

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-00832982

Submitted on 11 Jun2013

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.



0.02

0.015 0.01 0.005 0

-20 1

z/100 pf



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, Mg⁺@He_n, Ar⁺@He_n

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

Nottingham: Prof. Tim Wright

r/100 pm

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~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!

Marius Lewerenz

U. Leicester, 10 July 2009

3

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 ··· 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?

Marius Lewerenz

U. Leicester, 10 July 2009

5

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 \rightarrow 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

$$rac{\partial oldsymbol{C}(ec{r},t)}{\partial t} = \left\{ \sum_{j=1}^n oldsymbol{D}_j
abla_j^2 - oldsymbol{k}(ec{r})
ight\} oldsymbol{C}(ec{r},t) \; .$$

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

Marius Lewerenz

U. Leicester, 10 July 2009

Pair potentials involving helium and metals



Alkali-helium dimers

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



Comparison between silver and magnesium

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



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.

Marius Lewerenz



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)

U. Leicester, 10 July 2009

11

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

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





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.

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



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.



Marius Lewerenz

U. Leicester, 10 July 2009

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⁺ (3s¹) - 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 C₄ 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.

Marius Lewerenz

U. Leicester, 10 July 2009

19

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



Communications

Coordination in the Gas Phase

DOI: 10.1002/anie.200604148

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 Pb²⁺ with He atoms results in remarkably stable PbHe₁₅²⁺ 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 $(N_{\text{max}}, \text{ called the kissing number or Newton number})$ of a given radius R can be





conjunction with coordination numbers higher than 12

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 ($\alpha_{ffe} = 1.38 au^{[10]}$ 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, Pb²⁺ He does not undergo a Coulomb

Herein we take a different approach. We look for a single

stabilized by the surrounding matrix.[2]

Figure 4. E_{IB} for PbHe_N²⁺. Circles: minima of one-shell structures; squares: minima of two-shell structures.

Marius Lewerenz

U. Leicester, 10 July 2009

23

DMC calculations for Pbq+He_n

Pb²⁺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⁺ s²p 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

Pair interaction potentials for Pbq+He_n



Marius Lewerenz U. Leicester, 10 July 2009

Minimum energy structures for Pb^{q+}He_n



DMC ground state energies for Pb²⁺He_n



Radial densities for Pb²⁺He_n



Ground state energies for Pb+He_n



Radial densities for Pb⁺He_n



Ar⁺**He**_n: **Experimental evidence for shells**



Marius Lewerenz

U. Leicester, 10 July 2009

31

DMC calculations for Ar⁺He_n

Potential model:

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

IP(Ar)=15.76 eV \rightarrow 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 $\alpha_{\text{He}} = 1.41 \text{ a}_0^{-3}$.

Strong spin-orbit interaction in Ar⁺ ($\Delta = 1432 \text{ cm}^{-1}$): Non additive many body potential model including induced dipoles on He with additional spin-orbit mixing included using atomic $\Delta_{\text{Ar+}}$ (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







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

Marius Lewerenz

U. Leicester, 10 July 2009

35

Ar⁺**He: spectroscopic observables**

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

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		A -+1		. 4 . 1	
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

Marius Lewerenz

U. Leicester, 10 July 2009

39

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 $((H_2)_n, He_n(H_2)_m \text{ possible})$.

ANR project DYNHELIUM (Toulouse, Rennes, Paris)