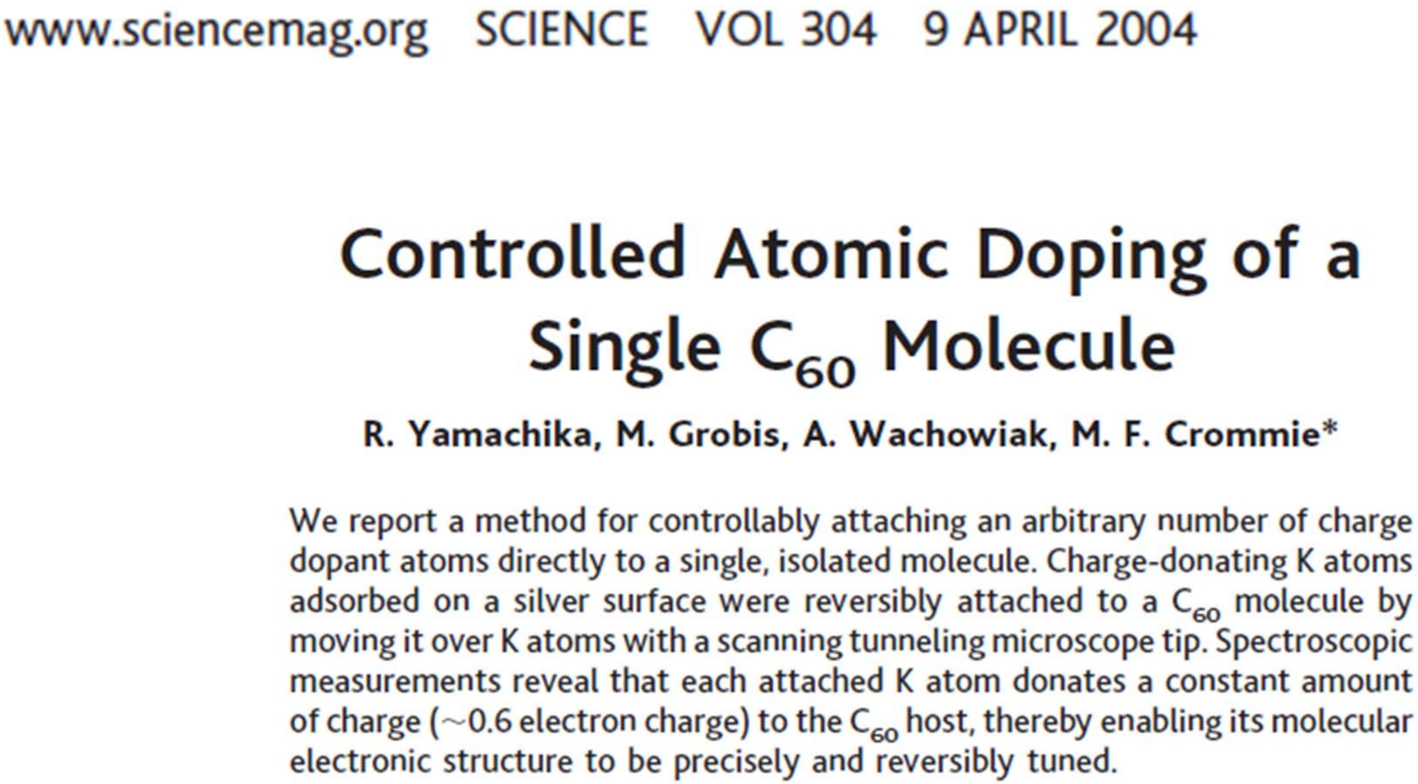
Manipulation with STM (2)

Outline

- Controlled atomic doping of a single C60 molecule
- Atomic collapse resonance on graphene
- Self regulated Gd atom trapping in open Fe nanocorrals
- Lock-in technique (brief introduction)

- Controlled atomic doping of a single C60 molecule



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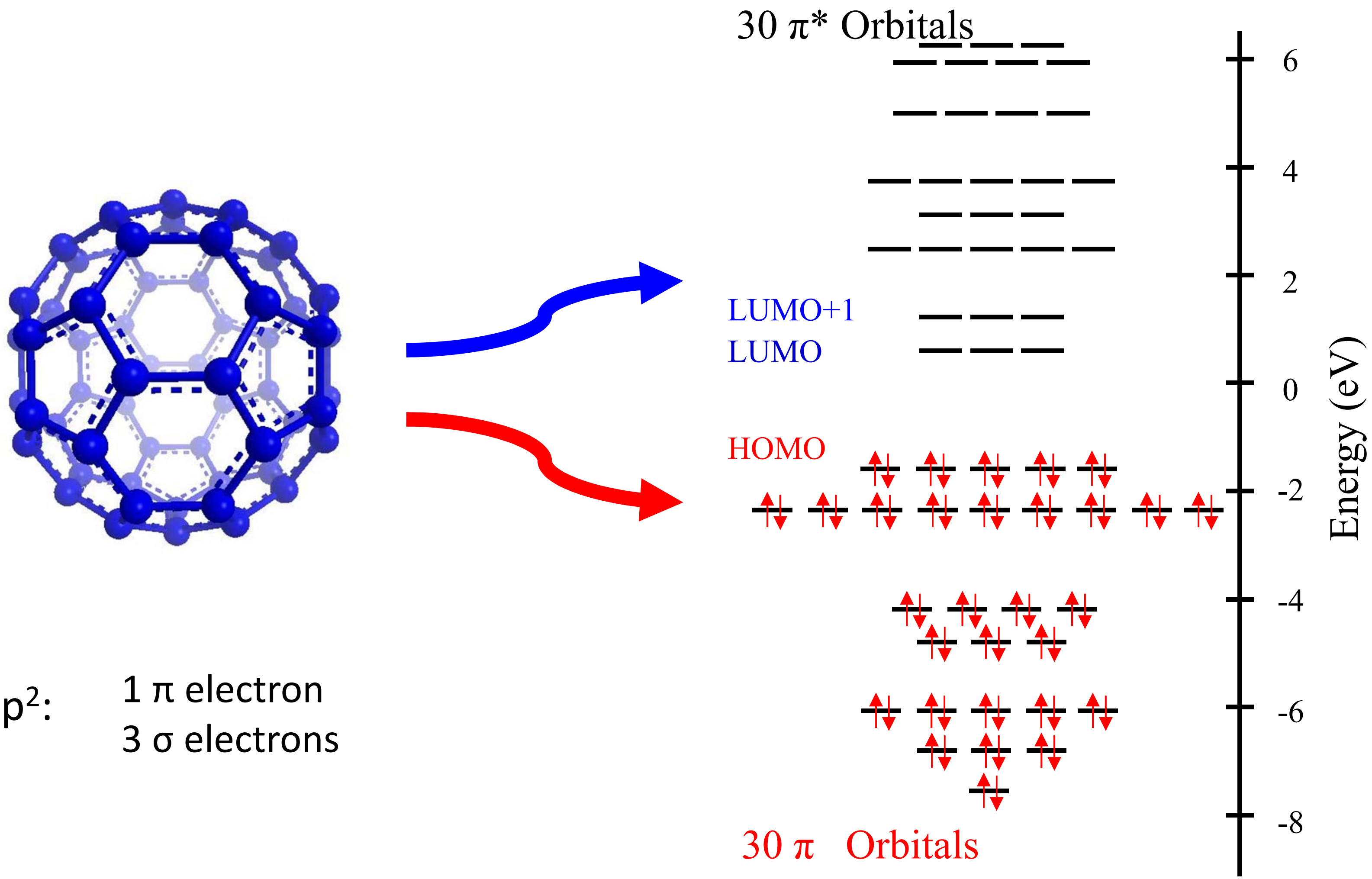
Controlled Atomic Doping of a Single C_{60} Molecule

R. Yamachika, M. Grobis, A. Wachowiak, M. F. Crommie*

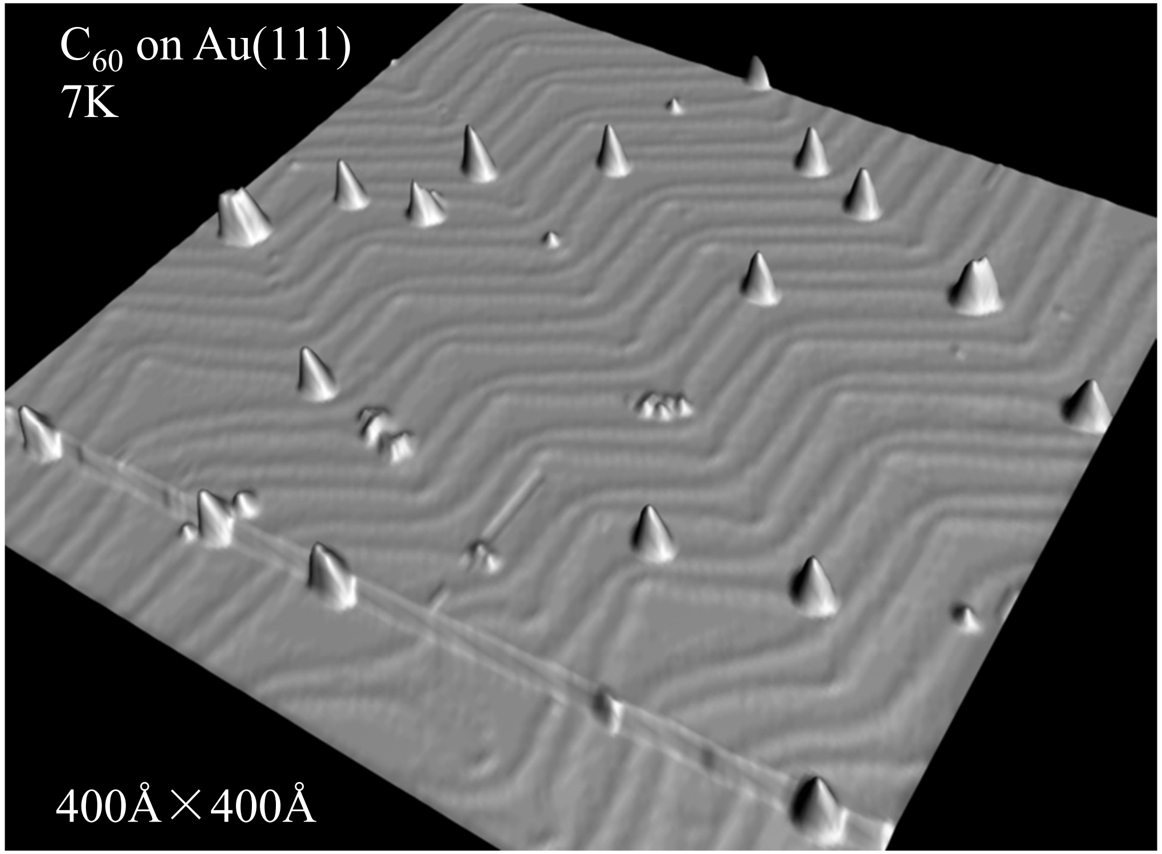
We report a method for controllably attaching an arbitrary number of charge dopant atoms directly to a single, isolated molecule. Charge-donating K atoms adsorbed on a silver surface were reversibly attached to a C_{60} molecule by moving it over K atoms with a scanning tunneling microscope tip. Spectroscopic measurements reveal that each attached K atom donates a constant amount of charge (~0.6 electron charge) to the C_{60} host, thereby enabling its molecular electronic structure to be precisely and reversibly tuned.

Free C_{60} Electronic Structure

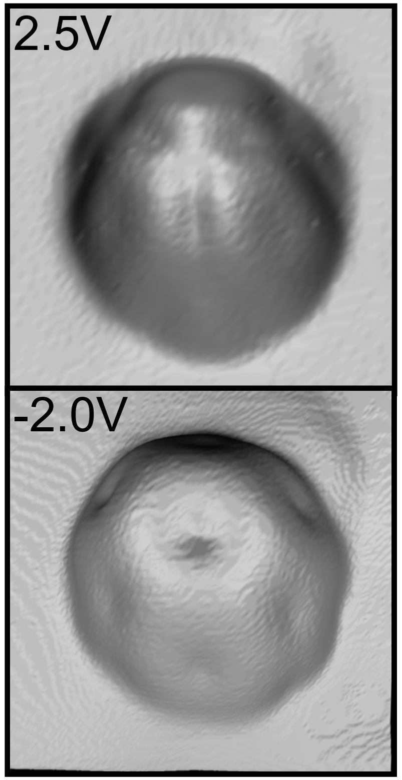


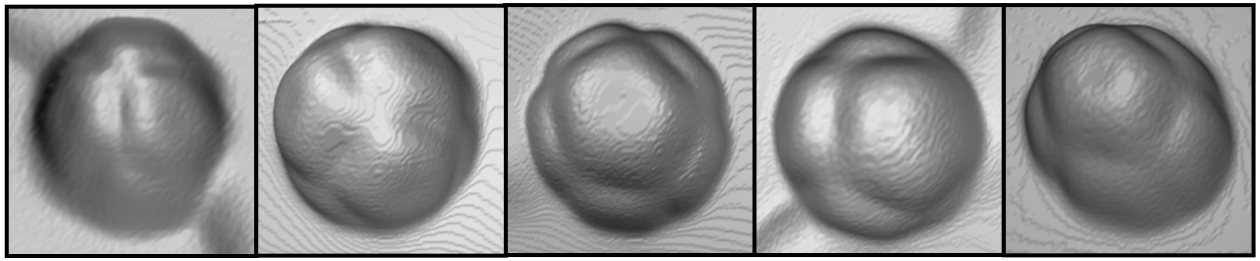
sp^2: 1 π electron
3 σ electrons

C_{60} on Au(111): topograph

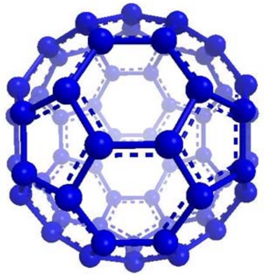


Bias Dependence

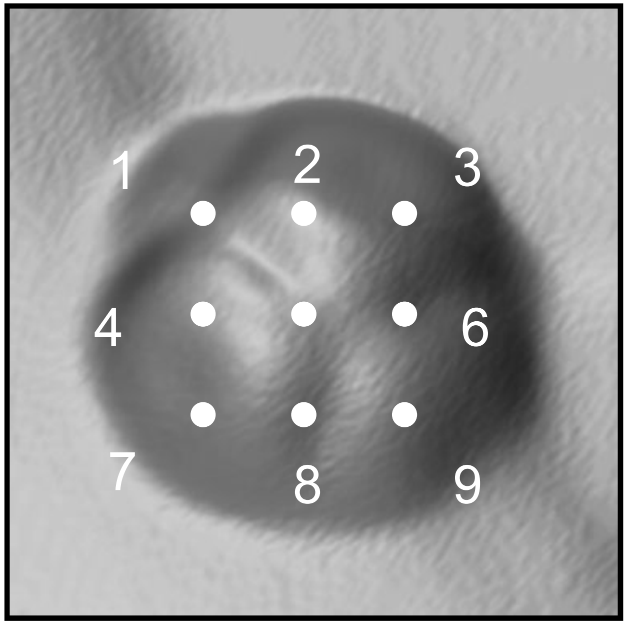


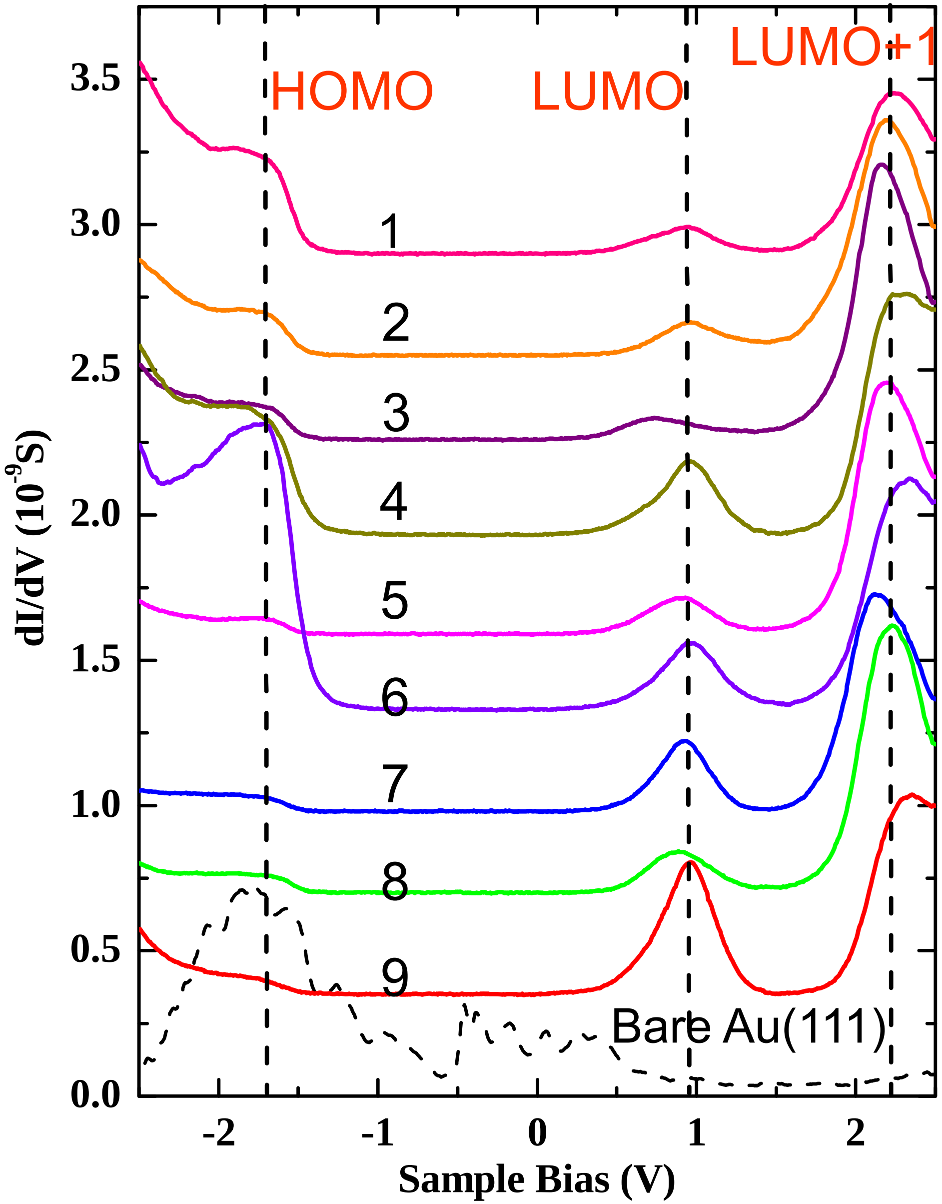


6-6 Hex. Pent. 5-6 Apex



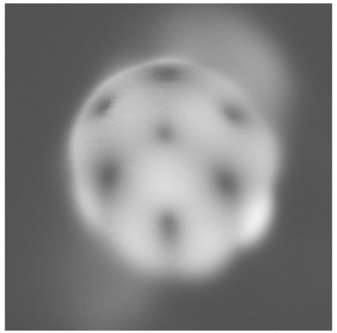
C_{60} on Au(111): spectroscopy



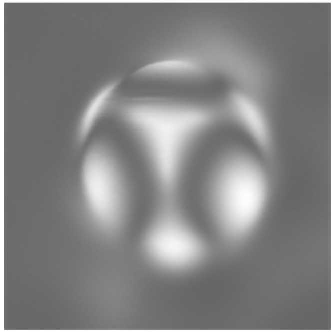


C_{60} on Au(111): Molecular orbitals

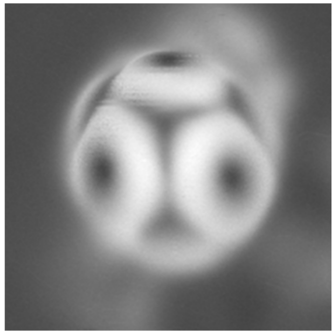
HOMO

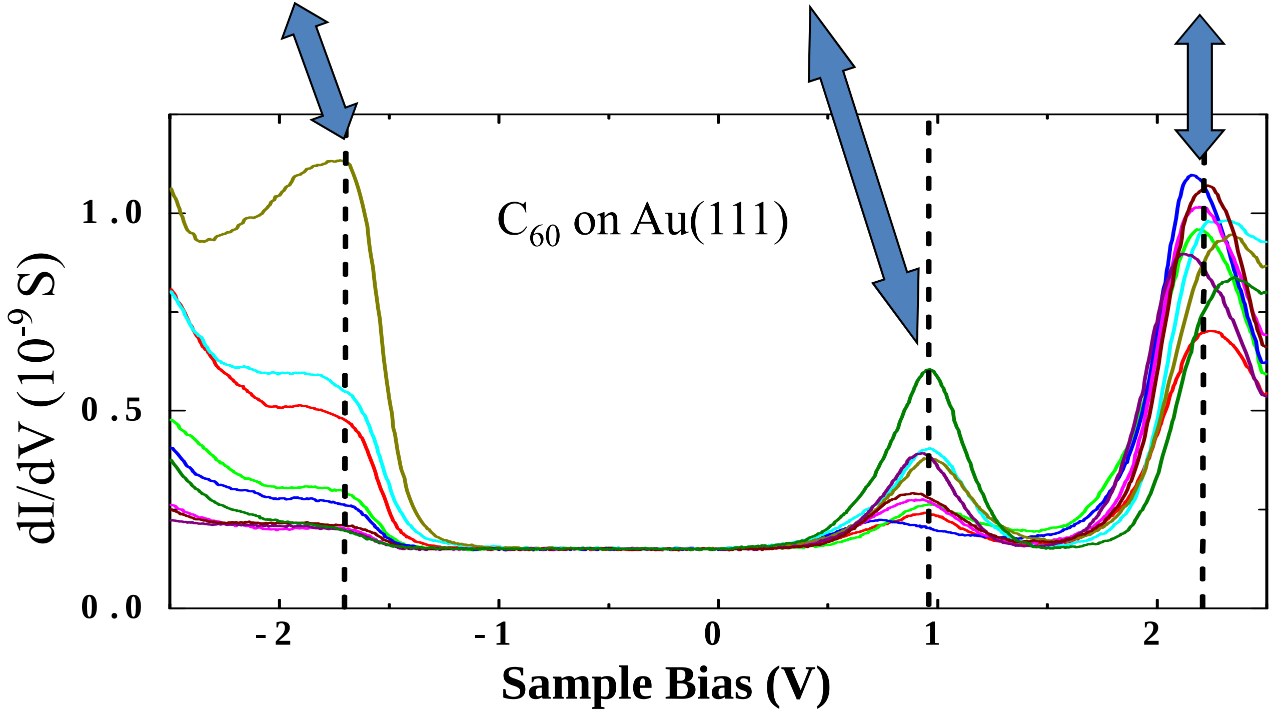


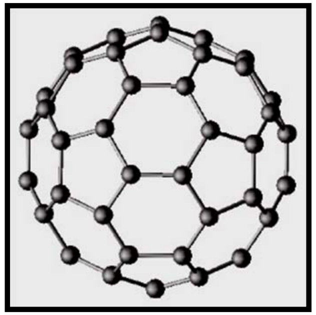
LUMO

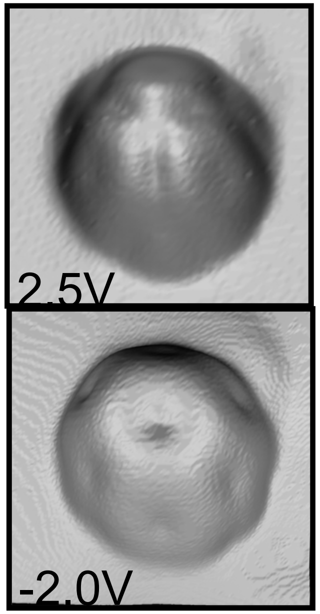


LUMO+1





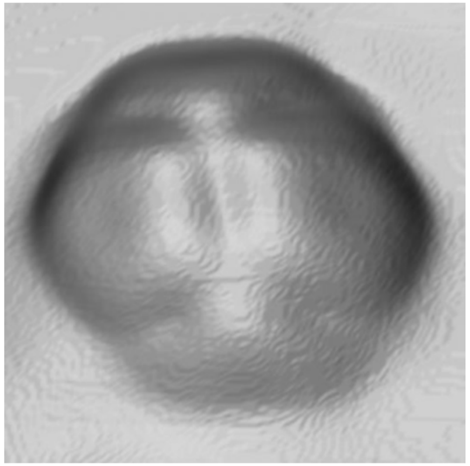




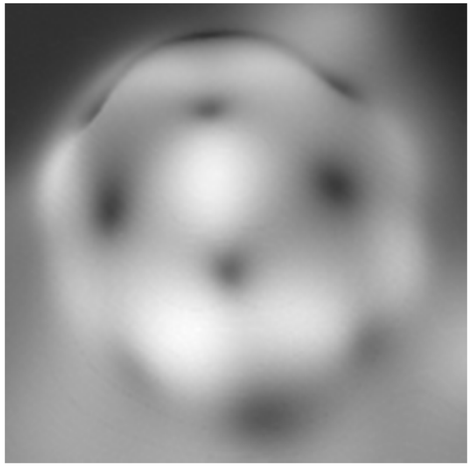
Topograph

C_{60} on Au(111): Understand Molecular Orbitals

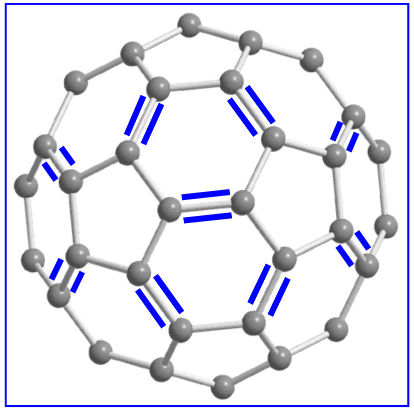
C_{60} Topograph



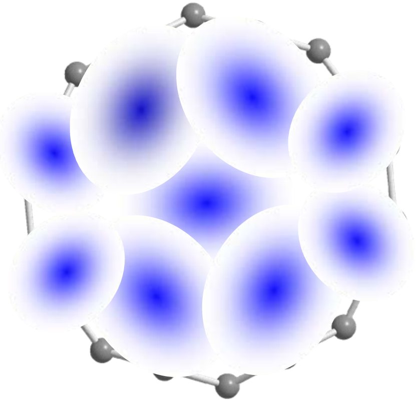
HOMO



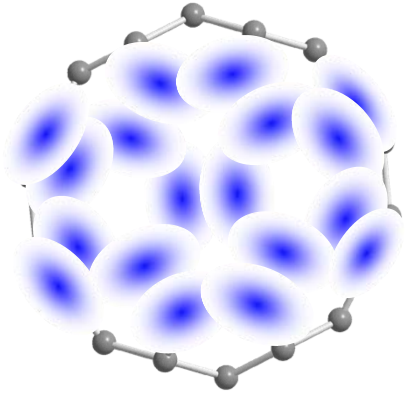
LUMO + 1



6-6 bonds

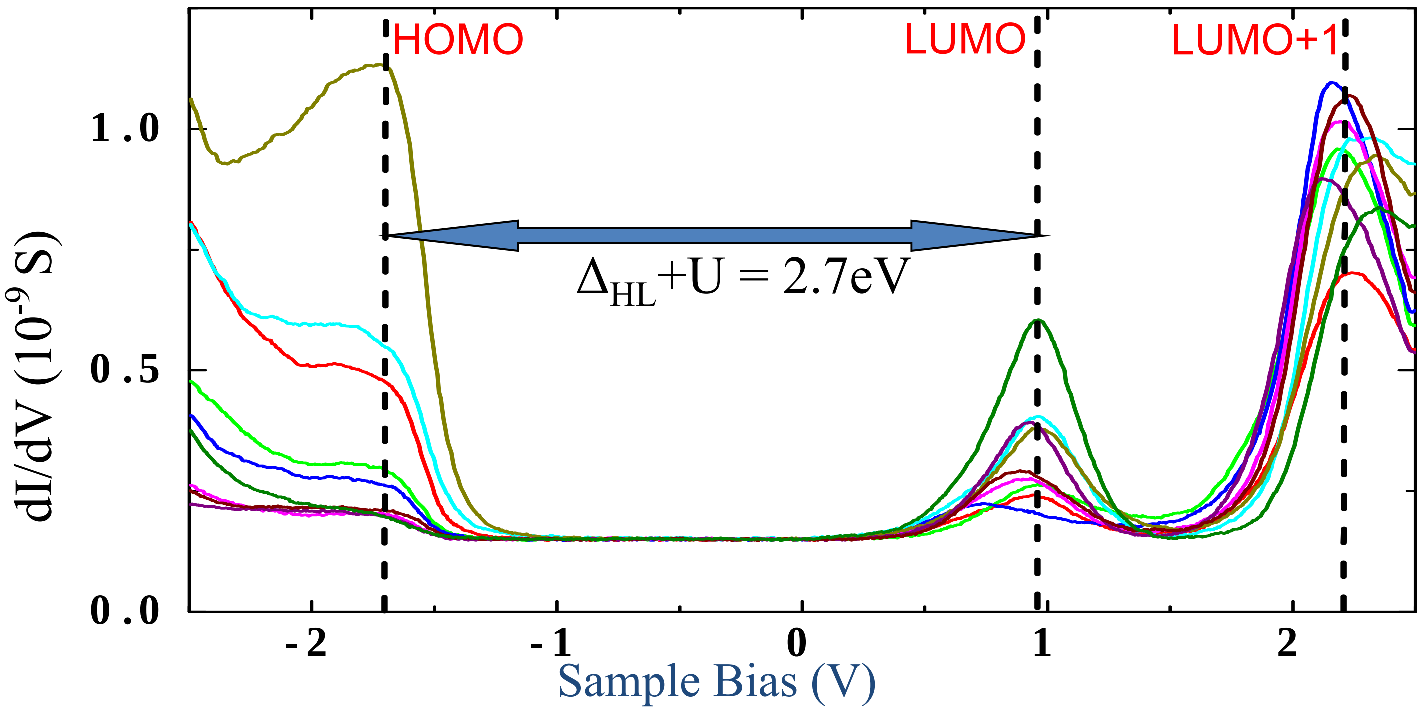


bonding

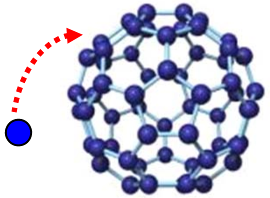


anti-bonding

C_{60} on Au(111): Reduced Charging Energy



Intrinsic H-L gap:
Δ_{HL} ~ 1.7eV

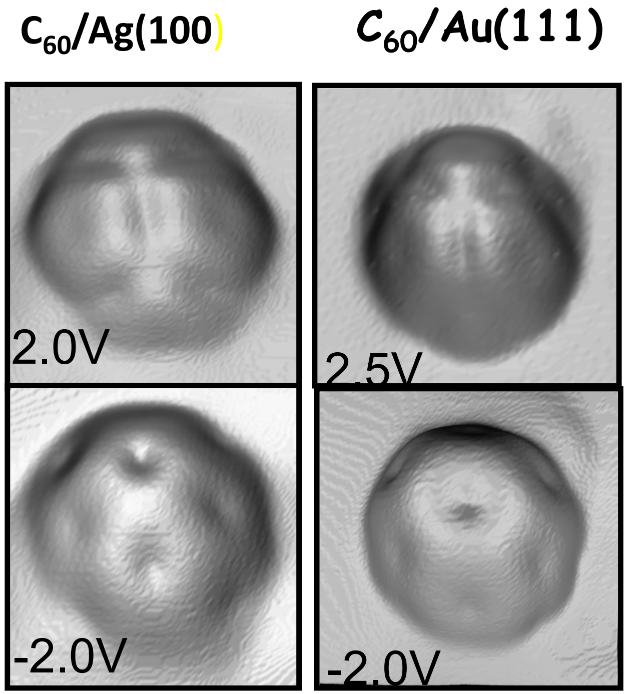


C_{60}/Au(111): U = 2.7eV – 1.7eV
= 1.0eV

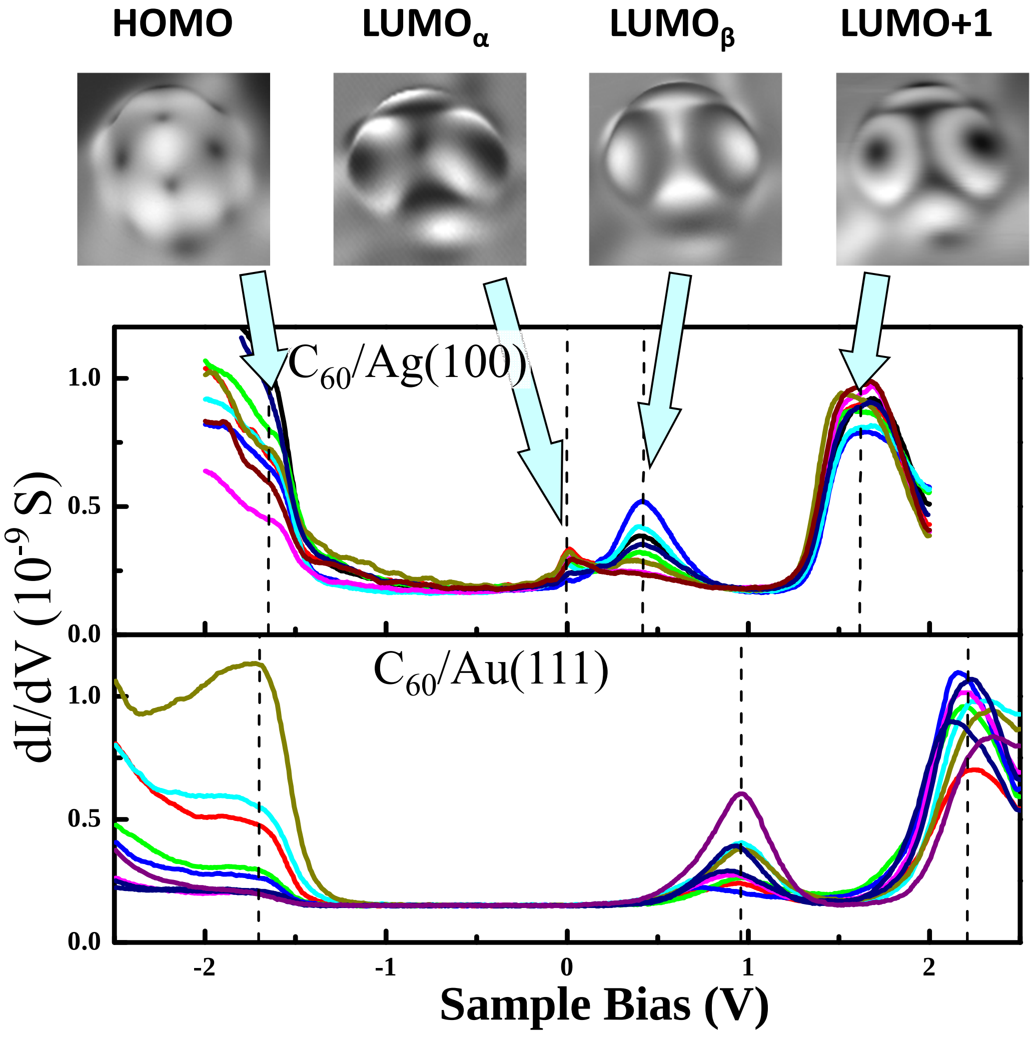
Free C_{60}: U ~ 3.2eV

Metal substrate screening

Topographs

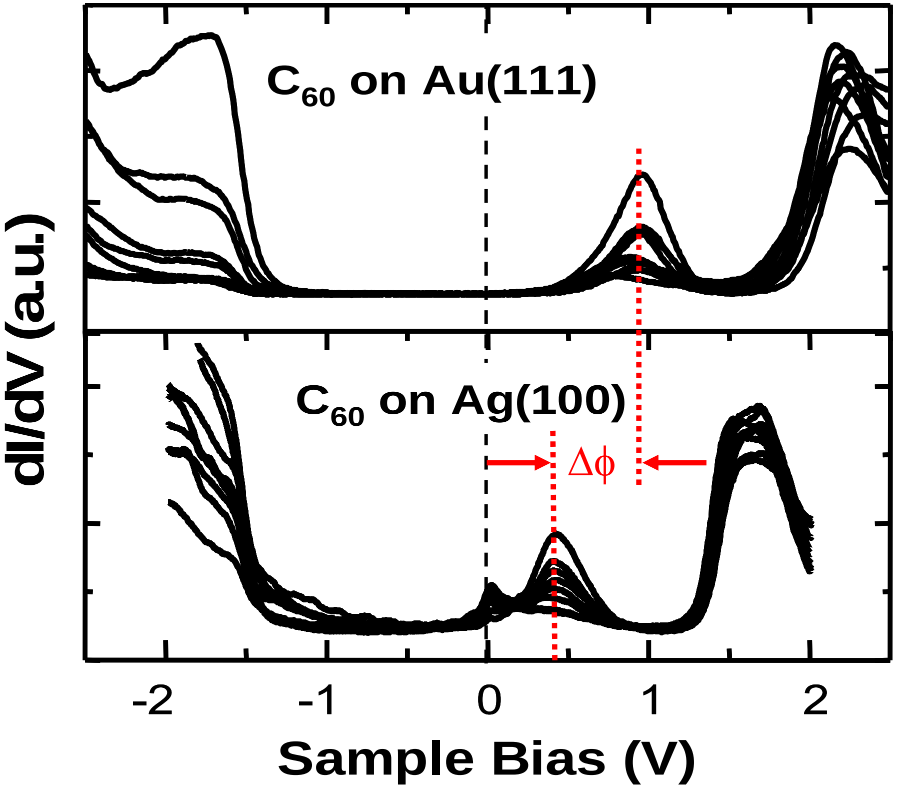


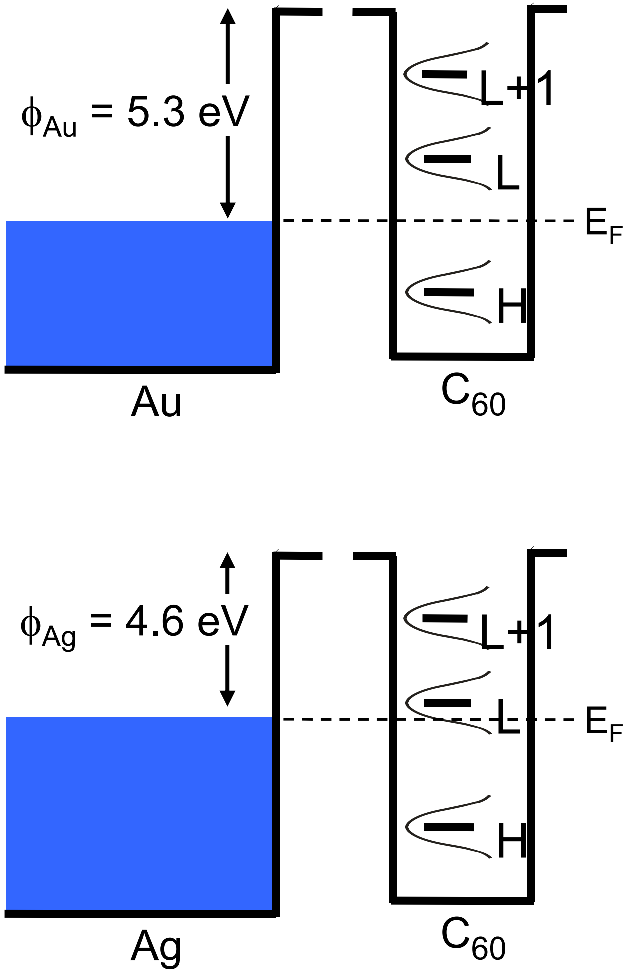
Spectroscopy



Level Shifting; LUMO Splitting

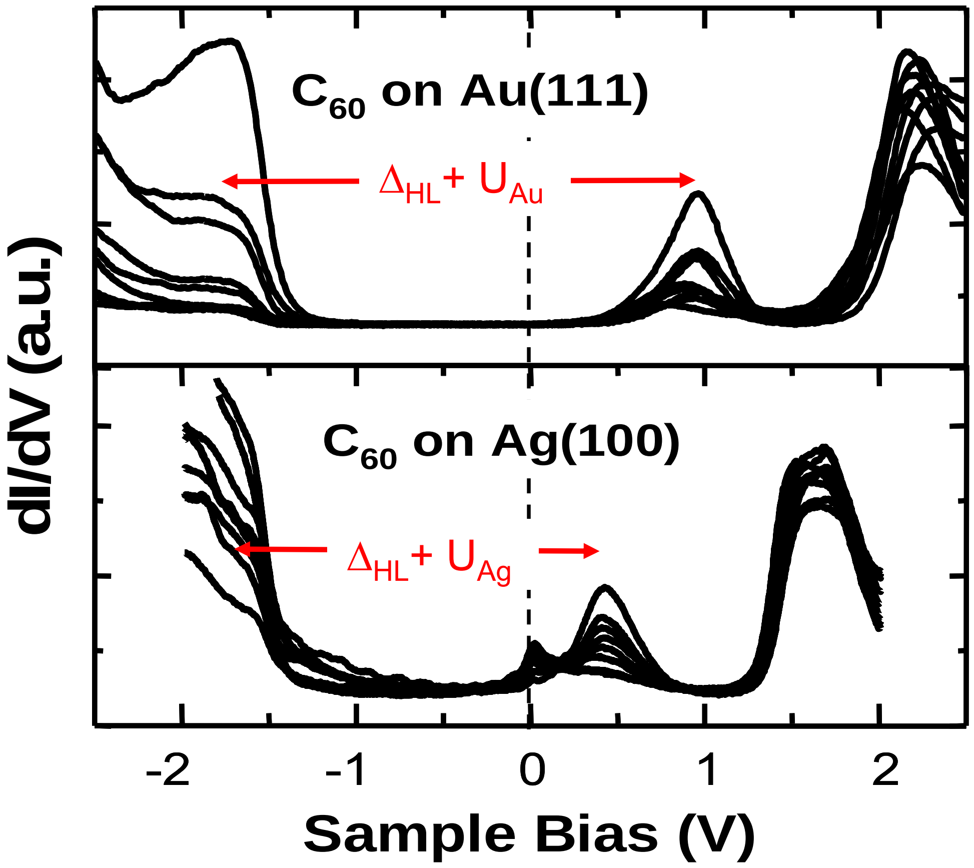
Workfunction and Level Alignment

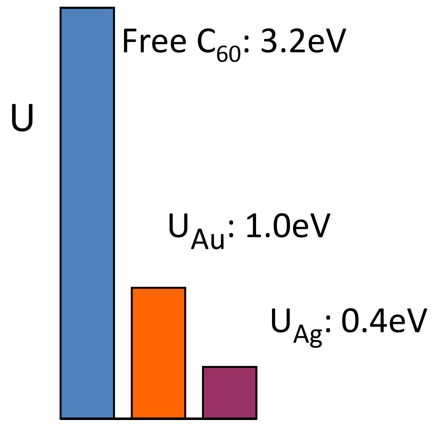




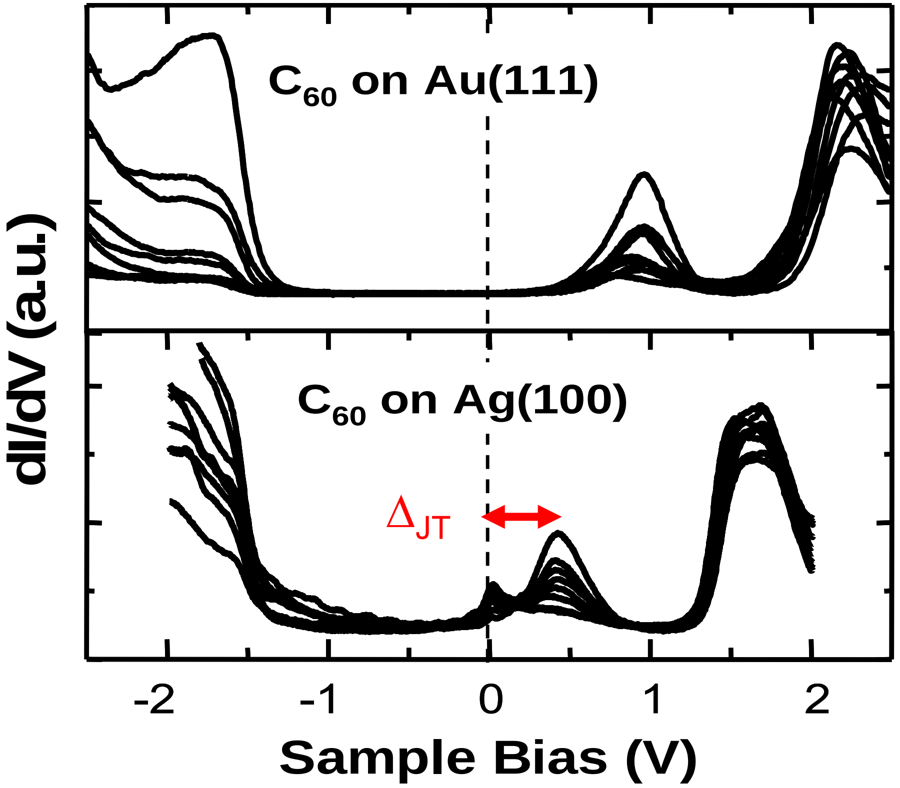
$\Delta\phi = \phi_{Au} - \phi_{Ag} = 0.7eV$

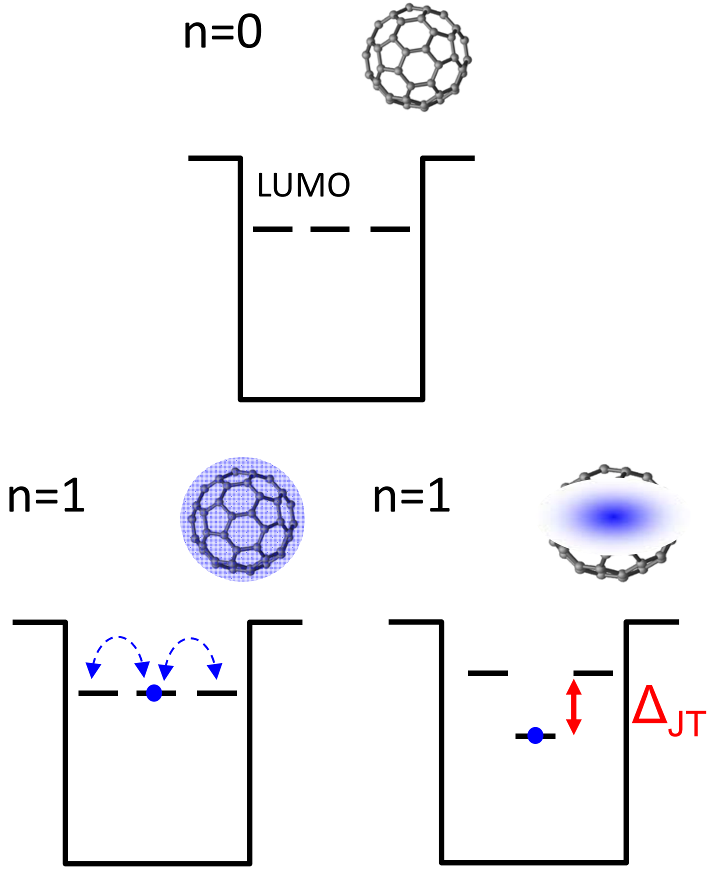
Charge Transfer: Enhanced Screening





Charge Transfer: Jahn-Teller Effect



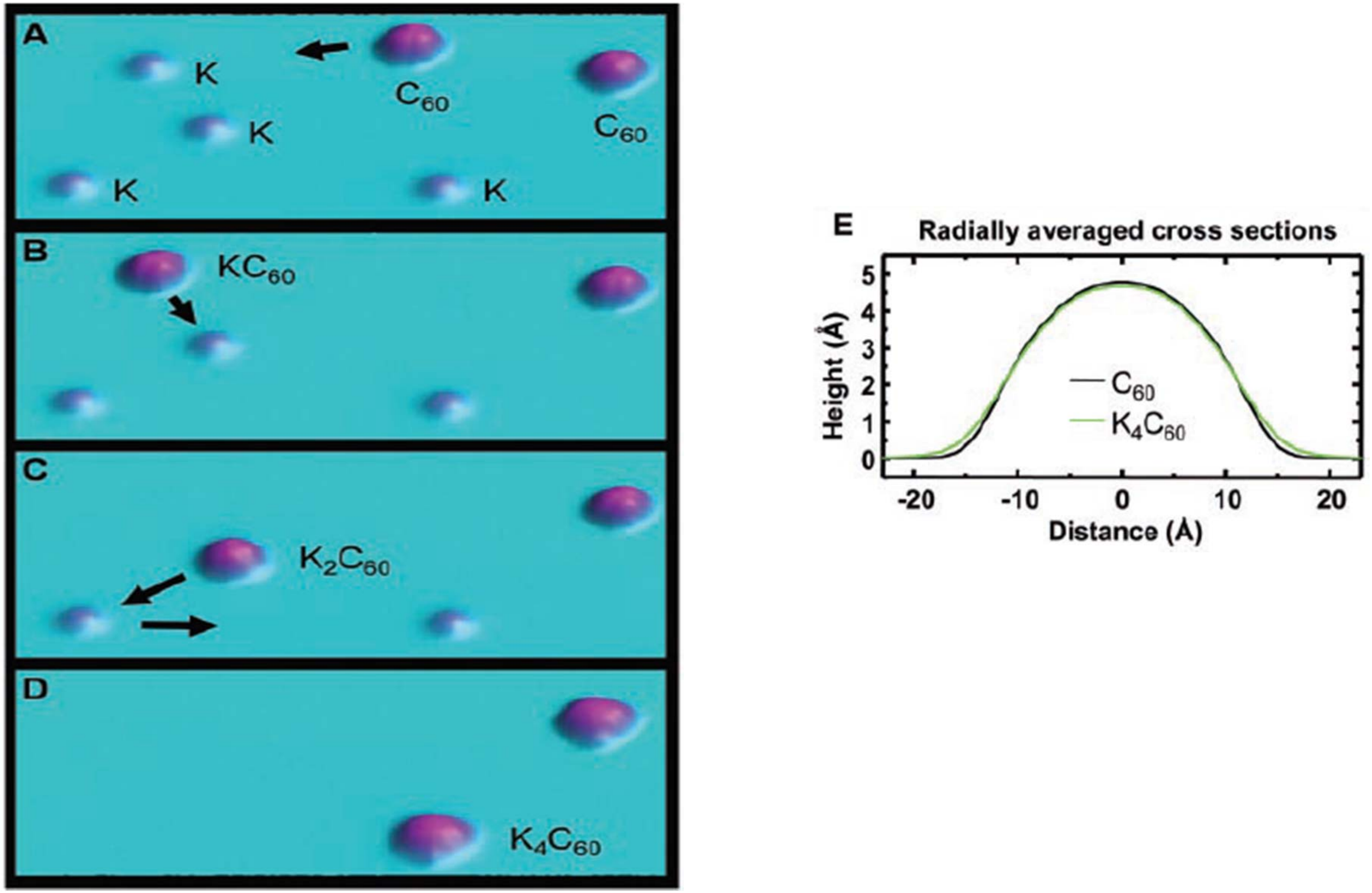


Experiment: Δ_{JT} = 0.4 - 0.1eV

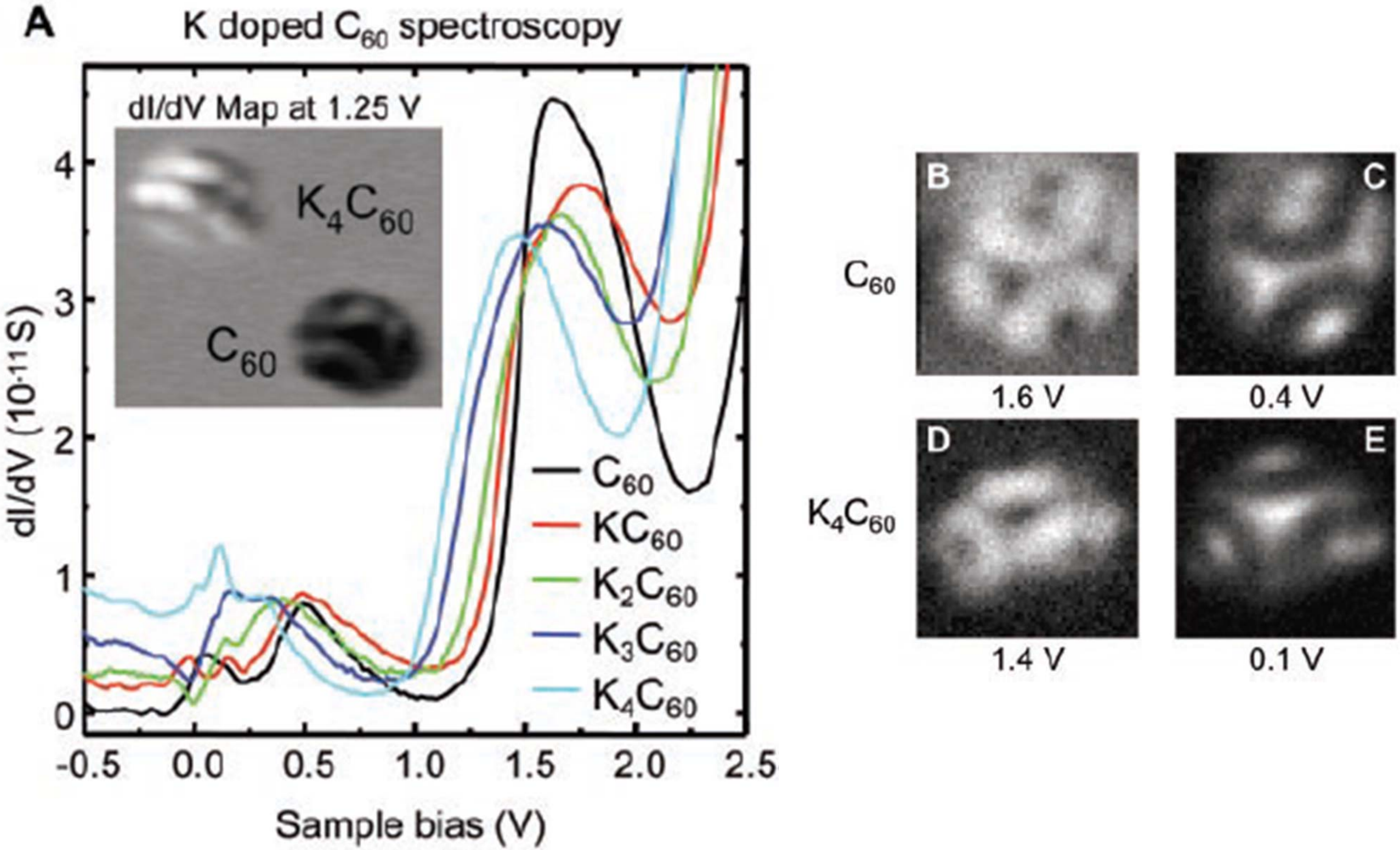
Theory for C_{60}^-: Δ_{JT} = 0.2eV

A. Auerbach, *et al.*, PRB 49, 12998 (1994)
O. Gunnarsson, PRB 51, 3493 (1995)
V. Brouet, *et al*., Struct. & Bonding 109, 165 (2004)

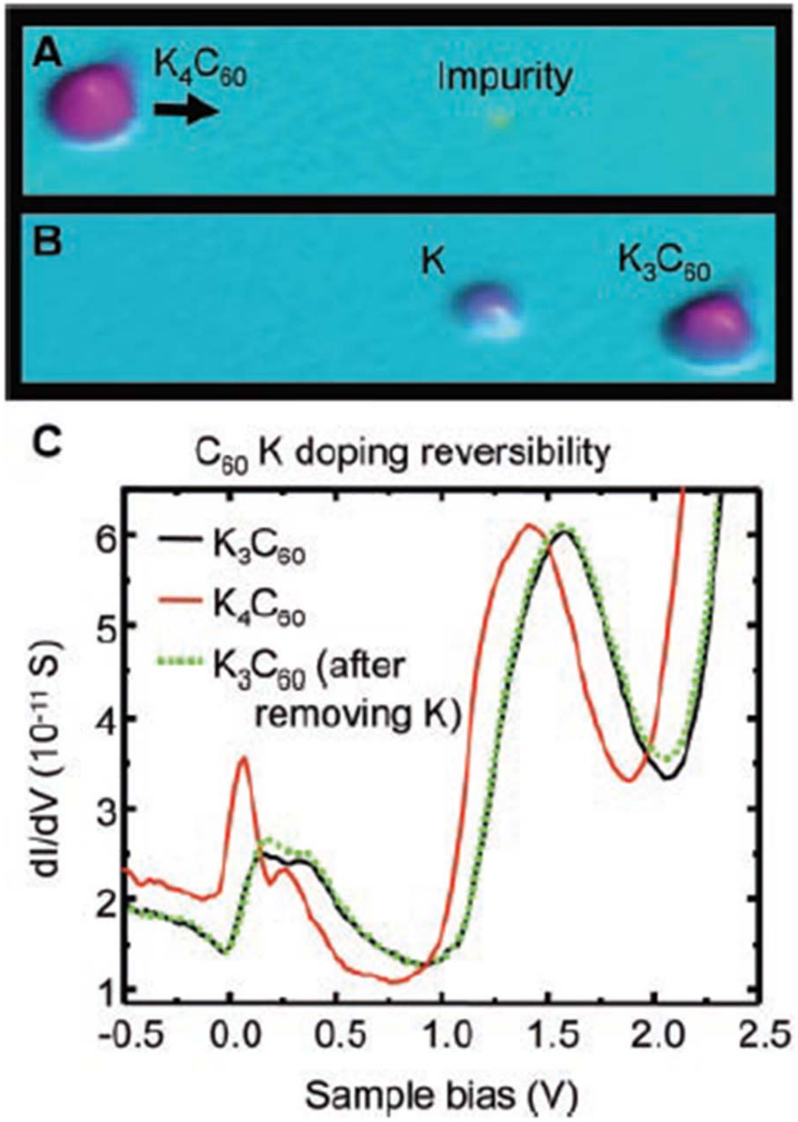
- Controlled atomic doping of a single C60 molecule



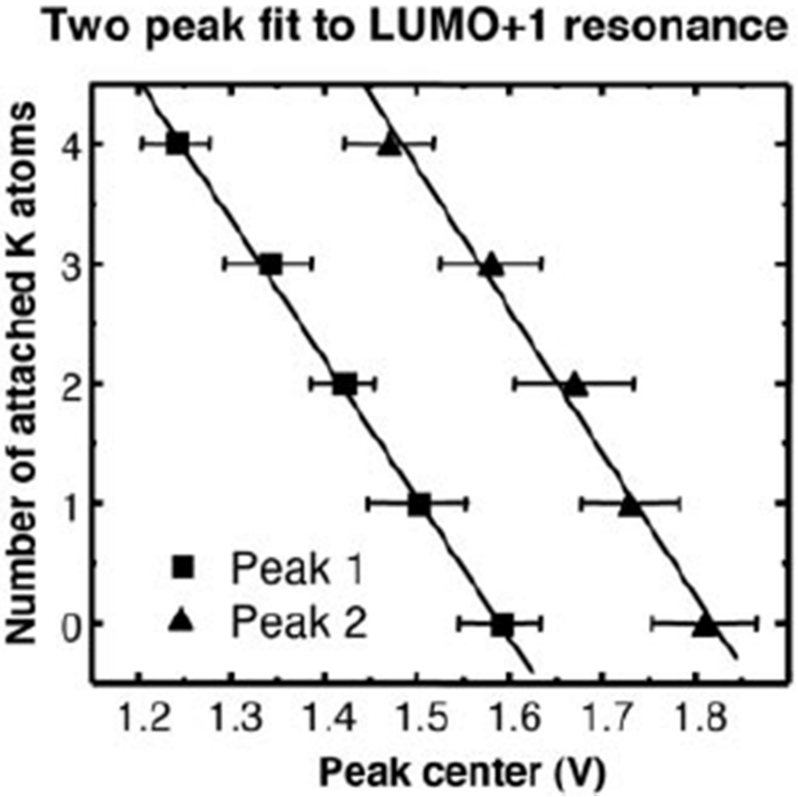
- Controlled atomic doping of a single C60 molecule



- Controlled atomic doping of a single C60 molecule

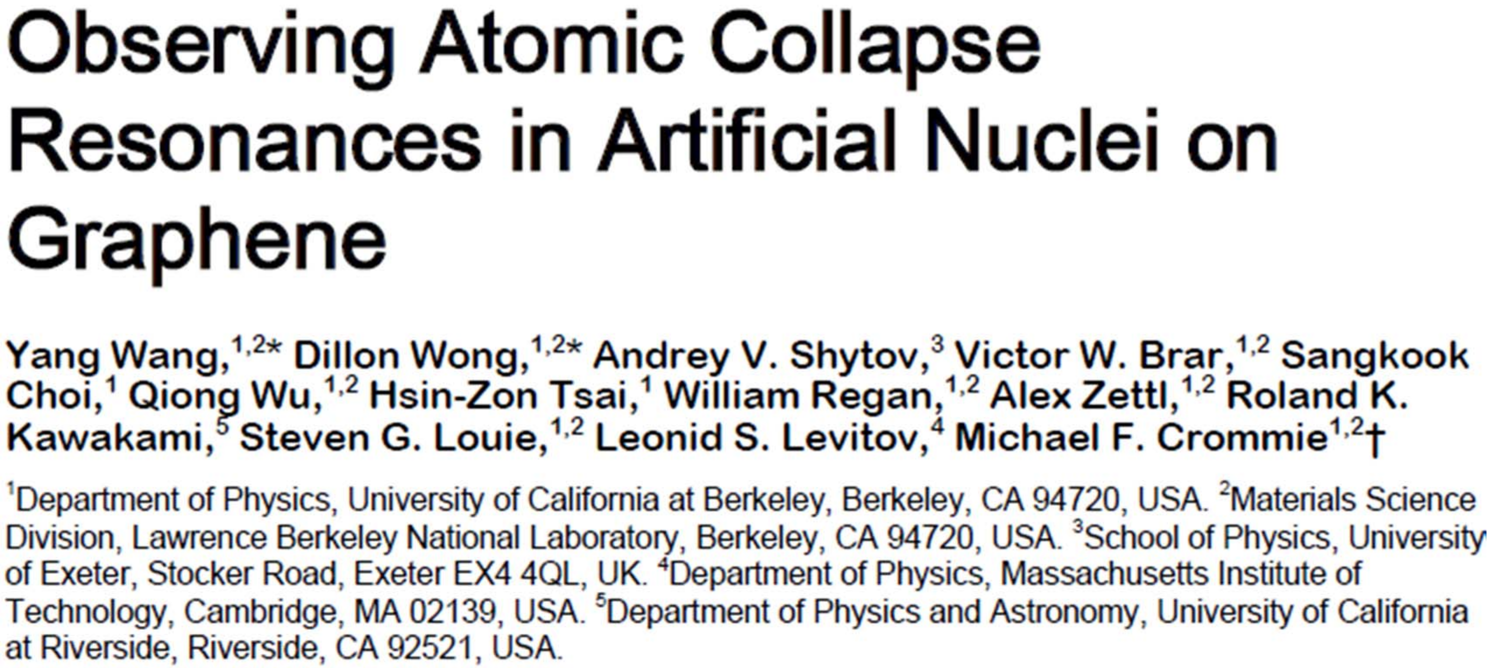


- Controlled atomic doping of a single C60 molecule



- Atomic collapse resonance on graphene

Science: Vol. 340, p. 734 (2013)



Observing Atomic Collapse Resonances in Artificial Nuclei on Graphene

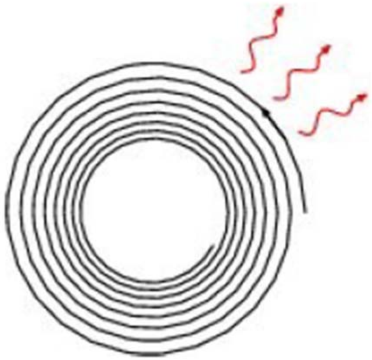
Yang Wang,[1,2]* Dillon Wong,[1,2]* Andrey V. Shytov,[3] Victor W. Brar,[1,2] Sangkook Choi,[1] Qiong Wu,[1,2] Hsin-Zon Tsai,[1] William Regan,[1,2] Alex Zettl,[1,2] Roland K. Kawakami,[5] Steven G. Louie,[1,2] Leonid S. Levitov,[4] Michael F. Crommie[1,2]†

[1]Department of Physics, University of California at Berkeley, Berkeley, CA 94720, USA. [2]Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA. [3]School of Physics, University of Exeter, Stocker Road, Exeter EX4 4QL, UK. [4]Department of Physics, Massachusetts Institute of Technology, Cambridge, MA 02139, USA. [5]Department of Physics and Astronomy, University of California at Riverside, Riverside, CA 92521, USA.

- Atomic collapse resonance on graphene

Stability of Atom

Classical physics: unstable (energy is unbounded)

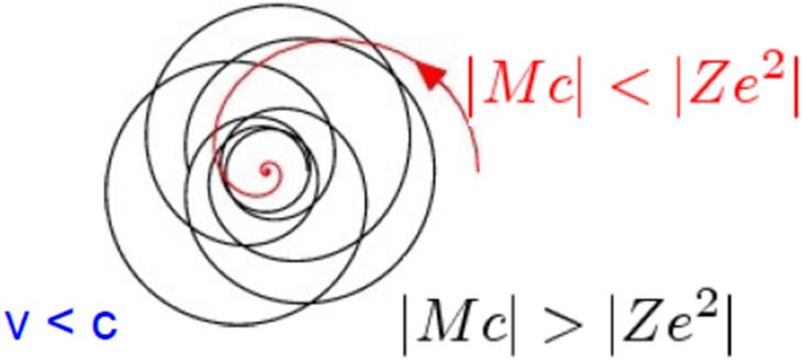


QM: stable orbits, zero point motion stops the collapse

$$K_{\mathrm{nr}} = \frac{p^2}{2m} \sim \frac{\hbar^2}{2mr^2}$$

$$U = -\frac{Ze^2}{r}$$

Relativity: collapsing orbits



Relativity + QM: Collapse?

$$K = cp \sim \frac{\hbar c}{r}$$

But: position uncertainty:

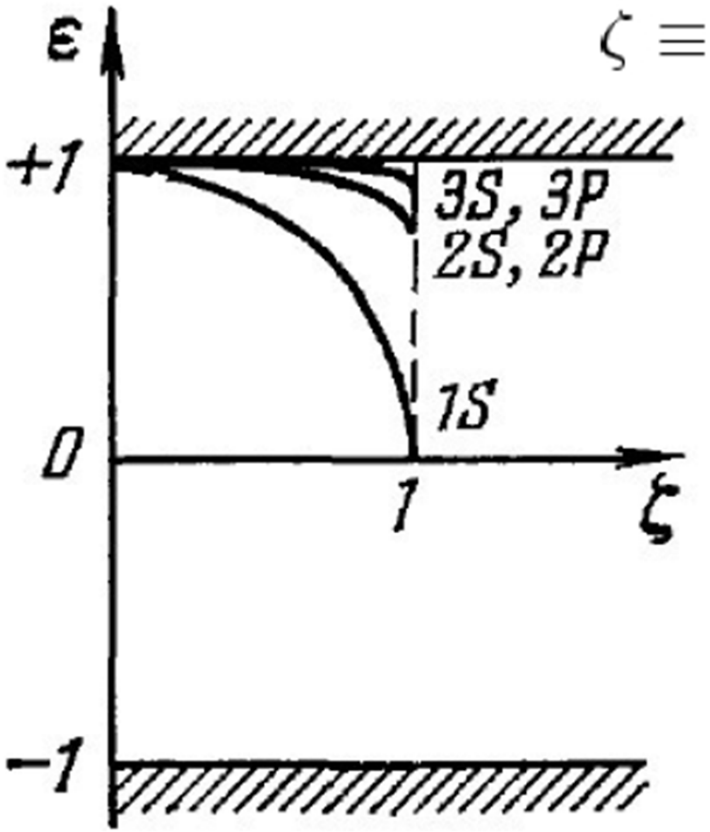
??? $\delta x > \frac{\hbar}{mc}$

- Atomic collapse resonance on graphene

Dirac-Keple Problem

$$m \neq 0 \qquad \epsilon_1 = m\sqrt{1-\zeta^2}$$

$$\zeta \equiv \frac{Ze^2}{\hbar c}$$



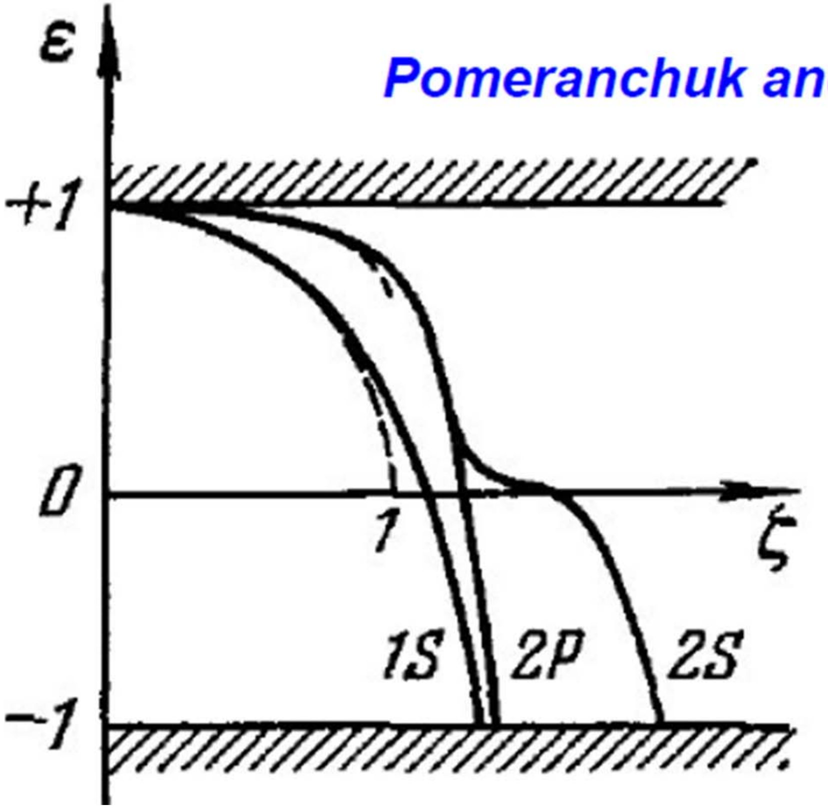

Dirac (1929)

What happens at Z > 137?

Atomic collapse resonance on graphene

Dirac-Keple Problem

$m \neq 0$

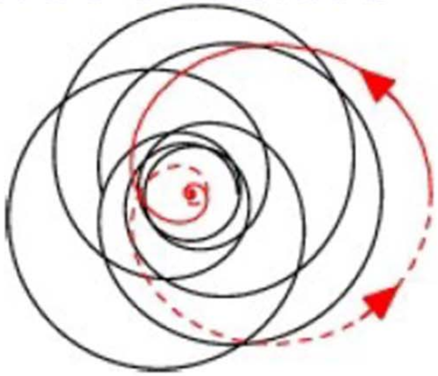


Pomeranchuk and Smorodinskii (1945)

Finite size of nucleus (regularization)

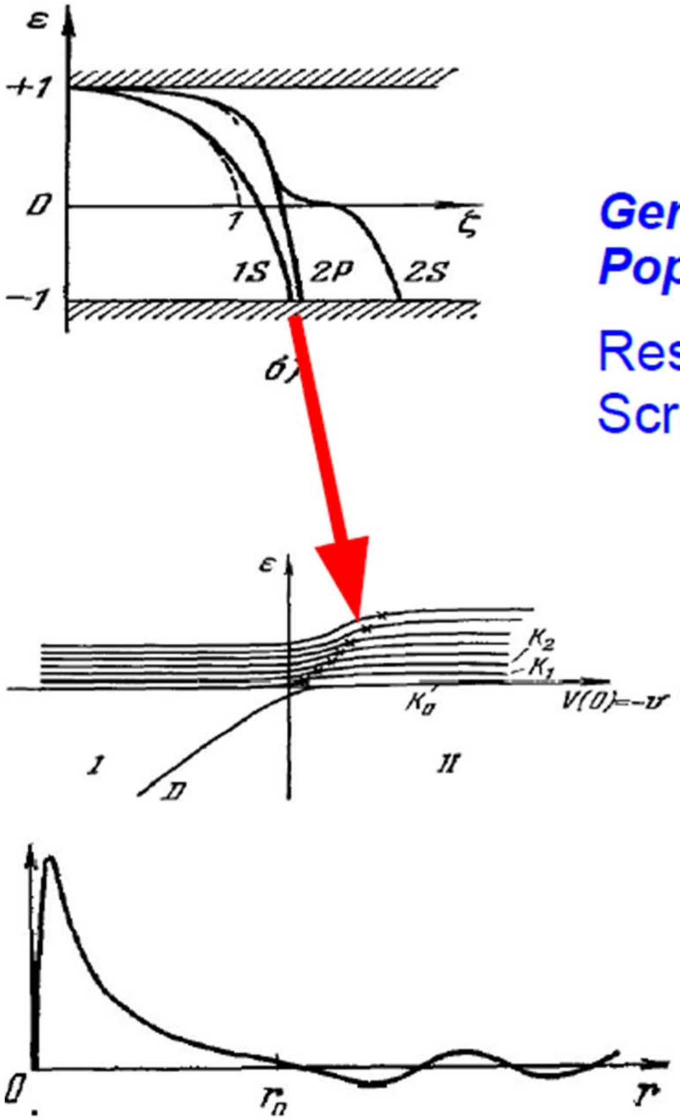
Solution can be continued to Z > 137.

1S level merges into Dirac sea at Z = 170



- Atomic collapse resonance on graphene

Dirac-Keple Problem



Gershteyn, Zeldovich (1969)
Popov (1970)

Resonant electron state in Dirac sea
Screening by pair production?

$$\epsilon = \epsilon_0 - i\gamma \qquad \epsilon_0 = -m - a(Z - Z_c)$$

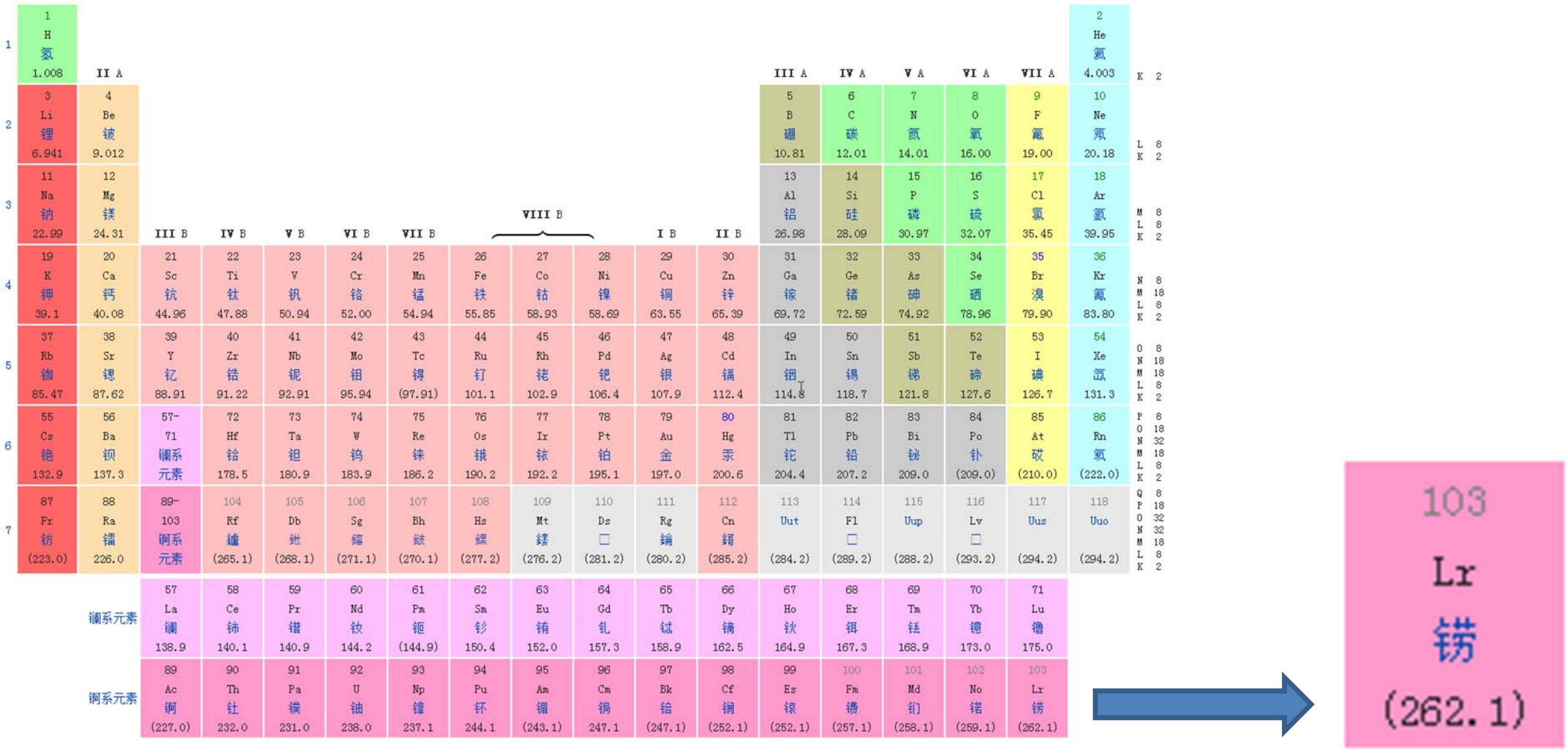
$$\gamma \sim \exp\left(-\frac{b}{\sqrt{Z - Z_c}}\right)$$

Quasilocalized state

- Atomic collapse resonance on graphene

Dirac-Keple Problem

Challenge: How to verify such theory?

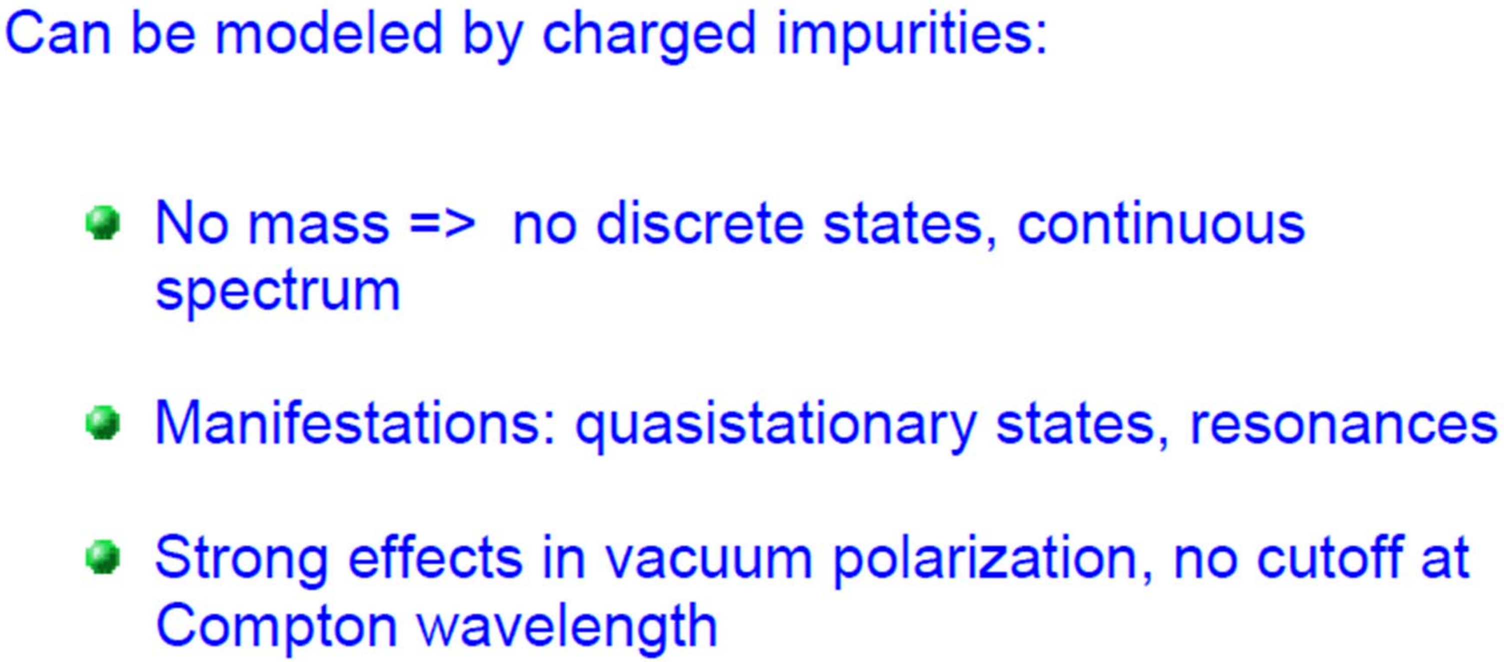


		II A	III B	IV B	V B	VI B	VII B	VIII B			I B	II B	III A	IV A	V A	VI A	VII A		
1	1 H 氢 1.008																	2 He 氦 4.003	K 2
2	3 Li 锂 6.941	4 Be 铍 9.012											5 B 硼 10.81	6 C 碳 12.01	7 N 氮 14.01	8 O 氧 16.00	9 F 氟 19.00	10 Ne 氖 20.18	L 8 K 2
3	11 Na 钠 22.99	12 Mg 镁 24.31											13 Al 铝 26.98	14 Si 硅 28.09	15 P 磷 30.97	16 S 硫 32.07	17 Cl 氯 35.45	18 Ar 氩 39.95	M 8 L 8 K 2
4	19 K 钾 39.1	20 Ca 钙 40.08	21 Sc 钪 44.96	22 Ti 钛 47.88	23 V 钒 50.94	24 Cr 铬 52.00	25 Mn 锰 54.94	26 Fe 铁 55.85	27 Co 钴 58.93	28 Ni 镍 58.69	29 Cu 铜 63.55	30 Zn 锌 65.39	31 Ga 镓 69.72	32 Ge 锗 72.59	33 As 砷 74.92	34 Se 硒 78.96	35 Br 溴 79.90	36 Kr 氪 83.80	N 8 M 18 L 8 K 2
5	37 Rb 铷 85.47	38 Sr 锶 87.62	39 Y 钇 88.91	40 Zr 锆 91.22	41 Nb 铌 92.91	42 Mo 钼 95.94	43 Tc 锝 (97.91)	44 Ru 钌 101.1	45 Rh 铑 102.9	46 Pd 钯 106.4	47 Ag 银 107.9	48 Cd 镉 112.4	49 In 铟 114.8	50 Sn 锡 118.7	51 Sb 锑 121.8	52 Te 碲 127.6	53 I 碘 126.7	54 Xe 氙 131.3	O 8 N 18 M 18 L 8 K 2
6	55 Cs 铯 132.9	56 Ba 钡 137.3	57- 71 镧系 元素	72 Hf 铪 178.5	73 Ta 钽 180.9	74 W 钨 183.9	75 Re 铼 186.2	76 Os 锇 190.2	77 Ir 铱 192.2	78 Pt 铂 195.1	79 Au 金 197.0	80 Hg 汞 200.6	81 Tl 铊 204.4	82 Pb 铅 207.2	83 Bi 铋 209.0	84 Po 钋 (209.0)	85 At 砹 (210.0)	86 Rn 氡 (222.0)	P 8 O 18 N 32 M 18 L 8 K 2
7	87 Fr 钫 (223.0)	88 Ra 镭 226.0	89- 103 锕系 元素	104 Rf 鑪 (265.1)	105 Db 𨧀 (268.1)	106 Sg 𨭎 (271.1)	107 Bh 𨨏 (270.1)	108 Hs 𨭆 (277.2)	109 Mt 䥑 (276.2)	110 Ds □ (281.2)	111 Rg 錀 (280.2)	112 Cn 鎶 (285.2)	113 Uut (284.2)	114 Fl □ (289.2)	115 Uup (288.2)	116 Lv □ (293.2)	117 Uus (294.2)	118 Uuo (294.2)	Q 8 P 18 O 32 N 32 M 18 L 8 K 2
		镧系元素	57 La 镧 138.9	58 Ce 铈 140.1	59 Pr 镨 140.9	60 Nd 钕 144.2	61 Pm 钷 (144.9)	62 Sm 钐 150.4	63 Eu 铕 152.0	64 Gd 钆 157.3	65 Tb 铽 158.9	66 Dy 镝 162.5	67 Ho 钬 164.9	68 Er 铒 167.3	69 Tm 铥 168.9	70 Yb 镱 173.0	71 Lu 镥 175.0		
		锕系元素	89 Ac 锕 (227.0)	90 Th 钍 232.0	91 Pa 镤 231.0	92 U 铀 238.0	93 Np 镎 237.1	94 Pu 钚 244.1	95 Am 镅 (243.1)	96 Cm 锔 247.1	97 Bk 锫 (247.1)	98 Cf 锎 (252.1)	99 Es 锿 (252.1)	100 Fm 镄 (257.1)	101 Md 钔 (258.1)	102 No 锘 (259.1)	103 Lr 铹 (262.1)		

103
Lr
铹
(262.1)

- Atomic collapse resonance on graphene

Dirac-Keple Problem



Can be modeled by charged impurities:

- No mass => no discrete states, continuous spectrum
- Manifestations: quasistationary states, resonances
- Strong effects in vacuum polarization, no cutoff at Compton wavelength

- Atomic collapse resonance on graphene

Dirac-Keple Problem

Dirac equation:

$$\epsilon\psi = -\frac{Ze^2}{\kappa r}\psi - i\hbar v_F \boldsymbol{\sigma}\boldsymbol{\nabla}\psi$$

Ansatz:

$$\psi(r,\varphi) = \begin{pmatrix} w(r) + v(r) \\ [w(r) - v(r)]\, e^{i\varphi} \end{pmatrix} r^{s-1/2} e^{im\varphi} e^{ikr}$$

$$\psi(r \to 0) \sim r^{s-1/2}$$

- Atomic collapse resonance on graphene

Dirac-Keple Problem

$$\psi(r \to 0) \sim r^{s-1/2}$$

$$s = \sqrt{\left(m + \frac{1}{2}\right)^2 - \beta^2} \qquad \beta \equiv \frac{Ze^2}{\kappa \hbar v_F}$$

Subcritical: $|\beta| < \left|m + \frac{1}{2}\right|$

Supercritical: $|\beta| > \left|m + \frac{1}{2}\right|$ Oscillations small r !

Critical value: $\beta_c = \frac{1}{2}$ $\frac{e^2}{\hbar v_F} \approx 2.5$

$$\kappa_{\text{RPA}} = 1 + \frac{\pi N}{8} \frac{e^2}{\hbar v_F}$$

$$\boxed{Z_c \approx 1}$$

- Atomic collapse resonance on graphene

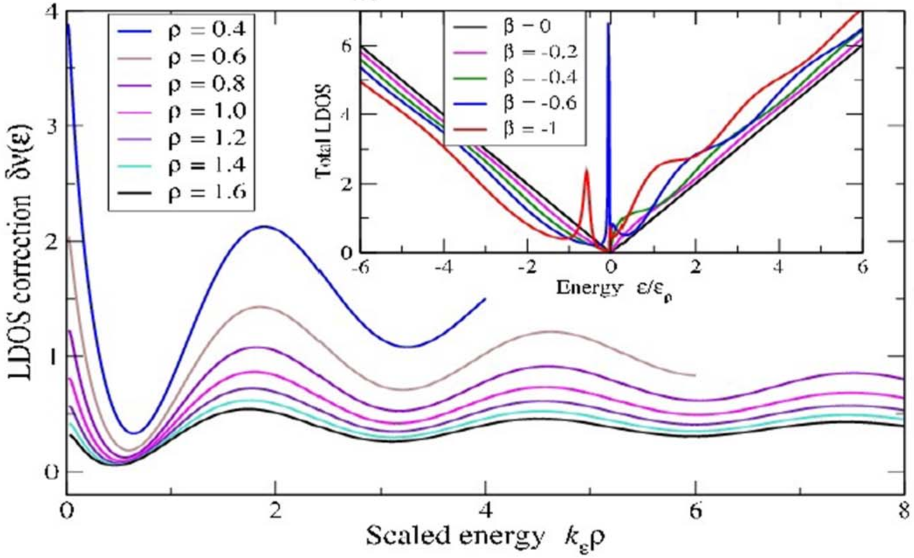
Dirac-Keple Problem

Subcritical case:

$$\left.\begin{matrix} v \\ w \end{matrix}\right\}^{+} = \left\{ \begin{matrix} {}_1F_1(s-i\beta, 2s+1, -2ikr) \\ \frac{s-i\beta}{m+\frac{1}{2}}\, {}_1F_1(s+1-i\beta, 2s+1, -2ikr) \end{matrix} \right.$$

Scale-invariant solution (depends only on *kr*)

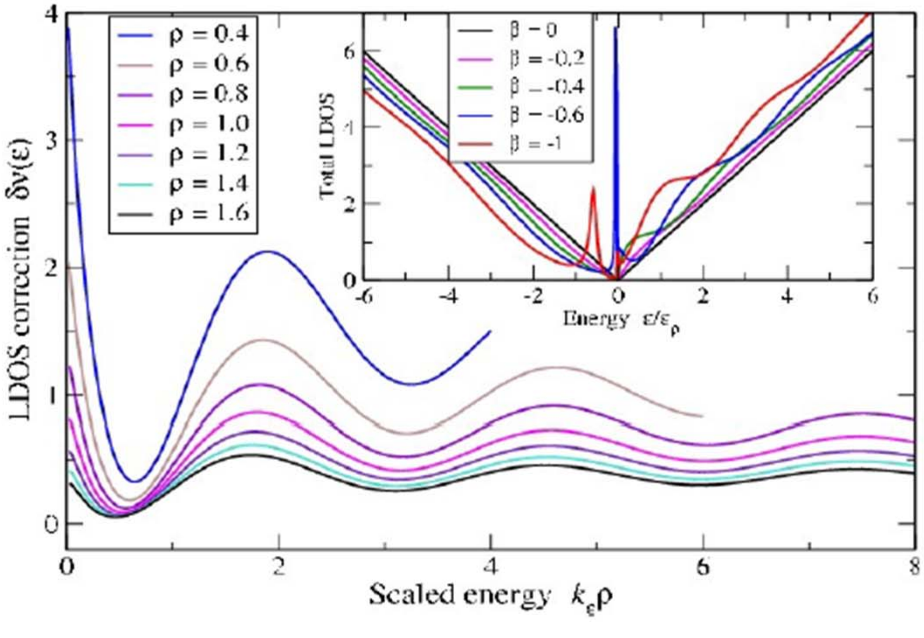
$$\nu(\epsilon, r) = \frac{N}{\pi\hbar v_F} \sum_m |\psi_m(\epsilon, r)|^2$$

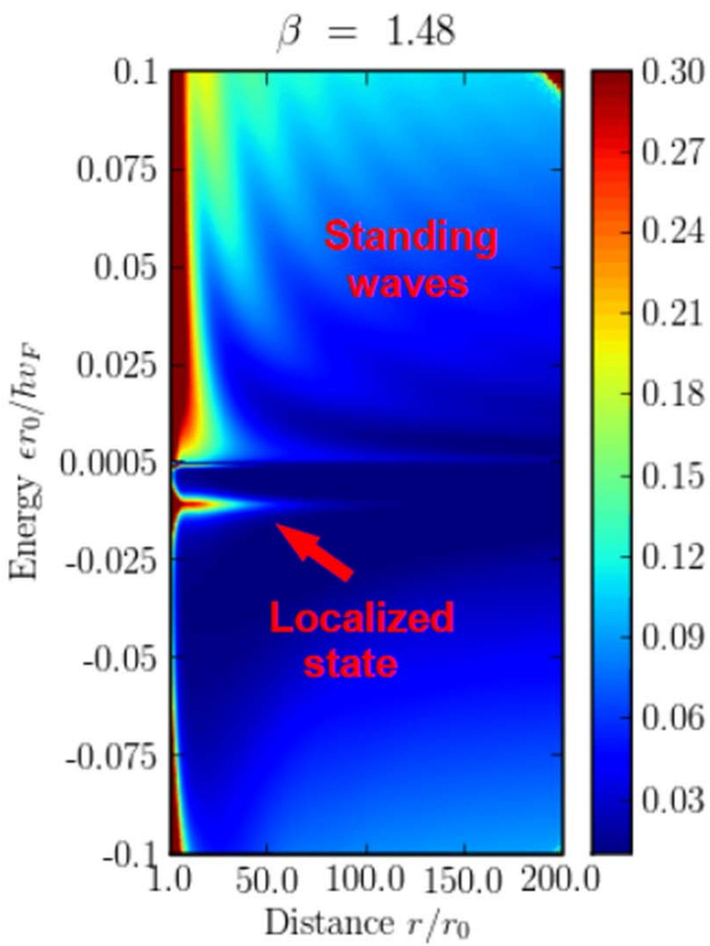


- Atomic collapse resonance on graphene

Dirac-Keple Problem

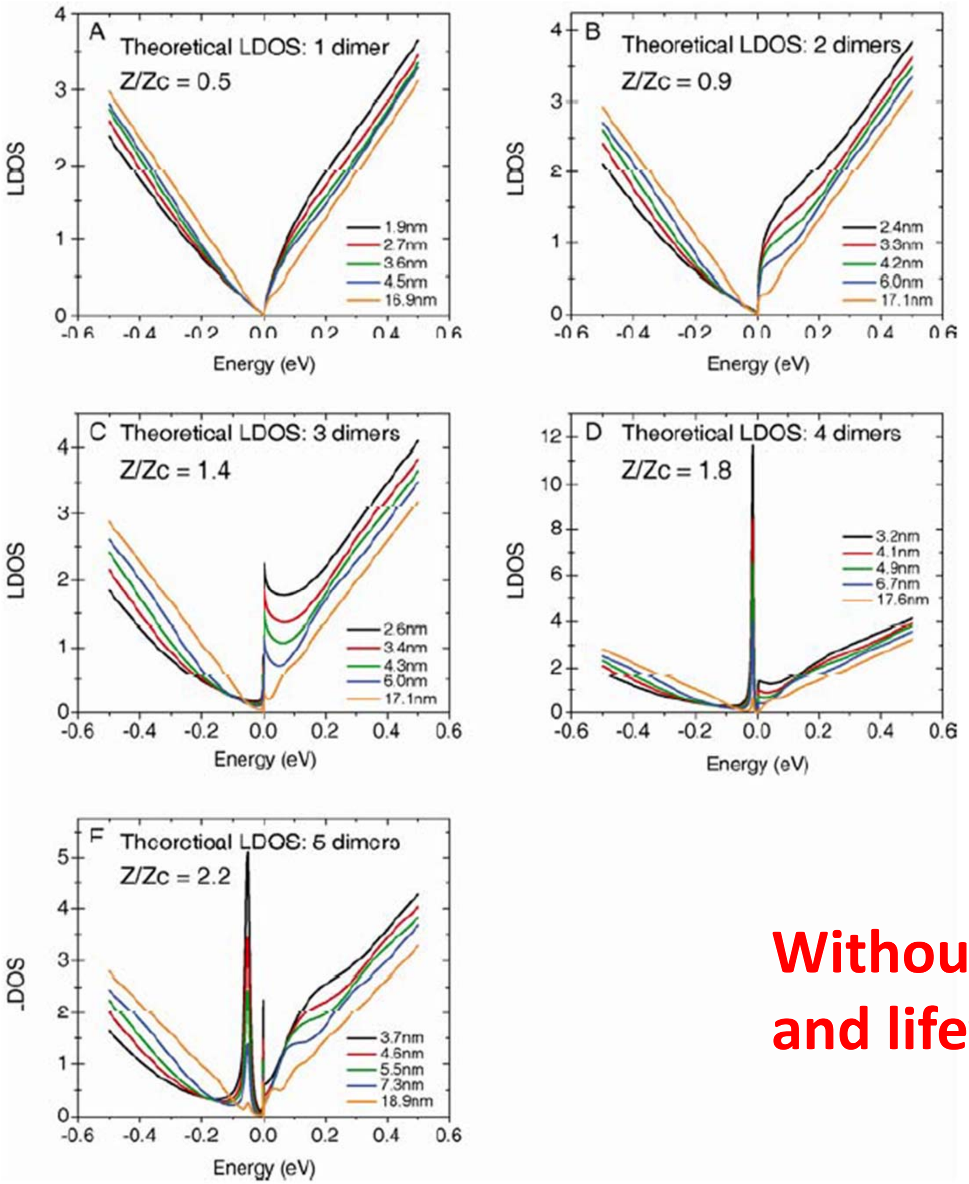
$$\nu(\epsilon, r) = \frac{N}{\pi \hbar v_F} \sum_m |\psi_m(\epsilon, r)|^2$$





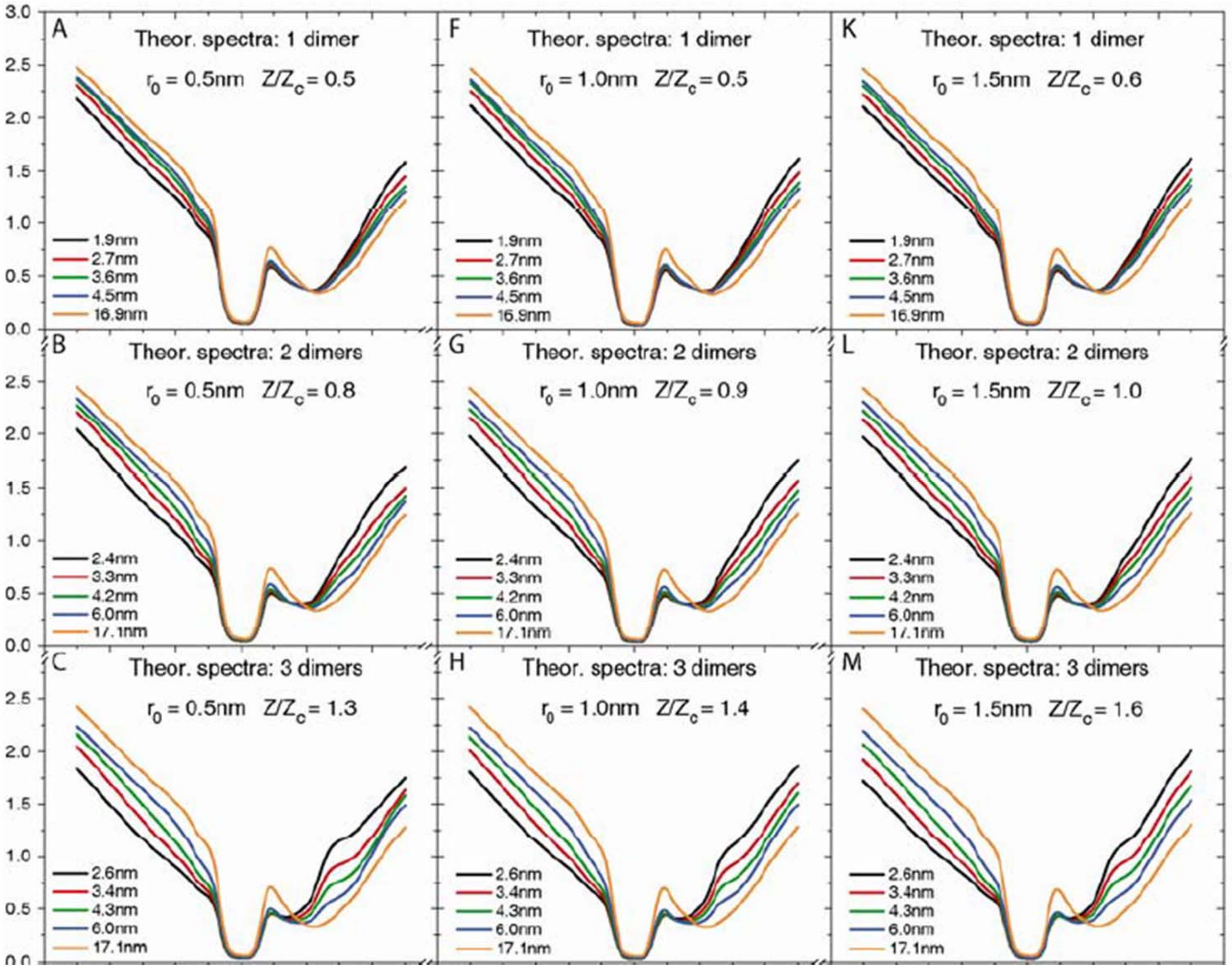
- Standing waves
- Bound states

- Atomic collapse resonance on graphene



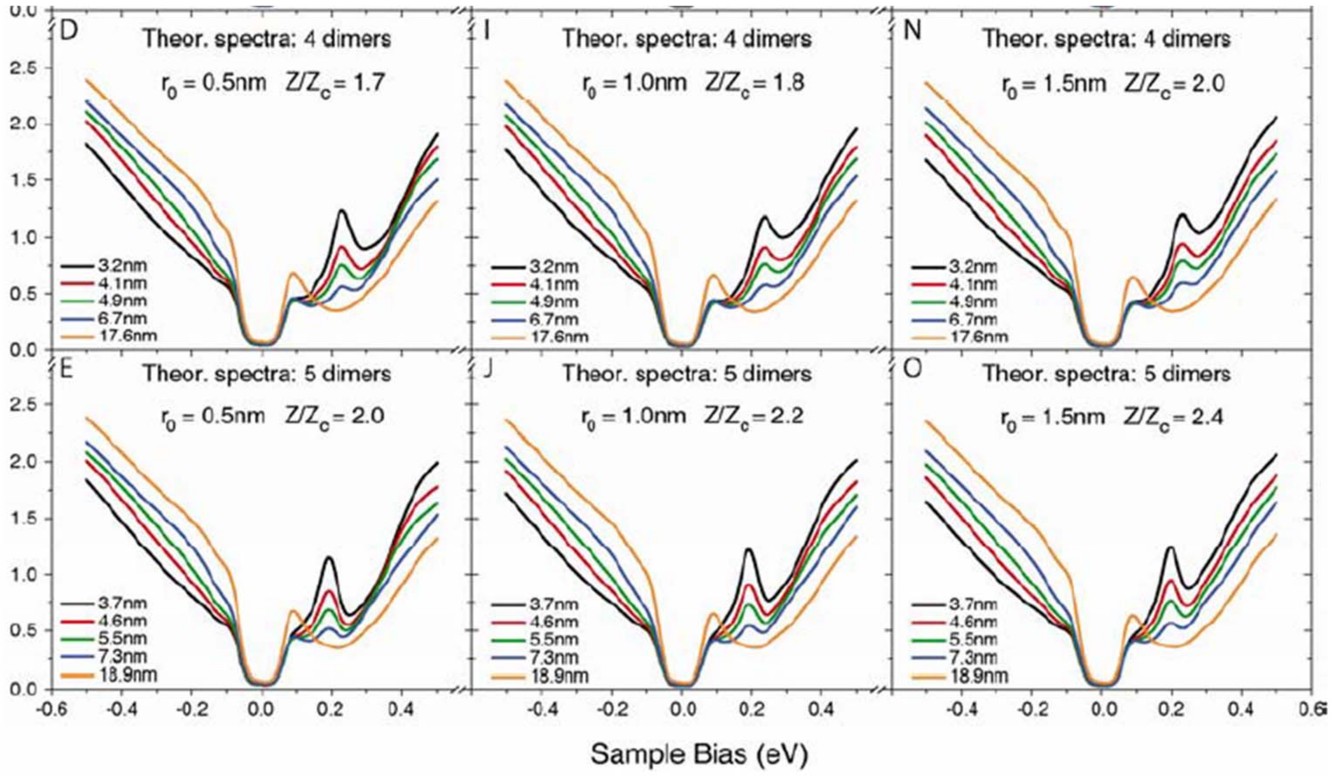
Without inelastic tunneling and lifetime broadening

- Atomic collapse resonance on graphene



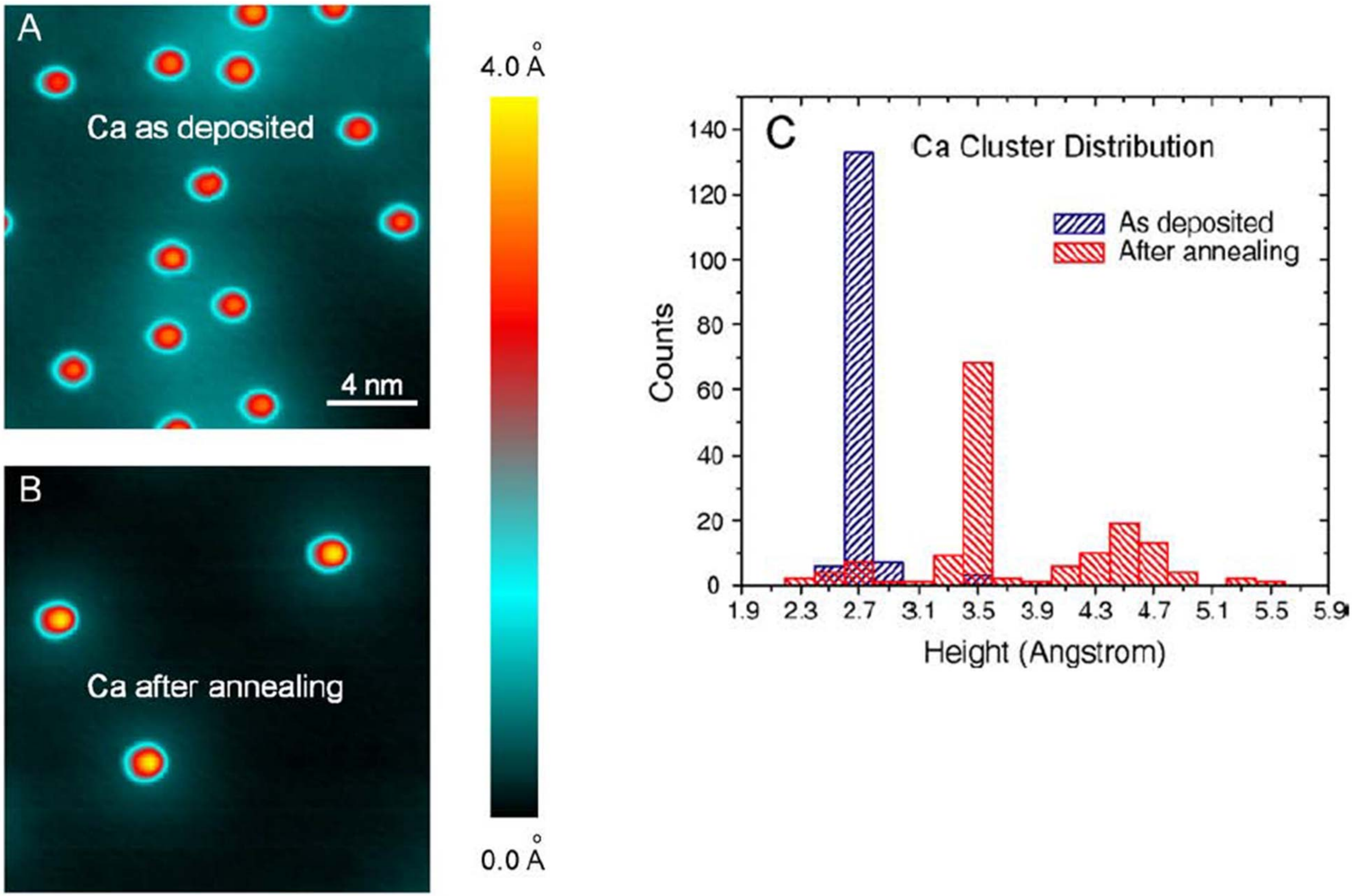
With inelastic tunneling and lifetime broadening

- Atomic collapse resonance on graphene

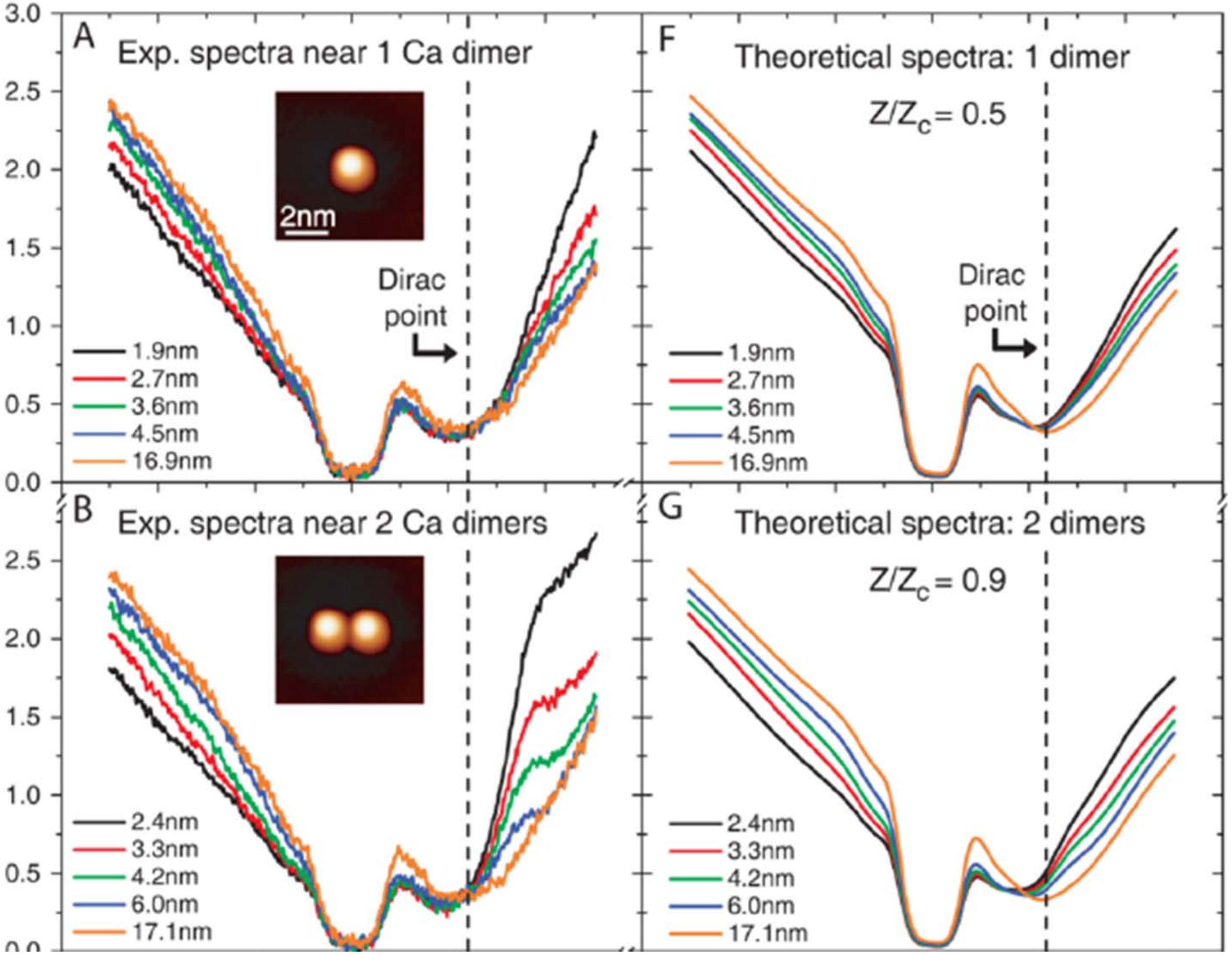


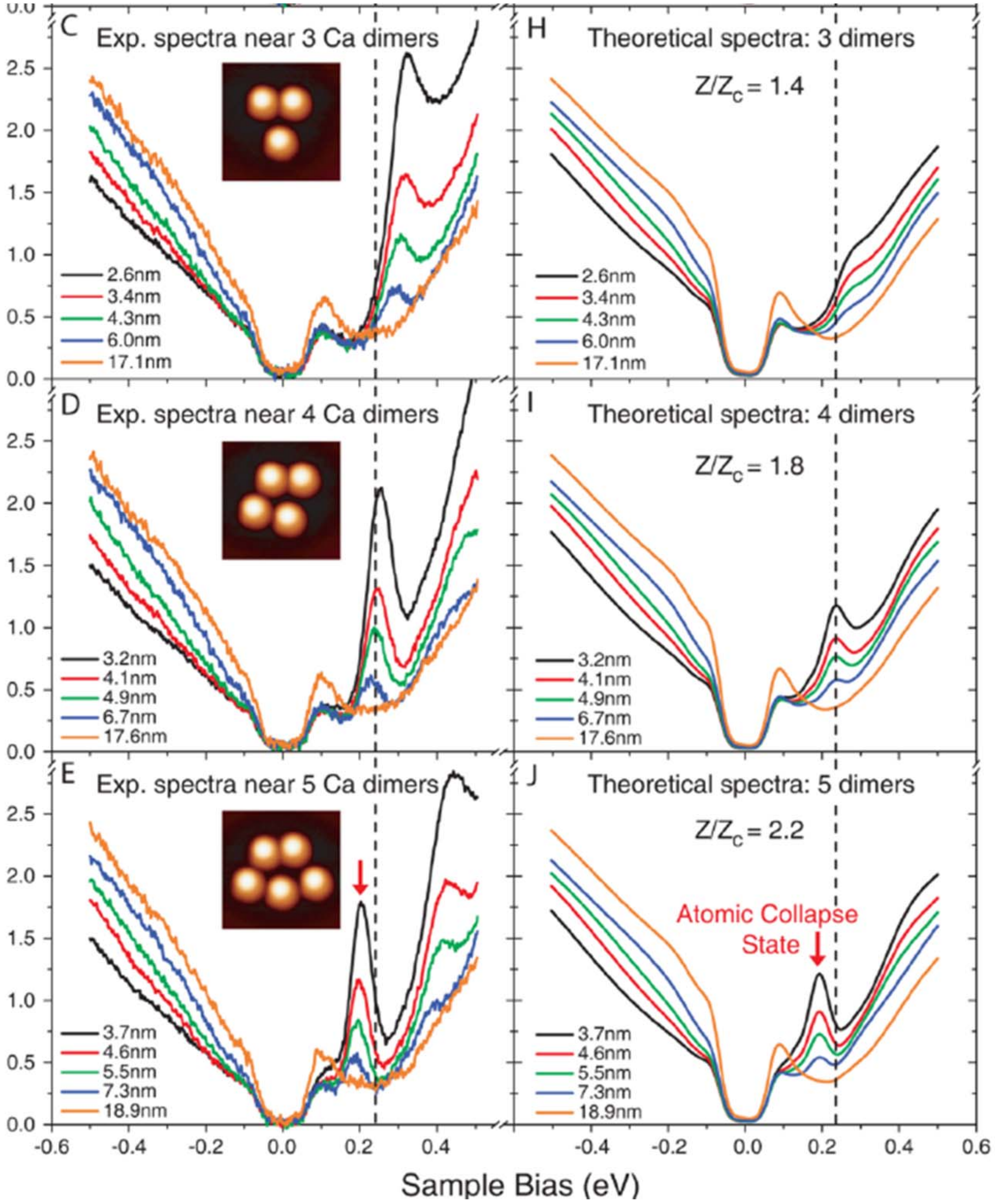
With inelastic tunneling and lifetime broadening

- Atomic collapse resonance on graphene

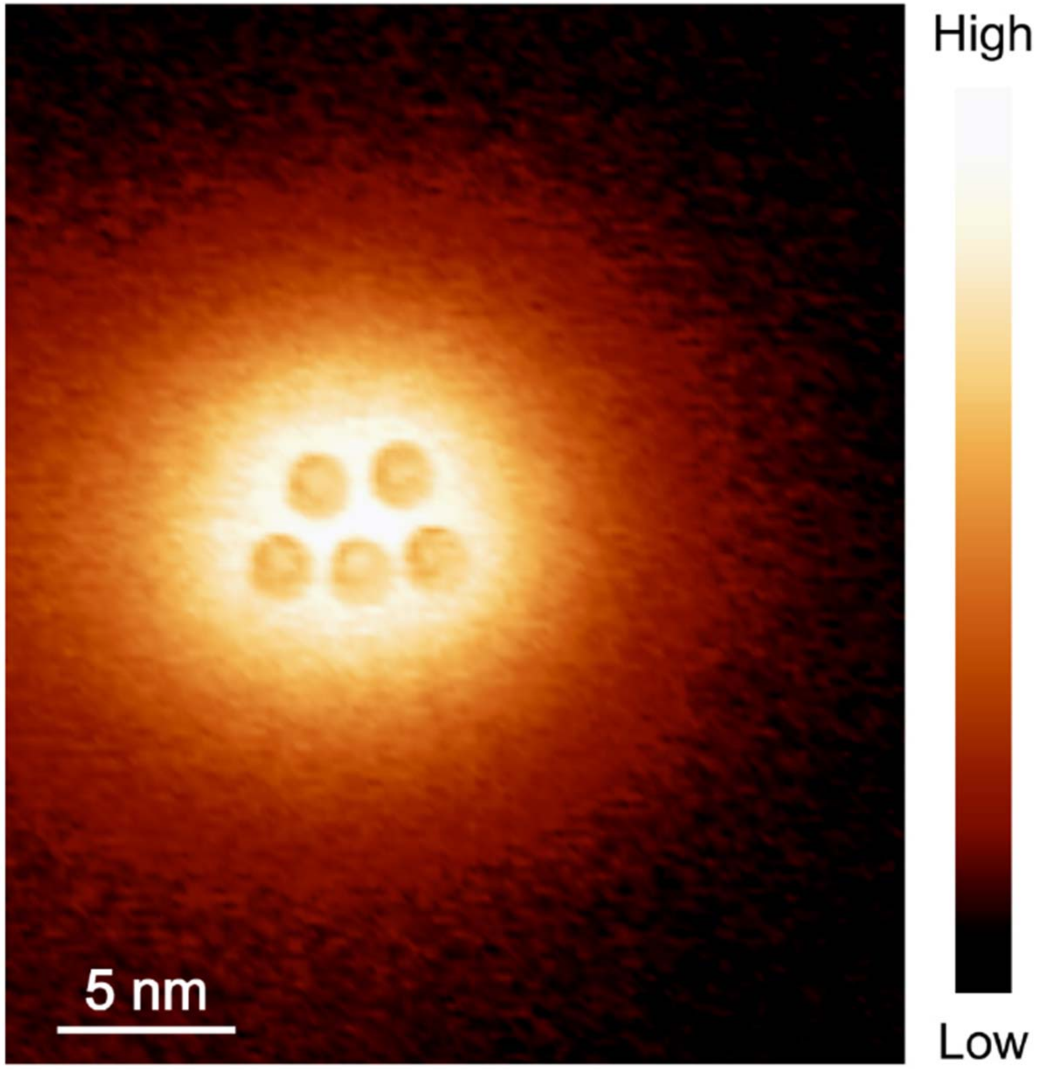


- Atomic collapse resonance on graphene

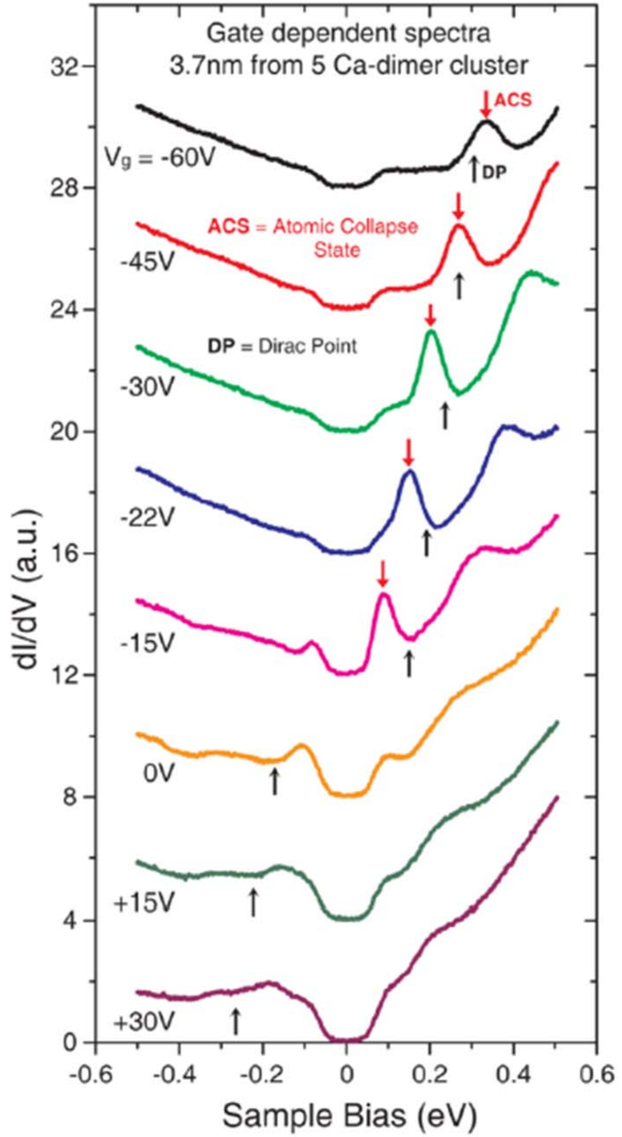



C
Exp. spectra near 3 Ca dimers
2.6nm
3.4nm
4.3nm
6.0nm
17.1nm
H
Theoretical spectra: 3 dimers
Z/Z$_c$ = 1.4
2.6nm
3.4nm
4.3nm
6.0nm
17.1nm
D
Exp. spectra near 4 Ca dimers
3.2nm
4.1nm
4.9nm
6.7nm
17.6nm
I
Theoretical spectra: 4 dimers
Z/Z$_c$ = 1.8
3.2nm
4.1nm
4.9nm
6.7nm
17.6nm
E
Exp. spectra near 5 Ca dimers
3.7nm
4.6nm
5.5nm
7.3nm
18.9nm
J
Theoretical spectra: 5 dimers
Z/Z$_c$ = 2.2
Atomic Collapse State
3.7nm
4.6nm
5.5nm
7.3nm
18.9nm
0.0
0.5
1.0
1.5
2.0
2.5
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
Sample Bias (eV)

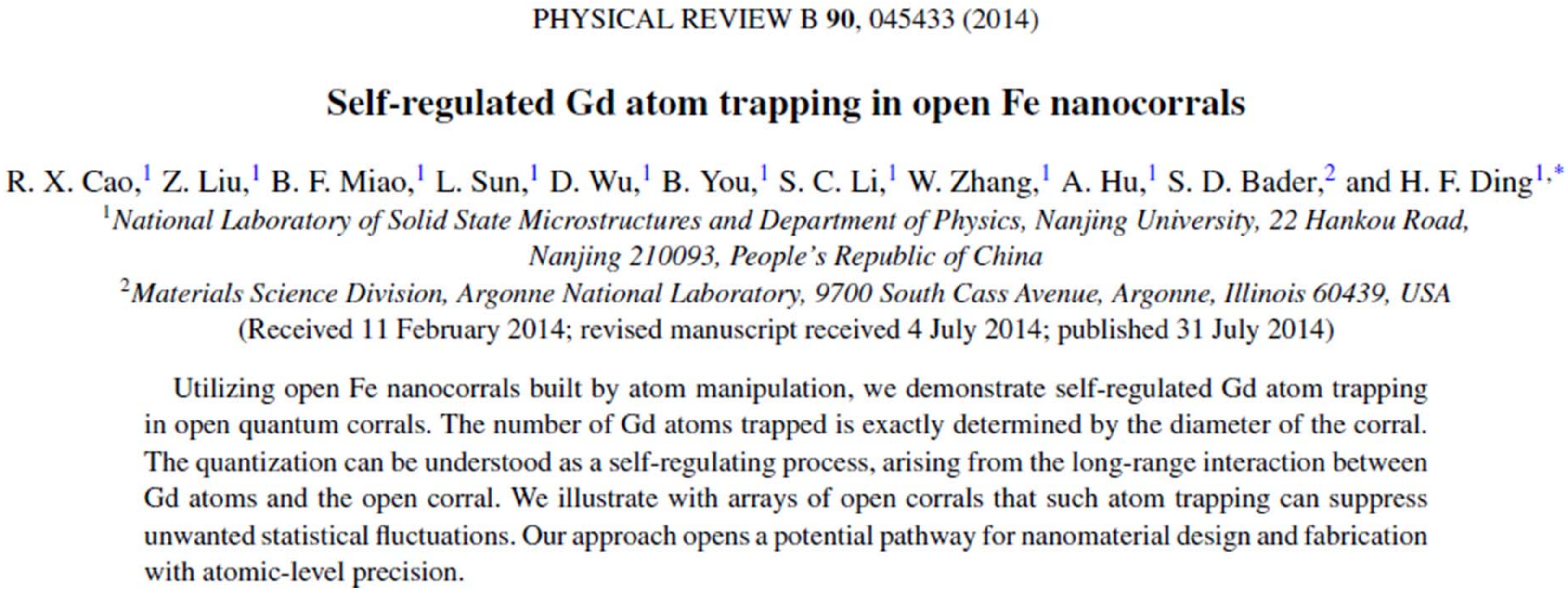
- Atomic collapse resonance on graphene



- Atomic collapse resonance on graphene



- Self regulated Gd atom trapping in open Fe nanocorrals



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Self-regulated Gd atom trapping in open Fe nanocorrals

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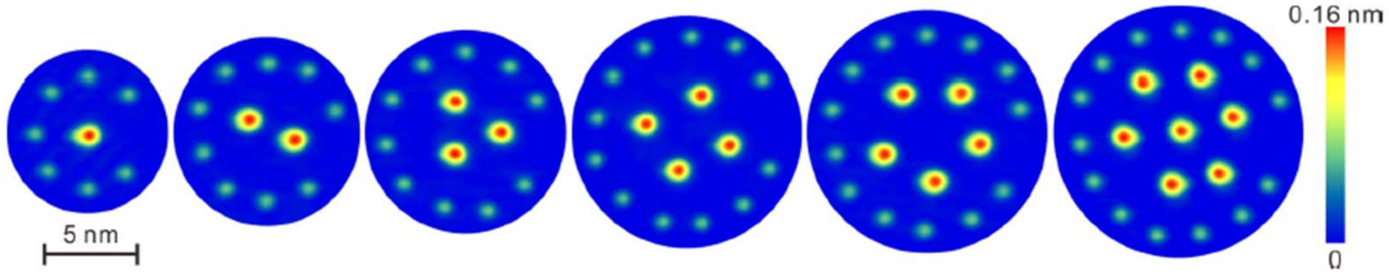
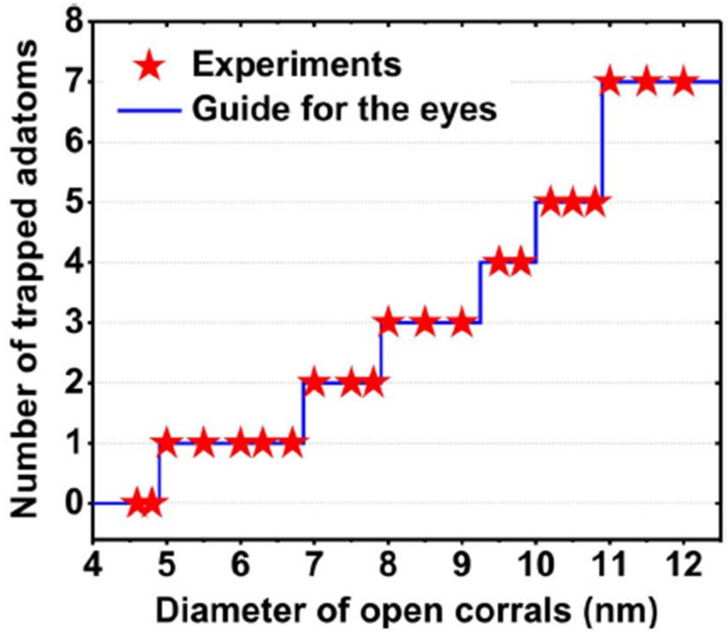
Utilizing open Fe nanocorrals built by atom manipulation, we demonstrate self-regulated Gd atom trapping in open quantum corrals. The number of Gd atoms trapped is exactly determined by the diameter of the corral. The quantization can be understood as a self-regulating process, arising from the long-range interaction between Gd atoms and the open corral. We illustrate with arrays of open corrals that such atom trapping can suppress unwanted statistical fluctuations. Our approach opens a potential pathway for nanomaterial design and fabrication with atomic-level precision.

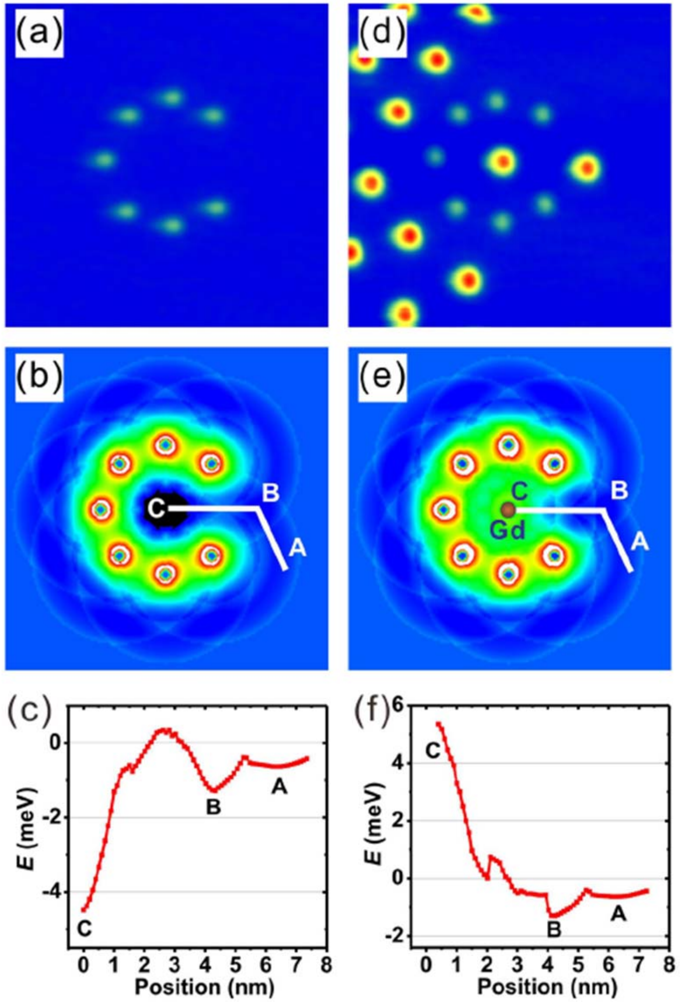
- Self regulated Gd atom trapping in open Fe nanocorrals

Gd in Fe corral on Ag(111)

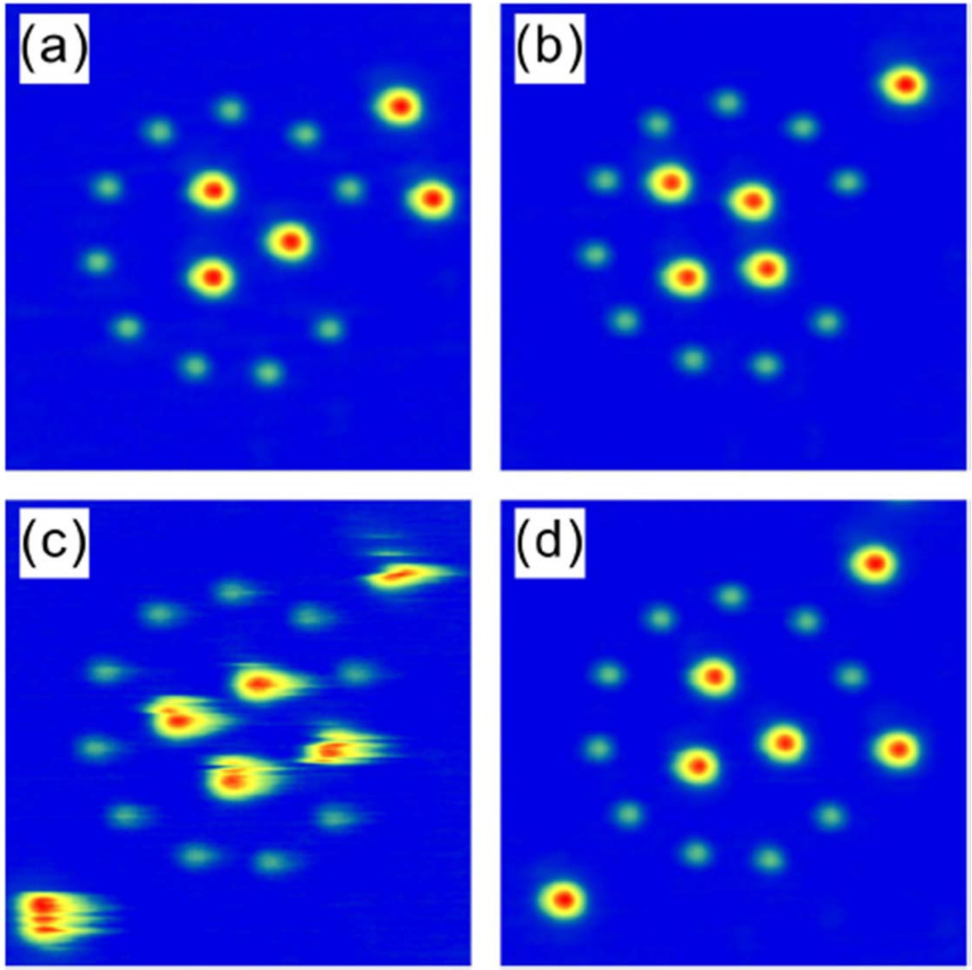




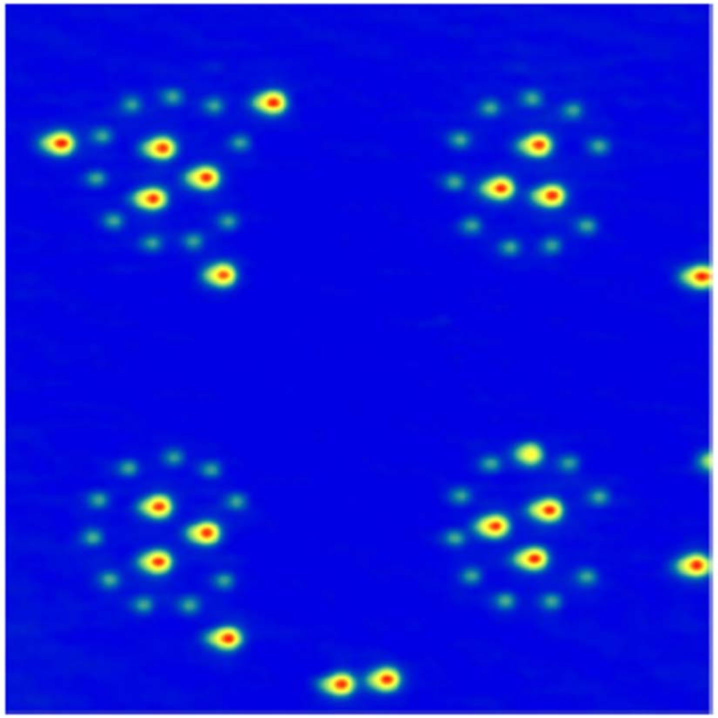
- Self regulated Gd atom trapping in open Fe nanocorrals



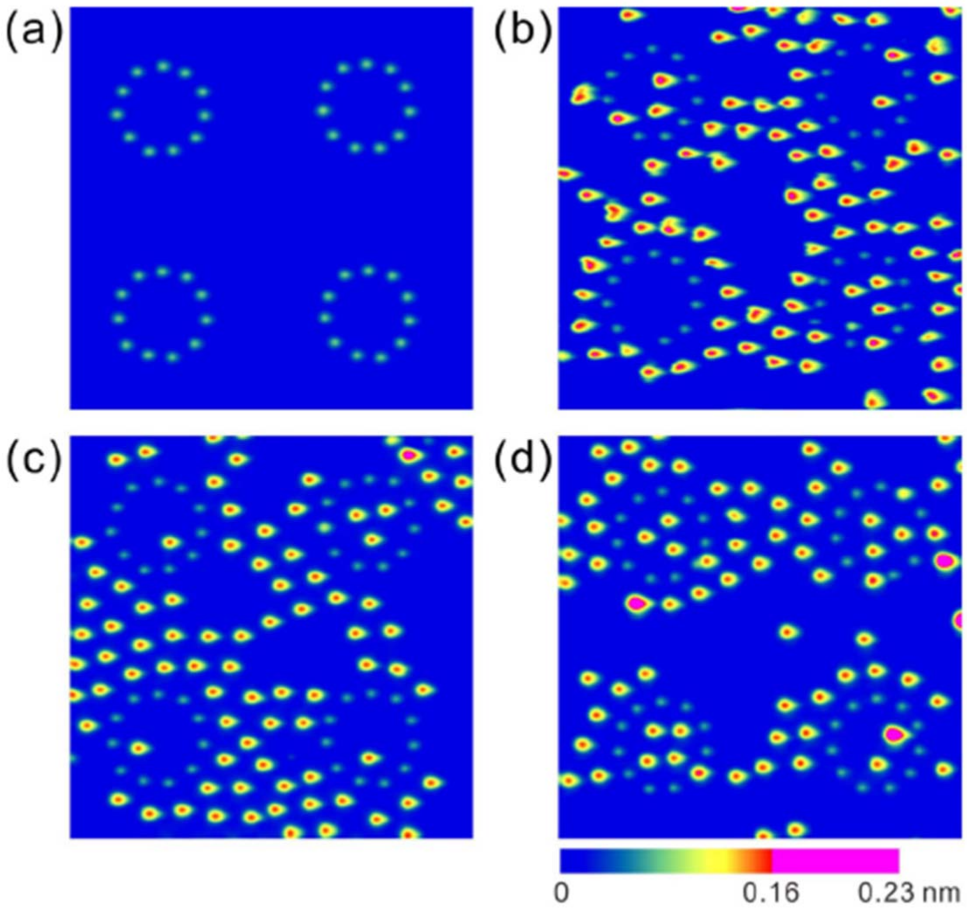
- Self regulated Gd atom trapping in open Fe nanocorrals

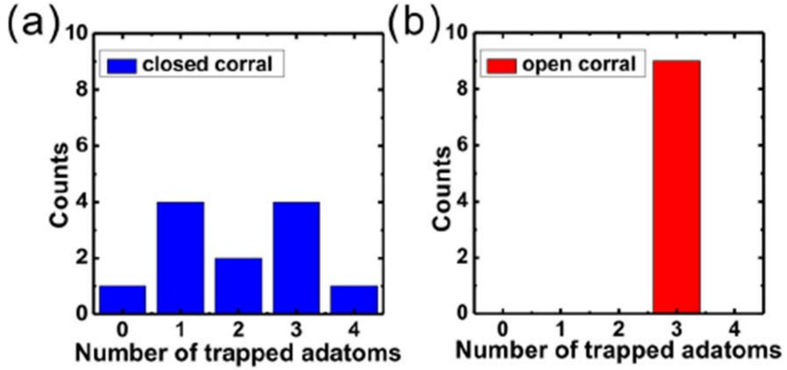


- Self regulated Gd atom trapping in open Fe nanocorrals



- Self regulated Gd atom trapping in open Fe nanocorrals





- Lock-in technique (brief introduction)

Stanford Research System

Signal Recovery

Zurich Instruments

Scitec Instruments

- Lock-in technique (brief introduction)

Basic idea behind the Lock-in

- Lock-in technique (brief introduction)

Basic idea behind the Lock-in

How to find a person in such situation?

- Lock-in technique (brief introduction)

Basic idea behind the Lock-in

Ways to find a person:

- **Position**
- **Color**
- **Wave hand/flag**
- **Synchronized action**

- Lock-in technique (brief introduction)

Basic idea behind the Lock-in