Quantum Chemistry in Croatia – Beginnings*

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Early days of Quantum Chemistry, and people responsible for its beginning in Croatia, are presented. The role of Milan Randić in initiating research in quantum chemistry and in theoretical chemistry in Croatia, is stressed.

Key words: Quantum chemistry in Croatia

The aim in this essay is to describe briefly the early days of quantum chemistry in Croatia. The development of quantum chemistry in Croatia was far behind that in England and the USA, but in parallel with most European countries. The first work in quantum chemistry in Croatia was the 1954 diploma work of *Milan Randić* (b. 1930) entitled *Electronic Structure of Benzene* ("Elektronska struktura benzena", Department of Physics, Faculty of Natural Sciences and Mathematics, University of Zagreb). Randić did this work under the guidance of Professor *Ivan Supek* (b. 1915; student of Heisenberg). Thus, Randić appears to be the first quantum chemist in Croatia. Presumably Supek selected Randić for this task because Randić, before starting to study physics in the Department of Physics at the Faculty of Natural Sciences and Mathematics attended one semester of chemistry at the Faculty of Technology in Zagreb.

After returning to Zagreb from Cambridge where he got a Ph.D. in spectroscopy (the title of his thesis was *Some Studies of Infrared Spectra of Molecules*) under Professor *Norman Sheppard* FRS, Randić founded in 1958 the Theoretical Chemistry Group in the Rugjer Bošković Institute. In these early years the main research of the group was that in quantum chemistry. Randić left Zagreb for good in 1971 for the USA, and there he stopped doing research in conventional quantum chemistry and started doing highly original research in mathematical chemistry.[1]

The first members of the Theoretical Chemistry Group were *Zlatko Meić* who came in December of 1962 (b. 1938; left the group in 1987 and formed the Laboratory for Molecular Spectroscopy; presently he is a professor of analytical chemistry at the Department of Chemistry, Faculty of Sciences and Mathematics, University of Zagreb), *Zvonimir Maksić* joined the Group in February of 1963 (b. 1938; left in 1994 and formed the Quantum Chemistry Group), *Tomislav Cvitaš* joined in September 1966 (b. 1943; left the group in 1997 and is currently professor of physical chemistry at the Department of Chemistry, Faculty of Sciences and Mathematics, University of Zagreb and a part-time researcher in the Department of Physical Chemistry, The Rugjer Bošković Institute) and *Nenad Trinajstić* (b. 1936) joined in October 1966 (coming from the Department of Organic Chemistry and Biochemistry). Of these four people, two (Cvitaš and Meić) chose to do research in the field of molecular spectroscopy, and two (Maksić and Trinajstić) did research in quantum chemistry. Cvitaš later switched to problems of air pollution kinetics. Trinajstić, after initial work in quantum chemistry, pursued research in mathematical chemistry, especially chemical graph theory, and only ocassionally returning to quantum-chemical problems.

Randić initially published three papers dealing with the spectral characteristics of some molecules. His fourth paper published in 1961 and entitled *Ligand Field Splitting of d-Orbitals in Eight Coordinated Complexes of Square Antiprism Structure* (*Croatica Chemica Acta* **32** (1961) 189–192) could be considered as the first paper by a Croatian author in quantum chemistry. This is also the first quantum chemical paper that appeared in *Croatica Chemica Acta*, a chemistry journal published by the Croatian Chemical Society since 1927.

While *Randić* was in Zagreb he had several M.Sc. and Ph.D. students who did research for their degrees in quantum chemistry. The first M.Sc. thesis in quantum chemistry in Croatia was in 1966 by Trinajstić entitled *Method of the Maximum Overlap*

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and Its Application to Calculation of Hybrids in Some Methyl-Substituted Cyclopropanes ("Metoda maksimalnog prekrivanja i primjena na izračunavanje hibrida nekih metil-supstituiranih ciklopropana", Faculty of Natural Sciences and Mathematics, University of Zagreb). In this thesis use was *made* of the maximum overlap method developed by Coulson and his graduate student *William E. Moffitt*,[2] and extended by Randić and Maksić,[3] a graduate student of Randić. The second M.Sc. thesis in quantum chemistry was in 1967 by Maksić, entitled *Study of Some Cycloalkanes by the Method of Maximum Overlap* ("Ispitivanje nekih cikloalkana metodom maksimalnog prekrivanja", Faculty of Natural Sciences and Mathematics, University of Zagreb).

The first Ph.D. thesis in quantum chemistry in Croatia was in 1967 by Nenad Trinajstić entitled *Electronic Structure of Some Polyatomic Molecules* ("Elektronska struktura nekih višeatomskih molekula", Faculty of Natural Sciences and Mathematics, University of Zagreb). The research leading to his dissertation Trinajstić did under the guidance of Professor *John N. Murrell* FRS at the University of Sheffield (1964–1965) and University of Sussex, Brighton (1965–1966). In his thesis he used the Pariser-Parr-Pople (PPP) SCF MO method to interpret the UV/VIS spectra of alternant hydrocarbon anions and cations, and reported several criteria for obtaining localized orbitals. Trinajstić also spent two years (1968–1970) with Professor *Michael J.S. Dewar* FRS (1918–1997) at the University of Texas (Austin) and as a *Robert A. Welch* postdoctoral fellow doing the SCF MO studies of various large molecular systems.

The second Ph.D. thesis in quantum chemistry was in 1968 by Zvonimir Maksić entitled *Some Problems of Electronic Structure of Complexes* ("Neki problemi elektronske strukture kompleksa", Faculty of Natural Sciences and Mathematics, University of Zagreb). Maksić did his research for the Ph. D. thesis under the guidance of Randić and his dissertation appears to be the first Croatian Ph. D. thesis in quantum chemistry based on research entirely carried out in Zagreb. Maksić in his Ph.D. thesis discussed the electronic structure of several inorganic complexes using the crystal field theory, the application of the maximum overlap method to adamantanes and some electron-deficient molecules, and produced a derivation of some molecular integrals needed in the *ab initio* calculations. Maksić spent one year (1970–1971) as a postdoctoral fellow with Professor *John Bloor* at the University of Tennessee (Knoxwille) and one year (1971–1972) as a *Robert A. Welch* postdoctoral fellow with *Dewar* at the University of Texas (Austin).

Randić was elected as the first professor of quantum chemistry at the University of Zagreb. He became in 1965 associate professor in the Department of Chemistry, Faculty of Natural Sciences and Mathematics. There he was promoted to full professorship in 1971 just before he left Zagreb for the USA. He lectured on quantum chemistry for undergraduate and graduate students. His undergraduate lectures were based on the books by *Walter, Eyring* and *Kimball*,[4] and by *Coulson*,[5] while for his graduate lectures besides these books he also recommended Streitwiser's book[6] and F. Albert Cotton's book on symmetry.[7] Randić did not write a book on quantum chemistry, but wrote an article entitled *"Atom"* in *Technical Encyclopaedia* ("Tehnička enciklopedija", Leksikografski Zavod, Zagreb 1963, Part 1, pp. 456–479) in which he introduced some quantum-chemical concepts such as hybridization, crystal field theory, elements of the VB and MO theory, many-body wave functions, etc., and he also wrote a chapter entitled *Molecular quantum mechanics* in the book of Ivan Supek *"Theoretical Physics and the Structure of the Matter"* ("Teorijska fizika i struktura materije", Školska knjiga, Zagreb 1962–1963; the second part, third edition) in which he presented some elementary concepts of quantum chemistry. These were the first introductory texts in Croatia on quantum chemical topics.

After *Randić* left Zagreb, Trinajstić took over his lectures in quantum chemistry and prepared a book for graduate students on the MO theory in chemistry entitled *"Molecular Orbitals in Chemistry"* ("Molekularne orbitale u kemiji", Školska knjiga, Zagreb, 1974; this book was translated into Albanian for the use of students in Albania and at the University of Prishtine, Kosovo). However, the first Croatian book with some quantum-chemical ideas was written by Professor *Drago Grdenić* (b. 1919): *Molecules and Crystals – Introduction to Structural Chemistry* ("Molekule i kristali – Uvod u strukturnu kemiju", Školska knjiga 1973.), so far was reprinted four times. The first Croatian book on quantum chemistry in general is Maksić's book *Quantum Chemistry* ("Kvantna kemija", Sveučilišna naklada Liber, Zagreb, 1976). *Leo Klasinc* (b. 1937), who was and is still engaged in applied quantum chemistry since the early sixties, together wrote with Maksić and Trinajstić a book for undergraduate students on the use of symmetry in quantum chemistry, entitled *Symmetry of Molecules* ("Simetrija molekula", Školska knjiga, Zagreb, 1979).

After Maksić and Trinajstić, a number Croatian researchers was trained in Zagreb or abroad in quantum chemistry, in computational chemistry, or in oft-related mathematical chemistry. This includes: *Dragan Amić, Darko Babić, Slobodan Danko Bosanac, Nađa Došlić, Ante Graovac, Ivan Gutman, Predrag Ilić, Albin Jurić, Krešimir Kovačević,*

Vlasta Bonačić-Koutecky, Bono Lučić, Milorad Milun, Sonja Nikolić, Dejan Plavšić, Krešimir Rupnik, Aleksandar Sabljić, Sanja Sekušak, Alka Velenik, Tomislav Živković. In the seventies and later, senior members of the Theoretical Chermistry group raised through their teaching and collaboration a new generation of Croatian quantum chemists many of which were located outside the Rugjer Bošković Institute and in other places than Zagreb (Osijek, Križevci, Split) and a few of which, unfortunately, emigrated to the USA. Currently the fourth generation of Croatian quantum chemists is making its mark.

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SAŽETAK

Kvantna kemija u Hrvatskoj – počeci

N. Trinajstić

Prikazan je rani razvoj kvantne kemije i spomenute su osobe koje su sudjelovale u početnom razvoju kvantne kemije u Hrvatskoj te su opisani njihovi doprinosi kvantnoj kemiji. Naglašena je vidovitost i zalaganje Milana Randića u započimanju istraživanja u kvantnoj kemiji i teorijskoj kemiji u Hrvatskoj.

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