



**The Abdus Salam  
International Centre for Theoretical Physics**



**2145-6**

**Spring College on Computational Nanoscience**

*17 - 28 May 2010*

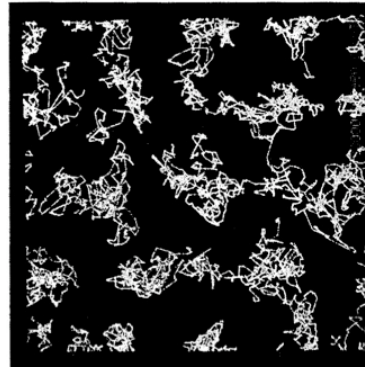
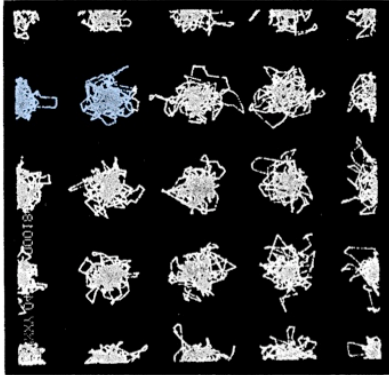
**INTRODUCTION SPEECH DIRAC MEDAL IN HONOUR OF ROBERTO CAR  
and MICHELE PARRINELLO**

Erio TOSATTI

*SISSA  
Trieste  
Italy*

circa 1980

“molecular dynamics” computer simulations of condensed matter: solids, liquids, etc

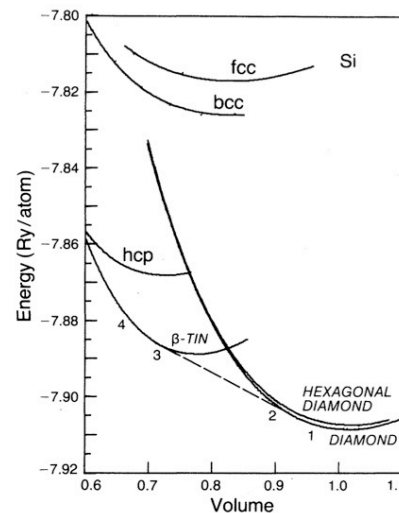
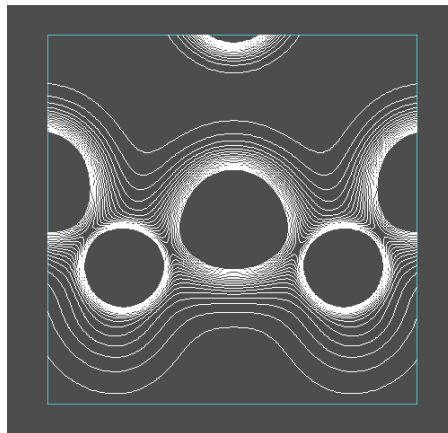


Berni Alder



Aneesur Rahman

“density functional” electronic structure and total energy calculations of solids, etc



Walter Kohn



Lu Sham



Marvin Cohen



FRANCO BASSANI 1929-2008

ROBERTO CAR

ROBERTO  
CAR



ALFONSO  
BALDERESCHI

Modena 18 Oct 1981

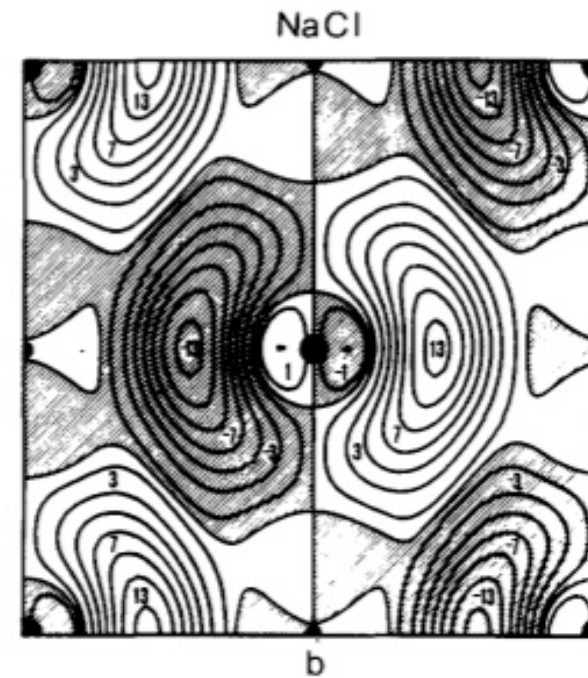
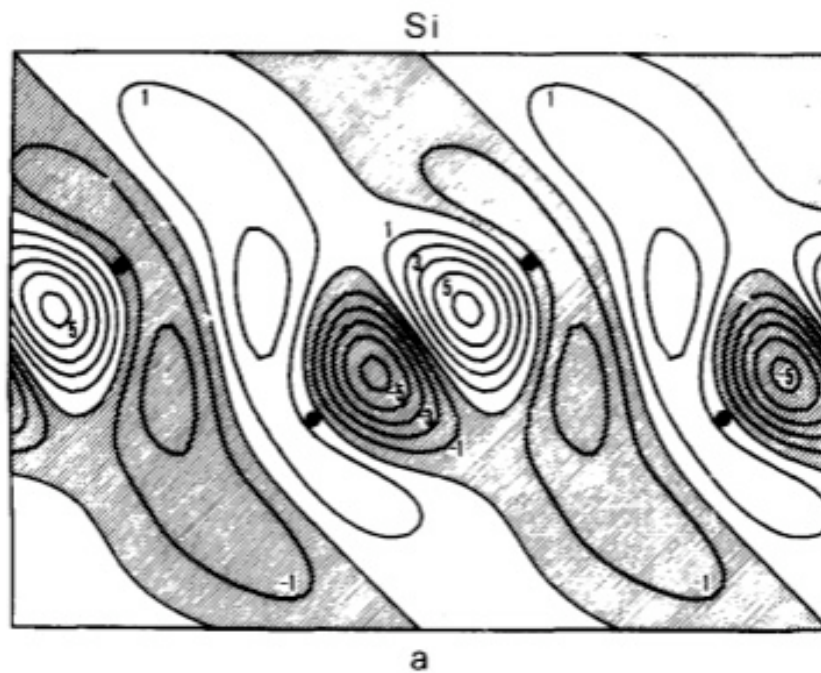
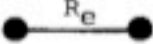
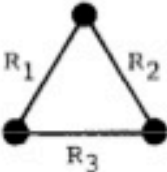
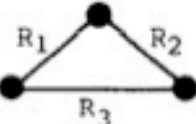
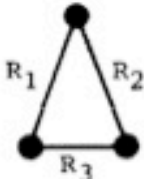
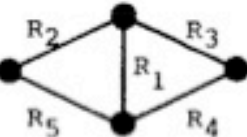


Table 1

Calculated ground state properties of Li clusters; values given in parentheses refer to experimental data as well as to other calculations; distances are in au, energies are in eV, vibrational frequencies  $\omega_e$  are in  $\text{cm}^{-1}$ ; see text for the meaning of symbols

Cluster	Geometry	Results
Li <sub>2</sub>		$R_e = 5.13$ (exp. [21]: 5.05; CI [19]: 5.09; AE-LD [9]: 5.13) $BE = 0.82$ (exp. [21]: 1.03; CI [19]: 0.99; AE-LD [9]: 0.83) $\omega_e = 354$ (exp. [21]: 351; CI [19]: 345; AE-LD [9]: 340) $IP = 5.18$ (exp. : 5.15, photoionization [22]; 4.86, electron impact appearance potential [23])
Li <sub>3</sub> <sup>‡</sup>		$R_1 = R_2 = R_3 = 5.59$ $BE = 2.70$
Li <sub>3</sub> (a)		$R_1 = R_2 = 5.32$ (CI [5]: 5.25) $R_3 = 6.29$ (CI [5]: 6.25) $BE = 1.32$ (exp. [23]: 1.79; CI [5]: 1.49) $IP = 4.17$ (exp. [23]: 4.35; CI [5]: 4.0)
Li <sub>3</sub> (b)		$R_1 = R_2 = 5.83$ (CI [5]: 5.82) $R_3 = 5.07$ (CI: 5.26) $BE = 1.31$
Li <sub>4</sub>		$R_1 = 5.1$ $R_2 = R_3 = R_4 = R_5 = 5.8$ $BE = 2.70$ $IP = 4.97$

ROBERTO



ANNABELLA...

VOLUME 42, NUMBER 20

PHYSICAL REVIEW LETTERS

14 MAY 1979

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**Local-Field Effects in the Screening of Impurities in Silicon**

R. Car

*Laboratoire de Physique Expérimentale, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland*

and

Annabella Selloni

*Laboratoire de Physique Théorique, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland*

(Received 7 November 1978)

...HELPED YANKING BOTH OF THEM AWAY FROM IBM.....

VOLUME 52, NUMBER 20

PHYSICAL REVIEW LETTERS

14 MAY 1984

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## Microscopic Theory of Atomic Diffusion Mechanisms in Silicon

Roberto Car,<sup>(a)</sup> Paul J. Kelly,<sup>(b)</sup> Atsushi Oshiyama,<sup>(c)</sup> and Sokrates T. Pantelides  
*IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598*  
(Received 17 February 1984)

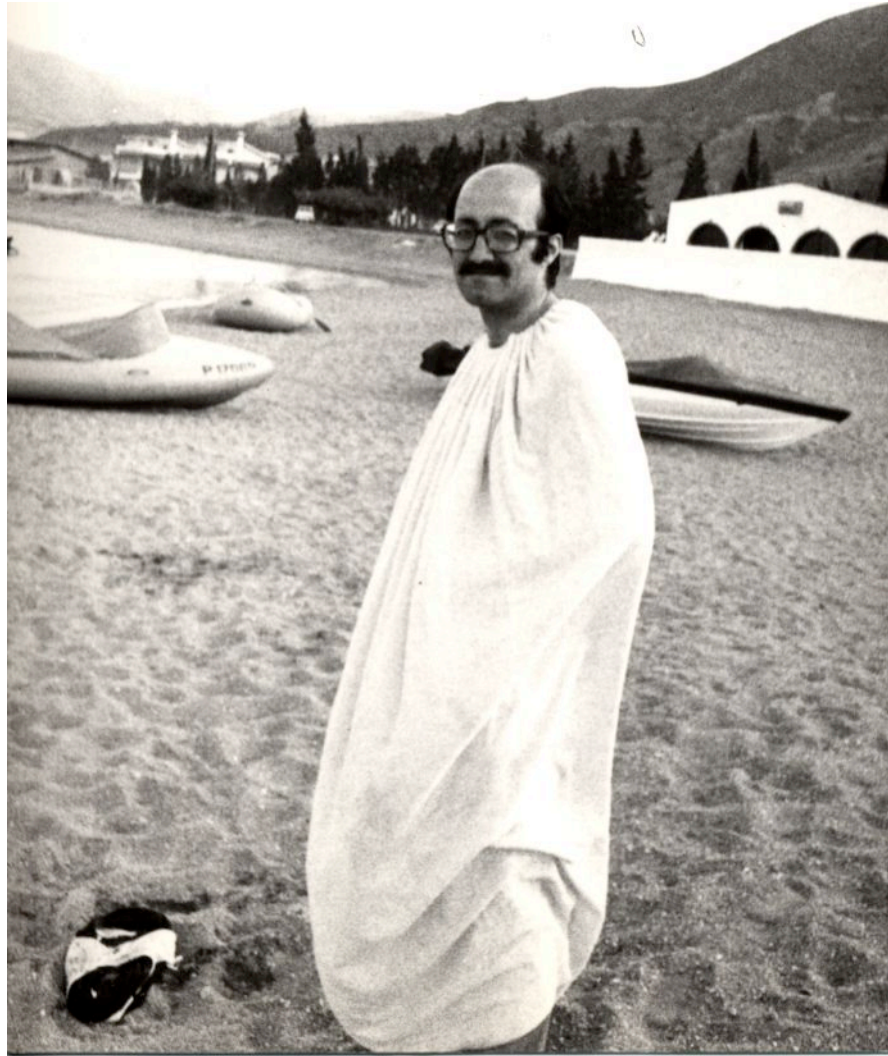
We report self-consistent Green's-function *total-energy* calculations which provide, for the first time, a firm theoretical framework for understanding the microscopic mechanisms of atomic diffusion in Si. We find that the self-interstitial has *negative-U* properties, roughly the same formation energy at several sites, small migration barriers, and charge-state instabilities that allow athermal migration along several paths. We also find that *both* vacancies and interstitials mediate self-diffusion and reconcile contrasting low- and high-temperature data.

....TO TRIESTE!





**MICHELE PARRINELLO**



1970s: MICHELE PARRINELLO  
IN A TYPICAL COSTUME OF HIS NATIVE SICILY....

# Ionic radii and diffraction patterns of molten alkali halides<sup>a)</sup>

M. C. Abramo, C. Caccamo, G. Pizzimenti, and M. Parrinello

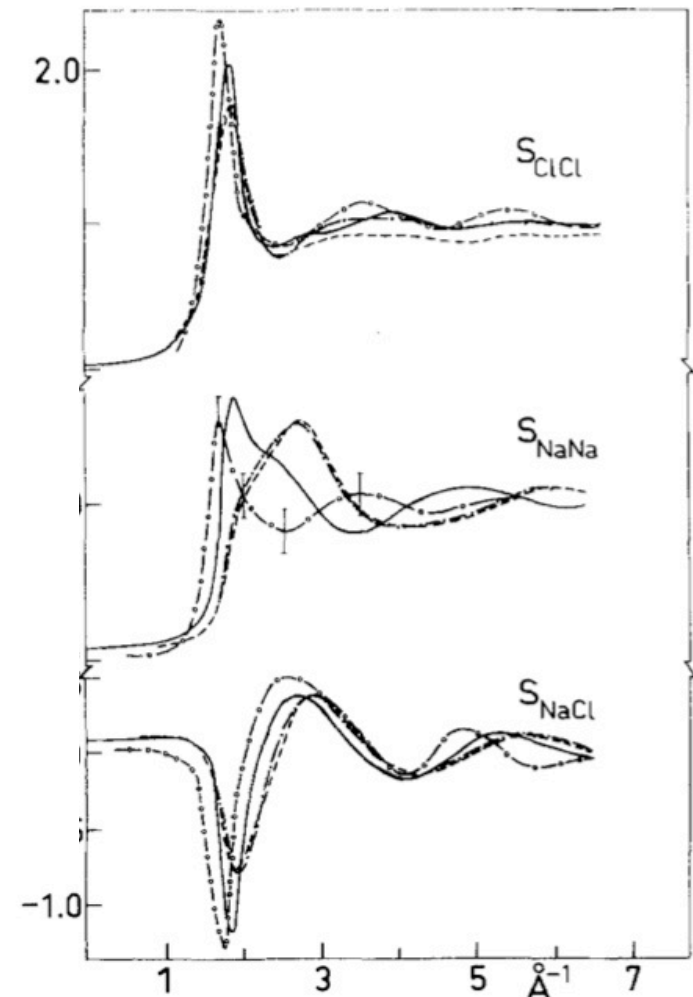
*Istituto di Fisica dell' Universita', Messina, Italy*

M. P. Tosi

*Istituto di Fisica dell' Universita', Roma, Italy*

(Received 20 July 1977)

The mean spherical approximation for a fluid of charged hard spheres of different radii is applied to the evaluation of diffraction patterns for the whole family of molten alkali halides. The ionic radii entering the model are determined from the liquid-state compressibility. The liquid-state radii are shown to be characteristic temperature-dependent lengths for each ion through the family of salts, and a good one-parameter fit of the whole set of compressibilities at each temperature is obtained through the assumption that the radius ratios are those for basic radii yielded by the Born-Mayer theory of alkali halide crystals. The analysis also provides new evidence against the older sets of crystal ionic radii. Calculations of partial structure factors and of x-ray diffraction patterns are then reported for all the salts and compared with the results of x-ray and neutron diffraction experiments wherever possible. The model emerges as having semiquantitative value in the prediction of x-ray diffraction from simple ionic fluids and in its detailed interpretation.



Excerpt from a longer love letter of Michele to Erio, late 1970s or early 1980s

$$v_{IJKL} = \int d^2 r_1 \int d^2 r_2 \overline{\psi_I(r_1)} \psi_L(r_1) \overline{\psi_J(r_2)} \psi_K(r_2) \frac{1}{|r_1 - r_2|}$$

$$\psi_L(\vec{r}) = N_L z^L e^{-\frac{1}{4}|\vec{r}|^2} = N_L z^L e^{i\theta_L} e^{-\frac{1}{4}r^2}$$

$$\frac{1}{|r_1 - r_2|} = \sum_{\ell=0}^{\infty} \frac{r_1^\ell}{r_2^{\ell+1}} P_\ell(\cos(\varphi_1 - \varphi_2))$$

$$v_{IJKL} = \iiint e^{-i\theta_1 I + i\theta_1 L - i\theta_2 J + i\theta_2 K} dr_1 dr_2 d\theta_1 d\theta_2$$

$$\cdot \int_0^{2\pi} \int_0^{2\pi} r_1^{I+L+1} r_2^{J+K+1} e^{-\frac{1}{2}r_1^2 - \frac{1}{2}r_2^2} \sum_{\ell=0}^{\infty} \frac{r_1^\ell}{r_2^{\ell+1}} P_\ell(\cos(\theta_1 - \theta_2))$$



$$\text{ma } I + J = K + L \implies L - I = -(K - J) = M$$



$$i(-\theta_1 I + \theta_1 L - \theta_2 J + \theta_2 K) = i\theta_1 M - i\theta_2 M = iM(\theta_1 - \theta_2)$$

$$v_{IJKL} = 2\pi \int_0^\infty dr_1 \int_0^\infty dr_2 \sum_{\ell=0}^{\infty} \frac{r_1^\ell}{r_2^{\ell+1}} r_1^{I+L+1} r_2^{J+K+1} e^{-\frac{1}{2}r_1^2 - \frac{1}{2}r_2^2}$$

$$\int_0^{2\pi} d\theta e^{iM\theta} P_\ell(\cos\theta) \leftarrow \text{ci sono gli } e^{-iM\theta} \text{ fino a } \ell \text{ (} u \leq \ell \text{, } \text{ma } M \leq \ell \text{)}$$

Dal. sp. p. 1015 prende  $\varphi_1 = \varphi_2 = \frac{\pi}{2}$

$$P_n(\cos\theta) = P_n(\theta)^2 + 2 \sum_{m=1}^n \frac{(n-m)!}{(n+m)!} (P_m(\theta))^2 \cos m\theta$$

MICHELE AND I  
HAD A LOT  
OF COMMON  
INTERESTS...

## Plasmon Bands and Gaps in Metal Crystals

R. Girlanda and M. Parrinello

*Istituto di Fisica, Università di Messina, Messina, Italy*

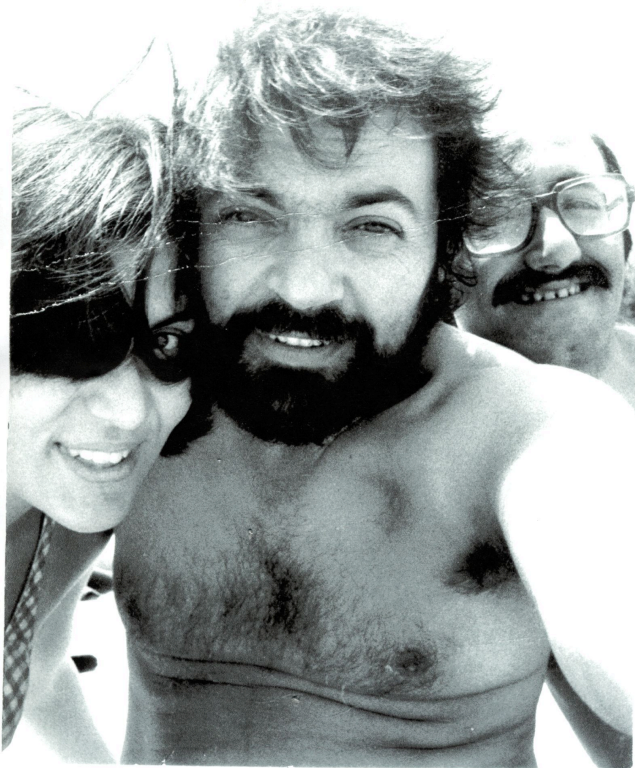
and

E. Tosatti

*Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche, Istituto di Fisica,  
Università di Roma, Rome, Italy*

(Received 22 September 1975)

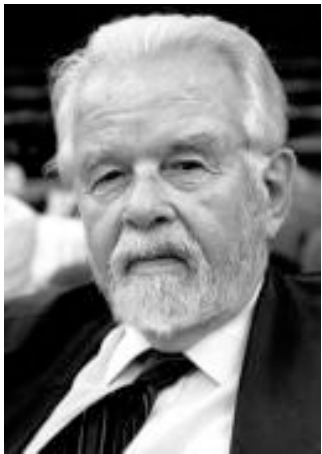
We consider the influence of a periodic lattice upon the plasmon energy in a metal, by means of the equation of motion proposed by March and Tosi. The solution, within the random-phase approximation and for a weak periodic potential, shows the existence of two plasmon bands separated by a *complex* energy gap near the Brillouin zone border. This gap, due to plasmon Bragg diffraction, is rapidly quenched in presence of damping in simple metals. Group-IV metals and semiconductors should offer better chances for the observation of these "nearly-free-plasmon" bands near the Brillouin zone border.



1977--1980:  
all together in  
Miramare!



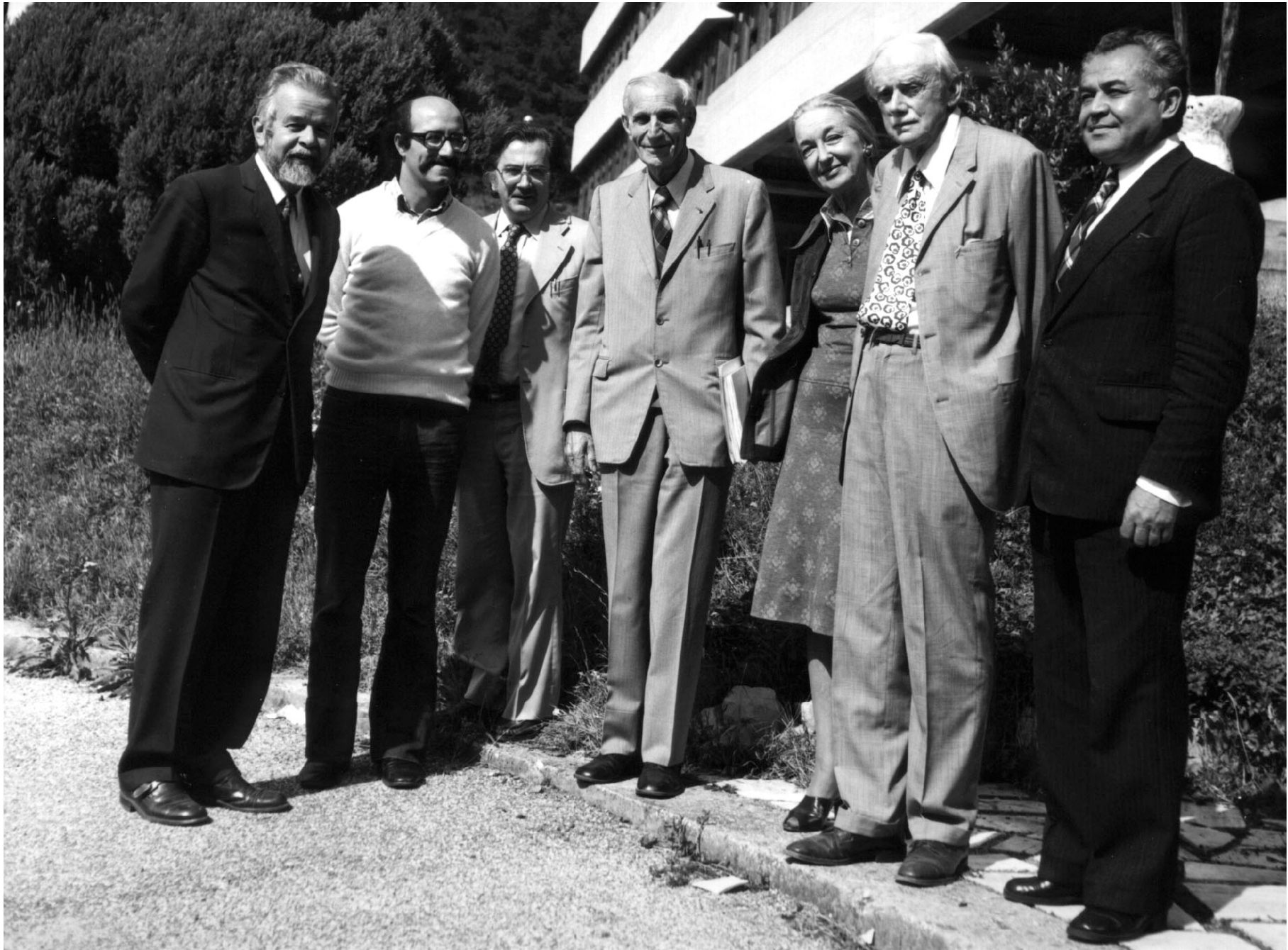
ABDUS SALAM



PAOLO BUDINICH







Michele with Dirac, Kastler, Budinich, Hamende, et al. (1978)



Simona Parrinello and  
Valentino Tosatti, Trieste,  
circa 1984



Roberto and Martina Car  
circa 1989



IN THE EARLY 80s....



## **Crystal Structure and Pair Potentials: A Molecular-Dynamics Study**

M. Parrinello<sup>(a)</sup> and A. Rahman

*Argonne National Laboratory, Argonne, Illinois 60439*

(Received 31 July 1980)

With use of a Lagrangian which allows for the variation of the shape and size of the periodically repeating molecular-dynamics cell, it is shown that different pair potentials lead to different crystal structures.

**MICHELE VISITS ANEES RAHMAN'S GROUP**

# WHILE WE COLLABORATE....

PHYSICAL REVIEW B

VOLUME 24, NUMBER 2

15 JULY 1981

## Dielectric band structure of crystals: General properties and calculations for silicon

R. Car\*

*Scuola Internazionale Superiore di Studi Avanzati, Trieste, Italy  
and Laboratoire de Physique Experimentale, Ecole Polytechnique Federale, Lausanne, Switzerland<sup>f</sup>*

E. Tosatti

*Gruppo Nazionale di Struttura della Materia, Istituto di Fisica Teorica, Università di Trieste, Trieste, Italy  
Scuola Internazionale Superiore di Studi Avanzati, Trieste, Italy,  
and International Center for Theoretical Physics, Trieste, Italy*

S. Baroni

*Laboratoire de Physique Theorique, Ecole Polytechnique Federale, Lausanne, Switzerland*

S. Leelaprute

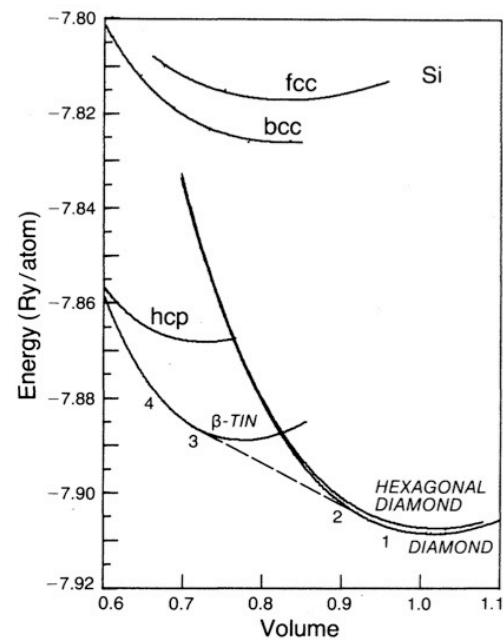
*International Center for Theoretical Physics, Trieste, Italy  
and Scuola Internazionale Superiore di Studi Avanzati, Trieste, Italy*

(Received 9 March 1981)

We develop the dielectric band-structure method, originally proposed by Baldereschi and Tosatti, for the

# ROBERTO GETS MORE AND MORE ENTANGLED WITH KOHN-SHAM DFT

Yin Cohen  
PRL 1980



WINTER 1984-85:  
WORKING IN THE  
NIGHT...



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## Unified Approach for Molecular Dynamics and Density-Functional Theory

R. Car

*International School for Advanced Studies, Trieste, Italy*

and

M. Parrinello

*Dipartimento di Fisica Teorica, Università di Trieste, Trieste, Italy, and  
International School for Advanced Studies, Trieste, Italy*

(Received 5 August 1985)

We present a unified scheme that, by combining molecular dynamics and density-functional theory, profoundly extends the range of both concepts. Our approach extends molecular dynamics beyond the usual pair-potential approximation, thereby making possible the simulation of both covalently bonded and metallic systems. In addition it permits the application of density-functional theory to much larger systems than previously feasible. The new technique is demonstrated by the calculation of some static and dynamic properties of crystalline silicon within a self-consistent pseudopotential framework.

$$L = \sum_i \frac{1}{2} \mu \int_{\Omega} d^3r |\dot{\psi}_i|^2 + \sum_I \frac{1}{2} M_I \dot{R}_I^2 + \sum_{\nu} \frac{1}{2} \mu_{\nu} \dot{\alpha}_{\nu}^2 - E[\{\psi_i\}, \{R_I\}, \{\alpha_{\nu}\}],$$

where the  $\psi_i$  are subject to the holonomic constraints

$$\int_{\Omega} d^3r \psi_i^*(\mathbf{r}, t) \psi_j(\mathbf{r}, t) = \delta_{ij}. \quad (4)$$

In Eq. (3) the dot indicates time derivative,  $M_I$  are the physical ionic masses, and  $\mu$  and  $\mu_{\nu}$  are arbitrary parameters of appropriate units.

The Lagrangean in Eq. (3) generates a dynamics for the parameters  $\{\psi_i\}$ 's,  $\{R_I\}$ 's, and  $\{\alpha_{\nu}\}$ 's through the equations of motion:

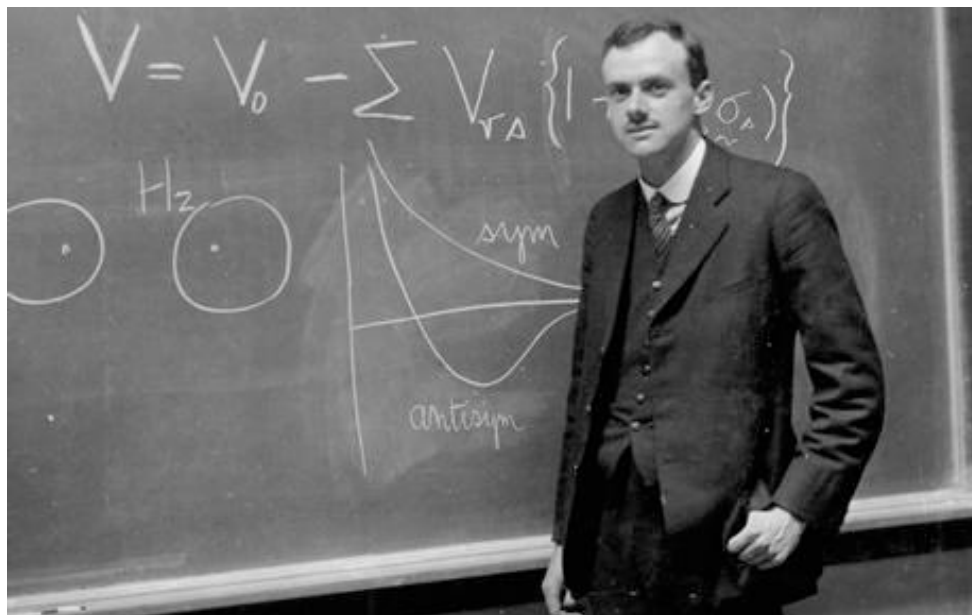
$$\mu \ddot{\psi}_i(\mathbf{r}, t) = -\delta E / \delta \psi_i^*(\mathbf{r}, t) + \sum_k \Lambda_{ik} \psi_k(\mathbf{r}, t), \quad (5a)$$

$$M_I \ddot{R}_I = -\nabla_{R_I} E, \quad (5b)$$

$$\mu_{\nu} \ddot{\alpha}_{\nu} = -(\partial E / \partial \alpha_{\nu}), \quad (5c)$$

laxation, and achieved *simu* kinetic energy tem from the s ergy.

It should be annealing techn quite general a minimization. of physics. For of classical field energy in Har schemes. We minimization is



The mathematician plays a game in which he himself invents the rules while the physicist plays a game in which the rules are provided by nature, but as time goes on it becomes increasingly evident that the rules which the mathematician finds interesting are the same as those which nature has chosen.

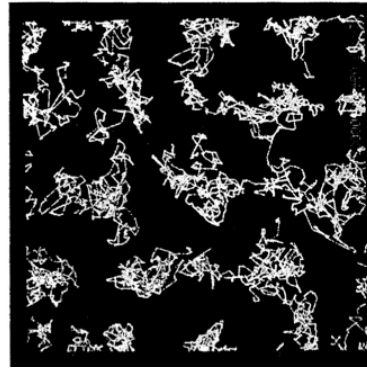
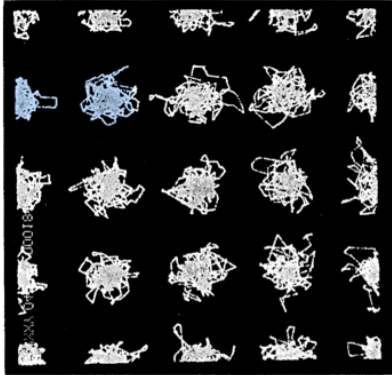
Paul A. M. Dirac

In Ian Stewart, *Why Beauty is Truth* (2007), 279.



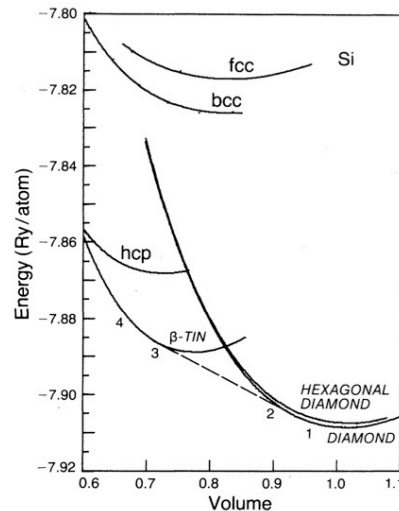
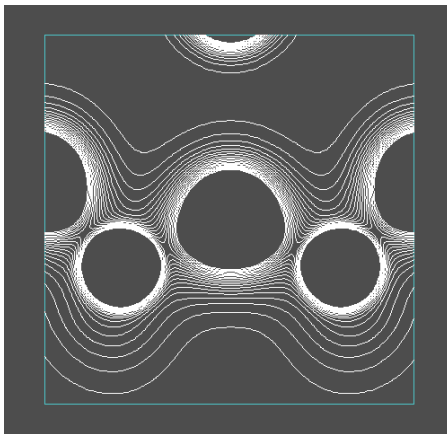
1985!

“molecular dynamics” computer simulations of condensed matter: solids, liquids, etc



Michele

“density functional” electronic structure and total energy calculations of solids, etc



Roberto

# IMPACT & CHALLENGES

SOLIDS, LIQUIDS, SURFACES....

CLUSTERS, NANOSYSTEMS, NANOBIO...

EXTREME PRESSURES, TEMPERATURES...

MOLECULES, CHEMISTRY, REACTIONS,.....

MATERIALS SCIENCE...

DYNAMICS, OPTICS,...

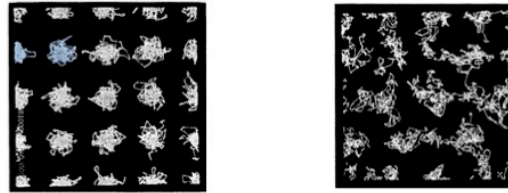
BIOCHEMISTRY, BIOLOGICAL PROCESSES,...

ENERGY

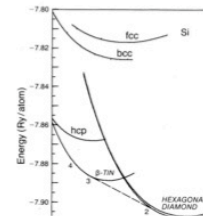
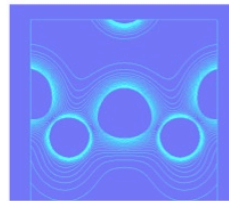
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1985!

“molecular dynamics” computer simulations  
of condensed matter: solids, liquids, etc



“density functional” electronic structure and  
total energy calculations of solids, etc



Michele



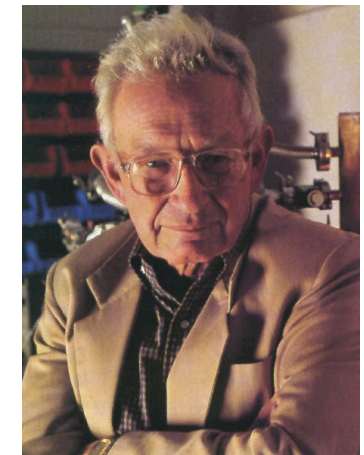
Roberto

STRONGLY CORRELATED ELECTRON SYSTEMS  
(MOTT INSULATORS, HIGH  $T_c$  SUPERCONDUCTORS, etc)

KONDO EFFECTS, QUANTUM TRANSPORT

DISORDER, AND “TOPOLOGICAL” PHYSICS  
IN CORRELATED SYSTEMS

DYNAMICS OF INTERACTING QUANTUM SYSTEMS



PHIL ANDERSON

THANKS, ROBERTO AND MICHELE!!



The 2009 Dirac Medal recognizes the joint contributions of Roberto Car and Michele Parrinello in developing the ab initio simulation method in which they combined, elegantly and imaginatively, the quantum mechanical density functional method for the calculation of the electronic properties of matter with molecular dynamics methods for the Newtonian simulation of atomic motions. The Car-Parrinello method has had an enormous impact, joining together the fields of simulation and of electronic structure theory, and has given rise to a variety of applications well beyond condensed matter physics.