

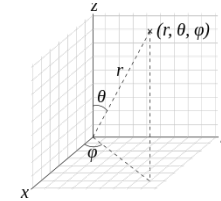
PC3130

Quantum Mechanics II

Hydrogen atom and
Wavefunctions

Eigenstate Wavefunctions of Hydrogen Atom

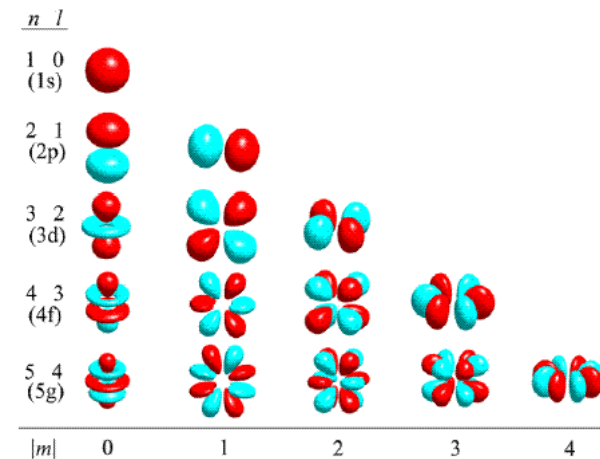
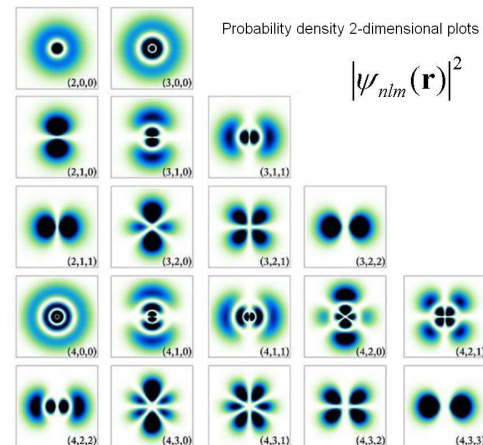
$$\psi_{nlm} = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} e^{-r/na_0} \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) Y_l^m(\theta, \phi).$$



$$n = 1, 2, 3, \dots; \quad l = 0, 1, 2, \dots (n-1); \quad m = -l, -l+1, \dots, 0, 1, 2, \dots, +l$$

$Y_l^m(\theta, \phi)$ are Spherical Harmonics

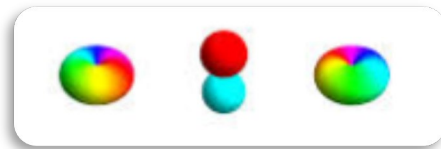
- Orbitals



Linear Combination of Orbitals

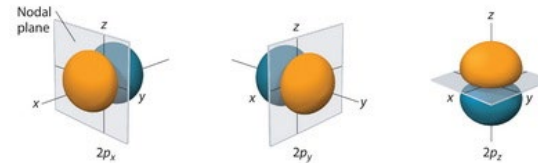
- 2p orbitals

$$\begin{aligned}
 \psi_{211} &= -\frac{1}{2}\sqrt{\frac{3}{2\pi}}R_{21}(r)\sin\theta e^{i\phi} & \phi_{2p_x} &= \frac{1}{\sqrt{2}}(\psi_{211} - \psi_{21-1}) = \sqrt{\frac{3}{4\pi}}R_{21}(r)\frac{x}{r} \\
 \psi_{210} &= \frac{1}{2}\sqrt{\frac{3}{\pi}}R_{21}(r)\cos\theta & \phi_{2p_y} &= \frac{i}{\sqrt{2}}(\psi_{211} + \psi_{21-1}) = \sqrt{\frac{3}{4\pi}}R_{21}(r)\frac{y}{r} \\
 \psi_{21-1} &= -\frac{1}{2}\sqrt{\frac{3}{2\pi}}R_{21}(r)\sin\theta e^{-i\phi} & \phi_{2p_z} &= -\frac{i}{\sqrt{2}}\psi_{210} = \sqrt{\frac{3}{4\pi}}R_{21}(r)\frac{z}{r}
 \end{aligned}$$



(Spherical Harmonics)

$$R_{21}(r) = \frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$$



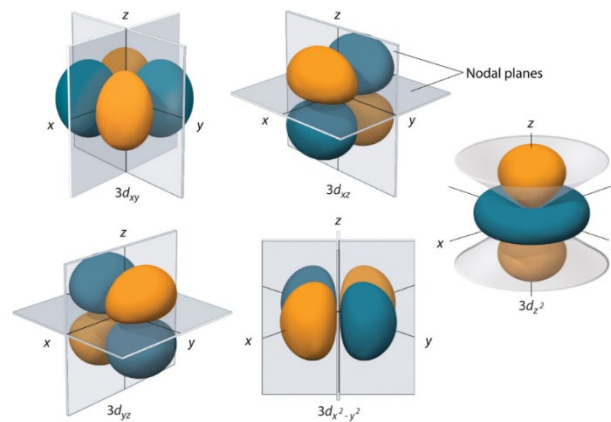
(Atomic Orbitals)

d atomic orbitals

Spherical
Harmonics



d atomic
orbitals



Linear
combination

n = 1: 1s

**n = 2: 2s, three 2p orbitals
(degeneracy of 4 = 1+3)**

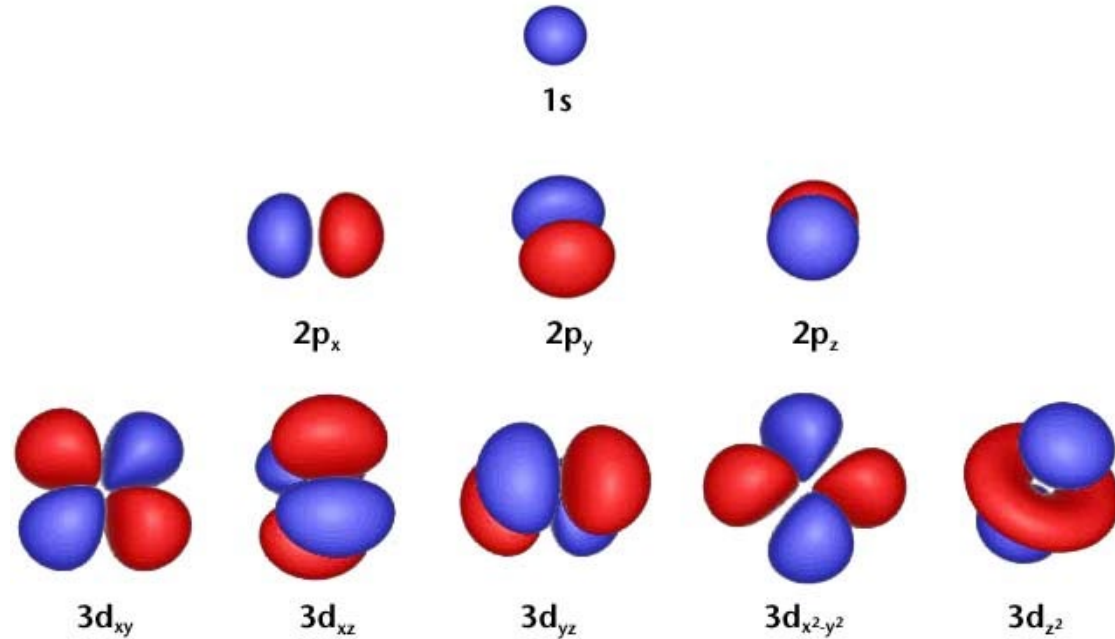
**n = 3: 3s, three 3p orbitals,
five 3d orbitals
(degeneracy of 9 = 1+3+5)**

l = 0: s orbitals (total: 2.0+1 = 1)

l = 1: p orbitals (total: 2.1+1 = 3)

l = 2: d orbitals (total: 2.2+1 = 5)

Atomic orbitals



Quantum numbers in Hydrogen atom
(there is one more quantum number later)

Quantum number (QN)	Name	Allowed values	Number of allowed states
n	Principal QN	$1, 2, 3, \dots$	No limit
l	Angular QN	$0, 1, 2, \dots, (n - 1)$	n
m	Magnetic (azimuthal) QN	$0, \pm 1, \pm 2, \dots, \pm l$	$2l + 1$

The values of n can range from 1 to ∞

For each given n , the values of l can range from 0 to $n - 1$

For each given l (and n), the values of m can range from $-l$ to l .

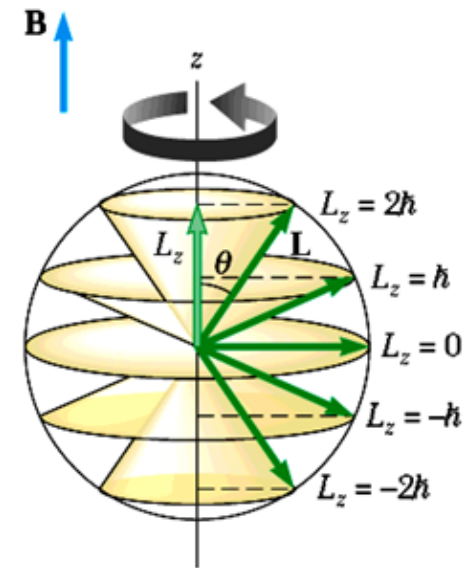
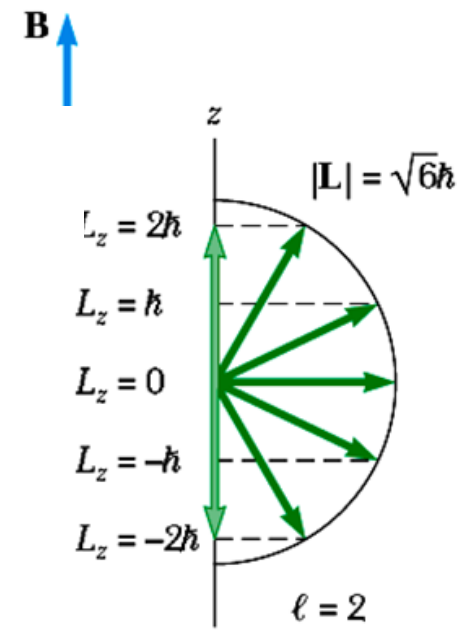
$$L = \sqrt{l(l+1)}\hbar$$

$$l = 0, 1, 2, \dots, n - 1$$

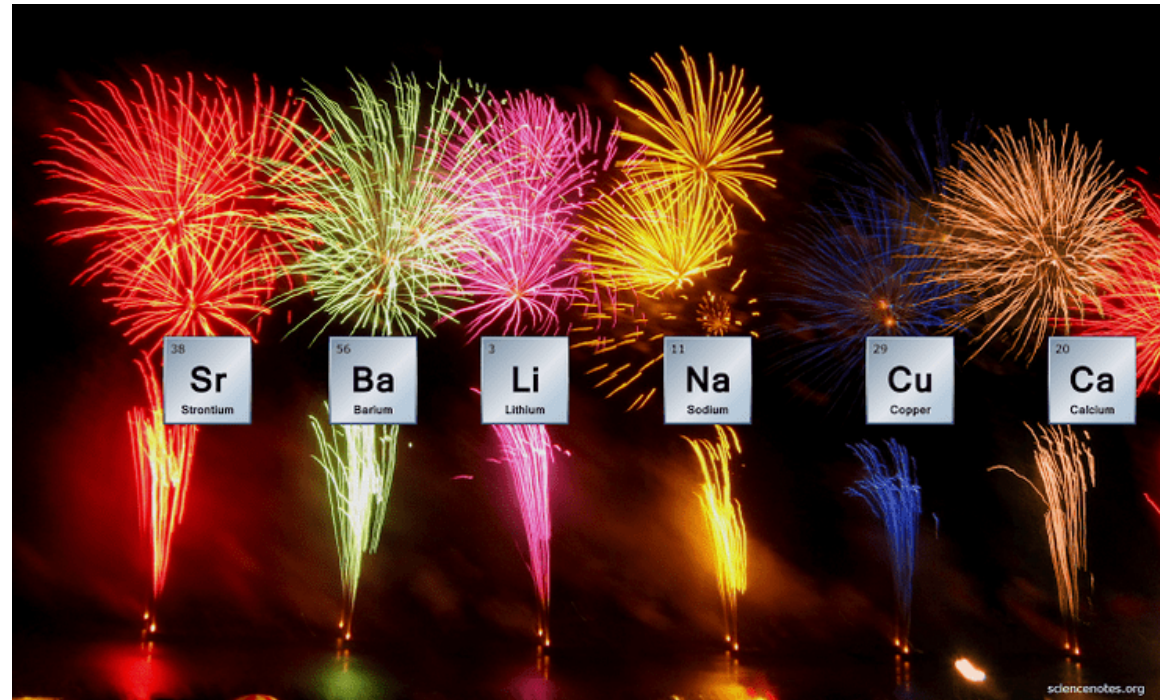
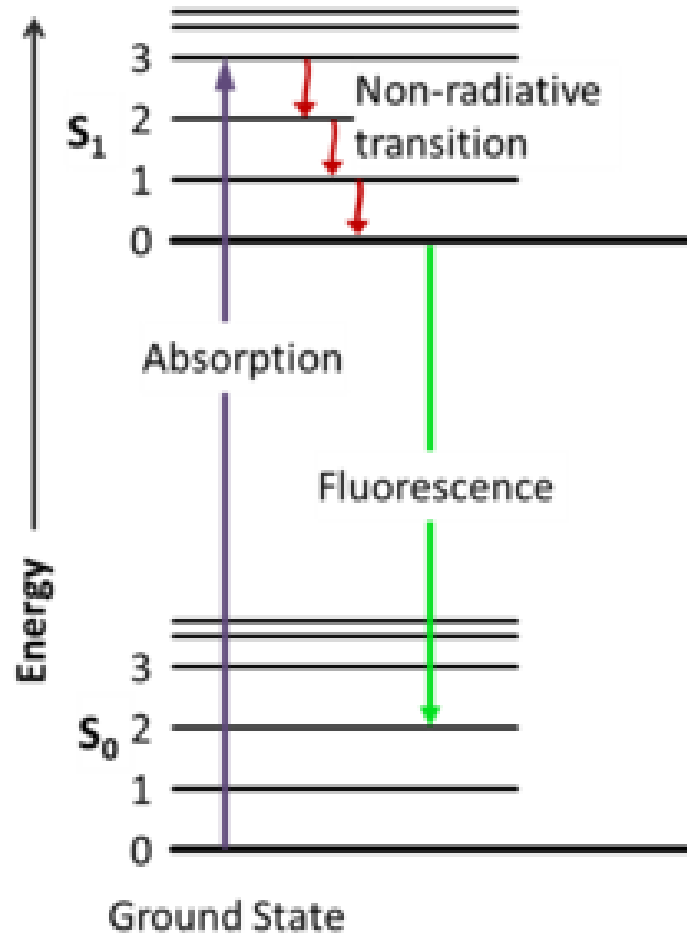
n is the **principal quantum number**.

$$L_z = m\hbar$$

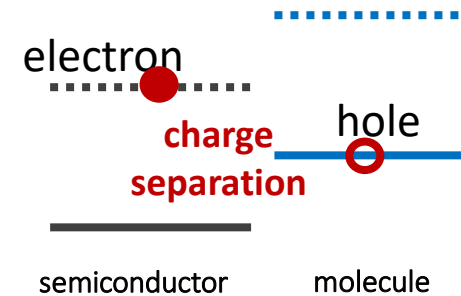
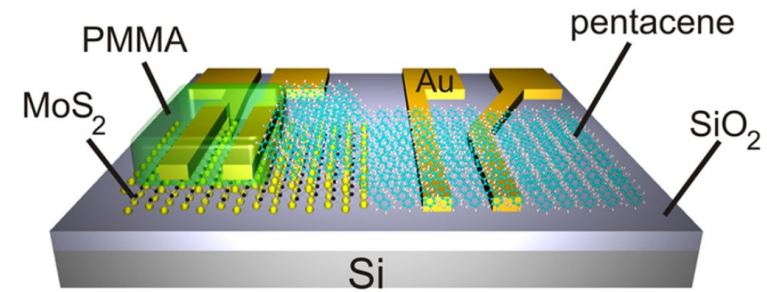
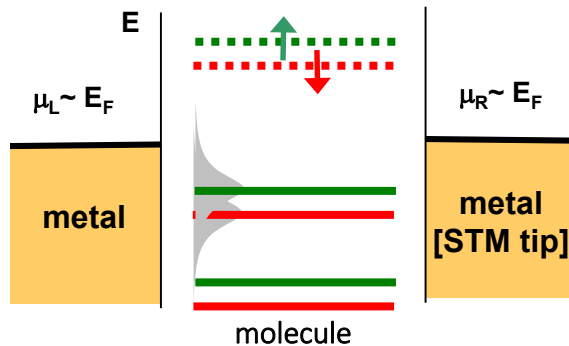
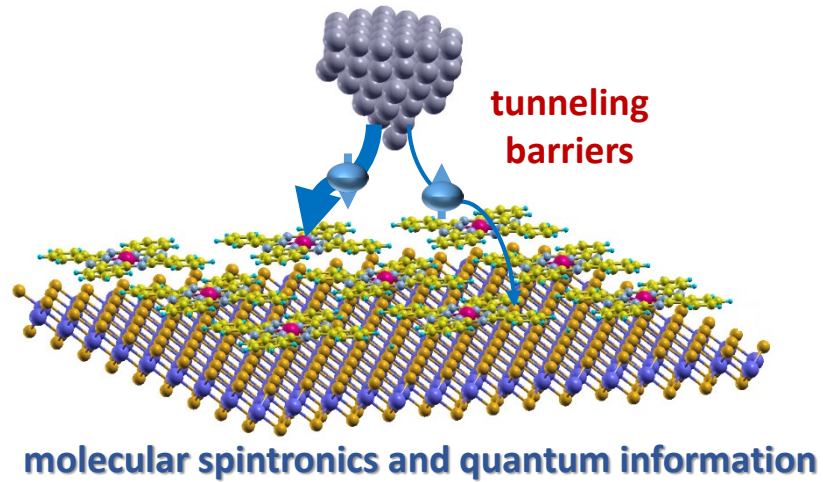
$$m = -l, -l + 1, \dots, -1, 0, 1, \dots, l - 1, l$$



Discrete Energy Levels and Fireworks



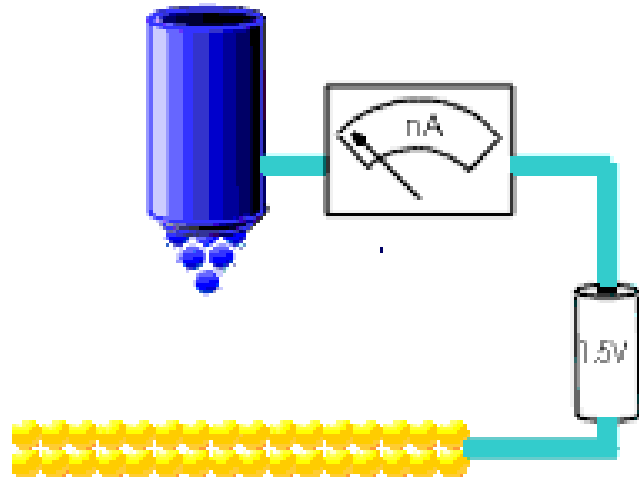
Importance of Energy Levels



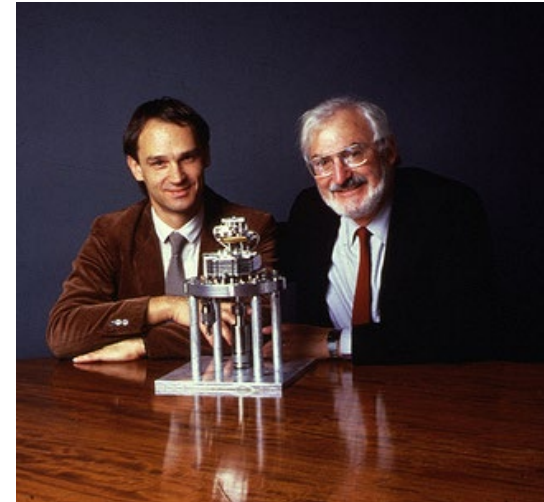
Experimental reconstruction of real-space wavefunctions

- $\psi(\mathbf{r}) = \langle \mathbf{r} | \psi \rangle$ can be reconstructed experimentally. Most commonly, $|\psi(\mathbf{r})|^2$ is visualized, most typically with scanning tunnelling microscopy. But phase information is lost in the measurement.
- Recent approaches have enabled the phase information to be deduced, and thus the real-space wavefunction can be reconstructed from experimental measurements.

Scanning Tunneling Microscope (STM)



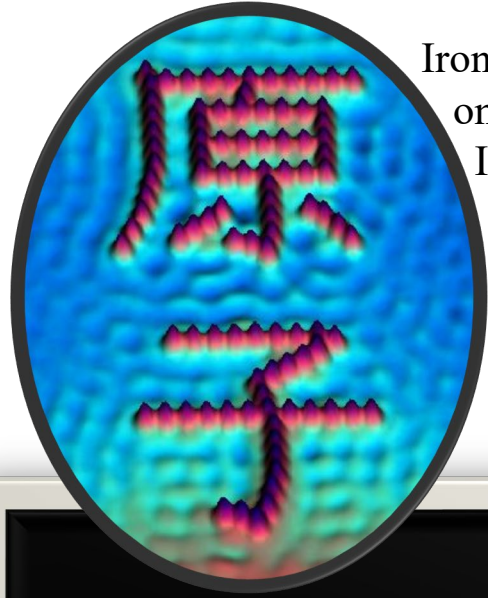
A man-made
application of
quantum tunnelling



Gerd Binnig and Heinrich Rohrer
(IBM Zürich)
Nobel Prize in Physics in 1986

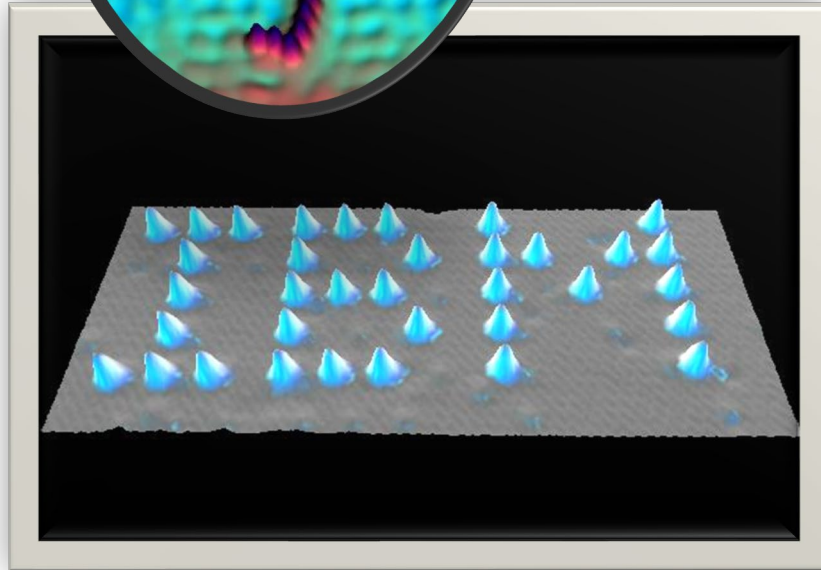
Scanning Tunneling Microscope Images

Visualization of
 $|\psi(\mathbf{r})|^2$

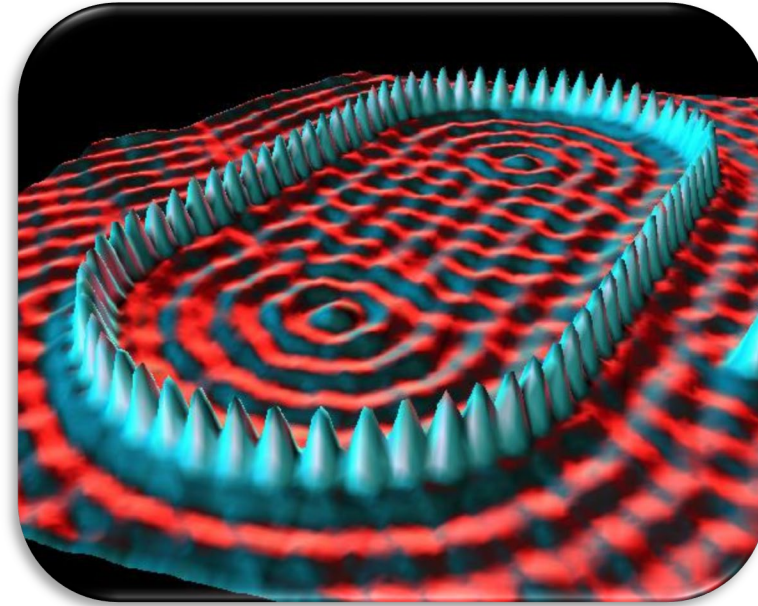


Iron atoms positioned
on copper (111) –
IBM

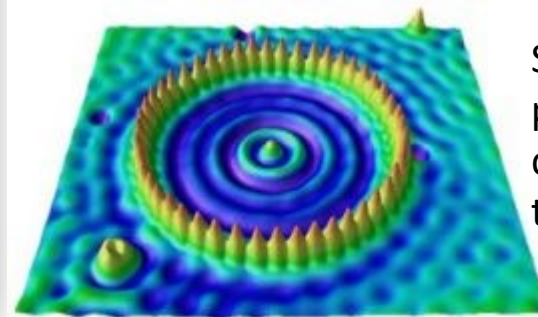
Iron atoms placed
using an STM on
copper (IBM)

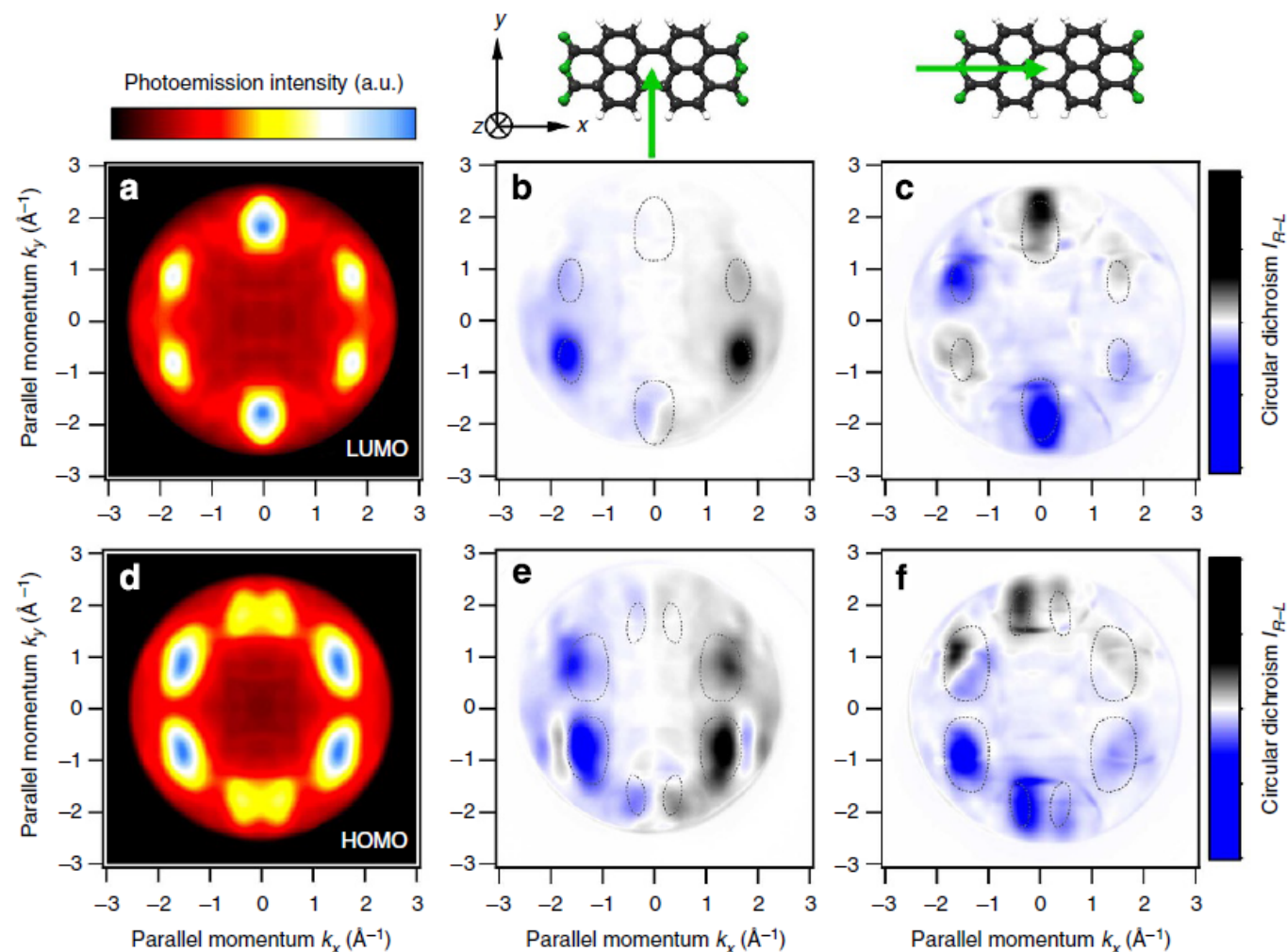


Zenon atoms positioned on Nickel written as 'IBM'



Standing-wave
patterns in the local
density of states of
the Cu(111) surface





Reconstruction of **phase information** of the wavefunction, using angle-resolved photoemission spectroscopy with circularly-polarized light (2014 paper).

Note: this is a challenging experiment. Theoretically, it is quite routine to predict the wave functions of these molecules. This is one example where theory can make predictions on properties that are difficult to measure.

Figure 2 | CDAD for the PTCDA LUMO and HOMO. (a) $k_{||}$ -dependent photoelectron intensity patterns of the PTCDA monolayer on Ag(110) recorded for the LUMO with a photon energy of $h\nu = 27$ eV as the sum of left- and right-handed polarized light, that is, equivalent to unpolarized light. (b) difference between the $k_{||}$ -dependent intensity patterns recorded with right- and left-circular polarized light, that is, the circular dichroism $I(k_x, k_y)_{R-L}$, for light incidence along the y direction and (c) for light incidence along the x direction. For both plots, dotted iso-intensity contours of **a** indicate the momentum positions of the molecular structures. (d-f) analogous data for the PTCDA HOMO. On top, the PTCDA molecule is sketched together with green arrows indicating the direction of the incoming light corresponding to the panels below.

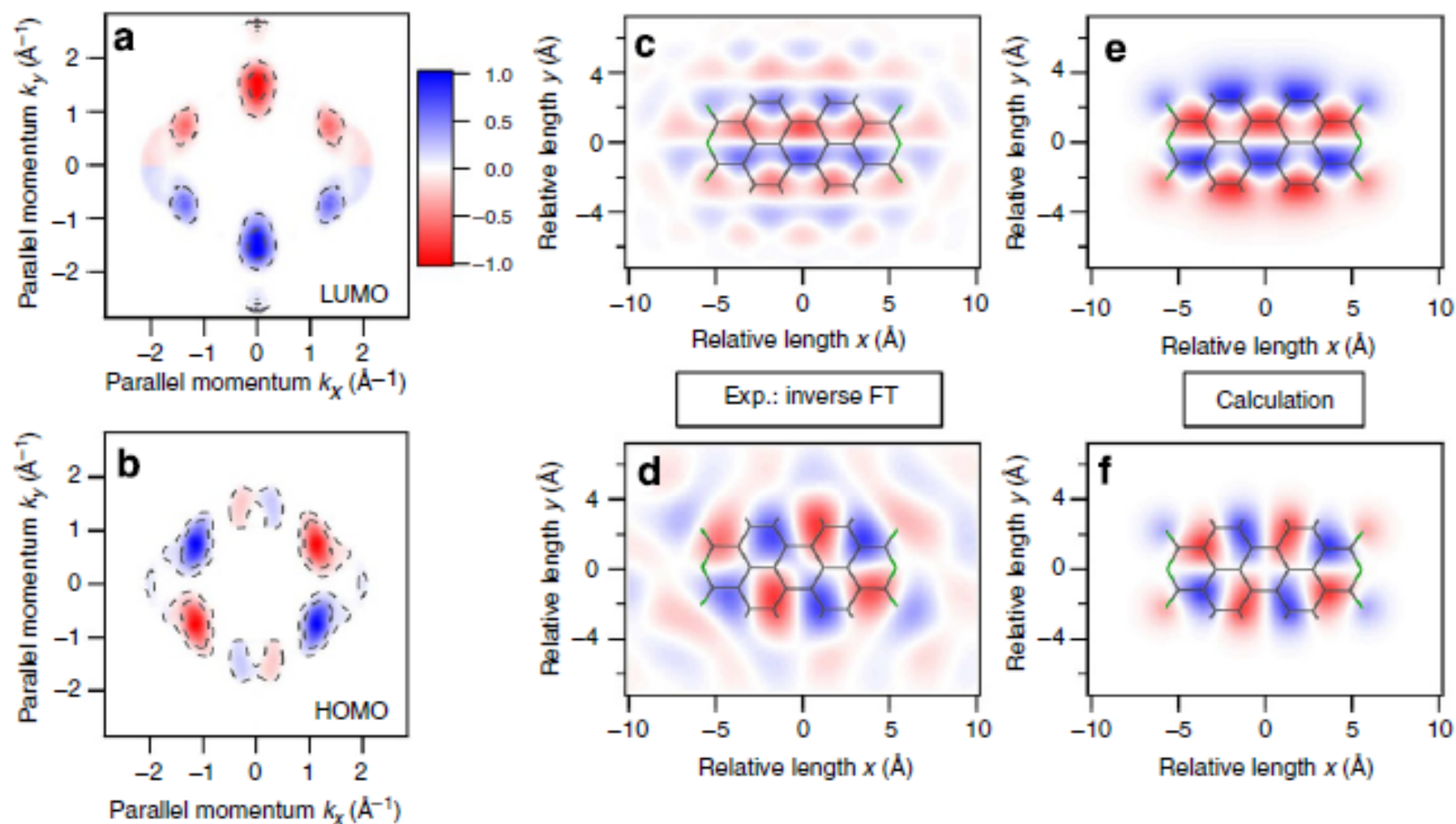


Figure 3 | Reconstruction of the phase distribution and transformation to real space. $k_{||}$ -dependent photoelectron intensity distributions ($h\nu = 55$ eV, sum of the left- and right-handed polarized light) of the PTCDA LUMO in **a** and HOMO in **b** with superimposed phase (positive: blue, negative: red) derived from the CDAD. The dashed lines indicate iso-intensity contours of the unpolarized signal. The inverse Fourier transformation leads to the sectional real space views of the real part of the LUMO shown in **c** and the HOMO in **d**. For illustration, the molecular structure of the PTCDA molecule is superimposed. For comparison, **(e)** and **(f)** show the respective real space orbital pictures derived from ab initio calculations for the isolated molecule.