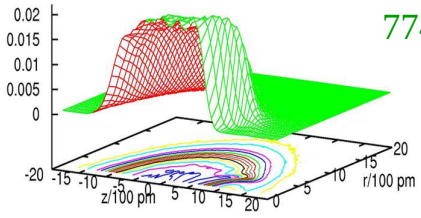
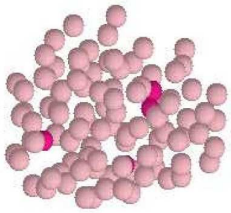
Stability, structure and dynamics of doped helium clusters from accurate quantum simulations

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Jiang Ji, Masters student, $Mg^+@He_n$, $Ar^+@He_n$

Prague:
Prof. Petr Slavíček, $Pb^{q+}@He_n$

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, $D_e \approx 7.6\ cm^{-1}$**
- **Helium atoms have a relatively small mass.**
- **Large zero point energy effects (D_0 for $He_2 \approx 0.001\ cm^{-1}$).**
- **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?**

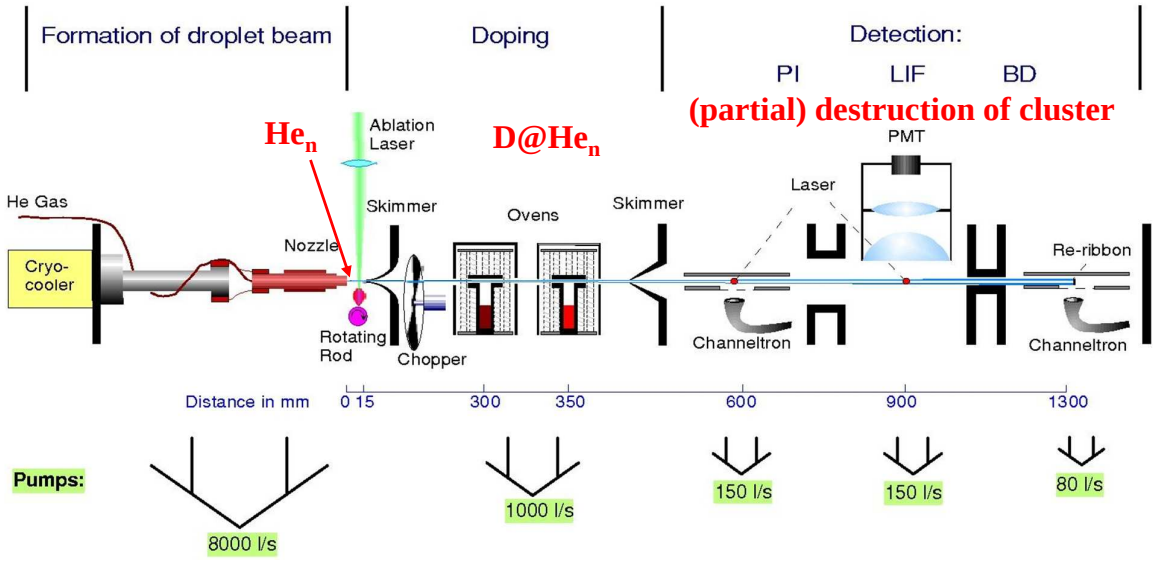
- **Implantation of dopants through (multiple) inelastic collisions.**
- **Weak interactions with dopant.**
- **Binding energy and position of dopants depend on quantum effects.**

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: $Ba + N_2O \rightarrow BaO + N_2$**
- **Preparation of reactive intermediates: $HF \cdots CH_3$, $HCN \cdots CH_3$ etc.**
- **Preparation of high spin metal polymers: Na_3, K_3, Rb_3 etc.**
- **Assembly of cold clusters: Ag_n, Mg_n**
- **Thermodynamically unstable isomers: linear $(HCN)_n$**
- **Nanomodels for molecule-surface interactions: $HCN \cdots Mg$ 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

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

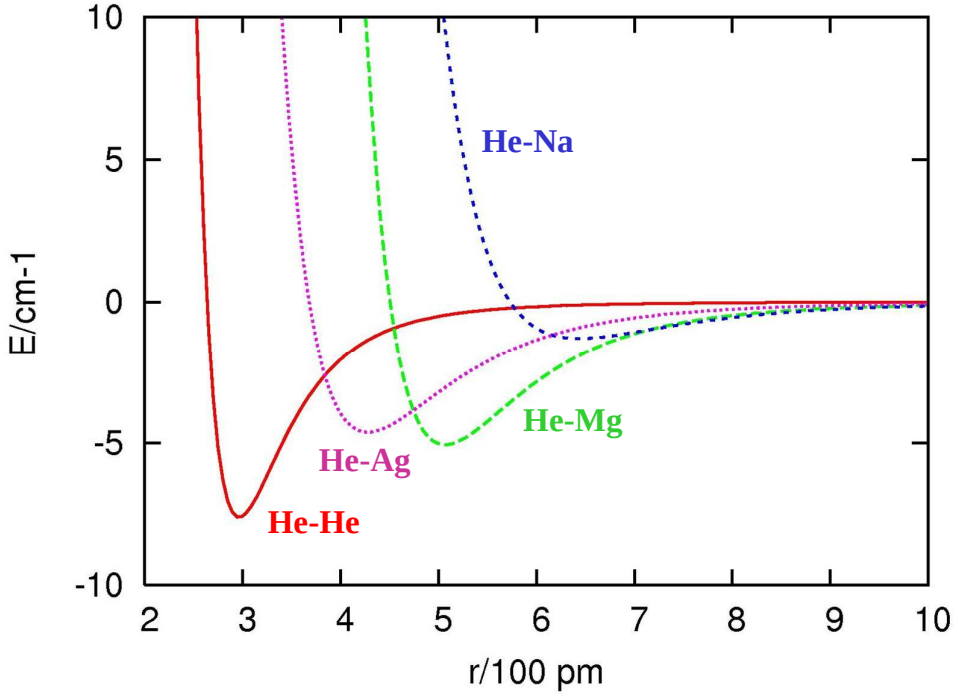
$$\frac{\partial C(\vec{r},t)}{\partial t} = \left\{\sum_{j=1}^{n} D_j\nabla_j^2 - k(\vec{r})\right\}C(\vec{r},t)\ .$$

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



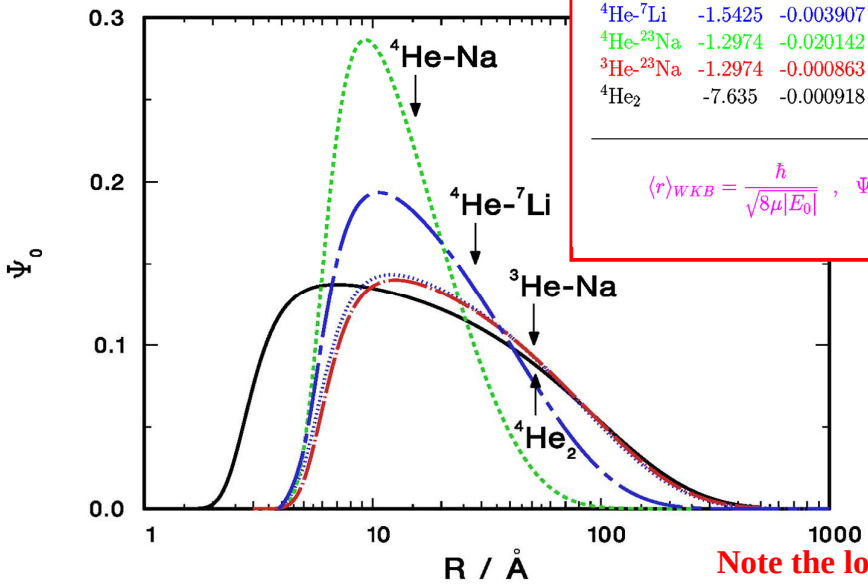
Alkali-helium dimers

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}He-^{6}Li	-1.5425	-0.001053	6.16	48.53	40.80	0.033457
^{4}He-^{7}Li	-1.5425	-0.003907	6.16	28.15	20.56	0.063601
^{4}He-^{23}Na	-1.2974	-0.020142	6.43	15.41	7.83	0.125440
^{3}He-^{23}Na	-1.2974	-0.000863	6.43	50.85	42.79	0.027745
^{4}He$_2$	-7.635	-0.000918	2.97	51.68	47.89	0.069649

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



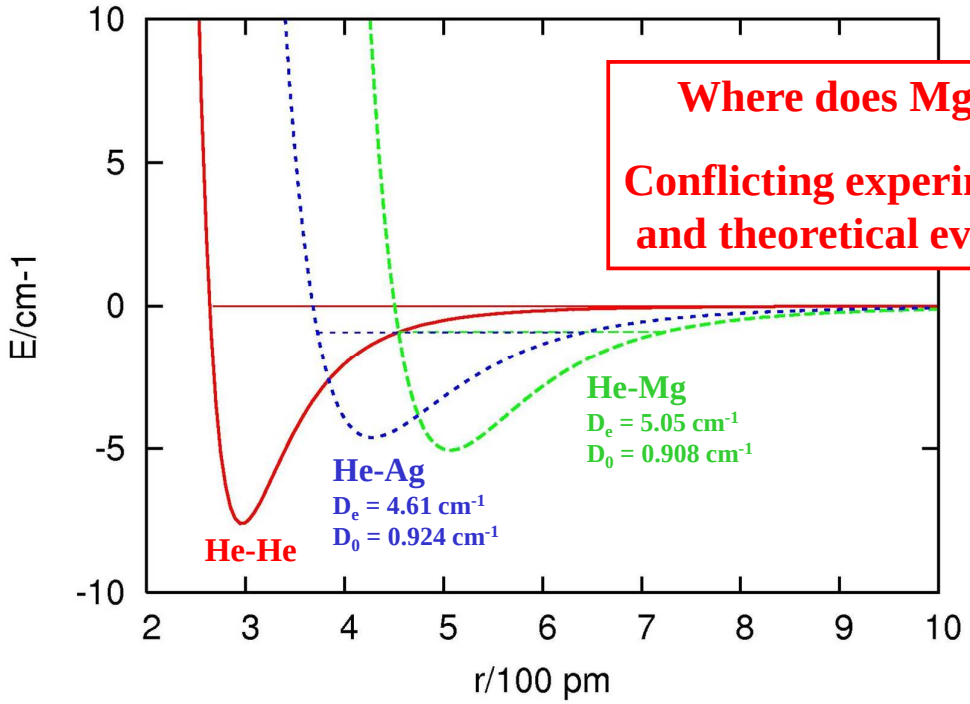
Predicted to be extremely weakly bound and diffuse

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

Incomplete aggregation of Mg atoms inside helium clusters?

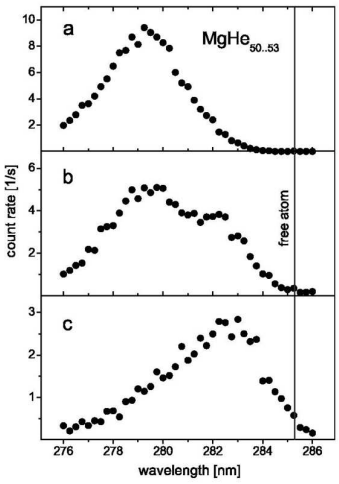


FIG. 2. R2PI spectra of magnesium doped helium droplets consisting of 6000 atoms detected on the Mg monomer mass channel [15] at different doping conditions. With fewer than one Mg atom on average [panel (a)] the spectrum shows a single maximum centered at 279 nm. At a higher doping with two Mg atoms 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.

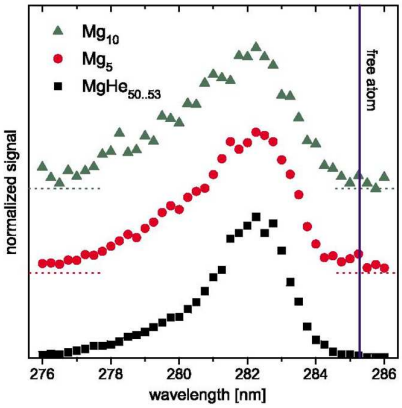
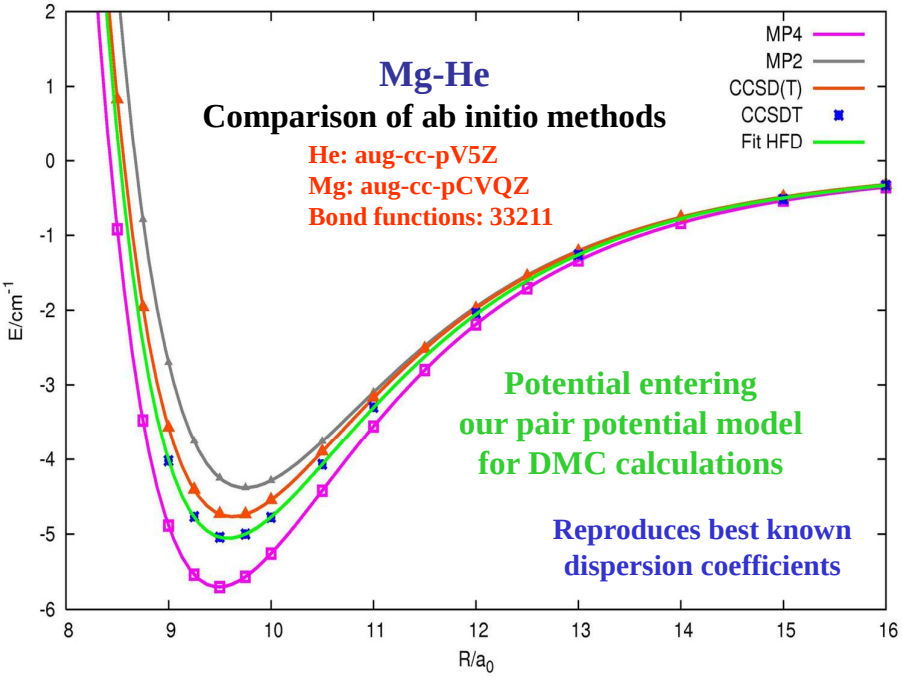


FIG. 3. (Color online) R2PI spectra of helium droplets consisting of 40 000 atoms doped with an average of 8 Mg atoms for different mass channels. The high similarity to the monomer spectrum recorded at the same conditions implies that all species originate from the same atomic precursor.

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

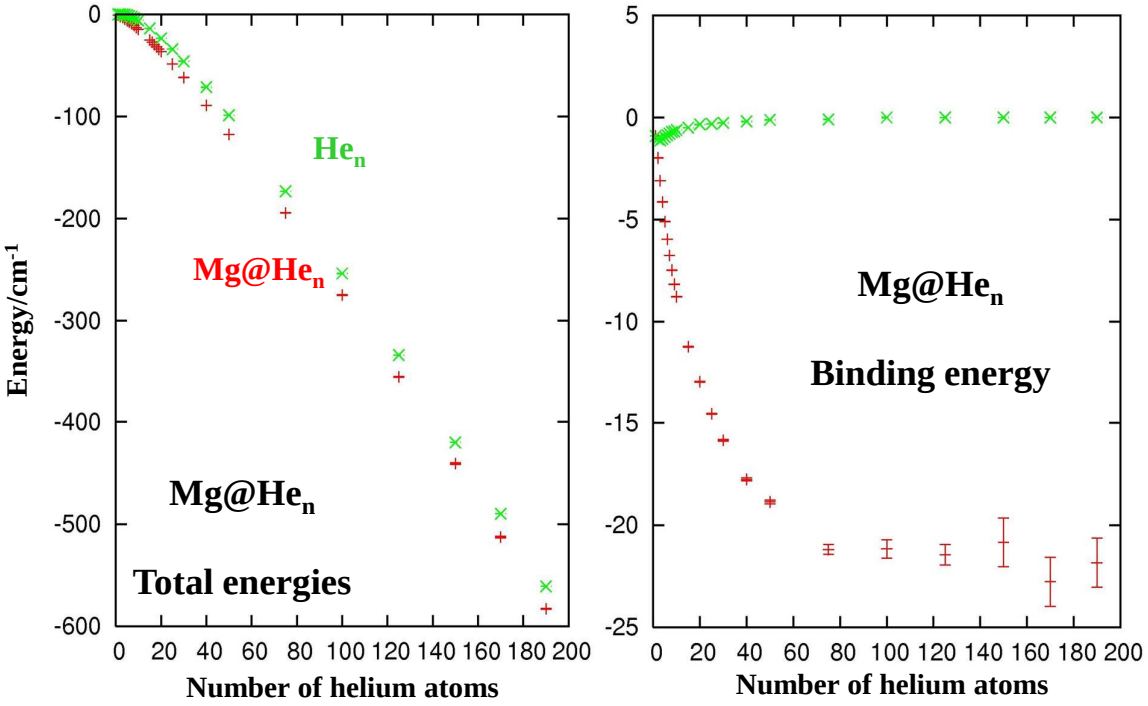
Mg-He $^1\Sigma^+$ electronic ground state calculations

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



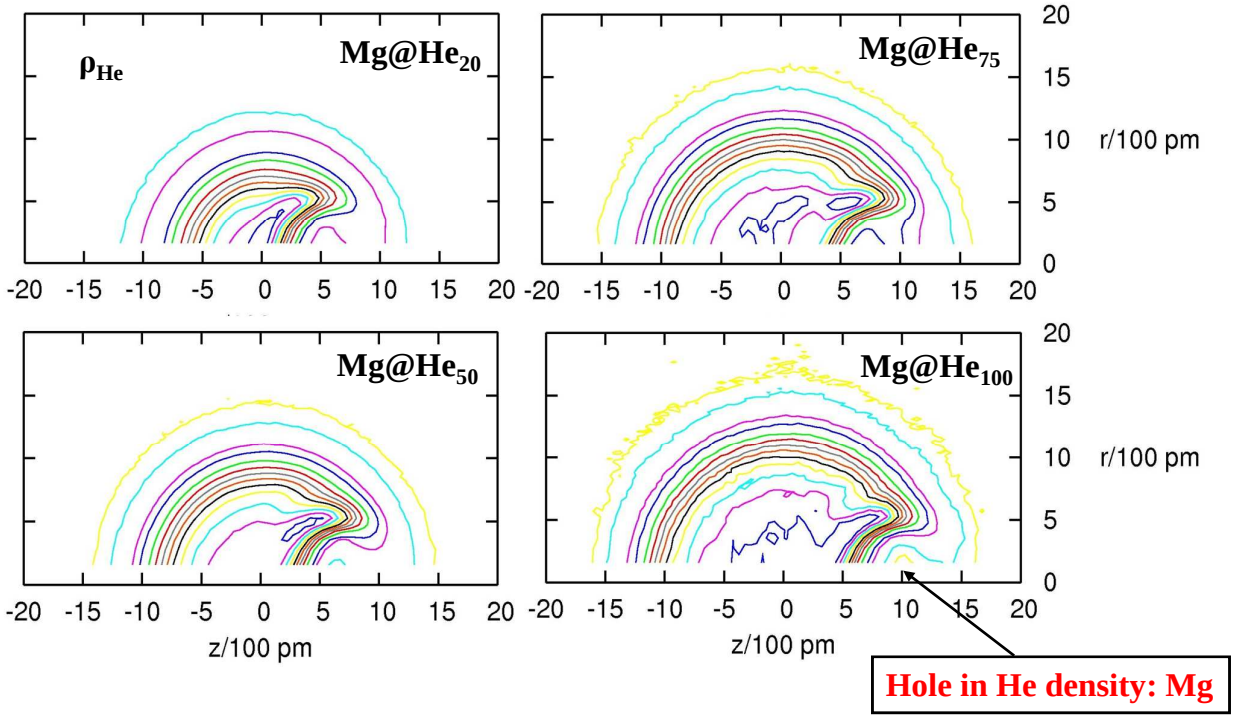
DMC results: total and binding energies

CCSDT(MgHe)+HFDB(HeHe) potential

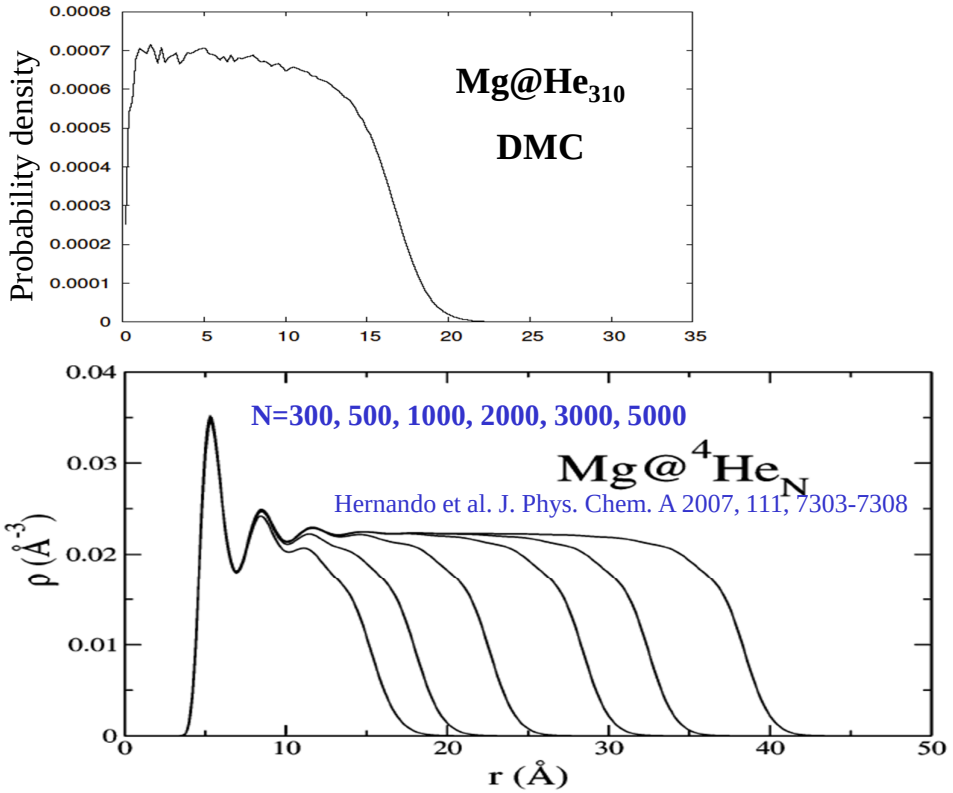


DMC: He density contours in cylinder coordinates

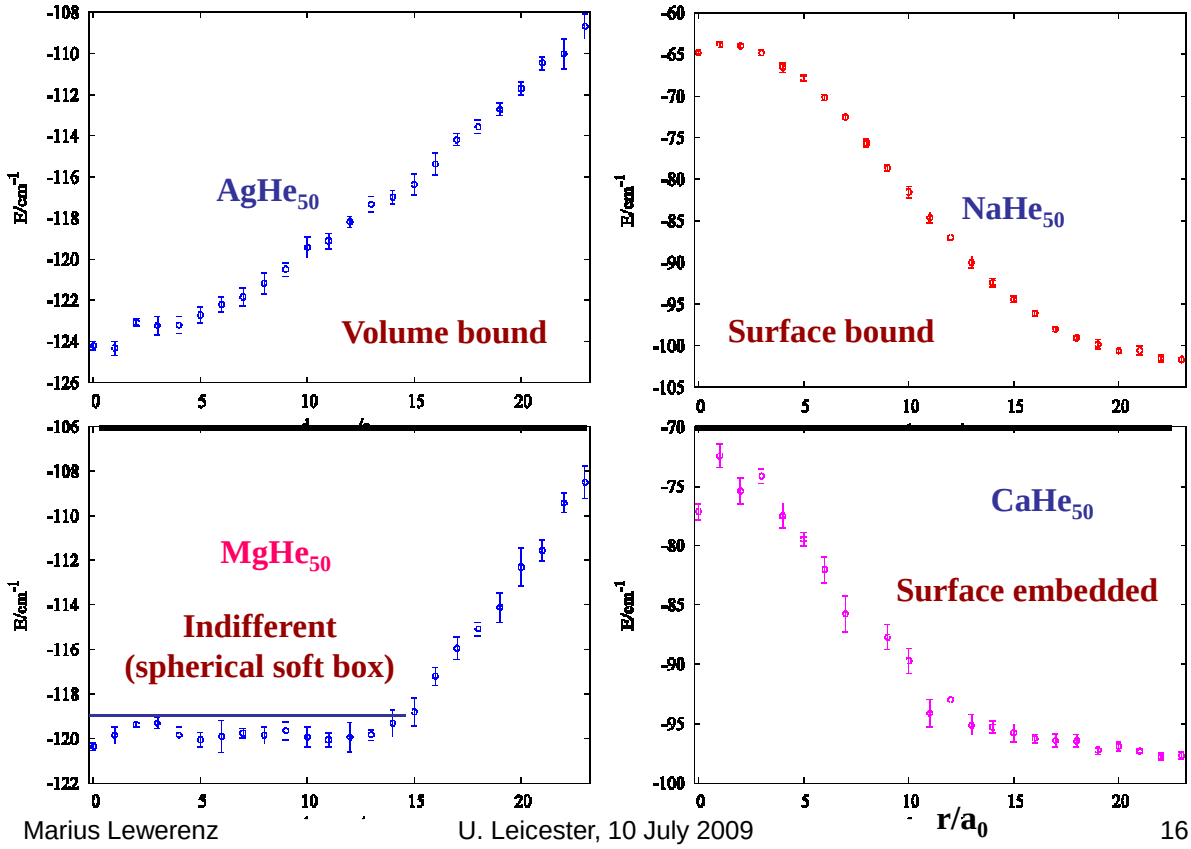
(descendent weighting)



Radial helium density profiles for $Mg@He_n$



DMC calculation with radial constraint



Quantum gel of neon atoms in liquid helium

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

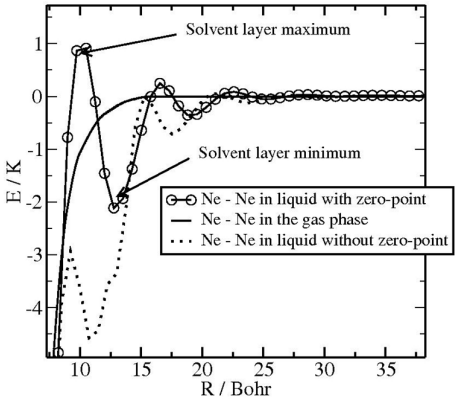


FIG. 1. Ne-Ne pair potentials in the gas phase (solid line) and in superfluid ^{4}He (circles with zero point; dotted without zero point) as a function of atomic distance are shown.

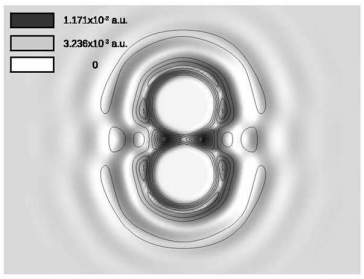
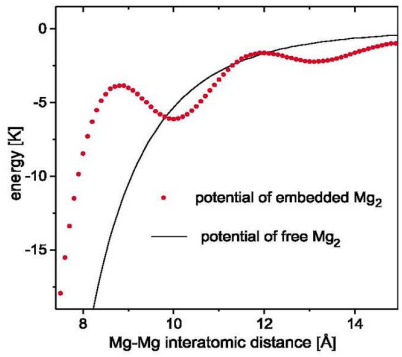


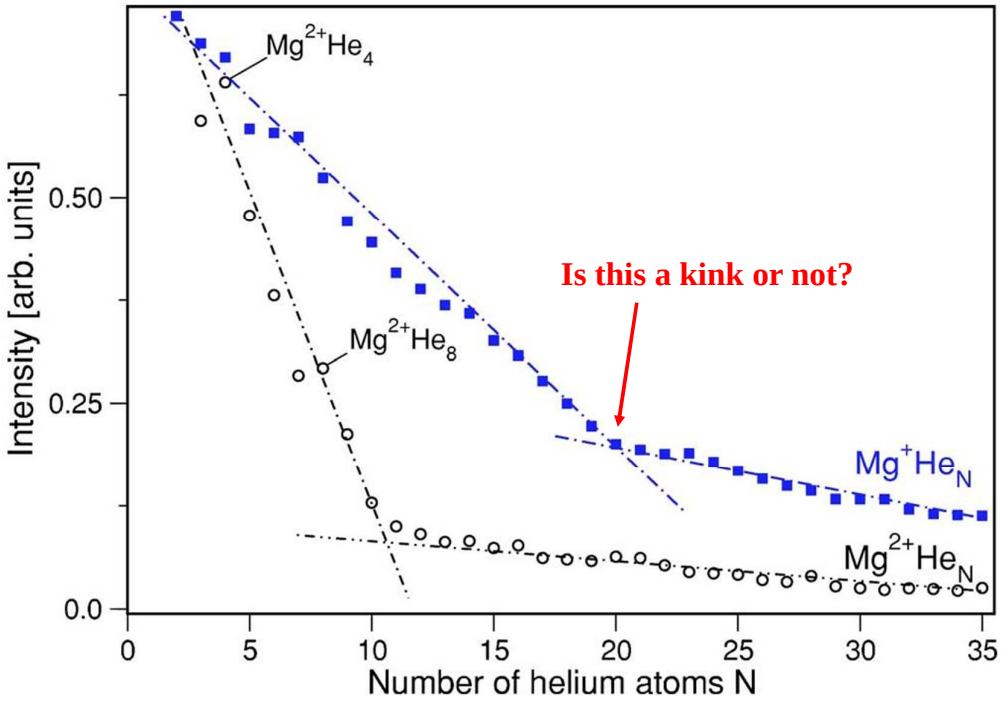
FIG. 3. 2D contour plot of superfluid helium density at the solvent layer minimum geometry for Ne-Ne. Note that a ring of solid helium exists around the neck of the molecular axis. The data shown in Fig. 2 correspond to a one-dimensional cut along the axis.

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



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

Döppner et al. 2007



DMC calculations for Mg^+He_n

Isotropic interaction, moderate non-additivity:

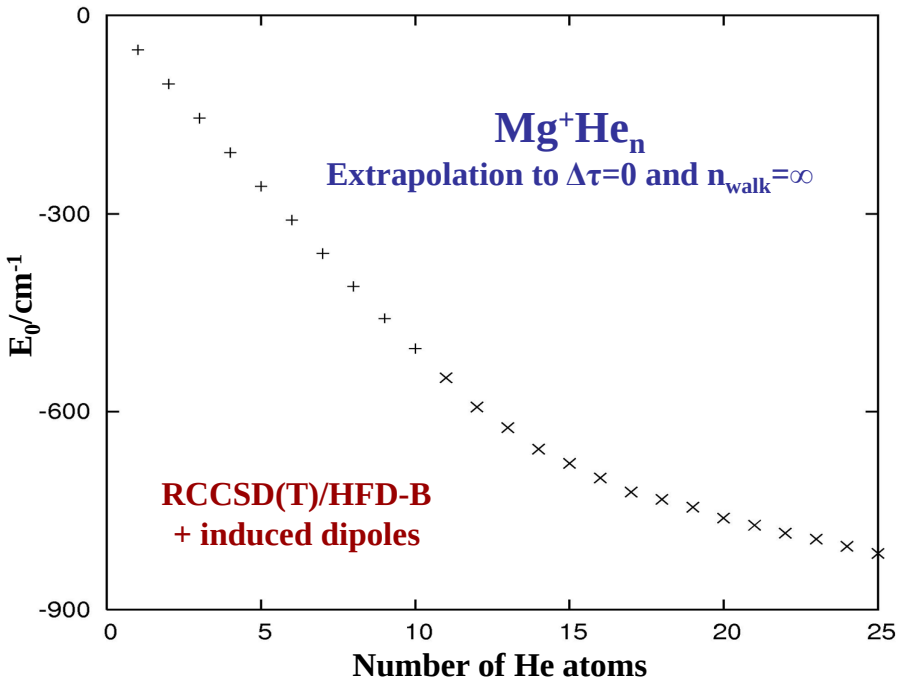
$^2\Sigma^+$ ground state potential for Mg^+ ($3s^1$) - He interaction (RCCSD(T)/core correlation/infinite basis extrapolation) from T. G. Wright, A. Gardner (unpublished).

Ab initio points fitted to HFD-style analytical form with fixed C_4 coefficient computed from $\alpha_{He} = 1.41\ a_0^3$.

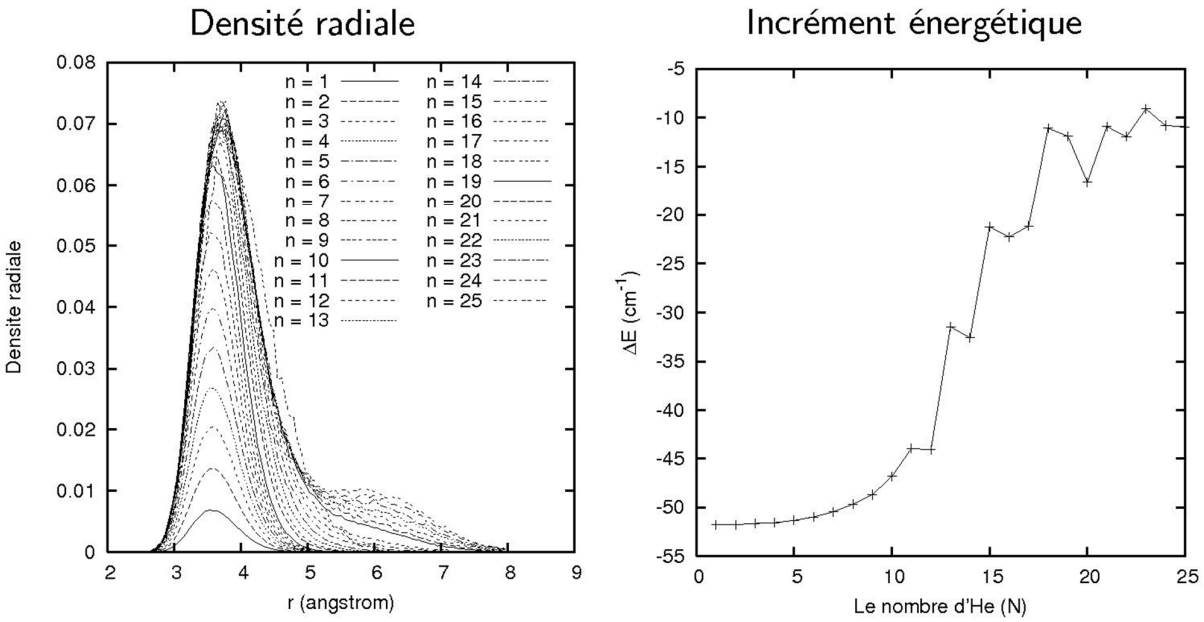
Standard van der Waals He-He potential.
Additional interaction between induced dipoles on He atoms.

Optimised trial wave functions with correct permutational symmetry.

DMC ground state energies for Mg^+He_n

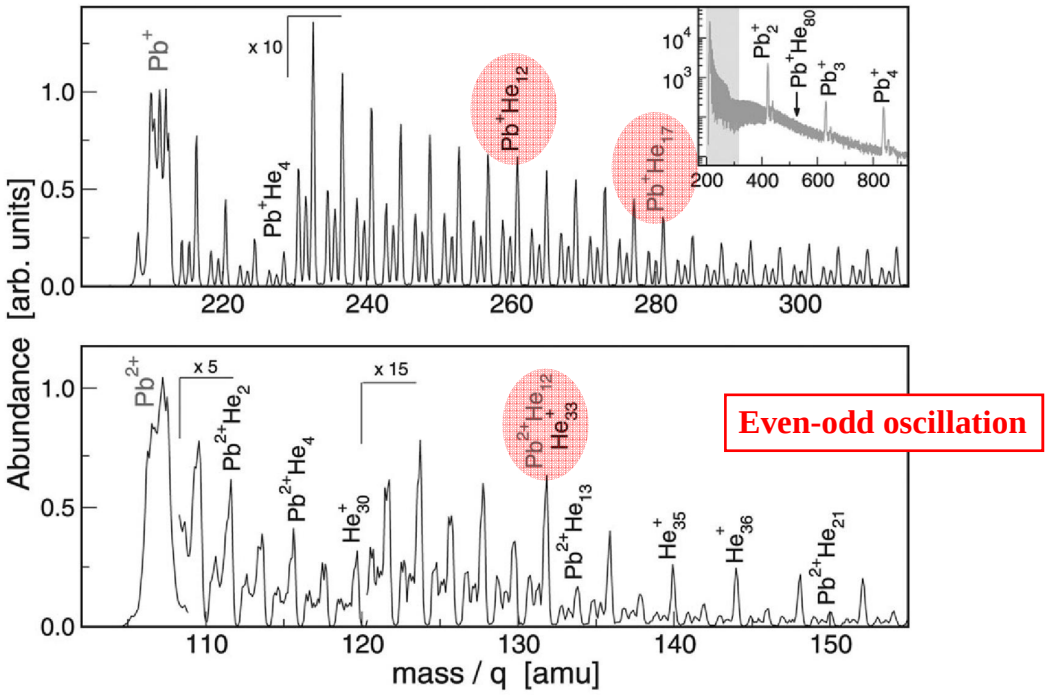


DMC radial density and energy for $Mg^{+}He_n$



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

Döppner et al. 2007



DOI: 10.1002/anie.200604148

Coordination in the Gas Phase

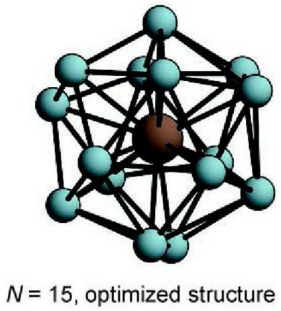
The Search for the Species with the Highest Coordination Number**

*Andreas Hermann, Matthias Lein, and Peter Schwerdtfeger**

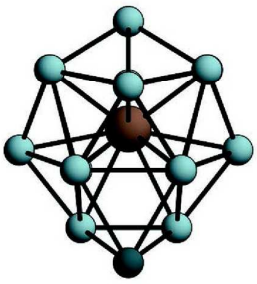
The question of the highest possible coordination number for an atom is addressed as this is related to the Gregory–Newton problem of kissing hard spheres.[1] Using first-principles quantum chemical simulations we show that the interaction of Pb^{2+} with He atoms results in remarkably stable $PbHe_{15}^{2+}$ 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, $M = Pb^{2+}$, and a very small ligand, X = He. Both atoms have reasonably small polarizabilities ($\alpha_{He} = 1.38$ au[10] and $\alpha_{Pb^{2+}} = 14.1$ 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



$N = 16$

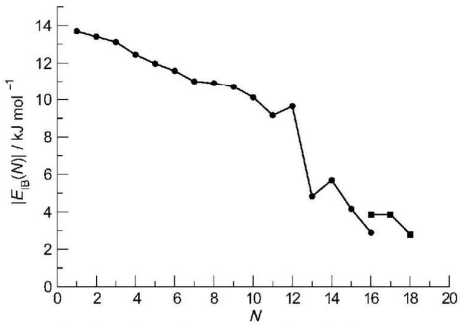


Figure 4. E_{IB} for $PbHe_N^{2+}$. Circles: minima of one-shell structures; squares: minima of two-shell structures.

DMC calculations for $Pb^{q+}He_n$

$Pb^{2+}He_n$:

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.

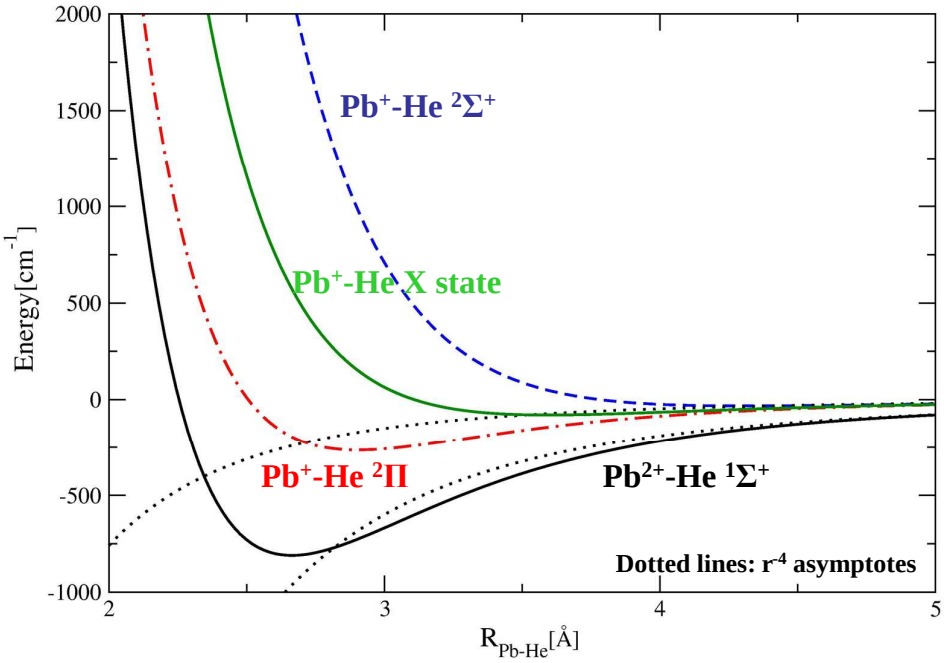
$Pb^{+}He_n$:

Anisotropy due to Pb^+ s^2p valence shell → $X^2\Pi$ and $A^2\Sigma^+$ states for Pb^+He.
Strong spin-orbit interaction in Pb^+ (Δ = 14081 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).

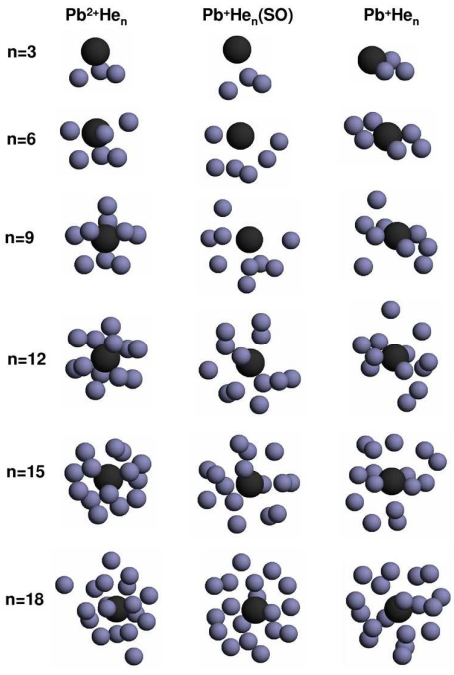
CCSD(T) calculations with Stuttgart pseudopotentials for both systems in collaboration with Petr Slavíček.

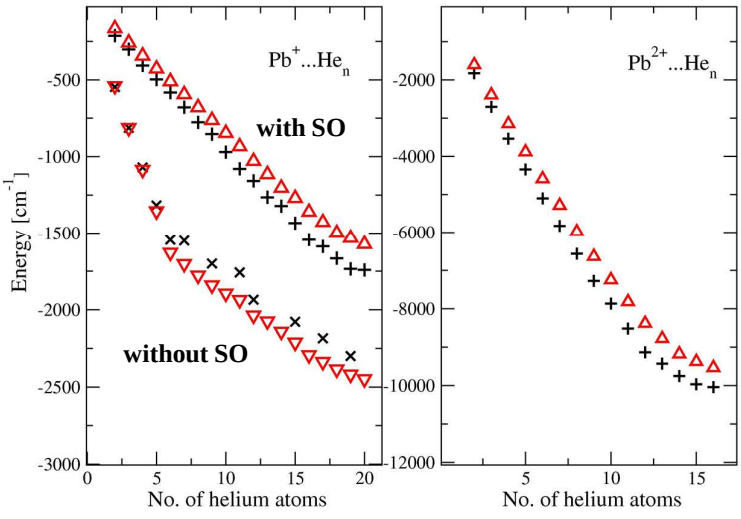
> 10^9 DMC samples, large ensemble sizes to suppress ensemble size bias

Pair interaction potentials for $Pb^{q+}He_n$



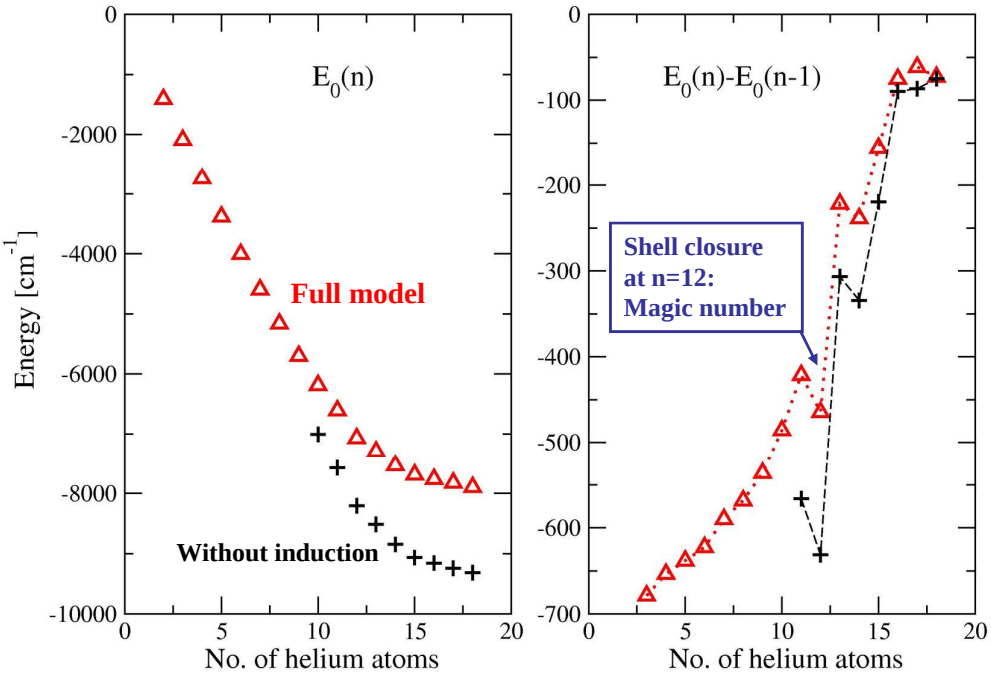
Minimum energy structures for $Pb^{q+}He_n$



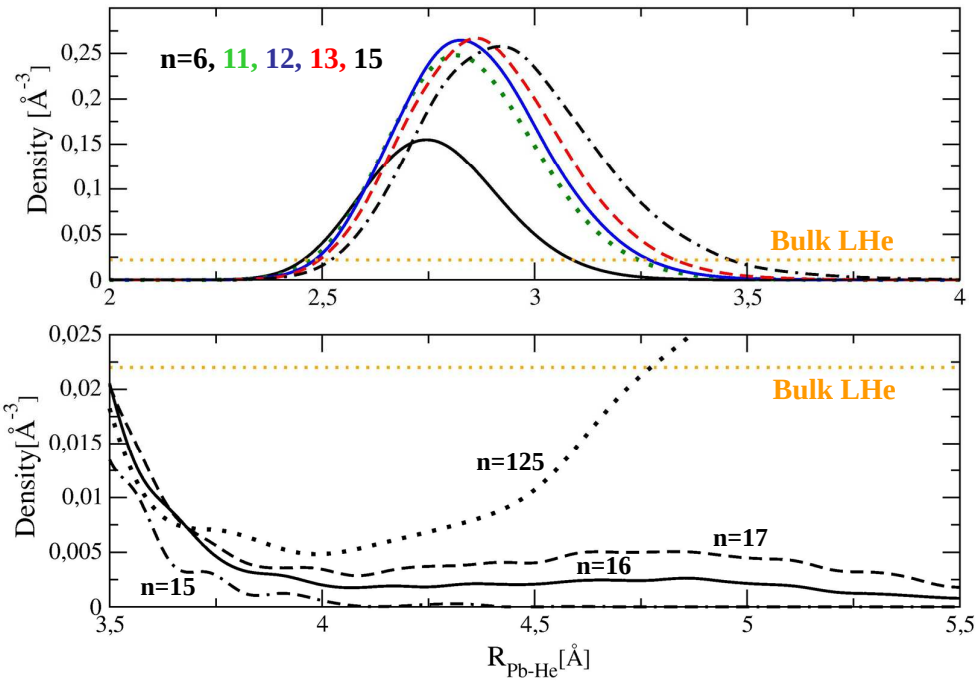


Red triangles: Model potential
Black crosses: DFT minimisation

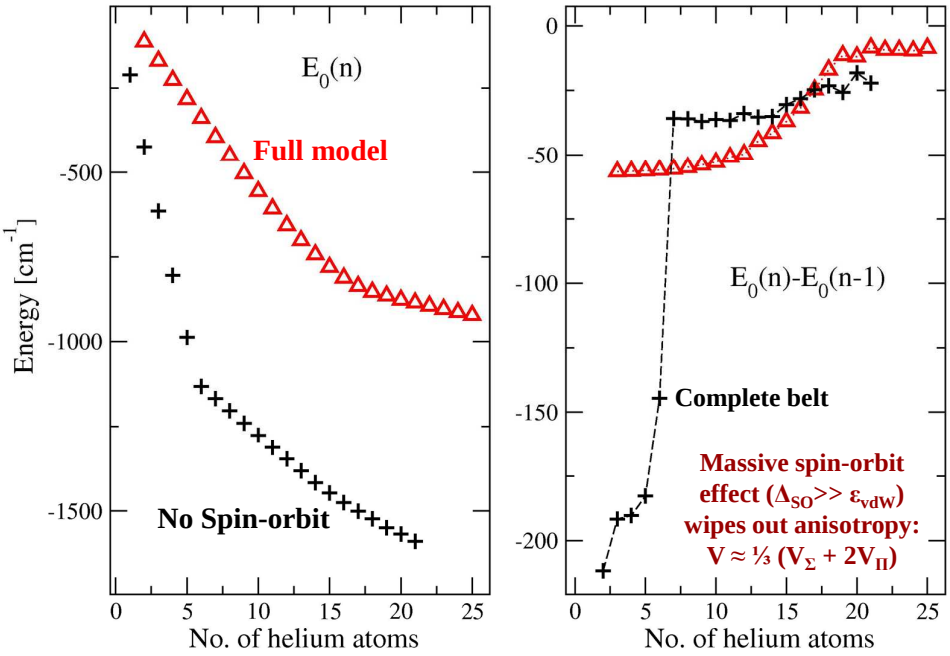
DMC ground state energies for $Pb^{2+}He_n$



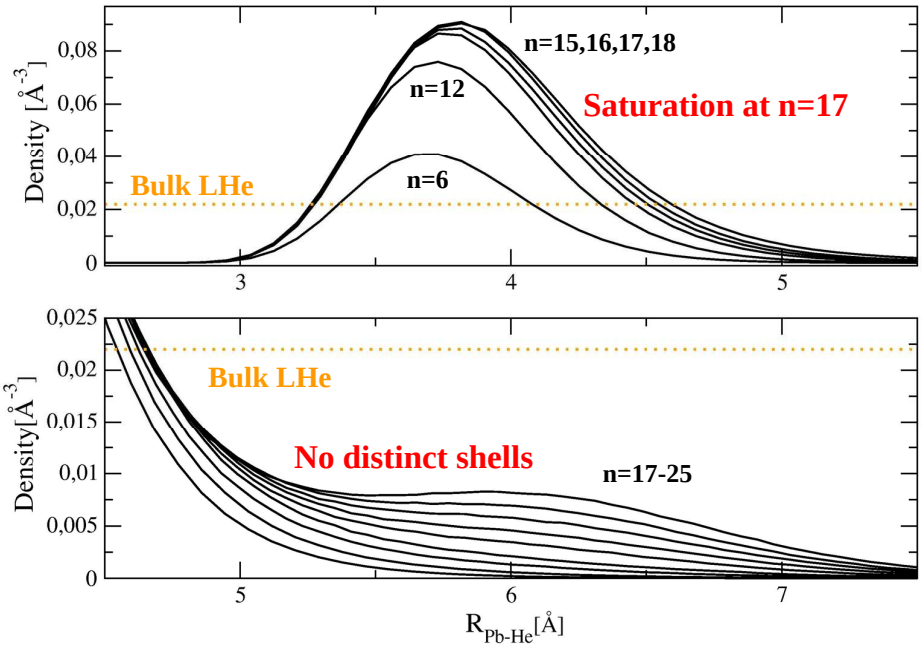
Radial densities for $Pb^{2+}He_n$



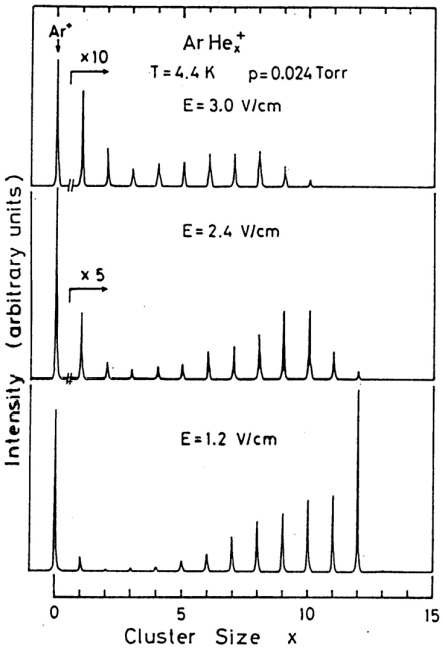
Ground state energies for Pb^+He_n



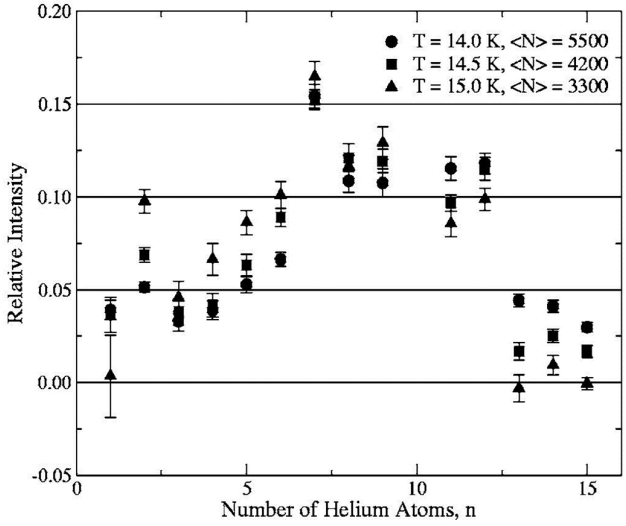
Radial densities for Pb^+He_n



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^+ s^2p^5 valence shell → $X^2\Sigma^+$ and $A^2\Pi$ states for Ar^+He.

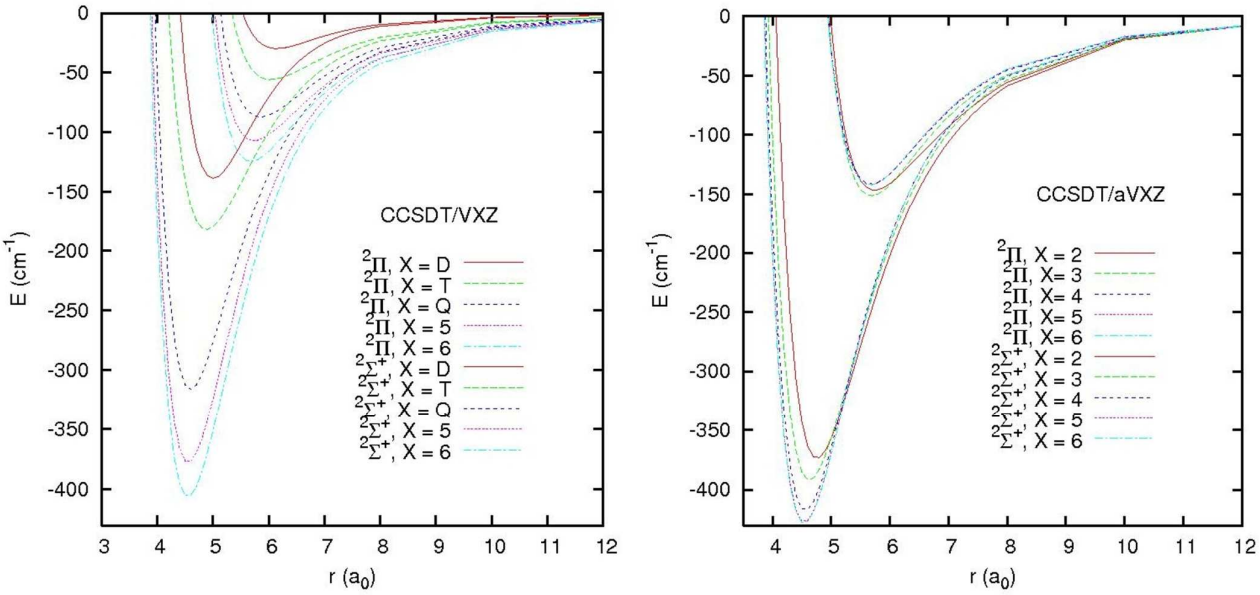
IP(Ar)=15.76 eV → He^++Ar channel is unimportant, single configuration. CCSD(T) calculations with (aug)-cc-pVXZ basis sets.

Ab initio points fitted to HFD-style analytical form with fixed C_4 coefficient computed from $\alpha_{He} = 1.41\ a_0^3$.

Strong spin-orbit interaction in Ar^+ ($\Delta = 1432\ cm^{-1}$): 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).

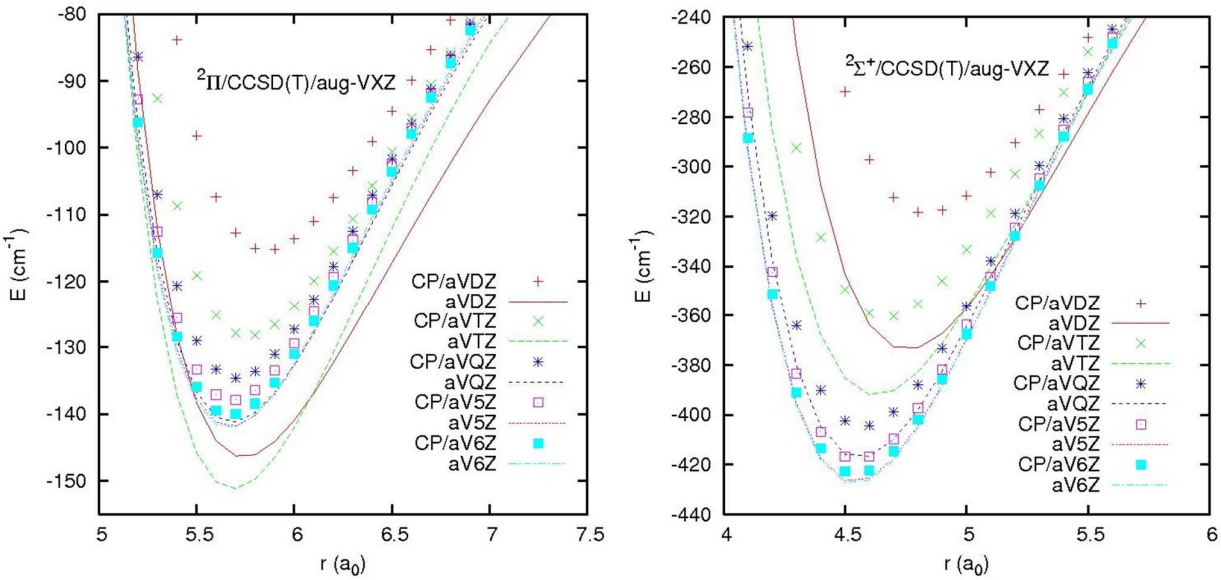
Ar^+He: convergence of interaction energy

CCSD(T) calculation



Ar^+He: BSSE counter poise correction

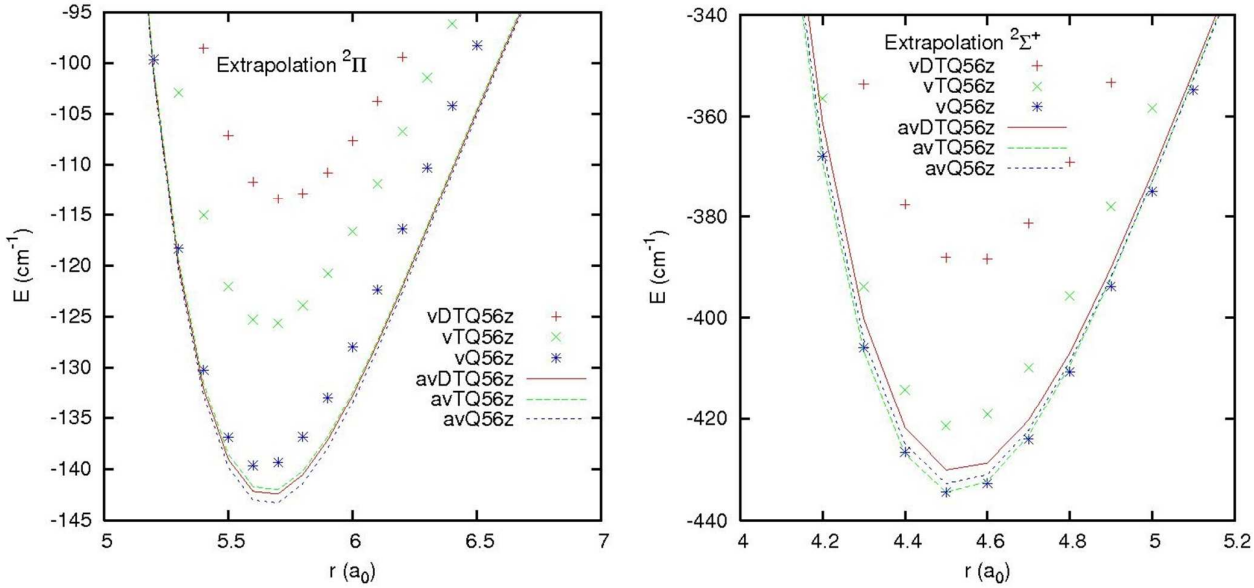
CCSD(T) calculation



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 $^2\Pi$ state

Ar^+He: spectroscopic observables

extrapolated potentials (aQ56), atomic spin-orbit splitting, variational rovibrational calculation in Laguerre basis, $^4He^{40}Ar^+$

Vibrational transition frequencies

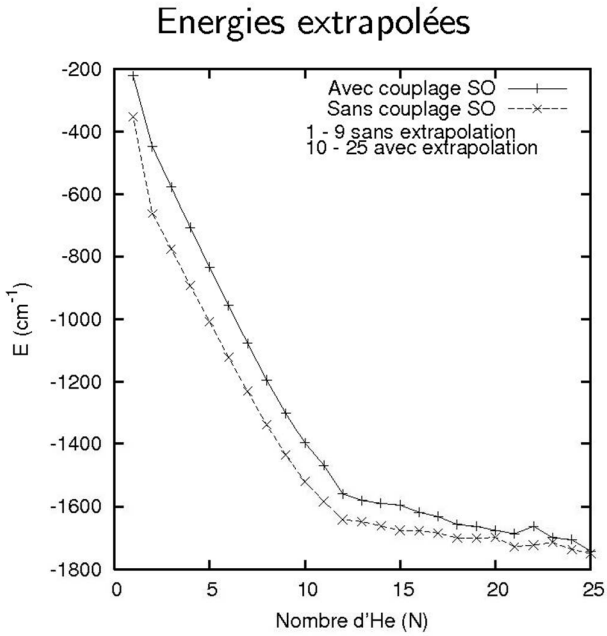
v	$X\ ^2\Sigma^+_{1/2}$			$A_1\ ^2\Pi_{3/2}$		$A_2\ ^2\Pi_{1/2}$		
	exp	S96	Fit	S96	Fit	exp	S96	Fit
0	**92.9**	83.9	**92.47**	52.9	55.91	**69.2**	64.0	**69.19**
1	**66.2**	55.2	**64.88**	26.9	29.20		35.1	38.82
2		30.7	38.55	11.9	11.73		15.7	17.59
3		14.1	17.81					

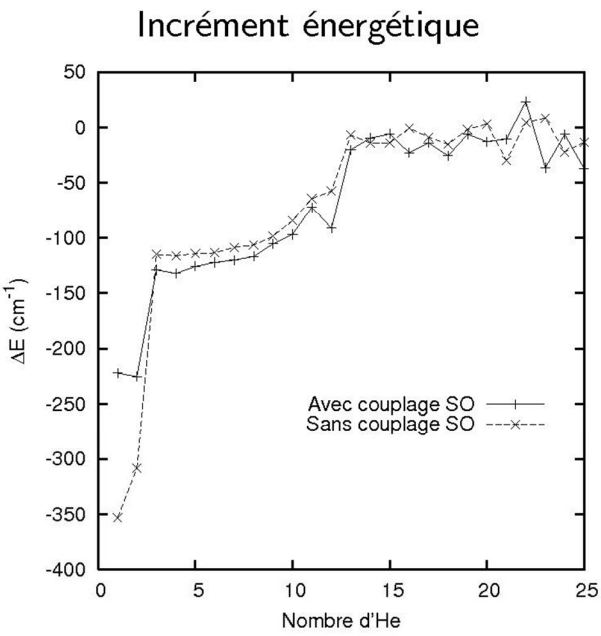
Expectation values for rotational constants

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					

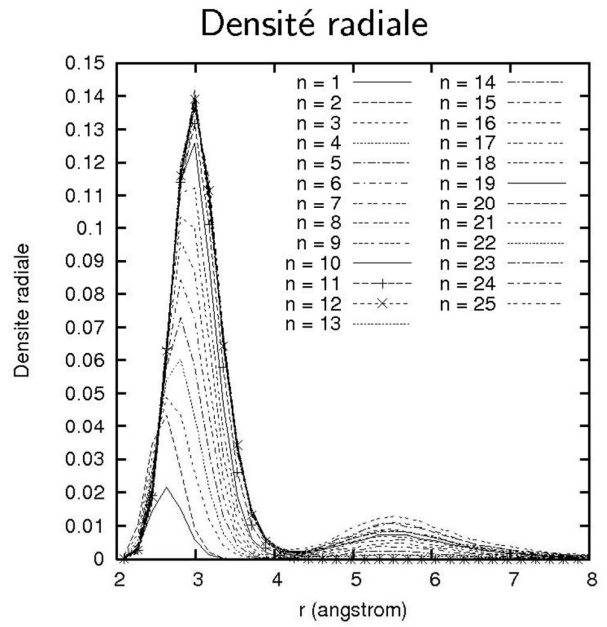
Our Ar^+He potential is excellent !

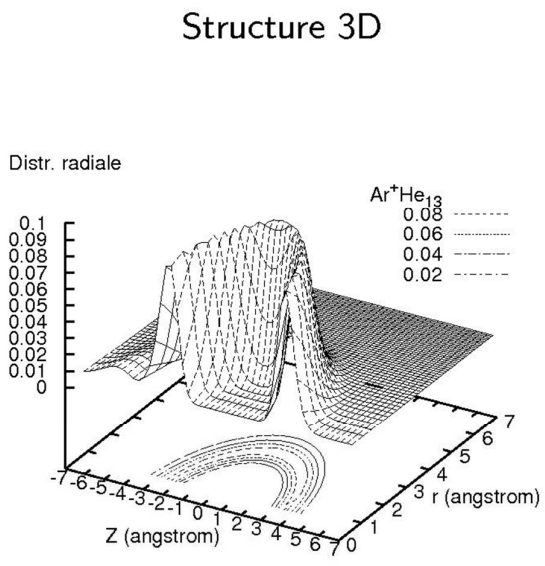
Ar^+He: DMC ground state energies





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 Pb^{2+} 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 CH_3I and CF_3I (ZPAD, DMC etc.)
- DMC with constraints ($(H_2)_n$, $He_n(H_2)_m$ possible).

ANR project DYNHELIUM (Toulouse, Rennes, Paris)