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# Chemistry, Spectroscopy, and the Question of Reduction

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## Modern Chemical Education. Too Much So-Called Theory?

The modern approach to chemical education appears to be strongly biased toward theories, particularly quantum mechanics. Many authors have remarked that classical chemistry and its invaluable predictive rules have been downgraded since chemistry was put into orbit around physics. School and undergraduate courses as well as textbooks show an increasing tendency to begin with the establishment of theoretical concepts such as orbitals and hybridization. There is a continuing debate in the chemical literature on the relative merits of theory as opposed to qualitative or descriptive chemistry (1–6). To quote the late J. J. Zuckerman who supported the latter approach (3).

Inorganic chemistry is facing an identity crisis. The old jumble of facts has given way to the new jumble of theories. Worse still the distinction between fact and theory itself has been allowed to blur. Inorganic chemists have been coaxed away from their formerly strong, central position based on a monopoly of information on syntheses, reactions, and properties of the elements and their compounds by the more ephemeral allure and false sophistication of spectroscopy and theory.

The supporters of this view appear to be fighting a losing battle if one considers the pervasiveness of the current orbitals paradigm in chemistry (2). Atomic and molecular orbitals are freely used at all levels of chemistry in an attempt to explain chemical structure, bonding, and reactivity. This is a very unfortunate situation since the concept of orbitals cannot be strictly maintained in the light of quantum theory from which it supposedly derives.

The notion of electrons in orbitals consists essentially of ascribing four distinct quantum numbers to each electron in a many-electron atom. It can be shown that this notion is strictly inconsistent with quantum mechanics (7). Definite quantum numbers for individual electrons do not have any meaning in the framework of quantum mechanics. The erroneous view stems from the original formulation of the Pauli principle in 1925, which stated that no two electrons could share the same four quantum numbers (8). This version of the principle was superseded by a new formulation that avoids any reference to individual quantum numbers for separate electrons. The new version due to the independent work of Heisenberg and Dirac in 1926 states that the wave function of a many-electron atom must be antisymmetrical with respect to the interchange of any two particles (9, 10).

The use of the older restricted version of the Pauli principle has persisted, however, and is routinely employed to develop the electronic version of the periodic table. Modern chemistry appears to be committing two mistakes. Firstly, there is a rejection of the classical chemical heritage whereby the classification of elements is based on the accumulation of data on the properties and reactions of elements. Secondly, modern chemistry looks to physics with reverence and the false assumption that therein lies the underlying explanation to all of chemistry. Chemistry in common with all other branches of science appears to have succumbed to the prevailing tendency that attempts to reduce everything to physics (11). In the case of the Pauli principle, chemists frequently fall short of a full understanding of the subject matter, and

advocate its use without realizing that their version of the principle is strictly inconsistent with current physics.

## The Periodic Table According to Chemistry or According to Spectroscopy

There are two ways to develop the periodic table of elements. The first is based on chemical evidence and is the version originally proposed by Mendeleef and others. The second method is based on the electronic configurations of atoms, as first suggested by Bohr, and based on atomic spectroscopy (12). The second scheme is the more recent, of course, and, since it was first proposed, numerous examples have been found where the two approaches show disagreement as to how the elements should be arranged in the periodic table. Some of these differences persist up to the present time. The periodicity in the chemical properties of the elements is a complicated matter and is only approximately reflected in the electronic configurations of atoms. This need not be cause for concern, however, since electronic configurations themselves represent an approximation. The simple notion that elements in the same group of the periodic table share the same outer electron configuration shows a number of exceptions. The elements helium and beryllium for example have the configurations of  $1s^2$  and  $2s^2$ , respectively, but are certainly not in the same group of the periodic table. On the other hand, nickel, palladium, and platinum are in the same group (10 according to the new 18 group scheme) and yet have very different outer shell configurations. Jorgensen (13) has concluded that,

no simple relation exists between the electron configuration of the ground state of the atom and the chemistry of the element under consideration.

The inability to reduce chemistry to electronic configurations does not in itself rule out the reduction of chemistry to physics, and quantum mechanics in particular, as some authors seem wrongly to conclude. Those who favor the spectroscopic or electronic version of the periodic table have explored whether there may be some underlying symmetry that governs the building-up of electronic orbitals (14, 15). This work has led to the proposal of a new form of the periodic table in which the alkaline earth elements, instead of the noble gases are placed at the right-hand edge (16, 17).

Empirically, the electron shells are not filled in a strict sequential order according to their average distance from the nucleus (18). In the element scandium, for example, the  $4s$  orbital is thought to be filled before the  $3d$  orbital begins to fill. This effect may be explained in terms of the relative stabilities of the two orbitals and interelectronic repulsive effects. It emerges that, although the  $3d$  orbital has a lower energy, it is less stable when electron repulsion effects are taken into account correctly (19). The greater overall stability of the  $4s$  orbital occurs due to a greater degree of electron penetration in  $s$  orbitals. Similar effects occur at other positions in the periodic table, and the correct sequence of electron filling is given by the following order, although there are about 20 exceptions for neutral atoms:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f \\ < 5d < 6p < 7s < 5f, \text{ etc.}$$

This sequence is not theoretically derivable but based on spectroscopic data. This fact is seldom stressed in textbook accounts, which imply that it refers to the energies of the various orbitals as calculated from the theory. As was mentioned above, the stated sequence refers strictly to the order of filling of orbitals, which may be rationalized by the correct inclusion of electronic repulsion effects.

Confusion is created by the often-quoted results of calculations by Latter that did predict some of the above ordering on the basis of the rather crude Thomas-Fermi method of approximation (20). More recent Hartree-Fock calculations on atoms show, for example, that the 3d level is definitely of lower energy than that of 4s (21).

Various mnemonic diagrams have been suggested for remembering the sequence of filling of orbitals (22-25), and they have been generally adopted in chemical education. Most chemistry texts include a form of the diagram shown in Figure 1.

If we consider the angular momentum quantum number of each of these orbitals,  $s = 0$ ,  $p = 1$ ,  $d = 2$ ,  $f = 3$ , etc., we obtain the following sequence of numbers for the order of filling. Each sequence shown on consecutive lines, is repeated just once.

0,
0,
1, 0,
1, 0,
2, 1, 0,
2, 1, 0,
3, 2, 1, 0,
3, 2, 1, 0,
.....
.....

The periodic table may be seen to take on a more symmetrical or systematic form with respect to these numbers if the elements are arranged so that the alkaline earths occur at the right-hand edge of the table as shown below. It is claimed that in the conventional form of the periodic table the inherent symmetry in electronic configurations is not emphasized and that the order of filling of electronic orbitals takes on a puzzling form (16). The proposed new f.d.p.s version shown in

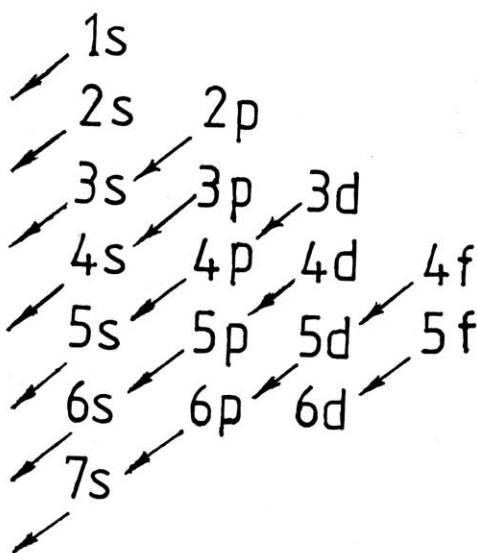


Figure 1. Mnemonic to obtain the order of filling of orbitals.

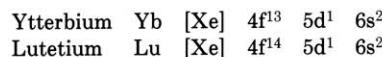
Figure 2 does not yield any new predictions as to chemical or physical behavior of the elements, and this in itself argues against its adoption. Moreover, the proposed version leads to the grouping together of the element helium with the alkaline earth metals, which is a little difficult to accept in chemical terms. The conventional periodic table places helium in group 8 of the periodic table in keeping with its close similarities with the other noble gases. This form of adjustment should not be possible in a table that is strictly committed to regularities based on particular sequences of quantum numbers, but precisely such an adjustment was made for helium by the originators of the scheme (17). Not surprisingly this proposed electronic form of the periodic table has not been generally adopted by chemists, although the quantum mechanical development of the subject through electronic orbitals is now very widespread. It should be mentioned, however, that some authors feel that a good case does exist for putting helium above beryllium in the same group. They claim that first members are frequently anomalous and that the ionization energy of helium can be predicted quite well from those of other elements to its left and below it, in the f.d.p.s form of the periodic table (26).

s										
(0)										
p										
(1)										
H He										
Li Be										
d										
(2)										
B C N O F Ne Na Mg										
Al Si P S Cl Ar K Ca										
f										
(3)	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
	Er	Tm	Yb						In	Sn
	Fm	Md	No	Lw					Sb	Te
									I	Xe
									Cs	Ba

Figure 2. New proposed form of the periodic table based on symmetry of electronic configurations and quantum numbers.

#### A Recent Modification to the Form of the Periodic Table

It is interesting to note that the adoption of electronic configurations as a means of developing the periodic table has led to some regressions in our understanding of atomic chemistry. A good example is provided by the question of which element to place under scandium and yttrium in the first column of the transition metals. Prior to the introduction of electronic configurations, the choice was invariably in favor of the element lutetium, which shows a number of chemical similarities with the two above-named elements. Until relatively recently the use of electronic configurations dictated that the element lanthanum should appear in this position instead of lutetium. In order to appreciate this situation, we need to consider the electronic configurations that were supposed to occur in the atoms of ytterbium (atomic number 70) as well as lutetium (atomic number 71).



According to this assignment the differentiating electron, that is, the final electron to enter the atom of lutetium, was seen as an f electron. This suggested that lutetium should be the final element in the first row of the rare earth elements, in which f electrons are progressively filled, and not a transition element as had been believed by the chemists. As a result of more recent spectroscopic experiments the configuration of ytterbium has been altered to (27)

while that of lutetium remains unchanged. Ytterbium therefore now appears to mark the end of the rare earths, and the subsequent element lutetium shows a d differentiating electron and thus makes it an equally good candidate as lanthanum, of configuration [Xe] 5d<sup>1</sup> 6s<sup>2</sup>, for the role of the first element in the first transition. Renewed chemical and physical measurements then showed conclusively that lutetium rather than lanthanum bears a close similarity with scandium and yttrium (28–30). Electronic configurations have re-established what was already known from old-fashioned chemical evidence. Precisely analogous arguments have been used to show that the fourth transition series should begin with the element lawrencium and not actinium as had been generally supposed on the basis of earlier electronic configurations. The older as well as the revised forms of the periodic table are shown in Figure 3.

#### Other Changes In Electronic Configurations Including the Rare Earths

The approximate nature of orbitals and configurations is reflected in the changes that have occurred in the supposed ground state configurations of 20 or so elements, even following the introduction of electron spin. If we were to consider earlier changes in electronic configurations, they would be far more numerous. The configurations ascribed to various elements by Bohr and Stoner underwent several important changes following the introduction of the fourth quantum number and the Pauli exclusion principle. Alterations that have occurred since Pauli's principle was first used to

#### Idealized and Observed (36) Outer Shell Configurations for the Rare Earths

Element	Atomic number	Idealized configuration	Observed configuration
La	57	5d <sup>1</sup> 6s <sup>2</sup>	5d <sup>1</sup> 6s <sup>2</sup>
Ce	58	4f <sup>1</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>2</sup> 6s <sup>2</sup>
Pr	59	4f <sup>2</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>3</sup> 6s <sup>2</sup>
Nd	60	4f <sup>3</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>4</sup> 6s <sup>2</sup>
Pm	61	4f <sup>4</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>5</sup> 6s <sup>2</sup>
Sm	62	4f <sup>5</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>6</sup> 6s <sup>2</sup>
Eu	63	4f <sup>6</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>7</sup> 6s <sup>2</sup>
Gd	64	4f <sup>7</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>7</sup> 5d <sup>1</sup> 6s <sup>2</sup>
Tb	65	4f <sup>8</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>9</sup> 6s <sup>2</sup>
Dy	66	4f <sup>9</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>10</sup> 6s <sup>2</sup>
Ho	67	4f <sup>10</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>11</sup> 6s <sup>2</sup>
Er	68	4f <sup>11</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>12</sup> 6s <sup>2</sup>
Tm	69	4f <sup>12</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>13</sup> 6s <sup>2</sup>
Yb	70	4f <sup>13</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>14</sup> 6s <sup>2</sup>

order the elements do not involve any major conceptual changes but depend on detailed spectroscopic experiments. Several theoretical studies have also been conducted aimed at finding which element marks the true beginning of the rare earths (31, 32). The section above mentioned a change in the configuration of ytterbium. Indeed most rare earth elements have undergone recent changes with regard to their supposed ground state configurations. To judge by the variations in inorganic texts, the precise configuration of the cerium atom appears to be particularly troublesome (33–35).

The table shows the most definitive and currently available outer shell configurations for the rare earths (36).

The idealized configurations refer to those expected on the basis of Hund's rule, that is configurations in which spin multiplicity is maximized. The only elements where the idealized configurations are found to occur are Ce, Gd, and Lu. Many early assignments of rare earth configurations had assumed the above-given idealized versions, due to the predominant trivalence of the rare earths. This provides another example of a difference between the chemical and spectroscopic periodic tables.

The identification of the ground state configuration is obtained from measurements of the splitting of spectral lines in an external magnetic field (Zeeman effect). The degree of splitting depends on the Landé splitting factor, *g*, which is related to the quantum numbers of the atom, *L*, *S*, and *J*, where *L* represents the orbital angular momentum, *S* the spin angular momentum, and *J* the overall angular momentum.

$$g = 1 + J(J + 1) - L(L + 1) - S(S + 1)/2J(J + 1)$$

The same *g* value may often arise for different spectroscopic terms, having differing values of *L*, *S*, and *J*, such as to render the deduction of the configuration ambiguous. For example, Moore's tables list as many as 30 terms corresponding to *g* = 1.500 (37). As a result, it is not always possible to obtain an unambiguous assignment of configurations from spectral measurements.

Furthermore, Landé's theory only represents a first-order approximation, and the *L* and *S* quantum numbers only behave as good quantum numbers when spin-orbit coupling is neglected. It is interesting to note that the most modern method for establishing the atomic ground state and its configuration is neither chemical nor spectroscopic in the usual sense of the word but makes use of atomic beam techniques (38).

#### The Actinides. A Case Where Spectroscopy Triumphs over Chemistry?

Up to this point we have argued in favor of chemical evidence over physical evidence with regard to the form of the periodic table. We now turn briefly to the controversy

Figure 3. The old (a), and revised version (b) of the periodic table showing changes with regard to the first elements in the third and fourth transition series.

regarding the elements from numbers 89 to 102 where spectroscopic evidence appears to have settled the question as to where these elements should be placed. It would seem that in this case the chemical evidence available confused the issue. In the 1950's several authors including F. Paneth argued that these elements should be regarded as transitional in view of chemical similarities (39).

Seaborg and those who follow him like to break off the last row of the periodic table at actinium and to write the elements 89–96 (and now 98) as the group of "actinides" under the group of "lanthanides" 57–72. They can point out in favour of this arrangement that in this way the probable similarities in the electronic structure of the respective members of the two groups are clearly indicated. However, those similarities, even if present, do not manifest themselves in the chemical behaviour of the first members, and those chemists who want to show above all in the periodic table the a grouping according to chemical relationships, hold that the discovery of the transuranium elements does not justify the neglect of the old-established and obvious correspondence between thorium and hafnium, protactinium and tantalum, and uranium and tungsten. They prefer to leave the periodic system up to uranium unchanged, and to put the group of transuranic elements, or "uranides" as they are sometimes called, at the end of the table.

Two years later H. R. Paneth reassessed this question and took a more impartial view (40). He considered the possible analogies of the element plutonium (93) with osmium (76), treating the elements in question as transition elements, or with the rare earth samarium (62), treating the elements as rare earths. If the analogy holds with osmium we would expect higher valencies up to 8 to be displayed by the elements, whereas, if it behaves more like samarium, its valency should typically be 3. Chemical evidence shows that plutonium shows its most stable valency as 4, while 3 and 6 also occur. This finding suggests that plutonium be regarded as one of the rare earth metals, which generally show low valencies. Transition metals, however, show higher valencies by promoting available d electrons to the outer valency shell, according to the electronic configuration model. This form of electron promotion does not readily take place in rare earths due to the deeper lying nature of its supposedly occupied f electrons. However, the author points out that, if we consider the elements preceding plutonium, the analogy with the rare earths is far from perfect particularly in the case of thorium and uranium. The latter is most stable in the 6 state, thus suggesting an analogy with the transition elements instead of the rare earths.

Earlier, in 1945, Seaborg had proposed that the elements starting at number 89 should be considered as a rare earth series. This resulted from attempts to synthesise elements 95 and 96. Seaborg suggested that the new series of rare earth elements should not begin after uranium as had been supposed but instead earlier, with the element actinium (41). He found that his proposed version of the periodic table suggested an analogy between elements 95 and 96 with europium and gadolinium, respectively. On the basis of this analogy he was able to identify the two new elements. The concept also led to the discovery of the remainder of the actinide elements and their eventual acceptance by the scientific community. The general opinion is now that the gradual increase in the oxidation states of thorium, protactinium, and uranium misled chemists into believing that these elements were members of a transition series in which the 6d levels were being built up. Following the discovery of the transuranium elements, it was found that successive elements ceased to show an increase in oxidation states and behaved like a second series of rare earth elements. More recently obtained spectral evidence has also been interpreted to mean that these elements add successive electrons to orbitals of the f type. Figure 4 shows the periodic tables given by F. Paneth and Seaborg, respectively.

## Conclusion

The greatest success of quantum mechanics has been in the field of spectroscopy, and there are some striking analogies between chemical periodicity and the periodicity shown by atomic spectra. However, an analogy does not imply an identity (42) between the two forms of the periodic table.

There are also a number of differences between chemistry and spectroscopy with regard to the properties of atoms. For example, according to spectroscopic measurements, it should be more energetically favorable for the element aluminium to form  $\text{Al}^{1+}$  or  $\text{Al}^{2+}$  ions, whereas in chemical compounds only  $\text{Al}^{3+}$  is formed. This chemical fact may be explained by recourse to the Born–Haber cycle, which shows that, when all relevant energetic terms are considered, the  $\text{Al}^{3+}$  ion represents the most favorable possibility. On the other hand, spectroscopy knows nothing of these chemical arguments involving energetic terms such as the lattice enthalpy. The attempt to reduce chemistry to quantum mechanics through electronic configurations was prompted by the analogies with optical and X-ray spectra (43). The failure to reduce chemistry to electronic configurations is hardly surprising since configurations represent an approximation that is strictly inconsistent with quantum mechanics. At the same time, this failure to reduce chemistry to electronic configurations does not rule out the possibility of reducing chemistry to quantum mechanics.

Most of the arguments presented in the present paper may be resolved if one accepts the coexistence of many forms of the periodic table that are similar but far from identical, rather than trying to reach one single compromise version. The electronic forms of the periodic table should not be considered as being more fundamental in some way.

	Group																	
Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
I																		H He
II	Li	Be												B	C	N	O	F Ne
III	Na	Mg												Al	Si	P	S	Cl Ar
IV	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br Kr	
V	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
VI	Cs	Ba	57-71	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
VII	Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf						

	Rare Earths																	
VI	La	Ce	Pr	Nd	Pu	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
57-71																		

H																		H He
Li	Be													B	C	N	O	F Ne
Na	Mg													Al	Si	P	S	Cl Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	57-71	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	89-																

Lanthanides	La	Ce	Pr	Nd	Pu	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
	57																

Actinides	Ac	Th	Pa	U	Np	Pu											
	89																

Figure 4. Comparison of periodic tables given by Paneth (42) and Seaborg (44).

The more general question of whether chemistry is reducible to quantum mechanics is more subtle and requires a consideration of the nature of ab initio calculations. According to some authors, the question even depends on the problems in the foundations of quantum mechanics (44).

The use of atomic orbitals in ab initio calculations has yielded some very accurate results, but this should not be taken to indicate the truth of the orbital model. The zero-order orbital model consists in assuming the electrons of a many-electron atom to be independent and that they possess definite quantum numbers. The wavefunction for a many-electron atom is expanded by taking an infinite series whose terms consist of a complete set of orthogonal functions. More precisely the expansion consists of a series of terms that are members of a set of normalized orthogonal functions each multiplied by a constant coefficient or weighting factor. Provided that sufficient terms are considered and that the series converges, it is possible to approach progressively closer to the experimentally observed energy of the atom in question. This feature is quite general and applies to the mathematical modelling of any arbitrary function. The mistake is to attribute some significance to the zero-order approximation, that is, to take the zero order approximation out of its mathematical context.

It should also be acknowledged that in recent years computational quantum chemistry has achieved a number of predictions that have since been experimentally confirmed (45–47). On the other hand, since numerous anomalies remain even within attempts to explain the properties of atoms in terms of quantum mechanics, the field of molecular quantum mechanics can hardly be regarded as resting on a firm foundation (48). Also, as many authors have pointed out, the vast majority of ab initio research judges its methods merely by comparison with experimental data and does not seek to establish internal criteria to predict error bounds theoretically (49–51). The message to chemical education must, therefore, be not to emphasize the power of quantum mechanics in chemistry and not to imply that it necessarily holds the final answers to difficult chemical questions (52).

As to the general issue of reduction, chemists would do well to consider the work of philosophers of science, who have for some time renounced the notion that any particular branch of science may be strictly reduced to a more basic science. The classic work giving conditions for strict reduction is by Nagel (53), and several detailed criticisms of his views have been published (54, 55). More recently there appears to be a partial return to reductionism under the guise of "supervenience". Chemistry is said to supervene over physics even though it cannot be shown to be strictly reducible in the sense of Nagel. Whether supervenience represents merely a hope and whether it holds any explanatory power is the focus of much current work in philosophy (56–58).

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