Lecture 3: Helium

Last Week: the hydrogen atom, eigenstate wave functions, and the *gross* and *fine* energy structure for hydrogen-like single-electron atoms

$$E_n = -\frac{Z^2}{n^2} hcR_\infty \left(\mu / m \right) = -\frac{1}{2} \mu c^2 \left(\frac{Z\alpha}{n} \right)^2 \qquad \text{Rydberg formula}$$

+ fine-structure terms coming in at higher powers of α

This week: multi-electron atoms (helium, alkali metal atoms),

What we'll learn from helium

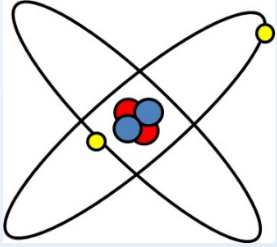How to deal with electron-electron interactions (screening)

How to deal with quantum statistics

    -restrictions on filling

    -exchange terms
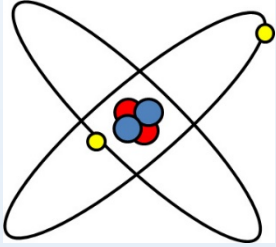
Consequence of transition selection rules for spin

Helium – gross structure and eigenstates

$$H = H_1^0 + H_2^0 + H_{\text{int}}$$

$$H = -\frac{\hbar^2}{2m}\vec{\nabla}_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{\hbar^2}{2m}\vec{\nabla}_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$
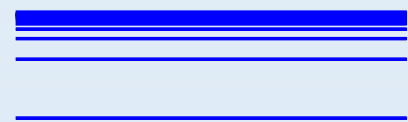
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0th order approx: just ignore H_{int}

For He⁺: $E_{gs} \approx \left(\frac{Z=2}{n=1}\right)^2 \times \left(-13.6\,\text{eV}\right) = -54.4\,\text{eV}$

$n = 2$
$(n, l, m_l) = (2,0,0)$
$(2,1,-1)$
$(2,1,0)$
$(2,1,1)$

$n = 1$
$(n, l, m_l) = (1,0,0)$

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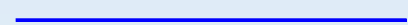
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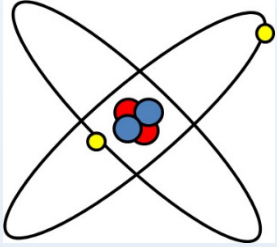For He⁺: $E_{gs} \approx \left(\frac{Z=2}{n=1}\right)^2 \times (-13.6\,\text{eV}) = -54.4\,\text{eV}$

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$(n, l, m_l) = (2,0,0)$
$(2,1,-1)$
$(2,1,0)$
$(2,1,1)$

Pauli exclusion: 2 electrons can't have all the same quantum #'s

$$\psi_{gs,spatial}^{(0)} = \psi_{1s}(r_1)\psi_{1s}(r_2) \equiv 1s^2$$

$m_s \in \{-1/2, 1/2\}$

$n = 1$
$(n, l, m_l) = (1,0,0)$

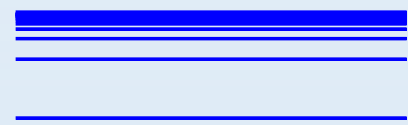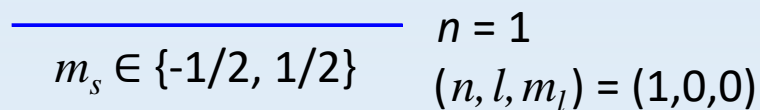# Helium – gross structure and eigenstates

$$H = H_1^0 + H_2^0 + H_{int}$$

$$H = -\frac{\hbar^2}{2m}\vec{\nabla}_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{\hbar^2}{2m}\vec{\nabla}_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

0th order approx: just ignore H$_{int}$

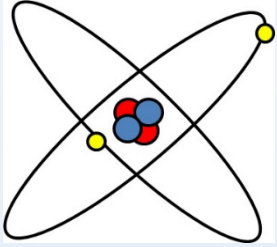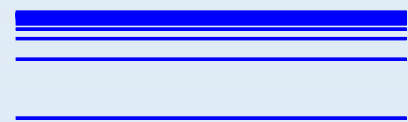For He$^+$: $E_{gs} \approx \left(\frac{Z=2}{n=1}\right)^2 \times (-13.6\,\text{eV}) = -54.4\,\text{eV}$

$\psi_{gs,spatial}^{(0)} = 1s^2 \qquad E_{gs}^{(0)} \approx -109\,\text{eV}$

$E_{gs}^{\text{expt}} \approx -79\,\text{eV}$

$n = 2$
$(n, l, m_l) = (2,0,0)$
$(2,1,-1)$
$(2,1,0)$
$(2,1,1)$

$m_s \in \{-1/2,\ 1/2\}$

$n = 1$
$(n, l, m_l) = (1,0,0)$

Helium – gross structure

Now let's estimate, to first order, the effect of interactions

$$\psi^{(0)}_{gs,spatial} = 1s^2 = \frac{1}{4\pi} R^{Z=2}_{1s}(r_1) R^{Z=2}_{1s}(r_2) = \frac{Z^3}{\pi a_0^3} e^{-Zr_1/a_0} e^{-Zr_2/a_0}$$

$$\Delta E = \left\langle H_{\text{int}} \right\rangle = \frac{e^2}{4\pi\varepsilon_0} \left\langle \frac{1}{r_{12}} \right\rangle \approx 34 \text{ eV}$$

The derivation of this result is basically HW question #3a – so won't go through it in detail

The basic idea is to consider the effective potential felt by electron #2 due to Coulomb interactions with *average* distribution of electron #1's charge (and vice versa)

This is <u>not</u> a great estimate – it's based on first-order perturbation theory and assumes that the eigenstates don't change much due to H_{int}. However, ΔE is on the order of E, so H_{int} is a large perturbation.

>> HW question 3b asks you to use a variational approach to minimize the energy

Multi-electron wave functions - symmetry

Electrons, being fermions, must* have a total wave function that is <u>antisymmetric</u> under the exchange of two particles

* in 3 dimensions

$$\psi\left(r_1, r_2, \ldots, r_N\right) = -\psi\left(r_2, r_1, \ldots, r_N\right)$$

Let's restrict to just two particles, and label states by all their relevant quantum numbers $Q = (n, l, m_l, m_s)$

spatial quantum numbers: n, l, m_l for our hydrogen-like orbitals

spin quantum number: each electron can have $m_s = \pm 1/2$,

which we'll write as $\uparrow$ and $\downarrow$

Multi-electron wave functions - symmetry

The solution $\psi(r_1, r_2) = \psi_{Q_1}(r_1)\psi_{Q_2}(r_2)$ is not allowed for $Q_1 = Q_2$

We can exclude this possibility by instead taking the superposition state

$$\psi(r_1, r_2) = \frac{1}{\sqrt{2}}\left(\psi_{Q_1}(r_1)\psi_{Q_2}(r_2) - \psi_{Q_2}(r_1)\psi_{Q_1}(r_2)\right)$$

which vanishes for $Q_1 = Q_2$

→ naturally gives us $\psi(r_1, r_2) = -\psi(r_2, r_1)$

Multi-electron wave functions - symmetry

The g.s. spatial wave function ($1s^2$) for helium is <u>symmetric</u>

$$\psi_{space}(r_1, r_2) = \psi_{1s}(r_1)\psi_{1s}(r_2)$$

The spin part of the g.s. wave function must be <u>antisymmetric</u>

$$\psi_{spin}(r_1, r_2) = \frac{1}{\sqrt{2}}\left(\psi_{\uparrow}(r_1)\psi_{\downarrow}(r_2) - \psi_{\downarrow}(r_1)\psi_{\uparrow}(r_2)\right)$$

singlet state with total spin S = 0 and m_S = 0

(parahelium)

Multi-electron wave functions - symmetry

The two-electron spin wave function can also be <u>symmetric</u>, and there are three possibilities:

$$\psi_{spin}(r_1, r_2) = \begin{cases} \psi_\uparrow(r_1)\psi_\uparrow(r_2) & m_S = +1 \\ \frac{1}{\sqrt{2}}\left(\psi_\uparrow(r_1)\psi_\downarrow(r_2) + \psi_\downarrow(r_1)\psi_\uparrow(r_2)\right) & m_S = 0 \\ \psi_\downarrow(r_1)\psi_\downarrow(r_2) & m_S = -1 \end{cases}$$

These are the *triplet* states with total spin S = 1

These configs require an antisymmetric spatial wave function

(orthohelium)

Excited states

Let's consider the most relevant class of excited states where one of the electrons remains in the 1s orbital.

Excited states can be both singlet and triplet spin configurations, and thus both symmetric and antisymmetric spatial configurations

At this "gross structure" level, the energies are not explicitly tied to the spin of the electrons, but we'll find that the symmetric & antisymmetric spatial wave functions can have different energies (Hund's rule #1)

Which state do you expect to have a lower energy, 2^1P or 2^3P?

- A) 2^1P

- B) 2^3P

- C) the same energy

Which state do you expect to have a lower energy, 2^1P or 2^3P?

- A) 2^1P

- B) 2^3P This triplet, symmetric spin state has an antisymmetric spatial wave function with reduced screening
→ it is more tightly bound

- C) the same energy

What is (approximately) the total energy of a state with electrons in the 1s and 3p orbitals?

What is (approximately) the total energy of a state with electrons in the 1s and 3p orbitals?

Electron-electron interactions are not that important for these far-separated orbitals (also recall that the 3p orbital goes to zero at the nucleus).

For the 1s electron, we can ignore shielding by the 3p electron, and so it's energy is roughly $-(Z=2/n=1)^2$ 13.6 eV = -54.4 eV

The 3p electron orbital experiences almost full shielding by the 1s electron, effectively seeing a hydrogen-like potential with $Z_{eff} = 1$, and has an energy of roughly $-(Z_{eff}=1/n=3)^2$ 13.6 eV = -1.5 eV

The total energy should be roughly -59.9 eV

a bit on notation / selection rules

Spectroscopic notation:

$$(n, l) \rightarrow nL_J \qquad \text{(shorthand for } n^{2S+1}L_J)$$

Spin term is typically omitted for hydrogen and alkalis, as
S = 1/2 for the single (unpaired, valence) electron, so all states have 2S+1 = 2

For **electric dipole transitions**
(basically assuming E-field of
absorbed/emitted light is uniform
over the size of the atom)

$$H_d = -\vec{d} \cdot \vec{E}$$

$$H_d = -(-e\vec{r}) \cdot \vec{E}$$

$$H_d \approx eE_0 e^{-i\omega t} (\vec{r} \cdot \hat{\varepsilon})$$

Δn: no limit

$\Delta l = \pm 1$

$\Delta m_l = 0, \pm 1$

$|\Delta l|, |\Delta j| \leq 1$ from cons. of angular momentum
$\Delta l \neq 0$ from symmetry of dipole operator

$\Delta j = 0, \pm 1$

$\Delta m_j = 0, \pm 1$

<u>always</u>: no $j = 0 \rightarrow j = 0$ from conservation of angular momentum

Dipole-forbidden transitions

One consequence: direct s $\rightarrow$ s, p $\rightarrow$ p, etc. transitions are forbidden. $2S_{1/2}$ state is metastable (can't decay directly via stimulated emission)

FIG. 4. Modified schematic block diagram of apparatus.

Lamb shift experiment – relied on *long* lifetime of $2S_{1/2}$

$$\tau \approx 0.12 \text{ seconds}$$

$2S_{1/2}$ can undergo two-photon decay [through intermediate state(s)]

Metastable helium

The net spin of multi-electron atoms like helium will give a new important selection rule, $\Delta S = 0$ (dipole operator doesn't act on spin)

$2^3S_1 \rightarrow 1^1S_0$ transition is <u>doubly</u> forbidden ($l = 0 \rightarrow l = 0$, $\Delta S = 0$)

metastable helium lives for over 2 hours!
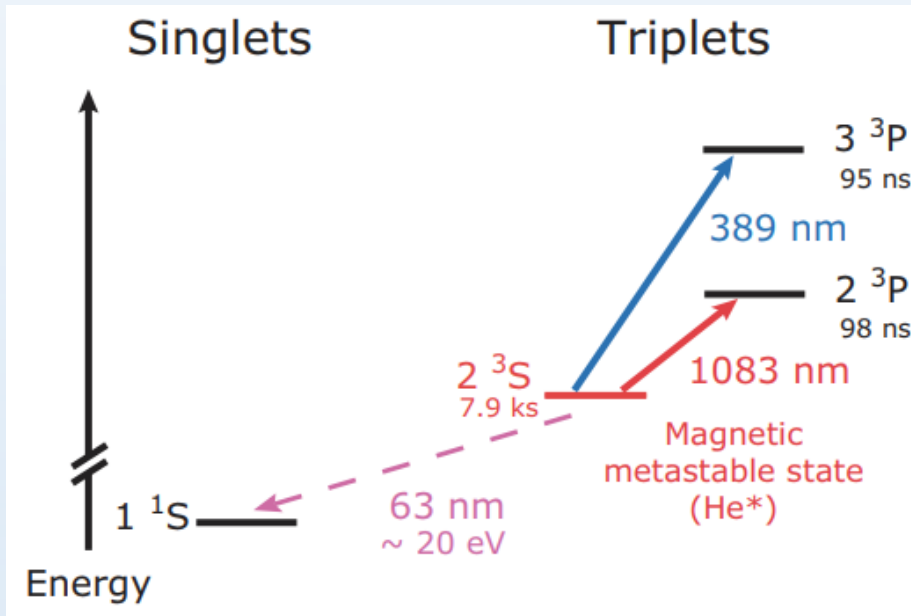
$\rightarrow$ long enough to do some cool science

Long lifetimes also for of neon (15 s), argon (38 s), krypton (39 s), xenon (43 s)
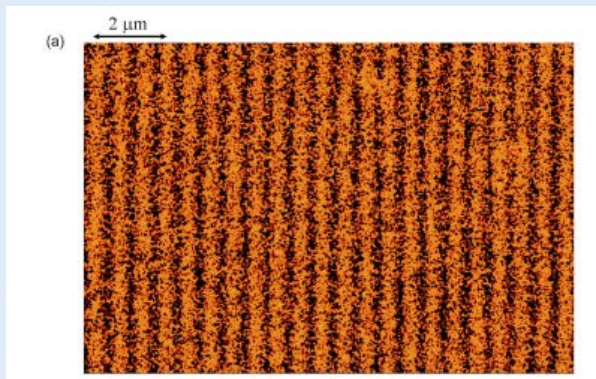
Laser cooling of noble gases
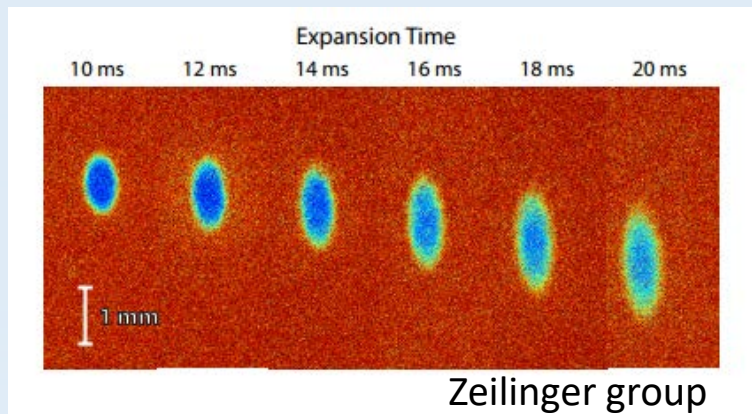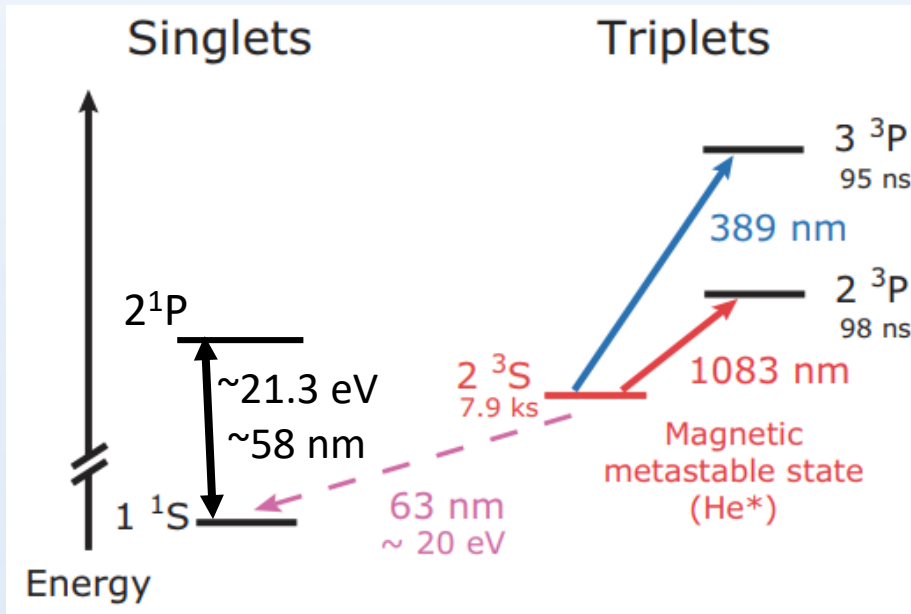
Also, laser-cooling and trapping of neon, argon, krypton, xenon

"Metastable helium: Atom optics with nano-grenades"

Singlets   Triplets

Energy

$3\ ^3P$ — 95 ns
389 nm
$2\ ^3P$ — 98 ns
1083 nm
$2\ ^3S$ — 7.9 ks
Magnetic metastable state (He*)
$1\ ^1S$
63 nm ~ 20 eV
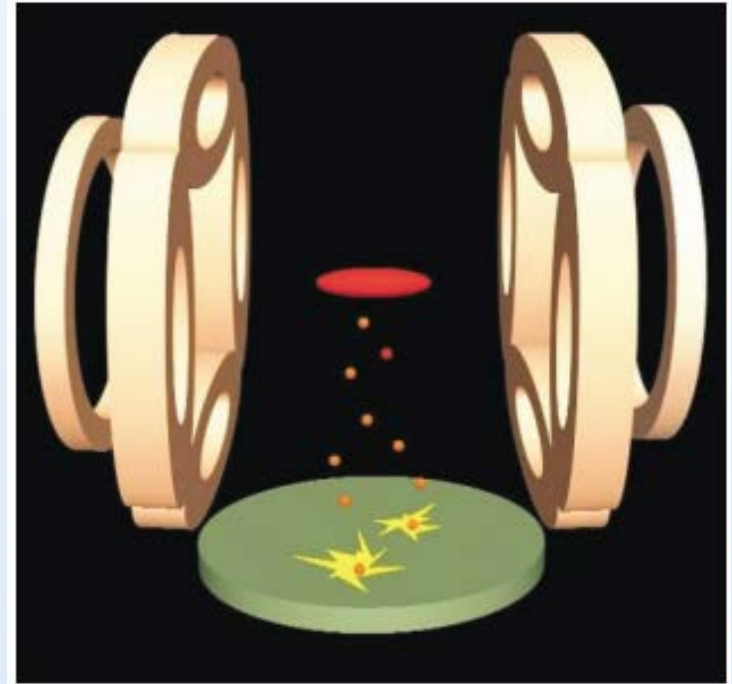
Lot's of internal energy left to "give up"

Olivier Sirjean, Orsay group
From Physics Today article 2001
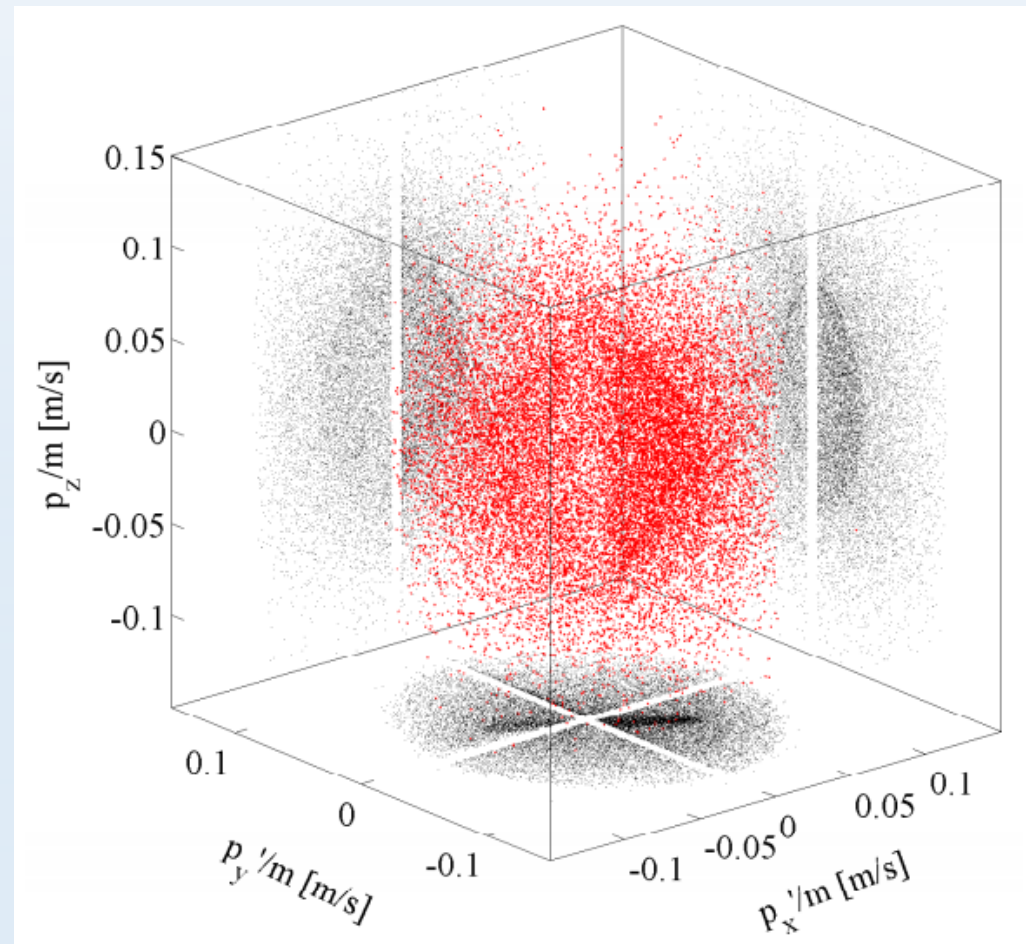

2 μm

Can kick out electrons / be used for lithography

← etched gratings in gold

"Metastable helium: Atom optics with nano-grenades"
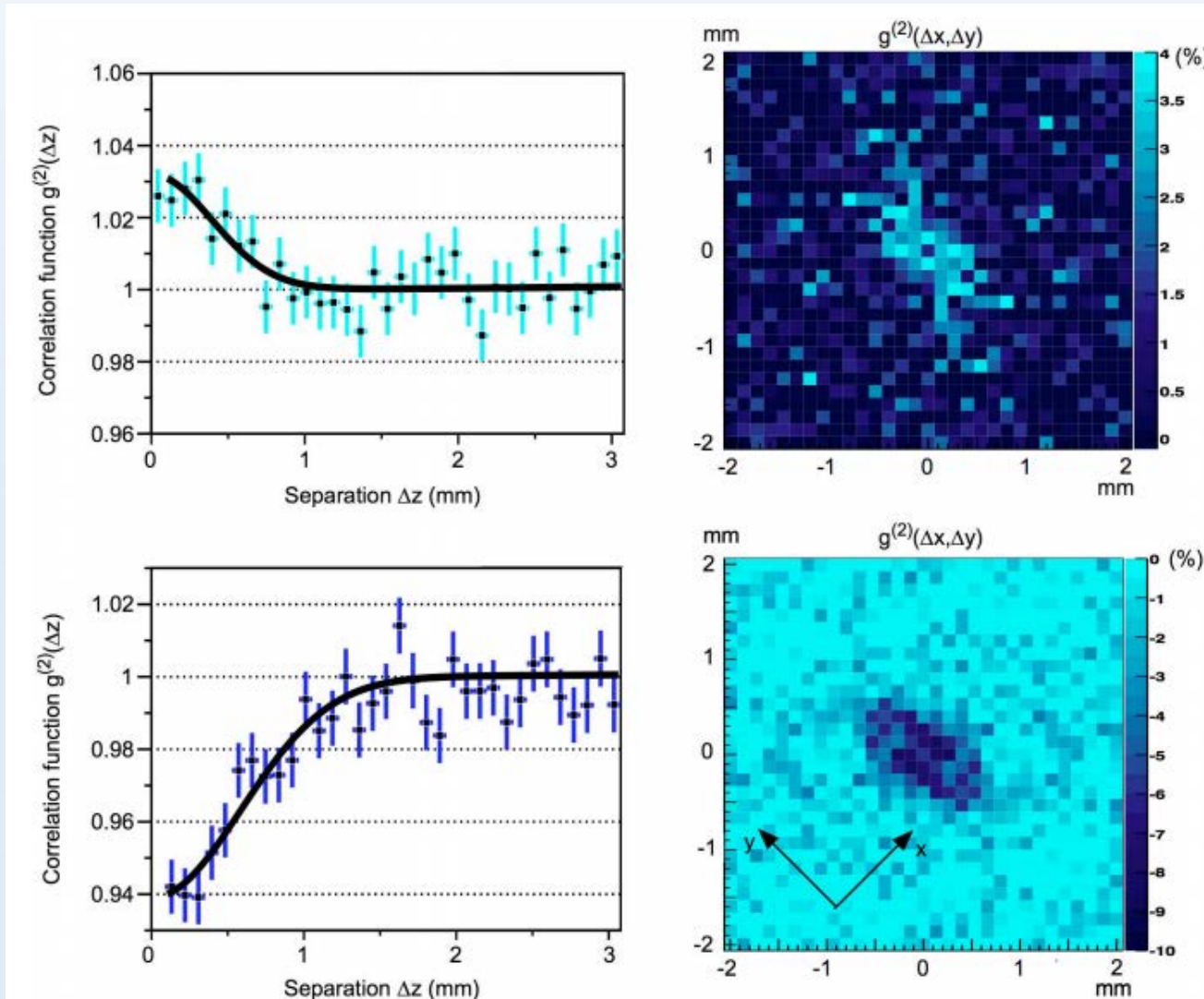
high-efficiency single atom detection
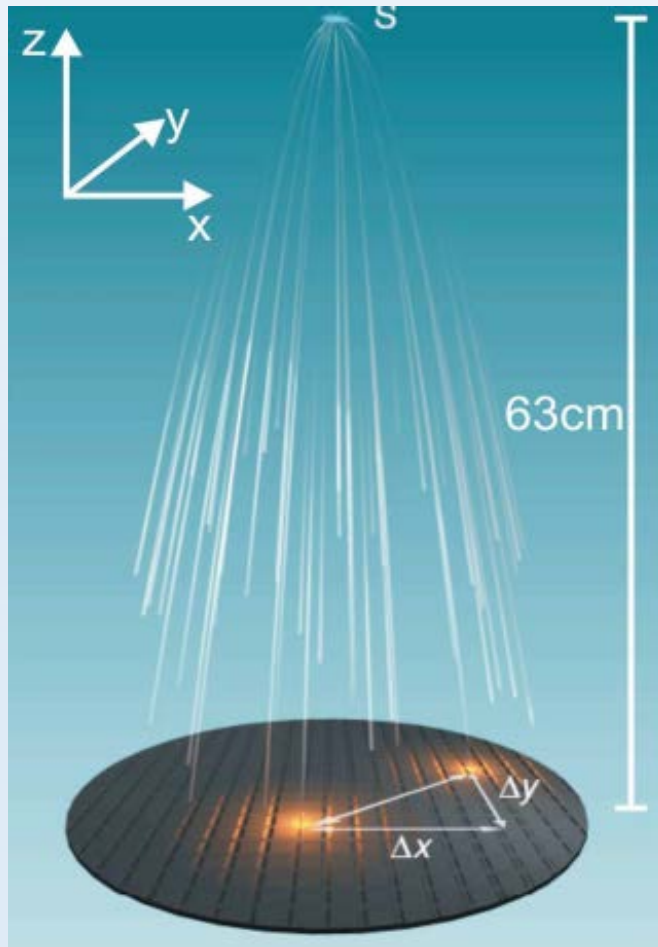
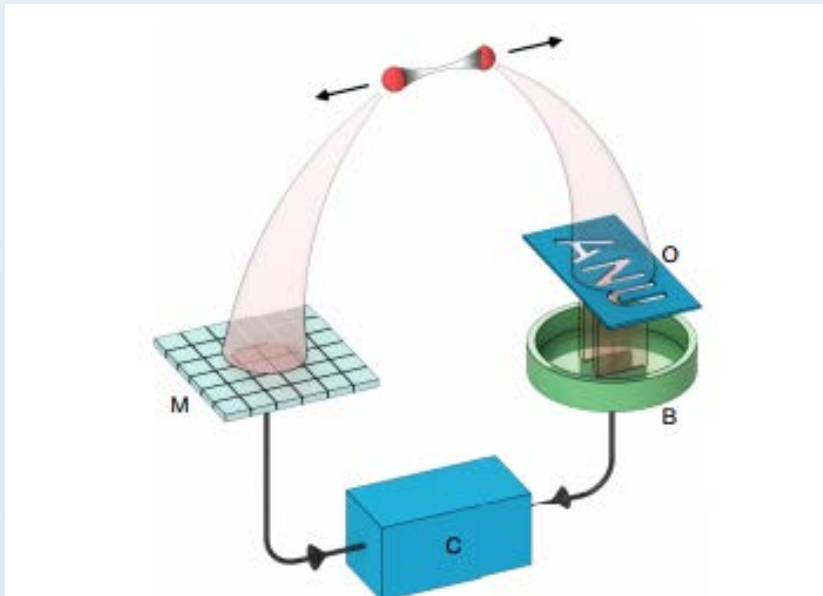
Palaiseau group

Vienna group

Bosons and fermions

Palaiseau group

Other cool stuff

ANU group