# Dipolar quantum gases, exciplex formation in $^4$He, and surface condensate

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Robert E. Zillich
D. Hufnagl, E. Krotscheck; F. Mazzanti, G. Astrakharchik, J. Boronat; A. Viel, M. Leino; J. Mayrhofer

Institut für Theoretische Physik, Johannes Kepler Universität, Linz, Austria

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# Outline

## Strongly correlated dipolar quantum gases

- Introduction
- (time-dependent) hyper-netted chain Euler-Lagrange
- 2D dipolar quantum gas
- Quasi-2D dipolar quantum gases
- Conclusion/Outlook

## $Rb^*$-He Exciplex formation on $^4$He surface

- Helium matrix isolation spectroscopy (HENDI)
- Diffusion and Path Integral Monte Carlo
- Rb-He and $Rb^*$-He Interaction
- $Rb^{*1}He_N$: 1st excited state, $^2\Pi_{1/2}$
- $Rb^{*2}He_N$: 2nd excited state, $^2\Pi_{3/2}$
- $Rb_2$ on $^4$He surface
- Conclusion and Outlook

## Surface condensate of doped $^4$He clusters

- Helium matrix isolation spectroscopy (HENDI)
- Description of BEC in clusters
- Path Integral Ground State Monte Carlo (PIGSMC)
- Results
- Conclusion/Outlook

# Introduction to dipolar QGs

## experiments:

- permanent magnetic dipole moments of atoms (Cr): Pfau group (Lahaye et al, Nature **448**, 672 (2007))
- permanent electric dipole moments of heteronuclear dimers (RbCs, etc): transfer atom pairs to weakly bound state by Feshbach resonance $\longrightarrow$ transfer to rovibrational g.s. by STIRAP laser pulses (Innsbruck; JILA, NIST: Ni et al., Science **322**, 231(2008),...)

## dipole-dipole interaction:

$$\text{polarized:} \quad v_{dd}^{\parallel}(\mathbf{r}_{12}) = d^2 \frac{1 - 3\cos^2\theta_{12}}{r_{12}^3}$$

$$\text{unpolarized:} \quad v_{dd}(\mathbf{r}_{12}) = d^2 \frac{\hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2 - 3(\hat{\mathbf{e}}_1 \cdot \hat{\mathbf{r}})(\hat{\mathbf{e}}_2 \cdot \hat{\mathbf{r}})}{r_{12}^3}$$

in this talk, only polarized QGs, no internal (rotation, spin) degree of freedom

# (time-dependent) hyper-netted chain Euler-Lagrange

(deeper theoretical background → E. Krotscheck's talk)

## HNC-EL

$$\Phi_0(R) = \prod_i \varphi(\mathbf{r}_i) \prod_{i<j} f(\mathbf{r}_i, \mathbf{r}_j) \cdots = e^{\frac{1}{2}\sum_i u_1(\mathbf{r}_i)} e^{\frac{1}{2}\sum_{i<j} u_2(\mathbf{r}_i,\mathbf{r}_j)} \cdots$$

$$\frac{\delta\langle H\rangle}{\delta u_1(\mathbf{r})} = 0\ , \qquad \frac{\delta\langle H\rangle}{\delta u_2(\mathbf{r}_1,\mathbf{r}_2)} = 0\ , \qquad \frac{\delta\langle H\rangle}{\delta u_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)} = 0$$

## TDHNC-EL

$$\Psi(R;t) = e^{-iE_0 t}\, \frac{e^{\frac{1}{2}\delta U(R;t)}}{\langle\Psi|\Psi\rangle^{1/2}}\, \Phi_0(R)$$

$$\text{with} \quad \delta U(R;t) = \sum_i \delta u_1(\mathbf{r}_i;t) + \sum_{i<j} \delta u_2(\mathbf{r}_i,\mathbf{r}_j;t) + \ldots$$

$$\delta \int dt \langle\Psi(t)|H(t) - i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = 0$$

- $\delta u_n = 0$ for $n > 2$ & uniform limit approximation: CBF approximation
- "..." & *no* uniform limit approximation: see EK's talk

# 2D dipolar quantum gas

- dipolar quantum gas in 2D, polarized in 3rd direction:

$$H = -\frac{\hbar^2}{2m}\sum_j \nabla_j^2 + d^2 \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|^3}$$

- interaction obviously isotropic
- characteristic length scale $r_0 = md^2/\hbar^2$
  characteristic energy scale $E_0 = \hbar^2/mr_0^2$

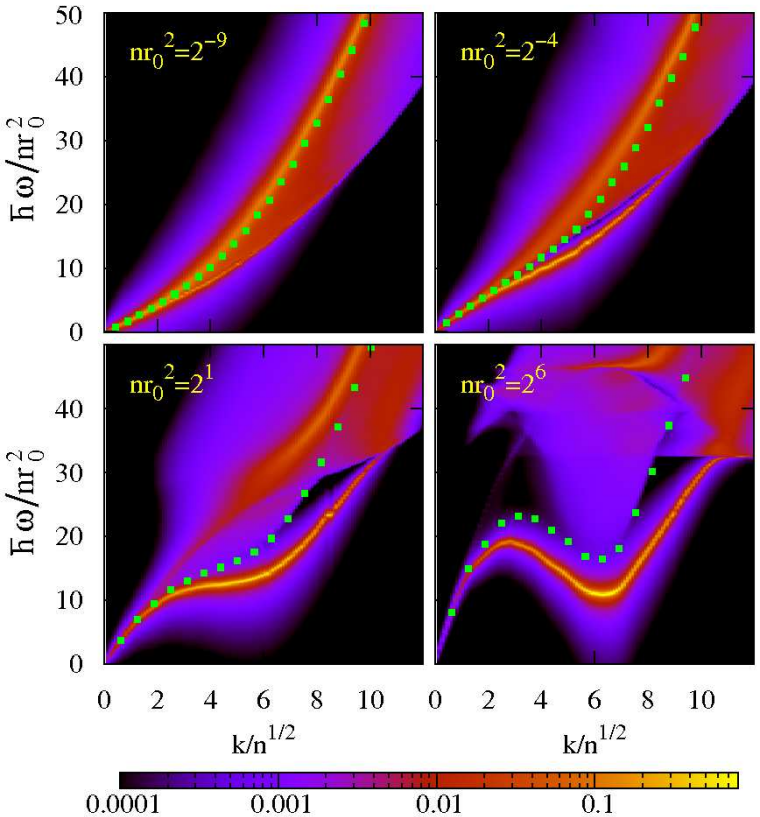
## ground state

DMC simulations: G. E. Astrakharchik et al. PRL **98**, 060405 (2007)

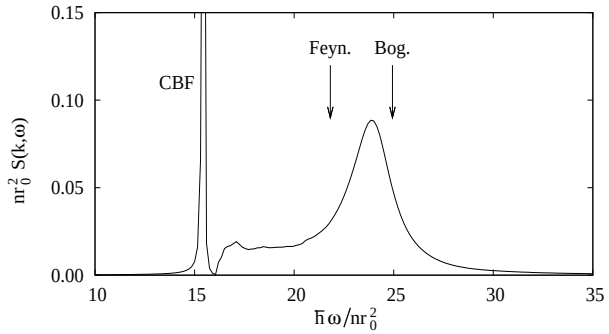
## excitations

CBF approximation, compared to Bjil-Feynman spectrum $\epsilon_F(k) = \frac{\hbar^2 k^2}{2mS(k)}$ and to Bogoliubov spectrum $\epsilon_B(k)$

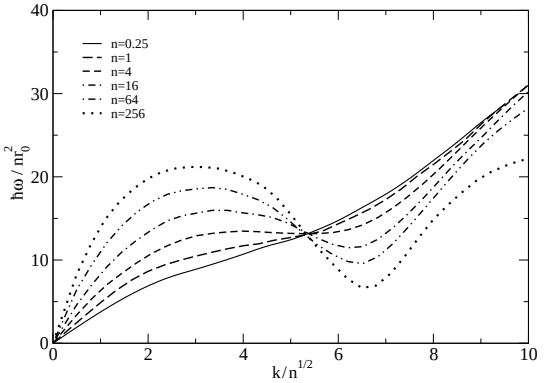
# Dynamic structure function $S(k,\omega)$ of 2D dipolar QG




- at very low $n$: Bogoliubov + damping
- increase $n$: splitting into phonon and multi-excitation




- appearance of roton at $nr_0 \approx 4$




F. Mazzanti, REZ, G. Astrakharchik, J. Boronat, PRL **102** 110405 (2009)

# *Work in progress*: Quasi-2D dipolar quantum gases

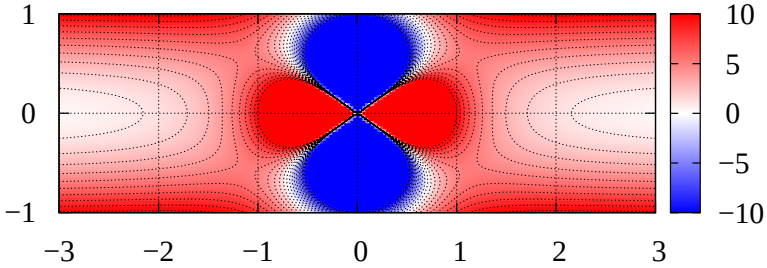
## experiment

- real trapped quantum gases: confinement in all 3 directions (oblate or prolate).
- tight confinement in $z$-direction: $v_{\mathrm{ext}}(z) = \alpha z^2$

## theory

- without short-range repulsion (s-wave scattering length $a$), polarized quasi-2D QG is only *metastable*: tunneling into attractive region of $v_{dd}^{\parallel}(\mathbf{r}_{12}) = (1 - 3\cos^2\theta_{12})/r_{12}^3$

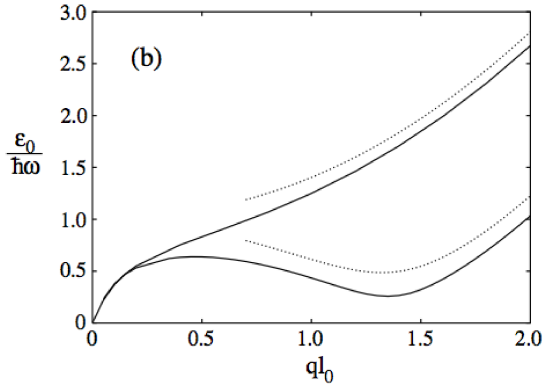
$v_{dd} + v_{\mathrm{ext}}$ for particle 1 at (0,0) and particle 2 at ($x$,$z$)




- only GP (mean field) calculations available: stable/unstable, depending on $a, d, \alpha, n, g$
  close to instability: appearance of "roton" ($\neq$ roton in $^4$He!)
- $\Rightarrow$ use *inhomogeneous* HNC-EL!
  non-trivial: "ground state" is only meta-stable (see figure)
  (GP does not "see" this problem, since there are no correlations)

# Quasi-2D dipolar quantum gases with repulsion

linearized GP results by Santos, Shlyapnikov, Lewenstein, PRL **90**, 250403 (2003):

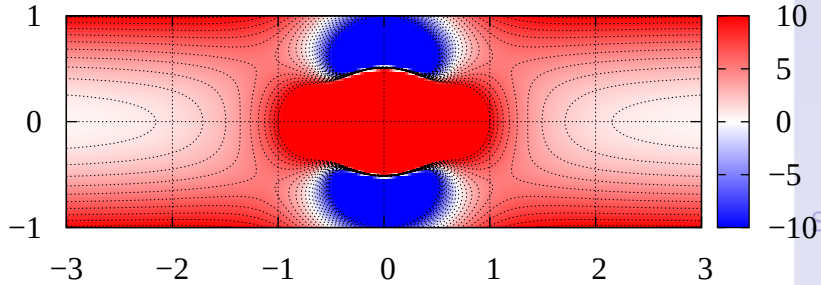



dipole + contact interaction $g\delta(\mathbf{r}-\mathbf{r}')$
top: $g/g_d > 1/2$
bottom: $g/g_d < 1/2$ — **"rotonization"**

mean field: hard to know what is happening microscopically

## hard-sphere repulsion $v_{\rm hs}(r) = (\sigma/r)^{12}$

$v_{dd} + v_{\rm ext} + v_{\rm hs}$ for particle 1 at (0,0) and particle 2 at $(x,z)$



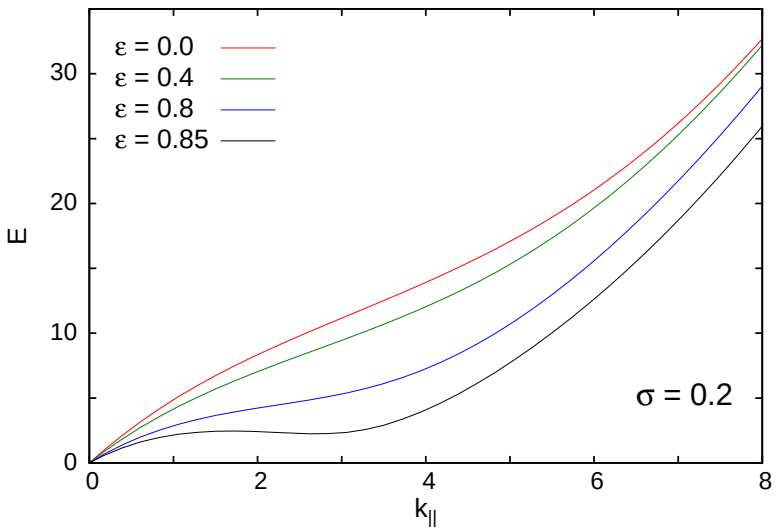

- stabilization w/resp. to tunneling to infinitely strongly bound state
  $\Rightarrow$ no need to avoid attractive potential region
- dependence on $\sigma$, $\rho$, $\alpha$, $d$

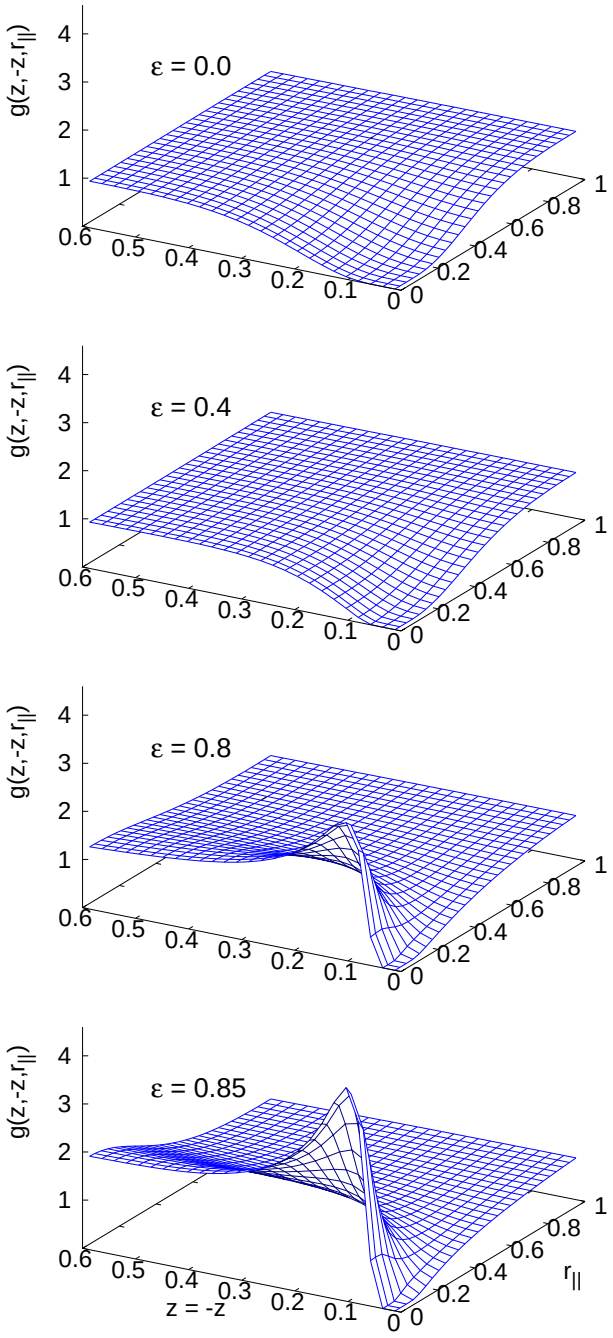
# Quasi-2D dipolar quantum gases

## Results with $\sigma = 0.2$, $\rho = 2$:

- rotonization $\longrightarrow$ possibly **dimerization**
- careful approach: $v_{dd}^{\parallel}(\mathbf{r}_{12}) = (1 - 3\varepsilon \cos^2\theta_{12})/r_{12}^3$
- peak in $g(z, -z, r_{\parallel})$
- signature of dimerization: emergence of "roton" — similar to GP results for collapse
  $k_{\parallel}^r \approx 3 \longrightarrow \lambda^r \approx 2 <$ confinement size
- dimerization happens at $\varepsilon$ similar to occurrence of bound state of free dimer
- *caveat*: description in terms of *s*-wave scattering length?

dispersion of lowest mode $\omega(k_{\parallel})$ in *Bjil-Feynman* approximation:



# Conclusion/Outlook

## Conclusion:

- 2D: transition from weakly interacting to strongly interacting: splitting of Bogoliubov spectrum $\longrightarrow$ phonon-roton and multi-excitation continuum
- 2D: roton due to strong correlation
- quasi-2D: instability due to "head-to-tail" attraction of dipoles possible dimerization phase transition

## Outlook for quasi-2D:

- mapping out $(\sigma, \rho, \alpha, d)$ space
- searching for spectrum with both kinds of rotons:
  1. strong correlations due to repulsion
  2. "rotonization" due to attraction
- full understanding of possible dimerization
- Bjil-Feynman $\rightarrow$ CBF $\rightarrow$ ...
- no hard-sphere repulsion: make HNC-EL work

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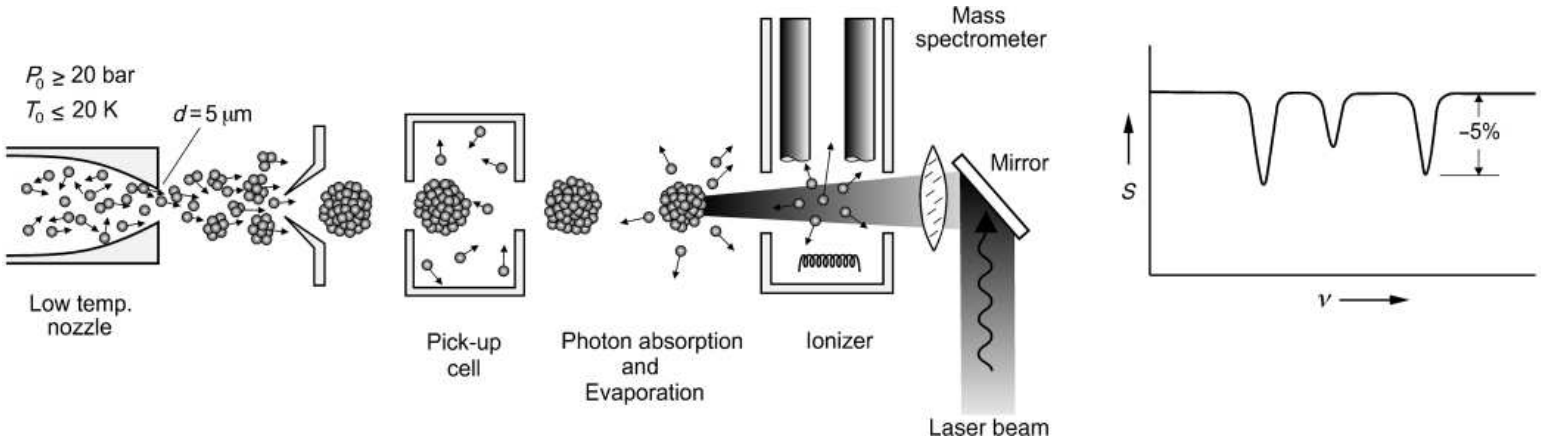
# Experiments: Helium matrix isolation spectroscopy

Spectroscopy of doped superfluid $^4$He clusters/droplets ($\sim$ 0.4K)
depletion spectroscopy: chromophore excitation detected by evaporating $^4$He atoms.




from J. P. Toennies and A. F. Vilesov

$\longrightarrow$ measureing sharp rovib. spectra of *isolated* molecules at low $T$
$\longrightarrow$ stabilizing transition states (conformations)
$\longrightarrow$ assembly of small clusters in He

$\longrightarrow$ probing $^4$He: superfluidity on microscopic scale – microscopic Andronikashvili exp.
(Grevenev et al., Science'98)
$\longrightarrow$ theoretical understanding of rotational spectra in terms of superfluidity
(Paesani, Kwon, Whaley, PRL'05)

$\longrightarrow$ electronic excitation of adsorbed atoms
$\longrightarrow$ exciplex formation; Rb$^*$ on $^4$He surface

# Rubidium adsorbed on $^4$He clusters

Motivation for this work:

- 1st electronically exited Rb state, $^2\Pi_{1/2}$ ($Rb^{*1}$):
  Experiment by group of W. Ernst: excitation-deexcitation cycles of Rb on He surface – electron spin pumping
  G. Auböck et al., PRL **101**, 035301 (2008)
- 2nd electronically exited Rb state, $^2\Pi_{3/2}$ ($Rb^{*2}$):
  exciplex formation Rb$\longrightarrow$Rb$^*$He
  Reho et al., JCP **113**, 9694 (2000)
  Droppelmann et al., PRL **93**, 023402 (2004)
- more than 1 adsorbate/dopant: spin-aligned alkali clusters (only on He!)
  trimers: Nagl et al., PRL **100**, 063001 (2008)
  dimers: Auböck et al., JPC (2007)
- electronically excited alkalis in *solid* He
  Nettels et al. (Fribourg), PRL **94**, 063001 (2005)

# Diffusion and Path Integral Monte Carlo

$$H = -\frac{\hbar^2}{2M}\nabla_0^2 - \frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 \; + \; V_{RbHe}(\{\mathbf{r}_j\}) + \sum_{i<j} V_{HeHe}(|\mathbf{r}_i - \mathbf{r}_j|)$$

## $T = 0$: Diffusion Monte Carlo

- Schrödinger equations in imaginary time = diffusion equation
- diffusion towards ground state by stochastic Langevin process (random walk)
- exact ground state energy $E_0$
  exact expectation values for diagonal operators ($\rho(\mathbf{r})$, etc.): descendent weighting
  (J. Casulleras, J. Boronat, PRB 52, 3654 (1995))
- efficiency: importance sampling using optimized trial wave function

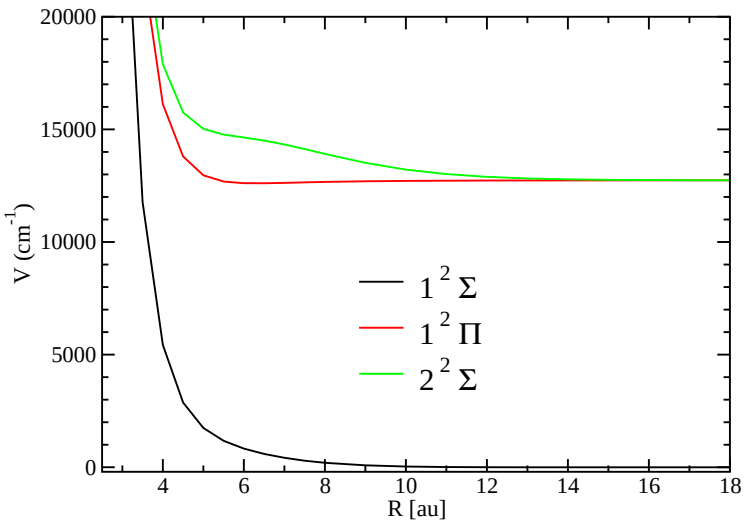
## $T > 0$: Path Integral Monte Carlo

- Monte Carlo sampling à la Metropolis of $N$-body density matrix
  $$\rho(R, R'; \beta) = \langle R|e^{-\beta H}|R'\rangle$$
- short-time approximation of $\rho(R, R'; \beta)$: pair-density approximation for He-He and He-Rb interaction, 2nd-order ("primitive") approximation for He-Rb$^*$
  (D. M. Ceperley, RMP 67, 279 (1995))
- quantum-classical isomorphism: quantum particle $\longrightarrow$ "polymer" chain of classical particles; Bose exchange $\longrightarrow$ reconnecting polymers

# Rb-He and Rb*-He Interaction

## w/o spin-orbit coupling

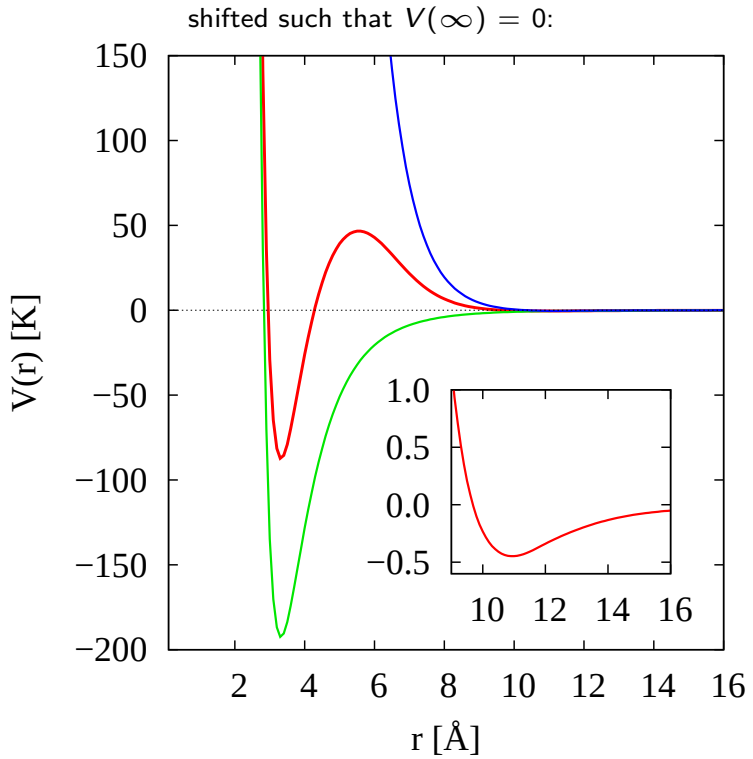
Rb-He and Rb-He* due to Pascale (1983)




interaction: 1 surface for Rb-He and 2 surfaces for Rb*He

## with spin-orbit coupling

$\Rightarrow$ splitting of Rb*-He interaction surfaces
Nakayama et al., JCP **114**, 780 (2001)



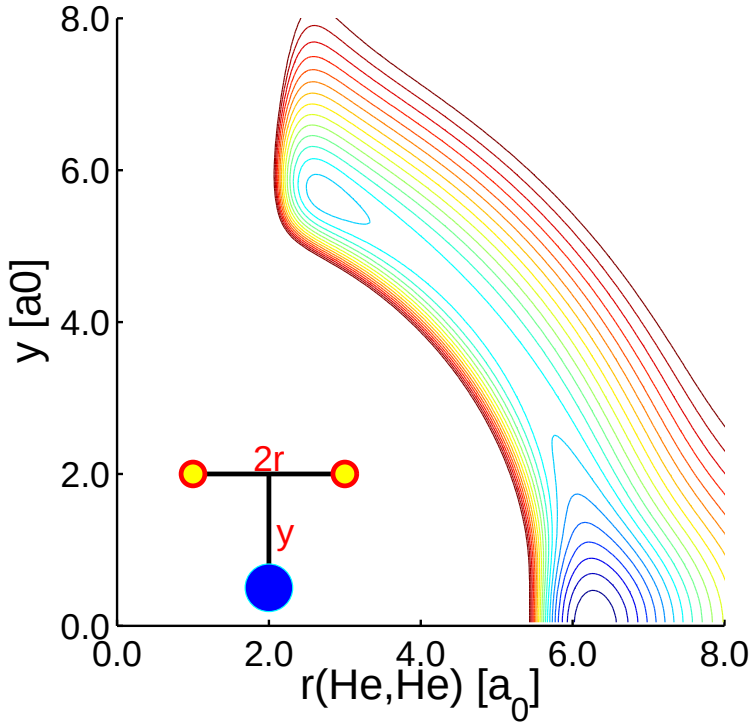

1. lowest, $^2\Pi_{1/2}$ (Rb$^{*1}$): attractive + barrier
2. middle, $^2\Pi_{3/2}$ (Rb$^{*2}$): purely attractive
3. highest, $^2\Sigma_{1/2}$: purely repulsive

# $Rb^{*1}$-$He_N$ Interaction: Many-Body Interaction

add more He atoms: DIM approximation $\Rightarrow$ not pairwise additive

Nakayama et al., JCP **114**, 780 (2001)

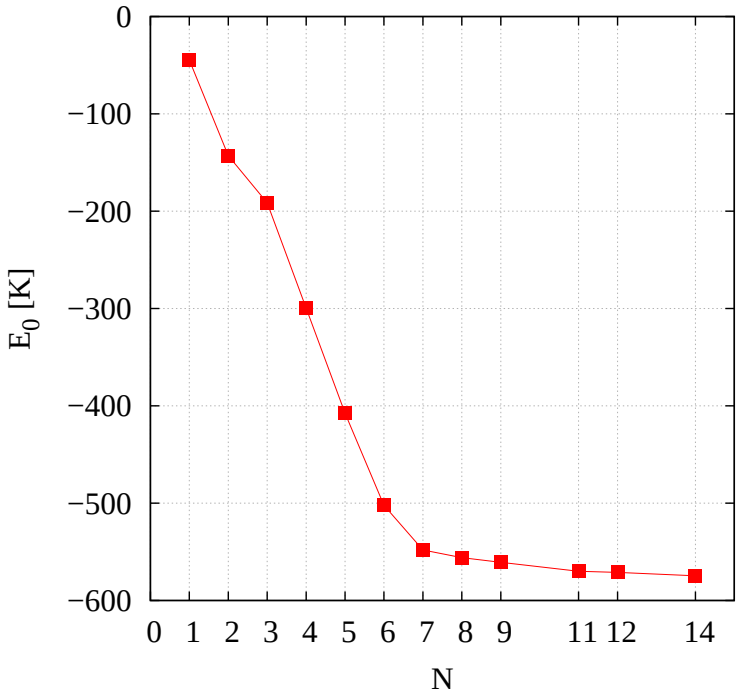
$N = 2$: miminum energy for linear He-Rb*-He configuration
(also true for 2nd excited state of Rb)




$N > 2$: minimum configurations?
(different from 2nd excited state of Rb)

# $Rb^{*1}He_N$: 1st excited state, $^2\Pi_{1/2}$

small clusters:




DMC simulation details:

- for $N > 7$: importance sampling: Jastrow wave function for He-He, Fermi well for He

results:

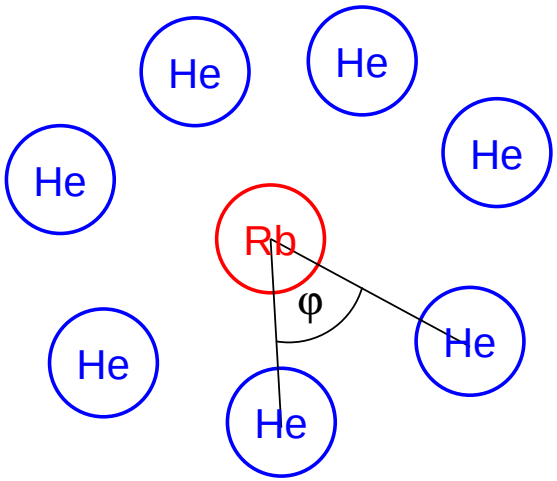
- $E_0(N)$ has kink at $N = 7$ – 1st shell closure?

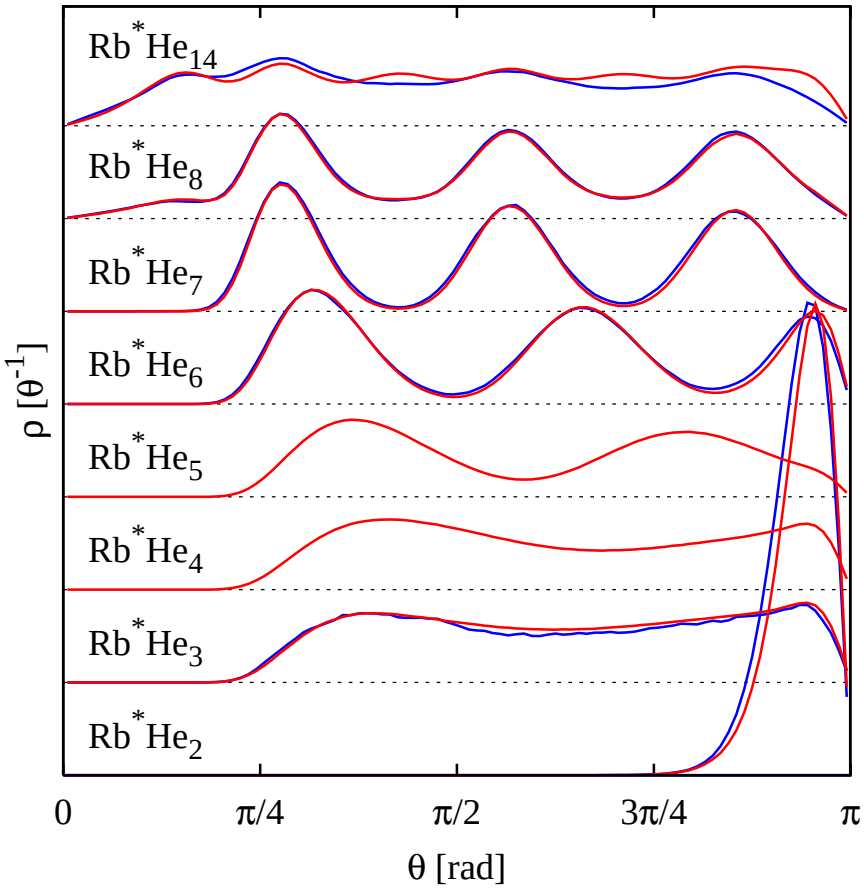
M. Leino, A. Viel, REZ, JCP **129**, 184308 (2008)

# Structure: Angular Distribution $\rho(\varphi)$

Q: What is structure of He solvation shell around $Rb^*$? $\rightarrow \rho(\varphi)$

- $\varphi$ is He-Rb-He angle
- $N = 2, 3, 4, 5, 6, 7$ (bottom to top)
- PIMC and DMC (descendent weighting, Casulleras & Boronat, PRB (1995))



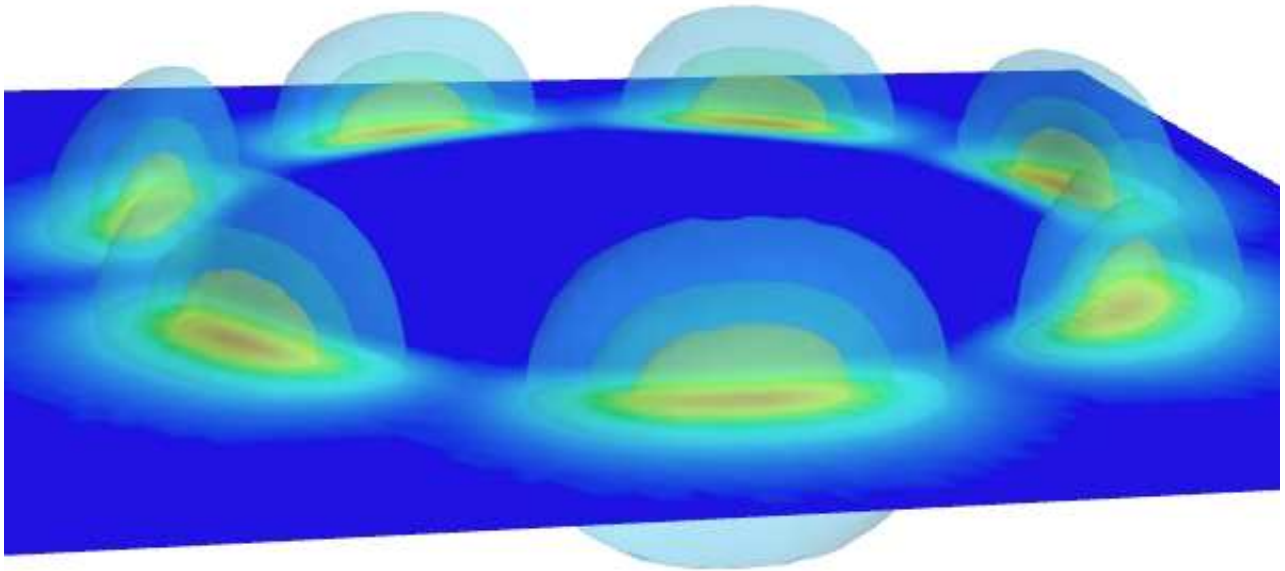




$N = 1 \ldots 7$: He forms ring around $Rb^*$ — symmetry breaking due to non-pairwise additive interaction

$N = 8, 9, \ldots$: further He atoms form weakly bound "tire" around "hub cap"

# Structure: He density of $Rb^{*1}He_7$ exciplex

iso surfaces and $(x, y)$ cut plane:



definition of body-fixed frame: see Baroni, Moroni, Comp. Phys. Comm. **6**, 1884 (2005)

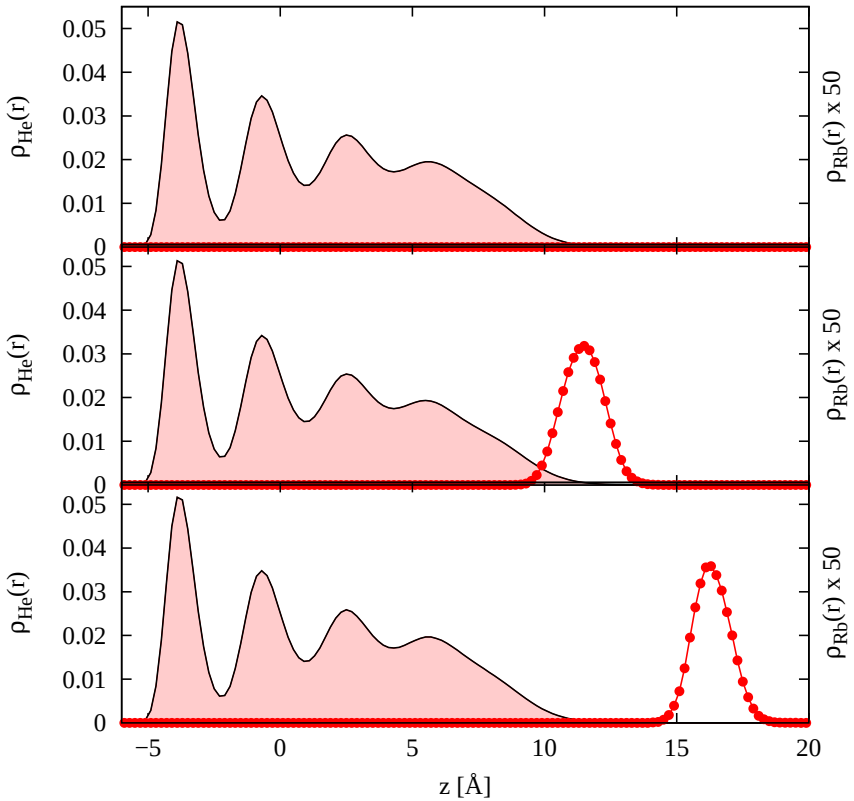
# Rb and $Rb^{*1}$ on He Surface

## experiment

Auböck et al. (Graz), PRL **101**, 035301 (2008): Optical spin pumping of Rb on He
excitation Rb→$Rb^{*1}$; relaxation $Rb^{*1}$ →Rb ⇒ $Rb^{*1}$ bound

## simulation (PIMC): "vertical Monte Carlo transition"

$RbHe_N$ configurations → switch to PES for 1st excited state → relax $Rb^{*1}He_N$ configurations: **no information about true dynamics, dissipation etc.**




PIMC simulation details:

- $T = 0.31$K
- thin $^4$He film on frozen He (instead of large droplet $N = O(10^5)$)
  ⇒ possible bias from finite thickness

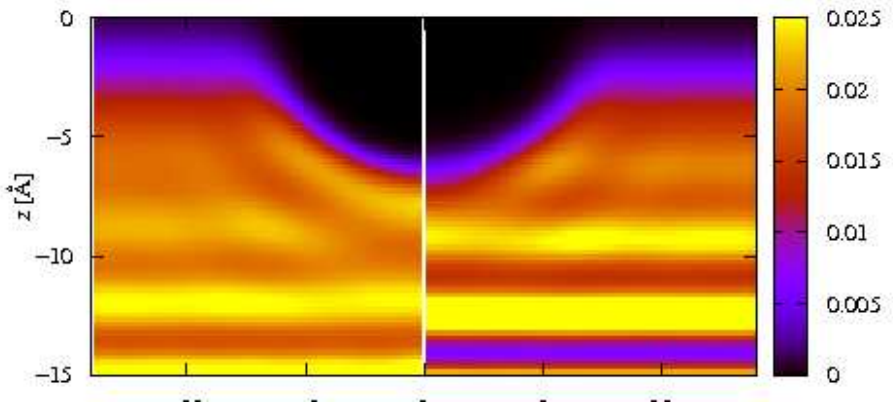
result:

$Rb^*$ relaxes to *metastable* surface state farther away than Rb
where is the ring of 7 He atoms?
**He cannot cross the barrier of $^2\Pi_{1/2}$ potential.**

# Rb and $Rb^{*1}$ on He Surface: Dimples

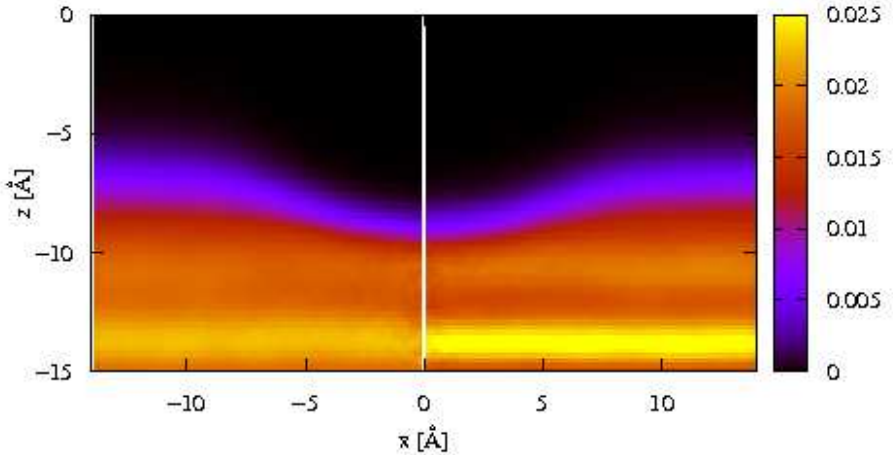
## Rb

- deep dimple
- $E_B \approx -15$K




## $Rb^{*1}$

- shallow, metastable dimple
- $E_B \approx -8$K
- transition/relaxation to ground state (w/ring of 7 He) never observed in PIMC
  → *no formation of exciplex*




Dynamics? — MC good for equilibrium ⟶ correlated basis function (CBF) theory?

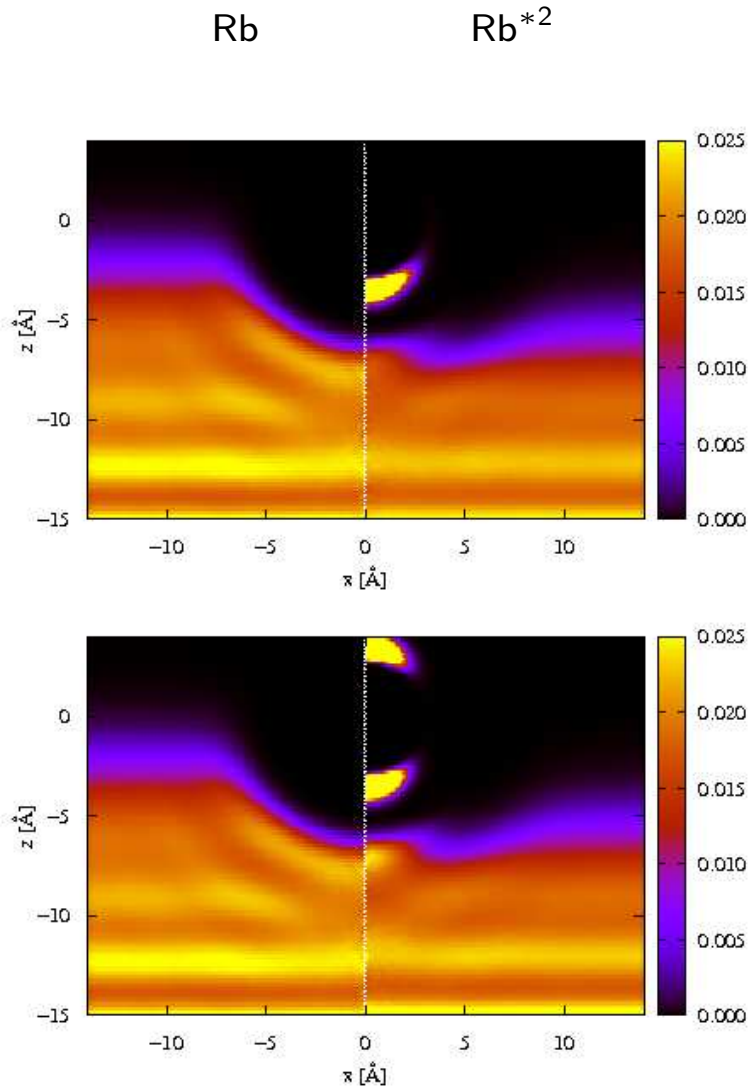
# $Rb^{*2}He_N$: 2nd excited state, $^2\Pi_{3/2}$

## Experiment

formation of $Rb^{*2}He$ exciplex upon excitation of Rb on He surface $\longrightarrow$ desorption

## our results

- $Rb^{*2}$ can form linear trimer with He: $Rb^{*2}He_2$
- further He atoms are very weakly bound
- "vertical MC transition" Rb $\longrightarrow$ $Rb^{*2}$ on He surface: formation of $Rb^{*2}He$ exciplex
- $Rb^{*2}He_{1/2}$ bound to surface ($\sim -15$K)

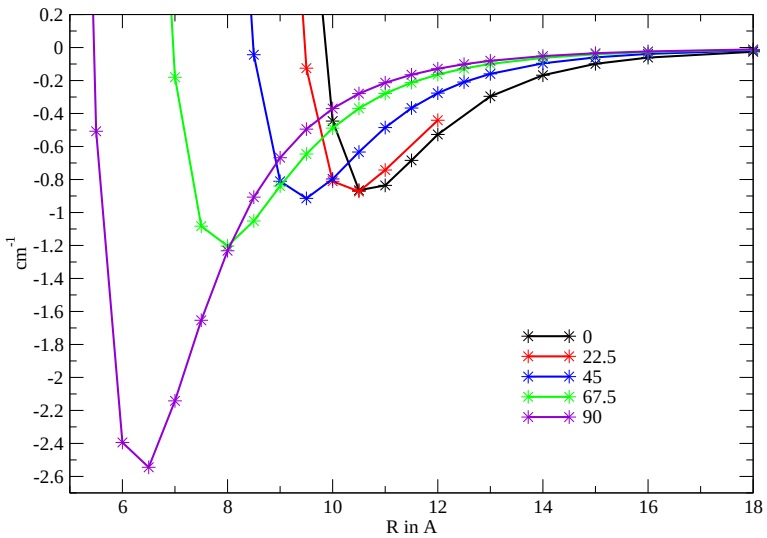


# $Rb_2$ on $^4$He surface

## Experiment

*spin-aligned* alkali clusters on He (Stienkemeier et al., Ernst et al.):
adsorb alkali one by one ⇒ formation of alkali dimer, trimers which are weakly bound ⇒ no desorption

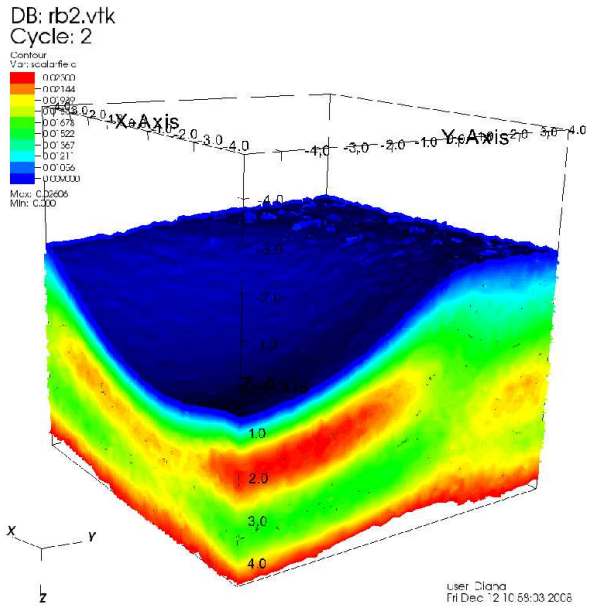
- Auböck et al. (Graz), JPC (2007): electronic spectrum split by presence of He surface, modeling of spectrum requires "crystal field" parameters, *i.e.* structural information, such as orientation of molecular axis, distance from surface




## $Rb_2$ in triplet state + $^4$He

- Rb-Rb = 6.1181 Å⇒ $B_0 = 0.0152$K
- RCCSD(T) with the aug-cc-pV5Z for He atom and the basis set augmented MDF small-core ECP (aug-ECP28MDF) basis set in uncontracted form for Rb.
- basis set superposition error (BSSE) correction has some effect
- potential minimum: T-shape
  same for $Li_2$, Mol. Phys. **103**, 3223 (2005)
- $Rb_2He_N$: $Rb_2$ lying flat on He surface?
- rotational dynamics? only in plane or also out of plane?

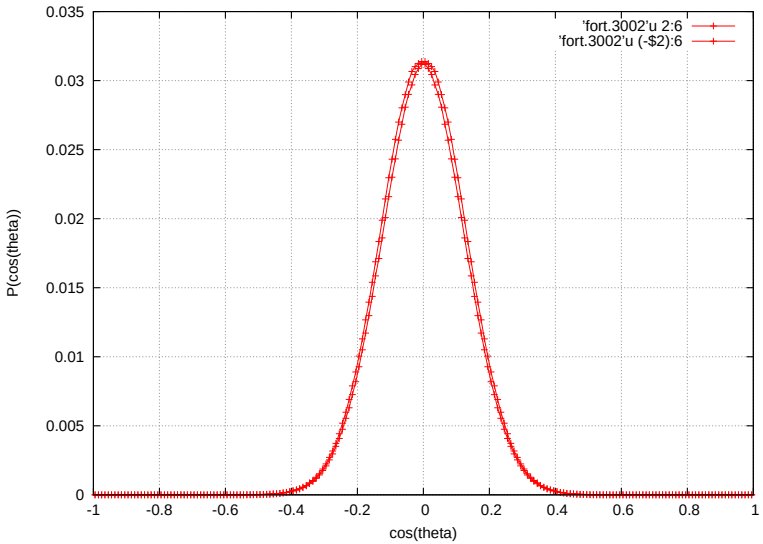
# $Rb_2$ on $^4$He surface: structure, pendular modes




## dimple @ $T = 0.3$K:

- isosurface of $^4$He density w/resp to $Rb_2$
- anisotropic (dumb bell shape)
- $Rb_2$ parallel on He surface

molecule axis orientation $\rho(\theta)$:




## pendular motion @ $T = 0.3$K:

- free rotation in surface (see below)
- pendular modes out of surface plane
- assume $\rho(\theta; T) = \rho(\theta, 0) \longrightarrow$ harmonic mean field pendular modes: $\hbar\omega = 0.94\,\mathrm{K}$

# $Rb_2$ on $^4$He surface: rotational dynamics

## PIMC simulation

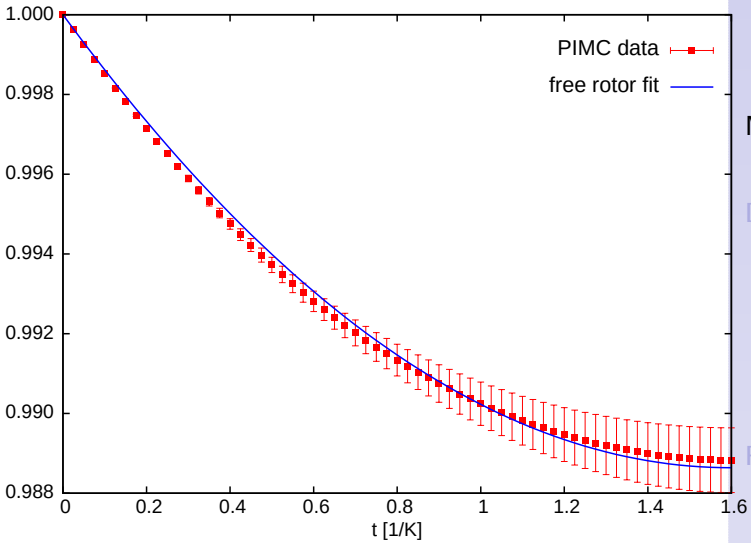
spectrum of 2D rotor (=dynamic structure function)

$$S_M(\omega) = \frac{1}{Z}\sum_{mn}\delta(\hbar\omega - E_m + E_n)e^{-\beta E_n}|\langle m|e^{iM\phi}|n\rangle|^2$$

$\Rightarrow$ imaginary-time correlation function

$$F_M(t) = \int_{-\infty}^{\infty} d\omega e^{-\omega t} S_M(\omega)$$
$$= \frac{1}{Z}\mathrm{Tr}\left[e^{-\beta H} e^{iM\phi(\tau)} e^{iM\phi(0)}\right]$$

$F_M(t)$ for $M = 1$ and free 2D rotor fit:




## Analysis

- fitting free 2D rotor correlation function to PIMC result:

$$F_M^{\mathrm{free}}(t) = \frac{1}{Z}\sum_n e^{-B(M+n)^2 t} e^{-Bn^2(\beta - t)}$$

- reduced effective rotational constant

$$B_{\mathrm{eff}} = (0.94 \pm 0.05) B_0$$

$\rightarrow$ almost indistinguishable from "gas phase" (=free) value $B_0 = 0.0152$K

# Conclusion and Outlook

## Conclusion

- Exciplex structure of 7 $^4$He atoms around Rb$^*$ — flat cluster
- Rb$\rightarrow$Rb$^{*1}$ [$^2\Pi_{1/2}$]: no exciplex formation, but metastable weakly bound surface state of Rb$^*$, consistent with experiments
- Rb$\rightarrow$Rb$^{*2}$ [$^2\Pi_{3/2}$]: *exciplex formation*
- spin-triplett $Rb_2$ on $^4$He:
  $\rightarrow$ flat equilibrium orientation on surface
  $\rightarrow$ 2D rotor with effective rotational constant $\approx$ gas phase value

## Outlook

- dynamics of (many-body!) excitation process with CBF method:
  $\rightarrow$ coupling to ripplons and phonons; dissipation?
- larger (earth) alkali clusters in/on $^4$He

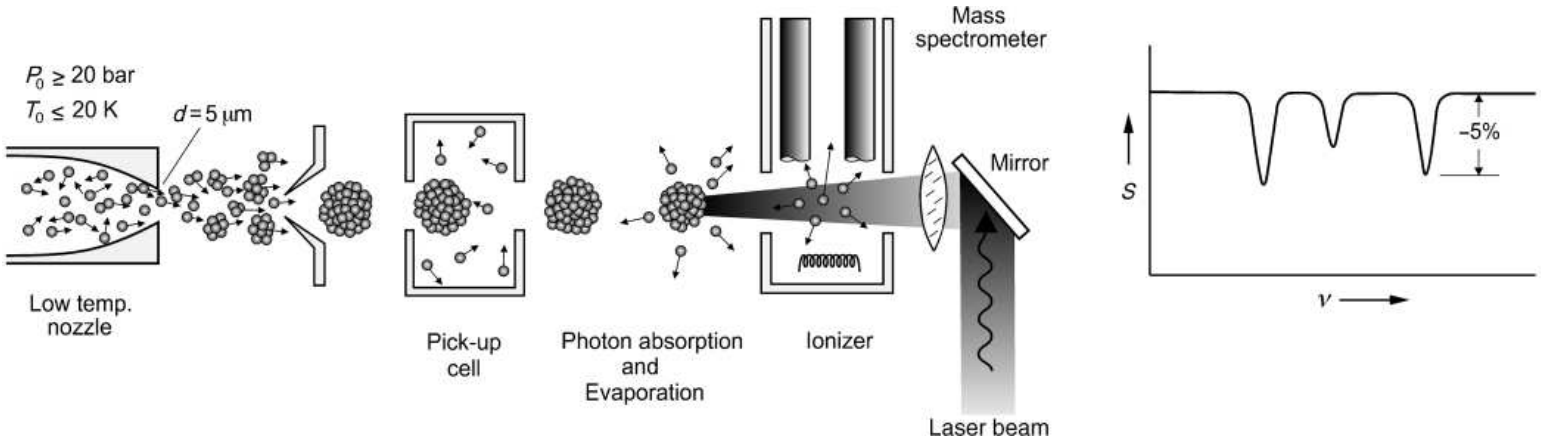
Strongly correlated dipolar quantum gases
- Introduction
- (time-dependent) hyper-netted chain Euler-Lagrange
- 2D dipolar quantum gas
- Quasi-2D dipolar quantum gases
- Conclusion/Outlook

Rb$^*$-He Exciplex formation on $^4$He surface
- Helium matrix isolation spectroscopy (HENDI)
- Diffusion and Path Integral Monte Carlo
- Rb-He and Rb$^*$-He Interaction
- Rb$^{*1}$He$_N$: 1st excited state, $^2\Pi_{1/2}$
- Rb$^{*2}$He$_N$: 2nd excited state, $^2\Pi_{3/2}$
- Rb$_2$ on $^4$He surface
- Conclusion and Outlook

Surface condensate of doped $^4$He clusters
- Helium matrix isolation spectroscopy (HENDI)
- Description of BEC in clusters
- Path Integral Ground State Monte Carlo (PIGSMC)
- Results
- Conclusion/Outlook

# Experiments: Helium matrix isolation spectroscopy

Spectroscopy of doped superfluid $^4$He clusters/droplets ($\sim$ 0.4K)
depletion spectroscopy: chromophore excitation detected by evaporating $^4$He atoms.




from J. P. Toennies and A. F. Vilesov

$\longrightarrow$ measureing sharp rovib. spectra of *isolated* molecules at low $T$
$\longrightarrow$ stabilizing transition states (conformations)
$\longrightarrow$ assembly of small clusters in He

$\longrightarrow$ probing $^4$He: superfluidity on microscopic scale – microscopic Andronikashvili exp.
(Grevenev et al., Science'98)
$\longrightarrow$ theoretical understanding of rotational spectra in terms of superfluidity
(Paesani, Kwon, Whaley, PRL'05)

$\longrightarrow$ Bose-Einstein condensation on microscopic scale
$\longrightarrow$ *No* theoretical understanding of rotational spectra in terms of BEC

# BEC in Strongly Interacting Systems: One-Body Density Matrix (OBDM)

- ideal gas of non-interacting bosons: below critical temperature $T_C$, a macroscopic number $N_0$ of particles occupy the zero momentum state
  $\longrightarrow$ condensation in momentum space
  $\longrightarrow$ $N_0$ atoms described by "macroscopic" wave function
- concept of macroscopic wave function carries over from non-interacting to weakly interacting systems
- Need a generalization for *strong* interactions and to *inhomogeneous* systems such as droplets
- 1956: Penrose and Onsager generalize concept of BEC by using one-body density matrix (OBDM)
- At $T = 0K$ the OBDM can be written as

$$\rho_1(\mathbf{r}, \mathbf{r}') = N \int d^3 r_2 \ldots d^3 r_N \; \Phi_0(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N) \; \Phi_0(\mathbf{r}', \mathbf{r}_2, \ldots, \mathbf{r}_N) \qquad (1)$$

- sample $\rho_1(\mathbf{r}, \mathbf{r}')$ with *Path Integral Ground State* Monte Carlo... see later

# Bulk .vs. Inhomogeneous System

## Bulk

- Bulk: homogeneous and isotropic
- normalized OBDM

$$n(\bar{r}) = \frac{\rho_1(\bar{r})}{\rho_0} = \int \Phi_0(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \times$$
$$\Phi_0(\mathbf{r}_1 + \bar{\mathbf{r}}, \mathbf{r}_2, \ldots, \mathbf{r}_N) d^3 r_1 \ldots d^3 r_N$$

where $\Phi_0$ = ground state wave function

- condensate fraction is defined as

$$n_0 = \frac{N_0}{N} = \lim_{\bar{r} \to \infty} n(\bar{r})$$

D. S. Lewart et al., PRB'88 ⟵
S. A. Chin, JLTP'93 ⟵
J. L. Dubois et al., PRA'03 ⟵

## Natural Orbitals

- Expansion of the one-body density matrix (OBDM) in natural orbitals (NO) yields

$$\rho_1(\mathbf{r}', \mathbf{r}) = \sum_i N_i \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}')$$

- Largest eigenvalue $N_0$ corresponds to condensate if $N_0 = \mathrm{O}(N)$ and $N_i \ll N$, $i \neq 0$
- Inhomogeneous but spherical symmetry: expand the OBDM as

$$\rho_1(\mathbf{r}', \mathbf{r}) = \sum_\ell \frac{2\ell + 1}{4\pi} P_\ell(\hat{\mathbf{r}} \cdot \hat{\mathbf{r}}') \rho_\ell(r', r)$$

- defining $u_{n\ell}(r) \equiv r\phi_{n\ell}(r)$, we end up with the eigenvalue problem

$$\int \left[ r \rho_\ell(r, r') r' \right] u_{n\ell}(r') dr' = N_{n\ell} u_{n\ell}(r)$$

-

$$\rho_1(\mathbf{r}) = \sum_{\ell, n} (2\ell + 1) N_{n\ell} |\phi_{n\ell}(r)|^2$$

$$N = \sum_{\ell, n} (2\ell + 1) N_{n\ell}$$

# Path Integral Ground State — diffusion to ground state

## Imaginary Time Propagation

exact ground state wave function $\Phi_0(R)$, $R \equiv (\mathbf{r}_1, \ldots, \mathbf{r}_N)$, can be obtained from trial wave function $\Psi_T(R)$ as

$$\Phi_0(R) \sim \lim_{\beta/2\to\infty} \langle R e^{-\frac{\beta}{2}H} \rangle \Psi_T = \lim_{\beta/2\to\infty} \int G(R, R', \beta/2) \Psi_T(R') dR'$$

with the imaginary-time propagator or Greens function

$$G(R, R', \beta/2) = \langle R | e^{-(\beta/2)H} | R' \rangle.$$

Split $\beta$ into shorter imag. time steps, $\frac{\beta}{2} = M\tau$.

$$G(R, R', \beta/2) = \int G(R, R_1, \tau) G(R_1, R_2, \tau) \cdots G(R_{M-1}, R', \tau)\, dR_1 \cdots dR_{M-1}$$

good trial wave function $\Psi_T \Rightarrow$ short imaginary time $\beta$

## Split imaginary time into steps ($\rightarrow$ "beads"):

$$\left\langle \hat{O} \right\rangle \propto \lim_{\beta\to\infty} \int dY\, P'(Y, \beta) \hat{O}(R_M, \tilde{R}_M) = \lim_{N_{mov}\to\infty} \frac{1}{N_{mov}} \sum_{i=1}^{N_{mov}} \hat{O}(R_M^i, \tilde{R}_M^i)$$

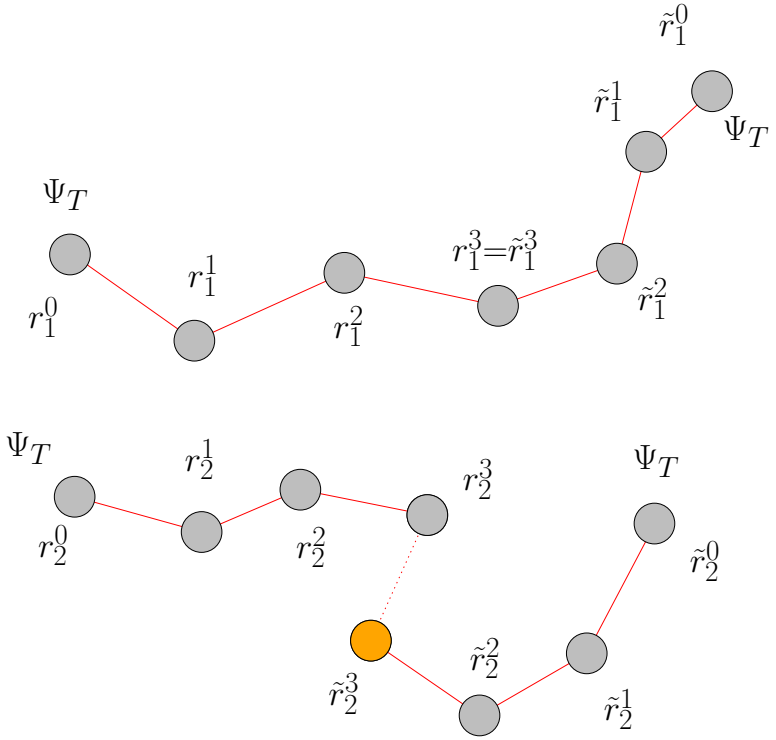
with

$$P'(Y, \beta) = \frac{1}{\text{Norm}} \Psi_T(R_0) \times \prod_{j=0}^{M-1} G(R_j, R_{j+1}, \tau) \times \prod_{j=0}^{M-1} G(\tilde{R}_j, \tilde{R}_{j+1}, \tau) \times \Psi_T(\tilde{R}_0)$$

(expectation value is not normalized correctly if $R_M \neq \tilde{R}_M$, such as for OBDM)

# PIGSMC sketch – classical isomorphism

imaginary time paths for 2 particles and 7 time slices ("beads").
path of particle 2 is cut in the center.




- each bead has weight $e^{-\alpha\tau V}$
- red lines: kinetic energy $e^{-(\mathbf{r}_i^\tau - \mathbf{r}_i^{\tau+1})^2/4D\tau}$
- end beads: trial wave function $\Psi_T$
- center bead: true ground state $\Psi_0$, unbiased by $\Psi_T$
- cut path in middle for off-diagonal properties such as OBDM
  caution: normalization
- Metropolis random walk using bisection method

$G(R, R', \tau)\ldots$ **quasi-6th** order PIGSMC, error$[E_0]$=O$(\tau^6)$
S. A. Chin and C. R. Chen, JCP'02
J. Casulleras, J. Boronat

# Quasi-6th order PIGSMC

$$G_0(R_j, R_{j+1}, \tau) = \rho_F(R_j, R_{j+1}, \tau')\rho_V(R_j),$$

$$\rho_V(R_j) = \begin{cases} \exp\left[-\tau v_0 V(R_j)\right] & \text{if } j = 0 \text{ or } j = 2M \\ \exp\left[-2\tau v_0 V(R_j)\right] & \text{else if } (j \bmod 3) = 0 \\ \exp\left[-\tau v_1 V(R_j) - \frac{u_0 \tau^3 \hbar^2}{m} \sum_{i=1}^{N} |\nabla_i V(R_j)|^2\right] & \text{else} \end{cases},$$

$$\tau' = \begin{cases} t_1 \tau & \text{if } (j \bmod 3) = 0 \\ t_2 \tau & \text{else} \end{cases}.$$

$\frac{1}{2}(1 - \frac{1}{\sqrt{3}}) \leqslant t_1 \leqslant \frac{1}{2}$ is a free parameter. Optimal value for $^4$He: $t_1 = 0.265$

$$t_2 = 1 - 2t_1$$

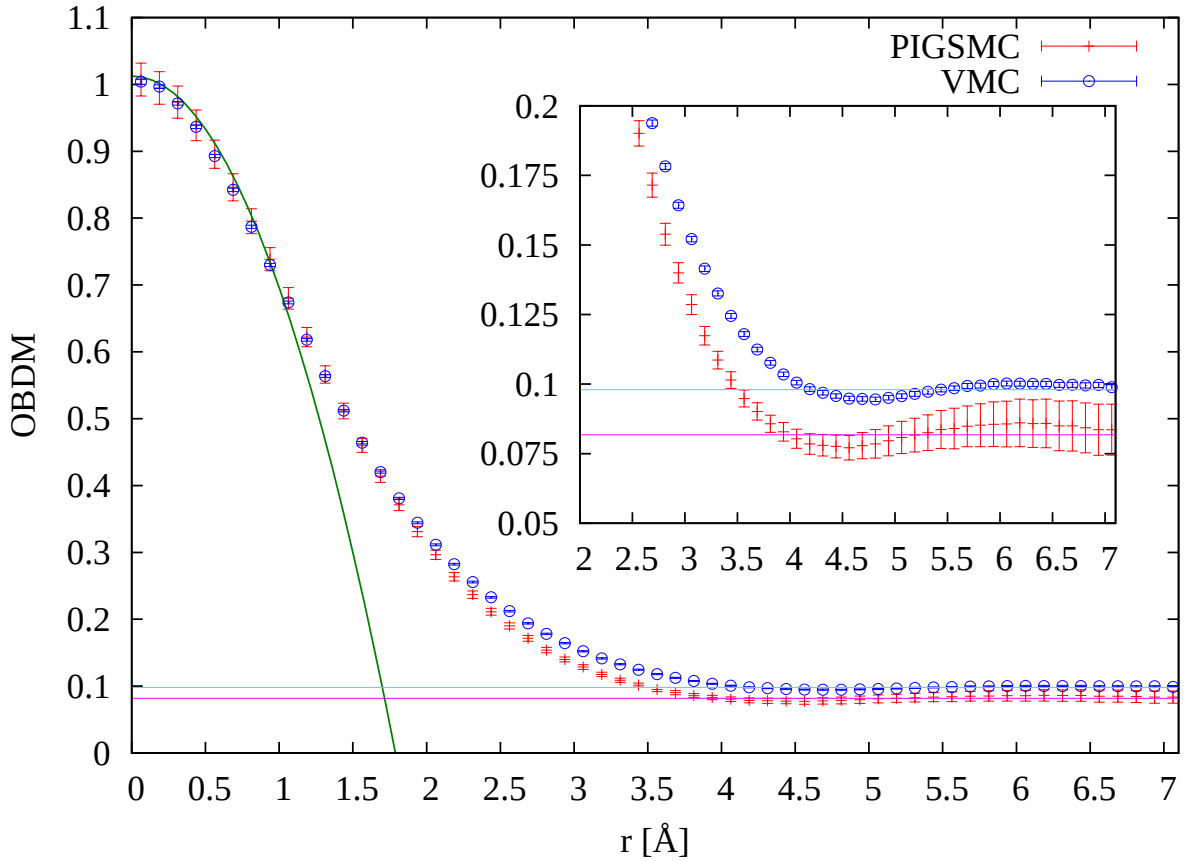
$$v_0 = \frac{6t_1(t_1 - 1) + 1}{12(t_1 - 1)t_1}$$

$$v_1 = \frac{1}{2} - v_0$$

$$u_0 = \frac{1}{48}\left[\frac{1}{6(1 - t_1)^2 t_1} - 1\right]$$

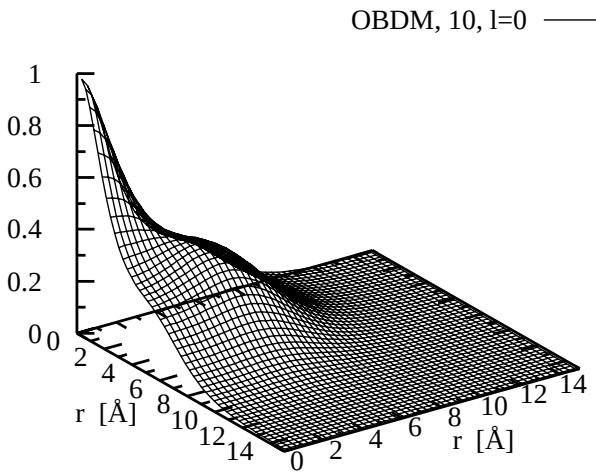
# Test of PIGSMC: bulk $^4$He

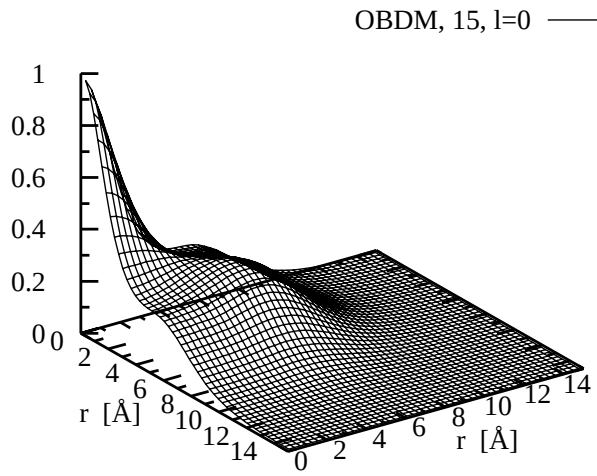
$n(\bar{r}) = \frac{\rho_1(\bar{r})}{\rho_0}$ for bulk $^4$He at equilibrium density ($N = 64$, pbc):

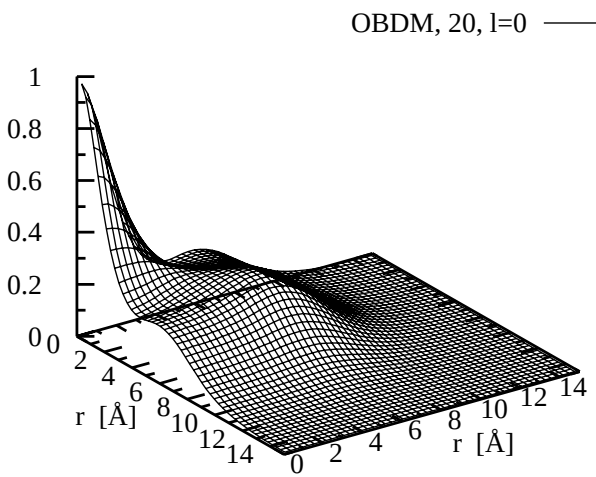


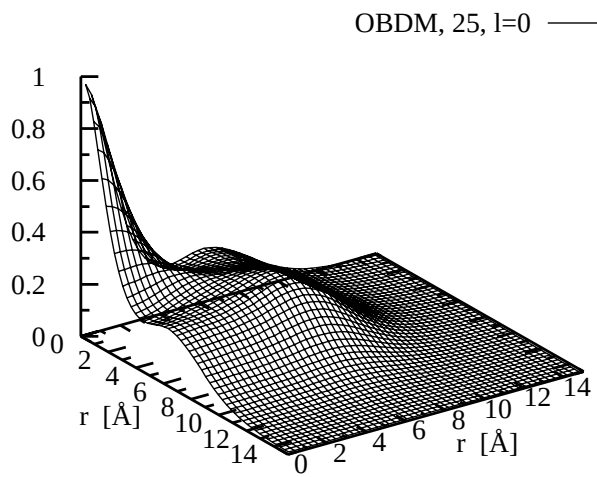

condensate fraction: $n(\bar{r} \to \infty) \approx 0.078$

# One-Body Density matrix for $\ell = 0$, pure $^4$He droplet

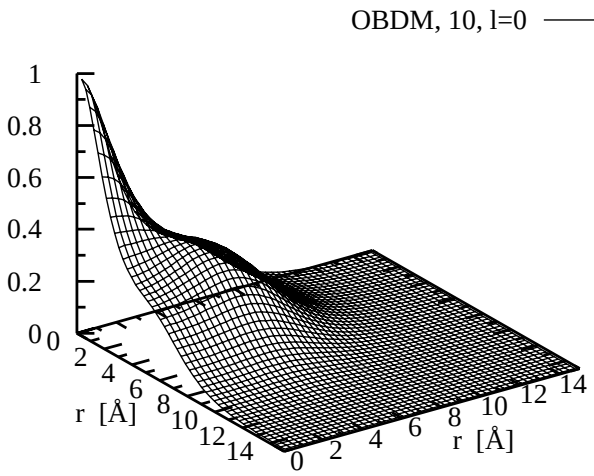


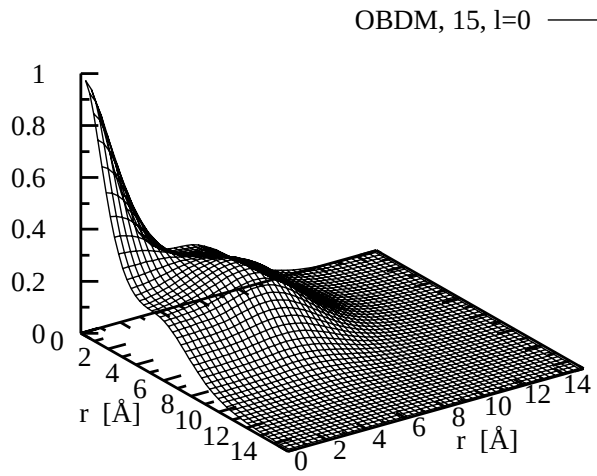



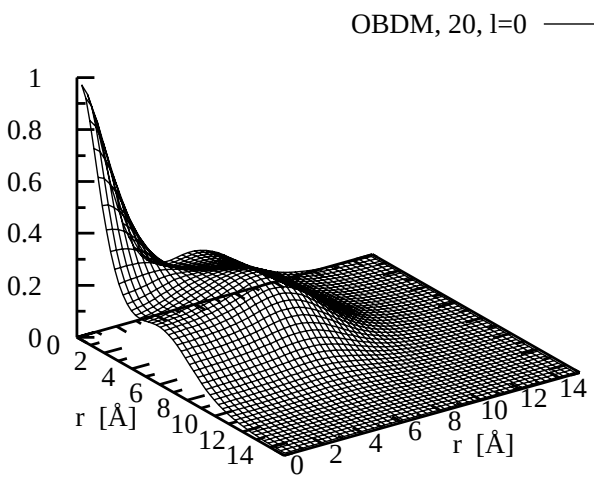



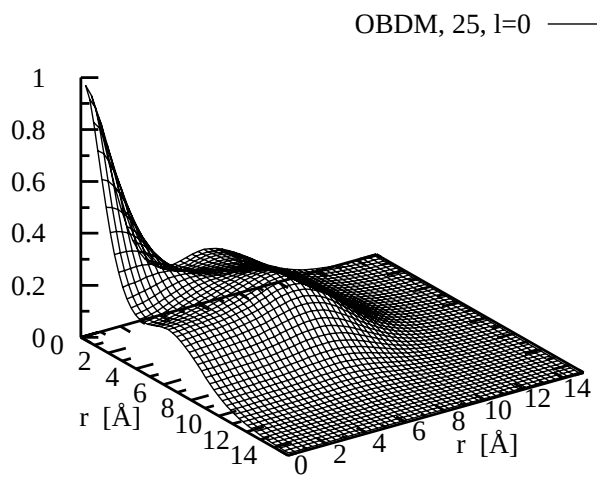
# One-Body Density matrix for $\ell = 0$, pure $^4$He droplet




**calculate for all $\ell$! diagonalize!**



# $SF_6He_N$ — Overview

plenty of experimental and theoretical work on doped $^4$He droplets

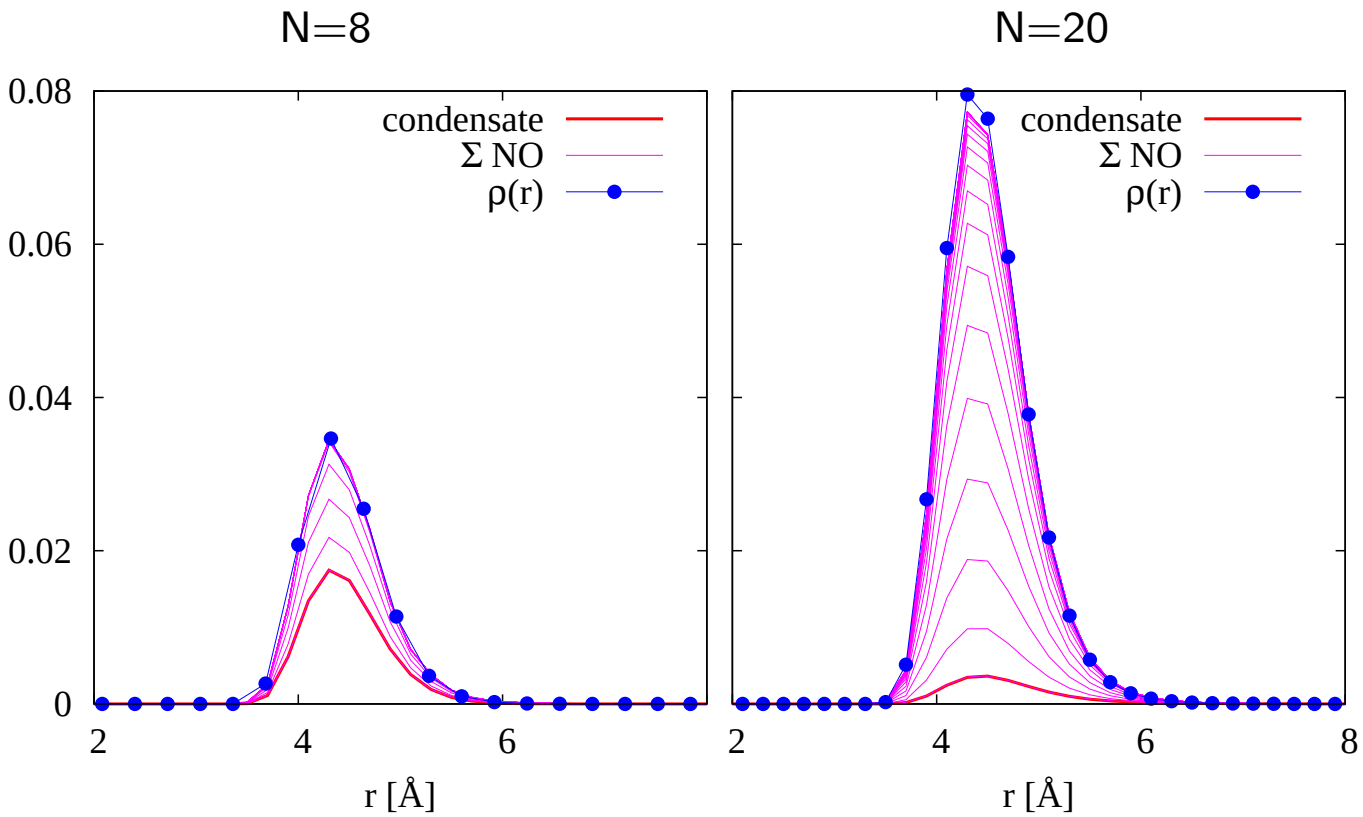
## previous work on $^4$He around $SF_6$

| | |
|---|---|
| experiment | Goyal et al, JCP (1993) |
| calculation | R. N. Barnett, K. B. Whaley, JCP (1993); Spherical Model for $SF_6$ |

## Model used in this work:

- $SF_6$ heavy ⇒ translational & rotational zero-point motion assumed negligible
- $SF_6$-He interaction assumed spherical

# $SF_6He_N$ — Natural Orbitals of $^4He$




$\Rightarrow$ filling of 1st solvation "shell" depletes the condensate (. . . obviously)

# $SF_6He_{20}$ — Solid or Liquid?

superfluid fraction about $x$-axis

$$f_x^s = 1 - \frac{I_x}{I_x^{cl}} = \frac{4m^2\langle A_x^2\rangle}{\hbar^2\beta\, I_x^{cl}}$$

Symmetry: $f_x^s = f_y^s = f_z^s$

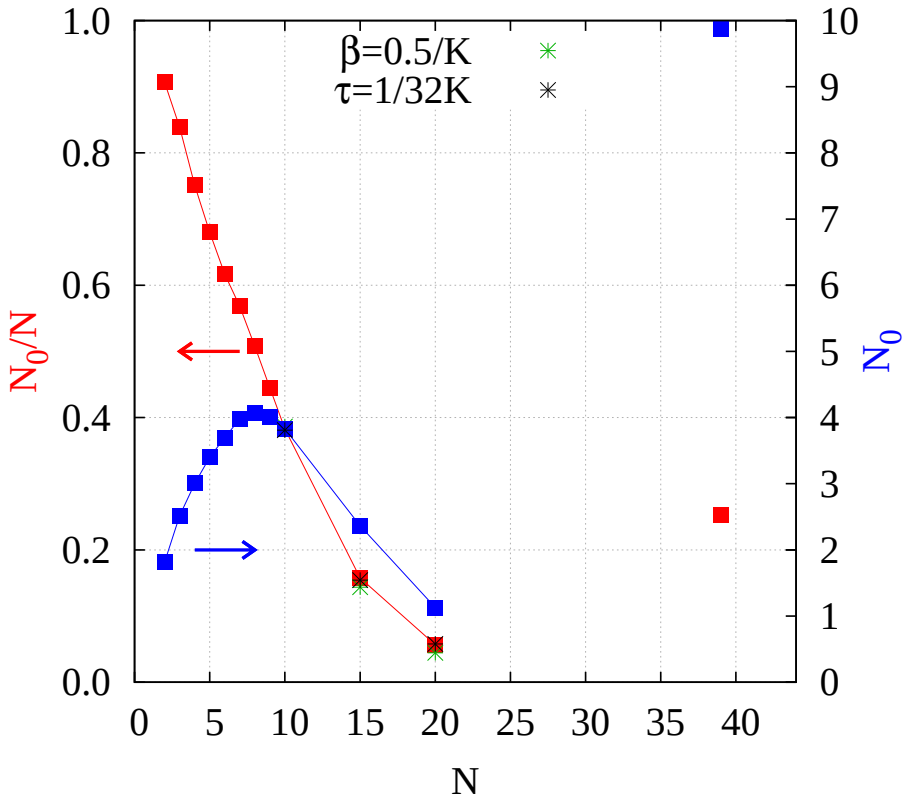
PIMC simulation of $SF_6He_{20}$ @ 0.3K:

$$f^s = 1.00 \pm 0.02$$

. . . as expected for an isotropic dopant surrounded by *liquid* $^4$He @ 0.3K.

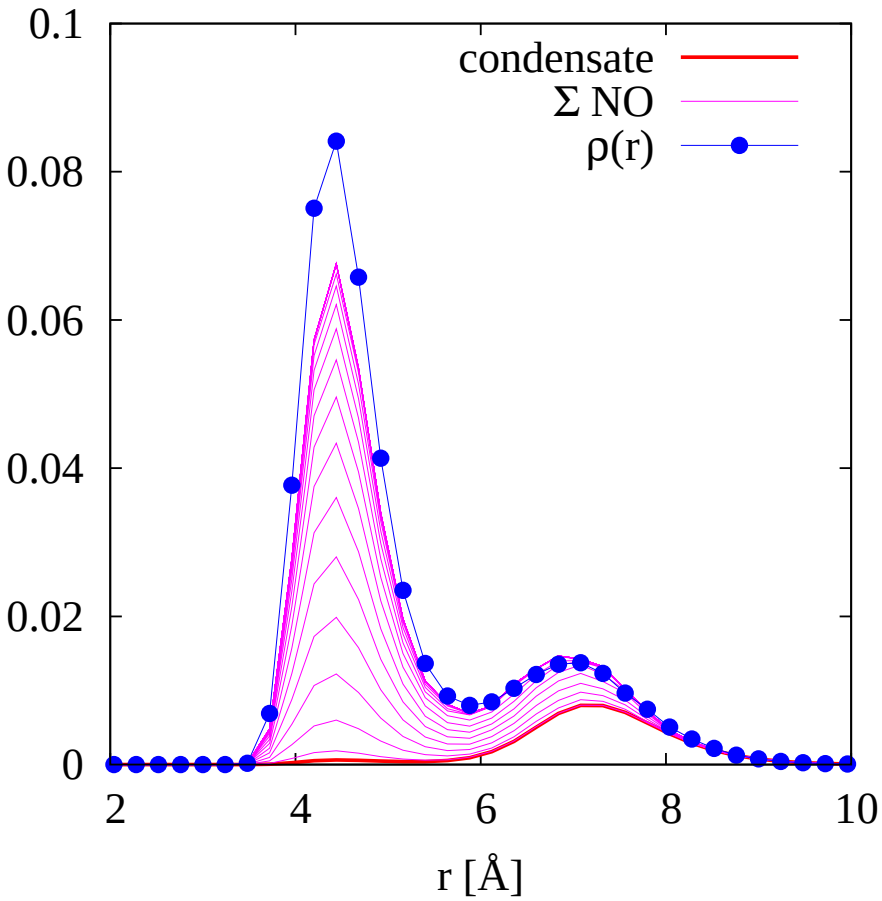
- $SF_6He_{20}$ is not solid but 100% superfluid
  true *an*isotropic $SF_6$-He interaction: $<$ 100% superfluid
- but BEC is supressed by interactions.

# $SF_6He_N$ — Condensate fraction




- condenstate fraction vanishes as $^4$He fills up 1st solvation "shell"
- technical: no $\tau$ bias, small $\beta$ bias ($\Rightarrow$ improve $\Psi_T s$)
- with occupation of 2nd "shell", condensate fraction increases, as exemplified by $N = 39\ldots$

# $SF_6He_N$ — Beyond 1st solvation "shell"




$N = 39$:

- no condensation in 1st "shell"
- about 2/3 of particles in 2nd "shell" are Bose condensed

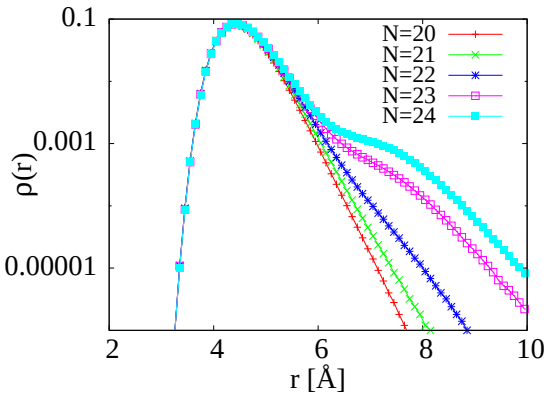
# Conclusion/Outlook

## Conclusion:

- PIGSMC allows calculation of NO's with negligible, controllable $\Psi_T$ bias
- non-monotonous $N$-dependence of condensate fraction due to layered growth of "shells"
- no condensate in 1st "shell"

## Outlook:

- Investigate 2nd "shell" growth $\longrightarrow$
- How to deal with rotational symmetry breaking induced by realistic dopant-He interaction?
- theory: coupling between local BEC and dopant molecule dynamics?
  $\longrightarrow$ can local BEC be measured by HENDI spectroscopy?
  (analog to bulk $^4$He: high momentum transfer of neutrons $\longrightarrow$ condensate fraction)
  (McKellar et al., PRL'06: oscillation of $B_{\mathrm{eff}}$ as function of $N$)



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**Surface Condensate**

Johannes Mayrhofer

*Thank you!*