Excitons in Confined Systems: in the memory of Prof. Rodolfo Del Sole.

The impressive improvement in deposition, characterization and manipulation of the samples in the last twenty years, has allowed to study the new physics of quantum confined systems and to extend the effects due to the strong radiation-matter interaction (polaritons).
The present series of Conferences on "Optics of Excitons in Confined Systems" , that the next September will open its 13^{th} meeting in Roma, has represented the ideal platform for discussing this interesting new physics, and has allowed the remarkable outcomes obtained in about twenty-six years of activity; in fact the first meeting was held in Roma in April of 1987.
I guess that this positive trend, that has overcomed the most optimistic expectation, is not over. In fact, strong non-linear effects, recently observed experimentally, namely: superfluidity, solitons, vortices and Bose-Einstein condensation, allow to hypothesize a new series of all optical devices based on Bose-Einstein condensation of polaritons that probably could be the core business of the future OECS conferences.
The study of all these interesting new effects has allowed to consider the "optics of exciton-polaritons in mesoscopic materials" as one of the most dynamic field of research in the condensed matter physics. Moreover, a long lasting discussion about the advantages and disadvantages of adopting different theoretical frameworks, based respectively on fermion, boson and composite-boson basis sets, for studying fundamental properties of exciton-polariton, was present in the past years. In order to evaluate the progress in this field, let me remind that, a framework well suited for computing self-consistent exciton-polariton linear and non-linear optical response, the so called "ABC free theory", was presented at the very beginning of OECS-Conferences, (Montelibretti, 13-16 April 1987) by Prof. Kikuo Cho, while, recently, Prof. Rodolfo Del Sole have shown that "ab initio" GW-calculation and Bethe-Salpeter electron-hole interaction is a correct framework for computing Wannier exciton-polariton in a surface of semiconductors.

Let me remind that in the first section of the present conference, some Collaborators of Prof. Rodolfo del Sole will illustrate the main scientific achievements, obtained in his not very long but intense carrier. Since, I am on the group of Colleagues that in a particular period of his carrier, have had the fortune of collaborating with Prof. Rodolfo Del Sole, let me spend some words about that period.
I guess that the problem of studying exciton-polariton by a self-consistent "ab initio" calculation was one of the main goals of the scientific activity of Prof. Rodolfo Del Sole, and, even if it was fully reached only recently, conceptually was present also at the very beginning of our collaboration.

I have met Rodolfo three times in my life, and each one in rather different contexts.
-The first one was at Roma La Sapienza University during the tutorial course of experimental physics, it was in the Autumn of 1966. That exam was compulsory for overcoming the threshold between the first and the second cycle of General Physics.
I was in the same team of Rodolfo, and our goal was to build up an experiment on the violation of parity conservation in beta decay. That experiment was a very difficult task for us, and our experimental results were not appreciated by our Tutor, and , therefore the evaluation of our work was very scarce for both. This experience probably accelerated the decision of looking for a theoretical degree.
-The second time that I met Rodolfo was at the "Cecchignola" place, the military town of Roma at about 1971. We performed a part of our compulsory period (about fifteen months) in the same barracks: the technical services of the Italian Army (STELA). In that period I also met his wife each evening picking him up.
-The third time was one year later (1972). In that period Rodolfo was in the group of Prof. Franco Bassani, at the Physics building of La Sapienza university, and he was teaching, as associated professor, at Camerino University; and I was a researcher at the Raman and Infrared Group (Prof.M.

Scrocco) of the Institute of Advanced Inorganic Methodology (IMAI), a chemical-physical institute of the National Research Council, located at the Chemistry building in front of the Physics one.
In the same year my scientific group participated to the International Conference on Polaritons held from 2nd to 6th of October in Taormina, Sicily (*"Polaritons"* Ed.: Elias Burstein and Francesco De Martini, Pergamon Press, 1972) organized by Elias Burstein and Francesco De Martini. In that Conference, Veselago illustrated some interesting effects, as the left propagation of photons, obtained when dielectric function and magnetic permeability are both negative, but what interested us was the concept of Polariton and its intriguing optical properties. Coming back from the Conference at the IMAI laboratory, we started to study phonon-polaritons for the optical characterization of molecular and ionic crystals.

phys. stat. sol. (b) 54, K131 (1972)

Subject classification: 6 and 13.5; 20.1; 22.8.1

C.N.R., Laboratorio di Metodologie Avanzate Inorganiche,
Istituto di Chimica Generale ed Inorganica, Università di Roma

Light Scattering from Polaritons in $NaBrO_3$ and $NaClO_3$

By

A. D'ANDREA, B. FORNARI, G. MATTEI, M. PAGANNONE, and M. SCROCCO

We have measured the polariton dispersion in two polyatomic crystals, sodium bromate and sodium chlorate, which are both cubic, space group $T^4(P2_13)$, with four molecules per unit cell and fourteen polar optical phonons of F-symmetry and whose Raman spectra have recently been measured by the laser Raman technique (1, 2).

Neglecting phonon damping, the frequencies and momenta of the transverse infrared-active vibrational excitations in a polyatomic crystal, assumed optically isotropic, are related as follows (3):

$$\varepsilon(\omega) = \frac{k^2c^2}{\omega^2} = \varepsilon_\infty + \sum_{j=1}^{n} \frac{S_j\,\omega_j^2}{\omega_j^2 - \omega^2}, \qquad (1)$$

My scientific collaboration with Rodolfo started at the 13th International Conference of Semiconductors held in Roma from 30th of August to 3rd of September 1976, where our work on *"The (e,2e) technique as a tool for surface spectroscopy: ideal and reconstructed surface"* was accepted as oral presentation in the section: Surfaces.
Very briefly, that technique, derived from nuclear techniques (p,2p) and (n,2n), was proposed by Ugo Amaldi as an experiment able to measure directly the dispersion curves in solids. We presented an application for studying a 2D dispersion curves on ideal (1x1) and reconstructed (2x1) Silicon surface.

Surface Science 71 (1978) 306–326

THEORY OF (e, 2e) REACTION NEAR SOLID SURFACES: APPLICATION TO Si

A. D'ANDREA
Laboratorio di Metodologie Avanzate Inorganiche, CNR di Roma, Rome, Italy

and

R. DEL SOLE
G.N.S.M., Istituto di Fisica dell'Università di Roma, Rome, Italy,

and

Istituto di Fisica dell'Università di Camerino

Received 25 April 1977; manuscript received in final form 18 July 1977

The use of the (e, 2e) technique in surface state spectroscopy is discussed. A general formulation based on Green function formalism is developed, that allows to take into account the electron–solid interaction. The case of the Si(111) surface is considered in detail. It is shown that the (e, 2e) cross section strongly depends on surface conditions; hence this technique could be an efficient tool for testing reconstruction models.

The success obtained with the participation to the 13^{th} Conference on Physics of Semiconductors, encouraged us in order to continue the collaboration that was extended to the optical properties of exciton-polaritons in surfaces and in semi-infinite solids.

Taking into account the Pekar's suggestion, where he claims: *"all boundary conditions in the problem under consideration (exciton-polariton), including the ABC as special case, must follow from the Schroedinger equation and the Maxwell system of equations"* (the former statement is also reported on the book: *"Crystal Optics and Additional Light Waves"* S.I. Pekar ,The Benjamin/Cummings Publishing Company, California 1974), our first paper on exciton-polariton in semi-infinite semiconductors had as title *"Excitons in semi-infinite crystals: microscopic calculation of optical reflectivity"* and it was published in Solid State Communication in 1979 (v.**30**,p.145, 1979).
The work was based on the so called D'Andrea-Del Sole exciton envelope function model, that is a solution of Schroedinger equation for semi-infinite solids and is expanded in a product of center-of-mass motion plane waves and hydrogenic wave functions:

$$\Psi_{ex}(\vec{r},\vec{R}) = N_{ex}\left\{\left[e^{-iK_zZ} + Ae^{iK_zZ}\right]\varphi_{1S}(r) + \sum_{n>1} c_n\varphi_n(\vec{r})\,e^{-P_nZ}\right\}e^{i\vec{K}_{//}\cdot\vec{R}_{//}}/\sqrt{S} \qquad (n \equiv n,l,m)\,,$$

supplemented by no-escape boundary conditions on the surface: $\Psi_{ex}(z_e = 0) = \Psi_{ex}(z_h = 0) = 0.0$. Notice, that the former boundary conditions give an intrinsic dead-layer (or transition layer) on the semiconductor surface. Moreover, the self-consistent solution is based on a variational principle for computing the exciton envelope function and an exact solution of the linear Maxwell's equations.

Solid State Communications, Vol. 30, pp. 145–149.
Pergamon Press Ltd. 1979. Printed in Great Britain.

EXCITONS IN SEMI-INFINITE CRYSTALS: MICROSCOPIC CALCULATION OF OPTICAL REFLECTIVITY

A. D'Andrea

Laboratorio di Metodologie Avanzate Inorganiche del CNR, Rome, Italy

and

R. Del Sole

Istituto di Fisica dell'Università di Camerino, Camerino, Italy

and

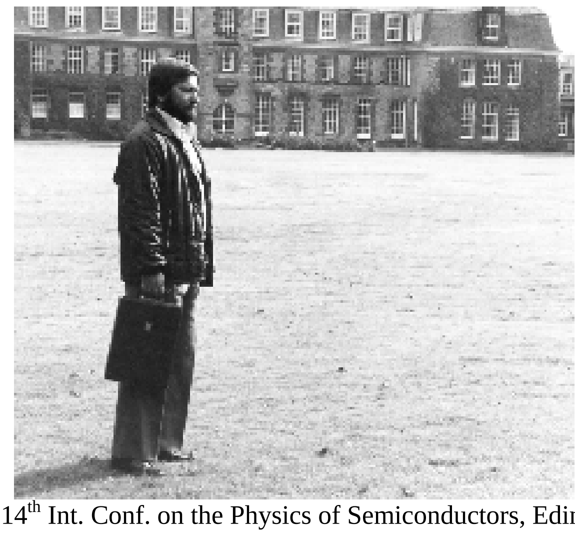
GNSM-CNR, Istituto di Fisica dell'Università di Roma, Rome, Italy

(*Received* 24 *November* 1978 *by F. Bassani*)

Expressions for exciton wavefunctions in semi-infinite crystals are derived in closed form within the effective mass approximation. From them the non-homogeneous non-local dielectric susceptibility is obtained showing the existence of the dead-layer and a new additional boundary condition. The results are compared with normal incidence reflectivity experiments in a number of semiconductors and the experimental lineshapes are reproduced.

The former envelope function was discussed more deeply in the paper *"Wannier-Mott excitons in semi-infinite crystals: wave functions and normal-incidence reflectivity"* Phys.Rev. B **25**, 3714 (1982), where a self-consistent calculation was presented for exciton-polariton computation.

Notice that the intrinsic dead layer of the exciton $(1/\bar{P})$, due to the exciton scattering on the solid surface, has a very different origin with respect to the extrinsic dead layer as discussed in Hopfield and Thomas paper (Phys.Rev.**132**, 563, 1963). Therefore, the **Pekar's dead layer on the semiconductor surface of real samples must take into account intrinsic and extrinsic dead-layer effects.** Moreover, the dead-layer strongly depress the image potential of the exciton on semiconductor surface.



Prof.Rodolfo Del Sole at the 14th Int. Conf. on the Physics of Semiconductors, Edinburgh, 4-8 September (1978).

The 1980 was a sabbatical year for both of us. Rodolfo was at Xerox Research Center in Palo Alto, working on Silicon surface reconstructions (Chadi's group), and I was at Surface Science Division of the National Bureau Standard in Washington DC for studying radiative and non-radiative decay from deep holes in solids (W. Gadzuk).

Coming back in Italy at the end of 1981, we started again our collaboration on the optical properties of Wannier excitons also under suggestion and in collaboration with Kikuo Cho, of Osaka University.

In the same period, I was sharing my scientific activity between exciton-polariton and Auger CVV decay, in collaboration with Michele Cini, that moved from the labs. of ENI in Monterotondo to the Institute of Inorganic Methodology of CNR at Research Area in Montelibretti. In that period, with Michele I have organized a school on "Auger decay in molecules and solids" , and had the opportunity of keeping in touch with Peter Weightman, of Liverpool University, that, some years later, proposed us to participate to the European Project, by name "Epioptics", that John McGilp, of the Trinity College of Dublin, was organizing. Obviously, the invitation was extended to Rodolfo as an expert on the optical response modelling in reconstructed semiconductor surfaces.

In the period from our return in Italy (1981) and the first Conference on "Excitons in Confined Systems" (ECS, 1987) our collaboration was threefolds, namely: i) a systematic study of the optical response at band edge of semi-infinite semiconductor solids (*"Wannier-Mott exciton in semi-infinite crystals: wave functions and normal incidence reflectivity"*,Phys.Rev.B **25**,3714,1982) ii) the extension of the former model for computing exciton-polariton propagation in semiconductor quantum confined systems (slabs, wires, dots) , and iii) to better understand the general computation framework adopted (*"New insight on exciton-polaritons based on a microscopic approach"* Phys.Rev.B **29**, 4782, 1984).

Even if our analytical exciton envelope function was assessed before our sabbatical year in the United States, the numerical results were presented seven years later at the first Conference on Exciton in Confined Systems (1987) (A.D'Andrea and R.Del Sole, "*Wave function and optical properties of excitons in a slab"* Springer-Verlag Proc.in Phys.v. **25**,p.102,1988).

The extension of the former exciton envelope function from semi-infinite to a self-sustained semiconductor slab, with thickness much greater than the Bohr radius of the Wannier exciton ($L_w \gg a_B$), was performed analytically:

$$\Psi_{ex}(\vec{r},\vec{R}) = N_{ex}\left\{\left[\cos(K_z Z) + A\sin(K_z Z)\right]\varphi_1(r) + \sum_{n>1}\left[\alpha_n e^{-P_n Z} + \beta_n e^{P_n Z}\right]\varphi_n(\vec{r})\right\} e^{i\vec{K}_{//}\cdot\vec{R}_{//}} / \sqrt{S}$$

where: $\varphi_1(r) = e^{-r/a_1}$, and by imposing the no-escape boundary conditions on both the surfaces of the slab: $\Psi_{ex}(z_e = \pm L_w/2) = \Psi_{ex}(z_h = \pm L_w/2) = 0.0$. The numerical solution was obtained by the minimization of two parameters: the effective Bohr radius (a_1) and the transition layer depth ($1/\overline{P}$).

Notice, that, even if the D'Andrea-Del Sole microscopic exciton model is a very simplified description of the reality, it allows to realize that: **optical response in confined systems can be obtained by self-consistent Schroedinger-Maxwell calculation, without "ad hoc" and/or fitting parameters (except for the non-radiative broadening)**, and therefore fully accomplish the Pekar's suggestion for Wannier excitons.

The 13th of April 1987 the Conference on "Excitons in Confined Systems" opened at the Conference Hall of the CNR Research Area at Montelibretti, about thirty kilometres at north of Roma, as claimed in the invitation card of the meeting.

"The aim of the meeting was to discuss the theoretical and experimental aspects of excitons in many different confined systems, from semi-infinite solids to quantum wells. The main idea was to bring together people with different cultural background to discuss and compare the concepts involved in the different confined systems", as reported on the preface of Springer Proceedings in

Physics of the Conference (*“Excitons in Confined Systems”*,Eds.: R.Del Sole, A.D’Andrea and A. Lapiccirella , Springer v. **25**,1988).
The scientific contributions to the Conference, about thirty papers, were divided in only three topics: i) Excitons in Semi-infinite Solids, ii) Excitons in Thin Films and iii) Excitons in Super-lattices and in Quantum Wells, and only one paper was devoted to the study of excitons in confined quantum wires. **Recently, this Springer Proceedings book has been selected to appear as an e-book in the Springer Book Archives**.
The Conference on “Excitons in Confined Systems” was though by us as a unique opportunity, as for instance the former conference on “Polaritons”, but three years later from the Montelibretti Conference, under suggestion of Raffaello Girlanda (Messina University) and Antonio Quattropani (Ecole Polytechnique Federale of Lausanne), we changed our mind and participated to the organization of a second Conference, that in reality was the first Conference by the title: “Optics of Excitons in Confined Systems” (OECS), that was held from 24^{th} to 27^{th} of September 1991 at Giardini Naxos (Taormina, Sicily).
At variance of the first Conference, where the main conceptual problem was to study the transition from free to confined dynamics of Wannier excitons, four years later we observed a real explosion of the number of papers devoted to different geometry of confinements (*“Optics of Excitons in Confined Systems”* Eds.: A.D’Andrea, R.Del Sole, R.Girlanda and A.Quattropani, Inst. of Phys. Conf. Series n. **123**, 1992), and also the participation made a jump of more than three times with respect to the former conference (about fifty participants).

Prof. Rodolfo Del Sole and his wife at the second conference on Confined Excitons- Giardini Naxos, Sicily (1991) (*courtesy of Prof.R.Girlanda*)

In that period the aim of our work on confined excitons was three-folds:
i) to use self-consistent Schroedinger-Maxwell framework in order to compute exciton-polariton optical response in different quantum confined structures (quantum slabs, wires and points) without “ad hoc” and/or fitting parameters, ii) to close the gap between very large (much greater than the exciton Bohr radius) and very thin slabs (much smaller than the exciton Bohr radius) in order to study the so called $3D \Rightarrow 2D$ exciton transition. Finally, iii) the extension of the former exciton model to different geometry of spatial confinements (quantum wires and boxes).
The first point was accomplished by using Green function formalism that changes the Maxwell equation from integro-differential to integral equation, where the kernel is degenerate (ABCs free

theory); while the second point was obtained by a very ingenuous procedure obtained by using two different exciton envelope functions. One model well suited for describing exciton dynamics in a thick, and another model for a thin self-sustained semiconductor slab (*"Excitons in confined systems: from quantum well to bulk behaviour"* L.C.Andreani, A.D'Andrea and R.Del Sole, Phys. Lett. A **168**, 451,1992). This method was validated by observing a rather astonishing agreement in the energy and in its oscillator strength values of the lowest exciton state (n=1) for slab thicknesses in the zone of $3D \Leftrightarrow 2D$ transition. Notice, that both the models adopted in our former calculation for describing Wannier exciton dynamics in thin and thick slabs were strongly criticized, many years later, in two papers of Monique Combescot et al. (*"Hydrogenic impurity ground state in quantum well: the envelope function revisited"*, Eur.Phys.B **22**, 89,2001, and *"The exciton dead layer revisited*", Eur.Phys.J. B **23**, 139, 2001).
The optical response of a grating of quantum well wires was presented at the conference on confined systems of Giardini Naxos (24-27 September 1991) and a long paper was published one year later (*"Exciton wave functions and optical properties in a grating of quantum well wires"*, Phys.Rev.B **46**, 2363, 1992).
I would like to remind that the study of the center-of-mass motion of Wannier exciton and the problem of the correct framework for computing exciton-polariton propagation by a self-consistent "ab initio" calculation were strongly encouraged by Franco Bassani (Scuola Normale Superiore - Pisa) and also discussed with Kikuo Cho, with whom we have been in touch from the very beginning of our activity till very recently. In fact, whenever Kikuo came in Roma for collaboration, we not lacked to meet Rodolfo and his wife Ambra in some typical roman restaurant.

Prof.Rodolfo Del Sole and his wife in a "Ghetto" restaurant of Rome (2009).
(*courtesy of Prof.K.Cho*)

I guess that the center-of-mass dynamics of Wannier exciton was thought as a key property that should be at basis of linear and non-linear effects, namely: the strong exciton-photon coupling (polaritons) and the exciton-exciton scattering respectively. In fact, this property has assumed a crucial role also in many new physical effects studied recently.
In that period Rodolfo was also active in the optical response in semiconductor surfaces, a topic of research that, many years later, could allowed to study Wannier exciton in bulk and in reconstructed surfaces by self-consistent GW "ab initio"calculation. In the same period I was working in a "self-consistent" Wannier exciton model, expanded in electron-hole subbands, for computing optical response in strained quantum wells (R.Atanasov, F.Bassani, A.D'Andrea, N.Tomassini, Phys.Rev.B **50**, 14381, 1994). The physical results were presented and discussed during the conferences of EPIOPTICS project (Springer, Basic Research Series Eds.: J.F.McGilp, D.Weaire, C.H.Patterson 1995).
The collaboration with Rodolfo was again active four years later, in occasion of Laura Pilozzi's thesis, by title: "Polaritoni eccitonici di buca quantica: eccitazione mediante reticoli" held at "Tor Vergata" University (1995). A series of two papers was also published on the same subject by titles: *"Electromagnetic properties of a dielectric grating. I Propagating, evanescent and guided waves"* Phys.Rev.B **54**,10751 (1996) and *"Electromagnetic properties of a dielectric grating. II Quantum wells excited by surface waves"* Phys.Rev.B **54**,10763 (1996).

In conclusion, I would like to note that the former chronological exposition of our scientific collaborations in many different periods of our scientific carriers is not reported for underlining the well known scientific contribution of Rodolfo, but for emphasizing the human aspect of Rodolfo; in fact, as a person totally dedicated to the research in physics, was able to change any scientific work into an extraordinary cultural adventure, and any adventure in an unforgettable friendship.

Roma 15^{th} of July 2013 Andrea D'Andrea