

Measuring Orbitals: Provocation or Reality?*

W. H. Eugen Schwarz*

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1. Introduction

The question in the title of this article has two aspects: How can one obtain the quantum mechanical description of matter through wave functions by reconstruction from experimental data? And can one represent chemical phenomena within a well-defined orbital approximation?

Wave functions, density matrices, orbital functions, Wigner functions etc. of electrons and atoms (i.e. nuclei) approximately reconstructed from experimental data have been published in scientific journals for decades. In the meantime reconstructions have been achieved even on the femtosecond timescale, which is of particular relevance for chemical reactions. An important step in this direction has recently been highlighted in a more general journal. The paper has provoked heated discussions in the scientific community focusing on secondary aspects. In the spirit of the

“Einstein Year” 2005,^[1] it seems timely to analyze scientific concepts and their experimental realization also in the present context.

Quantum reaction control and quantum stereochemistry control, quantum computers and quantum cryptography form a new and innovative field of research.^[2] This area contributes both to basic quantum theoretical understanding and to new promising techniques of applied physicochemical quantum engineering. Essential in this research are ultrafast manipulation methods: “femto techniques”.^[3] The timescale for movements of valence electrons is 10^{-17} s (10 as), and for molecular rearrangements by movements of nuclei, 10^{-13} s (100 fs). After more than a dozen years of continuous achievements, the field was acknowledged with the Nobel Prize in 1999 for molecular femtosecond investigations (Zewail).^[3b]

Quantum theory is a formal concept in effect “always and everywhere”. The philosophical interpretation, however, still creates problems. Basic quantum mechanical experiments are of help both for a deeper understanding of nature and for the further development of experimental techniques. And it is very satisfactory for a scientist to confirm experimentally the still-striking predictions of quantum theory. However, each time a paper with the provocative title “Orbital Measured” appears in a journal addressed to a more general readership, heated discussions are initiated in the pubs and on the Internet on whether the fundamental statements make any sense or the experiments have any meaning. This is remarkable, since orbitals reconstructed from experimental data have been described in the literature for decades (Section 4). Some

epistemological annotations therefore seem appropriate (Section 3).

Towards the end of 2004 a paper was published in *Nature* entitled “Tomographic imaging of molecular orbitals”.^[4a] The first response was: Again some orbital-like picture in *Nature*, or this time an orbital in real nature? Eloquent colleagues asked: “Imaging or Imagination?” Some background information: The paper was about an orbital corresponding to a specific electronic excitation, that is, an orbital well-defined by a photophysical process.^[5] Not a whole set of molecular orbitals (MOs) but only a single MO. Specifically, a nonbonding one of rather simple structure and high symmetry,^[6] which simplifies the experimental problems significantly. The amplitudes and phases of such an orbital function in three-dimensional space were reconstructed from measured data of higher harmonics generation (HHG) of laser pulses with the help of theoretical modeling. The most important aspect of this work was, however, the impressively short femtosecond timescale. Accordingly, an accompanying article in the same issue of *Nature* was entitled “Electrons frozen in motion”.^[4b]

For more than thirty years specific orbitals have been generated from experimental data of electron or X-ray scattering with the help of approximate theoretical assumptions. About twenty years ago sophisticated spectroscopic femtosecond techniques and the corresponding modern algorithms for processing the data were developed in order to reconstruct wave functions as empirically as possible.^[7] Attosecond experiments are already being designed.^[3,4,8] At present it is in general only possible to determine the wave function of a single particle or quasiparticle (phonon)

[*] Prof. emer. Dr. W. H. E. Schwarz
Theoretische Chemie
Universität Siegen
57068 Siegen (Germany)
and
School of Chemistry
Jiao Tong University
200240 Shanghai (China)
Fax: (+49) 271-740-4338
E-mail: schwarz@chemie.uni-siegen.de

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in one to three dimensions of space. In a few cases the quantum description of two-particle correlations could be reconstructed. All this refers to free atoms in a trap, to bound atoms in small molecules (rotation, vibration, dissociation), to electrons in free or bound atoms (e.g. dAOs in transition-metal complexes), to electrons in molecules or nanostructures (quantum dots).

On the other hand, it must be noted that the phrase “orbital measurement” is often used only as a catchword. Genuine “orbital measurements” have little in common with the determination of total electron density plots in position or momentum spaces, and certainly nothing to do with the somewhat arbitrary creation of difference densities between a “measured” density of unknown accuracy and a reference density of “clever” choice.^[9] It is also misleading to label photoelectron spectroscopy as “measuring orbitals on the energy scale”, or symmetry assignments of spectra as “measuring orbitals on the quantum number scale”. However, we may consider the experimental determination of some one-electron orbital densities as an acceptable limiting case of orbital measurement.

The recent reports in general scientific journals and in magazines of the scientific societies pose an interesting case for the sociology of science. Questions concerning the sources of experimental error or the serious approximations in the data analysis could have been commented on by experts. Mechanistic chemists could have commented on the potentialities of the femtosecond timescale. However, the discussion focused on only some secondary aspects, which were either positively exaggerated or incorrectly represented and then criticized on the basis of philosophical principles instead of scientific facts. Some comments were prefaced by the remark that familiarity with the new techniques, with modern quantum theory, or with the details of the respective publications is not required. However, the experiment^[4] will be reviewed and commented on in some detail in Section 2.

2. The Experiment

2.1. The Three Steps of the Experimental Procedure

Step 1: First the molecules of an N₂ molecular beam are aligned by the electric field of a linearly polarized red intense laser pulse of 60 fs ($h\nu = 1.5\text{--}1.6\text{ eV}$).^[10] Because of the different quantized rotational frequencies of the N₂ molecule, the molecular axis becomes smeared over all directions (Heisenberg uncertainty), but roughly every 4100 fs it becomes oriented (Figure 1, left).

Step 2: At this moment, a second significantly more intense laser pulse of only 30 fs is shot onto the oriented N₂, which becomes electronically excited in the keV range through multiphoton absorption of $m h\nu$ (Figure 1, middle). The partly ionized nonstationary state is many eV broad and emits higher harmonics $h m\nu$ of the original laser pulse.^[11] In the case at hand, these processes can be reasonably described within the orbital approximation: Large amplitude “vibrations” of a single electron from the least strongly binding σ_g orbital of the N₂ molecule (the lone-pair HOMO) in the direction of the polarization of the laser pulse are induced. Nineteen different angles 0°, 5°, 10°, ... 90° ($\pm 1\text{--}2^\circ$) between molecular axis and polarization were applied.

The laser field changes direction every 1.3 fs. In the quasiclassical description, the electrons (with mass M_e) move in this timespan up to a few 10 Å forth and back, as a wave packet of about 10-Å width. This wave packet φ can be approximated as a superposition of plane waves e^{ikr} of different speeds with electronic wave vectors k

[Eq. (1)];^[12] $a(k)$ is the complex “form

$$\varphi = \sum_m a(k_m) e^{ik_m r} e^{ix 2m\nu t} \quad (1)$$

$$k_m = \sqrt{2m\nu M_e/h}$$

factor” of the wave packet φ . φ coherently interferes with the partly ionized σ_g “home orbital” of the excited electron and will “scan” it: the photon emission by the time-dependent excited one-electron function $\sigma_g + \varphi$ carries the information about its amplitudes and phases (Figure 1, right). The interferences of φ with the other N₂ orbitals are incoherent and do not contribute to the photon emission. The important aspects of coherence and the common, though incorrect, arguments against short-time “chemistry at the uncertainty limit” have been discussed by Zewail.^[3c]

The maxima of the emission spectra at multiples $m h\nu$ of the irradiated photon energies $h\nu$ decay roughly exponentially. In the first Born and in dipole length approximations the intensities $I(m\nu)$ of the emitted photons of frequencies $m\nu$ are proportional to the square of the value of the optical transition dipole moment $\langle r \rangle$ and to the square of the number n of the simultaneously formed ions N₂⁺ [Eq. (2)].

$$I(m\nu) \approx n^2 (m\nu)^4 |\langle \sigma_g(r) | e | r | \exp(ik_m r) \rangle|^2 |a(k_m)|^2 \quad (2)$$

This comparatively simple expression results due to the inversion symmetry of the σ_g MO and from the simplifying assumption that in the moment of emission the N₂ wave function is deformed neither by the intense laser field nor by the field of the excited electron. Namely, in this moment the

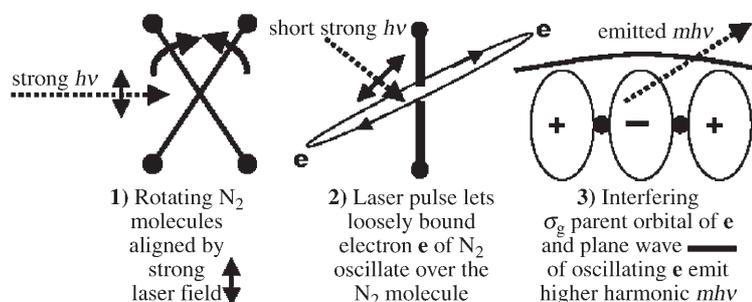


Figure 1. Sketch of the three experimental steps to reconstruct the highest occupied orbital of N₂ molecules.

laser field changes direction, and the electron is near the center of the molecule. Experiments have corroborated the theoretical prediction that a quadratic relation exists between the higher harmonics generation (HHG) intensity I and the ionization probability n .^[11] A quadratic relation between optical intensity and particle number is well known, for instance, for coherent X-ray diffraction by defect-free crystal domains.^[13] Another fortuitous circumstance is that electronic excitation of the nonbonding σ_g HOMO hardly excites nuclear vibrations of N_2 .^[6]

Step 3: The optical emission intensities $I(m\nu)$ and polarizations were measured as functions of the energies $m\nu$ in the X-ray range $\lambda = 15\text{--}50$ nm (photon energies 25–70 eV) for 27 higher harmonics of the initial laser frequency ν at the above-mentioned 19 angles. The relative phases of $a(k)$ were hypothetically determined by similar experiments with Ar and N_2 /Ar mixtures, and were in agreement with theoretical predictions.^[14]

2.2. Data Processing

From the experimentally determined form factors a , ion numbers n , HHG intensities I , and HHG frequencies $m\nu$ of sufficiently many energies, directions, and polarizations, the σ_g orbital function in 3D space can be reconstructed by a double Fourier and Radon transformation of $|\langle \sigma_g | e r | e^{ikmr} \rangle|$ in Equation (2). Several points facilitate the procedure.

Because of the high symmetry of the σ_g HOMO, the phase of the optical transition moment $\langle \sigma_g | e r | i e^{ikr} \rangle = \langle \sigma_g | r | \sin(kr) \rangle = \mu(k)$ is purely real ± 1 . From the theoretical analysis for an MO of $2p\text{-}\sigma_g$ topology with a length of a few Å, it follows that $\mu(k)$ for emission in the direction of the molecular axis should change sign at medium photon energies ($\lambda \approx 30$ nm), while $\mu(k)$ for emission orthogonal to the molecular axis should exhibit constant sign.^[15] The expected sign changes of μ show up as minima in the measured intensity “curves”. The most important term is the form factor $a(k)$.

Argon atoms and N_2 molecules have similar ionization potentials and

polarizabilities, and similar excitation and ionization characteristics. The complex form factor $a(k)$ has been determined from the measurements of Ar atoms, N_2 molecules, and Ar/ N_2 mixtures under the constraint that the data for Ar yield the theoretically calculated canonical Hartree–Fock $3p$ atomic orbital. Accordingly, errors in the diverse parameters of the instruments, detector, sensitivities etc. should basically cancel out in the reconstructed MO of N_2 .

The σ_g orbital function of N_2 was then reconstructed on a three-dimensional grid from the 27×19 basically empirical values of amplitude, phase, and polarization of the transition dipole moment vectors $\mu(k)$. This was achieved by Fourier unfolding of $\langle r \sigma_g | \sin(kr) \rangle$, and, for the transition matrix and the orbital function in different directions, by an algorithm similar to the Radon transformation used in medical tomography.^[16] The one-electron orbital obtained reproduces the measured excitation and emission processes within the independent-particle approximation.

Since the most weakly bound canonical Hartree–Fock orbital of Ar was used for calibration, the function generated from N_2 laser-pulse spectra shown in Figure 2 may be assumed to be a canonical Hartree–Fock HOMO or some similar type of orbital such as a Dyson orbital (see Section 3.9).^[17] Careful theoretical analyses of the experimental data production and of the data transformations are needed to distin-

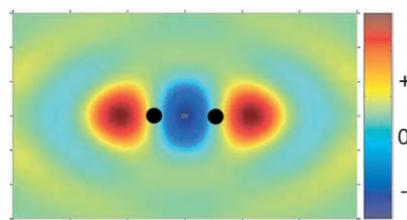


Figure 2. Orbital of the most weakly bound electrons of N_2 molecules, which reproduces (within the orbital approximation) the higher harmonics generation of a laser pulse interacting with N_2 (tomographically reconstructed from experimentally determined transition dipole moments of the short-wave XUV emission and complex form factors). The plot is in a plane passing through the N_2 molecular axis. The two dots indicate the positions of the N nuclei. The color scale on the right codes the positive and negative values of the orbital function.^[4a]

guish between these cases in the future. However, the accuracy of the fs-spectroscopic data achievable at present and the approximations introduced in the data processing so far do not permit the detection of differences between these different orbital types. In any case, the experimentally reconstructed function of Figure 2 qualitatively reproduces the typical topology of an $N2sp\text{-}N2sp\text{-}\sigma_g$ lone-pair MO with a negative lobe between the N nuclei and strong positive lobes on the left and right sides.

2.3. Evaluation

What has been measured on a femtosecond timescale are the optical intensities and polarizations of the higher harmonics generated by laser pulses interacting with N_2 molecules, with Ar atoms, and with N_2 /Ar mixtures to determine the relative interference phases (selected curves through the $m\nu$ intensity values are shown in Figure 3 of reference [4a]).

Most remarkable is the timescale. Within 1 fs a quasiclassical electron would revolve several times on Bohr's hydrogen orbit. Concerning nuclear motions in chemistry, 1 fs covers only a small fraction of a rotation, a vibration or a direct bond-rearrangement. Femtosecond measurements can analyze the electronic rearrangements during the comparatively slow nuclear motions in some detail. The “electron shifts” in reaction mechanisms can become more than just chemistry on paper, namely “well-defined quantum chemistry”, its experimental proof being within sight. The paper in *Nature*^[4] is indeed another step on this difficult path. The details described above indicate the large number of simplifications thrown in and the large number of problems still to be solved. Some of them have already been mentioned explicitly in the cited paper.^[4] In any case, at present the quantum chemical calculation of orbitals is the simpler and more reliable procedure.

An important aspect of experimental determination of orbitals is the well-defined orientation of the molecules. In the case of the gaseous phases, as in molecular beams, the molecular rotational states must be coherently super-

posed in an appropriate fashion. This was done here by a polarized laser pulse. Strongly polar molecules can be aligned with microwaves in multipole fields. Since the orientation of free molecules oscillates quantum mechanically, the “orbital measurement” must occur quickly. In the case of solids, the building blocks are in general stationary. Simpler, tried-and-true techniques can be applied easily (see Section 4.2).

Another point is the approximation of a complex many-electron phenomenon within the framework of the one-electron orbital model and the experimental reconstruction of the respective orbitals. Some theoretician’s wisdom on orbitals will be communicated below, which should be considered in future “philosophical” discussions among experimental and computational chemists and in the community of philosophers of material sciences.

Some experimental scientists argue that one should perform measurements in a well-defined manner and present only slightly processed raw data. They argue that representations of model concepts based on extensive theoretical analysis, or even the philosophical or linguistic analysis of those concepts, are irrelevant in experimental science. Quantum chemists argue correctly that theoretically and computationally experienced theoreticians can generate wave functions and orbitals quite reliably. But some argue furthermore that any efforts to develop experimental alternatives are pointless, since at present even small molecules require terribly complicated procedures. Both groups of readers should proceed to Section 4.

3. “Philosophy” of Orbitals and of Their Reconstructions

3.1. Objects

In the (natural) sciences only sections of the world are investigated. Considering an isolated object means that its interactions with the environment are neglected. Measurements of data of an object are always performed within the framework of some approximate theory of the isolated object. If these data can or could help answer a given question satisfactorily, then the

relations of the theoretical model represent some objective structure of reality. Whether an object may be said to exist objectively in this sense therefore depends on the internal physics of the system, its state, its environment,^[18] the type of question, and the timescale. For instance, the concept of an H₂O molecule makes sense in steam, but not in concentrated sulfuric acid, in particular not on an extended timescale.

3.2. Fields and Sets of Functions

Physical objects such as sections of electromagnetic or matter fields are represented by functions for fields and potentials.^[36] Fields on microscopic scales are at best determined from interference patterns with a carefully prepared reference wave. However, it is much easier to measure only the amplitudes or values of multicomponent field functions, for example, the light intensity or the electron density.

An electromagnetic field is represented by a “gauge-invariant set” of four-component potential functions $\{A(X,t) + \nabla f_j(X,t)\}$ at space-position X and time t . Here f_j is an arbitrary function, and ∇ the four-dimensional (X,t) derivative. All individual potential functions $A + \nabla f_j$ from the set $\{A + \nabla f_j\}$ are equivalent and yield the same, experimentally verifiable results. Similarly, a matter field is represented by a “gauge-invariant set” of complex wave functions $\{\Psi(X,t)e^{if_j(X,t)}\}$. All individual wave functions Ψe^{if_j} are equivalent. It depends on the personal preference whether $\{A + \nabla f_j\}$ and $\{\Psi e^{if_j}\}$ are interpreted as “elements of a deduced reality” or only as “mathematical constructs” that reproduce the reality as exactly as detectable by measurements.

3.3. Measured Intervals, Numbers, and Complex Components

Any elementary measurement yields numbers with a few decimal places; that is, there are no real numbers with an infinite number of digits in experimental science. All measured values come from a “small” set of discrete numbers. Multiply reproduced data, not just individual measured values, form the basis of

science. Because of the uncertainty of any experimental value, one can apply a mathematical simplification: calculations are performed with the help of continuous real values instead of the reliability intervals (of, say, $\pm 2\sigma$) obtained from repeated measurements. The basic equations of theoretical physics and chemistry hold in general for continuous differentiable functions.

Most physical quantities have several components. A vector field has three components; the so-called complex refraction index has two components for refraction and absorption; the nonrelativistically approximated wave function also has two complex components, in simple cases. Complex differentiable functions are mathematically distinguished and can represent the interrelationships of nature particularly clearly.

3.4. Wave Functions and Their Equivalents

All chemically interesting phenomena are many-particle phenomena that can often be described at the microscopic level with the help of many-particle wave functions $\Psi(X_1, \dots, X_N)$. Here, X_i may, for instance, indicate the position and spin direction of electron i in 3D space. Other variables can also be used as alternatives to the position representation. In the momentum representation, $\Theta(P)$ (an equivalent to $\Psi(X)$) is obtained by a Fourier transformation, $\Theta(P) = \int dX e^{iPX} \Psi(X)$.

If quantum electrodynamical and environmental effects can be neglected, an isolated molecular system can be approximately represented by a wave function, but only in the case where all observable parameters are well specified (“pure state”). If one has some ensemble (e.g. a thermodynamic one), several wave functions are needed to construct the “density operator kernel” $D(X_i, X_j)$. In the simplest case of a pure state, $D(X_i, X_j) = \Psi(X_i) \Psi(X_j)^*$. In general, $D(X_i, X_j)$ is complex. Equivalent descriptions of reality can be obtained by variable transformations, yielding the real Wigner function $w(X_i, P_j)$ or the positive Husimi function $h(X_i, P_j)$ as a quantum mechanical generalization of the classical X_i - P_j phase space density.^[19]

3.5. Orbitals

All experimental concepts are based on some idealized approximations. Correspondingly, any comparably accurate theoretical description also comprises approximations. It is important to introduce further approximations to obtain simple and intuitively clear theoretical explanations. The wave functions Ψ of many, though definitely not of all, states of an N -electron molecule can be approximated for many purposes by a “symmetry-adapted” product Φ of one-electron orbital functions $\varphi_j(X_i)$ ($j = a$ to n) for electrons $i = 1$ to N [Eq. (3)].

$$\Psi(X_1, \dots, X_N) \approx \Phi(X_1, \dots, X_N) \quad (3)$$

$$= \Lambda\{\varphi_a(X_1) \varphi_b(X_2) \dots \varphi_n(X_N)\}$$

Whether Φ is a satisfactory orbital approximation to Ψ depends on the type of the molecule, on its state, and also on the type of the question. The statement “this object or structure exists” has the meaning that there is some objective structure in the real world that is satisfactorily described by the applied approximate concepts (theory) for the chosen section of reality (the object). In this sense, also orbitals can “exist” depending on the circumstances, just as NaCl molecules can exist in the gaseous phase though in general not in condensed phases. If a molecule exists, then orbitals often exist in the above-mentioned sense in the molecular ground state. Concerning excited states, however, the orbital approximation often fails. For instance, the orbital approximation of Equation (3) does in general not work for states with an electron excited from a lower subshell, such as 3 s of transition metal atoms, or the lowest valence MO of a molecule. These are cases of “breakdown of the orbital approximation”.^[20] In such physical situations “there are no” orbitals.

3.6. Measurement of Model Parameters

There is a whole continuum of different cases of measurements with more or less theory-laden data conversion—from the simple direct “measurement” of a single number (e.g. the comparison of the “length of a desk” with a meter stick) to the sophisticated

semiempirical analysis of a large data set (e.g. the fitting of the parameters of a “static electron density model of a crystal” to the X-ray diffraction intensities). Concerning the extraction of physically relevant model parameters from the measured raw data, the last example is particularly strongly “theory- and model-laden”. Parameters such as “dynamically averaged chemical shifts” from NMR measurements, or “vibrationally averaged internuclear distances” from microwave measurements are comparatively closer to the measurements. The reconstruction of orbital functions from HHG intensity measurements lies somewhere in between. Any reconstruction of a continuous function from the limited number of measured data bears some model load, such as the concentration distribution in a reactor, or the Born–Oppenheimer energy surface of a molecule.

Another aspect is the amount of chemically useful information connected with experimentally determined parameters. It is quite considerable for internuclear distance distributions from X-ray diffraction intensities, which characterize the structure and flexibility of a molecule. At present the amount of chemically useful information is still low for experimentally based orbital pictures.

Some repeated experiments are performed with the same object. In other cases, different identically prepared objects have to be used, not only in the quantum regime. For example, for the determination of a single classical activation energy, several similar reaction mixtures at different temperatures are needed. For the determination of the HOMO of N_2 many differently aligned N_2 molecules are required.

3.7. Reconstruction from Insufficient Data

In the reconstruction of physical functions from experimental data sets on the basis of a theoretical model, two problems must be overcome: 1) Since the measured data carry errors, more data than absolutely necessary must be determined, for error reduction and reproducibility. 2) In many cases one always has an insufficient amount of data. A typical example is the so-called

“X-ray measurement of the electron density” of a crystal.^[13] For finite wavelength λ there is only a limited number of $\sin\theta/\lambda$ data. Their Fourier transform yields the Patterson density correlation function, and that only at an entirely insufficient quality. Therefore the broad qualitative and quantitative theoretical knowledge of chemistry is introduced. The approximate electron density distribution is constructed by fitting a superposition of vibrating “frozen” and “reasonably deformed” quantum-theoretical atomic densities, under the constraints of the already known chemical composition and under the restraints of “chemically reasonable” bonding and nonbonding interatomic distances. This approach now works routinely quite well after the introduction of a large number of tricks and educated guesses into the data-processing procedures, based on decades of experimental and computational experience.^[13] However, it still can happen that significantly different “measured electron densities” fit the same experimental data set.^[21]

3.8. Data Transformations

Fourier transformations of IR, NMR, and X-ray data are nowadays common between the time and energy domains, or between momentum transfers and position distances. In the cases of medical tomography and of atomic, electronic, or photonic scattering, projections upon different directions are measured. The data must be “inverted” to reconstruct the three-dimensional profile that causes the measured data. The previously mentioned Radon transformation developed for medical tomography and material investigations is also applied for “measuring orbitals”.^[16] It is not at all unique that engineering methods are also applied in quantum chemistry. The “Finite Elements” procedure, for instance, is used to predict tsunamis as well as the performance of new airplanes or cars, of large buildings and bridges, and of nanotubes, molecular orbitals, and nuclear dynamics in elementary chemical reaction steps.

3.9. Operational Definitions of Orbitals

“Orbitals” are concepts that are useful to approximately describe and efficiently manipulate structures, properties, and processes of real molecules, crystals, etc.^[5] Accordingly, orbitals are essentially determined by the nature of the molecules, as well as by the aspects to be highlighted by the experimental investigation and the theoretical analysis. The relation between wave function Ψ and corresponding orbital set $\{\varphi_j\}$ is made unique through the definition of the mathematical meaning of the “ \approx ” in Equation (3).

There are not “the orbitals” in molecules, just as there are not “the charges” on atoms in molecules. There are many kinds of atomic charges such as the Bader, Ahlrichs, Mulliken, IR, and dipole charges.^[22] Similarly, rigorous quantum theory offers a wealth of different, well-defined types of orbitals, appropriate for different physical phenomena, to be described in different frameworks.^[6,17] First, the *exact* wave function Ψ and the *exact* energy E can be generated from a simple orbital product function Φ by several theoretically well-defined techniques, for example, with the help of the Möller operator Ω or the coupled-cluster (CC) operator Ξ according to $\Psi = \Omega \Phi$ or $\Psi = e^{\Xi} \Phi$. Second, the popular density functional (DF) approaches of Kohn and Sham (KS) all aim at the calculation of highly *reliable* molecular energies with the help of a product wave function of “KS orbitals” of different kinds.^[23]

Third, the most famous orbital approach for *approximate* energies is the first-principles (or *ab initio*) model of the self-consistent field of Hartree and Fock (HF). There are also many semiempirical variants such as iterative extended Hückel (IEHT), CNDO, AM1, etc. For any of these approaches, there is a whole “continuum” of various equivalent sets of orbitals, such as the “canonically chosen” or the “localized-chosen” sets.

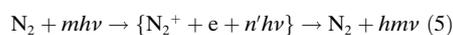
The description of arenes and pericyclic reactions, of periodic chains and crystals, of photo- and electrochemical excitations, and of charge-transfer processes by canonical orbitals delocalized over the molecule is particularly simple and concise. On the other hand, the discussion of σ systems, ordinary con-

jugated π systems and their substitution reactions, of valence-bond approaches, and of Lewis and VEPR models is most simple and straightforward, if orbitals are used that are localized according to Boys, von Niessen, Mezey etc. (the particular choice usually making no big difference).^[24]

Diagonalization of an (experimentally reconstructed) one-electron density kernel D yields the so-called (“experimental”) “natural orbitals”.^[17] The analysis of experimental data of simple one-electron ionization processes $M \rightarrow M^+ + e$ within the orbital approach according to the approximation in Equation (4) yields the “Dyson orbi-

$$\Psi(M) \approx_A \{\Psi(M^+) \varphi(e)\} \quad (4)$$

“tals”.^[5,17] The analysis of experimental HHG [Eq. (5)] in the framework of the



Hartree–Fock model should yield “experimental” “Hartree–Fock orbitals”.

3.10. The HOMOs of N_2

In the framework of the Hartree–Fock approximation of closed-shell systems, the energies of orbitals (chosen canonically delocalized) approximate simple direct one-electron ionization energies (theorem of Koopmans). Two assumptions are implicit: The orbitals of M^+ are taken over from M as unmodified (ionization reorganization error). And no change upon ionization of the total correlation effect between any two electrons due to their Coulomb repulsion is postulated (ionization correlation error).

Figure 3 shows the one-electron orbital ionization energies of N and N_2 (from reliable many-particle calculations and from reliable experiments) in the form of an MO scheme. The 2s AOs of the two N atoms give rise to the lowest bonding $\sigma_g(b)$ MO, which is particularly stable as a result of sp hybridization; the 2p π AOs give rise to the lower pair of binding $\pi_u(b)$ MOs. Also because of hybridization, the “antibonding” complement of $\sigma_g(b)$ becomes a nonbonding $\sigma_u(n)$ MO, and the “bonding” linear combination of the

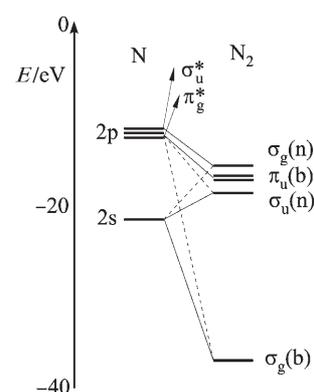


Figure 3. Negative one-electron orbital ionization energies E (in eV) of the N atom (2s and 2p, configuration average values) and the N_2 molecule ($2s\sigma_g(b)$, $2s\sigma_u(n)$, $2p\pi_u(b)$, $2p\sigma_g(n)$), with AO–MO correlations. (Note the deviation from the order of Hartree–Fock model orbital energies with π_u above σ_g .)

$2p\sigma$ AOs becomes a nonbonding $\sigma_g(n)$ MO. The two canonical MOs $\sigma_u(n)$ and $\sigma_g(n)$ correspond to the two localized N_2 lone pairs.

It has been known for decades that the π^4 correlation energy (e.g. of N_2) is particularly large. Reorganization and correlation errors nearly cancel each other in the case of the $N_2(\pi_u)$ ionization. The 2p-2p- $\pi_u(b)$ orbitals give rise to a vertical ionization potential (IP) at 17 eV; the corresponding orbital energy of the Hartree–Fock model is $\epsilon_{HF}(\pi_u) = -17.0$ eV. The smallest ionization energy of 15.6 eV is sufficient to eliminate an electron from the nonbonding 2p-2p- σ_g lone pair MO.^[6] Here the “Koopmans error” is as large as 1.8 eV ($\epsilon_{HF}(\sigma_g) = -17.4$ eV). While $IP(\sigma_g) < IP(\pi_u)$ holds for the ionization energies (according to experiment and theory), the Hartree–Fock approximation yields $|\epsilon_{HF}(\sigma_g)| > |\epsilon_{HF}(\pi_u)|$ for the orbital energies.^[25]

According to a theorem of Janak for the KS-DF approach, the energies of the delocal KS orbitals (approximately accounting for electron correlation) describe the occupation tendencies of the orbitals in the electronic ground state.^[23] Often the order of the approximate KS orbital energies corresponds to the order of the IPs. Indeed, we find $|\epsilon_{KS}(\sigma_g)| < |\epsilon_{KS}(\pi_u)|$. However, the values of the ϵ_{KS} are smaller than those of the IPs, as usual, by up to a few eV.

4. Different Experimental Reconstructions of Wave Functions

The reconstructions of total electron densities and orbital densities, of many-electron wave functions, and of one-electron orbitals each have their own problems related to the applied experimental procedures. Kapale noted that “*quantum state measurement is an immensely complicated endeavor*”.^[26a] A wealth of approaches for experimental data collection and for computational data processing have been suggested or realized. Neglecting transition cases, the “experimental” reconstructions of electronic quantum states can be classified as four or five types. The broad field of photonic and of nuclear wave functions (molecular translations, rotations, vibrations, dissociations) shall not be considered here.

4.1. Orbitals Reconstructed from Sufficient Experimental Data

Data sets sufficiently comprehensive for the direct reconstruction of amplitudes and phases of orbitals can be obtained from a whole series of different quite sophisticated experimental approaches. There are the spectroscopic homodyne and heterodyne techniques, the absorption, emission, fluorescence, and interference techniques of nonlinear and short pulse optics, which exploit the interaction of molecules with photons or electrons.^[26] The most recent example is reviewed in Section 2. If the state under investigation is nonstationary, changing on the fs or ns timescales, the orbital wave function is complex at each instance of time. Such an orbital, though a simple one of an alkali-metal atom, had been “measured” by Weihacht et al. already in 1998 (Figure 4).^[27]

4.2. Model Orbitals from Complementary Experimental Data Sets

An experimentally simpler approach towards orbitals, wave functions, density kernels, etc. is based on fitting a not-too-flexible orbital model ansatz to a data set that is still insufficient for direct reconstruction. The resulting orbitals depend both on the experimental data

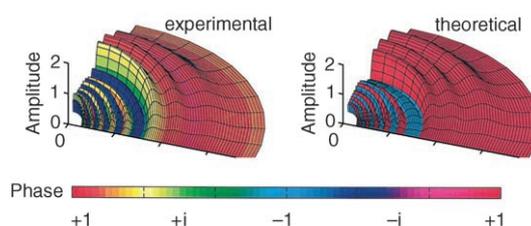


Figure 4. Nonstationary complex p_z orbital of a Cs atom (superposition of eight p states 25 p to 32 p obtained in a two-step excitation from 6 s by an appropriately shaped short laser pulse). Right: Theoretically expected orbital. Left: Reconstructed from experimental data. Plots are shown in a quadrant of the x - z plane. The complex values (phases) of the AO function from $+1$ to $+i$ to -1 to $-i$ to $+1$ are color coded.^[27]

and on the model assumptions. The most elaborate of such procedures is the joint use of complementary electron densities in position and momentum spaces for the generation of a “one-electron density matrix”.^[28] The one-electron position density expresses the multicenter character of the molecule, the momentum density succinctly describes the quantum chemical character of the covalent bonds. The eigenvectors of the density matrix are the “natural orbitals” projected onto the model basis. These “semiexperimental” orbitals also account for electron correlation effects, in contrast to those of the Hartree–Fock approximation. For instance, assuming $1s^2 2s^{2-\delta} 2p^\delta$ for beryllium with weakly occupied p shell, one obtains the shapes of 1s, 2s, and 2p, and the orbital occupations with $\delta \approx 0.15$. Most investigators do not plot orbital figures explicitly but construct the orbitals only implicitly on the computer and use them to calculate molecular properties from the reconstructed orbital wave function: measured data \rightarrow [semiempirical orbitals] \rightarrow property values.

4.3. Construction of Orbital Densities

Densities of individual Dyson orbitals can be reconstructed, first in momentum space, from inelastic energy-resolved triply differential electron-scattering data (e $-2e$ spectra of electron momenta spectroscopy, EMS).^[29] Similar results can be obtained from inelastic scattering data of high-energy photons (Compton spectroscopy) instead of high-energy elec-

trons.^[28b,c,30] Unfortunately the highly resolved gas-phase spectra yield only spherical averages of the orbital densities. We note a similarity between the EMS and HHG methods: The orbitals are scanned in momentum space by electronic plane waves, in the case of EMS by an “external” electron beam, in the case of HHG by a strongly oscillating electron from the excited molecule itself. Dyson orbital densities can also be generated from atomic scanning tunneling micro-

scopic (ASTM) data, in position space (Figure 5^[31]) or in momentum space (Figure 6^[29g]).

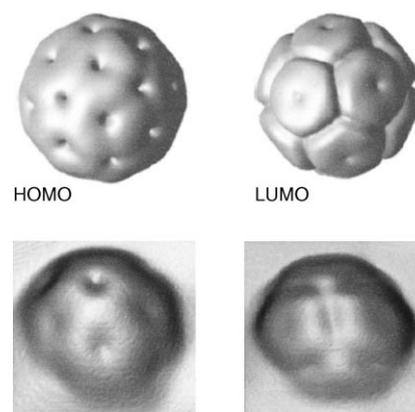


Figure 5. HOMO and LUMO densities of full-ene C_{60} . Top: from DFT calculations. Bottom: from scanning tunnel microscopy at $+2$ V (left) and -2 V bias (right).^[31a]

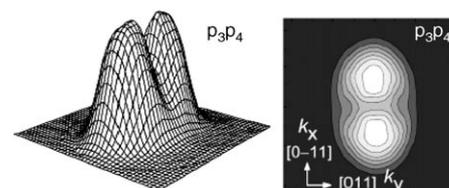


Figure 6. Momentum density of a localized p-like electronic state in an (InAs) quantum dot in gallium arsenide, in the [001] plane, from scanning tunnelling data in a sweeping magnetic field.^[29g]

4.4. Combined Theoretical–Experimental Determination of Wave Functions

Various authors have suggested solving the comparably simple theoretically

approximate Hartree–Fock orbital equations so that simultaneously reasonable agreement with some experimental data sets is achieved, for instance X-ray crystallographic data sets (“quantum crystallography”).^[32] In this way, not only electron correlation effects can be introduced semiempirically into molecular Hartree–Fock calculations but also environmental influences of the solid surrounding the molecule in the crystal. In principle, these are theoretical orbitals, obeying experimentally determined conditions.

In a highly simplified version one chooses a rather small atomic orbital basis set that is known to yield still reasonable results in approximate molecular quantum calculations. Introducing some further restrictions (e.g. the single-determinant approximation, leading to the idempotency condition of the one-electron density matrix), the MO coefficients can then be fitted to some experimental data sets.^[13a,33] For different opinions and critical comments on such semi-empirical and model-dependent MOs see footnote 1 in reference [28e].

4.5. Model Orbitals

It is common in crystallographic electron density studies to simulate the experimentally fitted total density distribution by a superposition of theoretical, empirically slightly deformed atomic orbital densities.^[34] In this approach, however, the quantum mechanical interference effects between bonded atoms (the physical origin of the covalences) are not explicitly accounted for in the density reconstruction. Thereby one can get only roughly approximated AO occupation numbers of the d shells of transition metal ions in complexes, or of p shells of bonded main-group elements.

5. Summary

5.1. So-Called Measurements

Every experimental result is obtained in the framework of some approximate model concepts and has only some mediocre numerical accuracy. Ev-

ery theoretical result is also based on some approximate assumptions and possesses only some numerical accuracy. This holds, for instance, even for the so-called exact hydrogen one-electron orbitals, which do not at all exactly reproduce reality.^[35]

The various experimental or theoretical approaches do not differ in principle, but in the extent and amount of approximations and accuracies. A “rather directly measured” quantity and one reconstructed in a complicated manner from sophisticated measurements do not differ in principle but in the amount of intervening concepts and theories. Formerly one could apply simple measurement procedures that were analyzed with simple theories (e.g. Euclidean geometry as an approximate theory of physical space). Nowadays highly developed equipments must be combined with elaborate theories. Present measurement devices often directly display results theoretically reconstructed with the help of integrated computational hard- and software. The statement that some quantity has been “measured” just means that it has been reconstructed from some measurements that were performed and analyzed on the background of conceptual and numerical approximations, assumed to be appropriately valid and reliable in the given case.

Electromagnetic and matter fields of molecules are idealized objects excised from their environment. Such objects can be described mathematically, in many cases by a “gauge-invariant set” of real or complex or vectorial numbers or functions. In order to perform a concrete computation, a single representative from that set must be selected, for example, an electromagnetic potential in “Coulomb gauge”, or a nonrelativistic wave function with α and β spin factors and a position space function with real phase. What is the most appropriate choice among more or less equivalent concepts depends on the case and on the purpose.

An N -electron wave function describing an approximately isolated molecule in an approximate manner can be represented, depending on the theoretical approach, more or less accurately with the help of N or more one-electron spin-orbitals. Whether canonical or lo-

calized orbitals, Hartree–Fock, density functional, or natural orbitals, or Dyson, Brückner, or Möller orbitals are most appropriate in a real problem also depends on the case and the accuracy desired. Anyhow, if one talks about orbitals one must always specify what kind is actually meant. This holds for calculated as well as for experimentally reconstructed orbitals.

5.2. Reconstruction of Orbitals and Orbital Densities from Experiments

Several experimental–theoretical hybrid approaches are on the market (Sections 2 and 4). The most developed one is based on a three-step femtosecond process consisting of: 1) tunnel ionization of an aligned molecule; 2) laser-driven motion of an electron in the continuum; 3) short-wave photoemission upon recombination. Whether and where the “experimental” constructions of total or orbital densities or wave functions are or may become superior to the purely theoretical ones depends on the molecular size and the thermodynamic conditions. When referring to empirically based electron deformation density maps or Laplacian density maps with all their incorporated assumptions as “measured ones”, then it is even more justifiable to call orbital maps directly reconstructed from experimental data also “measured ones”. However, the transformation of experimental data into orbitals has often not been analyzed sufficiently to specify the type of the reconstructed orbital. Today’s sophisticated experimental and theoretical techniques call for more cooperation between theory and experiment in physics and in particular in chemistry. The chemistry curricula must take this into account. The pertinent problems of orbital reconstruction lie in the technical details which should be discussed in an interdisciplinary fashion by the specialists. In Section 3 we have tried to clarify the more “trivial” principles.

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- [6] Constructive bonding AO interference in the overlap region is typical for two-center σ_g MOs. However, density accumulation of the second σ_g in the “lone-pair regions behind the nuclei” due to sp hybridization (see Figure 1) causes a nonbonding character: Vibrations are hardly excited, bond strength and length are hardly changed upon ionization of $^1\Sigma_g N_2$ to $^2\Sigma_g N_2^+$. In contrast, ionization from the bonding π_u MO leading to $^2\Pi_u N_2^+$ extends the bond length by 8 pm and reduces the force constant by one-third, see K. P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure IV*, Van Nostrand Reinhold, New York, **1979**.
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