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EU-India collaborations in molecular and materials science

Steven Blundell

CEA-Grenoble, France

Outline

- Collaborations between Univ. Pune (Prof. Dilip Kanhere) and CEA-Grenoble, France 2000–present

  Funded by: IFCPAR (2000–2003, 2004–2008) (Indo-French Centre for the Promotion of Advanced Research)

  EU-IndiaGrid2 (2010–)

  Collaborators:

  Prof. D. G. Kanhere (Univ. Pune, India)
  Dr. Kavita Joshi
  Soumyajyoti Haldar (student)
  Dr. Sajeev Chacko (now Jawaharlal Nehru Univ., New Delhi)
  Dr. Utpal Sarkar (now Assam University)

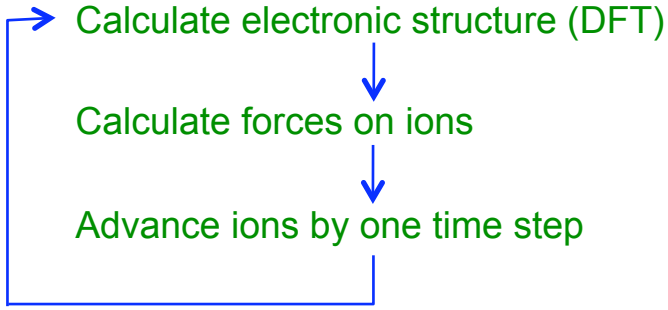
- Atomic clusters
  – structure
  – thermodynamics and melting
  – effect of substrate

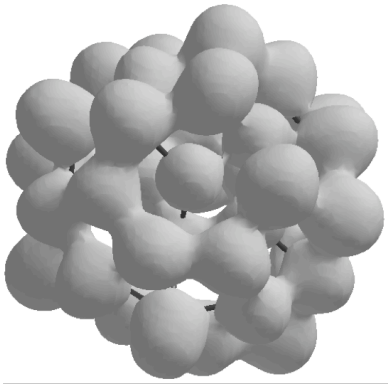
- Electronic structure of quantum dots
  – Wigner molecules

Clusters: methodology

- Density functional theory

- *Ab initio* molecular dynamics





Ga_{40}

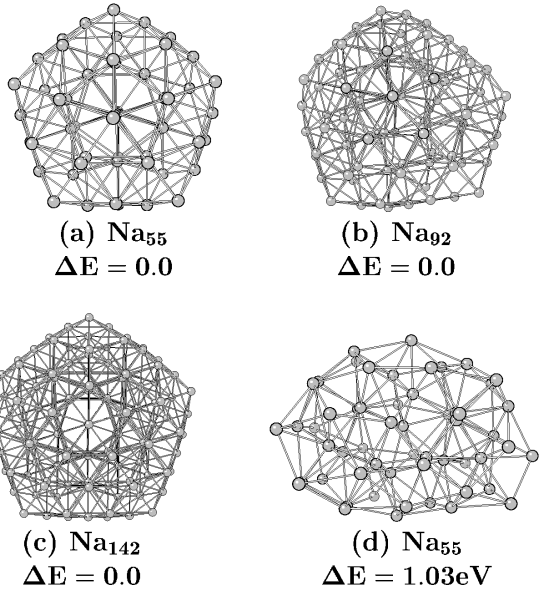
Clusters: properties can differ from bulk

- *Ab initio* statistical mechanics (melting)
  - sample ionic phase space (microcanonical or canonical MD, or Monte-Carlo)
  - extract classical ionic density of states $\Omega(E)$ (multihistogram fit)
  - thermodynamic averages

Melting of Na clusters

Aim: to understand the pattern of *size-dependent* (N = 50–300) melting temperatures measured by Haberland and co-workers (Nature, 1997)

- Find lowest-energy structures at T = 0 K
  ('basin hopping' with model potentials, local minimization with DFT)
- Large-scale *ab initio* (DFT) molecular dynamics simulations (1–2 ns per cluster size)
- Statistical analysis of data: classical density of states, entropy, specific heat, etc.
  (multiple histogram analysis, with isokinetic sampling of phase space)



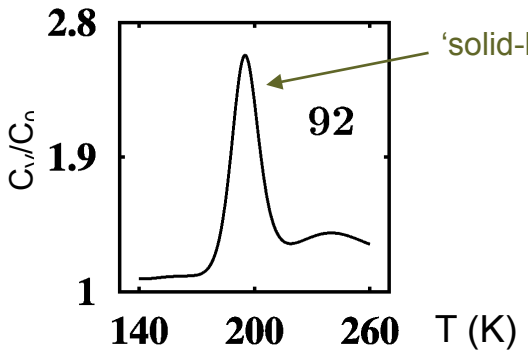


TABLE I. Theoretical and experimental melting temperatures in Na clusters.

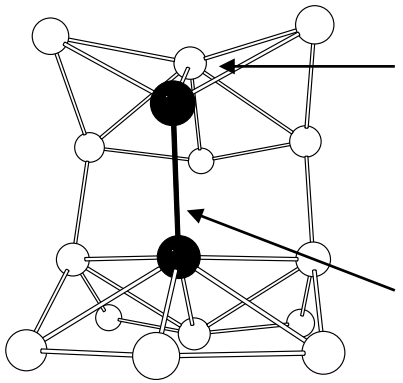
N	KS	Expt.	SMA[a]	SMA[b]	DB
55	280	290	175	162	190
92	195	210	170	133	240
142	290	270	240	186	270

First principles calculations of melting temperatures for free Na clusters
S. Chacko, D. G. Kanhere and S. A. Blundell, Phys. Rev. B **71**, 155407 (2005)

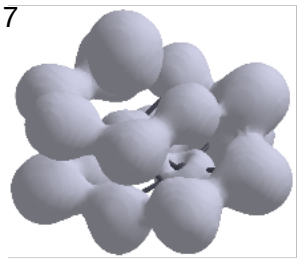
Experiment: Breaux *et al*.. PRL **91**, 215508 (2003)

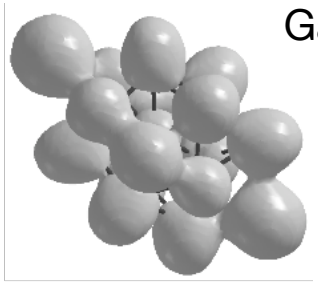
$T_m(Ga_{17}^+) \approx 700$ K
$T_m(Ga_{39}^+) = 550$ K
T_m(bulk) = 303 K

Bulk α-Ga



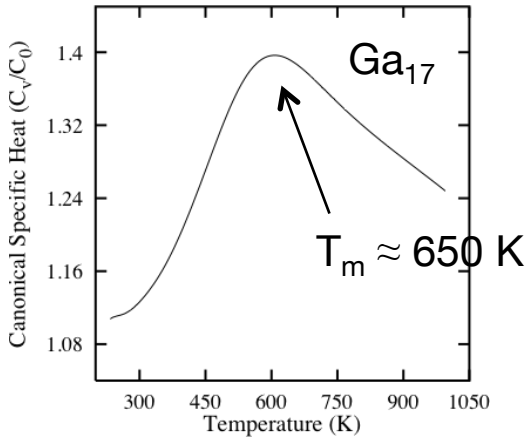
Ga_{17}

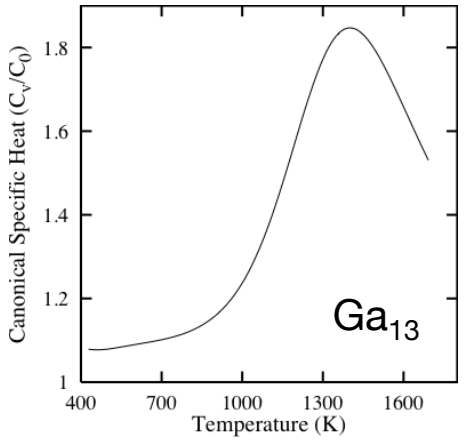


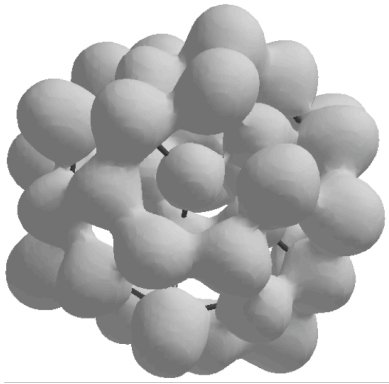


Ga_{17}^+

Theory: Joshi, Kanhere, and Blundell,
Phys. Rev. Lett. **92**, 135506 (2004)



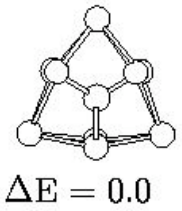




Ga_{40}

Thermal properties of Si and Sn nanoparticles

- Speculation that Si_N for $20 < N < 70$ fragments, rather than undergoes a solid to liquid transition (based on experiments by Jarrold *et al.*)

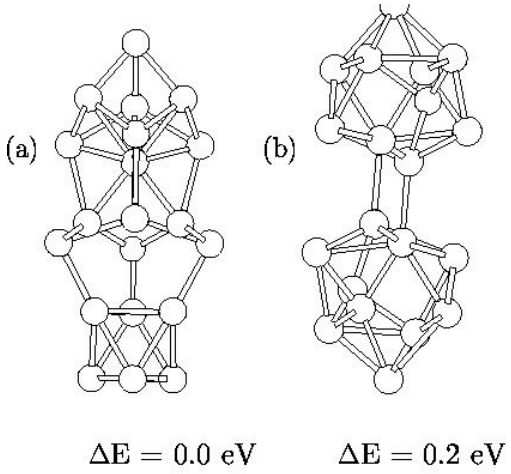


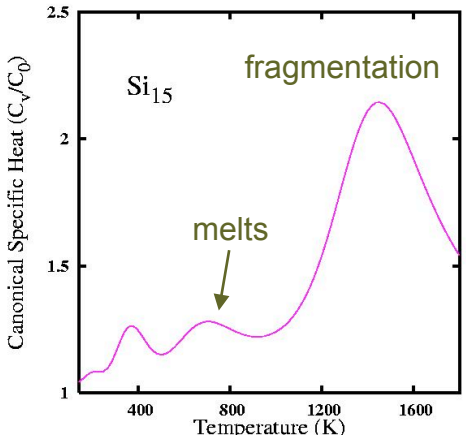
Si_{10}

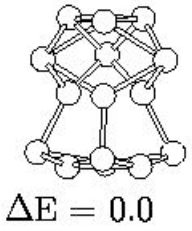
undergoes a conventional solid to liquid transition

Si_{20}

fragments (does not melt)

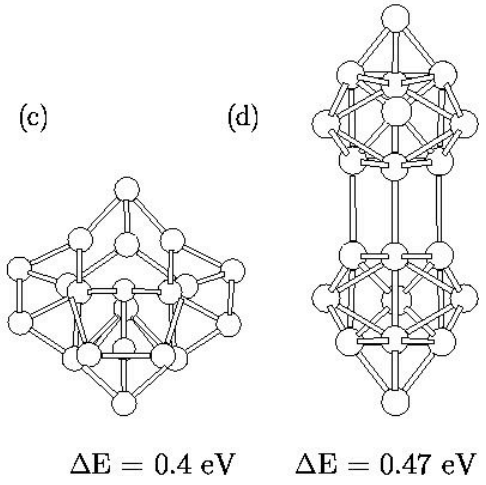






Si_{15}

initially melts, then fragments

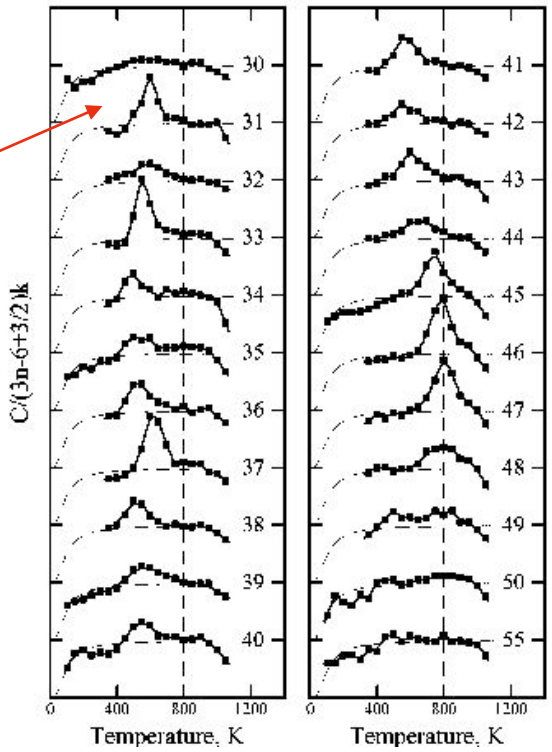


Finite-temperature behavior of small Si and Sn clusters: an *ab initio* molecular dynamics study
S. Krishnamurty, K. Joshi, D. G. Kanhere and S. A. Blundell, Phys. Rev. B **73**, 045419 (2006)

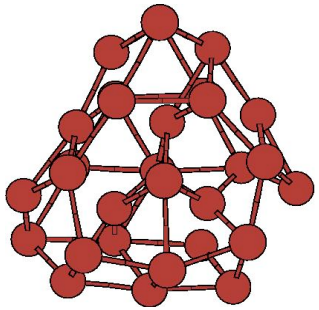
Ga clusters: “Magic melters”

Experiment:
M. F. Jarrold *et al.*, JACS comm. (2005)

“magic melter”

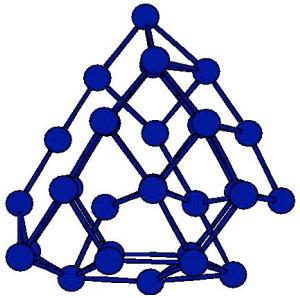


disordered

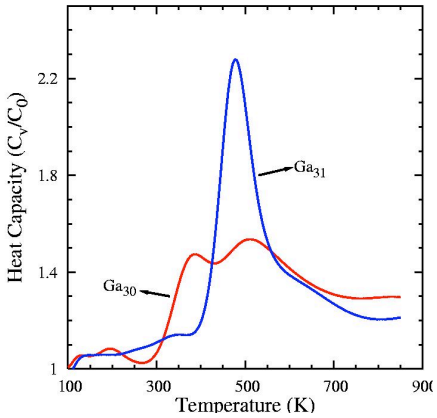


Ga 30

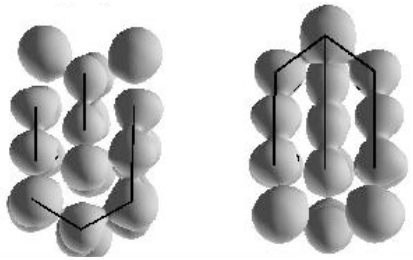
ordered



Ga31



Ga30 Ga31



ELF

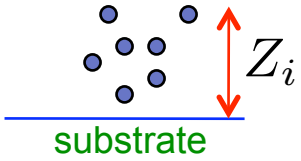
“Magic melters” have geometric origin
K. Joshi, S. Krishnamurty and D. G. Kanhere, Phys. Rev. Lett. **96**, 135703 (2006)

Thermodynamics of transition-metal clusters on a substrate

U. Sarkar and S. Blundell, Phys. Rev. B **79**, 125441 (2009)

Motivation: transition-metal clusters act as catalysts for the growth of carbon nanotubes

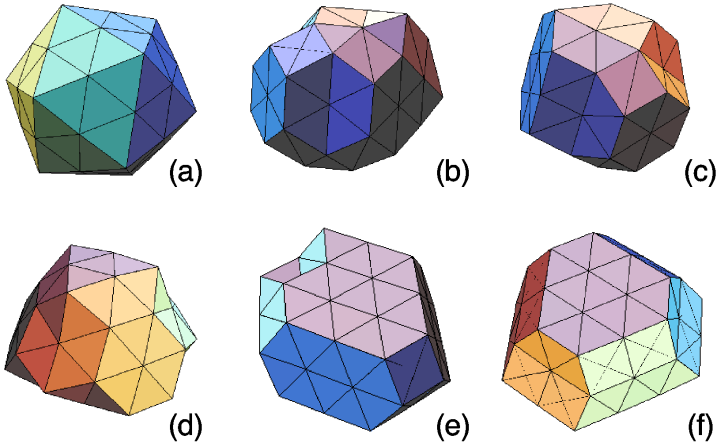
Cluster-cluster: Gupta potential

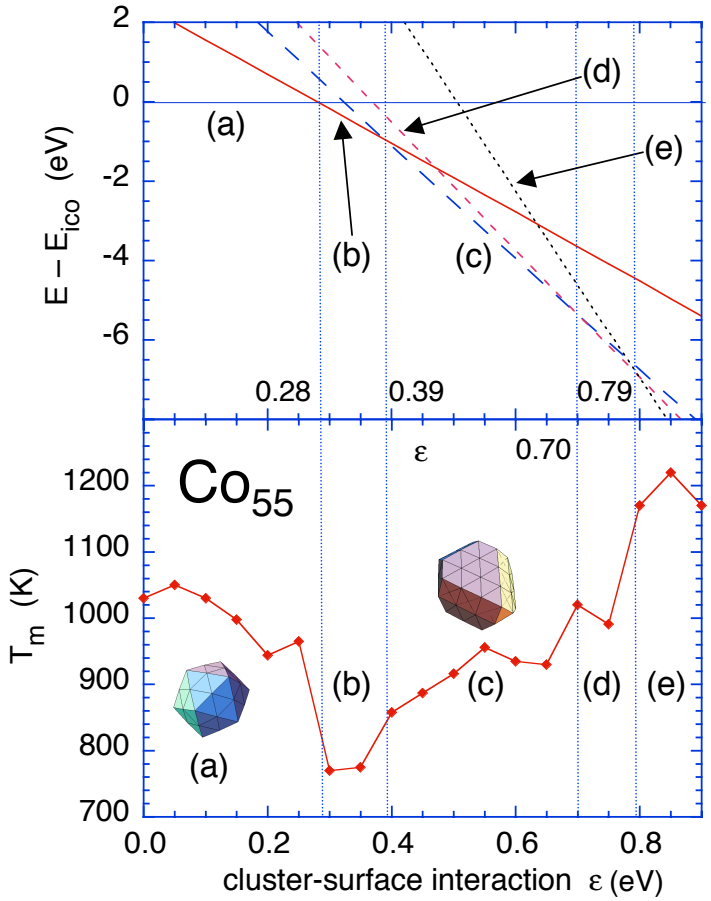


Cluster-surface:

$$E_{\mathrm{surf}} = \varepsilon \frac{3\sqrt{3}}{2} \sum_i \left[\left(\frac{\sigma}{Z_i} \right)^9 - \left(\frac{\sigma}{Z_i} \right)^3 \right]$$

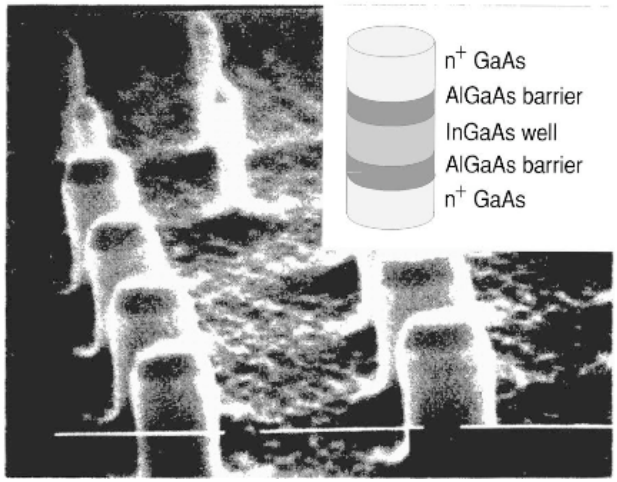
variable cluster-surface interaction strength



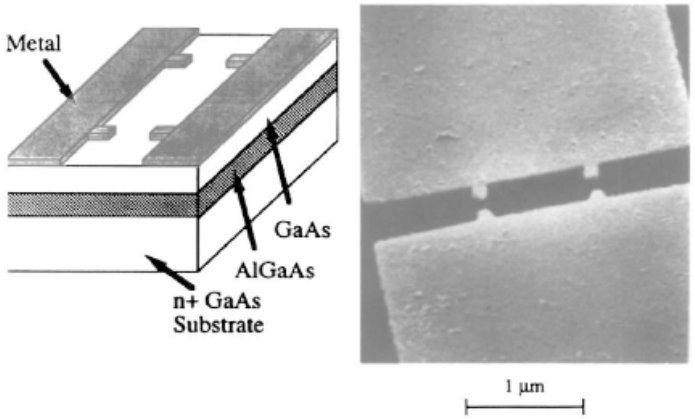


Semiconductor quantum dots

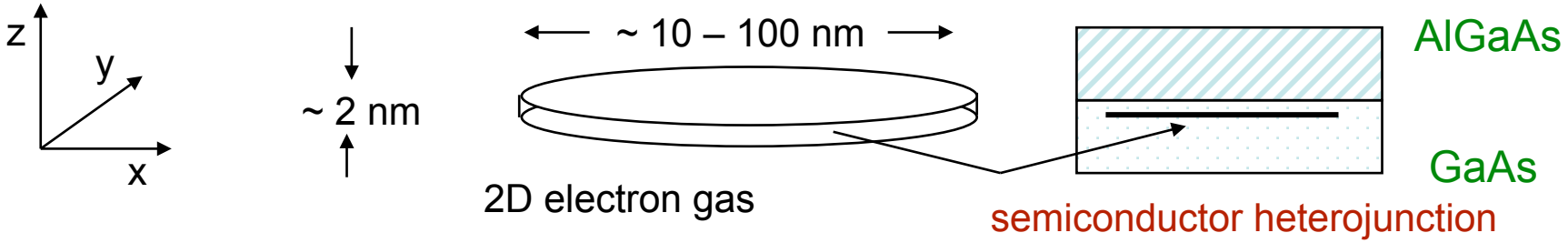
- nm sized region where carrier electrons (holes) are confined by electrostatic fields
- Examples: semiconductor heterostructures, vertical and lateral arrangements



Reed *et al*. (1988)

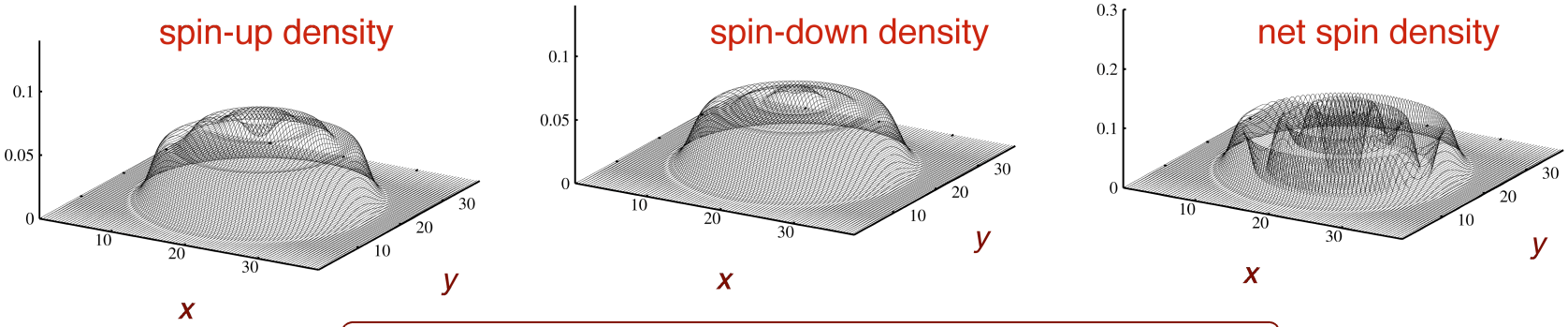


Meirav *et al*. (1990)



Artificial atoms

- Typical de Broglie wavelength in a semiconductor ~ 10 nm
- Confinement on nm scale ➔ discrete energy levels
- Lateral dimensions may be controlled experimentally
- Shell effects

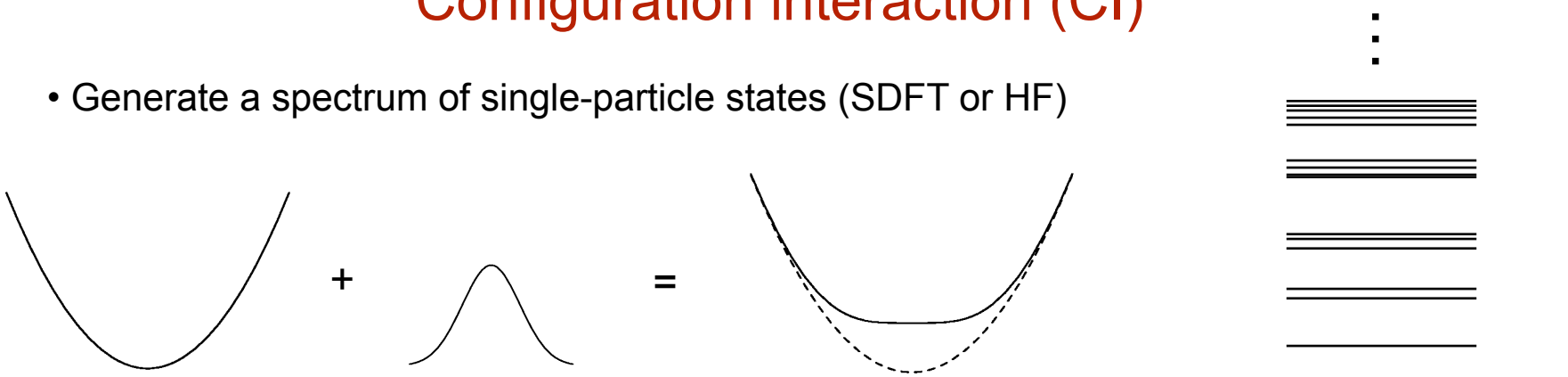


$N = 50$ electrons Ground state $S_z = 2$ $E = 236.126$ Ha*

(calculated by spin-density functional theory)

Configuration interaction (CI)

• Generate a spectrum of single-particle states (SDFT or HF)



• Construct many-electron basis of Slater determinants (with given S_z and optionally L_z)

• Diagonalize matrix of many-body Hamiltonian in these states

$$|\Psi\rangle = \sum_{\alpha} c_{\alpha} |\alpha\rangle$$

exact — Slater determinants

Large, sparse matrix ~ 10^6 x 10^6
Davidson methods

S. A. Blundell and Kavita Joshi (post-doc)
Phys. Rev. B **81**, 115323 (2010)

Full CI for $N = 6$ at low electronic density: low-lying states

S. A. Blundell and S. Chacko, Phys. Rev. B **81**, 121104(R) (2010)

circular parabolic confining potential $r_s = 12\ a_0^*$ Units: Ha^*

	^1S	^3P	^7S
Zeroth	0.96757	0.96454	0.96170
Singles	−0.01691(3)	−0.01350(3)	−0.01123(2)
Doubles	−0.00672(1)	−0.00649(1)	−0.00558(1)
Triples	−0.00153(1)	−0.00142(4)	−0.00109(1)
Quadruples	−0.00027(2)	−0.00024(2)	−0.00018
Quintuples	−0.00004(2)	−0.00002(2)	−0.00002(2)
Sextuples	0.00000	0.00000	0.00000
TOTAL	0.94211(6)	0.94287(6)	0.94360(4)
DMC(2007) [1]	0.94258(1)	0.94379(1)	0.94363(1)
CI-SHO(2006) [2]	0.948	0.949	0.950
PIMC(1999) [3]		0.9433(3)	0.9441(3)

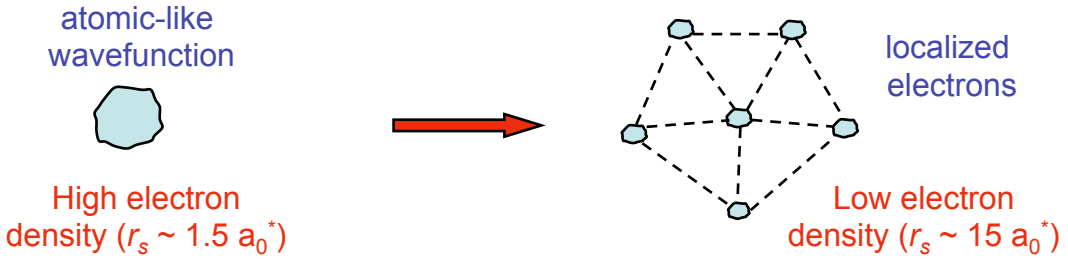
[1] A. Ghosal, A. D. Güçlü, C. J. Umrigar, D. Ullmo, and H. U. Baranger, Phys. Rev. B (2007); Nature Phys. (2006)
Variational + Diffusion Monte Carlo (fixed-node approximation)
$r_s \leq 18\ a_0^*$, lowest-energy state with a given symmetry (L_z, S)

[2] M. Rontani, C. Cavazzoni, D. Bellucci, and G. Goldoni, J. Chem. Phys. (2006)
CI with simple-harmonic-oscillator basis set

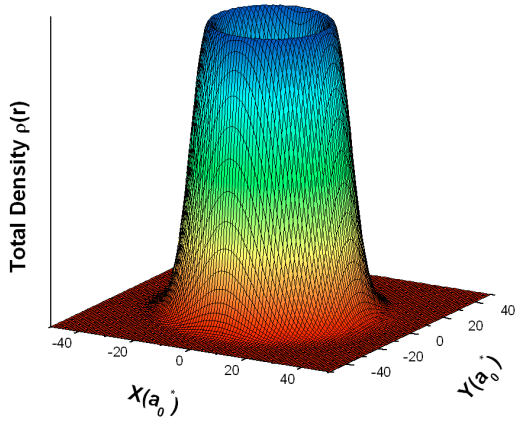
[3] R. Egger, W. Hausler, C. H. Mak, and H. Grabert, Phys. Rev. Lett. (1999)
Path-integral Monte-Carlo

Wigner molecules

- Low electron densities: electrons become localized into an ‘electron molecule’

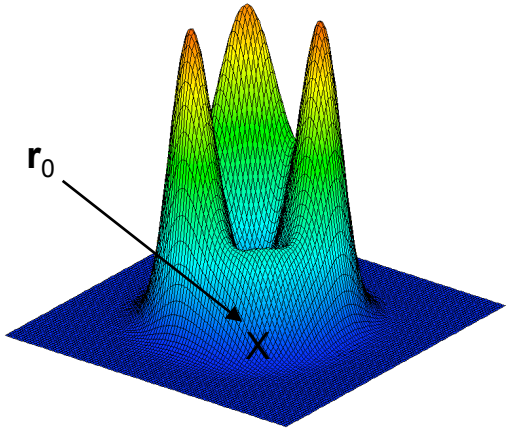


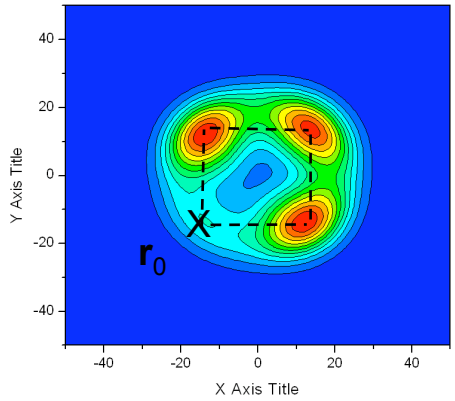
- Example with CI methods: $N = 4$, $r_s = 15\ a_0^*$



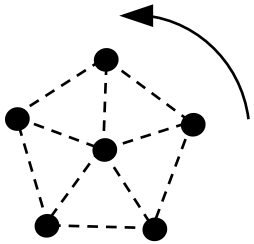
Total electron density remains
circularly symmetric

spin-spatial pair correlation function: $g(\mathbf{r}_0; \mathbf{r})$
(conditional probability)

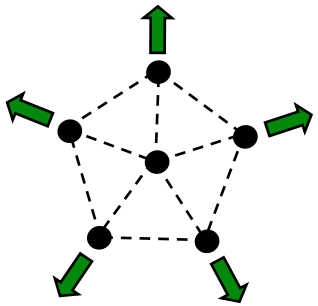




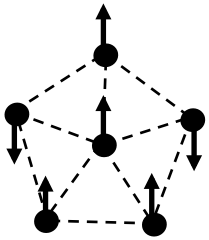
Excited states of Wigner molecules: classical limit



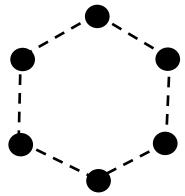
rotational



vibrational
(normal modes, w_a)



spin



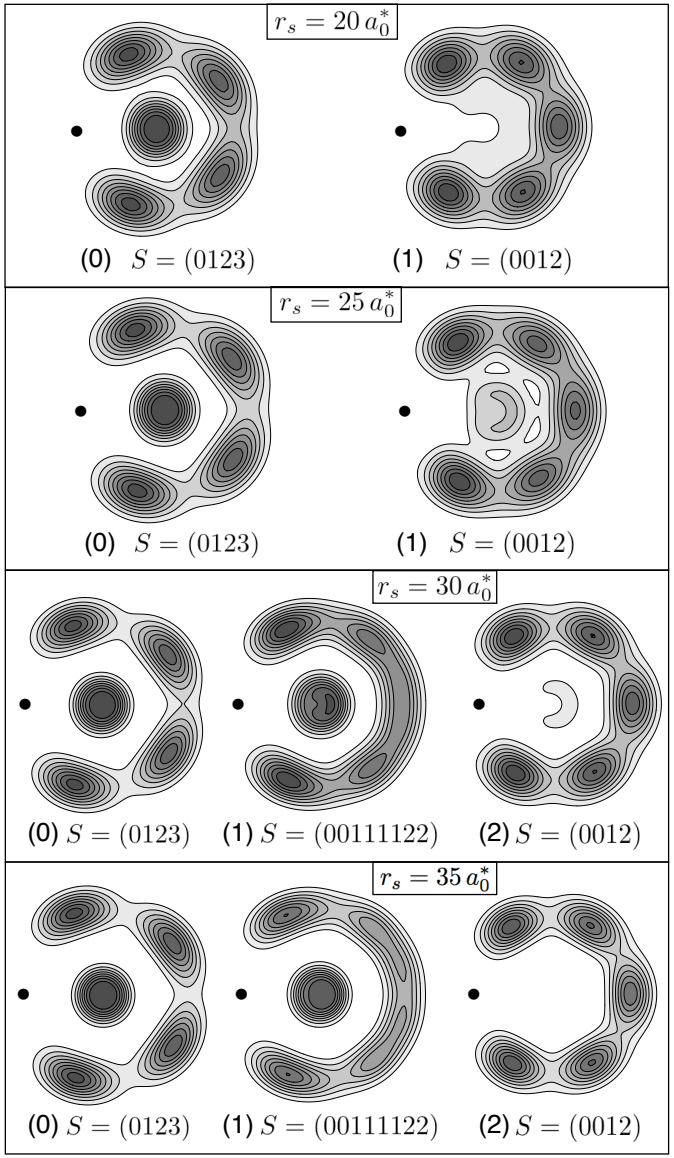
isomeric

- Effective Hamiltonian (classical limit, one isomer)

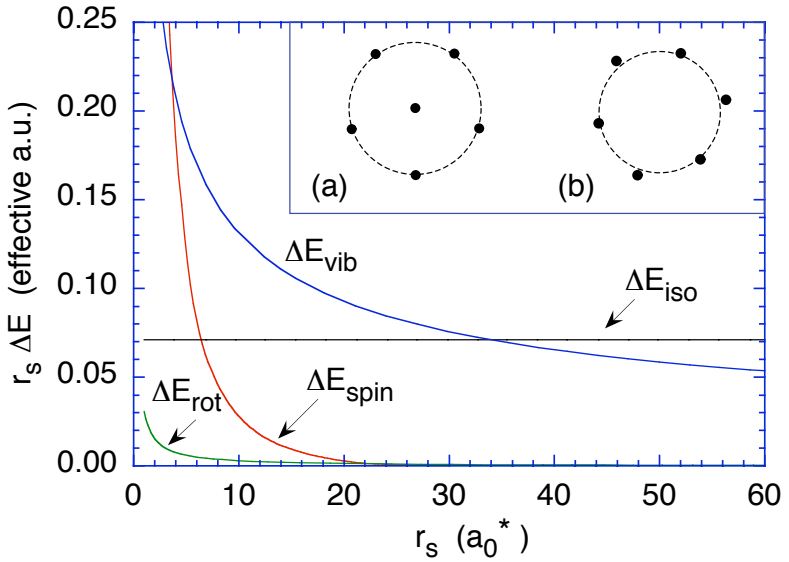
$$H_{\text{eff}} = \frac{\hbar^2 L_z^2}{2I} + \sum_a (\hbar\omega_a) n_a + \sum_{i>j}^{N} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

Excited states of Wigner molecules: CI

S. A. Blundell and S. Chacko, Phys. Rev. B **81**, 121104(R) (2010)



classical isomers



- *S*-wave states (L_z = 0)
- Non-Born-Oppenheimer ordering of vibrational and isomeric excited states