

## John C. Polanyi\*

### István Hargittai\*\*

Dudley R. Herschbach (b. 1932), Yuan T. Lee (b. 1936), and John C. Polanyi (b. 1929) received the 1986 Nobel Prize in chemistry for their contributions to the understanding of the dynamics of chemical elementary processes. Recently I recorded a conversation with Professor Herschbach in Boston and with Professor Polanyi in Toronto.

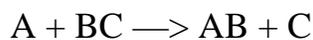
Dr. Herschbach is now Frank B. Baird, Jr. Professor of Science at the Department of Chemistry, Harvard University, Cambridge, Massachusetts, and Dr. Polanyi is University Professor at the Department of Chemistry, University of Toronto, Toronto, Canada.

Because of scheduling difficulties, the meeting with Dudley Herschbach took place in a noisy lobby at Logan Airport in the evening of July 23, 1995. ... The location of the conversation with John Polanyi, on Tuesday, August 1, 1995, was his quiet office but his schedule was only slightly less busy than Logan Airport. However, the conversations were very pleasant and informative in both cases. The interview with Professor Polanyi is augmented here by the [brief speech](#) he gave at the Stockholm City Hall on the occasion of the Nobel Prize ceremonies in December 1986.

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**István Hargittai (IH):** Let's jump in at the middle. What's the relationship between reaction dynamics and molecular structure?

**John C. Polanyi (JP):** I wish I knew. The beginnings of reaction dynamics, in which I was involved, hardly required penetrating insights into molecular structure, since the rules were being established for reactions in which an atom attacked a diatomic molecule. The type of question being asked was, does the atom approach the diatom along the axis of the two atoms or at right angles to that axis? What sort of forces does the atom feel, as it approaches? Is it immediately trying to climb over an energy barrier? When does it start to feel some attraction, as the new chemical bond begins to form? In answering these questions, one must understand the structure of the *transition state*; it simply isn't enough to look at the structure of the molecule under attack. In fact, whatever the reaction, we directed our attention to the attacking atom and to the two atoms that constituted the bond under attack. The first thing we did was to write



People laughed, because that was how Dudley Herschbach, Yuan Lee, myself, and many others in the dynamics community routinely began our lectures.

**IH:** Does the reaction dynamics approach now extend to complicated molecules?

**JP:** Yes, it is beginning to, but the simple framework of  $A + B$  remains useful. Our finding was that most of the interesting things were related to the bond that was being formed and to the bond that was being broken. If you start to hang complex structures on the attacking species or on the species under attack, the focus of your attention remains on the atoms that comprise the bond being formed and those that comprise the bond being broken. As reaction dynamics invades organic chemistry, where more intricate rearrangements are observed, this will cease to be so true.

**IH:** At the end of your Nobel lecture, as if projecting into the future, you mentioned two directions. One was *transition-state spectroscopy* and the other was *surface aligned photochemistry*. That was nine years ago. Was this a prediction?

**JP:** It was in a sense, because both these fields were very much in their infancy. The question was, how far would they go? As it turns out, both of them are maturing today in a very satisfying way.

I was involved with both early on. In the case of transition-state spectroscopy, we had the idea that we could see the very short-lived intermediate between reagents and products by means of something like line broadening. The spectral line broadening would be due to the strong repulsion for a millionth of a millionth of a second ( $10^{-12}$ s) between the pair of particles that were in the process of separating as reaction products. So we looked at spectral lines in chemiluminescence and found very great broadening, that is to say, what are called „wings” on the lines emitted in a chemical reaction that was forming electronically excited atoms.

This was a beginning to a field that has matured in surprising and marvellous ways. One way is due to Neumark and his co-workers at the University of California, Berkeley, who obtain the transition states of chemical reactions not by bringing the reagents together but by first forming a negative ion incorporating them and then removing an electron. It's a beautiful method. It plunges you right into the heartland of a chemical reaction. Another approach is well advanced in the laboratory of Zewail and co-workers at Cal Tech and involves the use of femtosecond lasers to actually clock the reaction as it passes through the transition state. Again a fabulous development. Neither of those things was anticipated.

The way new fields are born is as a consequence, first of all, of a surmise that there is something new that can now be done. In the case of transition-state spectroscopy, the surmise was that one could study the interaction of light with the very short-lived collocation of atoms that we are talking about here. These are subpicosecond collocations which constitute the successive intermediate configuration between reagents and products. As it turned out, it could be done in much better ways than were initially dreamed of.

So much for transition-state spectroscopy, a field in which I am still enthusiastically involved.

At the same time I am heavily involved with what we call „surface-aligned photochemistry”. There are quite a number of machines in my laboratory devoted, as in the past, to getting information about the motions of newly born reaction products. Previously, however, we were getting some evidence about the

molecular dance in cases in which the dancers could come onto the stage in any configuration they wished; that's what happens in gas-phase chemical reactions. But if you start with your reagents in the adsorbed state on a single crystal, the forces that adsorb them also order them. Then you trigger the reaction by sending a pulse of light through the ordered species. That's usually an ultraviolet laser pulse. The reaction now starts to unfold, that is to say, the dancers start to engage in their dance. The novelty is that they have started their movements this time from defined positions, marked by chalk on the stage. If you look at their unfolding motions following this ordered start, it should now be easier to infer what they did in the transition state, which is the most mysterious and interesting stage in a chemical reaction.

**IH:** Do calculations parallel the experiments?

**JP:** Our work has always included experiment and theory proceeding in parallel. We're just writing a paper which is part experimental, part theoretical, describing how photofragments leave the surface after a photolysis event. In the same paper we report the calculations (the theory) of the initial geometry of the molecular species, which we then check experimentally with polarized infrared spectroscopy. We then simulate the action of the light theoretically by considering the effect of changing a bond into an antibond. Our theoretical molecule flies apart. Next the classical and quantum equations of motion are used to predict the outcome. Finally, and crucially, we compare the computed outcome in terms of energy distributions and angular distributions with those we measure in the lab. This to-and-fro between theory and experiment has been typical of our *modus operandi*.

**IH:** What molecules are involved in such a study?

**JP:** The simplest ones are hydrogen halides. We just had a discussion in this room, before you came in, about hydrogen iodide adsorbed on lithium fluoride and on sodium fluoride. The crystalline surface of lithium fluoride is an alternating pattern of big  $F^-$  ions and little  $Li^+$  ions. Even a perfect crystal will have, therefore, a rather rough surface. When we change our surface to *sodium* fluoride, we are changing the unit-cell size. In each case we adsorbed the same molecule, which is HI at the moment. The HI molecules try to get comfortable on the surface by bringing the iodine over  $Li^+$ , to maximize attraction. They also try to bring their hydrogen end over  $F^-$ , and that's an operation that involves them in making compromises, since the fit is imperfect as with a grown-up riding a child's bicycle. Then, as one increases the coverage, the adsorbed HI molecules become aware of each other's affected not just by the adsorbate-substrate forces but by adsorbate-substrate forces.

One of the variables we use in order to change the pattern of adsorbate is the pattern of adsorbate is the nature of the substrate, but it's a pain in the neck to change the substrate. Another variable, as I was saying, is the coverage. It's very common in surface science for molecules at low coverage to lie down and then at higher coverage, as they start to crowd each other, to stand up. If these molecules are the reagents for some photoreaction, then, with changing coverage, they change their relative orientation. Why does this matter? Because we have a basis for expecting the outcome of the chemical reaction to change with orientation, and hence it must change between low coverage and high.

In a sense the crystal is *catalyzing* the photoreaction. More interesting still, this is *geometrical* catalysis,

brought about by aiming things differently. It is a form of catalysis that should be of particular interest to people in the dynamics community, like myself. We have been discussing the effect of different arrangements and alignments of molecules on chemical reactions for decades. Now we are developing a means of manipulating our reagent species by adsorbing them on different surfaces and with different coverages on a given surface so as to produce different alignments and arrangements at will.

**IH:** Apparently, you are a public figure in Canada. You have a busy waiting room with magazines like in a dentist's office. What's your experience in communicating with people outside the scientific community?

**JP:** Perhaps you'll concede that my magazines are better than most dentists'?

You are right that I've been engaged in various political debates, such as those sponsored by Pugwash, for over 55 years. My experience is that one can readily get access to senior politicians. The real question is, can one get them to listen? I would claim that if you make a sufficiently cogent argument, they will have to listen. I think we scientists have some training in organizing our thoughts and in trying to persuade difficult audiences.

In fact, our colleagues constitute just such an audience. When you go to a scientific meeting with a new idea, you don't expect people to applaud. What they do is to tear it apart. That's their function. In science we arrive at the truth through an adversarial dialogue. So we are used to having to make a case, and shouldn't be frightened to do so.

In the past, it is true, we were frightened to speak out on larger issues. We felt that we'd be trafficking in our reputation as scientists in order to get a hearing and that as a result we could bring science into disrepute, since people could say that we had abused our credentials.

As with most criticisms, there is something to this one. We do have to be careful about this. We have to explain what our expertise is.

But were we to take the opposite view that science is a sort of priesthood and that to keep it in high esteem we must keep it pure by ensuring that no scientist or group of scientists meddles in things outside their own discipline, then we would be involved in a different sort of irresponsibility.

The fact is that science is having a colossal effect on the world scene, and as a result we cannot responsibly opt out of the debate on world affairs. Earlier today, I had somebody in here who wanted to talk about the fiftieth anniversary of the dropping of the first atomic bomb in Japan. I was 16 in 1945 when that bomb was dropped. Though it came at the end of a huge and terrible war, it was a transforming moment in other respects, too. My own thinking was deeply affected by it, as it should have been. It transformed, for example, the relations between nations. But it was only one of a whole series of technological changes, to which we scientists have contributed, that have changed the world. It would be irresponsible, therefore, for us not to be involved in the debate that follows.

Often, all that we have been able to contribute has been technological solutions. But even these can have

tremendous impact. I have, for example, been involved in a lot of arms control discussions with Russian scientists. They way perhaps seem peripheral now, but at the time two colossal adversaries were threatening each other and the world. The danger of the arms race was very real. Nonetheless, the political community, our leaders, were saying that we can't do anything about it for a whole lot of technical reasons. It was necessary for the technical community to say quite specifically, „yes, we can”. If we fail to stop testing of nuclear weapons, or if we fail to reduce the number of nuclear weapons, it's not because it's impossible to verify these things. We explained in some detail how we could do it. If then we *didn't* do it, it was because we didn't want to. By clearing the way on the technological level, one has an undoubted influence on the way history unfolds.

**IH:** Let's speak about your teachers. Was your father your teacher?

**JP:** Formally he was my teacher for one year. I entered Manchester University in 1946 when I was 17. He lectured to me in the first year. That was the last year he lectured in science. Then he transferred to philosophy. He also taught me a great deal in conversations despite my many absences away from home, first in boarding school and then for three years as an evacuee in Canada.

Most of what he taught me about physical chemistry I learned at one remove from him. I was a student for six years in the Department that he had shaped in Manchester. My professor Meredith Evans, was one of his favorite students, and my Ph.D. supervisor Ernest Warhurst was another student of his. What I learned from his students gave me a sense of scientific values—where the field was going, what were the important questions to tackle, and to a degree, how to tackle them. Without those things I would have been lost. But it happens that I didn't get them directly from him, but from people who owed a lot to him.

**IH:** When you speak about transition-state spectroscopy, it seems to me to have a close relationship to Michael Polanyi.

**JP:** It does, of course, but I don't think that's the closest I got to his interests. He would have thought it far-fetched that one might get light to interact with this subpicosecond entity which is neither reagents nor products. Though it was not first done with lasers, it was the existence of lasers-of which of course, he never dreamed—that got people thinking about „seeing” the transition state.



*John C. Polanyi, Michael Polanyi, and Eugene P. Wigner around 1934, on the lawn of the Polanyi home in Didsbury Park, Manchester, England*



*Michael Polanyi in his lab about 1940 with Dr. A.G. Evans on his right*

*Photos courtesy Professor J.C. Polanyi*

I find myself now at the age of 66 engaged with great excitement in some novel experiments in which we are trying to look at transition states for sodium-atom reactions. It is this project that brings me eerily close to my father's interests of 1929 and subsequent years.

When I was being conceived (I was born in 1929), my father was establishing himself as the most perceptive interpreter of sodium-atom reactions, which he understood as being in a sense the simplest of all reactions. They are so simple that even a physicist can understand them. The sodium, which is easily ionized, comes up to a molecule with high electron hops a large distance, my father coined the term „harpooning” for this. It is also called this because the positively charged sodium hauls in its negative catch. This is a uniquely simple reaction. It is different from most reactions which are fascinating because they are *not* sequential events. Harpooning reactions can however be described as sequential. Step 1, reagent approaches; step 2, the harpoon jumps across; step 3, the alkali fisherman pulls in the catch. The end.

Today, in my lab, we are finding that it is possible to access the harpooning event, not by taking the reagents and bringing them together, but by forming a loose complex which is in the configuration of the transition state, that is to say, by starting in the middle of the reaction. That is what we are currently doing. And that is indeed a lineal descendent of my father's interests.

I am, however, only one of many who have seen the extraordinary possibilities offered by harpooning reactions. For example, Dudley Herschbach began his life as a dynamicist by studying that type of reaction. One should also add that my father himself was part of a continuous progression. What drew him to sodium reactions was that Fritz Haber had been studying an unexplained chemiluminescence from them. This was in Berlin and my father was in Haber's Institute as a young researcher. The history, as is usual in

science, constitutes an unbroken chain.

**IH:** Was he the determining influence in the direction you took in science?



*Michael Polanyi, Professor  
of Physical Chemistry,  
around 1937*

**JP:** He personally wasn't. But where I trained for six years was. If the question is whether he was the determining influence in my going into science, then, yes, but I should qualify that answer. At the time when I learned most from my father, in my late teenage years, his interests were even livelier in nonscientific fields than in scientific ones. He had another son, George, who went into the humanities, equally under his influence. I could just as easily have gone into economics or philosophy or theology and have ascribed it to my father's stimulus. He was, of course, delighted to see me go into science, just as he would have been delighted to see me go in many other directions.

Perhaps I am being disingenuous. I can only say that if he steered me toward science, I didn't notice.

**IH:** How did he make the transition from physical chemistry to philosophy? Were you a witness to this?

**JP:** We seem destined to discuss transition states. Yes, I witnessed this one directly. I got back to England right at the beginning of my fifteenth year, and until I was well into my twenties I saw a good deal of my father. That was the time, beginning in 1944, when he was making the transition. The fact that he made that transition isn't so surprising. There are a lot of scientists who have started to ruminate about how discoveries are made, how people learn anything, and the role of logic in this as compared with faith. And all this was of interest to him too.

What is striking, in my view, is the originality and impact that he had in his new field of epistemology, the theory of learning. He would have said confidently that what he did in that area was much more important than what he did in science.

I have a sense of wonder at all he did in science, and yet I believe he may easily have been right that his contribution to epistemology will turn out to be more lasting. The sales of his books and the interest in his ideas continue to be great. Eventually his name will, of course, be forgotten, but his philosophical ideas will live on as a significant contribution to the development of philosophical thought.

What is remarkable, then, is the quality of the contribution he made in his decades as a philosopher. Actually, his first book on a nonscientific theme was being conceived in the 1950s when he attacked the Russian economic system and at the same time confronted the leading British social scientists of his day, Sydney and Beatrice Webb, who'd published a learned volume explaining how the Soviet five-year-plan constituted a superb innovation and was bringing prosperity to the USSR. My father took this thesis apart in a series of essays, which became a book in 1940, that went far beyond economics and inquired why it

was that British liberals, the so-called Fabians, were so careless of the freedoms that they enjoyed; the book was called *The Contempt of Freedom*. It was an influential book and a prescient one. It is forgotten today. His best known book is, instead, *Personal Knowledge*.



*Michael Polanyi addressing the Congress of Cultural Freedom in Milan about 1956 with French political scientist Raymond Aaron*

As with new scientific theories, my father's thinking was initially rejected by the professionals. He was not embraced by the philosophers of his day, who felt that he was an ignorant outsider. This lasted for a large part of his time in philosophy. The people who paid attention to his work were closer to theology. This was in part because the philosophy of the time was „linguistic analysis”. That brand of philosophy, centered on the study of the structure of language, passed. I don't know whether my father contributed at all to its passing. It is an interesting question. Whatever the case, there followed a school of philosophy far more friendly to his ideas.

**IH:** Do you share his interest in philosophy?

**JP:** Just as a human being; not as a philosopher. I have no qualifications or ambitions in that area. It was a very brave and extraordinary undertaking on his part to do something so ambitious in the realm of philosophy. Unless you read widely and deeply, you are vulnerable to attack. But he did read widely and could withstand a skeptical and at times hostile audience.

**IH:** It wasn't only Michael Polanyi who made the name of Polanyi famous. It was a very extraordinary family in Hungary. Are your children aware of their family background?

**JP:** They are well aware. The spirit of curiosity and creativity is very evident in them. Our daughter is a journalist and TV producer (in science, to her surprise), and our son has done a lot of things starting with science and leading into the heartland of politics and social science.

**IH:** Earlier you mentioned that your father shaped his department in Manchester. Have you shaped your department at the University of Toronto?

**JP:** No I haven't. The structure of science in the academic world is totally different here. In England, as on the continent the Head of the Department shaped the interests for the whole department. That's not the case here. Nobody who has worked with me since I've been here, starting in 1956, has been appointed to a position at the University of Toronto. There is no „School”. It's not like that. But I do have students in other places working on things that had their origins in interests the encountered while working in this laboratory. I'm happy about that.

Whatever the structure of the academic community, one expect one's influence to be fleeting. What people hope for is that this fleeting influence will, on balance, be positive. Perhaps it is as well that they never find

out.

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\* Polanyi, John Charles, chemist, educator; b. Jan. 23. 1929; m. Anne Ferrar Davidson, 1958: 2 children. Bsc, Manchester \*Eng.) U., 1949, Msc, 1950 PhD, 1952 Dsc, 1964: DSc (hon.), U. Waterloo, 1970, Meml. U. 1976, McMaster U., 1977, Carleton U., 1981. Harvard U., 1982. Rensselaer U., Brock U., 1984, Lethbridge U., Sherbrooke U., Laval U., Victoria U., Ottawa U., 1987, Manchester U. and York U., Eng., 1988, U. Montreal, Acadia U., 1989, Weizmann Inst., Israel, 1989, U. Bari, Italy, 1990, U.B.C., 1990, McGill U., 1990, Queen's U., 1992, Free U. Berlin, 1993, Laurentian U., 1995, U. Toronto, 1995, U. Liverpool, 1995: LLD (hon.), Trent U., 1977, Dalhousie U., 1983, St. Francis-Xavier U., 1984: LLD (hon.), Concordia U., 1990: LLD (hon.), Calgary U., 1994, Mem. faculty dept. chemistry U. Toronto, Ont, Can., 1956- prof. U. Toronto, 1962/: William D. Harkins lectr. U. Chgo., 1970: Reilly lectr. U. Notre Dame, 1970: Purves lectr. McGill U., 1971: F.J. Toole lectr. U. N.B., 1974: Philips lectr. Haverford Coll., 1974: Kistiakowsky lectr. Harvard U., 1975: Camille and Henry Dreyfus lectr. U. Kans., 1975: J.W.T. Spinks lectr. U. Sask., Can., 1976: Laird lectr. U. Western Ont., 1976: CIL Disting. lectr. Simon Fraser U., 1977: Gucker lectr. Ind. U., 1977: Jacob Bronowski meml. lectr. U. Toronto, 1978: Hutchinson lectr. U. Rochester, N.Y.1979: Priestley lectr. Pa. State U., 1980: Barré lectr. U. Montreal, 1982. Sherman Fairchild disting. scholar Calif. Inst. Techn. 1982: Chute lectr. Dalhousie U., 1983: Redman lectr. McMaster U., 1983: Wiegand lectr. U. Toronto, 1984: Edward U. Condon lectr. U. Colo., 1984: John A. Allan lectr. V. Alta., 1984; John E. Willard lectr. U. Wis., 1984, Owen Holmes lectr. U. Lethbridge, 1985: Walker-Ames prof U. Wash., 1986: John W. Cowper disting. vis. lectr. U. Buffalo, SUNY, 1986: vis. prof. chemistry Tex. A&M U., 1986: Disting. vis. spkr. U. Calgary, 1987:Morino lectr. U. Japan, 1987; J. T. Wilson lectr. Intario Sci. Ctr., 1987: Welsh lectr. U. Toronto, 1987: Spiers Meml. lectr. Faraday div. Royal Soc. Chemistry, 1987: Polanyi lectr. Internat Union Pure & Applied Chemistry, 1988. W. B. Lewis lectr. Atomic Energy of Can. Ltd., 1988: Cogsol Bathurst vis. lectr. Concordia U., 1988: Priestman lectr. U. N. B., 1988: Killam lectr. U. Windsor, 1988: Herzberg lectr. Carleton U., 1988: Falconbridge lectr. Laurentian U., 1988: DuPont lectr. Ind. U., 1989: C.R. Mueller lectr. Purdue U., 1989: Luther lectr. U. Regina, 1989: Franklin lectr. Rice U., 1990: Launer lectr. Wilfred Launer U., 1990: Pratt lectr. U. Va., 1990: Goodrich lectr. Case Western Rex. U., 1990: Phillips lectr. U. Pitts., 1991: Albert Noyes lectr. U. Tex., 1992: John and Lois Dove Meml. lectr. U. Toronto, 1992: Fritz London lectr. Duke U., 1993: Castle lectr. U. South Fla., 1993: Linus Pauling lectr. Calif. Inst. Tech., 1994: Hagey lectr. U. Waterloo, 1995: Larkin Stuart lectr. U. Toronto, 1995: Hungerford lectr., 1995: York Club, 1995: disting. lectr. ser. Meml. U., 1995: John C. Polanyi nobel laureate lectr. U. Toronto, 1995: Floyd E. Bartell Meml. lectr. U., Mich., 1996: Christian Culture award lectr. Assumption U., 1996: Liversidge lectr. U. Sidney, Australia, 1996: mem. sci. adv. bd. Max Plank Inst. for Quantum Optics, Fed. Republic Germany, 1982-92: mem. nat. adv. bd. on Sci. and Techn., 1987-89: hon. cons: Inst. Molecular Sci., Okazaki, Japan, 1989-94: bd. dirs. Steacie Inst. Molecular Scis., Ottawa. Can., 1991-founding mem., pres. Can. Com. of Sci. and Scholars. Beam Disting. vis. prof. U. Iowa, 1992, Charles M. & Martha Hitchcock prof. U. Calif. Berkeley, 1994: Young Meml. visitor Royal Mil. Coll., 1994: Co-editor: (with F.G. Griffiths) *The Dangers of Nuclear War*, 1979: contrb. articles to jours., mags., newspapers: producer: film *Concepts in Reaction Dynamics*, 1970. Mem. Queen's Privy Coun. for Can., 1992: bd. dirs. Can. Ctr. for Arms Control and Disarmament: founding mem. Can. Pugwash Com., 1960. Decorated officer Order of Can., companion Order of Can., knight grand cross Order St. John of Jerusalem: recipient Marlow medal Faraday Soc., 1962, Centenary medal Chem. Soc. Gt.

Brit., 1965, Noranda award Chem. Inst. Can., 1967, award Brit. Chem. Soc., 1971, Mack award and lectureship Ohio State U., 1969, medal Chem. Inst. Can., 1976, Remsen award and lectureship Am. Chem. Soc., 1978, Nobel Prize in Chemistry, 1986, Izaak Walton Killiam Meml. prize, 1988. John C. Polanyi award Can. Soc. Chemistry, 1992. Floyd E. Bartell Meml. lectureship U. Mich., 1996. Liversidge lectureship U. Sydney, Australia, 1996, Christian Culture award and lectureship Assumption U., 1996: co-recipient (with N. Bartlett) Steacie prize, 1965, Wolf prize in chemistry, 1982: named Sloan Found. fellow, 1959-63, Guggenheim fellow, 1979-80 Geoffrey Frew fellow, 1996, Fellow Royal Soc. Can. (founding mem., pres., com. on scholarly freedom, Marshall Tory medal 1977), Royal Soc. London (Royal medal 1989, Bakerian Lectr. and award 1994), Royal Soc. Edinburgh, Royal Soc. Chemistry (hon., Michael Polanyi medal 1989), Chem. Inst. Can. (hon.): mem. NAS (fgn.) Am. Acad. Arts and Sci. (hon. fgn. mem. com. on internat. Security Studies), Pontifical Acad. Scis., Rome. Office: U Toronto Dept. Chemistry, 80 St George St. Toronto, ON Canada M5S 1A1

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