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Nano Innovation 2016 Rome, 20-23 September
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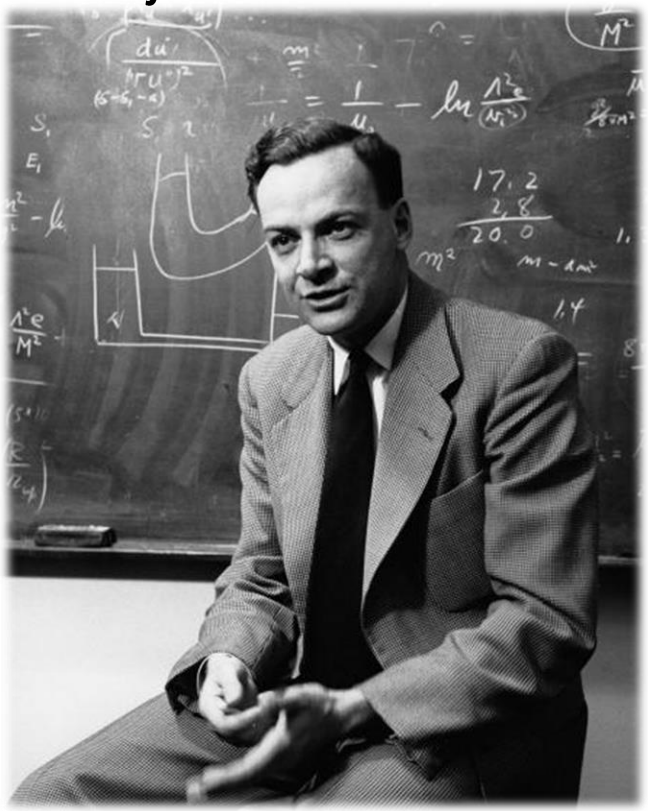
The Role of Electronic Excitations in Solution-Processed Oligothiophene Small-Molecules for Organic Solar Cells from First Principles.

Dr. Fabrizio Gala

Dipartimento di Scienze di Base e Applicate

Per l'Ingegneria (SBAI)

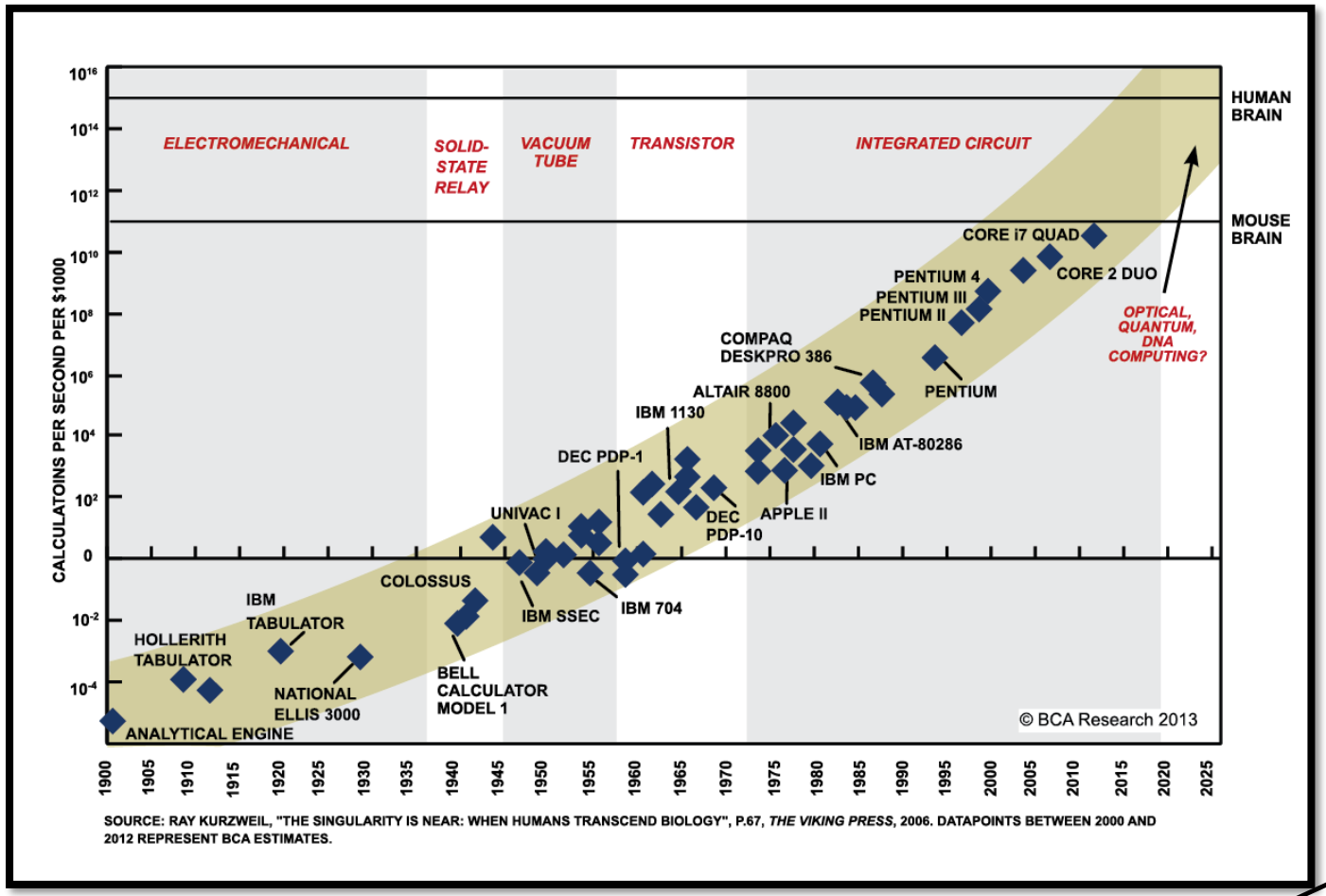
R.P. Feynman



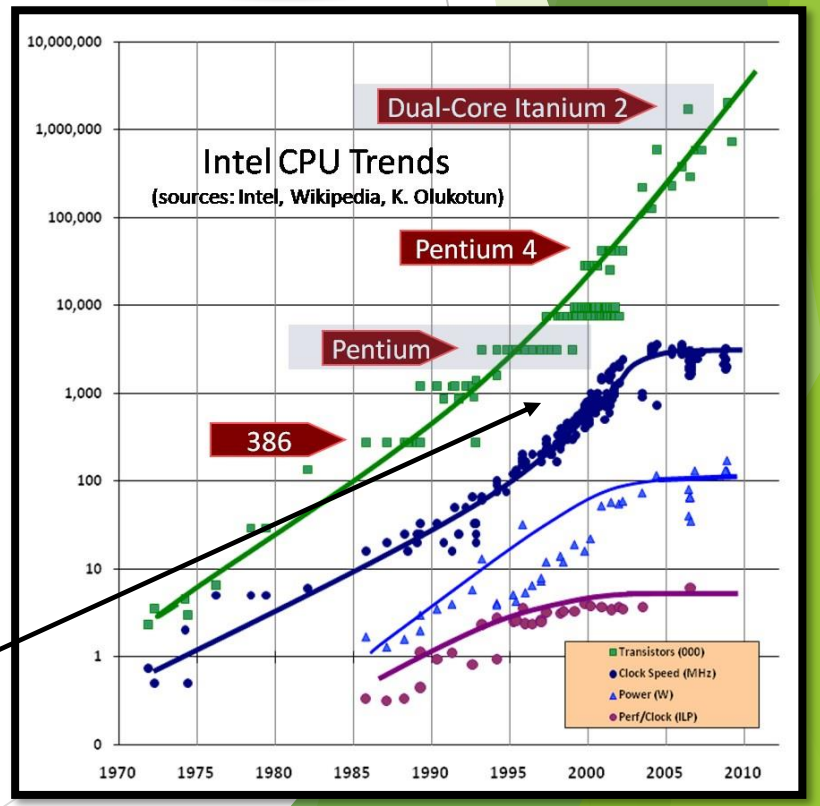
«Nature isn't classical, dammit, and if you want to make a simulation of nature, you'd better make it quantum mechanical, and by golly it's a wonderful problem, because it doesn't look so easy.»

from "Simulating Physics with Computers",
International Journal of Theoretical Physics, volume 21, 1982, p. 467-488

What about Computing Power ?



Moore's law: $y \propto 2^{\frac{2}{3}x}$



Moore's law keeps going, defying expectations
(thanks mainly to transistor size miniaturiazion)

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TOP500 Computers

Nano 2016 Innovation Conference & Exhibition — Rome, 20-23 September

TOP500 - Wikipedia - Mozilla Firefox

Posta in arrivo - fabrizio.g... | Posta in arrivo - fabrizio.g... | ScholarOne Manuscripts | TOP500 - Wikipedia | Exploration & Production ...

https://it.wikipedia.org/wiki/TOP500#cite_note-4

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Altre 10
Modifica collegamenti

quello esistente nel novembre del 1993, il Connection Machine CM-5/1024 (con 1024 core ed un Rpeak di 131 GFLOPS).

Lista (prime 10 posizioni) [modifica | modifica wikitesto]

La seguente tabella mostra le prime dieci posizioni della 44ª TOP500, pubblicata nel novembre 2014[3]

Posizione	Rmax Rpeak (TFLOPS)	Nome	Computer Core, Architettura	Produttore	Sito Nazione, Anno	Sistema operativo
1	33.863 54.902	*Tianhe-2*	**NUDT** Xeon E5-2692 + Xeon Phi 31S1P, TH Express-2	NUDT	National Supercomputing Center in Guangzhou Cina, 2013	Linux
2	17.590 27.113	*Titan*	**Cray XK7** Opteron 6274 + Tesla K20X, Cray Gemini Interconnect	Cray Inc.	Oak Ridge National Laboratory Stati Uniti, 2012	Linux
3	17.173 20.133	*Sequoia*	**Blue Gene/Q** PowerPC A2, Custom	IBM	Lawrence Livermore National Laboratory Stati Uniti, 2013	Linux
4	10.510 11.280	*K computer*	**RIKEN** SPARC64 VIIIfx, Tofu	Fujitsu	RIKEN Giappone, 2011	Linux
5	8.586 10.066	*Mira*	**Blue Gene/Q** PowerPC A2, Custom	IBM	Argonne National Laboratory Stati Uniti, 2013	Linux
6	6.271 7.779	*Piz Daint*	**Cray XC30** Xeon E5-2670 + Tesla K20X, Aries	Cray Inc.	Swiss National Supercomputing Centre Svizzera, 2013	Linux
7	5.168 8.520	*Stampede*	**PowerEdge C8220** Xeon E5-2680 + Xeon Phi, Infiniband	Dell	Texas Advanced Computing Center Stati Uniti, 2013	Linux
8	5.008 5.872	*JUQUEEN*	**Blue Gene/Q** PowerPC A2, Custom	IBM	Forschungszentrum Jülich Germania, 2013	Linux
9	4.293 5.033	*Vulcan*	**Blue Gene/Q** PowerPC A2, Custom	IBM	Lawrence Livermore National Laboratory Stati Uniti, 2013	Linux
10	3.577 6.132		**Cray CS** Xeon E5-2660v2 10C and Nvidia K40, Infiniband	Cray Inc.	Stati Uniti, 2014	Linux

Lista (supercomputer in Italia) [modifica | modifica wikitesto]

La seguente tabella mostra i supercomputer in Italia:

Posizione	Sistema	Core	Rmax TFLOPS	Rpeak TFLOPS	Produttore	Sito	Anno
19	HPC2 - iDataPlex DX360M4, Intel Xeon E5-2680v2 10C 2.8GHz, Infiniband FDR, NVIDIA K20x	72,000	3,188.0	4,605.0	IBM	ENI[4]	Novembre 2015
37	Fermi - BlueGene/Q, Power BQC 16C 1.60GHz, Custom	163,840	1,788.9	2,097.2	IBM	CINECA[5]	Novembre 2015
130	GALILEO - IBM NeXtScale nx360M4, Xeon E5-2630v3 8C 2.4GHz, Infiniband QDR, Intel Xeon Phi 7120P	50,232	684.3	1,103.1	IBM	CINECA	Novembre 2015
206	HPCC1 - iDataPlex DX360M4, Xeon E5-2670 8C 2.600GHz, Infiniband FDR14	24,000	454.1	499.2	IBM	ENI	Novembre 2015

ENI CRENC (Centro Ricerche per le Energie Rinnovabili) Istituto ENI Donegani Novara

Measuring heat of formation for a single molecule is 50 times more expensive than accurate quantum chemistry calculation

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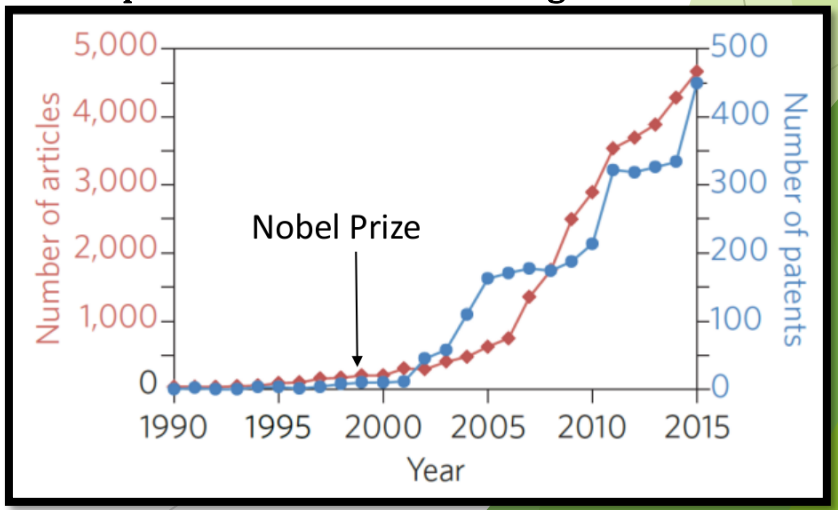
Atomic-scale modelling in the industry

INDUSTRIAL USERS

- **Chemical** – major chemical companies have modeling groups since the 1980's using discrete models; modelling of solid state systems (heterogeneous catalysis) started later; smaller chemical companies are still in the process of adopting discrete models
- **Electronic** - leading electronics companies have been pioneering discrete models on the electronic and atomistic levels since the 1970's (IBM, NEC, Bell Labs); today major players like Intel, Samsung, Fujitsu, Panasonic, TSMC use commercial software
- **Oil, gas, energy** – leading companies like Shell and ExxonMobil have in-house modelling groups using atomic-scale models; government supported research organizations (IFPEN, Mexian Petroleum Institute) support industrial efforts

IPC	Description	Percentage
H01	Basic electric elements	~26 %
C07	Organic chemistry	~21%
C …	Other areas of chemistry	~24 %
B01	Physical or chemical processes	~10 %
A	Health, Medical	~ 6%
G06	Computing, Calculating, Counting	~ 5%

From "the Economic impact of molecular modelling" – Goldbeck Consulting Ltd (2012)



Number of articles and patents in materials science including the term "density functional theory" published per year during the past 25 years.

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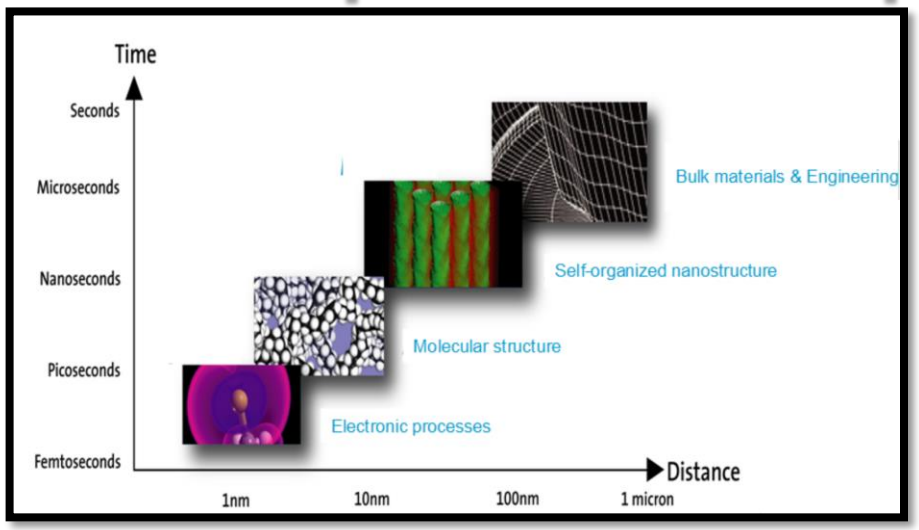
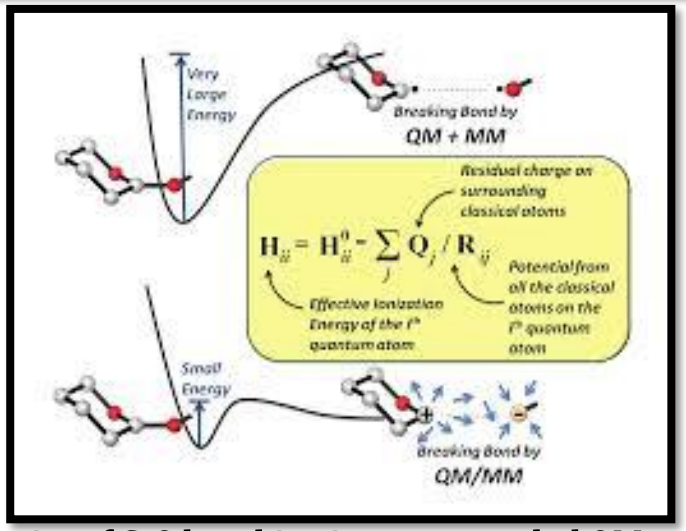
Multiscale computational approaches

The **Nobel Prize** in Chemistry 2013 was awarded jointly to M. Karplus, M. Levitt and A. Warshel "for the development of **multiscale models** for complex chemical systems".



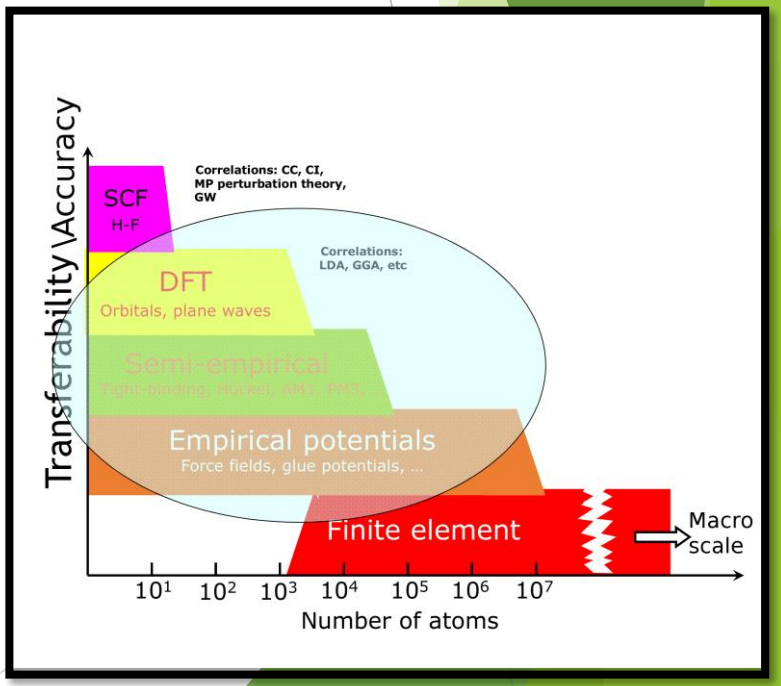


Energetics of C-O breaking in an uncoupled QM + MM (upper diagram) and in a coupled QM/MM (lower diagram)

Different length/time scales

Different physical phenomena

Multiscale approach (QM/MM for instance)



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AB-INITIO CALCULATIONS: Density Functional Theory(1)

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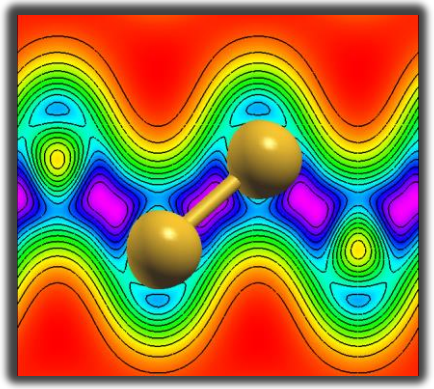


Silicon electron charge density in a FCC crystal.

The total energy is a functional of the electron density only, then:

1) A universal Hohenberg-Kohn Functional $F_{HK}[n(r)]$ exists
2) The external potential corresponds to a given density and viceversa

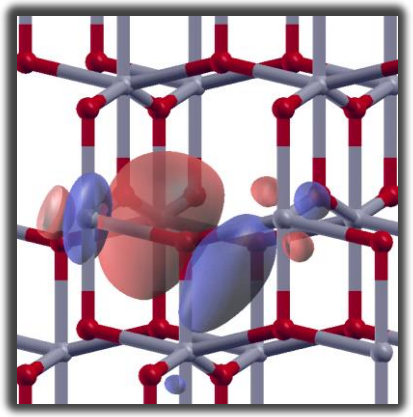
$$F_{HK}[n_{\boldsymbol{R}}(\boldsymbol{r})] = T[n_{\boldsymbol{R}}(\boldsymbol{r})] + U_{ee}[n_{\boldsymbol{R}}(\boldsymbol{r})]$$

$$E[n_{\boldsymbol{R}}(\boldsymbol{r})] = F_{HK}[n_{\boldsymbol{R}}(\boldsymbol{r})] + \int V_R^{ext}(\boldsymbol{r}) n_{\boldsymbol{R}}(\boldsymbol{r}) d^3r$$

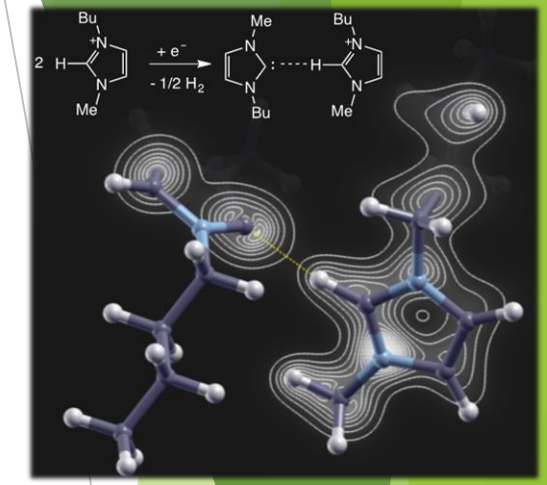
Contains all the complicated physical aspects of electron-electron interactions

ELECTRON DENSITY

$$n_{\boldsymbol{R}}(\boldsymbol{r}) \equiv n(\boldsymbol{r}) = \sum_k f(\epsilon_k) \|\psi_k(\boldsymbol{r})\|^2$$



Pseudo sp^2 orbital in TiO_2 anatase bulk phase



Charge density profile of N-Heterocyclic carbenes

Energy Minimization is carried out by solving (self-consistently) the Khon-Sham (KS) Equations:

$$\left(-\frac{1}{2}\nabla^2 + \int \frac{n_{\boldsymbol{R}}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d^3r' + V_{xc}(\boldsymbol{r}) - \sum_I \frac{Z_I}{|\boldsymbol{r}-\boldsymbol{R}_I|}\right)\psi_k(\boldsymbol{r}) \equiv h_0(\boldsymbol{r})\,\psi_k(\boldsymbol{r}) = \epsilon_k \psi_k(\boldsymbol{r})$$

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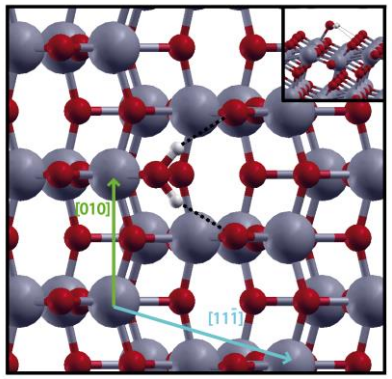
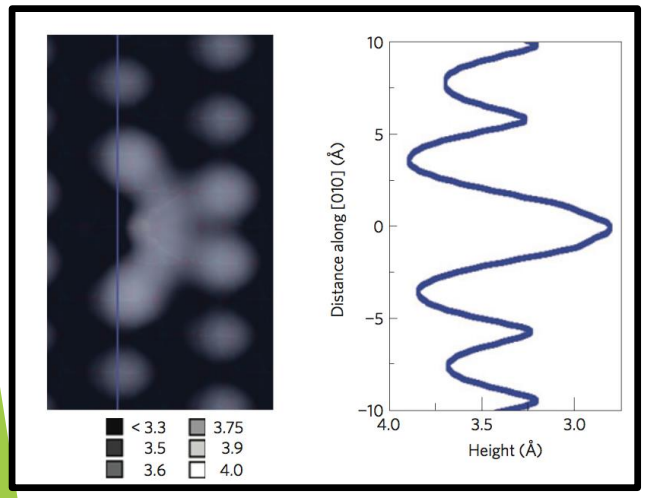
AB-INITIO CALCULATIONS: Density Functional Theory(2)

STM images

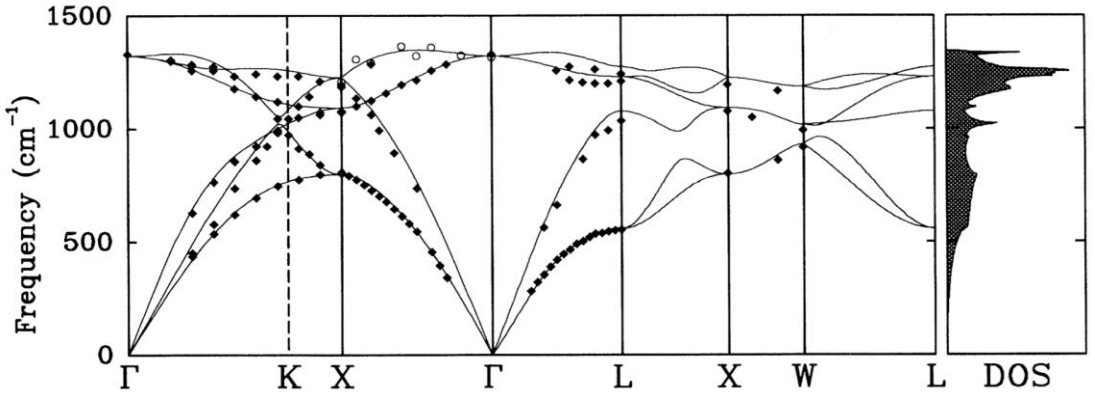


F. Gala et al. J. Phys. Chem. C 2016, 120, 450-456



Y. He et al. - Nature Material 8, 585-589 (2009)

Crystal Vibrations



S. Baroni et al. - Rev. Mod. Phys. 73, 515 (2001)

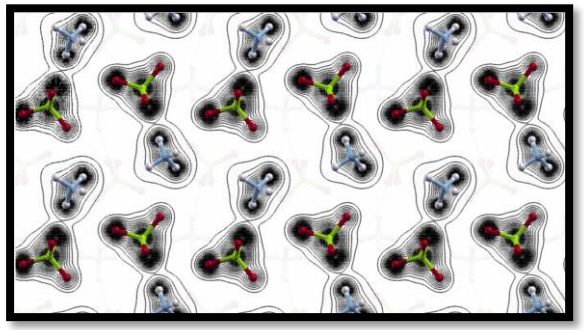
Phonon Dispersion in Diamond

$$\frac{\partial^2 E(\boldsymbol{R})}{\partial \boldsymbol{R}_I \partial \boldsymbol{R}_J} = -\frac{\partial \boldsymbol{F}_I}{\partial \boldsymbol{R}_J}$$

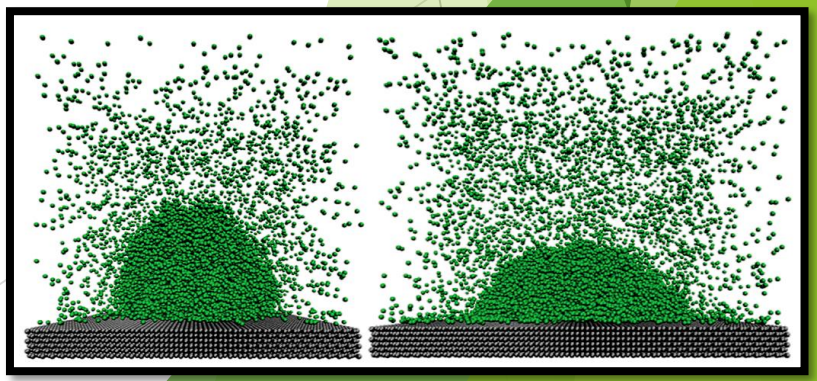
Ionic Forces (Helmann-Feynman Theorem):

$$\boldsymbol{F}_I = -\frac{\partial E(\boldsymbol{R})}{\partial \boldsymbol{R}_I} = -\int n_{\boldsymbol{R}}(\boldsymbol{r}) \frac{\partial}{\partial \boldsymbol{R}_I}\left(-\sum_I \frac{Z_I}{|\boldsymbol{r}-\boldsymbol{R}_I|}\right) d^3r \; - \frac{\partial}{\partial \boldsymbol{R}_I} \sum_{I \neq J} \frac{Z_I Z_J}{|\boldsymbol{R}_J - \boldsymbol{R}_I|}$$

Electrostatic Potential

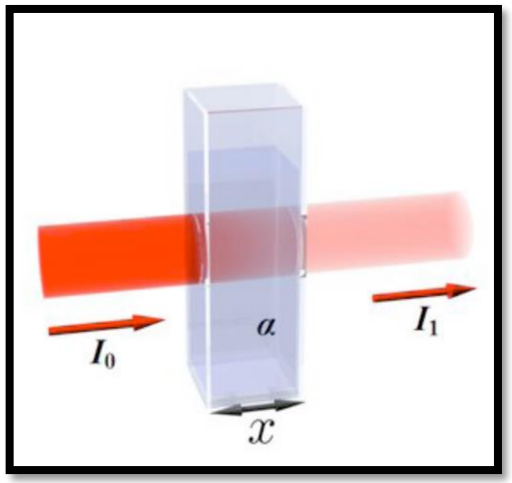


Molecular Dynamics

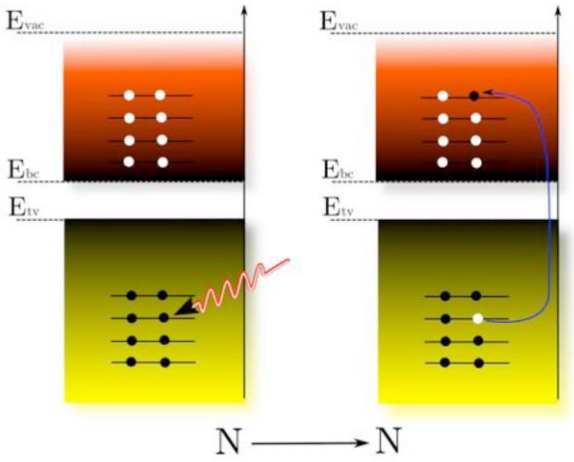


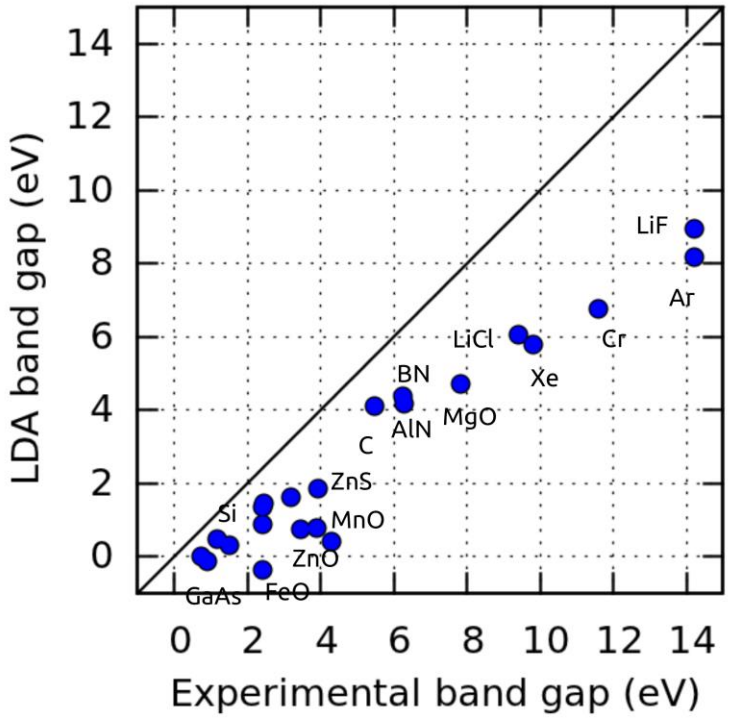
Beyond DFT(1)

Light Absorption



Beer–Lambert law: $I_1 = I_0 e^{-\alpha x}$





F. Tran et al. – Phys. Rev. Lett. 102, 226401 (2009)

DFT underestimate experimental band gaps (since $V_{xc}(r)$ as a function of N is not a continuos function)

In absorption (as well as in direct/inverse photoemission) measurements, the excited electron interacts with a hole in the Fermi sea and can not be supposed to be a free electron decoupled from the surrounding.

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GW approximation and Bethe-Salpeter Equations

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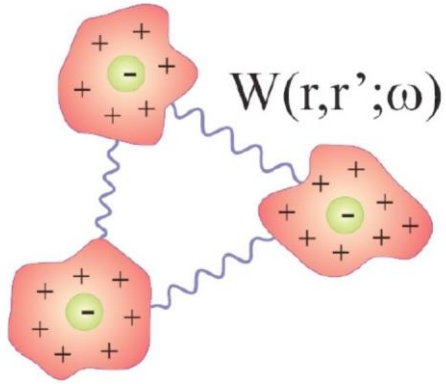
Quasi Particle Picture

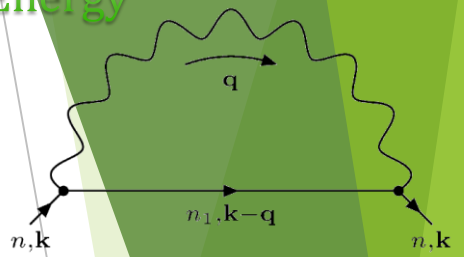


$$G(\boldsymbol{r}t,\boldsymbol{r}'t') = -i\frac{\langle\Psi_0|T\{\psi(\boldsymbol{r}t)\psi^\dagger(\boldsymbol{r}'t')\}|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle}$$

(Non Local)Self-Energy Term

$$[\omega - h_0(\boldsymbol{r}) - V_{xc}(\boldsymbol{r})]G(\boldsymbol{r},\boldsymbol{r}') - \int d^3r_1\Sigma(\boldsymbol{r},\boldsymbol{r}_1;\omega)G(\boldsymbol{r}_1,\boldsymbol{r}') = \delta^{(3)}(\boldsymbol{r}-\boldsymbol{r}')$$

$\Sigma_{n\mathbf{k}}(\omega) =$

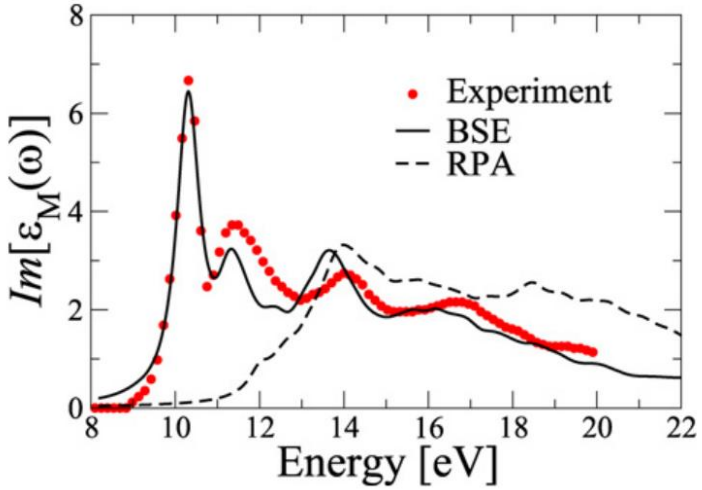


Excitonic Effects = Electron/Hole interaction

W is an effective screened potential

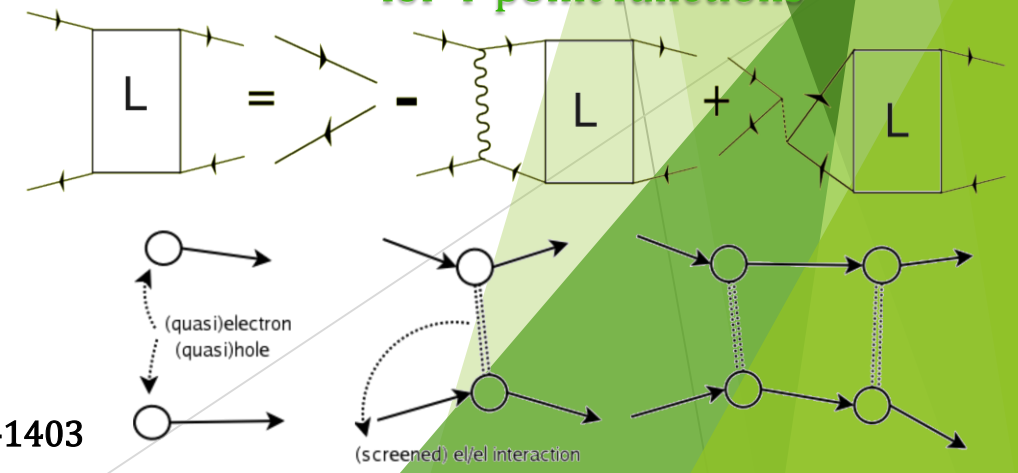
$$W(\boldsymbol{r},\boldsymbol{r}',\omega) = \int \frac{\varepsilon^{-1}(\boldsymbol{r},\boldsymbol{r}'',\omega)}{|\boldsymbol{r}''-\boldsymbol{r}'|}d^3r''$$

weaker than the bare Coulmb interaction



Absorption Spectra of Solid SiO_2
from Marini et al. - Comp. Phys. Comm. 180 (2009) 1392-1403

Bethe-Salpeter Equation for 4-point functions



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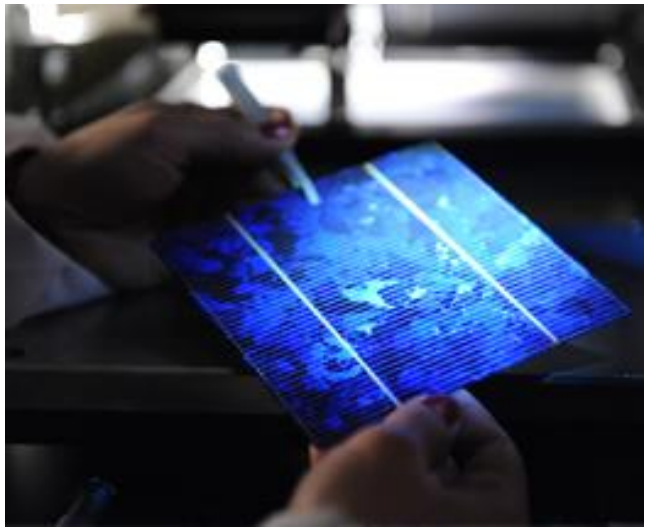
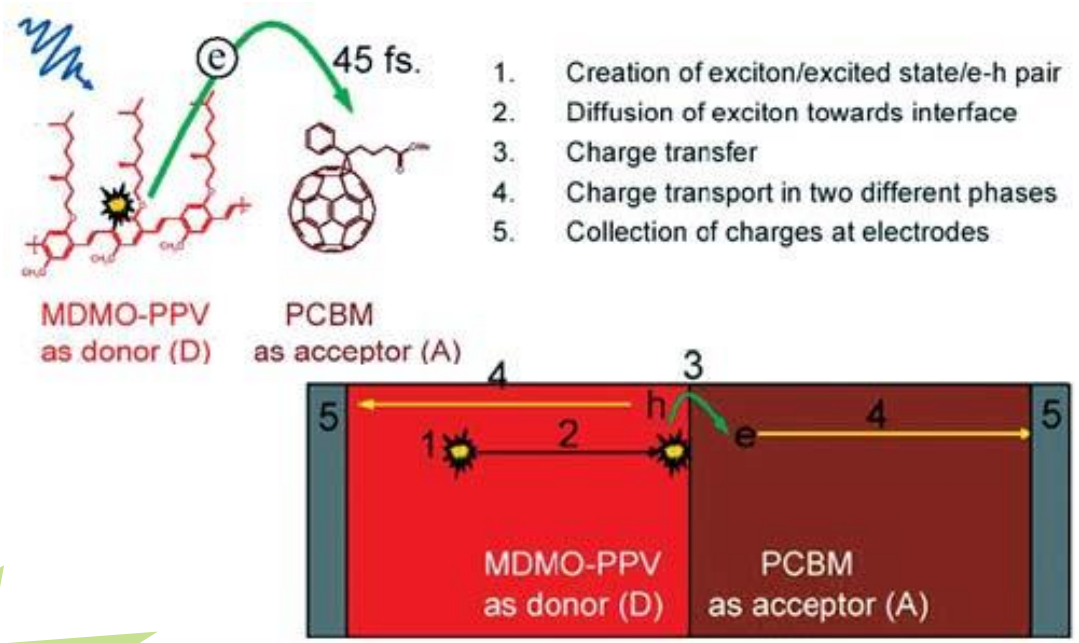
Bulk Heterojunction (BHJ) Solar Cells





KITCHEN SCIENCE

«*The initial discovery of ultrafast electron transfer occurred in late 1992.* ***It was a discovery based purely on curiosity****. At that time, we had been working on the optical properties of semiconducting polymers for many years. Then, the fullerenes were discovered[…]. During a* ***random discussion*** *in my offi ce, we speculated on what would happen if we mixed these two novel materials. We made several speculative guesses, but decided to do some initial experiments even though* ***the idea was not yet well formed in our minds****. We obtained the now famous soluble fullerene derivative, PCBM, from Fred Wudl and the story began to unfold.»*

Alan J. Heeger

(Nobel Prize in Chemistry 2000)

Heeger A. J. - Adv. Mater. 2014, 26, 10-28

PCBM : Phenyl-C61-butyric acid methyl ester
MDMO-PPV: Poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene]

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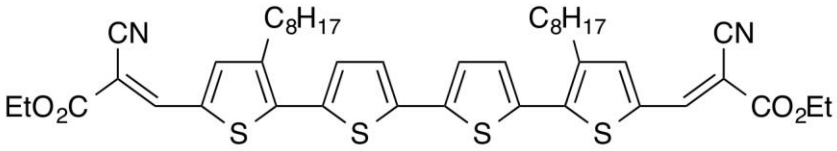
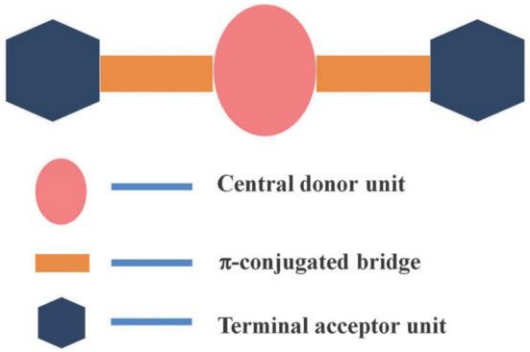
BT2N as donor material in BHJ: Experimental Evidences

BT2N Molecular Formula :

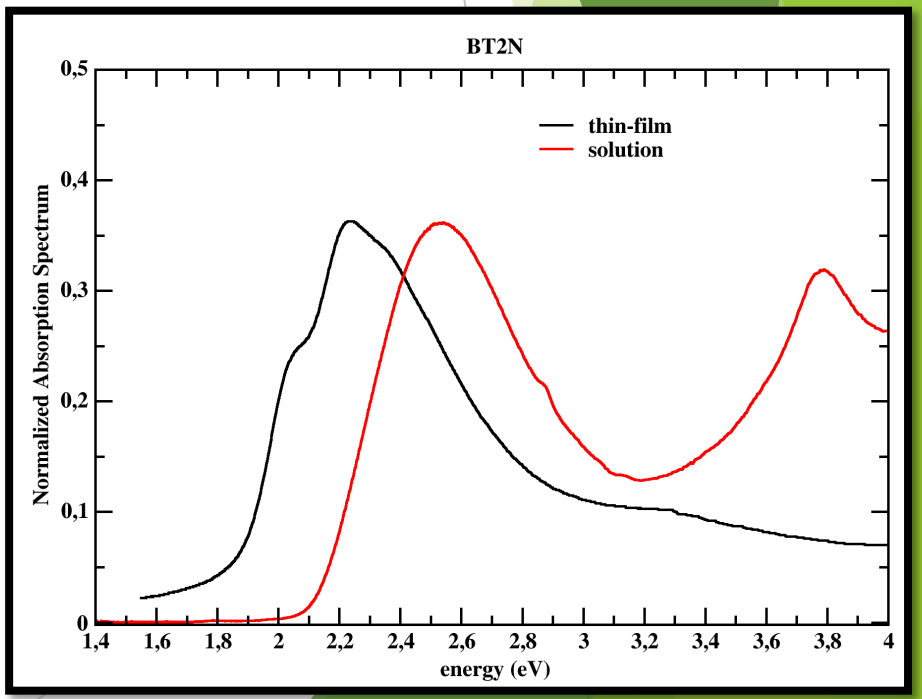


Oligothiophene derivatives exposed to ultraviolet light at 254 nm (left) and 365 nm (right)

Acceptor-Donor-Acceptor (A-D-A) Structure



from Ni W. et al. - Chem. Commun., 2015, 51, 4936-4950



BT2N absorption spectrum

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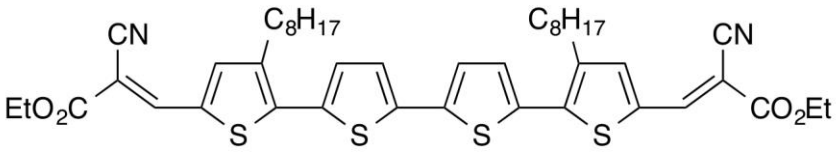
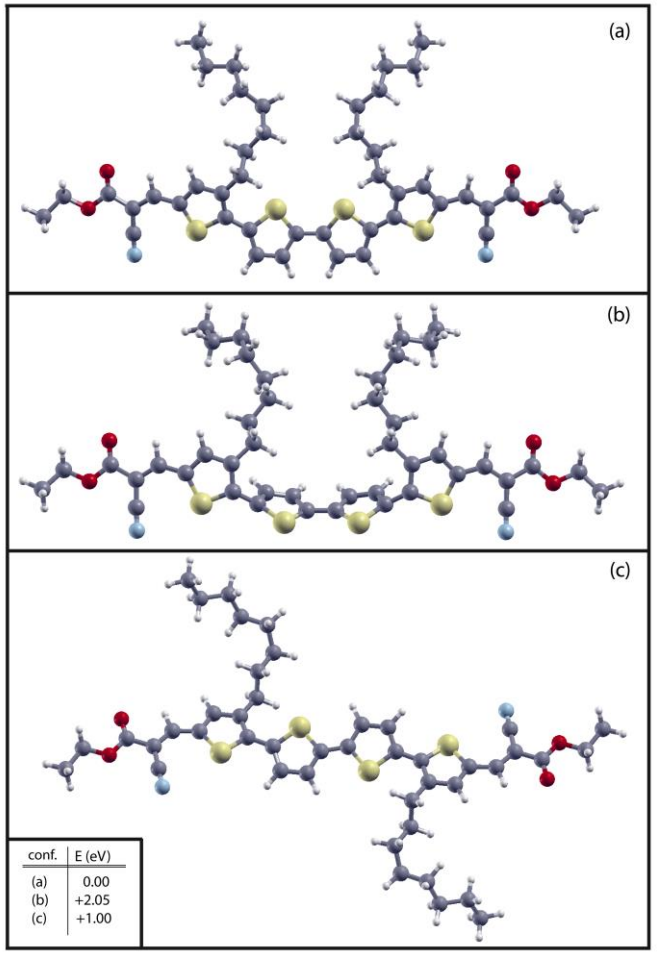
Modelling oligothiophene small-molecules from first principles

BT2N Molecular Formula :



The bare chemical formula does not give any insight about the relaxed geometry of the molecule



Starting trial configurations have been chosen according to:

- Symmetry Considerations
- Hindrance minimization

IONIC RELAXATION

from Gala F. et al. – J. Chem. Phys., 144, 084310 (2016)

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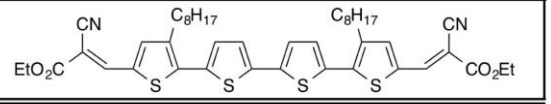
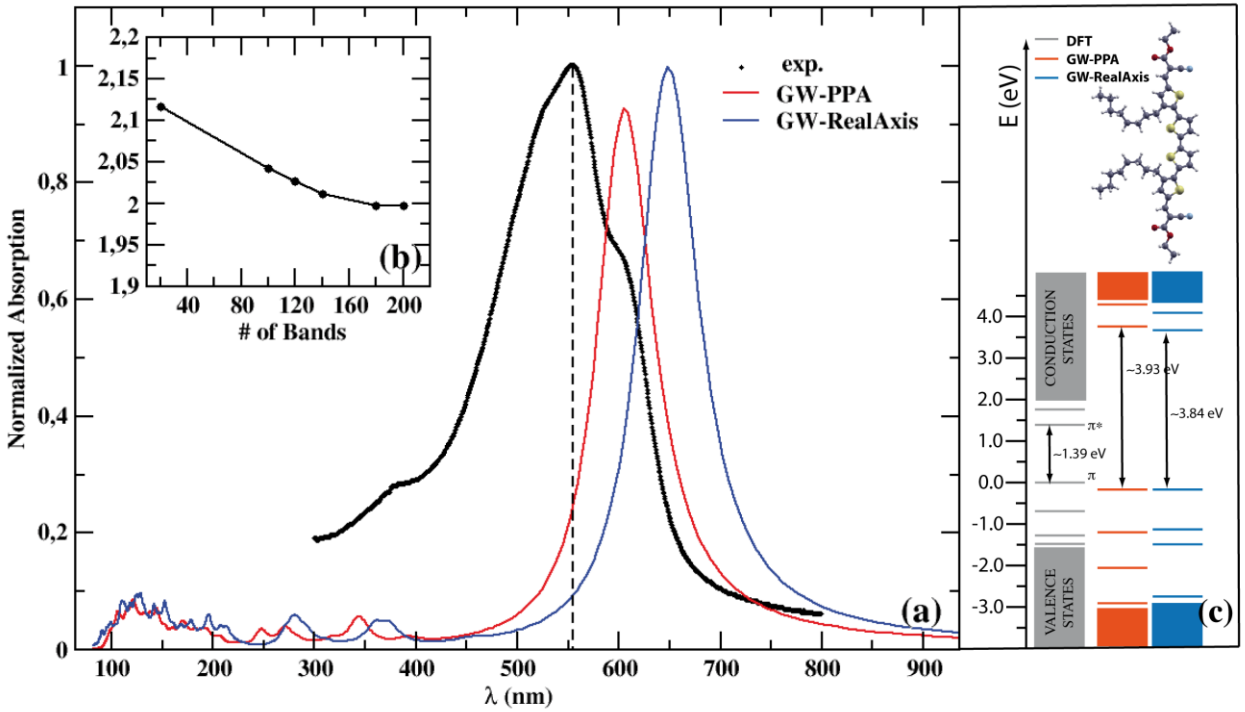
BT2N Electronic Properties: Gas Phase

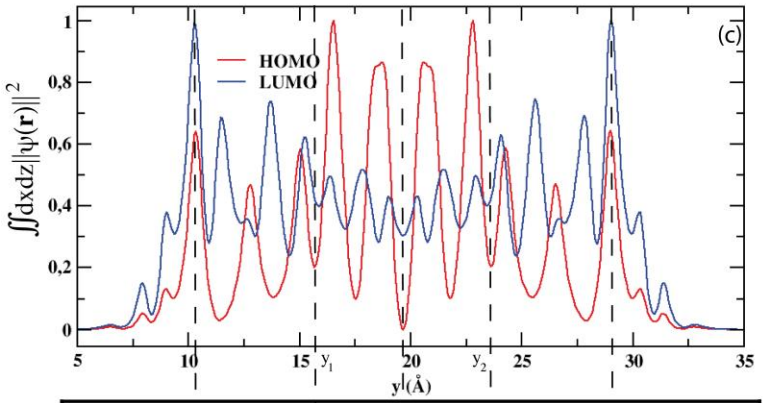
Name	ε_{HOMO} (eV)		ε_{LUMO} (eV)		ε_{gap} (eV)		Structure
	DFT-PBE	exp.	DFT-PBE	exp.	DFT-PBE	exp.	
BT2N	-4.96 (-4.56)	-5.49	-3.57 (-3.27)	-3.47	1.39 (1.30)	2.02	



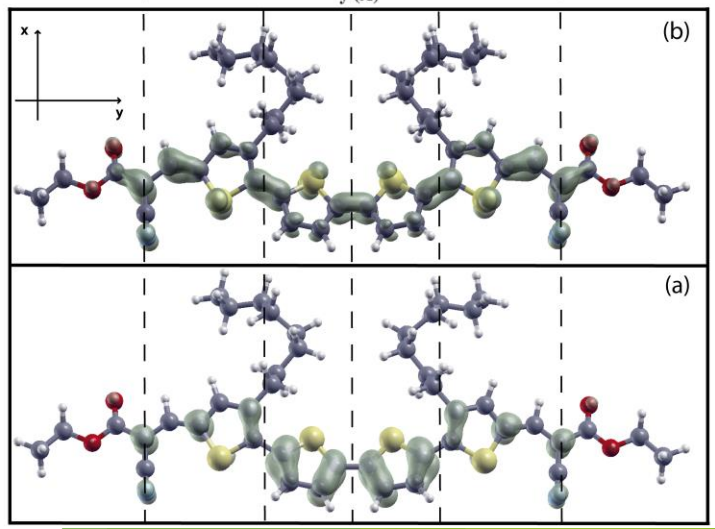
$P_{y_2-y_1}^{HOMO} \sim 0.53$

$P_{y_2-y_1}^{LUMO} \sim 0.31$

Isosurface plots for the calculated HOMO and LUMO orbitals ((a) and (b), respectively), together with their normalized *xz* average values (c).



A-D-A Structure ??



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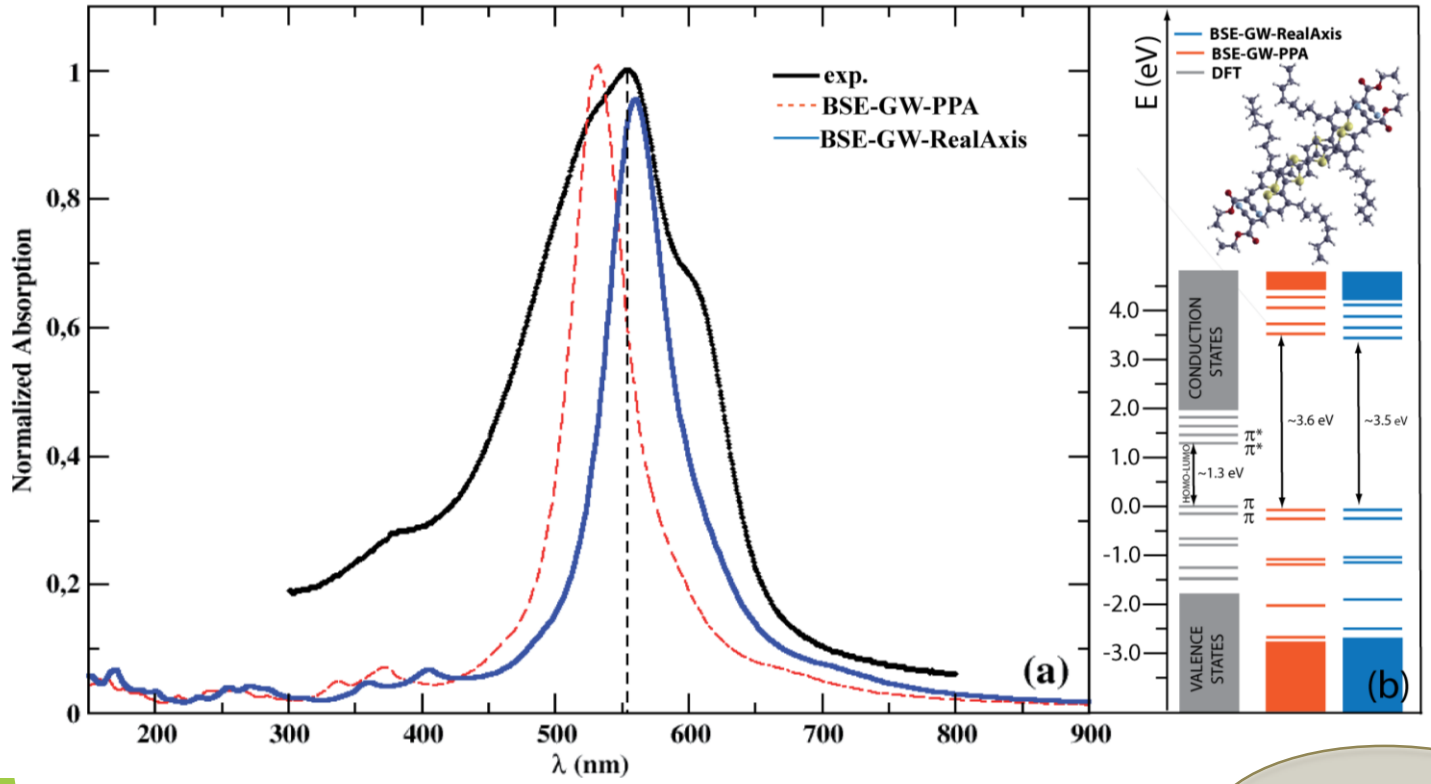
BT2N Electronic Properties: Solid State Phase

π conjugation between BT2N molecules



The absorption properties of small oligothiophene molecules are tightly related to the way they are arranged in the matrix of organic solar cell device.

Clausius-Mossotti relation: $\alpha_{\parallel} = \frac{3\Omega}{4\pi}\frac{\epsilon_{\parallel}-1}{\epsilon_{\parallel}+2}$

$$\epsilon_M(\omega) = 1 - \lim_{\mathbf{q}\to 0} V(\mathbf{q}) \lim_{\eta\to 0^+} \sum_{\lambda\lambda'} \sum_{n_1 n_2} \langle n_1 | e^{-i\mathbf{q}\cdot\mathbf{r}} | n_2 \rangle \frac{A^{\lambda}_{n_1 n_2}}{\omega - E_\lambda + i\eta}$$
$$\times S^{-1}_{\lambda\lambda'} \sum_{n_3 n_4} (f_{n_3} - f_{n_4}) \langle n_4 | e^{i\mathbf{q}\cdot\mathbf{r}'} | n_3 \rangle (A^{\lambda'}_{n_3 n_4})^*$$

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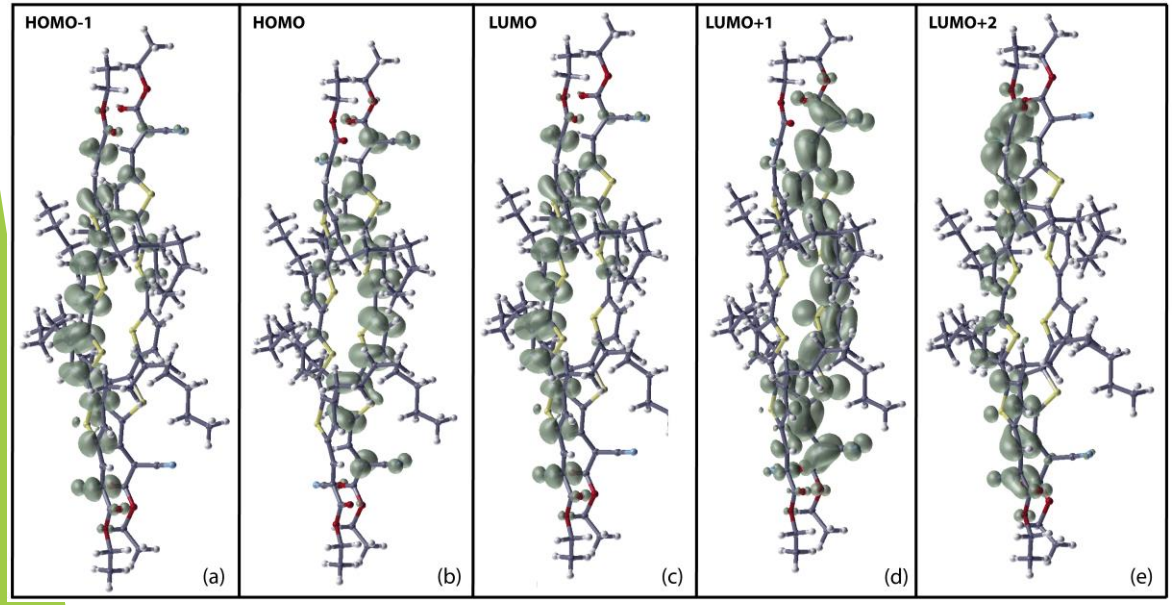
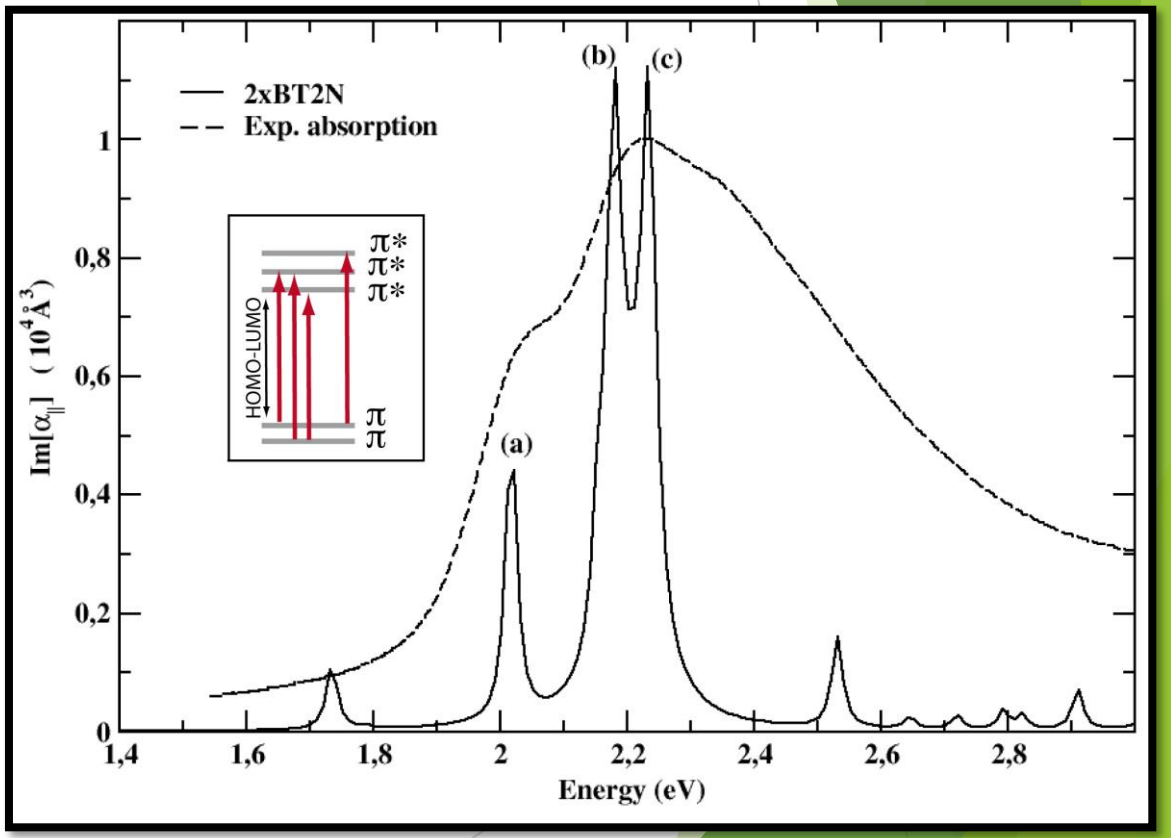
BT2N Excitonic Properties

experimental band gap!

Peak	E (eV)	eh pairs	Weight $A^{\lambda}_{nn'}$
(a)	2.02	HOMO-1→LUMO+1 HOMO→LUMO+1 HOMO-1→LUMO	0.61 0.25 0.12
(b)	2.18	HOMO → LUMO + 2	0.87
(c)	2.23	HOMO-1→LUMO HOMO-1→LUMO+1 HOMO→LUMO+1	0.30 0.30 0.25

$$\Phi^{\lambda}(\boldsymbol{r}_e, \boldsymbol{r}_h) = \sum_{nn'} A^{\lambda}_{nn'}\, \phi_n(\boldsymbol{r}_e))\phi^*_{n'}(\boldsymbol{r}_h)$$





Future Developments

- Evaluation of Exciton Lifetime/Diffusion Length in small molecules

$$L = (D\tau)^{\frac{1}{2}} \propto \tau^{\frac{1}{2}}$$

- Inspect the role of ionic degrees of freedom (phonons) in the exciton formation
- Evaluate the charge transfer rate at the interface with PCBM

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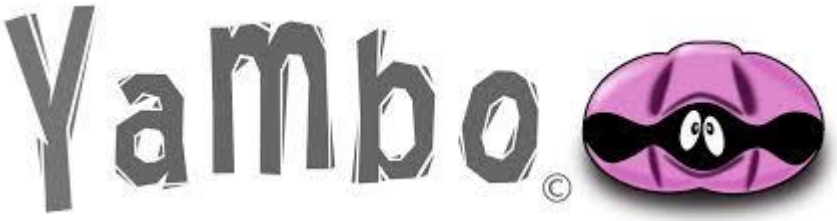
Thanks To the Audience

Calculations performed with:



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