REVIEW ARTICLE

Charge-Transfer Integrals for Perylenetetracarboxylic Dianhydride (PTCDA) – Critical Overview of Available Computational Methods[*]

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An attempt is made to estimate the nearest-neighbour charge-transfer integrals for the crystal of perylenetetracarboxylic dianhydride (PTCDA). Several alternative methodologies are applied; the case of PTCDA is used to discuss their advantages and shortcomings.

Introduction

The recent discoveries of superconductivity and laser action in solid polyacenes [1,2], followed by successful construction of a pentacene-based field-effect transistor [3], have prompted considerable revival of interest in the electrical properties of organic molecular crystals. The new discoveries emphasize the need to develop a reasonable strategy for attaining an acceptable degree of understanding of the underlying fundamental phenomena, which in a long run would enable one to make useful predictions. One of the possible strategies entails the study of a wide range of related organic systems, representing a large diversity of chemical and crystallographic features. Owing to its structure, the crystal of perylenetetracarboxylic dianhydride (PTCDA, *cf*. Fig. 1) is one of intriguing cases, intensively studied in the recent years [4–9]. In this paper, it will be used to exemplify a problem ubiquitous in the theoretical description of organic solids.
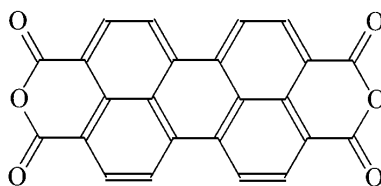

Figure 1. Perylenetetracarboxylic dianhydride (PTCDA).

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[*]Dedicated to the memory of Professor Krzysztof Pigoń.

The charge-transfer (CT) states and their coupling with the Frenkel states are one of the primary targets both for experimental and theoretical studies. The evaluation of the diagonal energies of localized charge pairs is nowadays a more or less standard procedure: the electrostatic stabilization can be accurately calculated by Self-Consistent Polarization Field (SCPF, [10]) or Fourier-Transform (FT, [11,12]) methods; although the accuracy of the standard quantum chemical methodologies for calculating the energies of isolated ions (molecular ionization potential and electron affinity) are less accurate, when combined with a judicious correcting scheme [13], they may provide a reasonable starting point for interpretational purposes. On the other hand, there seems to exist no accepted standard routine for the calculations of the CT integrals, crucial for spectroscopic applications and for the description of charge transport. As the computer codes for the well founded and well tested classic approach [14–16] are practically extinct, there is a natural tendency to harness for this purpose the existing quantum chemistry packages. Unfortunately, most of them are not adequate in this context, which is not always recognized. The objective of this paper is to show the limits of their performance.

Classic approach

The standard way of calculating the CT integrals, developed by Katz *et al.* [14,15], consists of two steps. In the first step, the molecular orbitals of the molecules involved in the transfer are generated by one of the standard quantum chemical methods (either semi-empirical or *ab initio*). Within reasonable limits, at this stage, the quality of the atomic orbitals is practically irrelevant [14,15] and any standard basis set may be applied. In the second step, the calculated LCAO coefficients are used to calculate the CT integrals from definition, *i.e.* as the matrix elements $<AB^{\pm}|H|A^{\pm}B>$ of the crystal Hamiltonian H, off-diagonal in the basis spanned by the products of the molecular orbitals of individual molecules A,B (the superscripts $\pm$ denoting the corresponding ions). As was shown for polyacenes in the early papers on the subject [14], the CT integrals are extremely sensitive to intermolecular overlap, limited by the long-range behaviour of the wavefunctions; accordingly, at this stage the best available SCF atomic orbitals are used [14,15]. The great advantage of calculating the CT integrals in this way consists in the fact that the time- and memory-consuming LCAO MO calculations can be done for a single molecule and in a modest basis set, while the main source of order-of-magnitude errors, *i.e.* poor description of intermolecular overlap, is eliminated. So far, this classic approach was used only for aromatic hydrocarbons, and only the π-orbitals were explicitly taken into account, which was justified by their dominant role at a large distance from the molecule. In effect the program codes, that implement the second step of the procedure described above, can handle only the contributions from carbon atoms. Nowadays, when many systems of actual interest contain heteroatoms, this is a very serious limitation.

One might argue that most molecules of interest contain few heteroatoms, which should affect the molecular orbitals only to some extent, not necessarily crucial for the CT integrals. In a different context, valuable hints could be obtained when a non-hydrocarbon molecule was mimicked by its hydrocarbon analogue [17]. It is tempting to apply a similar approach for calculating the CT integrals. In order to test this idea, we have applied it to calculate them for the nearest-neighbour molecules in the PTCDA crystal.

In the first step, the PTCDA molecular orbitals were generated by the standard GAMESS program at the RHF STO-3G level. In the second step, based on the known crystal structure [18], the CT integrals were calculated using an adapted version of the program originally written by Yokoi for anthracene [19]. The PTCDA molecule was represented as a fictitious pseudo-hydrocarbon system, where the oxygen atomic orbitals were modified in two alternative ways. 1. The oxygen orbitals were assumed to have a negligibly short range, so that their contributions to the CT integrals (weighted by the LCAO coefficients obtained in the first step for the actual oxygen atoms) were entirely neglected; 2. The oxygen orbitals were replaced by carbon orbitals (again weighted by the LCAO coefficients obtained in the first step for the actual oxygen atoms). Neither of the above representations is realistic. Nevertheless, if the results turned out to exhibit a not too strong sensitivity to the level of approximation, the program code strictly applicable only for hydrocarbons might provide some indirect clues also for other systems.

Table 1. Electron and hole transfer integrals estimated by various methods. The transfer is assumed to take place between the molecule located at (0,0,0) and that at the position indicated in the table. O→C: oxygen orbitals are replaced by carbon orbitals; O→0: oxygen orbitals are assumed to have negligible range. ± marks the cases where the applied method does not allow one to determine the sign of the corresponding integral. All integrals are expressed in units of 10^{-4} eV.

Crystal/Method	Electron	Hole	Electron	Hole
Anthracene	(1/2,1/2,0)		(1,1,0)	
Classic, [16]	434	−303	258	−453
STO-3G, [23]	±340		±240	
STO-631G, [23]	±910	±320	±580	±560
DFT band calcns [26]	±590	±174	335	−378
PTCDA	(1,0,0)			
Classic, O→C	−170	−213		
Classic, O→0	31	−433		
Dimer, RHF 321G	±90	±440		
Dimer, RHF 631G	±80	±515		
Dimer, RHF 631G*	±55	±530		
Dimer, ZINDO/S, [9]	−70	−610		
DFT band calcns/fit	±180	±440		

Unfortunately, this is not the case. The results are shown in Table 1. It is readily seen that they differ drastically; even the sign of the integrals may be different. A change of even very few atomic orbitals substantially affects the values of the CT

integrals; the latter turn out to be very sensitive to the chemical identity of every single atom of the molecule. In this respect PTCDA may be somewhat exceptional, owing to the unusual plane-to-plane arrangement of the nearest-neighbour molecules and to phase alternation in the HOMO and LUMO, peculiar to PTCDA and related systems [20]; when combined, the two effects result in a near-cancellation of the terms of different sign [20], so that even a few contributing atoms may substantially change this fragile balance. However, it is difficult to rule out that a similar situation may be encountered also in other systems; the bottom line is that the existing programs, based on the classic approach, are not a feasible tool to estimate the CT integrals in systems containing heteroatoms. This motivates the search for alternative methods.

Supermolecule LCAO MO approach

A seemingly feasible alternative was first applied by Grant [21]. It is based on the following argument: Consider a dimer, composed of two moieties related by a point-group symmetry operation. To a good approximation, its orbital energies are split symmetrically with respect to the corresponding energy in the monomer (modified by the diagonal part of the intermolecular interaction, which, by virtue of symmetry, is the same for both moieties). Upon closer scrutiny, the splitting of the HOMO may be identified as twice the hole transfer integral, and the splitting of the LUMO – as twice the electron transfer integral. Therefore, the transfer integrals may be easily found by analyzing the eigenenergies calculated by any standard quantum chemical method, applied to the dimer viewed as a supermolecule. Only a rather special analysis of the eigenvectors allows one to determine the signs of the integrals [9,22]; usually this is not done. Silinsh *et al*. [23] performed the dimer-type MO calculations for anthracene, using state-of-the-art Gaussian basis sets. In their calculations the relative orientation of the moieties mimicked the arrangement of the molecules in the anthracene crystal for the directions corresponding to the largest CT integrals. The results are quoted in Table 1. It is readily seen that the integrals strongly depend on the basis size; for the STO-3G basis they are smaller, but for the STO-631G basis they are considerably larger than those of Tiberghien and Delacote [16], obtained within the classic approach (also shown in Table 1).

This provokes the obvious question: which of the obtained results, if any, is trustworthy? As an indicator we have used the ratio of the carbon 2p orbital, represented by different state-of-the-art Gaussian basis functions, to the SCF carbon orbital represented by a superposition of three p-type Slater functions [24] (more extended Slater basis sets yield practically the same results). In Fig. 2 the dependence of this ratio on the distance from the nucleus is displayed for two representative Gaussian basis sets.
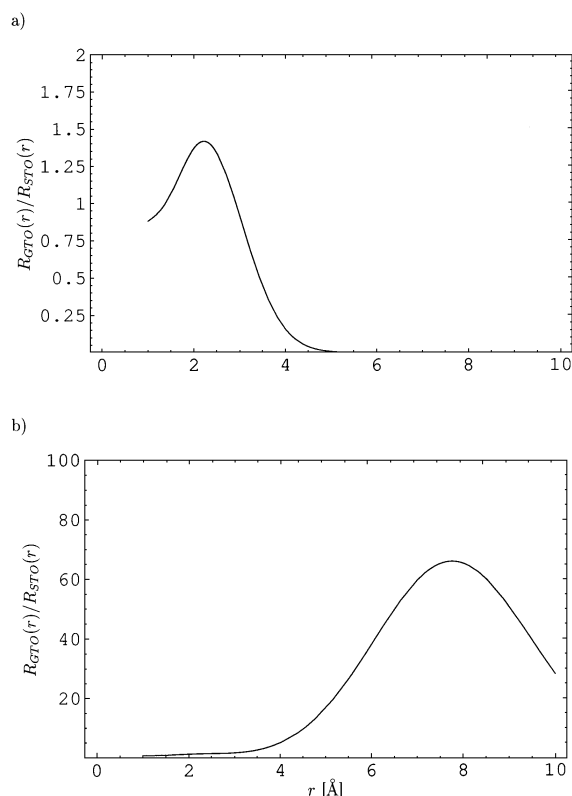
a)

b)

Figure 2. Dependence of the ratio of the various Gaussian representations (panel a: 631G, panel b: 631+G) of the carbon 2p orbital to the corresponding SCF carbon orbital, on the distance from the nucleus.

It is readily seen that the Gaussian representation poorly reproduces the shape of the carbon orbital at typical intermolecular distances. At some distances the wave-function is underestimated, at other distances it may be overestimated by more than one order of magnitude. The actual value of the CT integral is composed of contributions corresponding to different interatomic distances, weighted by factors dependent on the number of atoms separated by a given distance, *i.e.* on the geometry of the molecules and on their relative orientation, defined by crystal structure. In any actual case it is practically impossible to foresee, whether the overestimated or the underestimated terms would dominate. In effect, not only is it impossible to predict, which of the Gaussian sets would produce the most realistic CT integrals, but it is even difficult to anticipate, whether any given set would yield a big-side or a small-side estimate. In this respect, the smallest Gaussian basis sets are probably the safest, as they are expected to consistently underestimate the actual integrals.

For comparison, we have used the same methodology, with various Gaussian basis sets, to calculate the CT integrals for PTCDA. The results are again collected in Table 1.

In contrast to the anthracene case, for PTCDA the dependence of the results on the basis size is marked, but not as strong as it is for polyacenes. This is probably another manifestation of the near-cancellation of the terms of different sign, due to phase alternation in the HOMO and LUMO [20] (*vide supra*). When a more extended basis set is used, most of the contributions from distant atoms, exposed by the longer range of the basis orbitals, cancel out anyway, so that their net effect on the integral value is dramatically reduced. This observation is consistent with the results of the preceding section. It is worth noting that a more extended basis does not necessarily imply larger values of the CT integrals (in fact, the electron transfer integral *decreases* with increasing size of the basis set).

With respect to the classic approach, the supermolecule approach gives one the advantage of using a standard program package for molecular orbital calculations. However, it involves considerable computational effort: the eigenstates have to be calculated for a system twice as large as is necessary for the classic approach described in the preceding section. The numerical effort is much larger for extended basis sets. The above results obtained for the Gaussian basis suggest that for some molecules containing heteroatoms, the calculations based on a very simple representation of atomic orbitals cannot be dismissed off-hand, as is normally done for hydrocarbons: it seems more important to account properly for the chemical nature of the constituent atoms than to reproduce the long-distance tails of their wavefunctions. Admittedly, the values obtained in this way are expected to provide a crude estimate, but it seems that in contrast to the situation typical for hydrocarbons [14], no order-of-magnitude errors are expected.

This suggests that much less sophisticated calculations might provide about the same information at a much lower cost. Hoffmann *et al*. [9,22] calculated the PTCDA charge transfer integrals by means of the simple ZINDO/S semiempirical method. This simplistic calculation, where the carbon orbitals are represented by only one Slater function, yields the transfer integrals of the same order of magnitude as our calculations in a small Gaussian basis sets (*cf.* Table 1), which is again the expected effect of the near-cancellations mentioned above.

Unfortunately, even if this level of approximation were deemed acceptable in some contexts, the supermolecule approach is not general enough to provide all the necessary CT integrals. In fact, it cannot be used for calculating the transfer integrals between the molecules, which in the crystal are related only by space-group symmetry, and there is no point-group symmetry element, which would transform one of them into the other. In that case the dimer extracted from the crystal consists of inequivalent moieties. The supermolecule orbitals are localized predominantly on one of the monomers, as the diagonal part of the intermolecular interaction is different for each of the two molecules. This difference contributes to the resultant splitting of the orbital energies, which is no longer simply related to the CT integral.

This is well illustrated on the example of PTCDA. The nearest-neighbour molecules are located in the (1,0,0) relative position, in plane-to-plane orientation; in addition to the translation by one lattice period (about 3.5 Å), they are related by a centre

of inversion. The transfer integrals, estimated from orbital splittings in the dimer, are affected to an unknown extent by the shortcomings of the Gaussian basis set. Yet, as discussed above, the calculated values remain within a reasonable range (*cf.* Table 1). On the other hand, our calculations reveal that for the molecules in the (0,1/2,1/2) relative position, the HOMO and LUMO splittings are on the order of 0.5 eV. If these splittings were attributed to the CT integrals alone, it would yield about 0.25 eV, evidently unphysical for molecules with centres some 10 Å apart and in an orientation that rules out substantial π-orbital overlap.

So far, the difficulties described above seem to have passed unnoticed in the literature; some of the past results have to be reassessed in the new light. In [23] it was noted that the CT integrals for anthracene, calculated in extended Gaussian basis sets, exceed those obtained in the basis of the best SCF carbon orbitals. In view of Fig. 2, there is little doubt that the earlier results of Tiberghien and Delacote [16] must be considered as the more reliable ones. For the transfer between the molecules in the (0,1,0) relative position, which are related by a centre of symmetry, the discrepancy may be attributed entirely to the contributions from those parts of space, where the Gaussian representation overestimates the corresponding SCF orbital. However, for the molecules in the (1/2,1/2,0) relative position the results of [23] are even less accurate, since they contain inevitably a contribution due to the difference in the diagonal part of the intermolecular interaction; the (very large) value of about 0.09 eV obtained for the (1/2,1/2,0) electron transfer integral has probably this provenance.

Band structure calculations

Solid state band structure calculations provide another alternative for evaluating the CT integrals. In fact, the analogues of quantum chemical methods applied for molecules may be used to generate the crystal counterparts of molecular orbitals. In view of the translational symmetry of the solid, the eigenstates are now labelled by the values of quasimomentum **k**, and there are standard program packages to calculate the **k**-dependence of orbital energies, often referred to as "orbital dispersion relations". On the other hand, simple geometric considerations, based on the specific crystal structure in hand, allow one to pinpoint several transfer integrals that are of primary relevance for the actual band structure (*e.g.* those involving the nearest neighbours in each of the main crystal directions), and these may be used as parameters for fitting the calculated HOMO and LUMO dispersion relations. As long as the fitting procedure is based on those points of the Brillouin zone, where the HOMO and LUMO energies are well separated from other orbital levels, successful simulation of the band structure should provide a reasonable estimate of the relevant CT integrals. This approach was used for instance for the fullerene crystal [25].

The DFT approach implemented in the plane-wave basis (available in the commercially accessible CASTEP program) provides an efficient means of generating the band structure that is to be fitted. For PTCDA the crystal structure suggests that the dominant contribution to the dispersion relations should be limited by the transfer

between the nearest neighbours in the (1,0,0) direction. This allowed us to evaluate the corresponding electron and hole transfer integrals by single-parameter fits; an elementary derivation shows that the difference in the corresponding orbital energies at $\mathbf{k} = (0,0,0)$ and $\mathbf{k} = (\pi,0,0)$ is given as four times the relevant integral.

The integrals estimated in this way are listed in Table 1. Their absolute values are almost the same as those obtained by Hoffmann from supermolecule-type ZINDO/S calculations [9,22]. (There is a difference in the sign of the hole integral, which probably follows from a different convention used by the two programs to generate the relative phase of the basis orbitals centred at different molecules; an analogous problem was encountered in the classic calculations for polyacenes [16] when a different symmetry element was used to generate the phases for translationally inequivalent molecules).

On the one hand, the very good agreement between the two estimates lends additional credence to the result [9,22], based on a simple semiempirical scheme. On the other hand, as it is known that the ZINDO/S wavefunction (using the basis of single Slater functions) is bound to underestimate the orbital at typical intermolecular distances, it suggests that both results may represent a small-side estimate of the transfer integrals.

In order to give this conjecture some independent verification and to assess in a more general context the probable quality of the CT integrals estimated from band structure fits, we have done similar calculations for the naphthalene and anthracene crystals [26] for which the classic results [16] provide benchmark values. These results suggest that for the polyacene crystals only the integrals for the molecules in the (1/2,1/2,0), (0,1,0) and (1/2,1/2,1) positions are not negligible; therefore, our fits of the dispersion relations were based on these three parameters. The sample results for anthracene are shown in Table 1 (for naphthalene similar trends are observed [26]). Evidently, the estimates obtained from this procedure may either overestimate or underestimate the actual integrals even by a factor of two. On this view, it is quite probable that the values for PTCDA are indeed underestimated, possibly grossly.

Discussion

The calculations of the present paper, combined with the literature results, consistently yield the nearest-neighbour CT integrals for PTCDA on the order of 0.005–0.01 eV for the electron and 0.05 eV for the hole. These figures are probably underestimated. In a broader context, our results have some more general ramifications. Firstly, it follows that the presence of heteroatoms is of crucial importance for the transfer integrals and there is no simple way to simulate it by calculations for fictitious hydrocarbon systems. In effect, the error introduced by a poor representation of atomic orbitals (reaching one order of magnitude for polyacenes [14]), for systems containing heteroatoms may be exceeded by the error due to the neglect of the drastic differences of chemical nature. However, as this results from the peculiarities of crys-

tal and molecular structure, there is no way of predicting in advance which of the two factors would be the one limiting the CT integrals in a given system.

Assuming that the chemical factor dominates, the supermolecule approach based on the available INDO-type methods offers the most economic way to get crude estimates of the CT integrals. In this respect, the applicability of the sophisticated quantum chemistry packages based on the Gaussian basis is poorer. Small Gaussian sets grossly underestimate the wavefunction at relevant distances; in this sense they fare no better than the primitive Slater basis of INDO-type methods. Typical sets of more extended type underestimate the wavefunction in some parts of space and overestimate it in other parts, so that it is not even possible to foresee on which side of the correct value the calculated CT integral would be. This could probably be remedied by still larger basis sets, designed specifically for this purpose, which would be prohibitively time consuming and hence not practically feasible. Effectively, the Gaussian basis is rather unsuitable for evaluating the CT integrals.

Another method that could potentially be used for this purpose is rooted in solid-state band structure calculations (*e.g.* CASTEP). A fit of the dispersion relations calculated for the valence and conduction band yields the values of the relevant transfer integrals. For PTCDA, the CT integrals evaluated in this way are somewhat smaller than those obtained from ZINDO/S calculations, which suggests that they are probably underestimated. The results obtained for polyacenes, where the benchmark values of Tiberghien and Delacote are available [16], suggest that the estimates may be wrong by a factor of two. Very likely, the inherent accuracy of other methods based on standard programs, described in this paper, may be similar.

The classic approach [14–16] where the CT integrals are calculated from definition (as matrix elements of the crystal Hamiltonian in the localized basis set), is not used in current literature, since the corresponding computer codes are no longer accessible; moreover, they were originally developed only for hydrocarbons, while most of the systems of current interest contain heteroatoms. The more recent approximate version developed by Yokoi [19], based on Monte Carlo integrations, also suffers from this latter shortcoming.

There is little hope for progress, since in this approach the atomic orbitals are represented by superpositions of Slater functions and these are rarely used nowadays, because they require clumsy numerical integrations. Consequently, the task of developing new software of this kind is a tedious and unrewarding one: the computer routines that might be created for calculating the CT integrals would be unlikely to find other applications. Yet, in view of the imminent demand, due to the revival of interest in the electro-optical properties of organic solids, the effort might be worth investing.

Acknowledgments

REFERENCES

1. Schoen J.H., Kloc C. and Batlogg B., *Nature*, **406**, 702 (2000).
2. Schoen J.H., Kloc C., Dodabalapur A. and Batlogg B., *Science*, **289**, 599 (2000).
3. Schoen J.H., Berg S., Kloc C. and Batlogg B., *Science*, **287**, 1022 (2000).
4. Shen Z., Burrows P.E., Forrest S.R., Ziari M. and Steier W.H., *Chem. Phys. Lett*., **236**, 129 (1995).
5. Shen, Z. and Forrest S.R., *Phys. Rev. B*, **55**, 10578 (1997).
6. Bulović V., Burrows P.E., Forrest S.R., Cronin J.A. and Thompson M.E., *Chem. Phys*., **210**, 1 (1996).
7. Bulović V. and Forrest S.R., *Chem. Phys*., **210**, 13 (1996).
8. Hennessy M.H., Soos Z.G., Pascal R.A. Jr. and Girlando A., *Chem. Phys*., **245**, 199 (1999).
9. Hoffmann M., Schmidt K., Fritz T., Hasche T., Agranovich V.M. and Leo K., *Chem. Phys*., **258**, 73 (2000).
10. Silinsh E.A., Organic Molecular Crystals: Their Electronic States, Springer, Berlin 1980.
11. Bounds P.J. and Munn R.W., *Chem. Phys*., **44**, 103 (1979); **59**, 47 (1981); **59**, 47 (1981).
12. Eisenstein I. and Munn R.W., *Chem. Phys*., **77**, 47 (1983); **79**, 189 (1983).
13. Andrzejak M., Mazur G. and Petelenz P., *J. Mol. Struct. (Theochem)*, **527**, 91 (2000).
14. Katz J.I., Rice S.A., Choi S.I. and Jortner J., *J. Chem. Phys*., **39**, 1683 (1963).
15. Silbey R., Jortner J., Rice S.A. and Vala M.T. Jr., *J. Chem. Phys*., **42**, 733 (1965); **43**, 2925 (1965).
16. Tiberghien A. and Delacote G., *J. Phys. (Paris)*, **31**, 637 (1970).
17. Soos Z.G., Hennessy M.H. and Wen G., *Chem. Phys*., **227**, 19 (1998).
18. Ogawa T., Kuwamoto K., Isoda S., Kobayashi T. and Karl N., *Acta Cryst. B*, **55**, 123 (1999).
19. Yokoi K., *Phys. Rev. B*, **45**, 5919 (1992).
20. Kazmaier P.M. and Hoffmann R., *J. Am. Chem. Soc*., **116**, 9684 (1994).
21. Grant P.M., *Materials Science*, **10**, 95 (1984).
22. Hoffmann M., Doctoral Thesis, Dresden Technical University, Dresden 2000.
23. Silinsh E.A., Klimkans A., Larsson S. and Cápek V., *Chem. Phys*., **198**, 311 (1995).
24. Huzinaga S., Approximate Atomic Functions, University of Alberta 1971.
25. Janner A.-M., Eder R., Koopmans B., Jonkman H.T. and Sawatzky G.A., *Phys. Rev. B*., **52**, 17158 (1995).
26. Andrzejak M., Doctoral Thesis, Jagiellonian University, Cracow 2000.