Theor Chem Acc (2004) 111:58–60
DOI 10.1007/s00214-003-0559-7

Theoretical
Chemistry Accounts

Introduction

Jacopo Tomasi

Maurizio Persico

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, 56126, Pisa, Italy
e-mail: mau@dcci.unipi.it

Received: 19 December 2002 / Accepted: 19 December 2002 / Published online: 21 January 2004

Introduction

Jacopo Tomasi was born in Diano Marina, a sea town in the north-west of Italy, on 14 September 1934. During his youth he went through the harshness and upheaval of World War II, and to this period belong the first reminiscences we share of his – occasionally dangerous – adventures: mother cooking with TNT, for lack of a tamer fuel; or young Jacopo following his father into a minefield to gather firewood. ''We'' here means the friends, coworkers and other charmed listeners who have profited from the first quality of Jacopo we wish to point out: that of being a gifted, cultured and entertaining talker and storyteller, in spite of his characteristic stuttering. Surely this quality was reinforced by his unestinguished and omnivorous curiosity, which he has always tried to satisfy by travelling, reading, talking to people, and, of course, by doing research. A broad range of scientific (and extra-scientific) interests, an enviable memory and very effective organization of bibliographic work make him an exceptionally cultured chemist.

Jacopo moved to Pisa in 1952, having won a scholarship from the Scuola Normale Superiore to study chemistry at the University of Pisa. In the next few years he witnessed the flourishing of a vital and innovative school of chemistry, thanks to the impulse of two leading figures, Eolo Scrocco and Piero Pino, and of their younger coworkers. It was a time of creativity and ''big science'' at our university: following the advice of Enrico Fermi, professors and technicians designed and built the first electronic computer in Italy, the ''Calcolatrice elettronica Pisana'', which was operative in 1960. With that machine Jacopo and other young researchers (R. Moccia, G. P. Arrighini, and C. Guidotti), together with their senior fellows in theoretical chemistry (O. Salvetti and M. Maestro) entered the era of electronic computing, after years of painstaking calculations with crank calculators and handwritten four-index matrices.

Jacopo's first research works, under the guidance of Professor Scrocco, concerned quantum chemistry methods, as the times required: use of polarized basis functions or bond functions in ab initio calculations [1, 2], implementation of a Hartree–Fock (HF) scheme based on density matrix partitioning [3] and, later on, configuration interaction expansions [4]. Very soon they tackled problems of interest for the experimental community, such as the determination of nuclear quadrupole coupling constants [5, 6], at the time when nuclear quadrupole resonance spectroscopy was being developed in Pisa.

The main thrust, however, was towards the development of theoretical concepts and tools, suitable to extend the range of applicability of ab initio calculations and to extract from their results at least semiquantitative information about complex phenomena, such as chemical reactivity. The strategy, easily recognized in the pattern of Jacopo's publications since the late 1960s, and explicitly stated later on [7–11], was articulated in two points. The first point stems from the observation that the ''brute force'' ab initio technique was not (*is* not) powerful enough to account for all the important chemical phenomena, and its limitations may drive a theoretician to oversimplify in a misleading way chemical reality; hence, we need physical models of the complex systems and processes we are studying, whereby the core features are treated at the highest level of accuracy (e.g. ab initio) and other important but complementary aspects are taken into account in a less detailed way. The second basic observation is that 1, 10 or 100 calculations will add little to our knowledge, if we cannot use the computational results to formulate and validate general laws, trends and concepts which help us to understand and predict chemical phenomena at a qualitative or semiquantitative level. This effort of generalization is necessary if we do not want theoretical chemistry to be ''a deluge of numbers on a desert of concepts'', according to Bernard Lévy's colourful expression.

Along these lines, in the 1970s and early 1980s Jacopo explored the predictive power of the molecular electrostatic potential (MEP) for chemical reactivity and intermolecular interactions [12, 13], devised an early version of what we would now call a quantum mechanical/molecular mechanics method [14, 15], studied crystal field effects on embedded ions [16],

demonstrated the additivity of group contributions to the MEP [17], and investigated the validity of energy and wavefunction decomposition schemes in intramolecular and intermolecular interactions [18–20]. The quest for simplified models and qualitative explanations is also apparent in the intense work on chemical reactivity [21–23] and in the first investigations on excited states [24], which triggered interest in photochemistry among younger coworkers in Pisa [25]. Of this period, the most lasting success is certainly the introduction of the MEP as a tool for characterizing the reactivity of functional groups, enzyme active sites, host–guest and solute–solvent interactions, crystal surfaces and cavities; the origin and the development of MEP concepts, techniques and applications were nicely reviewed by Náray-Szabo and Ferenczy [26] in 1995.

The investigation of reaction mechanisms and of biochemical processes, among other fields in which Jacopo was very active in the 1970s and 1980s, required the development of a theoretical tool to deal with solvent effects. This came in 1981, with the first implementation of the polarizable continuum model (PCM) [27]. The lasting impact of this paper in the next 2 decades has been well documented by Luque et al. [28]. The formulation of the PCM put forward by Miertuš, Scrocco and Tomasi was not the first based on an effective Hamiltonian and on the representation of the solvent as a continuum dielectric [29]. Yet, since it was based on a solvent cavity of realistic shape, it had a wider applicability than previous continuum models. On the other hand, it also proved more difficult to supplement Tomasi's PCM with certain technical features such as analytic derivatives of the free energy with respect to nuclear coordinates: such developments had to wait until 1994 [30–33]. The implementation of the model itself was reformulated several times in the last 2 decades: important steps in this process were the introduction of a matrix-inversion technique [34] and of an integral equation formalism [35], the coupling with ab initio methods beyond the HF approximation [36–39], and the inclusion of dispersion–repulsion interactions [40, 41]. The generality of the model and the aforesaid reformulations have allowed it to be adapted to a wide range of problems and physical situations: nonequilibrium solvation [38, 42, 43], interfaces [44–46], anisotropic and nonhomogeneous media [35, 47, 48], and transition states in chemical reactions [49–52]. In the last few years, Tomasi's group has shifted the focus to spectroscopic, optical, magnetic and other molecular properties of solutes [46, 53–58], but many other groups around the world have contributed to the development of the PCM and have applied it in the investigation of a great variety of chemical problems, especially since it has been implemented in widely employed packages, such as GAUSSIAN and GAMESS.

Of course these achievements are not the work of one or a few people, yet Jacopo's research group has never been large. A cursory look at the list of his publications shows that he has worked with more than 110 other scientists, mostly younger people and mostly foreigners, who have been attracted to Pisa by Jacopo's scientific personality and have enriched our small party of quantum chemists with new ideas, different points of view and interests, and precious technical skills. In this way Jacopo has played a fundamental role in opening Pisa's group to the direct contact and beneficial influence of the greater international community.

To many of these people Jacopo has been "the boss", for a few months or for several years, in his peculiar way. He has always felt one of his main responsibilities is to ensure that everyone in his entourage does research (and teaching, and other academic duties) to the best of his or her skill and aptitude. But, at the same time, he has been very generous in granting full freedom and support to everybody who wished to develop a new research line, however far from the "core business" of the group. For this, all of us, Jacopo's former students and younger coworkers, are extremely grateful.

References

1. Scrocco E, Tomasi J (1961) Mol Phys 4: 193
2. Bonaccorsi R, Salvetti O, Scrocco E, Tomasi J (1966) J Chem Phys 44: 4361
3. Scrocco E, Tomasi J (1964) A study of Cl^- and HCl by a factorization technique of density matrix in the SCF-LCAO-MO method. Molecular orbitals in chemistry, physics and biology. Academic, New York
4. Alagona G, Tomasi J (1972) Theor Chim Acta 24: 42
5. Scrocco E, Tomasi J (1964) Theor Chim Acta 2: 386
6. Bonaccorsi R, Scrocco E, Tomasi J (1969) J Chem Phys 50: 2940
7. Scrocco E, Tomasi J (1978) Adv Quantum Chem 2: 115
8. Tomasi J (1988) J Mol Struct (THEOCHEM) 179: 273
9. Tomasi J, Alagona G, Bonaccorsi R, Ghio C, Cammi R (1991) In: Maksic ZB (ed) Theoretical models of chemical bonding, part 3 Springer, Berlin Heidelberg New York, p 545
10. Tomasi J, Bonaccorsi R, Cammi R (1991) In: Maksic ZB (ed) Theoretical models of chemical bonding, part 4. Springer, Berlin Heidelberg New York, p 229
11. Tomasi J (1996) In: Ellinger Y, Defranceschi M (eds) Strategies and applications in quantum chemistry Kluwer, Dordrecht, p 1
12. Bonaccorsi R, Scrocco E, Tomasi J (1970) J Chem Phys 52: 5270
13. Bonaccorsi R, Pullman A, Scrocco E, Tomasi J (1972) Theor Chim Acta 24: 51
14. Bonaccorsi R, Petrongolo C, Scrocco E, Tomasi J (1971) Theor Chim Acta 20: 331
15. Alagona G, Cimiraglia R, Scrocco E, Tomasi J (1972) Theor Chim Acta 25: 103
16. Ghio C, Scrocco E, Tomasi J (1976) In: Pullmann (ed) Environmental effects on molecular structure and properties. Reidel, Dordrecht, p 329
17. Bonaccorsi R, Scrocco E, Tomasi J (1976) J Am Chem Soc 98: 4049
18. Bonaccorsi R, Scrocco E, Tomasi J (1969) J Chem Phys 50: 2940
19. Ghio C, Scrocco E, Tomasi J (1980) Theor Chim Acta 56: 61
20. Cammi R, Bonaccorsi R, Tomasi J (1985) Theor Chim Acta 68: 271
21. Petrongolo C, Tomasi J (1984) In: Chemical and biochemical reactivity. The Jerusalem symposia on quantum chemistry and biochemistry VI, Jerusalem, p 513
22. Silla E, Scrocco E, Tomasi J (1975) Theor Chim Acta 40: 343
23. Alagona G, Tomasi J (1983) J Mol Struct (THEOCHEM) 91: 263
24. Cimiraglia R, Tomasi J (1977) J Am Chem Soc 99: 1135

25. Cimiraglia R, Persico M, Tomasi J (1977) J Phys Chem 81: 1876
26. Náray-Szabo G, Ferenczy GG (1995) Chem Rev 95: 829
27. Miertuš S, Scrocco E, Tomasi J (1981) Chem Phys 55: 117
28. Luque FJ, Lopez JM, Orozco M (2000) Theor Chem Acc 103: 343
29. Tomasi J, Persico M (1994) Chem Rev 94: 2027
30. Cammi R, Tomasi J (1994) J Chem Phys 101: 3888
31. Cancès E, Mennucci B, Tomasi J (1998) J Chem Phys 109: 260
32. Barone V, Cossi M, Tomasi J (1998) J Comput Chem 19: 404
33. Cammi R, Mennucci B, Tomasi J (1999) J Phys Chem A 103: 9100
34. Cammi R, Tomasi J (1995) J Comput Chem 16: 1449
35. Cancès E, Mennucci B, Tomasi J (1997) J Chem Phys 107: 3032
36. Olivares del Valle FJ, Tomasi J (1991) Chem Phys 150: 139
37. Fortunelli A, Tomasi J (1994) Chem Phys Lett 231: 34
38. Mennucci B, Cammi R, Tomasi J (1998) J Chem Phys 109: 2798
39. Cammi R, Frediani L, Mennucci B, Tomasi J, Ruud K, Mikkelsen K (2002) J Chem Phys 117: 13
40. Floris FM, Tomasi J (1989) J Comput Chem 10: 616
41. Amovilli C, Barone V, Cammi R, Cancès E, Cossi M, Mennucci B, Pomelli CS, Tomasi J (1998) Adv Quantum Chem 32: 227
42. Bonaccorsi R, Cimiraglia R, Tomasi J (1983) J Comput Chem 4: 567
43. Aguilar MA, Olivares del Valle FJ, Tomasi J (1993) J Chem Phys 98: 7375
44. Bonaccorsi R, Floris F, Palla P, Tomasi J (1990) Thermochim Acta 162: 213
45. Frediani L, Pomelli CS, Tomasi J (2000) Phys Chem Chem Phys 2: 4876
46. Corni S, Tomasi J (2002) J Chem Phys 116: 1156
47. Mennucci B, Cossi M, Tomasi J (1995) J Chem Phys 102: 6837
48. Mennucci B, Cancès E, Tomasi J (1997) J Phys Chem B 101: 10506
49. Bonaccorsi R, Cimiraglia R, Tomasi J, Miertuš S (1983) J Mol Struct (THEOCHEM) 94: 11
50. Pomelli CS, Tomasi J (1997) J Phys Chem A 101: 3561
51. Coitiño L, Ciuffarin E, Floris FM, Tomasi J (1998) J Phys Chem A 102: 8369
52. Amovilli C, Floris FM, Solá M, Tomasi J (2001) Organometallics 20: 1310
53. Cammi R, Cossi M, Mennucci B, Tomasi J (1996) J Chem Phys 105: 10556
54. Cammi R, Mennucci B, Tomasi J (1999) J Chem Phys 110: 7627
55. Cappelli C, Corni S, Cammi R, Mennucci B, Tomasi J (2000) J Chem Phys 113: 11270
56. Cammi R, Mennucci B, Tomasi J (2000) J Phys Chem A 104: 4690
57. Mennucci B, Tomasi J, Cammi R, Cheeseman JR, Frisch MJ, Devlin FJ, Gabriel S, Stephens PJ (2002) J Phys Chem A 106: 6102
58. Corni S, Cappelli C, Cammi R, Tomasi J (2001) J Phys Chem A 105: 8310