Is a molecular orbital measurable by means of tomographic imaging?

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Abstract Interpretation of experiments involving use of vacuum ultraviolet radiation to effect ionization of N_2 in terms of measurements of a molecular orbital is erroneous.

Keywords Orbital · Mathematical function · Experimental observable · Spectrometry

Itatani et al. (2004) claimed to measure a "molecular orbital" and presented a highly regular and detailed diagram of that claimed molecular orbital obtained through "tomographic imaging". As such a claim is incongruous with the established properties or nature of a molecular orbital (Pauling and Wilson 1935), the purpose of this essay is to challenge this assertion; we discuss also other aspects of their article that have a bearing on the credibility of their analysis as a basis of that claim.

According to a standard definition (Pauling and Wilson 1935), an orbital is a mathematical formula that arises as an exact algebraic solution, generally denoted ψ , of Schroedinger's temporally independent, partial-differential equation in three spatial dimensions, $H\psi = E\psi$, for a system of one electron; this system might be hydrogen atom H for an atomic orbital or dihydrogen molecular cation H_2^+ for a molecular orbital, or an equivalent system such as He^+ for an atomic orbital (Pauling and Wilson 1935). That orbital is hence an amplitude function or wave function that is required as an operand on which differential operator H, and other operators, operate. For this mathematical quantity, Pauling and Wilson (1935) used a precise term "orbital wave function". Although each such solution ψ is, for the corresponding system, an algebraically exact formula—but only with a fixed atomic nucleus for H or fixed nuclei for H_2^+ , the Schroedinger equation is a non-relativistic approximation, among other prospective deficiencies; if one were to postulate an exact wave function for a mathematical model to apply to a real atomic or molecular system involving only one electron,

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that orbital wave function would serve as only an approximation of that exact wave function. Another property of Schroedinger's equation is that each such amplitude function multiplied by any fourth root of unity yields invariant observable properties; no particular such fourth root is thus logically preferable. A further pertinent aspect is that Schroedinger's wave mechanics is only one particular mathematical method within quantum mechanics—one of two methods that together comprise *pioneer quantum mechanics*; in the other method called matrix mechanics, no wave function arises. For these reasons, an orbital wave function, or in general any formula ψ as a solution of Schroedinger's equation, is merely an artefact of one particular, and approximate, mathematical method among those several methods collectively comprising quantum mechanics; any one of these might serve for a calculation of a molecular property such as energy E. Moreover, as electrostatic repulsion between electrons, and their intrinsic angular momenta, are necessarily absent from that simple treatment of a hydrogen atom or a dihydrogen cation, but are important for an atomic or molecular system containing multiple electrons, an orbital wave function is rigorously extraneous to such a system. On this understanding of the definition and properties of an orbital, we proceed to consider the questionable claim.

The title of the article (Itatani et al. 2004) alludes to "orbitals"—i.e. plural; their text specifies, and accompanies a depiction of, only one, single, purported orbital, and the experimental method seems in general limited, according to the description, to the prospective measurement of merely a single "molecular orbital" of any molecule—the first of several instances of imprecision in this article (Itatani et al. 2004). These authors described what they claimed to measure as an "orbital", but analysis of their description makes clear that they likely meant instead a Feynman-Dyson amplitude function, which is an integral over all space of a total molecular wave function, ψ_n , for a neutral molecule with electrons numbering *m* and another total molecular wave function, ψ_c , for the corresponding molecular cation with *m*-1 electrons:

$$\varphi^{\text{Dyson}}(r_m) = \int \psi_n(r_1 \dots r_m)^* \psi_c(r_1 \dots r_{m-1}) \, \mathrm{d}r_1 \dots \mathrm{d}r_{m-1}$$

Although such a function has the same physical dimensions, $m^{-3/2}$ in SI units, as an orbital, it clearly fails to conform to the definition of an orbital as recalled above; the original designation of this quantity was Feynman-Dyson amplitude function (Ortiz 1990), which is more appropriate and precise than Dyson orbital or Dyson function. Such a Feynman-Dyson amplitude function $\varphi^{\text{Dyson}}(r_m)$ clearly depends on the state of the molecular cation to which putative wave function ψ_c pertains. Even within a primitive orbital approximation, wave function ψ_c of the cation is not simply that, ψ_n , of the neutral molecule but with one less electron with which is associated a particular constituent orbital wave function, $\varphi(r_m)$, because of both orbital relaxation—the nature of the other constituent orbital wave functions varies between the two molecular wave functions ψ_n and ψ_c —and electronic correlation-a single product of orbital wave functions is a poor approximation to the putative total molecular wave function. A notable instance of the failure of this approximation, attributed to Koopmans (1934), is, in particular, molecular dinitrogen, N_2 (Cederbaum et al. 1973). Either a Feynman-Dyson amplitude function or any atomic or molecular wave function has a formally infinite extent, whereas the "molecular orbital" depicted by Itatani et al. (2004) appears remarkably bounded, but that effect might reflect the poor quality or a truncation of their calculations, or experimental error.

All preceding remarks have a theoretical basis: an amplitude function, whether a direct solution from Schroedinger's equation or of type Feynman-Dyson, is a purely algebraic formula that exists in a purely mathematical domain as an artefact of a particular mathematical method within a collection of mathematical methods called quantum mechanics. The remainder of the article of Itatani et al. (2004) is inconsistent with a correct declaration, in the first sentence of their abstract, that "single-electron wave functions, or orbitals, are... mathematical constructs"; the definition (Cambridge Dictionary on internet) of construct is "an idea or an imaginary situation". On that basis, their claim (Itatani et al. 2004) to have measured, in a physical experiment, a mathematical formula is preposterous.

Regarding experimental aspects of the basis of their nonsensical claim, the formation of the molecular cation N_2^+ was effected by means of ionization of (gaseous) molecular dinitrogen N₂ in its electronic ground state, designated X ${}^{1}\Sigma_{g}^{+}$, with radiation generated simultaneously as harmonics 17-51 of light at 800 nm. As the energy of photons at the upper bound of that range is more than five times the first ionization energy of N₂ from its electronic ground state, clearly molecular cation N_2^+ formed might be present in multiple electronically excited states; through a spectral transition, at least four of these states are as readily accessible as the electronic ground state of this molecular ion. According to the claim that the rate of tunnel ionization depends (presumably negatively) exponentially on the ionization energy, the proximity of the first two single ionization energies of N_2 at 15.6 and 16.98 eV (Cederbaum et al. 1973) implies that the recorded signal from a first ionization is contaminated to at least 25 per cent with the signal from a second ionization. Associated with these excited states are thus, within the Schroedinger framework, at least two, and perhaps even five, distinct molecular wave functions ψ_c ; there is hence no logical basis for excluding any of them from participation in the allegedly measured function. In any case, because the first electronically excited state is associated not with a vacancy in the 'highest occupied molecular orbital' ('HOMO'), which is $1\pi_0$ (Cederbaum et al. 1973), a claim that the depicted (Itatani et al. 2004) quantity pertains to that particular orbital wave function must be incorrect, even if one might make a physical measurement of a mathematical formula, which is manifestly impossible. According to the designation X $^{1}\Sigma_{g}^{+}$ for the electronic ground state of N₂, and X $^{2}\Sigma_{g}^{+}$ for the electronic ground state of N₂⁺, the transition dipolar moment must lie along the internuclear axis, whereas the highestoccupied molecular orbital (Cederbaum et al. 1973) is aligned perpendicular to this axis, contrary to the depiction of Itatani et al. (2004). The assertion by Itatani et al. (2004) that "the orbital with the lowest ionization potential [sic, energy, according to the equation at top right of page 868] (the 'HOMO' in an unexcited molecule) is preferentially excited" demonstrates confusion between mathematical formulae, which can not be excited or ionized, and molecules, which can be ionized, but the 'HOMO' in this case of N_2 is not even 2p $\sigma_{\rm g}$ that is claimed to be measured but 2p $\pi_{\rm u}$ (Cederbaum et al. 1973).

The deduced picture in figure 4 (Itatani et al. 2004) that is "reconstructed" from a tomographic inversion of "high harmonic spectra" is purported to result from a Fourier transform of the measured squares of a transition electric dipolar moment, which is a complex tensor, calibrated on the basis of a supposed " $2p_x$ " orbital of Ar according to calculations of uncertain quality; this $2p_x$ amplitude function arises necessarily from a real, linear combination of complex $2p_{+1}$ and $2p_{-1}$ orbital wave functions of H, according to the standard convention of labeling atomic orbitals (Pauling and Wilson 1935). Moreover, the 'highest occupied *atomic* orbital' of Ar would—if one might describe a mathematical formula as being occupied—be 3p, not 2p. The authors claimed that the presence of positive and negative values of a quantity with symbol " $\psi(X)$ " proves this quantity to be "a wave function, not the square of the wave function, up to an arbitrary phase", but the authors made assumptions about the sign associated with the magnitude of the matrix element and about the polarization of the emission. As in other spectral experiments, the purportedly measured quantity (Itatani et al. 2004) is an intensity that is proportional to the

square of the modulus of that dipolar moment; this complex moment itself, rather than its measured square, is stated to be "a spatial Fourier transform of the [non-existent] orbital in the x direction" (the relation between x and X is undefined), so taken as lying along the internuclear axis, which is conventionally designated z (Pauling and Wilson 1935). A Fourier transform of a complex quantity can not yield a quantity symmetric, according to figure 4 (Itatani et al. 2004), with respect to a centre of inversion between the two atomic nuclei.

In view of not only the multiple assumptions and approximations in the calculations of multiple stages between the measured intensities, as a function of angle between the internuclear axis and the axis of polarization, in the experiment described as "tomographic imaging of an orbital" and the eventual purported picture of an orbital, but also the inaccuracies and confusion of the authors exhibited in their presentation, their claim (It-atani et al. 2004) of physical measurement of an orbital wave function is clearly incredible. As an example of understatement by the same authors, there appears a remark (Itatani et al. 2004) "Yet single orbitals are difficult to observe experimentally"—in truth, not merely difficult but *impossible*, for manifest reasons expounded above. As their second reference, these authors cite a book (Pauling 1960) of title *The Nature of the Chemical Bond…* by an author identified as "C. P. Linus"! If the quality of their analysis of experimental data match the quality of preparation of this article by these authors, one might, in any case, have no faith in their conclusions.

A "free public lecture" of title "Catching Electrons with Light" was advertised (Vancouver Sun newspaper) with an assertion that "lasers can now make light flashes fast enough to photograph the atoms and electrons in a molecule", to be presented on 2010 July 13 by Dr. Paul Corkum, a senior coauthor of the article by Itatani et al. (2004). A sheet of paper distributed at that lecture states "the world's shortest light pulses are measured in attoseconds-short enough to freeze the motion of valence electrons in atoms and molecules", but electrons are fundamentally indistinguishable-there is no valence electron, no core electron, no σ electron, no π electron—only an electron. That paper continues with a claim that "we have 'photographed' a molecule's electrons and the position of its atoms the first frame in a molecular movie which we plan to produce". Scrutiny of the figures in the article by Itatani et al. (2004) shows no photograph of an electron but only features possibly attributable to some aspects of a spatial electronic distribution; apart from the fact that there is no atom in a molecule—only electrons and atomic nuclei, these figures show nothing directly attributable to the relative location of the nitrogen nuclei. Needless to relate, during that public lecture there was shown no "photograph [of] atoms and electrons in a molecule", but there was stated inaccurate history: although that year 2010 was the fiftieth anniversary of the operation of the first laser, the first "movies" were made not "a century and a half ago" but in 1877 or 1881. Such gross exaggeration of the meaning of tenuous experiments and inaccurate scientific and historical fact is reprehensible.

A preceding discussion (Schwarz 2006) of the article by Itatani et al. (2004) appears to be based on an acceptance of an orbital as other than a mathematical or algebraic formula—although what an orbital is seems not to have been precisely defined—and, thus, an acceptance that a physical measurement of orbitals might be practicable, provided that orbitals are uniquely defined through real physical processes that might be reasonably approximated with a specified orbital model; that view of an orbital is contrary to established terminology (Pauling and Wilson 1935), and the proviso seems inconsistent with rigorous mathematical properties of wave functions (Pauling and Wilson 1935). Other discussion (Schwarz 2006) concerns aspects different from those examined here.

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There is no such (tangible) thing as an orbital (Ogilvie 1990)! There exist properties of atoms and molecules that one can measure experimentally, described as physical observables, but an orbital wave function, as a mathematical formula, is not one of them. Of two other erroneous claims about orbitals from experiments reflecting either wishful thinking or lack of understanding of fundamental concepts, a claim to have observed a $3d_{z^2}$ orbital of Cu (Zuo et al. 1999), based on comparison of results of an approximate calculation with necessarily imprecise experimental measurements of electronic densities with xray and electron diffraction of crystalline CuO, is deprecated (Wang and Schwarz 2000); even in this case, the authors conceded that what was claimed to be observed was not an orbital but merely its square, interpreted as an electronic density—or actually the lack thereof (Zuo et al. 1999). Further discussion of the physical and philosophical aspects of this experiment and of its interpretation is available elsewhere (Wang and Schwarz 2000; Scerri 2000). A claimed "wave function for Be" (Jayatilaka 2000) is likewise a result of calculations in several stages and with various assumptions and approximations, based on fitting 361 independent parameters with 58 experimental measurements from xray diffraction! All three instances of measurements or observations of an orbital or wave function from experiments represent pathological science (Rousseau 1992).

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