

# Spatial features and energetics of ultra weakly interacting three-particle systems: do they hold Efimov states?

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What do we mean by ultra weakly bound systems ?

- Weak atom-atom potentials (well depths of few  $\text{cm}^{-1}$ )
- Important long range dispersion component
- High Zero Point Energies
  - Extremely small binding energies
  - Very delocalized, floppy systems

Ultra weakly bound systems are the principal candidates which could support Efimov states

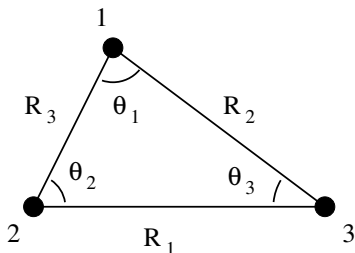
How can we characterize ultra weakly bound systems ?

- Challenging problem (very diffused states, very small energies, ...)
- Distributed Gaussian Function (DGF) Method: Energies, Possible Efimov Behaviour, Detailed geometrical characterization of bound wave functions

DGF treats trimer systems:

- $A_3$
- $A_2B$
- $ABC$

in terms of interatomic coordinates



Wave Function:

$$\Phi^{(k)}(R_1, R_2, R_3) = \sum_j a_j^{(k)} \phi_j(R_1, R_2, R_3)$$

$$\phi_j(R_1, R_2, R_3) = N_{lmn}^{-1/2} \sum_{P \in S_3} P [\varphi_l(R_1) \varphi_m(R_2) \varphi_n(R_3)]$$

Triangular Inequality Requirement (TIR):  $|R_l - R_m| \leq R_n \leq R_l + R_m$

$$H(R_1, R_2, R_3) = \sum_{k=1}^3 -\frac{\hbar^2}{2m_k} T_k(R_1, R_2, R_3) + \sum_{i,j,k=1}^3 V_{ij}(R_k)$$

- $T_k$  depends on the type of system ( $A_3$ ,  $A_2B$ ,  $ABC$ )
- $V_{ij}(R_k)$  sum of 2B interatomic potentials
- DGF also treats 3B potential contributions ( $V_{3B}$  in terms of  $R_1, R_2, R_3$ )  
 $V_{3B}$  is negligible for weakly bound systems

S.Orlandini *et al.* Mol. Phys. **106**, 573 (2008)

I.Baccarelli *et al.* J. Chem. Phys. **122**, 144319 (2005)

- 1D distribution

$$\mathcal{D}^{(k)}(R_i) = \iint |\Phi^{(k)}(R_1, R_2, R_3)|^2 dR_j dR_k$$

- 2D distribution

$$\mathcal{D}^{(k)}(R_i, R_j) = \int |\Phi^{(k)}(R_1, R_2, R_3)|^2 dR_k$$

- Pseudo Weights

$$1 = \langle \Phi^{(k)} | \Phi^{(k)} \rangle = \sum_j a_j^{(k)} \langle \Phi^{(k)} | \phi_j \rangle = \sum_j P_j^{(k)}$$

$$\langle x^n \rangle^{(k)} = \sum_j a_j^{(k)} \langle \Phi^{(k)} | x^n | \phi_j \rangle \approx \sum_j P_j^{(k)} x_j^n$$

## Basic Features:

- Description in terms of "natural" coordinates  $R_1, R_2, R_3$
- 3-dimensional problem factorized in 3 mono-dimensional integrals
- Simple computational setup

## New Features:

- Huge matrix size is now possible  
Very extended radial domains, millions of basis functions now solved with limited computational effort  
(not possible with standard techniques)
- Challenge of Collinear structures  
Ill-behaving DGF Wave Functions corrected with "Badness" indicator
- The familiar problem of a finite basis set  
Extrapolation to the "exact" DGF value of the energy  
(infinite number of  $\delta$ -function)

- The Gaussian basis set is not orthogonal  
Nuclear Schrödinger equation leads to a Generalized Eigenproblem:

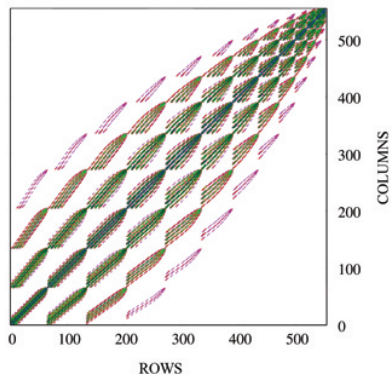
$$H \Phi^{(k)} = \left( E^{(k)} - S \right) \Phi^{(k)}$$

- matrix structure:
  - sparse
  - diagonally dominant
- Best solution for large sparse eigenvalues problems:  
Iterative method for the solution of the Schrödinger equation  
→ Jacobi-Davidson Method

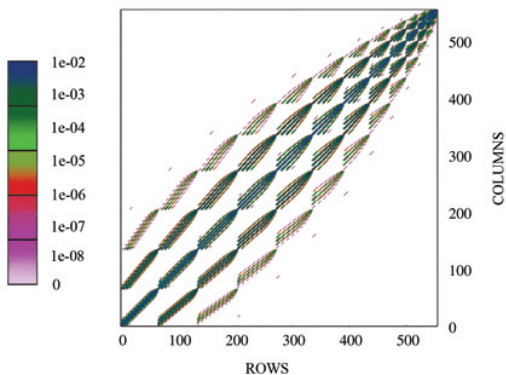
G.Sleijpen, H.van der Vorst, SIAM J. Mat. Anal. and Appl. 17, 401 (1996)

D.Fokkema, G.Sleijpen, H.van der Vorst, SIAM J. Sci. Comput. 20, 94 (1998)

HAMILTONIAN MATRIX



OVERLAP MATRIX



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Basic idea of Jacobi-Davidson Method:

$$\mathbf{H}_n x = \lambda x$$

- Generate a low dimensional subspace  $\mathcal{K}$  spanned by an orthonormal basis  $\{v_1, \dots, v_k\}$  ( $k$  dimensional,  $k \ll n$ )
- Project the matrix onto this subspace:  $\mathbf{M}_k = \mathbf{V}_k^* \mathbf{H}_n \mathbf{V}_k$
- Extract an approximate eigenpair  $(\theta, y)$  from the low dimensional eigenproblem:  $\mathbf{M}_k s = \theta s$  using standard technique ( $k \ll n$ )
- If the approximate eigenpair does not satisfy some convergence criteria expand the subspace using the orthogonal correction of  $y$
- If the convergence is reached:  
The eigenvalues of  $\mathbf{M}$  is the same of  $\mathbf{H}$   
The eigenvector of  $\mathbf{H}$  is  $\mathbf{V}_k s$

JDQZ Method: QZ-algorithm applied to the Jacobi-Davidson

D.Fokkema, G.Sleijpen, H.van der Vorst, SIAM J. Sci. Comput. **20**, 94 (1998)

JD performances with respect to original DGF:

- Number of basis functions
  - OLD max 60 000
  - JD-DGF until  $2 \cdot 10^6$
- Memory requirement
  - OLD  $\sim 30$  GB for 60 000 basis functions
  - JD-DGF  $\sim 20$  MB for 60 000 basis functions
- Parallel implementation
  - Speed-Up
  - Scale-Up
- Time
  - Problem with  $1 \cdot 10^6$  basis function requires few hours

	Processor	CPU	RAM	Performance
NEC	SX-6 single node	565 MHz	64 GB	72 Gflops
POS	AMD Opteron 246	2.0 GHz	4.0 GB	200 Gflops
CLX	Xeon Pentium IV	2.8 GHz	1.0 GB	238 Gflops
T23	AMD Athlon(tm) 64 X2	2.4 GHz	1.9 GB	

System: HeNeH

60720 basis functions

	proc.	NEC	POS	CLX	T23
OLD	1	41:13:17			
NEW	1	03:18:41	00:23:08	00:25:14	00:18:50
	2		00:12:41	00:16:27	00:10:08
	4		00:07:05	00:09:20	
	8		00:04:42	00:05:52	
	16		00:03:22	00:04:12	

Pathological region of the wave function

- Restricted TIR

$$|R_l - R_m| < R_n < R_l + R_m$$

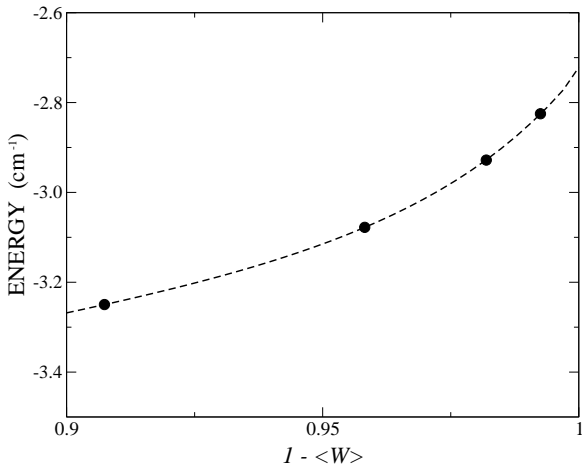
- "Badness" operator quantifies the pathology of the Wave Function

$$\mathcal{W}(R_1, R_2, R_3) = \begin{cases} 0, & |R_1 - R_2| \leq R_3 \leq R_1 + R_2 \text{ holds} \\ 1, & \text{otherwise} \end{cases}$$

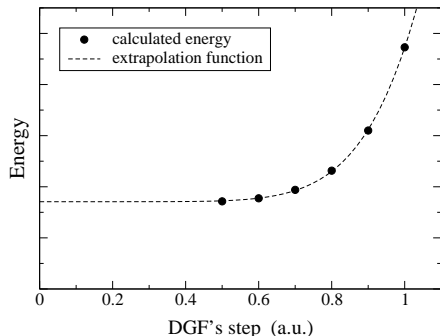
- Different calculation at different "Badness"  
(by shifts of the basis functions)
- Extrapolation of the Energy value at zero "Badness"

System: HeNeH

$$E = \sum_{k=0}^3 a_k x^{2k}$$



- We always use Gaussian functions with finite amplitude.
- The "exact" value of the DGF energy corresponds to the limit of using an infinite number of  $\delta$ -functions (computationally unreachable).
- We solve this problem with an extrapolation to the  $\delta$ -limit.



System: HeNeH

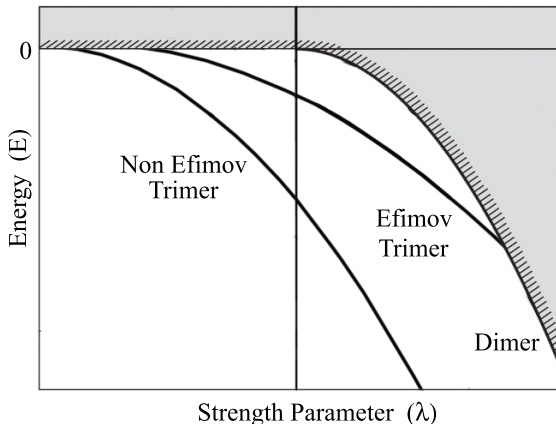
Functional Form:

$$E = a_0 + a_1 x^2 + a_2 x^4 + a_3 x^{a_4}$$

Std. Dev.:  $\sim 10^{-5}$

# How to search for an Efimov state

- Tuning the strength of 2B potential  
V.Efimov, Phys. Lett. **33B**, 563 (1970)
- We use a strength parameter  $\lambda$  to tune the 2B potentials



Ne with half mass ( $^{half}\text{Ne}_3$ ) as a benchmark system

M.Nightingale, P.Roy J. Phys. Chem. A **110**, 5391 (2006)

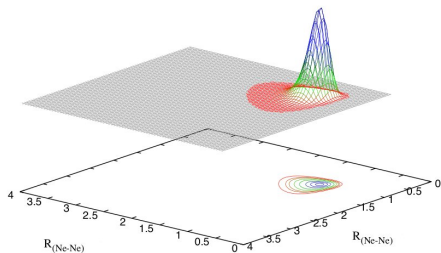
k	DVR	CFMC	DGF	DGF <i>zero badness</i>
0	-1.3086	-1.3086	-1.3086	-1.3086
1	-0.8803	-0.8803	-0.8863	-0.8808
2	-0.7594	-0.7594	-0.7752	-0.7597
3	-0.5671	-0.5671	-0.5847	-0.5682
4	-0.4804	-0.4804	-0.4861	-0.4853

All energies are in units of  $\epsilon$ .

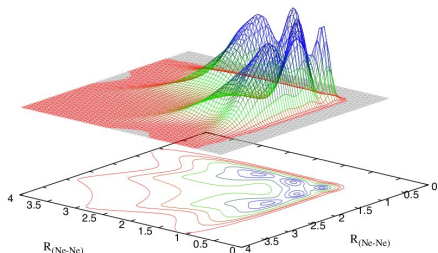
- No collinear for ground state  
The extrapolation at zero badness is not required
- For excited state the extrapolation at zero badness is required

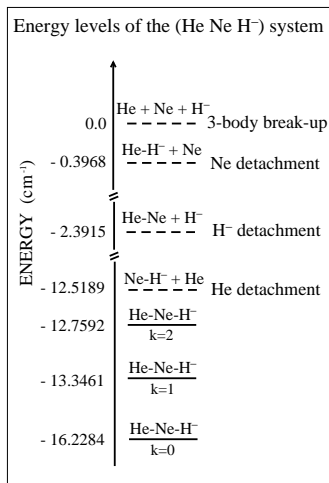
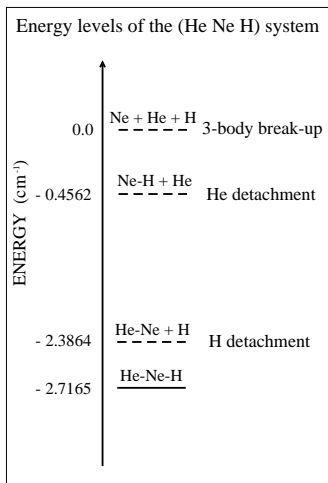
S.Orlandini, I.Baccarelli, F.A.Gianturco, Comp. Phys. Comm. **180**, 384 (2009)

$k = 0$



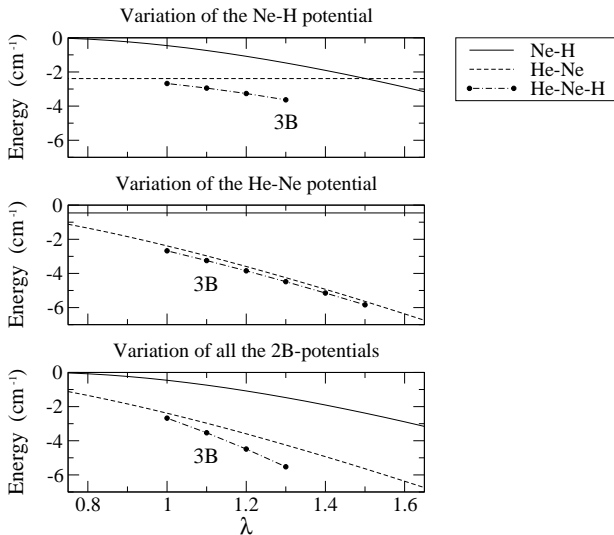
$k = 4$

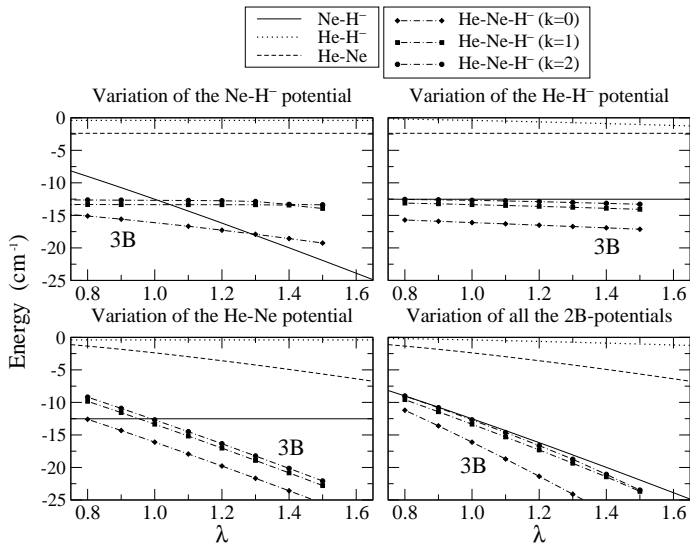




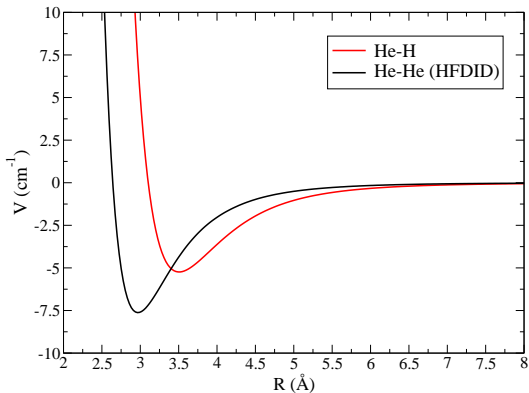
S.Orlandini, I.Baccarelli, F.A.Gianturco, J. Chem. Phys. **125**, 234307 (2006)

HeNeH:  $E_0 = -2.7122 \text{ cm}^{-1}$  Liu and Roy, J. Chem. Phys. **121**, 6282 (2004)

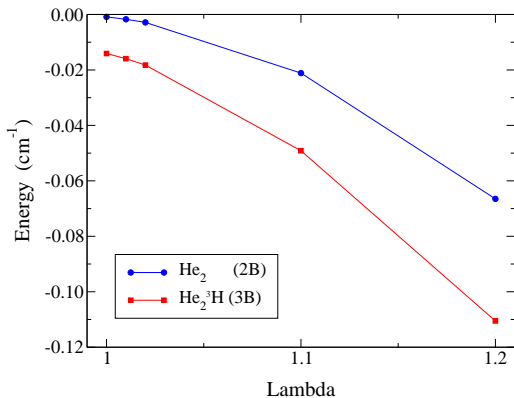




	DGF	Faddeev
He <sub>2</sub> - <sup>1</sup> H	-	-
He <sub>2</sub> - <sup>2</sup> H	-	-
He <sub>2</sub> - <sup>3</sup> H	-0.01407	-0.01409



	DGF	Faddeev
He <sub>2</sub> - <sup>1</sup> H	-	-
He <sub>2</sub> - <sup>2</sup> H	-	-
He <sub>2</sub> - <sup>3</sup> H	-0.01407	-0.01409



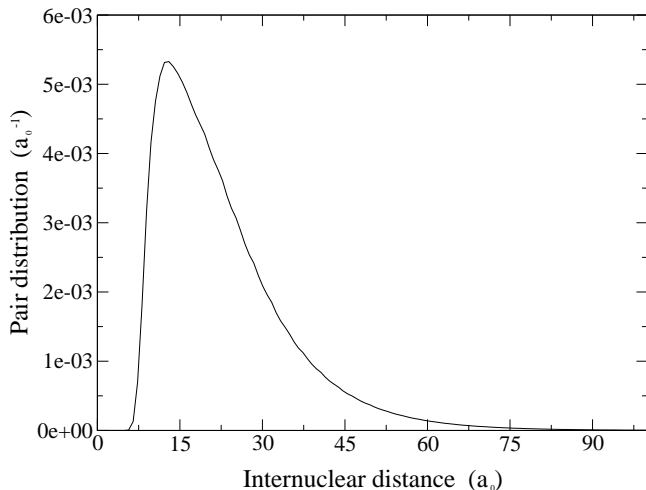
	$k = 0$	$k = 1$	References
DGF old	- 0.15	- $1.24 \cdot 10^{-3}$	PRL <b>82</b> , 1648 (1999)
DGF present	- 0.0873	- $1.56 \cdot 10^{-3}$	CPC <b>180</b> , 384 (2009)
Esry et al.	- 0.0737	- $1.47 \cdot 10^{-3}$	PRA <b>54</b> , 394 (1996)
Nielsen et al.	- 0.0870	- $1.96 \cdot 10^{-3}$	JPB <b>31</b> , 4085 (1998)
Blume et al.	- 0.0872	- $1.58 \cdot 10^{-3}$	JCP <b>112</b> , 8053 (2000)
Motovilov et al.	- 0.0875	- $1.58 \cdot 10^{-3}$	EPJD <b>13</b> , 33 (2001)

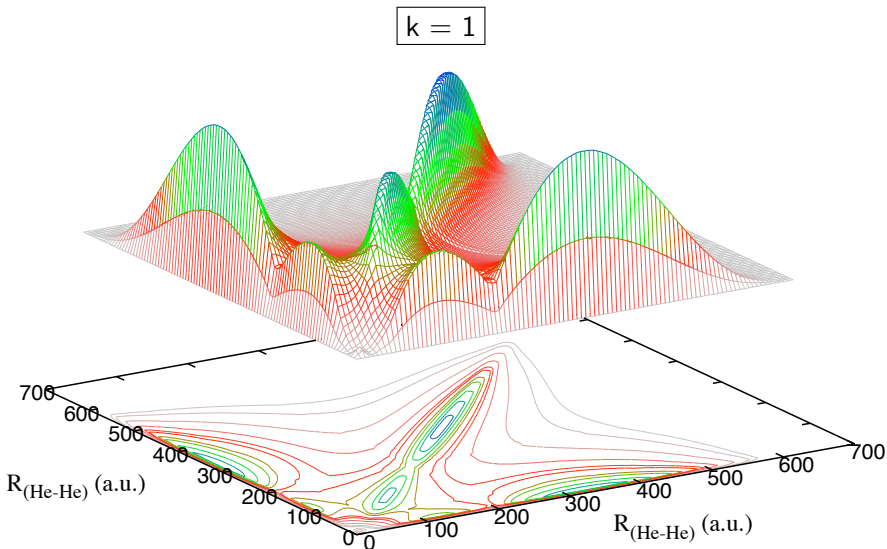
All energies are in  $\text{cm}^{-1}$ .

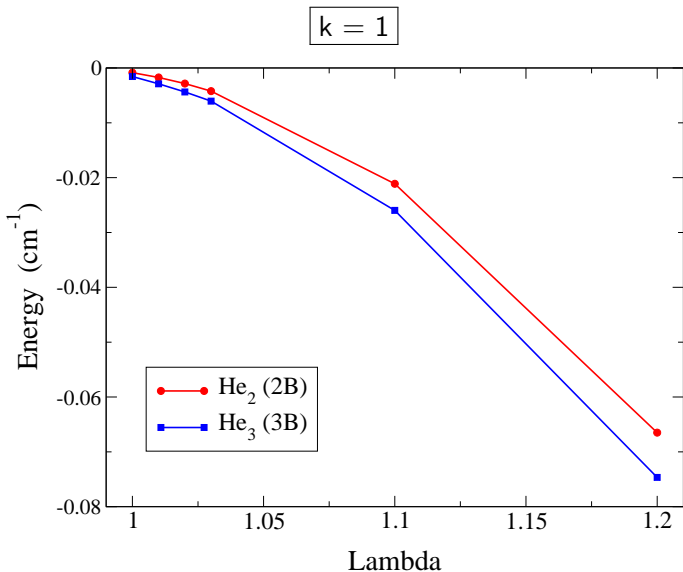
in %	Equil.	Coll.	Iso. Flat	Iso. Tall	Scal.
$k = 0$	1.8	15.2	9.9	0.0	73.1
$k = 1$	4.2	6.1	0.3	0.0	89.4

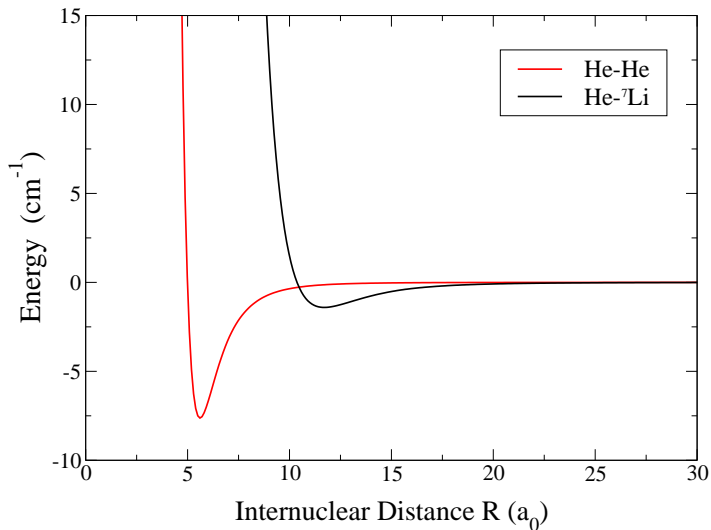
S.Orlandini, I.Baccarelli, F.A.Gianturco, Comp. Phys. Comm. **180**, 384 (2009)

$$k = 0$$

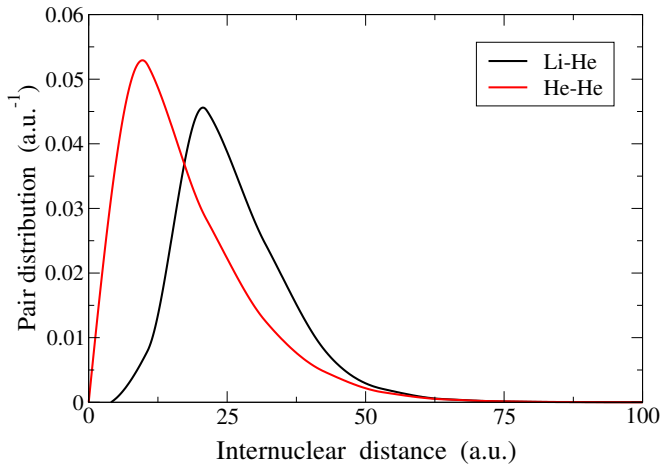








Dimer	$k = 0$	
He-He	$-0.091 \cdot 10^{-2}$	
He- ${}^7\text{Li}$	$-0.195 \cdot 10^{-2}$	
<hr/>		
Trimer $\text{He}_2{}^7\text{Li}$		
old DGF	$-5.10 \cdot 10^{-2}$	PCCP <b>2</b> , 4067 (2000)
new DGF	$-4.87 \cdot 10^{-2}$	
Yuan et al.	$-3.18 \cdot 10^{-2}$	JPB <b>31</b> , L637 (1998)



# Conclusion

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- Set up of DGF Method for ultra weakly bound systems
- Full characterization of the geometrical features for several systems
- We have not found Efimov states so far ... but we keep looking for other candidates

## Acknowledgements

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- The Spanish Crew
  - Prof. P. Villarreal
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