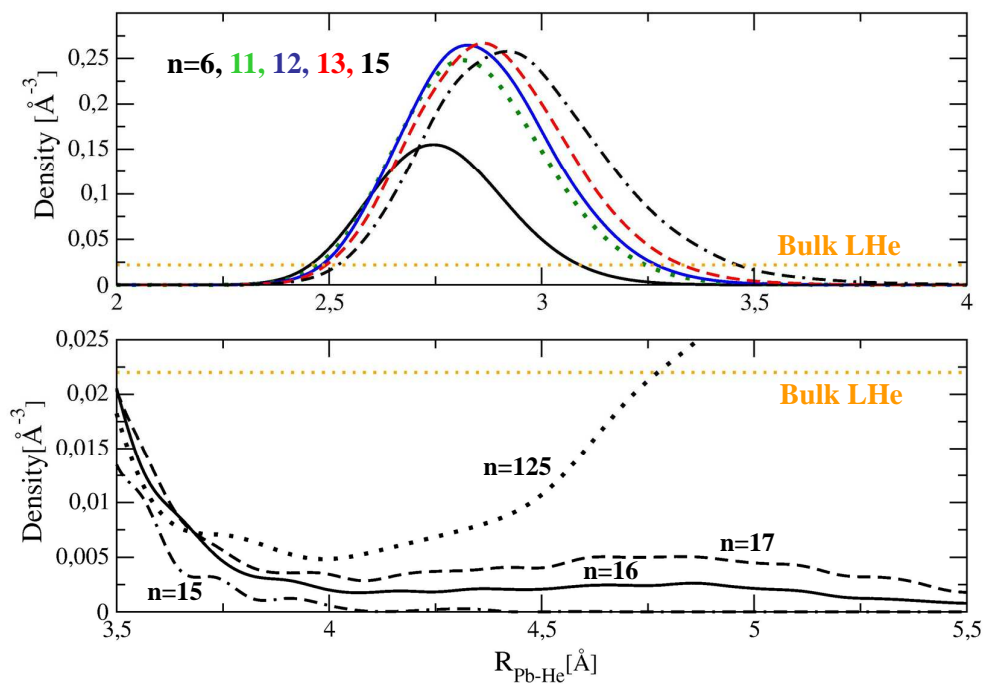
U. Leicester, 10 July 2009

26

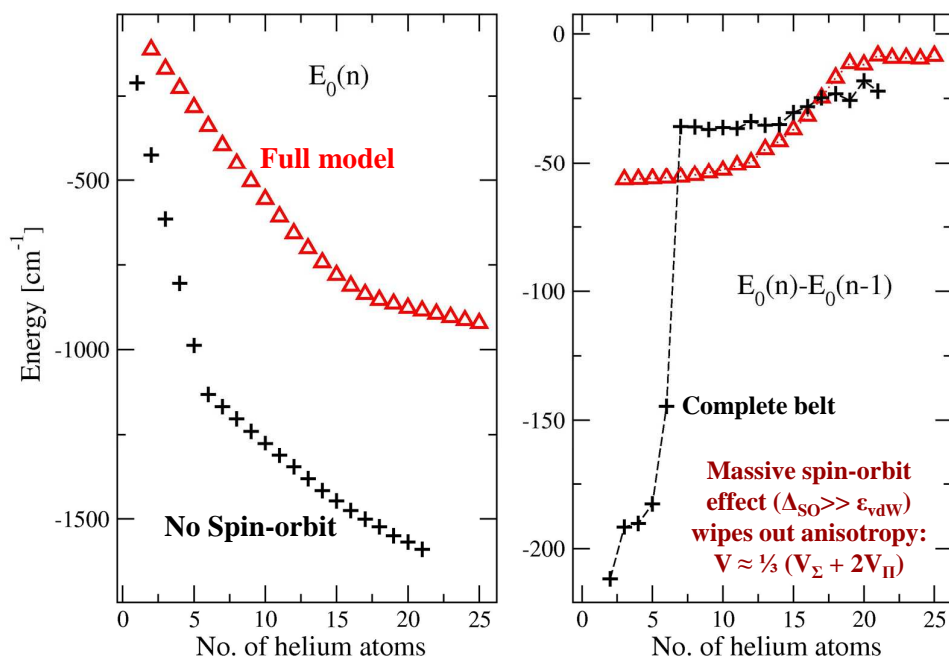
DMC ground state energies for $\text{Pb}^{2+}\text{He}_n$



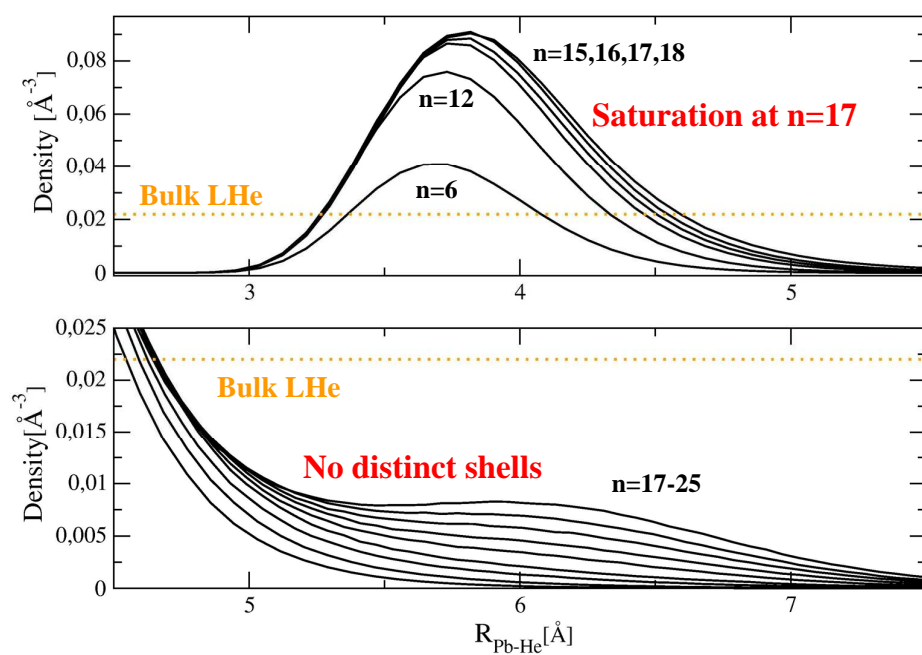
Radial densities for $\text{Pb}^{2+}\text{He}_n$



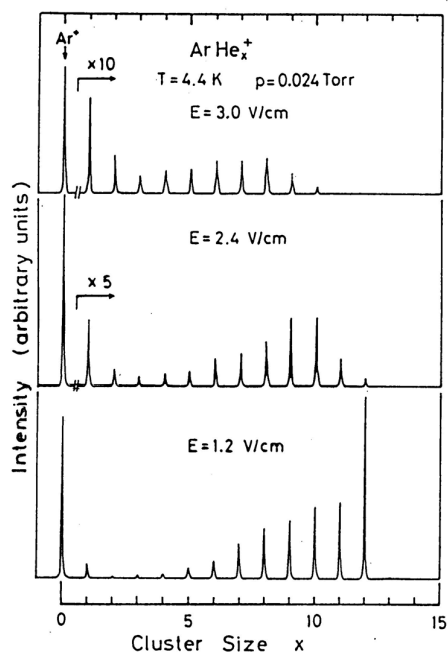
Ground state energies for Pb^+He_n



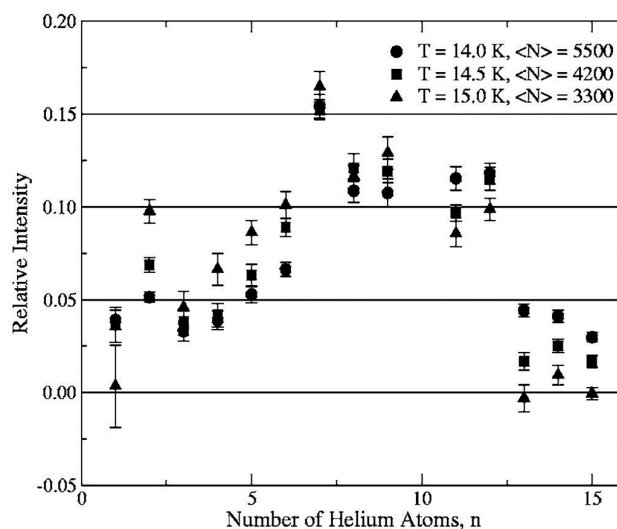
Radial densities for Pb^+He_n



Ar⁺He_n: Experimental evidence for shells



Drift tube experiment, Kojima et al. 1992



Fragmentation after ionisation of Ar@He_N,
Brindle et al. 2005

DMC calculations for Ar⁺He_n

Potential model:

Anisotropy due to Ar⁺ s²p⁵ valence shell → X²Σ⁺ and A²Π states for Ar⁺He.

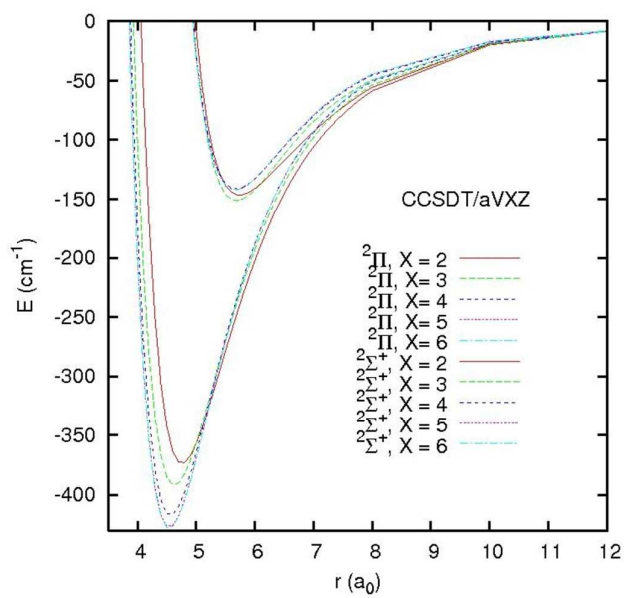
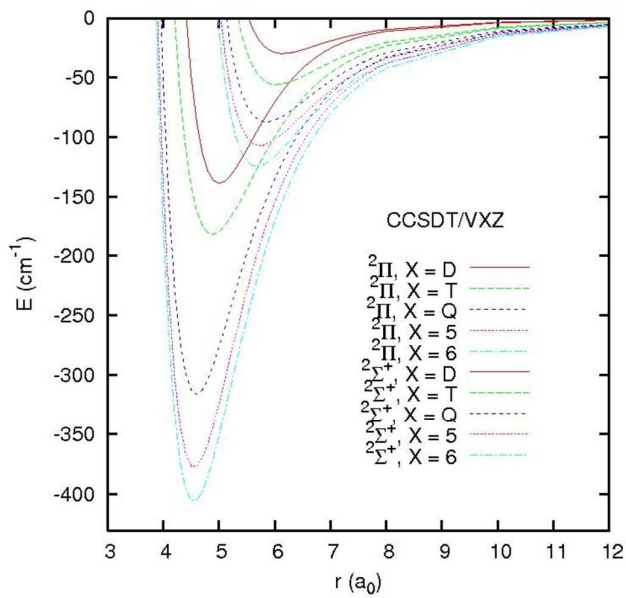
IP(Ar)=15.76 eV → He⁺+Ar channel is unimportant, single configuration.
CCSD(T) calculations with (aug)-cc-pVXZ basis sets.

Ab initio points fitted to HFD-style analytical form
with fixed C₄ coefficient computed from α_{He} = 1.41 a₀³.

Strong **spin-orbit interaction** in Ar⁺ (Δ = 1432 cm⁻¹):
Non additive many body potential model including induced dipoles on He
with additional spin-orbit mixing included using atomic Δ_{Ar+}
(**complex 6 x 6 matrix** to diagonalise in each DMC step).

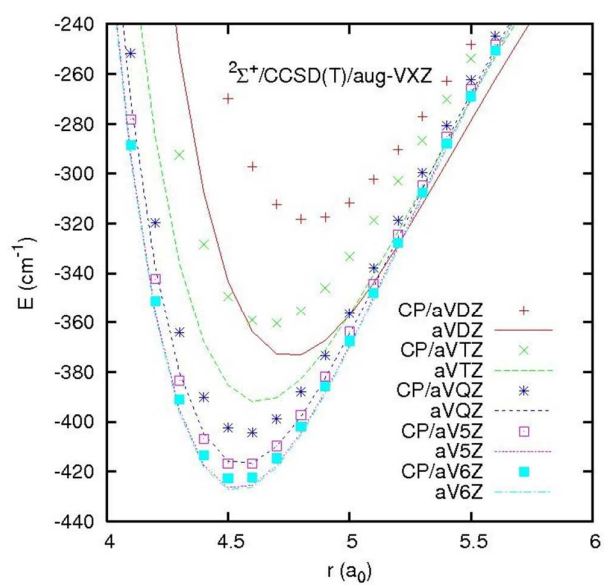
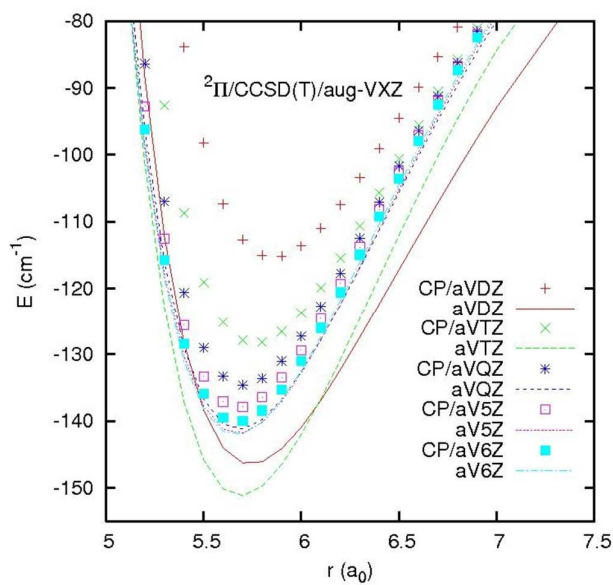
Ar⁺He: convergence of interaction energy

CCSD(T) calculation



Ar⁺He: BSSE counterpoise correction

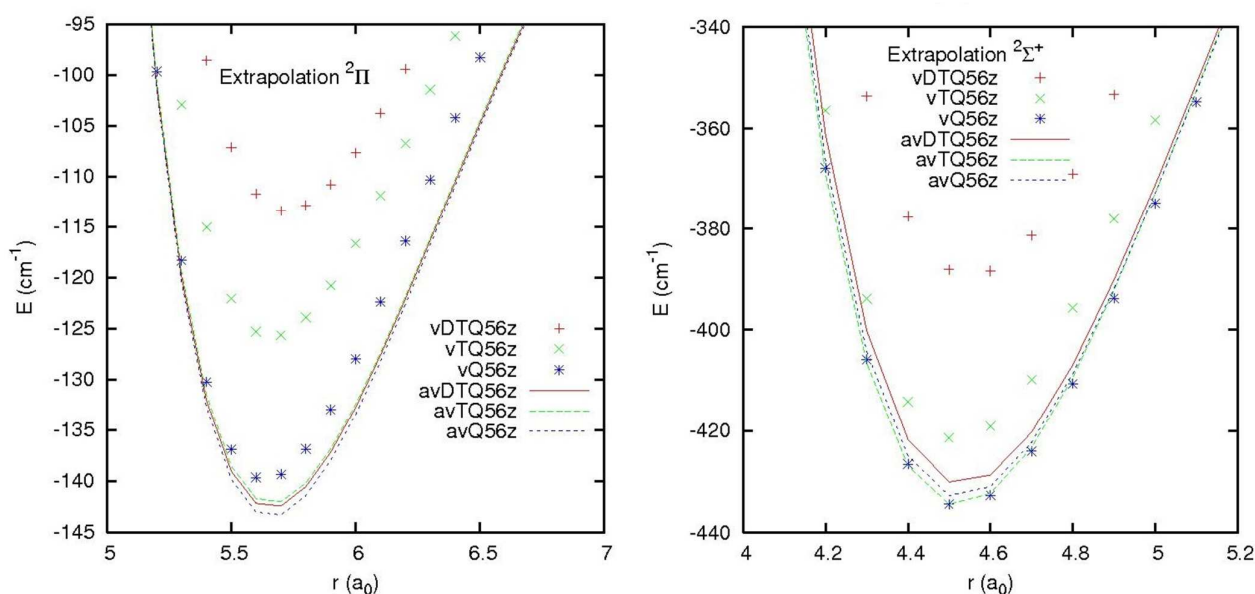
CCSD(T) calculation



Unsatisfactory convergence for $^2\Pi$ state, $^2\Sigma^+$ looks ok but

Ar⁺He: basis set extrapolation

(aug)-cc-pVXZ series, SCF: exponential, CCSD(T) correlation X⁻³



Augmented series is much more stable, remaining mismatch for ²Π state

Ar⁺He: spectroscopic observables

extrapolated potentials (aQ56), atomic spin-orbit splitting, variational rovibrational calculation in Laguerre basis, ⁴He⁴⁰Ar⁺

Vibrational transition frequencies

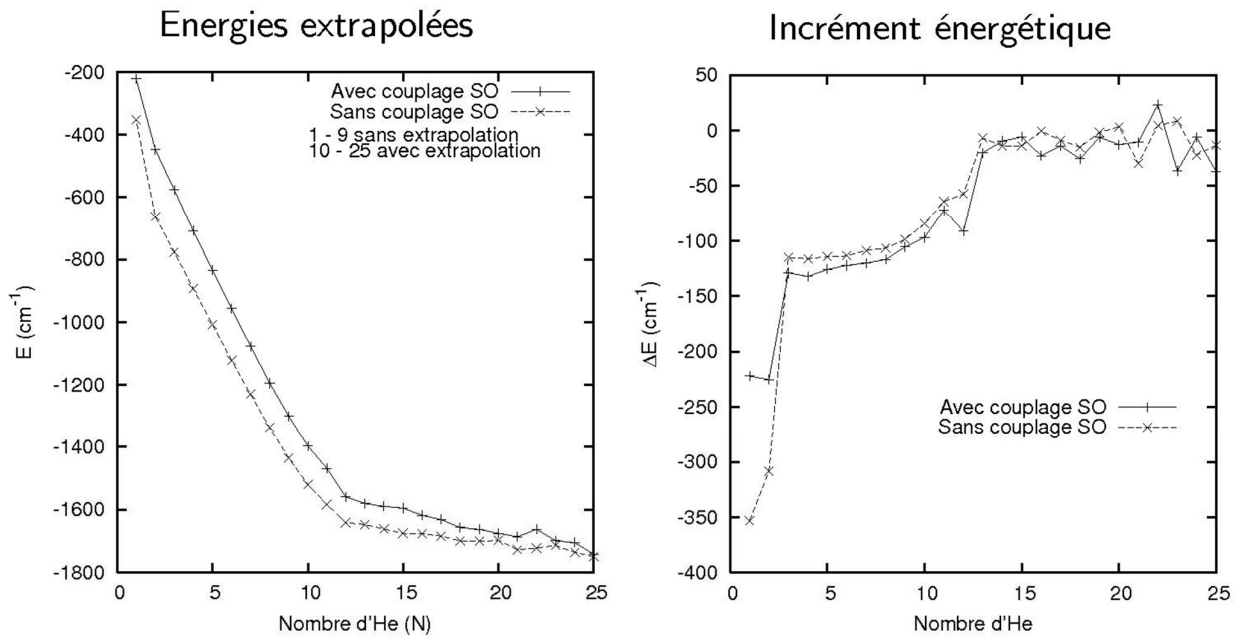
v	X ² Σ _{1/2} ⁺			A ₁ ² Π _{3/2}		A ₂ ² Π _{1/2}		
	exp	S96	Fit	S96	Fit	exp	S96	Fit
0	92.9	83.9	92.47	52.9	55.91	69.2	64.0	69.19
1	66.2	55.2	64.88	26.9	29.20		35.1	38.82
2		30.7	38.55	11.9	11.73		15.7	17.59
3		14.1	17.81					

Expectation values for rotational constants

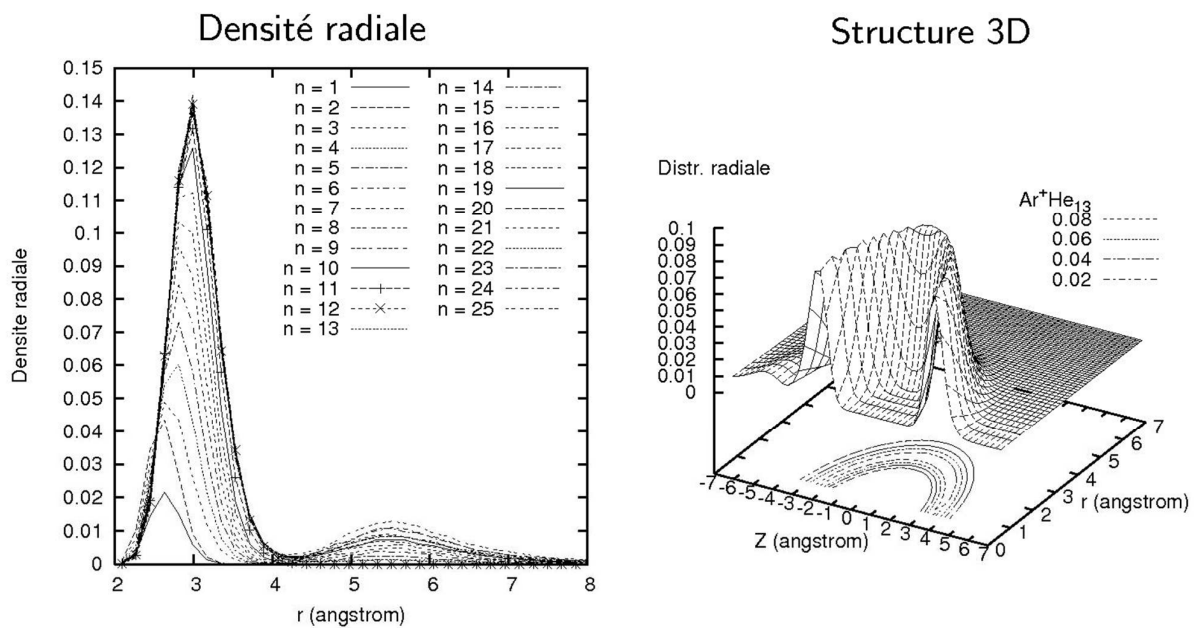
0	0.659	0.614	0.650	0.460	0.469	0.515	0.501	0.514
1	0.551	0.518	0.559	0.355	0.365	0.420	0.397	0.412
2	0.39	0.404	0.450	0.241	0.255		0.282	0.298
3		0.282	0.324	0.168	0.087		0.182	0.180
4		0.182	0.196					

Our Ar⁺He potential is excellent !

Ar⁺He: DMC ground state energies



Ar⁺He: ground state radial density



Conclusion

- DMC code with new features for constraints and treatment of spin-orbit coupled electronic states.
- **Mg@He_n is special**, structural debate largely closed, association dynamics still requires further studies.
- **Mg⁺He_n**: no snowball, soft build up of density.
- Coordination number 15 for **Pb²⁺** not robust with respect to quantum effects; softening of 1st solvation shell.
- Spin-orbit coupling has profound effect on stability pattern for **Pb⁺@He_n**, no clear shell separation.
- **Ar⁺He_n**: distinct shell closure in agreement with experiments, somewhat affected by spin-orbit coupling

Outlook

- Analyse inhibited/incomplete formation of Mg_n (constrained DMC and ZPAD).
- Dopant spectroscopy (Mg*, Ag*, Ag⁺ etc.).
- Transport properties (Mg⁺, Na⁺).
- DMC and ZPAD calculations on Xe_nHe_m.
- Photodissociation of CH₃I and CF₃I (ZPAD, DMC etc.)
- DMC with constraints ((H₂)_n, He_n(H₂)_m possible).

ANR project DYNHELIUM (Toulouse, Rennes, Paris)