

Preface to the Third Edition

More than ten years have passed since the publication of the second edition of *Introduction to Scanning Tunneling Microscopy* (STM). Significant advances in this research field have been made during that decade. One of the most important advances is the direct experimental observation of the wavefunctions of atoms and molecules (through field quantities representing local values of wavefunctions) down to picometer resolution with negligible disturbance. This advance was a result of two breakthroughs.

The first breakthrough came about 2005 when a group at IBM Zurich Laboratory discovered a method to image the wavefunctions of single atoms and organic molecules in pristine state using STM by separating the molecule and the metal substrate with an ultrathin film of insulator, typically NaCl [1, 2]. By using different biases, images of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are clearly observed, agreeing with the charge density contours of those wavefunctions calculated from first-principle quantum mechanical computations.

The second breakthrough took place around 2011, where the same group at IBM Zurich Laboratory imaged the organic molecules sitting on an insulating film using an STM tip functionalized with a CO molecule [3]. The STM images did not resemble the charge density contour at all, but rather the squares of the lateral derivatives of the molecular wavefunctions, which peak at the nodal structures of the molecular wavefunctions. For the first time in science history, the nodal structures inside molecular wavefunctions are directly observed and mapped in real space. That *Physics Review Letter* was reviewed by a Viewpoint article in *Physics* [4], entitled *Visualizing Quantum Mechanics*, which commented that the direct observation of the nodal structures inside molecular orbitals “will help future generations of chemists in obtaining an intuitive understanding of molecular properties that will guide them to novel solutions in all areas of chemistry.”

The direct observation of the wavefunctions and their derivatives touches a fundamental scientific question unresolved over almost one century: the interpretation of wavefunctions. In *A Brief History of Time* [5], Stephen Hawking said: “Quantum mechanics underlies all of modern science and technology. It governs the behavior of transistors and integrated circuits, and is the basis of modern chemistry and biology.” On the other hand, as Richard Feynman famously said, “If you think you understand quantum mechanics, you don’t understand quantum mechanics”—because the interpretation of its central subject, wavefunction, was highly controversial [6, 7]. The direct experimental observation of wavefunctions shows that they are observable physical reality, similar to Maxwell’s electromagnetic fields. This new edition features an added chapter on *Imaging Wavefunctions*, including a section *Meaning of Wavefunction Observation*.

During the writing of the new edition, an unavoidable difficulty was how to present the experimental observation of wavefunctions. According to the orthodox view of quantum mechanics, represented by the Copenhagen doctrine and the von Neumann axioms [7], wavefunction is not observable. Regarding this question, I communicated extensively with Franck Laloë, the author of *Do We Really understand Quantum Mechanics?* [8], and the coauthor of the well-known textbook *Quantum Mechanics* with Nobelist Claude Cohen-Tannoudji [9]. In the foreword of the 2019 edition of Laloë's book [8], Cohen-Tannoudji said that it “provides clear and objective presentation of the alternative formulations that have proposed to replace the traditional orthodoxy”. Accordingly, until about 1970 or 1980, most physicists took the Copenhagen interpretation as the orthodoxy. Nowadays, the attitude of physicists is more open concerning the matters [8]. Laloë recommended the three-volume masterpiece *Mécanique Quantique* [10] by Émile Durand, a graduate student of Louis de Broglie and a long-term dean of Toulouse University. Published in the 1970s, it started with a formulation that all wavefunctions are real, including Pauli and Dirac spinors [10]. By identifying real wavefunctions as the physical reality, the meaning of wavefunction observation becomes natural, as shown in Section 8.4.

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October 2019

Chapter 8

Imaging Wavefunctions

The concept of wavefunction was introduced in the first 1926 paper by Erwin Schrödinger entitled “*Quantisierung als Eigenwertproblem (erste Mitteilung)*” [11] as the central object of the atomic world and the cornerstone of quantum mechanics. It is a mathematical representation of de Broglie’s postulate that the electron is a material wave. In that historical paper, wavefunction $\psi(\mathbf{r})$ was defined as “everywhere real, single-valued, finite, and continuously differentiable up to the second order.” Schrödinger defined the quantity $-e|\psi(\mathbf{r})|^2$ as the charge density distribution of an electron extended in real space. The normalization condition

$$\int d^3\mathbf{r} |\psi(\mathbf{r})|^2 = 1 \quad (8.1)$$

is required because the total charge of an electron is always the elementary charge $-e$. The meaning of $-e|\psi(\mathbf{r})|^2$ as the charge density distribution of a single electron is the basis for quantum-mechanical treatments of many-electron atoms, molecules, and solid state. The wavefunction of a many-electron system is a Slater determinant of the wavefunctions of individual electron states. The wavefunction of each individual electron state, also known as an *orbital*, is the solution of the Schrödinger equation in a potential field formed by the nuclei and the electrical charge densities of all other electrons. It is the basis of the self-consistent field theory, including the Hartree method and the Hartree-Fock method, especially the DFT [12, 13]. It is documented in standard quantum mechanics textbooks [14, 15] as well as standard quantum chemistry textbooks [16, 17].

Nevertheless, for many decades since its introduction as a physical concept, wavefunction has not been characterized as an observable for legitimate reasons. First, it is too small. The typical size of a wavefunction is a fraction of a nanometer. Second, it is too fragile. The typical bonding energy of a wavefunction is a few electron volts. Using an optical microscope is out of the question: the wavelength of visible light is thousands of times greater than the size of a wavefunction. Heisenberg [18] suggested using a gamma ray microscope to observe electrons in a subatomic scale. However, the energy of such gamma ray photons is thousands of times greater than the bonding energy of the wavefunctions, which would severely disturb the electrons under observation. This was an argument for his uncertainty principle. An electron microscope has a much better resolution than an optical

microscope. However, to achieve spatial resolution smaller than a fraction of a nanometer, the energy of the electrons is still too high. According to de Broglie, the wavelength of an electron with energy E in eV is

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m_e E}} = \sqrt{\frac{1.504}{E}} \text{ nm.} \quad (8.2)$$

Table 8.1 shows some typical values of the wavelength λ of an electron. Therefore, wavefunction is not observable by an electron microscope.

The advancement of STM and AFM has made wavefunctions observable. First, the accuracy of position determination can be a fraction of a picometer. Second, both STM and AFM are nondestructive, which leaves the object of observation undisturbed. The importance of *nondisturbance* in quantum mechanical measurement process is discussed in Section 8.4.

The meaning of expression “imaging wavefunctions” needs to be clarified. To take advantage of the Euler formula $e^{ix} = \cos x + i \sin x$, many quantum mechanics textbooks define wavefunctions as complex. However, it contradicts the original definition of wavefunctions by Schrödinger, and it is often unnecessary. According to Wigner’s theorem, if the Hamiltonian is time-reversal invariant, all wavefunctions can be real, see Appendix B. For applications in STM and AFM, it is always fine to follow the original definition of Schrödinger that all wavefunctions of bound states are real. In most cases, the wavefunction has multiple lobes of opposite signs. By multiplying the wavefunction with -1 , it is still a good solution of the Schrödinger equation. Nevertheless, the signs of all lobes are reversed. The field quantities directly observed and mapped by STM and AFM are derived from the local values of wavefunctions, as shown by the following examples. First, the square of the wavefunction, which is proportional to the charge density distribution of the electron at that location, $\rho(\mathbf{r}) = -e|\psi(\mathbf{r})|^2$. Second, the square of the lateral derivatives of the wavefunction, as measured using a p -type tip wavefunction. Third, the absolute value of the wavefunction, as measured through the chemical-bond interaction energy between an s -type tip and the sample. Lastly, the absolute value of the lateral derivatives of the wavefunction by AFM using a p -type tip. If the wavefunctions are degenerate (in the tip or in the sample), then a linear superposition of the degenerate wavefunctions can change the observable quantity from an individual wavefunction. However, because the degenerate wavefunctions are orthogonal and normalized, the observable quantity arising from all de-

Table 8.1: Wavelength and electron energy

Energy (eV)	25	50	100	200
Wavelength (nm)	0.245	0.173	0.123	0.087

generate wavefunctions at the same energy level is invariant under a linear superposition, for example, due to a coordinate rotation. For all those cases, a field quantity representing the local values of wavefunctions is observed and mapped [3]. An umbrella term “imaging wavefunctions” is thus used. For more details, see Section 8.4.

8.1 Use of ultrathin insulating barriers

Atoms and molecules adsorbed on metal surfaces have been observed even in the early years of STM. However, in those early experiments, the wavefunctions of the adsorbed atoms and molecules are seriously perturbed by the metal substrate. The images are often interpreted as a disturbance of the LDOS of the metal surface at the Fermi level caused by the adsorbed atoms or molecules.

By placing an ultrathin insulating barrier between the atom or molecule under observation and the metal substrate, atoms and molecules, including the amplitudes and the derivatives of the wavefunctions, can be investigated in pristine condition. A well-verified system consists of two atomic layers of NaCl on a Cu(111) substrate [19, 20, 21]. The perturbations of the metal substrate to the wavefunctions become negligible.

The substrate with an ultrathin NaCl insulating film on Cu(111) is relatively easy to prepare and well studied. The underlying substrate, Cu(111) surface, can be prepared with repeated sputtering and annealing. NaCl is then evaporated thermally, with the sample temperature kept at about 320 K. NaCl forms (100)-terminated islands up to several microns in size, starting with a double layer [20]. Islands of three-layer film also exist, which can

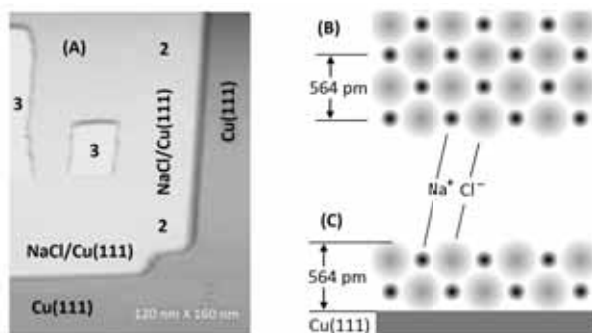


Fig. 8.1. Ultrathin insulating barrier for imaging wavefunctions. (A) An STM image of a NaCl film on Cu(111) substrate. (B) A schematic diagram of a top view, showing a (100) structure of NaCl on top of the Cu(111) surface. (C) A lateral view. The average thickness of the double NaCl film is about 564 pm. The interference to the atoms and molecules from the metal substrate is substantially reduced.

be identified by STM, see Fig. 8.1(A). The structure, with a lattice parameter of 0.564 nm, is shown in Fig. 8.1(B). The energy gap of NaCl is 8.5 eV, which has been shown to exist already for a bilayer [3]. It is equivalent to a vacuum gap of 0.564 nm, see Fig. 8.1(C). The work function of Cu(111) is 4.94 eV. The gap causes a decay constant

$$\kappa = 5.1 \times \sqrt{4.94} \approx 11.3 \text{ nm}^{-1}. \quad (8.3)$$

The reduction ratio for the tunneling current is

$$R = e^{-0.564 \times 11.3} \approx 1.7 \times 10^{-3}. \quad (8.4)$$

The tunneling current reduction can be compensated by increasing amplification, whereas the perturbation to the wavefunctions under observation is reduced by about three orders of magnitude.

8.2 Imaging wavefunctions with STM

8.2.1 Imaging atomic wavefunctions

One of the most well-known wavefunctions, described in all quantum mechanics textbooks, is the ground state of a hydrogen atom. It is

$$|1s\rangle = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}, \quad (8.5)$$

where

$$a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \approx 52.9 \text{ pm} \quad (8.6)$$

is the Bohr radius. The energy level is

$$E = -\frac{m_e e^4}{32\epsilon_0^2 \pi^2 \hbar^2} \approx -13.6 \text{ eV}. \quad (8.7)$$

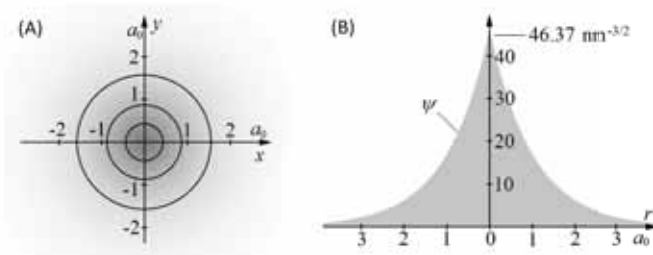


Fig. 8.2. Wavefunction of ground-state hydrogen atom. (A) Amplitude plot of the ground-state wavefunction of hydrogen. (B) The amplitude profile.

Table 8.2: Wavefunction radii and energy levels.

Atom	Configuration	Radius (pm)	Energy level (eV)
H	$1s$	53	-13.60
Li	$1s^2 2s$	167	-5.39
Na	$\dots 2s^2 2p^6 3s$	190	-5.14
K	$\dots 3s^2 3p^6 4s$	243	-4.34
Cu	$\dots 3p^6 3d^{10} 4s$	145	-7.72
Ag	$\dots 4p^6 4d^{10} 5s$	165	-7.57
Au	$\dots 5p^6 5d^{10} 6s$	174	-9.22

A density plot and an amplitude contour of the wavefunction of ground-state hydrogen atom are shown in Fig. 8.2. As shown, the equal-amplitude contours of the wavefunction are spheres. If it is possible to map the amplitude contours, the results should be spheres of different radii.

However, the size of the wavefunction of the ground-state hydrogen atom is very small, and the energy level is much too deep with respect to the work function of the metal substrate, typically 5 eV. Other atoms with a single outer electron are the alkali metals and noble metals. The size of the wavefunctions and the energy levels are shown in Table 8.2.

As shown, for alkali metal atoms (Li, Na, K), the energy level is very close to the Fermi level and roughly equals the work function of the metal substrate. Therefore, the wavefunction of those atoms tends to spread over to the surface. The three group-11 elements (Cu, Ag, Au), the so-called noble metals, have a single electron moving in the potential field of a spherical charge distribution formed by the nucleus and other electrons. The energy

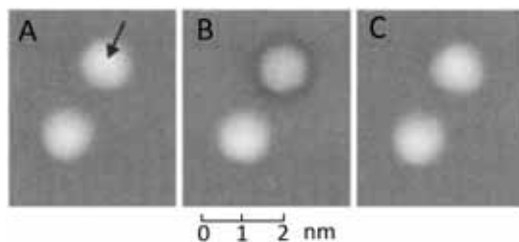


Fig. 8.3. STM images of Au atoms on NaCl film. The images of Au atoms on a NaCl insulating film appear as protrusions of apparent height of 0.20 nm to 0.25 nm, as part of a spherical electrical charge distribution. The charge state of the Au atom can be switched by applying electrical pulses. (A) By applying an electrical pulse of $V \geq 0.6$ V near the center of the Au atom, the charge state of the Au atom is apparently changed, as the diameter and height of the image is changed, see (B) By applying another electrical pulse of -1 V, the charge state of the Au atom is switched back, see (C).

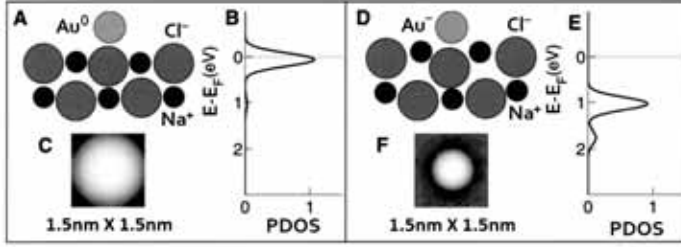


Fig. 8.4. Explanation of the charge-state switching of an Au atom. Calculated electronic and geometrical properties of the neutral (A and C) and negatively charged (D and F) Au atom. The geometry of the atomic arrangement and the energy levels are changed due to the state switching After Repp et al. [1].

levels are a few eV below the Fermi level. Those metal atoms are convenient for wavefunction observation and mapping.

Figure 8.3 shows examples of experimental observations of Au atoms on a NaCl insulating film. As expected, the images of the Au atoms appear as round-shaped protrusions of 0.20 to 0.25 nm, the top part of the contours of the spherical electrical charge distribution.

An interesting effect is, the charge state of the Au atoms can be switched using electrical pulses. As shown in Fig. 8.3(A), by applying a pulse of $V \geq 0.6$ V on top of an Au atom, the image is dramatically changed, see Fig. 8.3(B). By applying a pulse of higher voltage and opposite polarity, the state can be switched back, see Fig. 8.3(C).

Another interesting fact is, before and after state change, not only the shape of the image is changed, but also peak bias voltage to observe the images is changed. It is because the energy levels of different states are different, and the bias voltage realigns the energy levels. Figure 8.4 is an explanation of the process. The geometry of the atomic arrangement and the energy levels are changed due to the state switching.

8.2.2 Imaging molecular wavefunctions

The STM imaging of the wavefunctions of metal atoms on an insulating barrier showed definitively its observability, as its charge density distribution can be mapped in real space [1]. Much richer images can be observed on organic molecules on top of the ultrathin insulating films. With an s -wave tip state of a typical metallic apex atom, representing the square of wavefunctions at different energy levels [22]

$$I_s(x, y) \propto |\psi(x, y, z_0)|^2, \quad (8.8)$$

are mapped in real space [21, 23]. Not only are the structures of the wavefunctions more complex, for many organic molecules, but also both the

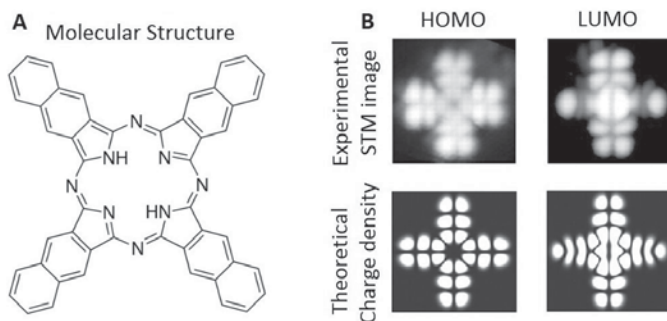


Fig. 8.5. Charge density and STM image of naphthalocynine. (A) The molecular structure of naphthalocynine. (B) The theoretical charge density distributions and STM images of naphthalocynine, for both HOMO and LUMO. The theoretical charge densities contours are computed using density-functional theory. The STM images closely resemble the theoretical charge density contours, represented by the square of the wavefunctions. [25].

HOMO (highest occupied molecular orbitals) and LUMO (lowest unoccupied molecular orbitals) states have energy levels within the reach of STM by using reasonable bias voltages. In 2005, the wavefunctions of both HOMO states and LUMO states of pentacene were observed by STM [21]. The images and the energy levels fit well with the wavefunctions and energy eigenvalues of the free molecules from first-principle numerical computations using DFT based on quantum mechanics [24], see plate 14. Figure 8.5 shows another example of imaging naphthalocynine molecule on a NaCl insulating film. (A) is the molecular structure. (B) shows the theoretical and experimental images. The HOMO state is observed with a bias of -1.75 V, and the LUMO state is observed with a bias of +0.6 V. The charge density contours, represented by the square of the wavefunctions, are computed using DFT methods. The STM images are shown to closely resemble the charge density contours, or the square of wavefunctions. Those STM images show clearly that the electron charge density distributions, or the square of the wavefunctions, are observable field quantities.

8.2.3 Imaging nodal structures

In 2011, using a tip functionalized by a CO-molecule to image organic molecules adsorbed on a NaCl thin film, completely different STM images were observed [3]. The process of controlled transfer of a CO atom between the STM tip and the sample was discovered in 1997 [26]. The physics of the process and the electronic states of the CO molecule is well understood [27], see Section ?? . The carbon atom is directly attached to the metal base. The oxygen atom has a pair of degenerate p_x and p_y states, that dominate the tunneling process. According to the derivative rule of tunnel-

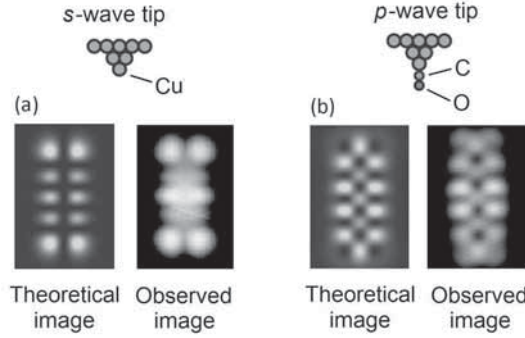


Fig. 8.6. STM images of HOMO wavefunctions of pentacene, *s*-wave-tip and *p*-wave-tip. (a) The theoretical and observed images of HOMO wavefunctions by an *s*-wave tip, from [21]. (b) The theoretical and observed images of HOMO wavefunctions by an *p*-wave tip, from [3].

ing theory [22, 28, 29], the tunneling matrix elements are proportional to the derivatives of the sample wavefunction ψ , which are

$$M_{p_x} \propto \frac{\partial \psi}{\partial x} \quad \text{and} \quad M_{p_y} \propto \frac{\partial \psi}{\partial y}, \quad (8.9)$$

respectively. The tunneling current $I_p(x, y)$ is proportional to the sum of the squared tunneling matrix elements. On a plane $z = z_0$, it is

$$I_p(x, y) \propto \left| \frac{\partial \psi(x, y, z_0)}{\partial x} \right|^2 + \left| \frac{\partial \psi(x, y, z_0)}{\partial y} \right|^2. \quad (8.10)$$

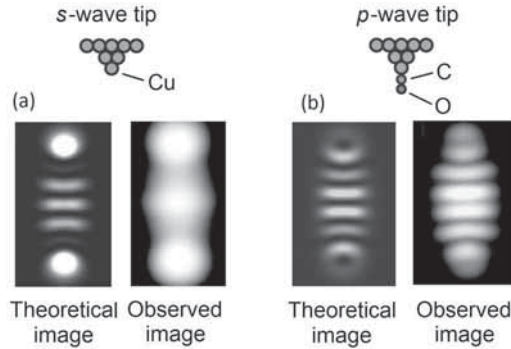


Fig. 8.7. STM images of LUMO wavefunctions of pentacene, *s*-wave tip and *p*-wave-tip. (a) The theoretical and observed images of LUMO wavefunctions by an *s*-wave tip, from [21]. (b) The theoretical and observed images of LUMO wavefunctions by an *p*-wave tip, from [3].

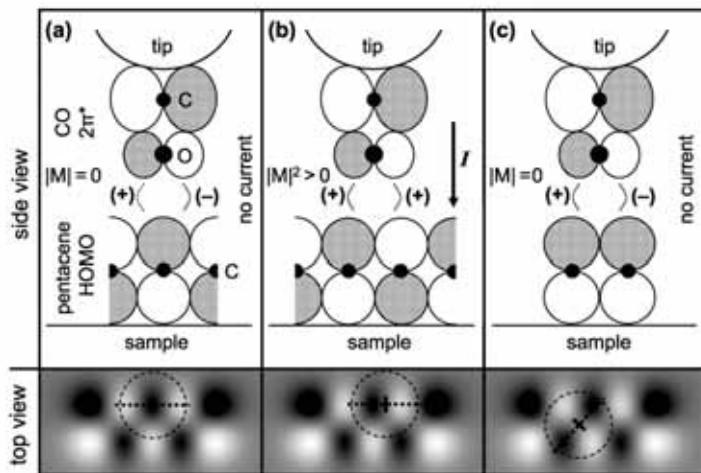


Fig. 8.8. Mechanism of STM imaging with a p -wave tip. (a) The tip wavefunction is dominated by the p_x and p_y orbitals of the O atom. At the center of a lobe of the sample wavefunction, the contributions to the tunneling current from the two lobes of the p -orbital cancel each other. The net tunneling amplitude is zero. (b) At a nodal plane of the sample wavefunction, the contributions from the two lobes of the p -orbital of the tip wavefunction are additive, and the tunneling amplitude reaches maximum. (c) At a site of four-fold asymmetry, the contributions of different lobes of the p -orbital of the tip again cancels each other.

The predicted and observed images from such a p -type tip for the HOMO wavefunction of pentacene are shown in Figure 8.6(b). Those for the LUMO wavefunction are in Figure 8.7(b). Those images resemble the squares of the *lateral derivatives of wavefunctions*.

A combination of images with an s -type tip and a p -type tip enables the experimental determination of complete wavefunctions up to a global sign. Typically, in many places where the tunneling current from a metal tip $I_s(x, y)$ (see Eq. 8.8) vanishes, the current from a p -type tip $I_p(x, y)$ (see Eq. 8.10) is at its maximum. As a consequence of Schrödinger's equation, the derivatives of the wavefunction should be continuous. A sign change in the wavefunction is observed. Consequently, *the phase contrast of different lobes of wavefunctions is observable*. Therefore, the entire wavefunction can be mapped experimentally up to a global sign.

Figure 8.8 is an intuitive explanation of the observed contrast. The CO molecule has two degenerate π_x and π_y orbitals near the Fermi level, that dominate the tunneling current. As shown in Fig. 8.8(a), on the O atom of the tip, the wavefunctions are basically a p_x and a p_y atomic orbitals, each has two lobes. Here the polarity (positive or negative) of the lobes are marked by grey or white. If the tip is located on top of the center of a lobe of the sample wavefunction, the tunneling current from the positive lobe and

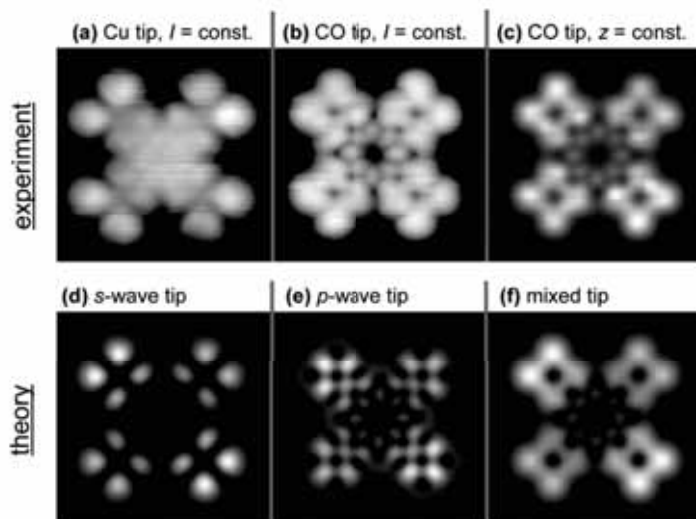


Fig. 8.9. Imaging naphthalocynine with a Cu tip and a CO tip. (a) The topographical image of naphthalocynine HOMO wavefunction using a Cu tip. The gross features are resolved. (b) and (c) Images of the same, using a CO tip. The fine features of the eight-fold patterns are clearly resolved. (d) Theoretical images of the square of the HOMO wavefunction, showing similar features as (a). (e) and (f) Theoretical images of the square of lateral derivatives of the HOMO wavefunction of naphthalocynine, showing great details of the eight-fold features. The theoretical image based on a mixture *s*-state and *p*-state in (f) fits perfectly with the observed image.

the negative lobe of the *p*-orbital cancel each other. The tunneling matrix element $|M|$ is zero. In Fig. 8.8(b), the tip axis is located at a nodal plane of the molecular orbital. The tunneling amplitudes from the two lobes of the *p*-orbital of the O atom to the two sides of the sample orbital have the same sign, thus are added together, similar to a constructive interference. The tunneling conductance reaches a maximum. Figure 8.8(c) shows a third case. At a sample site of a four-fold symmetry, the tunneling conductance from different lobes of the *p*-orbital again cancel each other, and shows a zero tunneling current.

Figures 8.9 and 8.10 show the images of another molecule, naphthalocynine, with more details on the effects of the combinations of different tip wavefunctions. Figure 8.9 shows the theoretical results and the observed images of the HOMO wavefunction of naphthalocynine with a Cu tip and a CO tip. As shown in (b) and (c), by using a CO tip, many more details of the wavefunction are resolved than the images with a Cu tip, as shown in Fig. 8.9(c). Furthermore, the theoretical image based on a mixture of *s*-tip wavefunction and *p*-tip wavefunction fits accurately to the observed image with a CO tip. It indicates that the actual tip wavefunction is a mixture *s*-tip wavefunction and *p*-tip wavefunction.

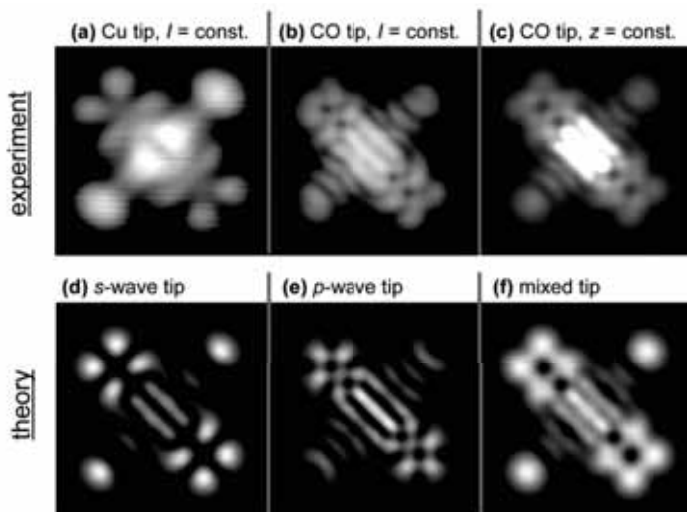


Fig. 8.10. Imaging naphthalocynine with a Cu tip and a CO tip. (a) The topographical image of naphthalocynine LUMO wavefunction using a Cu tip. The gross features are resolved. (b) and (c) Images of the same, using a CO tip. The fine features of the eight-fold patterns are clearly resolved. (d) Theoretical images of the square of the LUMO wavefunction, showing similar features as (a). (e) and (f) Theoretical images of the square of lateral derivatives of the HOMO wavefunction of naphthalocynine, showing great details of the eight-fold features. The theoretical image based on a mixture *s*-tip wavefunction and *p*-tip wavefunction in (f) fits perfectly with the observed image.

In Fig. 8.10, images of the LUMO wavefunction of naphthalocynine are presented. The images with a CO tip, Fig. 8.10(b) and (c), show more details of the internal structure of the LUMO wavefunction than with a Cu tip, Fig. 8.10(a). Again, the theoretical images based on a mixture of *s*-tip wavefunction and *p*-tip wavefunction makes a perfect match to the experimental images using a CO tip.

The interpretation of the STM images with a CO-functionalized tip as associated with lateral derivatives of sample wavefunctions has been extended and verified by further experiments. For example, in 2015, Corso et al. reported the observation of enhanced resolution of internal structures of acetylene by a CO-functionalized tip [30]. In 2018, Shiotari et al. reported the observation of lateral derivatives of molecules with a NO-functionalized tip, which also has $2p\pi^*$ states at the apex [31].

8.3 Imaging wavefunctions with AFM

As discussed in Chapter 4, the chemical bond energy can be represented by the Bardeen tunneling matrix elements. Therefore, the main component of

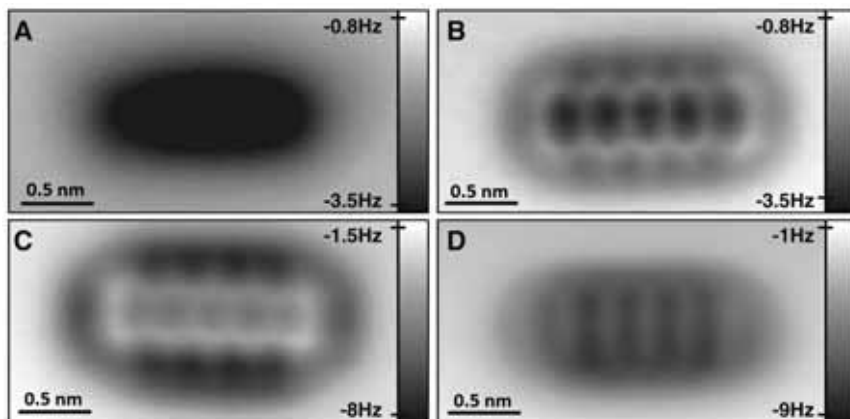


Fig. 8.11. AFM images of a pentacene molecule with different tips. The nature of the AFM image depends drastically on the tip. (A) Ag tip. (B) CO tip. (C) Cl tip. (D) Pentacene tip. See Gross et al. [32].

the attractive atomic force, the chemical bond energy, is capable of imaging the sample wavefunction. A straightforward inference from the STM imaging of wavefunctions in the previous sections is that the observed AFM images should dramatically depend on the atomic structure of the tip. A properly functionalized tip could improve the resolution.

One complication of AFM compared to STM is, the Pauli repulsive force is an unavoidable component. The repulsion between atomic cores would eventually appear at shorter tip-sample distances. In 2009, both the effects of tip functionalization and the Pauli repulsive force were observed with pentacene molecules on a Cu(111) substrate buffered by two atomic layers of NaCl, see Gross et al. [32].

Figure 8.11 shows four AFM images of a pentacene molecule with different tips. (A) is from an Ag tip. As shown, only a single broad peak is observed. (B) is from a CO tip. A lot of details, including the atomic skeleton, are apparent. (C) is from a Cl tip. The resolution is much higher than the Ag tip, but the image is somewhat different from that with a CO tip. (D) is from a pentacene tip. The image is very different from that with a CO tip. Apparently, using different tips, different features related to the molecular wavefunction are imaged.

Furthermore, by measuring the AFM frequency shift (Δf) versus voltage dependence to obtain the local contact potential difference (LCPD) at each point in the space, three-dimensional images of the charge distribution within a single molecule are obtained [33]. The experiment was done on naphthalocyanine on a Cu(111) substrate, with a two atomic buffer layer of NaCl, similar to the conditions in Sections 8.2.2 and 8.2.3. A plot of the three-dimensional electrical charge density inside the molecule is shown

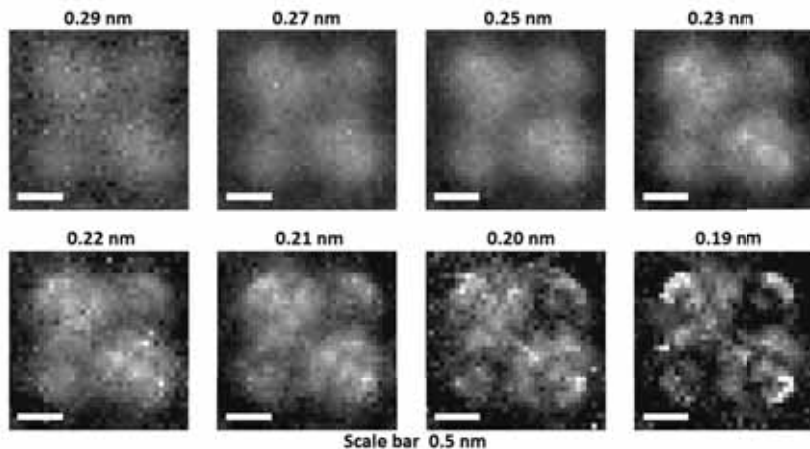


Fig. 8.12. Three-dimensional electrical charge map inside a molecule. The vertical height in nm on each cross-sectional plot is in reference to the STM set point. The scale bar in each graph is 0.5 nm. See Mohn et al. [33].

in Fig. 8.12. The vertical height in nm on each cross-sectional plot is in reference to the STM set point ($I = 2$ pa, $V = 0.2$ V). The scale bar in each graph is 0.5 nm. As shown, the closer the tip is to the molecule base plane, the more details of the charge distribution discovered. Therefore, the three-dimensional electrical charge distribution of the electron, or the square of the wavefunction, can be measured and mapped in real space without significant disturbance to the system under observation.

8.4 Meaning of wavefunction observation

The concept of wavefunction was introduced in the first 1926 paper by Schrödinger [11] as the mathematical representation of de Broglie's material wave of an electron, which is "everywhere real, single-valued, finite, and continuously differentiable up to the second order." Schrödinger defined the quantity $-e|\psi(\mathbf{r})|^2$ as the charge density distribution of an electron. It is the basis for quantum-mechanical treatments of many-electron atoms, molecules, and solid states [12, 13, 14, 15, 16, 17].

The experimental observation and mapping of wavefunction through local field quantities by STM and AFM, including the square of wavefunction and the square of the lateral derivative as well as their absolute values, implied that the wavefunction is a physical field. Schrödinger's original interpretation is confirmed. The statistical interpretation of the wavefunction, although valid and indispensable, has to be properly defined.

8.4.1 Interpretations of wavefunctions

Many quantum mechanics textbooks [34, 35, 36] present the following interpretation of wavefunction. Wavefunction as one of the representations of an abstract state is not observable. Its absolute square $|\psi(\mathbf{r})|^2$ as a real function in space is also not observable. As a material point, the position of an electron in real space is an observable. Each time a measurement of the position of an electron is conducted, values of its coordinates are returned. In general, the result of each position measurement is different. The only meaning of the wavefunction is: the probability of finding an electron in an elementary volume $d^3\mathbf{r}$ around $\mathbf{r}$ is

$$P(\mathbf{r}) d^3\mathbf{r} = |\psi(\mathbf{r})|^2 d^3\mathbf{r}. \quad (8.11)$$

Some textbooks [34, 35] further state that after a position measurement, the wavefunction collapses to a position eigenstate as a delta function $\psi(\mathbf{r}) \Rightarrow \delta(\mathbf{r} - \mathbf{r}_0)$, where $\mathbf{r}_0$ is the result of measurement.

Max Born was awarded a Nobel prize in physics in 1954 for his statistical interpretation of the wavefunction. Nevertheless, according to his Nobel Lecture, his statistical interpretation has a well-defined meaning. He did not mention anything related to wavefunction collapse [37]:

Wave mechanics enjoyed a very great deal more popularity than the Göttingen or Cambridge version of quantum mechanics. It operates with a wave function ψ , which in the case of one particle at least, can be pictured in space, and it uses the mathematical methods of partial differential equations which are in current use by physicists. Schrödinger thought that his wave theory made it possible to return to deterministic classical physics. He proposed (and he has recently emphasized his proposal anew), to dispense with the particle representation entirely, and instead of speaking of electrons as particles, to consider them as a continuous density distribution $|\psi|^2$ (or electric density $-e|\psi|^2$).

To us in Göttingen this interpretation seemed unacceptable in face of well established experimental facts. At that time it was already possible to count particles by means of scintillations or with a Geiger counter, and to photograph their tracks with the aid of a Wilson cloud chamber.

Born referred to the matrix mechanics of Heisenberg as the Göttingen version and the q -number formulation of Dirac as the Cambridge version of quantum mechanics. According to Born, Schrödinger's version is *a great deal more popular* because of its intuitiveness and easier mathematics.

According to Born, Schrödinger insisted that the electron is an extended physical field. And the quantity $-e|\psi|^2$ represents the charge density distribution of the electron as a continuous field. In other words, Schrödinger

disagreed with the view that the electron can be represented by a geometrical point of ultimate sharpness and arbitrary precision.

Later developments favored Schrödinger's definition of electron charge density distribution. It is the basis of the DFT, now a standard method for computational quantum mechanics [12, 13]. Accordingly, the total electron density in a many-electron system is the sum of the density distributions of individual electron wavefunctions,

$$n(\mathbf{r}) = \sum_{j=1}^N |\psi_j(\mathbf{r})|^2. \quad (8.12)$$

8.4.2 Wavefunction as a physical field

The experiments described in this Chapter indicate that the wavefunction is a physical field. Especially, $-e|\psi(\mathbf{r})|^2$ is a charge density distribution. The nature of wavefunction is similar to the Maxwellian electromagnetic fields, enabling a realistic interpretation of quantum mechanics.

In an article for the centenary of Maxwell's birth, *Maxwell's Influence on the Development of the Conception of Physical Reality*, Einstein wrote [38]:

Before Maxwell, people thought of physical reality—in so far represented events in nature—as material points, whose changes consist only in motions which are subject to total differential equations. After Maxwell, they thought of physical reality as represented by continuous fields, not mechanically explicable and subject to partial differential equations. This change in the conception of reality is the most profound and the most fruitful that physics has experienced since Newton.

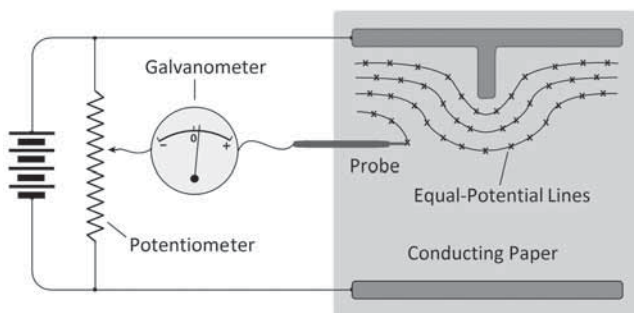


Fig. 8.13. Observing and mapping electrical fields. Using an electrical probe, the electrical field can be observed and mapped. Note the similarity to the STM mapping of wavefunctions by using another wavefunction as the probe.

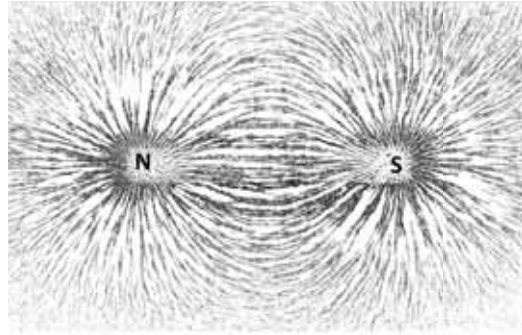


Fig. 8.14. Observing and mapping magnetic fields. Using iron filings, the magnetic field can be observed and mapped. Note the similarity to the STM mapping of wavefunctions by using another wavefunction as the probe.

For centuries after Newton, the forces between material points, including gravitational and electrical, were considered as acting over a distance. Maxwell introduced electromagnetic fields that exist outside the material points, governed by partial differential equations. The electromagnetic fields can be observed independently of the particles, and have energy density in the space; for example, the black-body energy of standing electromagnetic waves in a cavity, and the mass and momentum of gamma ray.

Figure 8.13 shows an apparatus for observing and mapping the electrical field. Note that the probe for observing and mapping is an electrical device, which is also governed by the same Maxwell equations.

Figure 8.14 shows an experiment for observing and mapping the magnetic field. Also note that the probes, iron filings, are magnetic devices, and the mapping process is governed by the same Maxwell's equations.

The observation and mapping of the wavefunctions by STM and AFM is similar to the observation and mapping of Maxwell's electromagnetic fields. In the same article about Maxwell's fields, Einstein made a criticism about the probabilistic interpretation of quantum mechanics [38]:

Nevertheless, I am inclined to think that physicists will not be satisfied in the long run with this kind of indirect description of reality, even if an adaptation of the theory to the demand of general relativity can be achieved in a satisfactory way. Then they must surely be brought back to the attempt to realize the program which may suitably be designated as Maxwellian: a description of physical reality in terms of fields which satisfy partial differential equations in a way that is free from singularities.

Einstein's prophecy may have been realized as the wavefunction becomes an observable physical reality because of STM and AFM.

8.4.3 Born's statistical interpretation

Although the experimental observations of wavefunctions showed the similarity of the wavefunction to the electrical field and magnetic field, as soon as quantization is brought up, including energy, charge, and mass, Born's statistical interpretation is valid and indispensable.

The statistical interpretation is necessary even for electromagnetic waves. Take an example of the double-slit experiment, see Fig. 8.15. A number of single-photon detectors of width δ are on the detector side, D. Each detector is made of thousands of atoms and has many energy levels. An electromagnetic wave with circular frequency ω causes a transition between two quantum states with energy difference $\hbar\omega$ of a detector. The transition rate is proportional to the square of the field intensity at the location of that detector. Therefore, the probability of photon detection is proportional to the square of the field intensity at the location of a detector. In certain sense, this is Einstein's statistical interpretation of electromagnetic waves. Note that in the entire space between the light source and the detectors, the only valid description of light is an electromagnetic wave. There is no point-like photons moving around. Energy is quantized only when light is produced or converted into other forms.

Born was the first scientist to publish a paper about the relation of the probability of particle detection with the wavefunction in 1926 [39]. As Born stated in his Nobel Lecture [37], his inspiration of statistical interpretation came from Einstein's idea that the probability density of the occurrence of light quanta is proportional to the square of field intensities. Born said, "This concept could at once be carried over to the ψ -function: $|\psi|^2$ ought to

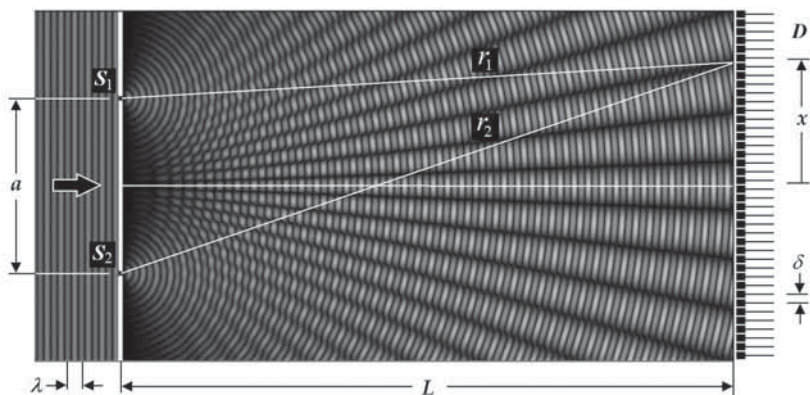


Fig. 8.15. Double-slit experiment with single-photon detectors. A plane wave of wavelength λ falls on a screen with two slits S_1 and S_2 of distance a . An interference pattern is formed on an array of single-photon detectors δ . The probability of photon detection is proportional to the square of field intensity at a detector.

represent the probability density for electrons [37].” Therefore, Born’s statistical interpretation of wavefunctions is an analogy to Einstein’s statistical interpretation of electromagnetic waves.

Note that Born’s statistical interpretation is valid only on a macroscopic scale, such as the double-slit experiment and the particle detection in scattering experiments, where each individual position detector (such as detector δ in Fig. 8.15, photographic plates, scintillators, Geiger counters, and tracks in Wilson chambers [37]) is composed of thousands of atoms. On the other hand, STM and AFM experiments show that wavefunction is an extended physical field on a subatomic scale. Although on a macroscopic scale the electrons appear as individual entities, on a subatomic scale, an electron is a continuous field. Both Born’s statistical interpretation and Schrödinger’s field interpretation are valid and indispensable.

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