Towards a Philosophy of Approximations in the 'Exact' Sciences

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Abstract: The issue of approximations is mostly neglected in the philosophy of science, and sometimes misinterpreted. The paper demonstrates that approximations are in fact in the core of some recent discussions in the philosophy of chemistry: on the shape of molecules, the Born-Oppenheimer approximation, the role of orbitals, and the physical explanation of the Periodic Table of Elements. The ontological and epistemological significance of approximations in the exact sciences is analyzed. The crucial role of approximations in generating qualitative images and comprehensible models is emphasized. A complementarity relation between numerically 'exact' theories and explanatory approximate approaches is claimed.

Keywords: *Approximations in quantum chemistry, complementarity, shape of molecules, orbitals, Born-Oppenheimer approximation, Periodic Table.*

1. Introduction

The issue of approximations appears, explictly or implicitly, in many discussions in the philosophy of chemistry. Do molecules have a shape? Can orbitals be observed in experiments? Is the physical explanation of the Periodic Table of Elements really an explanation? All these subjects involve an analysis of the role of approximations.

For instance, Garcia-Sucre & Bunge (1981) argued, "the Born-Oppenheimer approximation, although an artifact, does represent some important objective properties of quantum-mechanical systems, among them their geometry." How is that possible – an artifact representing some important objective properties? Is it by accident? Is this situation peculiar to the Born-Oppenheimer approximation? Could it be clarified or even remedied by a change of terminology, as suggested recently by Del Re 2003 (note 11)?

> We write "theorem" instead of "approximation" because the latter name has misled some researchers into believing that the Born-Oppenheimer study has

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> no physical content: actually, it is the proof that quantum mechanics is compatible with the separation of nuclear motion from electronic motions as revealed by observed molecular spectra; and novelties are only found when two hypersurfaces cross.

We meet a similar situation in the recent discussion on the status and observability of orbitals. According to Scerri (2001),

> Of course, the orbital model remains enormously useful as an approximation and lies in the heart of much of quantum chemistry but it is just that – a model, without physical significance, as all computational chemists and physicists are aware.

Is this again by chance – a model without physical significance lying in the heart of quantum chemistry? Moreover, Scerri (2001) explains the experimentally obtained images of orbitals by Zuo et al. 1999, "I suggest that any similarities between the reported images and textbook orbitals may be completely coincidental". Is all that not too much coincidence for the 'exact' sciences?

The examples illustrate that the discussions are not about some marginal technical details but about the very heart of quantum chemistry. Therefore, the meaning and significance of approximations in science deserve a deeper analysis from ontological and epistemological perspectives than it received before.[1] Are approximations necessary or can they be avoided in order to make a science really exact? Are they arbitrary and subjective (artifacts)? How can they be linked to something observable? These and other related issues are analyzed in this paper by further developing aspects of a previous paper (Ostrovsky 2001).

2. Approximations in physics: an insider's view

Although physics is considered an exact science, any practicing physicist knows that everything in physics is approximate. The prominent theoretical physicist A.B. Migdal starts his *Qualitative Methods in Quantum Theory* (1989) as follows:

> No problem in physics can ever be solved exactly. We always have to neglect the effect of various factors which are unimportant for the particular phenomenon we have in mind. It then becomes important to be able to estimate the magnitude of the quantities we have neglected. Moreover, before calculating a result numerically it is often necessary to investigate the phenomenon qualitatively, that is, to estimate the order of magnitude of the quantities we are interested in and to find out as much as possible about the general behavior of the solution.

> For the last dozen years theoretical physics has undergone strong changes. Under the influence of the theory, new fields of mathematics started being used and developed by theorists. Computational theoretical physics acquired a particular importance. Nevertheless, despite mathematization of physics, qualitative methods became even more important than before elements of the theory. They are sort of mathematical analog of the image-bearing mentality of sculptors and poets, feeding the intuition.
>
> I believe that now more than before, a beginning theoretician should master qualitative methods of reasoning.

This is not some marginal opinion, but an authoritative judgment of an outstanding professional. The English edition of Migdal's book was printed by one of the most authoritative publishing houses in the exact sciences, Addison-Wesley. In 1989 and 2000 the book reappeared in the series *Advanced Book Classics*. Its author, Professor A.B. Migdal, was a full member of the USSR Academy of Science, member of L. D. Landau Institute of Theoretical Physics and a Landau Prize Laureate. The book was translated from Russian by Anthony J. Leggett who became in 2003 the recipient of the Nobel Prize in physics. Migdal's views are universally accepted by the community of physicists.

Laypeople might be confused by such a statement as: 'In quantum mechanics one can obtain an exact solution only for the hydrogen atom, but not for a multi-electron atom.' In fact, such formulations contain implicit assumptions that are shared by specialists. In this particular example, it means that an exact solution is obtainable for the *non-relativistic* Schrödinger equation of the hydrogen atom. But the Schrödinger equation itself is an approximation: it does not account for relativistic effects. Strictly speaking, there is not such an object in nature[2] as a non-relativistic Schrödinger atom. It is a model, or an approximation, that allows calculating results that match only approximately experimental data.[3] An exact solution for the hydrogen atom can also be obtained from the Dirac equation that takes the relativity theory into account. It ensures a better agreement with experiment (for instance, by describing the fine structure of the energy levels), but again, it is an approximation. One need to take into account the size and structure of the atomic nuclei to improve the results. The Dirac equation does not account for the atomic interaction with the electromagnetic field. If one decides to go further and achieve higher accuracy (*e.g.*, to describe the Lamb shift of levels), one has to turn to quantum electrodynamics. Even the latter theory does not provide an 'exact' equation to be solved. It only allows calculating properties of atoms and ions at some order of approximation over small parameters that characterize relativistic effects.

Thus, physics is nothing else than a hierarchy of approximations, without a single exact equation or result. This is not a pitiful temporary drawback that might be removed in the course of time. It will continue forever, since it reflects the essence of the approach of physics to describing nature. First of all, the laws of physics are not given *a priori*, but are always experimentally tested with only some precision. Second, there are some inevitable approximations. Any researcher must select a piece of the universe to be studied and described (for instance, an atom, or a planetary system) and, by approximation, must neglect the rest of the world. Only some cosmological theories claim to avoid these limitations, but, of course, they contain an immense number of other approximations. Third, even if some more exact theory is known, it still makes a deep sense to resort to approximations, not only for pragmatic reasons, but also for epistemological reasons. Approximations immensely enrich our qualitative picture of nature. This aspect will be further discussed in Section 4, but it is worthwhile to indicate here that the basic models of chemistry (such as molecular shape, see Section 3.2) are not universal, but arise from appropriate approximations.

Apparently the laws of conservation in physics have a somewhat special status. Some of them, initially considered strict, later proved to be only approximate, as the parity conservation. The most important and widely known one is the energy conservation law that seems to remain unshaken. However, this law has a special character as emphasized by Feynman (1992). As our knowledge of nature expands, new forms of energy are embraced by the law to obtain the total energy that is conserved. Thus, energy conservation actually means that up to now we have always managed to find new terms to be added to keep the total energy constant. This availability is, of course, a deeply rooted principle of nature.

People interested in really exact results and statements should turn to mathematics rather than to physics. Mathematics is not a natural science, albeit widely applied in the natural sciences. Mathematics works with abstract constructions that should be internally consistent, *i.e.* without logical contradictions. No other restrictions are imposed. Mathematicians construct a logically non-contradictory 'universe' and work with it. They need not care if this universe is the one we live in. For instance, a mathematician is ready to consider a space of arbitrary dimensionality n. While this is extremely useful as a mathematical technique, a physicist is faced with fact that we live in a space with $n=3$, with all its peculiarities. Physicists cannot construct their universe; they have to study the only one available.

Thus, no physical theory can be blamed for using approximations because, in fact, all theories do that. The only question is how the approximation in a specific theory or a specific application is justified. To develop a proper approximation and to be aware of the limits of its applicability is an important element of defining the qualification of a physicist. This skill cannot be put in the form of an algorithm, which is one of the reasons why a physicist cannot be replaced by a computer. The great chain of approximations bears deep epistemological meaning that is frequently unrecognized or underestimated.

3. Approximations in physics: a view from the outside

Some nonphysicists seem to have radically different ideas about approximations. They adhere to an image of the ideal and immaculate exact science that does not resort to approximations. Since real science does not fit the ideal image but widely employs all kinds of approximations, some of its approaches and results are looked upon with skepticism, suspicion, and distrust.

The issue of approximations is important for chemistry. It is in the center of many philosophical discussions in chemistry, as mentioned in the Introduction, so that a proper philosophical understanding of approximations is particularly important here. Below we at first discuss some specific, albeit vitally important, approximations.

3.1. Born-Oppenheimer approximation

An issue much discussed in the recent literature is the problem of molecular shape. In quantum mechanics a multi-particle system generally does not possess such a property as a definite shape. However, a shape might be ascribed to a molecule within the Born-Oppenheimer approximation. The latter is instrumental in the quantum theory of molecules and therefore plays a very important role in quantum chemistry. In particular, chemical reactions that are not accompanied by a change of the electronic states are described within this approximation. Some authors exhibit deep dissatisfaction about the facts that chemistry is actually based upon approximations (and hence that more general theories exist) and that molecular shape is not an absolute but transient property with a limited domain of applicability.

Garcia-Sucre and Bunge (1981) call the Born-Oppenheimer approximation an artifact. They do not elucidate the meaning of this term, but the context suggests that an artifact is something human-made and unrelated to nature. However, 'human-made' is not alien to science, nor does it mean unrelated to nature. Take, for instance, the 'exact' Schrödinger equation basic to non-relativistic quantum mechanics. It was suggested by Schrödinger, not by nature. It was intensively used by other human beings. Nature does not solve Schrödinger equation; it does not know anything about the wave function. Instead, it seems that nature acts like an old-fashioned analogous computer, without resort to digitization. All science was created by humans in a pursuit to describe and understand nature. In this sense all science is an artifact.

Because the term ‘artifact’ is applied also to the material objects produced by humans, we may distinguish science and similar products by saying that they are *ideal artifacts*. Is there any principal difference between the two ideal artifacts of an ‘exact’ wave function and its approximate Born-Oppenheimer version? As discussed above, an exact solution of the Schrödinger equation describes something non-existent, as some philosophers would say. Actually this terminology is misleading, since in fact such an ‘exact’ wave function provides a good, physically justified *approximation*. However, the same might be said about wave functions obtained within the Born-Oppenheimer approximation.

Quantum chemists use the Schrödinger equation in the domain where it is appropriate, although this equation is not exact (since it does not include relativistic effects) and even not the most accurate known. Some researchers go beyond the Schrödinger equation and find interesting and chemically significant relativistic effects (see, *e.g.*, Pyykko 1988). Others go beyond the Born-Oppenheimer approximation and call this non-Born-Oppenheimer chemistry (Jasper *et al*. 2004). Thus, there is no principal difference between using the ‘exact’ (actually approximate) Schrödinger equation and the Born-Oppenheimer approximation. The difference is, first, in the numerical accuracy that can be ensured, and, second, in the possibility of developing a qualitative interpretation and understanding by different approximations. These two features are in a complementary relation, as discussed below in Section 4.

Moreover, the term ‘artifact’ gives the impression of something artificial and subjective, not directly related to nature. This meaning is misleading. The Born-Oppenheimer approximation directly reflects the specific nature of molecules as quantum systems, namely, the fact that molecules consist of heavy particles (atomic nuclei) and light particles (electrons). The ratio of masses governs the accuracy of the approximation. The constitution of molecules and the ratio of masses are all objective properties that in no way depend on the researcher’s will. In this regard, the Born-Oppenheimer approximation is dictated by nature, in a similar sense as quantum properties of microparticles are.

While myriads of approximations are feasible *a priori*, only a few of them are valid (applicable). This is not by accident, but because the latter ones reflect some important features of nature. These approximations reflect nature just as the ‘exact’ equations do, albeit in a different way. They reflect the more *qualitative* side of nature, whereas more exact theories tend to reflect *quantitative* aspects; but both sides are objective and not invented by researchers.

Del Re (2003) has suggested to switch to a more acceptable terminology and talk about the Born-Oppenheimer theorem instead of approximation. The theorem could read as: ‘In the limit $m_e/M \to 0$ the Born-Oppenheimer scheme of calculations provides an exact result, and thus nuclear and electronic motions are completely separated.' (Here, m_e is the electron mass and M is the characteristic mass of atomic nuclei.) The formulation could even be proved in a mathematically rigorous way. However, the problem is that in reality the ratio m_e/M is *not zero*, although fairly small ($m_e/M \approx 1/1837$ if the proton mass is chosen for M); this value is given by nature and cannot be varied. Therefore, the Born-Oppenheimer scheme for finite m_e/M inevitably remains an approximation, although it is well supported by the Born-Oppenheimer theorem. The example shows that, even if some exact mathematical results are available, they do not allow avoiding approximations in practical physical or chemical applications.

It might be mentioned that on a somewhat deeper level the ratio of the characteristic velocities of the particles is physically more relevant than the ratio of masses. Smallness of the velocities ratio serves as a basis for the *adiabatic* approximation that is in principle different from the Born-Oppenheimer approximation, although close in some aspects.

In molecules the characteristic velocities of electrons are usually much higher than those of atomic nuclei. However, in some molecular states the electrons are highly excited and might have velocities comparable to those of the nuclei or even lower. For these highly excited states the Born-Oppenheimer approximation becomes invalid. Such molecular states are less important to chemistry, although they play a significant role in atomic physics. Deviations from the Born-Oppenheimer approximation also occur when there are several equilibrium configurations of atomic nuclei (*i.e.* several minima on the potential surface) separated by potential barriers of moderate height. In this situation *non-rigid molecules* emerge, which are related to the issue of molecular shape discussed in the next subsection. The presence of several minima with the same depth is inevitable if a molecule contains two or more identical atomic nuclei. The permutation of these particles physically corresponds to the tunneling between different potential wells. The rate of such processes is usually very low, which explains why related effects are extremely small. In any case, they can be described within the general framework of the adiabatic approximation, so that the first principles of quantum mechanics are not violated.

The manifestations of the Born-Oppenheimer approximation are apparent in experimental observations, also outside of chemistry. In molecular spectra we see vibro-rotational bands, and not just chaotic sets of lines that would appear in the spectra of general multi-particle systems. This is visible evidence that the Born-Oppenheimer (approximate) separation of nuclear and electronic motion is a feature of nature and not some wishful invention of researchers. Of course, to understand that the band character of a spectrum has this meaning requires some scientific qualification. But this is inevitable in modern science. Below (Section 3.4) we return to the issue of the observability of ideal artifacts.

After this elucidation one might finally agree with Garcia-Sucre and Bunge (1981): an artifact (*i.e.* science created by human beings) does represent some important objective properties of nature. This is exactly what science is about, and there is nothing particular about the Born-Oppenheimer approximation here. Of course, some deeper questions might be pursued further. For instance, the eminent physicist E. Wigner (1995) was puzzled by "the unreasonable effectiveness of mathematics in the natural sciences". But the issue of the Born-Oppenheimer approximation does not present anything specific in this respect.

3.2. Molecular shape

A subject closely related to Born-Oppenheimer approximation is the issue of molecular shape. As already mentioned, in quantum theory a molecule might be ascribed a definite shape by using the Born-Oppenheimer approximation. Within this approximation one has first to replace atomic nuclei by force centers fixed in space and then to solve the quantum problem of the molecular electrons for varying sets of nuclear coordinates. The solutions provide a potential surface that depends parametrically on the coordinates of the atomic nuclei. The next step involves locating minima on the potential surface that indicate the (equilibrium) positions of nuclei in a molecule. At this stage of the approximate construction, a definite molecular shape emerges.

The status of molecular shape has induced much concern among philosophers. For instance, Ramsey (1997) remarks, "… shape is widely thought to be a physical as well as a chemical attribute of the world …" The paper contains an interesting discussion, but the cited statement expresses the origin of many philosophical misunderstandings. Indeed, the term 'attribute' is usually understood to describe some *indispensable* property of matter. The most popular examples are space and time: matter is invariably described in terms of space and time; but in no way does this apply to shape. The situation was well recognized already in antiquity: solid bodies have a shape and a fixed volume, while liquids possess only a volume, but no definite shape. As for gases, they have neither shape nor intrinsic volume, but fill any volume available. This trivial counterexample invalidates such statements as "Classically every physical thing has some geometry or other, but in the quantum theory the notions of spatial structure, shape, and size seem to become hazy if not outright inapplicable" (Garcia-Sucre & Bunge 1981). There is no need to resort to modern quantum physics to discover that some material entities (liquids or gases) do not have a shape of their own, but that the shapes are dictated by the environment (vessels). Interestingly, the analogy with molecules might be pursued further. When a molecule freely rotates, its field is averaged and the shape is not manifest. For instance, there are dipole molecules (such as H_2O), but a freely rotating molecule (in a stationary state with definite values of rotational quantum numbers) cannot possess a dipole momentum. When an external field is applied, or some other molecule approaches, a molecule becomes oriented in space, and its shape or dipole momentum become clearly exhibited. The fact that the molecular shape is recovered only under the perturbation by some external agent has induced some hesitation among philosophers, but we see from our example that such a situation is not unusual even in elementary classical physics.

Of course, the analogy is incomplete, since a molecule possesses some (maybe hidden) shape of its own while a gas or a liquid fits any shape. But since shape is not an attribute, it is not surprising that the molecular shape might remain latent in some situations (freely rotating molecule) while in other contexts it plays a crucial physico-chemical role (for instance, in the X-ray structural analysis of molecules oriented due to some reason, for example, by the surroundings in crystals).

Since shape is obviously a transient property in the macroworld, there is no reason to anticipate that the situation would be different in the microworld. Many phenomena in chemistry are well understood in terms of rigid structures of atoms with definite shapes. However, this cannot be a reason for treating shape as an absolute property in the realm of molecules. Physics clearly shows the limited applicability of the notion of shape in systems of several quantum particles. A shape emerges if two or more particles (nuclei) have masses much larger than the masses of other particles (electrons); in this situation the Born-Oppenheimer approximation is valid, see Section 3.1.[4]

A shape arises as a result of an *approximation*, and this is a common situation in the structure of the 'exact' sciences. A multitude of physically very useful and appealing concepts arise as a result of approximations to 'exact' physical equations; but they are not applicable to the most general systems or situations. Making some approximation-based concepts absolute without justification is a dangerous pitfall, both in practical and philosophical regards. On the contrary, the recognition of the approximate character of concepts does not denigrate them, but reminds us of the existence of applicability limits. Approximation-induced concepts remain illuminating and constructive, although one has to bear in mind the limitations of their use. In the case of chemistry, the limitations might be inferred from physics. This is a typical situation, since physics treats the basic properties of matter in a very broad scope of conditions (potentially it pretends to treat matter in any situation), whereas chemistry focuses on a limited range of conditions and studies the subject matter in more detail, especially concentrating on the structure and transformation of compounds. Chemical compounds cannot exist under certain conditions, for instance, in hot plasmas in the interiors of stars. Therefore it is not surprising that such a property as shape gradually looses its significance in some situations, outside the scope of chemistry. Atomic and molecular physics is a scientific discipline that studies atoms and molecules from a broader perspective, beyond that of chemistry. The outlook provided by this branch of science is useful when philosophical problems of chemistry are analyzed (see some further comments in Ostrovsky 2003a).

3.3. Orbitals

Orbitals appear in the theory that provides approximate solutions for Schrödinger equations of systems with a number of interacting particles larger than two. Many textbooks provide detailed descriptions of the theoretical scheme. A brief exposure suitable for general discussion is given in Ostrovsky 2001, 2003b, and 2004, and will not be repeated here. However, it can be clearly stated that, contrary to some claims, the scheme to construct orbitals lies fully within modern quantum theory (without resort to classical trajectories) and does not violate its general principles, such as the non-distinguishability of electrons. The key physical approximation in the scheme is that any electron moves in the *mean field* produced by the averaged motion of other electrons and nuclei. On the one hand, this physical image can be cast in the mathematical form of equations; on the other hand, it is very useful for developing explanatory patterns for many phenomena in atomic and molecular physics as well as in chemistry. Methodically the approximation is developed along the lines normally used in theoretical physics. It has no particular features that would justify the introduction of a special term, like 'floating model'.

The notion of orbitals has attracted much philosophical attention in recent years. Scerri (2000) describes the situation in theoretical physics and quantum chemistry as follows:

> According to accepted current theory atomic orbitals serve merely as basis sets – that is, as types of coordinate systems that can be used to expand mathematically the wave function of any particular physical system.

Thus, it is said sometimes that the continuing value of orbitals lies in their serving as a basis set, although the orbital model is an approximation in a many-electron system. The problem is that these two statements contradict each other. The same object of a theory cannot simultaneously serve as a basis and as an approximation. A basis in a Hilbert space is analogous to a coordinate frame in geometry. If we consider a point on a plane, we can characterize its position in rectangular, polar, parabolic, elliptic, etc. coordinate frames. All the frames provide equivalent information, and neither of them is approximate;[6] one frame can be only more convenient than the others, depending on the particular problem. The origin of the misconception lies in confusing basis functions $\eta_j(\mathbf{r})$ (which in principle are arbitrary) with orbitals $\varphi(\mathbf{r})$ that are expressed via the basis functions:

$$\varphi(\mathbf{r}) = \textstyle\sum_j c_j \, \eta_j(\mathbf{r}) \qquad (1).$$

The expansion coefficients c_j are found by solving approximate equations; for instance, the Hartree-Fock equations based on the *mean field approximation*. The equations depend on the specifics of a physical system (molecule) under consideration and thus bear the basic physical information about it (for instance, the number of particles, the type of interaction between them, the presence of external fields, *etc*.). So do the orbitals. One can replace the basis set $\eta_j(\mathbf{r})$ by some other set, which results in a different set of coefficients c_j, but the orbitals $\varphi(\mathbf{r})$ remain the same. The latter statement is mathematically exact when both basis sets are complete and thus infinitely large. In practice the basis sets are finite, such that computational chemists or physicists have to check the convergence. This is a purely technical business, inevitable in any application of numerical mathematics to a real problem – the case of orbitals does not bear any specifics.

Once the distinction between basis functions and orbitals is clarified, the puzzling situation described above is resolved: the basis functions $\eta_j(\mathbf{r})$ are indeed 'without physical significance' and might be chosen at the researcher's convenience. However, the orbitals $\varphi(\mathbf{r})$ obtained via solution of physical (albeit approximate) equations 'lie in the heart of much of quantum chemistry', 'as all computational chemists and physicists are aware'.

It is true that, "the term 'orbital' is a highly generic one. It is used to describe hydrogenic orbitals, Gaussian orbitals, natural orbitals, spin orbitals, Hyleraas orbitals, Kohn-Sham orbitals, and so on" (Scerri 2001). Sometimes the terminology might be too loose and thus misleading to blur the distinction between basis functions $\eta_j(\mathbf{r})$ and physical orbitals $\varphi(\mathbf{r})$. For instance, 'Gaussian orbitals' are in fact always basis functions. For physical orbitals, it does not matter if they are constructed as a superposition, according to equation (1), of Gaussian basis functions, or if some other functions, say, Slater functions, are employed for this purpose. To non-specialists that distinction is not obvious and could lead to unjustified bulk statements such as 'it does not matter whose orbitals are selected from the modern palette of choices since none of them refer'.

Further on, there is no ground to say that "the scientific term 'orbital' is strictly non-referring with the exception of when it applies to the hydrogen atom or other one-electron system". In fact, as already indicated (Section 2), the Schrödinger orbitals, strictly speaking, are not exact even for the one-electron hydrogen atom, and the Dirac orbitals are not exact as well. Therefore both the hydrogenic orbitals (*i.e.* the hydrogenic wave functions) and the orbitals in a multi-electron atom are approximations. In this regard, the term ‘orbitals’ is in both cases ‘strictly non-referring’, although that terminology is hardly appropriate, because it underestimates the physically justified approximation. Along these lines, it is worthwhile to correct such statement as ‘atomic orbitals are mathematical constructs’, in order to make it acceptable. Orbitals are not mathematical constructs, since they bear physical information; they are constructs of theoretical physics, or ideal artifact in the sense discussed above. In this respect they are not worse than ‘exact’ wave functions.[7]

In which sense then do orbitals exist? Here one can turn to the paper by Ogilvie (1990) entitled ‘There are no such things as orbitals’. In different terms, but equivalently, the author’s viewpoint might be cast as: orbitals are ideal artifacts. Then the preceding discussion of ideal artifacts fully applies. Orbitals do not exist in nature, just as ‘exact’ wave functions or the Schrödinger equation do not exist in nature: these are all creations of the human mind. Orbitals appear as a result of approximations, just as ‘exact’ wave functions (solutions of the Schrödinger equation). Better approximations are known in both cases, which ensure improved numerical results for quantitative comparison with experiments. Nevertheless, orbitals are important and in wide use for several reasons. First, they reflect some important qualitative features of nature and thus provide an instructive physicochemical insight. Second, they ensure reasonably good quantitative descriptions because of that. Third, orbitals technically serve as a convenient basis for further quantitative refinement of theory. Orbitals are not the result of wishful thinking of theoreticians, but stem from a very physical idea, namely, that an electron motion proceeds largely as if an electron moved in the mean field of other electrons and atomic nuclei. It is important to stress that the orbital picture provides a useful guideline for developing the numerical schemes. Some of the most accurate numerical schemes do not explicitly use the orbital picture and rely on the ‘brute force’ of the computers. The highest numerical accuracy is achieved in this way (for simpler atoms and molecules), but the qualitative understanding is inevitably lost. This is a manifestation of the complementarity discussed in more detail below (Section 4).

The orbital approximation plays a key role in the quantum explanation of the Periodic Table of Elements. This application of orbitals was thoroughly discussed in previous publications (Ostrovsky 2001, 2003a, 2003b, 2004). Here, I only want to indicate that attempts to discard the validity of the modern quantum explanation of the Periodic Table have been mostly based on the mere indication that the orbital picture used in this explanation is approximate. These arguments have been rejected, since an explanation requires the creation of a qualitative image that is usually done by using approximations (see Section 4).

3.4. Approximations and observability

Now I turn to another important question: can orbitals be observed? This is actually an instance of the more general question: can ideal artifacts be observed? Of course, the manifold of ideal artifacts needs to be limited: for instance, a centaur is an ideal artifact beyond the scope of our discussion. Here we discuss only *physical ideal artifacts*, which is just another name for *approximations*. As ideal entities, they cannot be observed in the most direct sense. At the same time, if we consider a valid physical approximation as being based in nature, it is manifested via phenomena of nature, and in this sense it is observable. I will call this *semi-direct observability*. Just in this respect the Born-Oppenheimer approximation or molecular shapes are observable, as discussed in Sections 3.1 and 3.2.

In our everyday life we observe effects and phenomena that are directly related to scientific ideal artifacts. Consider, for example, a shadow. Do shadows exist? Indeed, an unambiguously defined shadow exists only in geometrical optics, which is an approximate theory. The advanced theory of wave optics provides a better approach according to which an absolute shadow does not exist because of diffraction. In other words, it is impossible to define the boundaries of a shadow rigorously, since diffraction fringes appear near the boundaries. For a spectacular presentation of this situation we refer to the figure at the beginning of chapter 10 in a standard textbook of optics by Hecht (2002). It shows a shadow of a human hand holding a dime, illuminated by monochromatic laser light that allows discerning the fringes at the edges of this macroscopic shadow. The lower part of the figure shows the same phenomenon in the microworld, with electrons diffracted on a zinc oxide crystal. Diffraction phenomena depend on various parameters (the light wavelength, the size of the obstacle, the position of the observer), but in principle the phenomenon persists, whereas geometrical optics with its well-defined shadows is only an approximation.

Thus, in physical terms a shadow is an approximation. ('There are no such things as shadows', Ogilvie would say). In everyday life we observe shadows and have no problems to identify them, which is often due to the low resolution of our visual sense. This fact clearly demonstrates that a reasonable, physically justified approximation might be used to describe something real (within the limits of its applicability) and might be perceived by direct observation. The essence of this example is not so far from chemistry as one might imagine. It concerns the relation between the classical (geometrical) description and more general theories that include wave (quantum) features.

Orbitals have systematically been observed for a long time, but in the energy representation.[8] For instance, in the measured photoabsorption cross sections the prominent peaks appear as a result of photoionization from a particular orbital in an atom or molecule.[9] Consider, for example, figures 1 and 2 in Chung 2004.[10] They show the cross section of the photoionization (*i.e.* essentially the yield of photoelectrons) of a lithium atom. When the photon energy is high ($E_{\mathrm{ph}} \approx 60\mathrm{eV}$), the photoionization of valence electrons has a very low yield that smoothly depends on E_{ph}. Superimposed on this background are the sharp and high peaks that are interpreted in terms of photoionization via intermediate resonance states. Each of these states corresponds to the excitation of *two* atomic electrons to various unoccupied orbitals as detailed in the figures. The *doubly excited* states eventually decay with the emission of an electron that contributes to the photoelectron yield. Thus, the explanation of a prominent structure in the experimental observation is achieved solely within the orbital picture; and there is no way to do it without. In this sense we can say that orbitals are observed in the experimental data, albeit in this case on the energy scale, or in the *energy representation*.

In quantum mechanics a physical system is described by a wave function that can be represented in various ways. The space coordinate representation is probably most often employed. It provides standard probability densities in the coordinate space.[11] Along with the coordinate representation, the momentum representation of a wave function is frequently employed in theory. Various experiments directly measure the electron momentum distribution, which is represented by probability densities in the momentum space. In many cases, energy spectra provide the most convenient and direct way to describe a physical system. Nowadays virtually nothing is directly observed in physical experiments, but complicated experimental devices provide 'raw' data that need to be processed.[12] There is no fundamental reason to prefer an observation in the coordinate representation to an observation in the momentum or energy representation; and in the latter representation, as indicated already, the orbitals have been observed long ago.

The observation of orbitals in conventional coordinate space can be inferred from a recent experiment (Zuo *et al.* 1999). Much of philosophical criticism has followed. Meanwhile the imaging of orbitals by various experimental techniques has become commonplace (Feng *et al.* 2000, Litvinyuk *et al.* 2000, Brion *et al.* 2002, Hatani *et al.* 2004). I will not go into details of the interpretation of these experiments. The experiments were carried out using modern state-of-the-art sophisticated techniques and their analysis should be done in a physical or chemical publication, but not in a philosophical one. In some particular cases, the interpretation of an experiment can be doubtful; for instance, a critical analysis of the experiments by Zuo *et al.* (1999) was carried out by Wang and Schwarz (2000a, 2000b) and Zuo *et al.* (2000). I just want to indicate that the experimental observation of orbitals cannot be rejected on general philosophical grounds,[13] because there is no principal objection to the observation of orbitals based on approximations in quantum theory.

3.5. More on orbitals

Scerri (2001) devotes a significant part of his paper to emphasize the approximate status of orbitals in order to conclude only that this aspect is hardly relevant to the reality of orbitals:

> […] the fact that orbitals might only provide an approximation to the motion of many-electron systems is not a sufficient reason for the complete denial that they or something related to orbitals can possibly exist.

Therefore, he puts forward two more arguments to support the idea that orbitals are in principle not observable. However, both arguments refer not only to orbitals, but also to the 'exact' Schrödinger wave function.

The first argument is related to the well-known fact that the wave function $\psi(\mathbf{r})$ is generally complex-valued, $\psi(\mathbf{r}) = |\psi(\mathbf{r})| \exp[\mathrm{i}\, \phi(\mathbf{r})]$, so that its full description requires information not only on its modulus $|\psi(\mathbf{r})|$, but also on the phase $\phi(\mathbf{r})$. Complex-valued functions appear in quantum mechanics when two (or more) stationary states are populated coherently, or when the system is non-stationary (*i.e.*, when its Hamiltonian is time-dependent), or when a magnetic field is present. It is also known that the phase $\phi(\mathbf{r})$ is trivial in the case of *stationary* (bound) states (which were actually the object of experimental analysis) and in the absence of a magnetic field. The phase depends linearly on time t and not on the electron coordinate $\mathbf{r}$: $\phi = -\mathrm{i}E_\mathrm{b}\, t + \alpha$. Here E_b is the bound state energy and the constant α is independent of $\mathbf{r}$. This constant is insignificant since it does not influence any observable. Therefore, the phase can be treated as non-physical and neglected, such that the wave function may be considered a real-valued magnitude. A somewhat more complex situation emerges in the case of degeneracy, but this consideration can be restricted to real-valued functions.

Many experiments probe the electron charge density $\rho(\mathbf{r})$ that is proportional to the probability density $|\psi(\mathbf{r})|^2$, $\rho(\mathbf{r}) = e\, |\psi(\mathbf{r})|^2$, where e is the electron charge. Bearing in mind that the wave function phase might be omitted, one has to carry out only the square root operation, $\psi(\mathbf{r}) = \pm\, [(1/e)\, \rho(\mathbf{r})]^{1/2}$, to restore the wave function from the electron density. Here the symbol ± requires some attention, since in general even a real-valued wave function oscillates around zero and thus is positive or negative in different domains of space. The dividing boundaries are known as the nodal surfaces. Each crossing of a nodal surface means a change of the wave function sign. The nodal surfaces [*i.e.*, the zero value surfaces for the density $\rho(\mathbf{r})$] might in principle be defined from experiments. Then the wave function can be fully restored from the observable charge density. This might be considered a semi-direct observation, albeit not a direct observation of $\psi(\mathbf{r})$ in the strict sense. However, as already stressed, in modern experiments virtually nothing is directly observed and some processing of raw data is always required. With this in mind, we may conclude that there are no theoretical obstacles to the semi-direct observation of wave functions of stationary states.

The second argument reads:

> […] atomic orbitals are described in a many-dimensional Hilbert space which denies visualization since we can only observe objects in three-dimensional space. [Scerri 2001]

This point reveals a misinterpretation. The Hilbert space theory is a mathematical apparatus that has found useful applications in quantum theory, but which is in no way limited to it. Any regular function, for instance, any function of a coordinate, might be regarded as a function belonging to some Hilbert space. For example, the electron density might be considered as belonging to a Hilbert space, but this does in no way preclude its observability. When the Schrödinger equation is solved, the eigenfunctions can be regarded as elements in an infinitely-dimensional Hilbert space; but they are simultaneously defined in the conventional three-dimensional space.

A more reasonable point to consider is the fact that a wave function is defined in the configurational space. The latter is three-dimensional for a single electron, which allows visualization of the probability distribution. For two electrons the configurational space is already six-dimensional, and the complete probability distribution $\rho(\mathbf{r}_1, \mathbf{r}_2) = |\psi(\mathbf{r}_1, \mathbf{r}_2)|^2$ cannot be visualized.[14] The charge distribution is obtained by wave function convolution. For an N-electron system the electron density is

$$\rho(\mathbf{r}) = \int d\mathbf{r}_2\, d\mathbf{r}_{3\,\ldots}\, d\mathbf{r}_N \,|\, \psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \ldots \mathbf{r}_N)\,|^2 \qquad (2),$$

where $\mathbf{r}_j$ is the coordinate of the j^{th} electron. The formula suggests that the wave function cannot be exactly restored from the electron density. In terms of atomic orbitals this is reflected in the fact that in a multi-electron system all the orbitals filled by electrons contribute to the observed charge distribution. In order to separate the contribution of a single orbital, the experimentalists (Zuo *et al.* 1999) used a special technique critically analyzed in the subsequent discussion (Wang & Schwarz, 2000a, 2000b; Zuo *et al.* 2000). These developments are beyond the scope of the present study, however.

To conclude this section, it should be stressed that the orbital approximation, as any other approximate or ‘exact’ theory, has its limitations. The applicability of the orbital picture reflects *objective* properties of atomic and molecular states, which are not universal. For instance, for some doubly (or multiply) excited states the electron motion is strongly correlated and the mean field picture does not hold even as a first-order approximation (for a bibliography see Prudov & Ostrovsky 1998). Some examples of the orbital picture breakdown were discussed previously (Ostrovsky 2001, 2003b); often they belong to atomic physics rather than to chemistry. However, the applicability domain is still large enough for orbitals to be 'in the heart of most of quantum chemistry'.

3.6. Rejecting the existence of orbitals

There are various possibilities to reject the existence of orbitals on philosophical grounds. To start with, some philosophical systems deny the reality of an objective material world, *i.e.* nature. Then the orbitals are rejected as a part of it.

Another possibility is based on the philosophical distinction between properties and things, or properties and substances. It is impossible to object to statements like 'An orbital *as such* is not observable; what is observable are its properties'. I would like to indicate only that there is nothing special about orbitals. Any physical experiment implies observing (measuring) some properties of the object of study. The object *as such* is never observed – if one does not hold to the naive view that observing something means seeing it by someone's eyes. For instance, only the properties of molecules are observed, but not molecules *as such* – large molecules became accessible to some kind of experimental 'viewing' only recently, and in any case this is not viewing by someone's eyes. Such a situation provides a basis for skepticism that could last for a long time, as the widely known example of the prominent physicochemist Ostwald shows. Skepticism is a legitimate constituent of scientific approach; the point is that there is no fundamental difference in this respect between orbitals and molecules (the idea of this particular analogy belongs to W.H.E. Schwarz).

Yet another possible type of objection could be as follows. Imagine that someone attributes a peak in the photoelectron spectrum to the ionization from a particular electron orbital, and then quantitatively describes the peak position based on the orbital calculations. A skeptic is not convinced but says that from the very beginning the scheme of calculations already presupposes the orbital picture. Again, this argument is not specific to orbitals or any other approximate scheme, but in fact refers to the conventional physics approach. For instance, when the energy levels of a hydrogen atom are calculated, it is presumed that the stationary states and the energy levels exist and that they correspond to regular solutions of the Schrödinger equation.

Note that the fact that the theory operates with occupied (actual states) and non-occupied (potential states) electron orbitals is also not specific to the orbital approximation. ‘Exact’ quantum mechanics considers a variety of stationary states of any quantum system (for instance, an atom or a molecule) that are only potentially populated. For an atom in the ground state, all the excited states are potential states that might be excited under external perturbation.

3.7. Further examples of approximations

In this subsection we give two further examples of approximations that seems to be of interest in the present context.

According to modern theory, a chemical substance as common as water is only approximately stable. “Indeed, let us consider the system consisting of ten electrons, ten protons, and eight neutrons. These constituents can produce a water molecule or a neon atom with ^{18}Ne nucleus” (Belyaev *et al*. 2001). The probability of such a molecular-nuclear transition from the water molecule to the neon atom is expected to be very small from general considerations. However, it is enhanced due to the presence of a particular resonance state in the ^{18}Ne nucleus. At present it is difficult to evaluate the lifetime of water theoretically, and special experimental searches have not succeeded in detecting the reaction. Nevertheless, there is no rigorous conservation law that forbids such decay, and, as a general rule of quantum mechanics, everything that is not forbidden by strict selection rules proceeds with some probability.

In hydrodynamics an approximation of an *ideal liquid* has been employed for quite some time. It implies the neglect of liquid viscosity and hence the energy dissipation emerging due to viscosity. Originally this approximation was inspired by its mathematical simplicity and beauty. In reality viscosity becomes important in the boundary layer along the surfaces that limit the liquid flow. Garcia-Ripoll and Perez-Garcia (2001) state, “John von Neumann noticed that most mathematical models of the date [around 1900] did not take viscosity into account and thus could not explain the features of real fluids. He coined the term ‘dry water’ to refer disrespectfully to those idealized models that did not care take account of dissipation (R. Feynman, 1964). Bose-Einstein condensate represents an experimental realization of such a ‘dry fluid’ or superfluid”. This example teaches us that approximations have sometimes a particular fate. Starting as mathematical playgrounds, they can eventually find a manifestation in unusual states of matter. This is yet another case of “the unreasonable effectiveness of mathematics in the natural sciences” (Wigner 1995).

4. The epistemological value of approximations

A professor in theoretical physics at St. Petersburg State University used to say to his students, 'Imagine how poor, scarce and insufficient our knowledge would be if we knew only exact wave functions'. At first glance, that appears paradoxical. Indeed, according to quantum theory, the wave function contains all the information of a physical system and allows calculating any physical observable. Nevertheless the saying contains an ultimate truth. Knowledge of only numerical values is insufficient for understanding, because explanations are most often cast in terms of the qualitative images induced by approximations.

The term 'explanation' has several meanings. Quite often it is used to denote a deduction from a more general theory. However, it seems that the term 'prediction' is more appropriate than 'explanation' in this situation. In quantum measurements 'explanation' is often understood as a mapping from the quantum physics of the actual system onto the classical point of view of an observer. However, we believe that researchers in quantum mechanics develop a special kind of 'quantum intuition' that allows a direct understanding of quantum objects without appeal to classical analogues (see, *e.g.*, Zakhar'ev 1996).

The 'exact' equations for complicated physical systems provide only limited insight. Few general theorems can be proved rigorously, like the probability conservation for the Schrödinger equation, but only very restricted possibilities are available to create qualitative images and patterns. In our pursuit of exploring nature we need both quantitative information and qualitative understanding. It is useless to ask which of the two is more important; both aspects are essential. However, we cannot obtain both fruits in a single approach. When we make our numerical schemes more and more sophisticated, the physical meaning becomes non-evident and only numbers emerge from the computer black box. On the other hand, approximate models provide a qualitative and often semi-quantitative description, though not of highest precision.

Another example of very useful images created by approximations is the theory of chemical exchange reactions (without electronic transitions) viewed in terms of motion along a potential surface. This approach provides much understanding and is a quantitatively reliable tool, although it is based on an approximation, namely the Born-Oppenheimer approximation discussed in Section 3.1. My point is that in the preceding sentence it would be reasonable to replace 'although' by 'because'. As pointed out by Del Re 2003, some researchers believe that the Born-Oppenheimer approximation has 'no physical content'. My position is just the opposite: physical sense emerges in the frameworks of approximations.

Modern researchers, when obtaining some numbers from their computers, frequently remain dissatisfied and seek for the *physical sense* of the results. While it is difficult to provide a complete definition of what 'physical sense' means, it implies, to a significant extent, the capability to interpret the numerical results in terms of simple models and qualitative images. All this comes from approximations and models.

Approximations and models are a fully legitimate part of a theory, and not its temporary, abominable, and shameful part. Every textbook in quantum mechanics includes some *simple* problems, such as bound states in one-dimensional potential wells, scattering on a potential barrier, harmonic oscillator, hydrogen atom, *etc.* Most of these problems are included not because they provide an accurate description of nature, but because they allow students to understand important qualitative quantum concepts, such as the shape of the bound-state wave function, the tunneling phenomenon, the above-barrier reflection, *etc*. The basic approximations and the simple model problems with easily grasped properties form an appropriate language to develop explanations of more complicated situations. Of course, as with every language, such explanations are addressed to a knowledgeable audience.

The current progress in computer techniques makes the *complementary relation between calculations and explanation* even more important. Niels Bohr put forward the idea of complementarity first on the basis of physics where the complementarity between coordinate and momentum is expressed by Heisenberg's uncertainty principle. According to this principle one can measure with an arbitrary precision either the coordinate of a particle or its momentum, but not both simultaneously. Bohr realized that this type of relation is very generic. He applied the *complementarity concept* to a broad variety of fields outside of physics, such as psychology, biology, and anthropology (Bohr 1999). This concept is epistemologically significant because it is about a very general pattern of relations between subject and object. As to the complementary pair of numerical calculations and explanations, numerical calculations seek to reproduce a physical object with the highest possible quantitative precision, whereas explanations appeal to a subject and rely on qualitative images (Ostrovsky 2001). This also means that an explanation appeals to a community of researchers with a common background only, which may be different in other communities. The complementary pair numerical calculations/explanations might be considered as a particular implementation of the more general pair quantity/quality.

If one's objective is to obtain the best numerical results, then approximations are something to avoid or to limit as much as possible in the course of scientific progress: fewer approximations provide better numerical output. However, the bare 'exact' equations for a complex system provide very limited insight and are a barren ground for explanations. Explanatory concepts of high heuristic potential are born out of approximations. They inspire the intuition that is a powerful vehicle for the advancement of science. In Section 3 it was shown that key concepts of chemistry, such as molecular shape or molecular orbitals, directly emerge from approximations. If one seeks for explanations, then dropping some approximations might hopelessly destroy the entire framework. This, of course, does not necessarily mean that the same set of explanatory approximations or models would be retained forever. On the path of historical progress the models could be substantially modified or even completely new models could be developed. However, models and approximations remain a substantial and inevitable part of explanations of complex systems, and not some temporary deficiency.

5. Conclusion

Thus far I have discussed both objective and subjective features of approximations, and one might argue that approximations have either a subjective character or an objective one and that both cannot be true at the same time. However, the point is that these features are not manifested simultaneously and in the same meaning. It is worthwhile to summarize my view once again.

In many essential regards there is no basic difference between approximations and 'exact' equations. The natural sciences combine objective and subjective sides that are inseparable. On the one hand, the potential goal of science is to reflect nature in the most exact way, which means objectivity. On the other, science is created by humans and simply would not exist without the existence of subjects. Therefore science has inevitably subjective aspects. The technical aspects of the formulation of results and their dissemination, the particular ways of advancement in science, the existence of different although mostly complementary approaches – all these bear a strong flavor of subjectivity. Science cannot exist without such notions as understanding or intuition, which are clearly subjective. Science is a kind of interface between objects and subjects, and the same refers to its important part – approximations.

The term 'approximation' belongs to the well established and universally accepted terminology in the exact sciences, such that one should not change the terminology by replacing it with other terms, such as 'theorem'. The latter has a different meaning and cannot substitute 'approximation'. It is important to develop a proper meaning of the term 'approximation' and to appreciate its significance in all aspects of science, including ontological and epistemological implications.

Now I summarize the main points of this work.

- A physical theory should not be blamed for using approximations because approximations are ubiquitous in the 'exact' sciences. Only invalid, physically (and mathematically) unjustified approximations discredit a theoretical scheme, and an approximate approach should not inappropriately be extended beyond its applicability domain. Acknowledging the approximate character of a theory or an approach cannot terminate a scientific or philosophical discourse, but is only the beginning. The failure to recognize the approximate character of a notion leads to fallacious absolutization and philosophical confusion.
- A valid approximation is not a researcher's subjective and voluntaristic construction, but a reflection of nature's features; it is not inferior to 'exact' equations. Approximations reflect the more qualitative side of nature, while 'exact' theories tend to characterize its quantitative side. Valid approximations are deeply rooted in nature, in some sense they are observable via characteristic features of natural phenomena.
- The hierarchy of approximations creates a path (and probably a unique one) to scientifically constructed qualitative images, notions, and patterns that emerge from 'exact' equations. By basing studies on approximations, semi-quantitative and qualitative approaches are developed, which are invaluable in science, particularly in chemistry. Thus, approximations are the most precious fruits of theory, which should be considered in the philosophy of science.
- The 'exact' quantitative approaches and the intuition-inspiring approximations form a complementary pair in the universal sense of Niels Bohr's complementary relations in nature and society. In this dual relation, the quantitative results represent the more objective side of nature while the qualitative approximation-induced images rest on the subjective side of the researchers' interpretation of nature. Very often we progress in science via the development of approximate approaches.

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Notes

[1] Among the notable exceptions I indicate papers by Fock (1936, 1974), Pechenkin (1980), Ramsey (1997), Del Re (2000), and Friedrich (2004).

[2] It should be recognized that the present author, as a practicing physicist, holds to realism and understands by 'nature' an objective reality, as opposed to the subjective observer.

[3] The distinction between approximations and models is an interesting and sometimes subtle issue not pursued here. However, one aspect could be indicated: approximations are *derivable* from more general (*i.e.* more exact) theories, while models are *constructed* in order to grasp some important features of physical reality. From this point of view, the non-relativistic Schrödinger equation is rather an approximation (since it is derivable from the Dirac equation) than a model.

[4] Born-Oppenheimer and adiabatic approximations are often not properly distinguished in the literature. In the rigorous sense, the Born-Oppenheimer scheme implies expansion of the total (electronic and nuclear) molecular Hamiltonian in terms of a small parameter that proves to be $(m_e/M)^{1/4}$, which is much larger than the mere ratio m_e/M. In the lowest order of the approximation, the atomic nuclei are localized near their equilibrium positions and their motion proceeds in a harmonic oscillator potential. Anharmonicity appears in the higher orders of the approximation. Thus, the genuine Born-Oppenheimer scheme is inconvenient when the strongly anharmonic vibrational motion close to the dissociation limit is considered. Moreover, the scheme is fully inapplicable for the treatment of atom-atom (or atom-molecule, or molecule-molecule) collisions. The adiabatic approximation is devoid of these deficiencies.

[5] There are some other cases, not related directly to chemistry, where a composite quantum system exhibits some properties that are interpreted in terms of a shape. Some heavy atomic nuclei show rotational structures in their energy spectra, which is evidence of the non-spherical (ellipsoidal) shape of such nuclei. In the nuclei, all the constituent particles (nucleons) have comparable masses, and the spontaneous breaking of spherical symmetry cannot be explained via the Born-Oppenheimer approximation. A vibro-rotational structure was also found in the energy spectra of doubly excited atomic states (see, for instance, Prudov & Ostrovsky 1998 and the bibliography therein). Isolated atoms might have anisotropic properties that also do not rely on the Born-Oppenheimer approximation. For instance, the excited states of the hydrogen atom might possess an electric dipole momentum (so-called Stark or parabolic states). For an arbitrary atom the states with a non-zero total angular momentum J and definite projection M_J are magnetic dipoles. The states with $J > 1/2$ have an electric quadrupole momentum *etc.* All these anisotropic properties are revealed by the application of weak external fields.

[6] Note that the *truncation* of a basis set is an approximation.

[7] A careless characterization of orbitals as 'mathematical constructs' sometimes appears even in the professional physics literature. The most recent example is Hatani *et al*. 2004. The wording (cursory used in the abstract) is in contradiction to the content of the paper which discusses a sophisticated experimental technique employed for the *observation* of orbitals.

[8] In quantum mechanics a wave function might be expanded over different basis sets. It is said that the set of expansion coefficients provides a wave function *representation* in a given basis. Thus, representation is a rigorously defined notion of

quantum theory. All the representations contain equivalent information on the wave function. They are related to each other by unitary transformations. Among the most frequently used representations are coordinate, momentum, and energy representation; the latter one employs a basis of eigenfunctions of energy, *i.e.* the Hamiltonian operator.

[9] Note that not only the outer (valence) orbitals, but also the inner-shell orbitals might be probed in this way.

[10] The choice of the particularly recent review-type paper is rather casual, since observation and calculation of these types of phenomena have been carried out for decades.

[11] The actual experiment might measure the charge density of an electron cloud that is proportional to the probability density, see also Section 3.5.

[12] In the philosophical literature, some experiments are characterized as theory-laiden, implying that they are not trustworthy. Actually almost all serious current experiments are strongly theory-laiden. Of course, vicious circles are to be avoided and the applicability of theoretical formulations should be attentively controlled.

[13] Thus the philosophical criticism of the observability of orbitals was met with skepticism in the physics community.

[14] The configurational space is used to describe the motion of classical particles. For *N* particles it has dimensionality 3*N*. Nevertheless this does not preclude visualization of classical particles motion because classical objects are sharply localized, in contrast to quantum particles spread in space.

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