NICOLAUS COPERNICUS
UNIVERSITY
IN TORUŃ

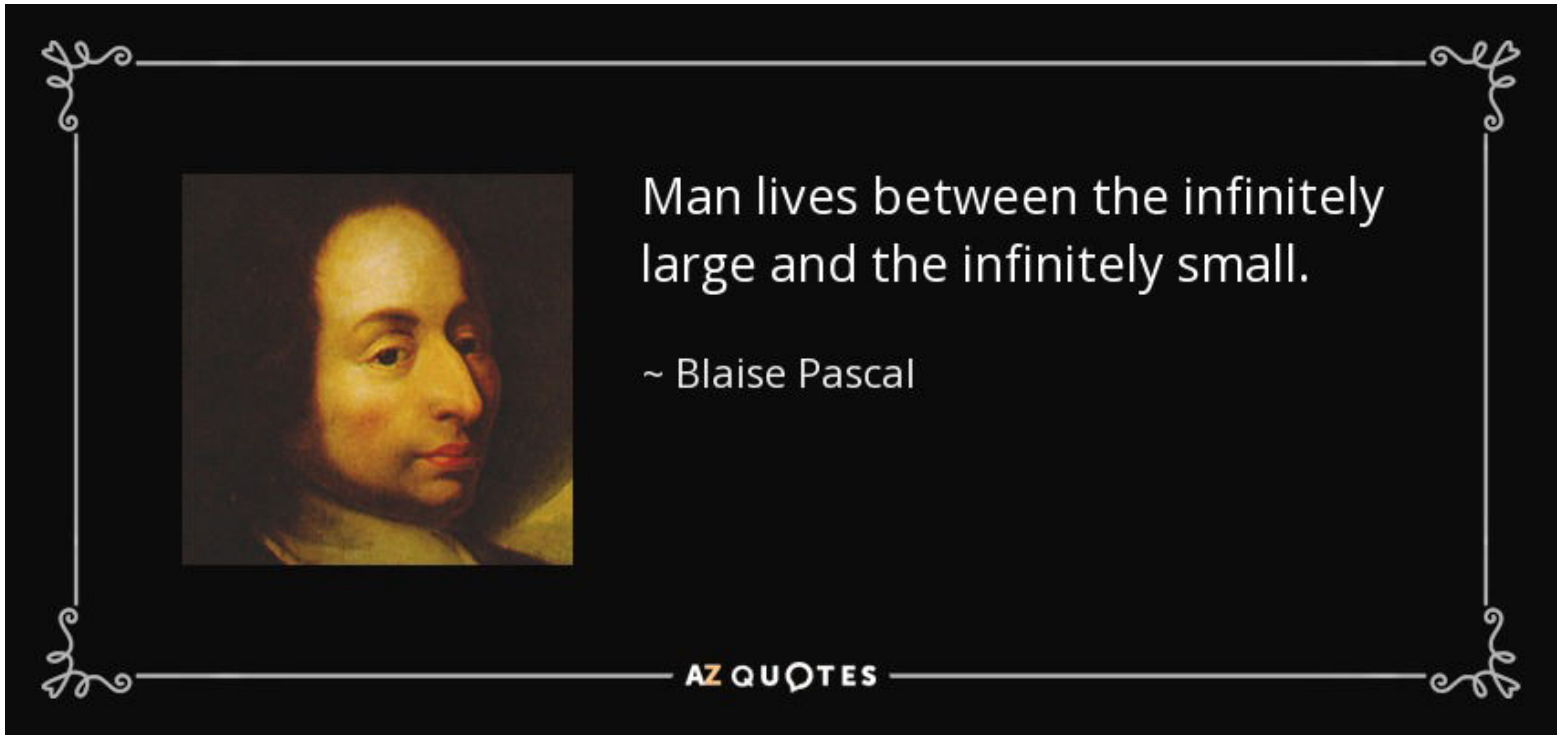
Materials design from first principles: minimizing energy

Igor Di Marco

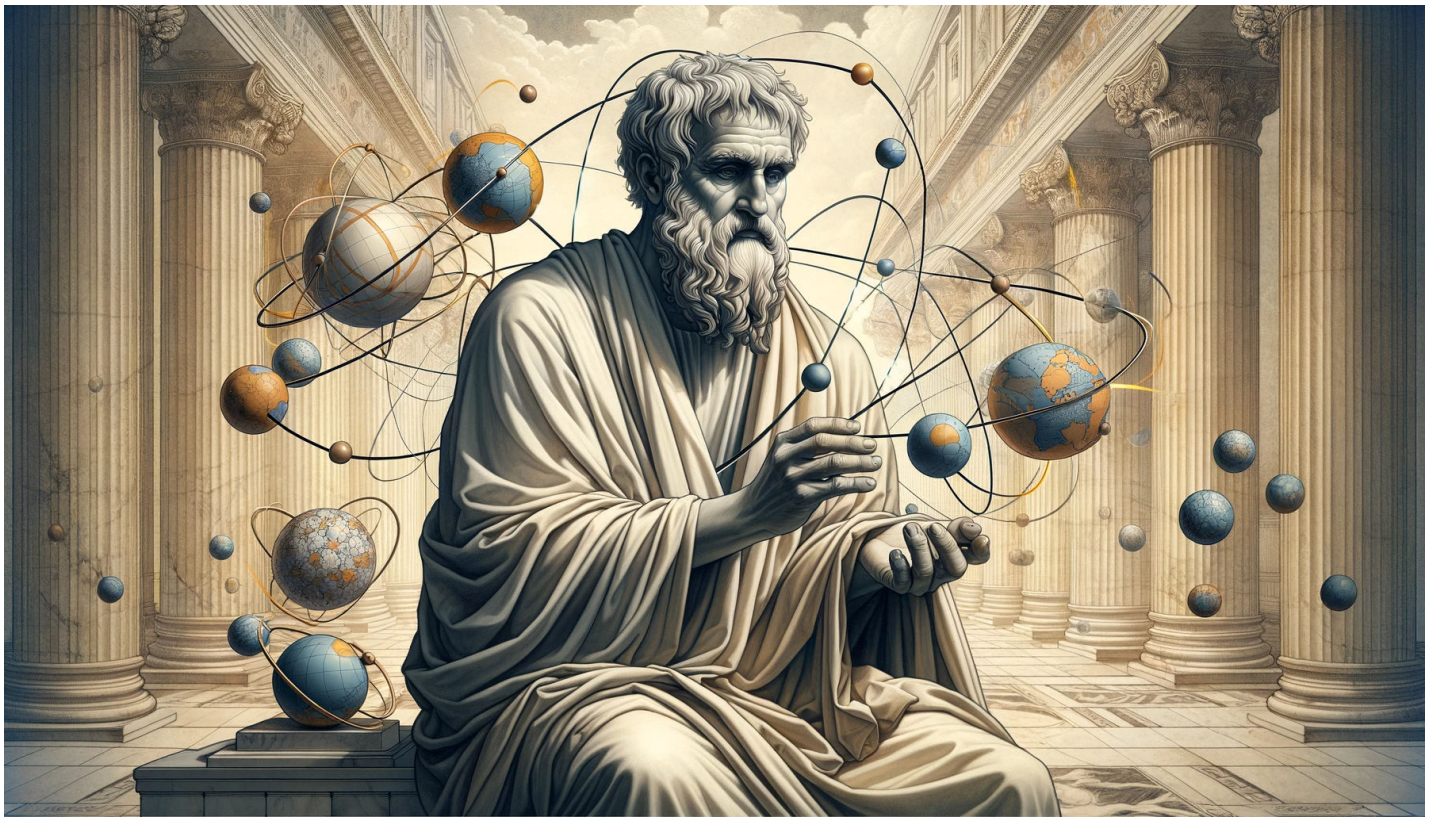
Nicolaus Copernicus University, Toruń, Poland
Uppsala University, Sweden

POLONEZ BIS

Humanity's interest in extreme phenomena



Democritus and the rise of the atomistic model



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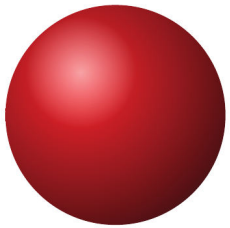
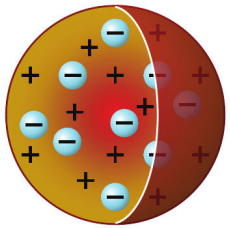
A long journey towards our current understanding

An atom can be modeled as a nucleus with a system of interacting electrons



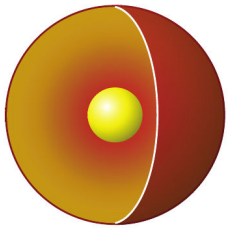
Atom model

Dalton (1803)



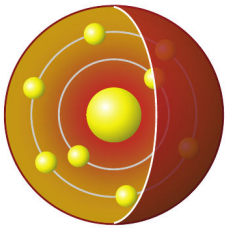
Pudding atom model

Thomson (1904)



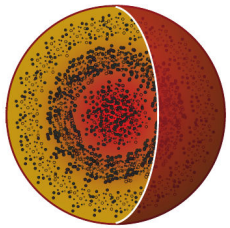
Planetary atom model

Rutherford (1911)



Orbital atom model

Bohr (1913)



Quantum mechanical atom model

Schrödinger (1926)

Energy Encyclopedia.com

A revolutionary theory that escapes human intuition

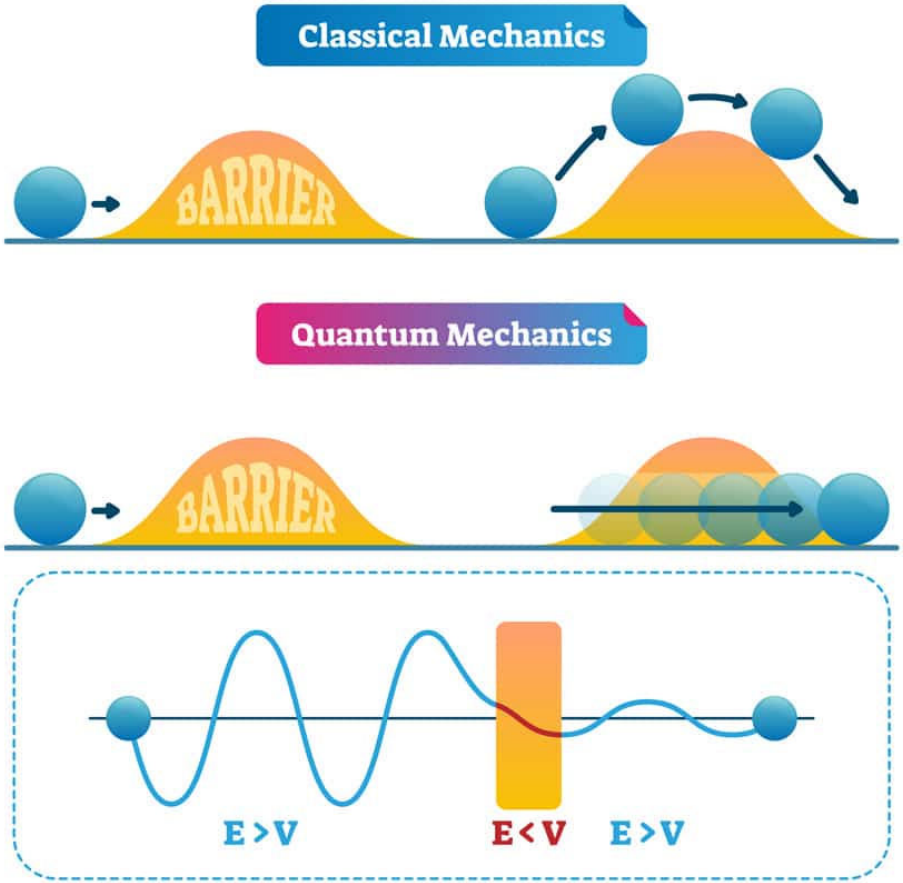


Image Courtesy: normaals/Getty Images

Wave-particle duality

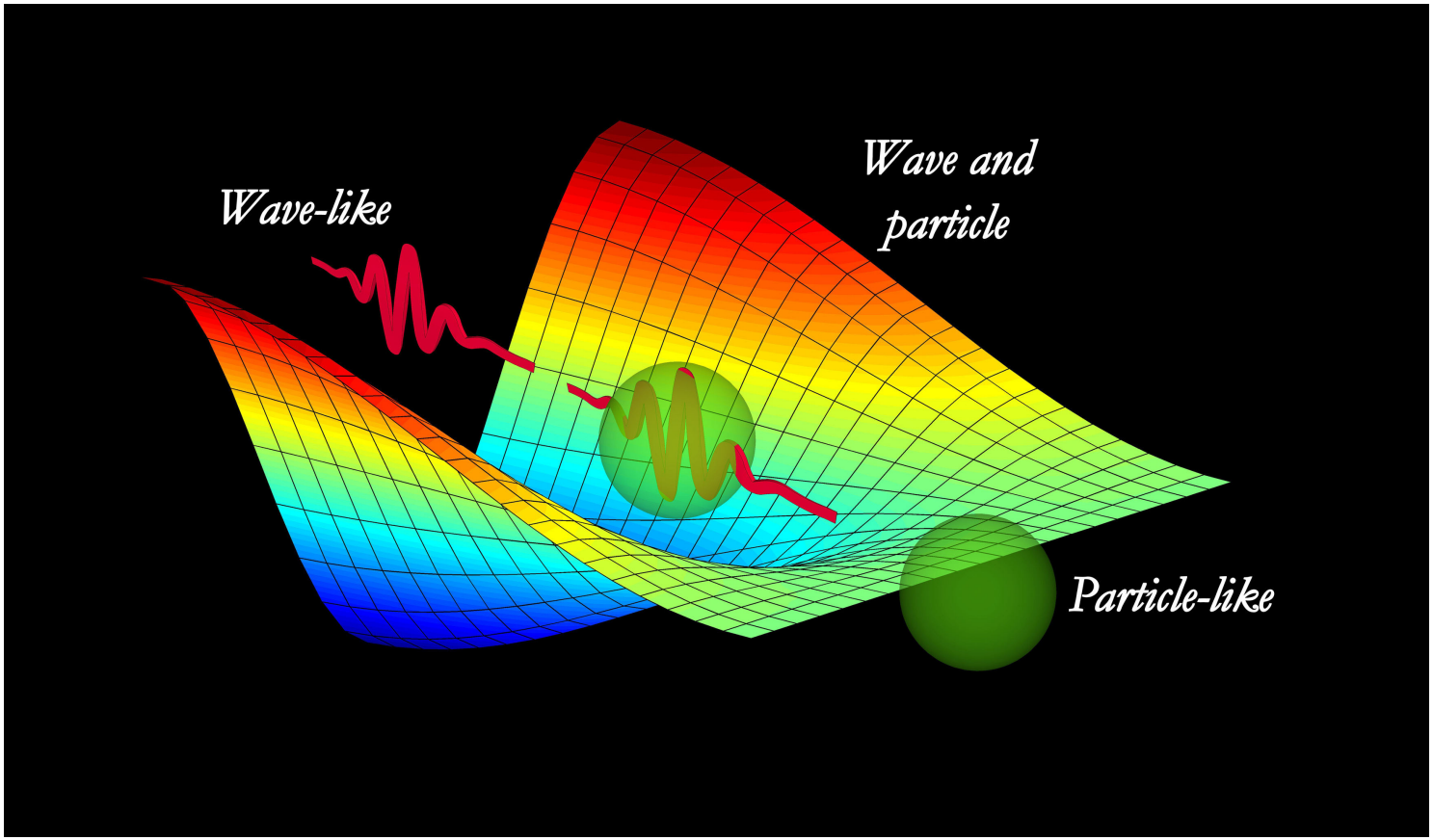


Image credit: S. Tanzilli, CNRS

Wanted! But dead or alive?

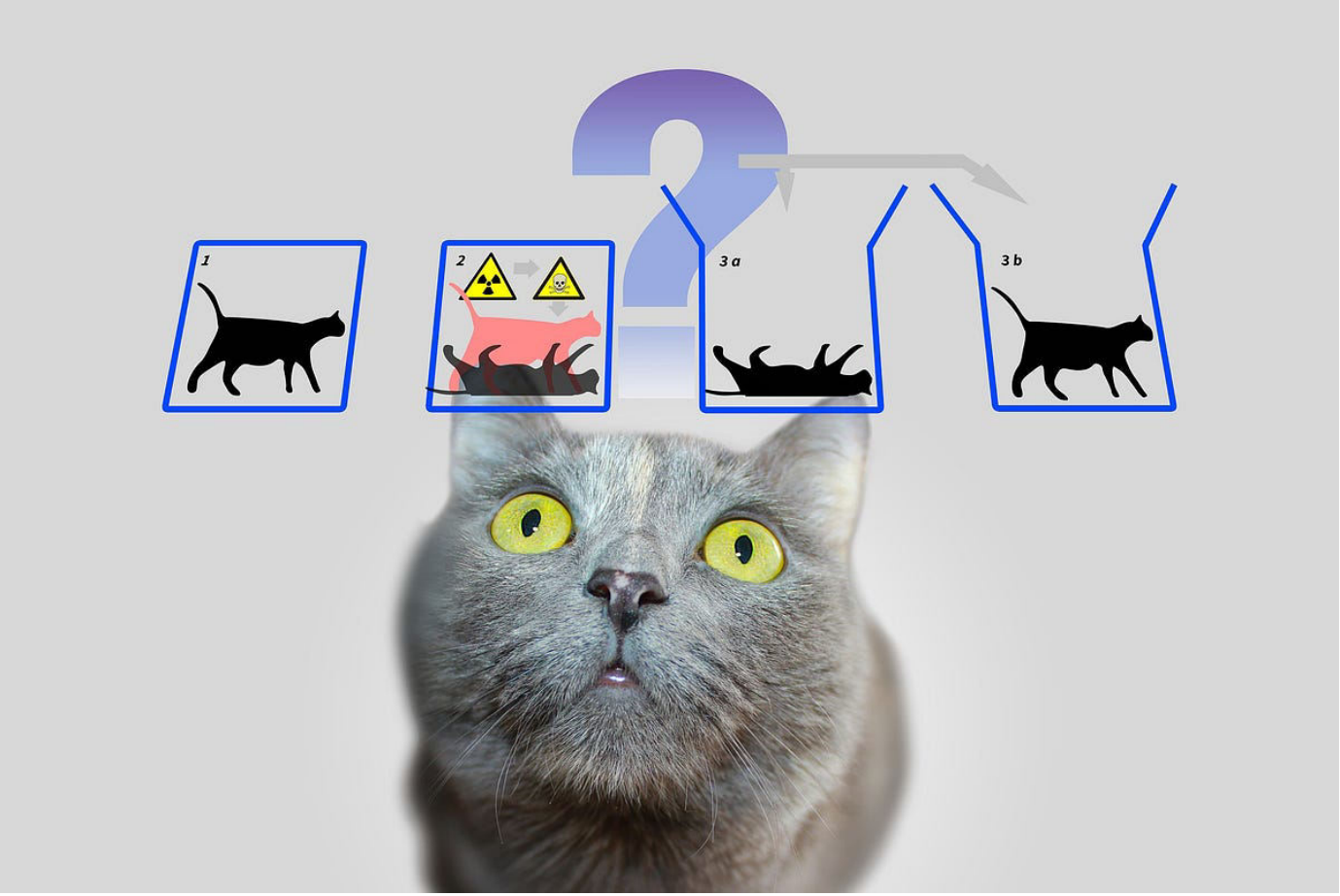
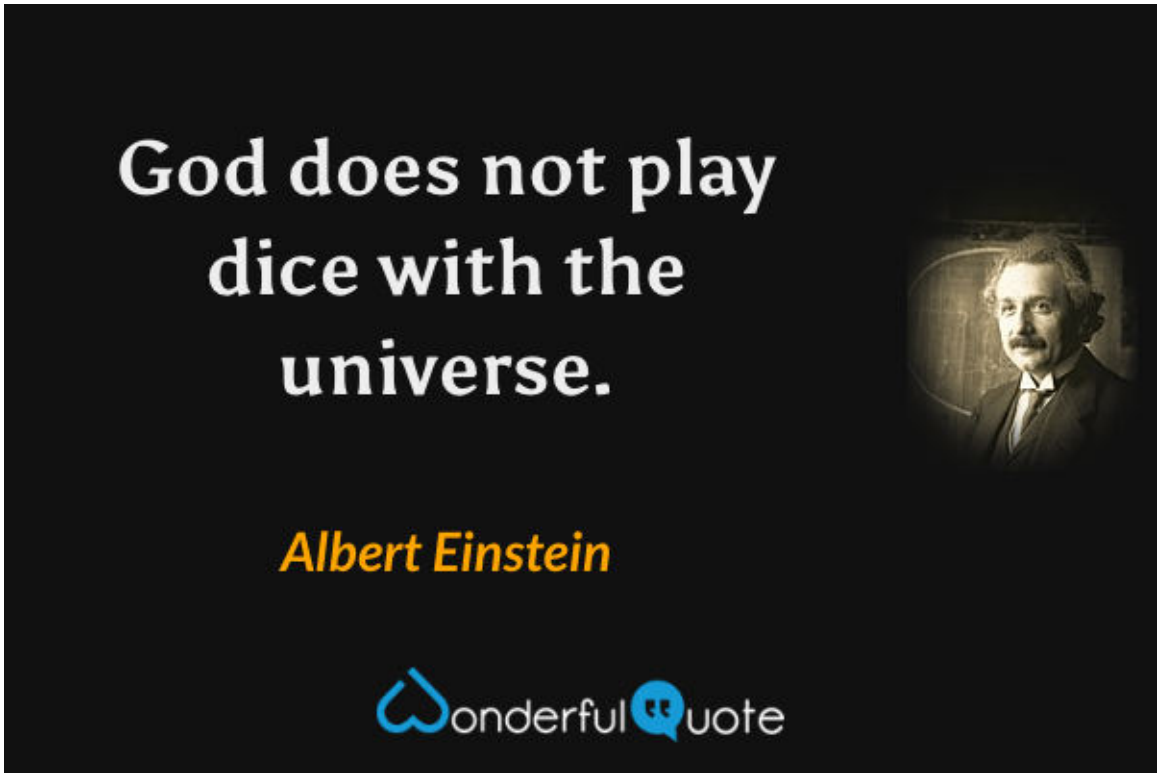
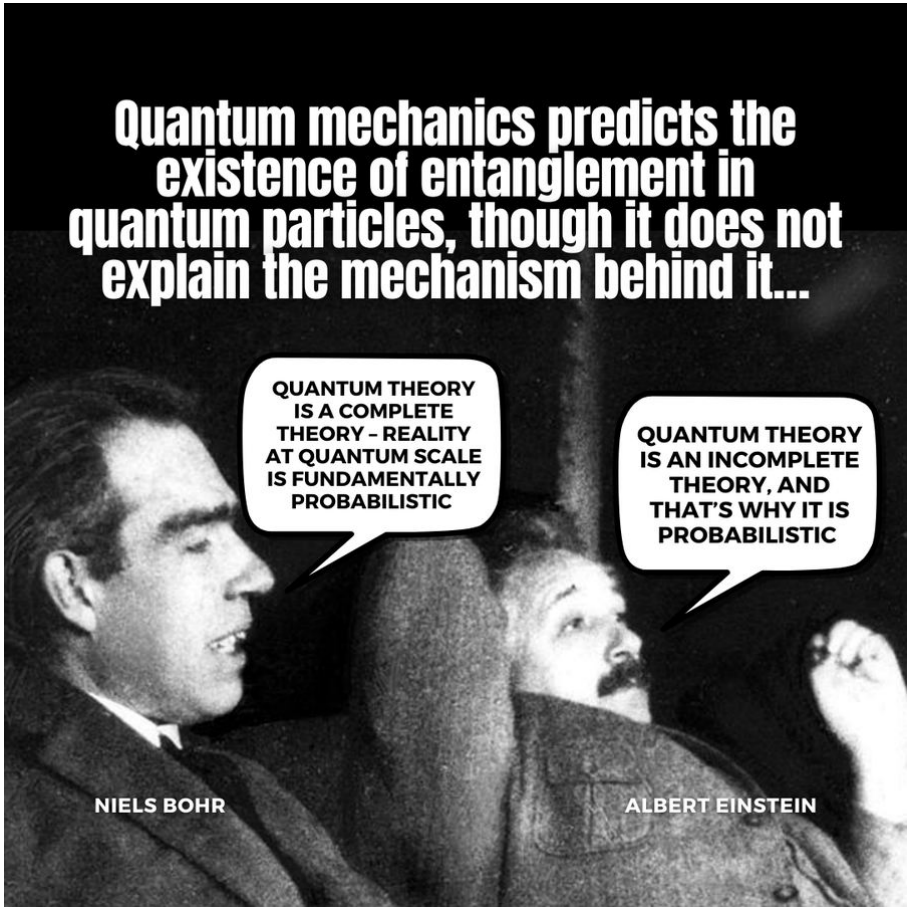


Image by Gerd Altmann, via Pixabay

The philosophical problems of a probabilistic theory

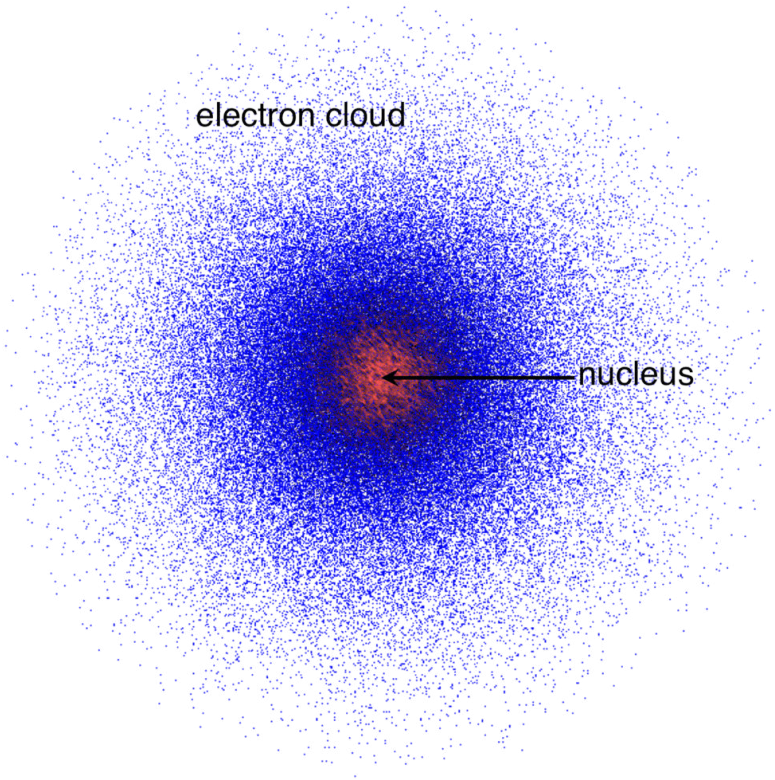


A solution that seemed far from complete (and still does)



The concept of electronic cloud

The electrons have a probability to be located in a given region around the nucleus



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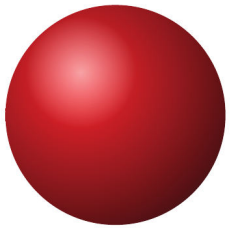
The end of a very long journey

An atom can be modeled as a nucleus with a system of interacting electrons



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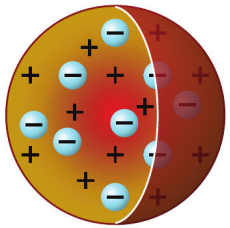

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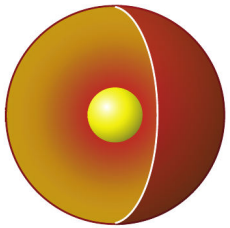

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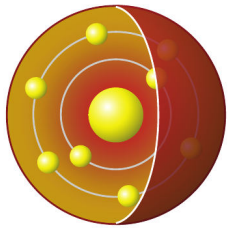

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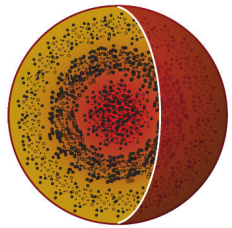


Quantum mechanical atom model

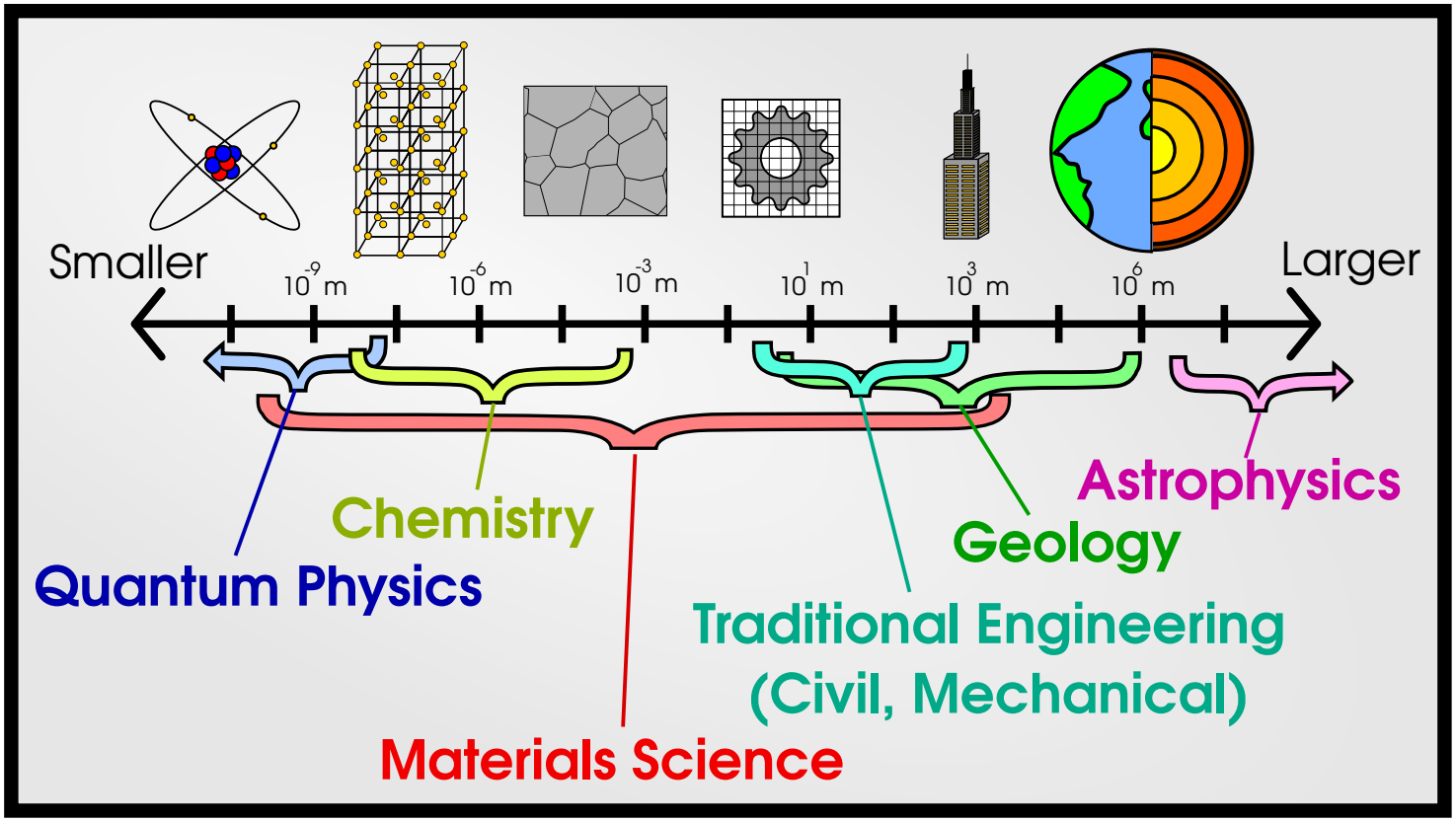
Schrödinger (1926)

Energy Encyclopedia.com

An atom is not the final indivisible component but remains still important

Can we go from small to big length scales?

What if had infinite mathematical or computational power?



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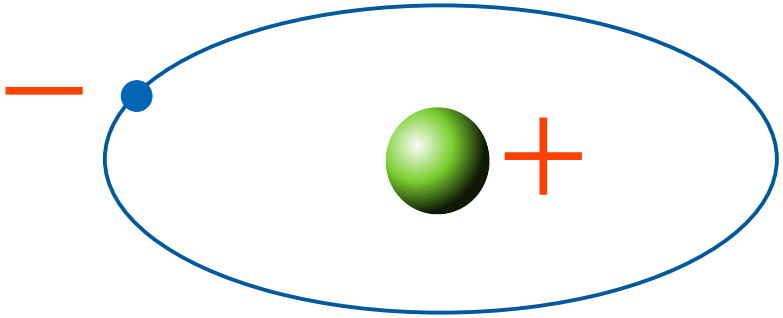
The rules of the game: the atomic model

An atom can be modeled as a nucleus with a system of interacting electrons



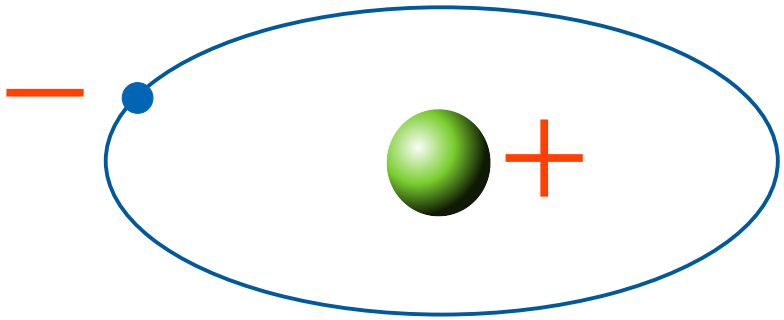
We must “simply” solve the Schrodinger equation of electrons and nucleus

 are much bigger than  and also heavier!

As in classical mechanics, the electrons can be decoupled

The rules of the game: the atomic model

An atom can be modeled as a nucleus with a system of interacting electrons



We must “simply” solve the Schrodinger equation of electrons and nucleus

Decoupling the nucleus, we are left with the equation for electrons only:

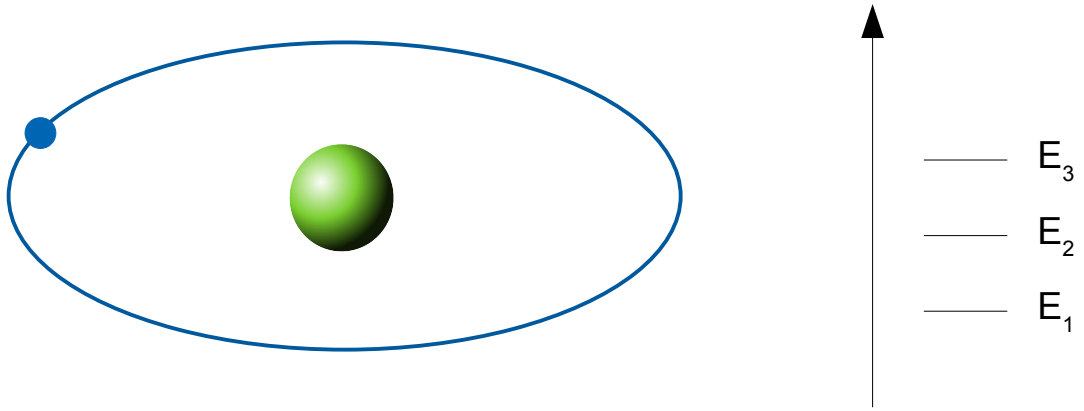
$$\left[T_e + V_{ne} + V_{ee}\right]\psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_N) = E\psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_N)$$

The crucial part is the electronic wavefunction ψ

The rules of the game: the atomic model

An atom can be modeled as a nucleus with a system of interacting electrons

The Schrodinger equation for the electrons is exactly or numerically solvable

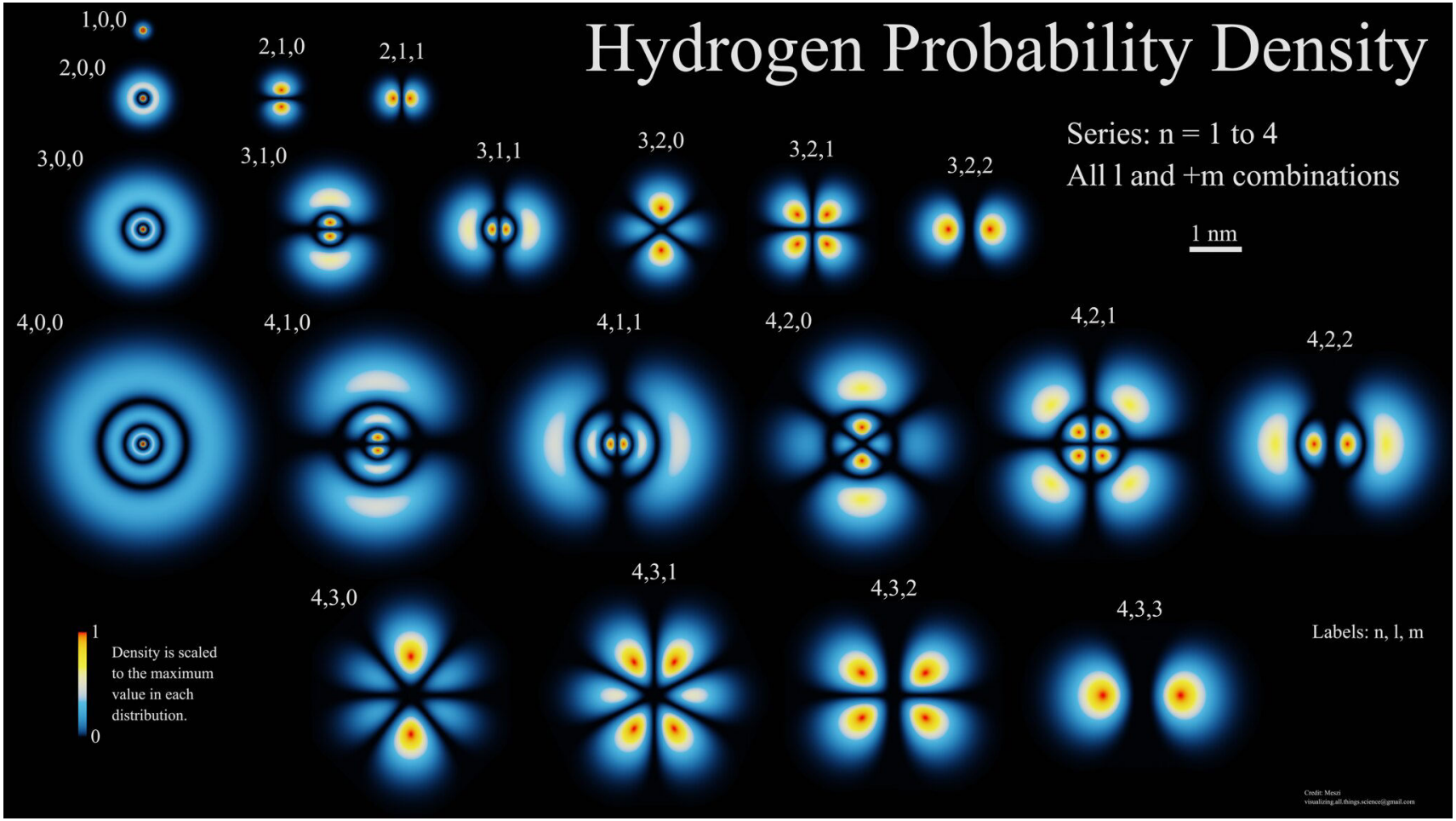


The electrons can occupy a set of discrete energy levels (**bound states**)

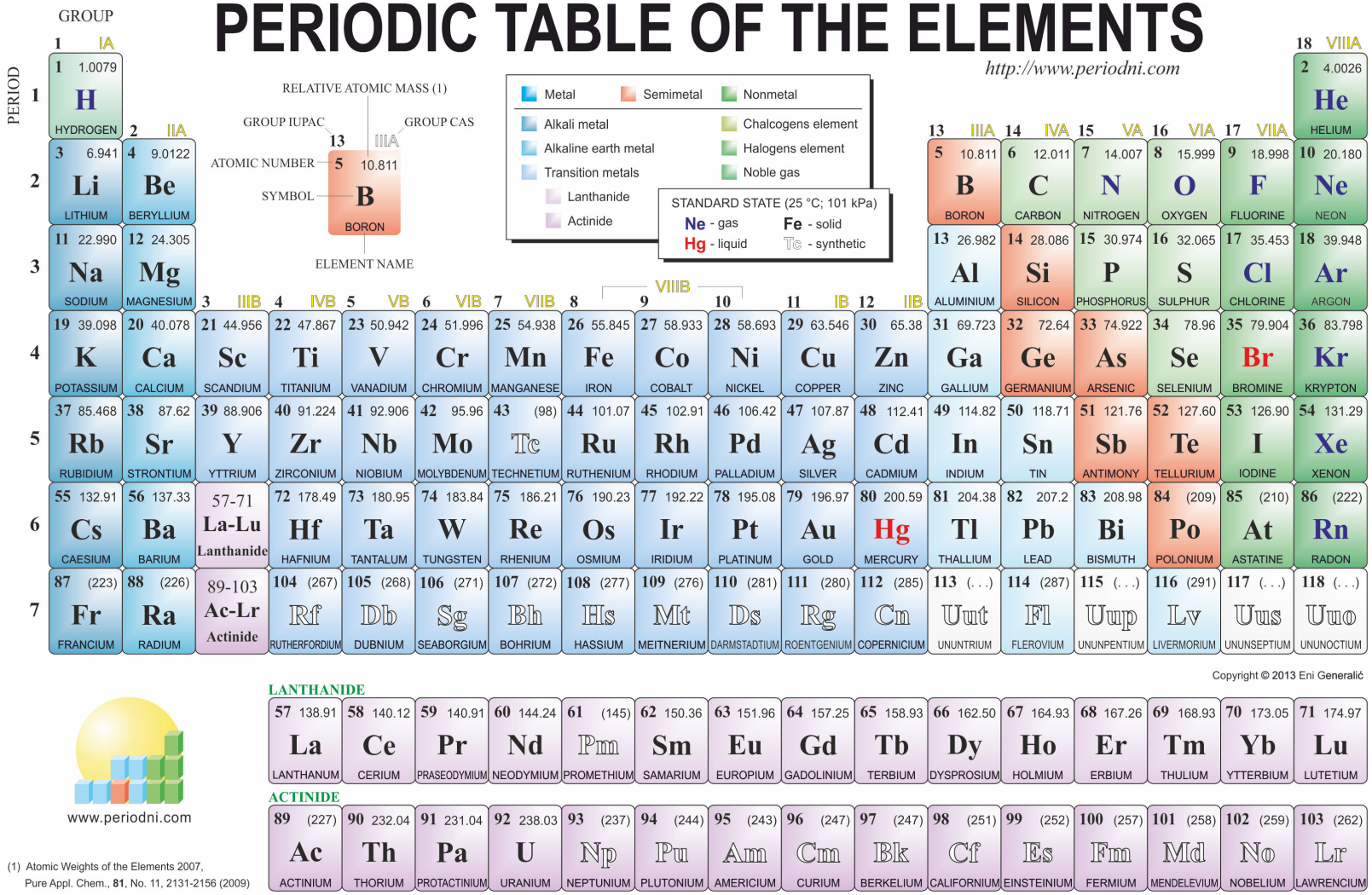
Electronic shells: 1s 2s 2p 3s 3p 3d 4s 4p 4d 4f 5s 5p 5d 5f ...

A bit of mathematics...

The only available analytical solution!



The periodic table explained several known chemical rules



The rules of the game: from atoms to solids

What does it happen when we bring a few atoms together?

The rules of the game: from atoms to solids

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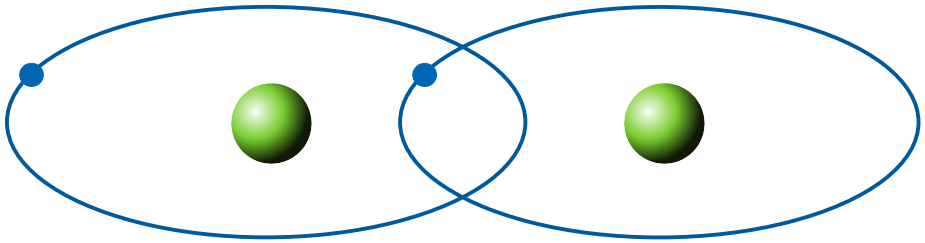


A chemical bond is formed and keeps these ions together

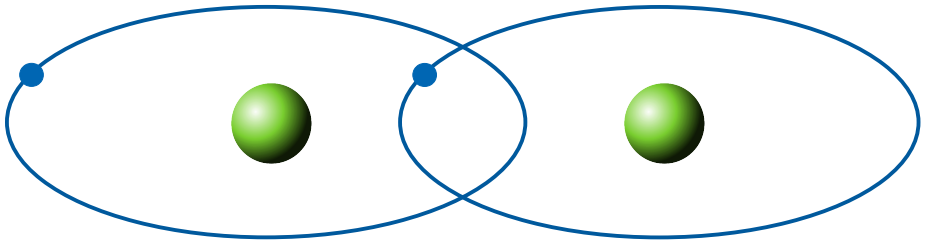
Small molecules or clusters are numerically solvable in quantum chemistry

- By decoupling electrons and nuclei, one obtains the electronic SE

$$\left[T_e + V_{ne} + V_{ee}\right] \psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_N) = E\psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_N)$$

The rules of the game: from atoms to solids

What does it happen when we bring a few atoms together?



A chemical bond is formed and keeps these ions together

Small molecules or clusters are numerically solvable in quantum chemistry

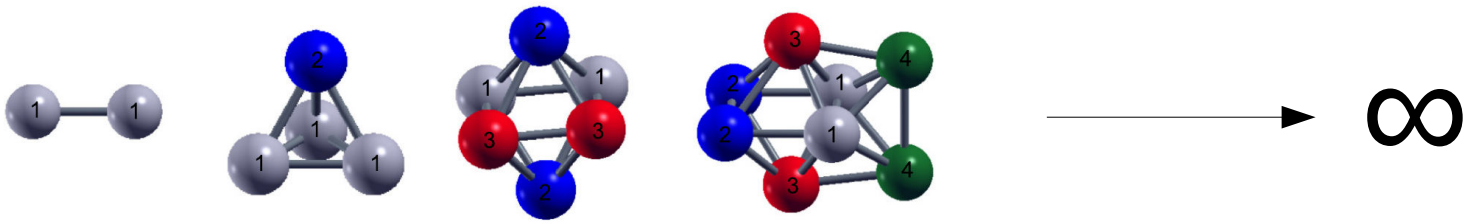
- By decoupling electrons and nuclei, one obtains the electronic SE
- Electronic problem solved via configuration interaction or coupled clusters
- The atomic positions are optimized

The rules of the game: from atoms to solids

Atoms and molecules are still elementary components

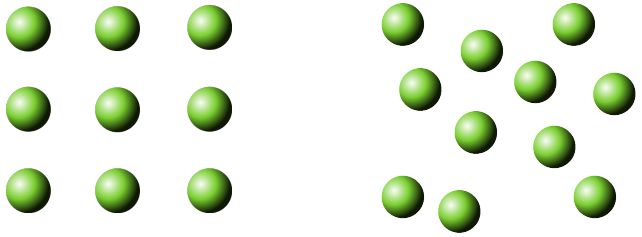
But how do we go from there to materials?

Let us consider a cluster of atoms, where we add one atom at the time



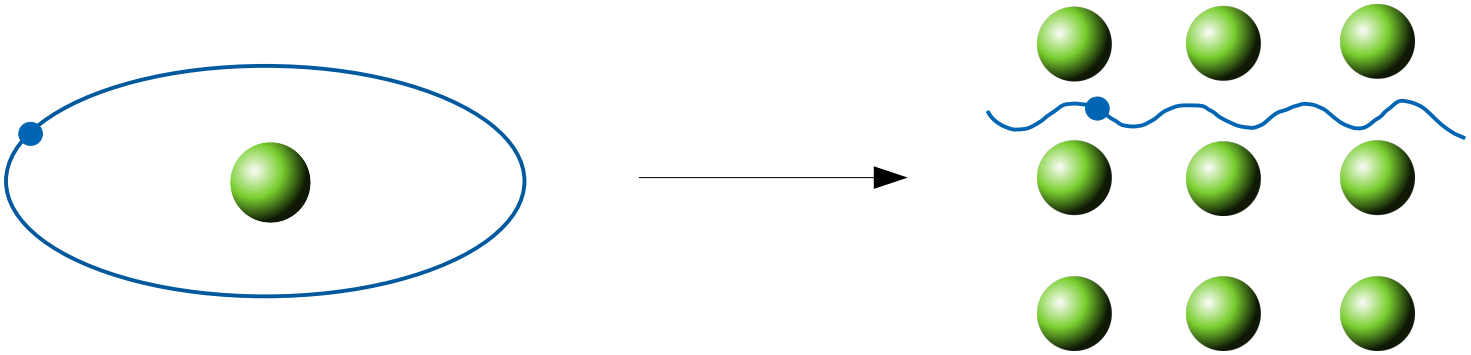
A periodic structure can be obtained

Crystalline vs amorphous solids



The rules of the game: from atoms to solids

A crystalline solid is composed by many atoms in a regular arrangement



A few interacting electrons

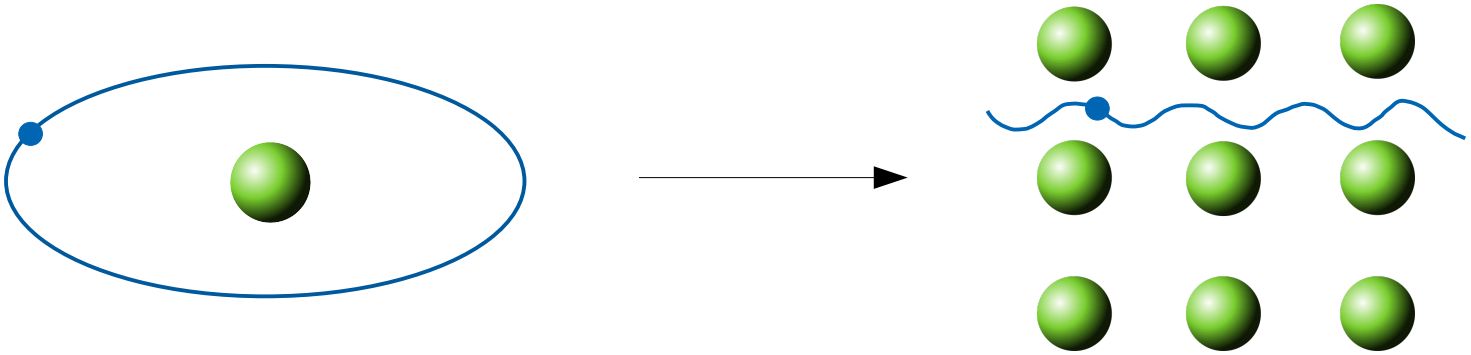
10^{23} electrons

10^{23} electrons = 100000000000000000000000 electrons

Let us remember that we must solve for an equation for $\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$

The rules of the game: from atoms to solids

A crystalline solid is composed by many atoms in a regular arrangement



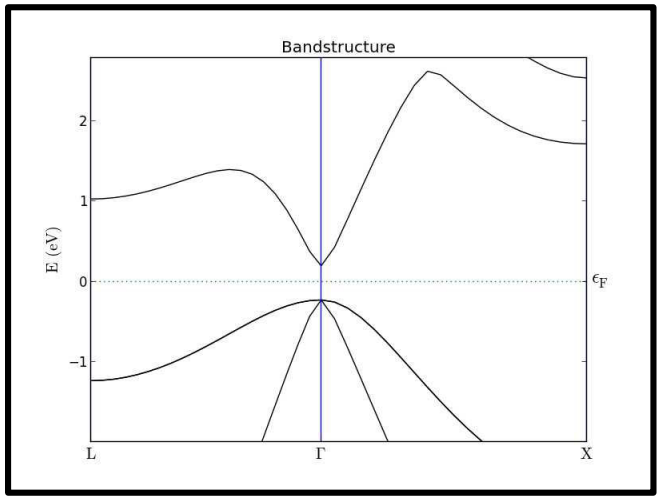
Too many particles (~10^{23}) for a solution!

In one-particle approximation, we obtain

1) <u>delocalized electrons</u>

2) <u>energy bands</u>

But how adequate is this simple picture?



Solving the many-electron problem in solids

Density-functional theory (DFT) is the most used electronic structure theory

DFT is based on two fundamental concepts

1) focus is shifted from the wavefunction $\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$ to the electron density $n(\mathbf{r})$

Solving the many-electron problem in solids

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100000000000000000000 variables

1 variable

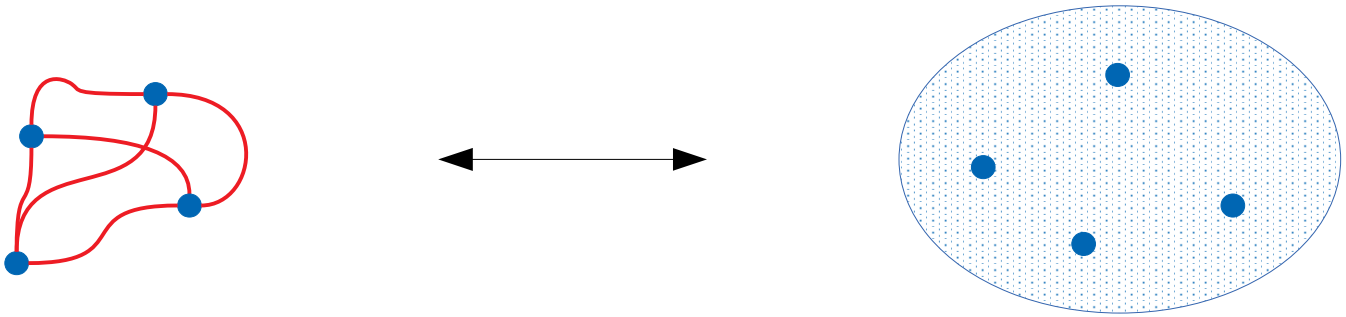
Solving the many-electron problem in solids

Density-functional theory (DFT) is the most used electronic structure theory

DFT is based on two fundamental concepts

1) focus is shifted from the wavefunction $\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$ to the electron density $n(\mathbf{r})$

2) a mapping onto a system of non interacting electrons in an effective potential



The key advantage is that we do not need to simplify the initial problem!

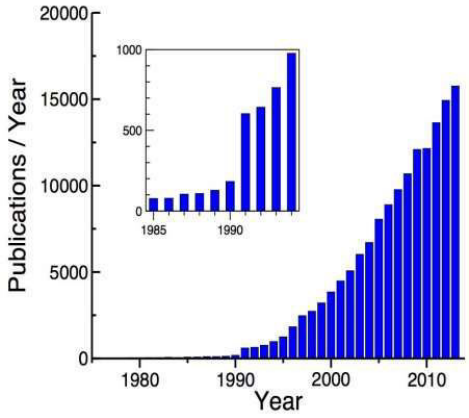
Solving the many-electron problem in solids

Density-functional theory (DFT) is the most used electronic structure theory

It is a very general approach, from atoms, molecules and clusters to solids

Provides access to a variety of properties

- equilibrium crystal structure
- elastic properties
- magnetic properties
- optical properties
- thermoelectric properties
- ...



A high accuracy and a high computational efficiency

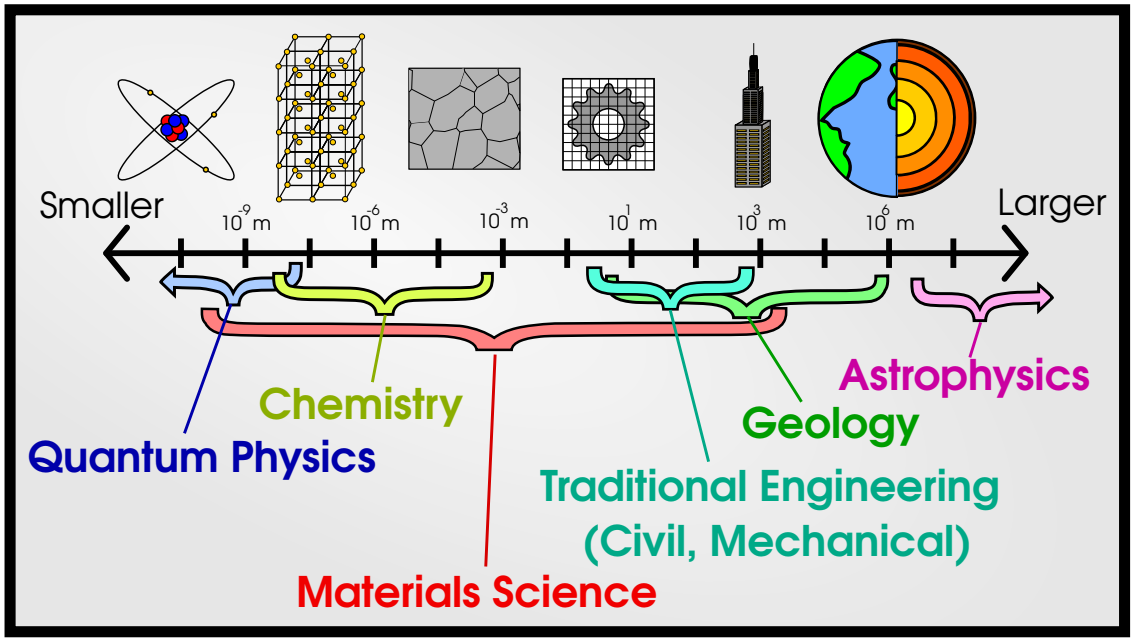
What is the limitation of not having the full electronic wavefunction?

Solving the many-electron problem in solids

Density-functional theory (DFT) is the most used electronic structure theory

It is a very general approach, from atoms, molecules and clusters to solids

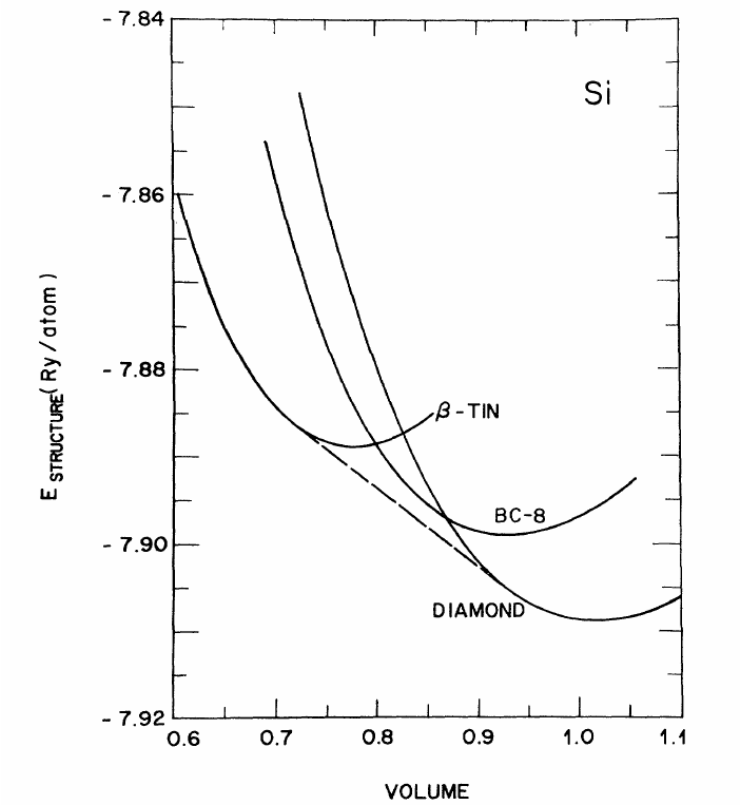
DFT provides a description of the macroscopic world in **ideal conditions**



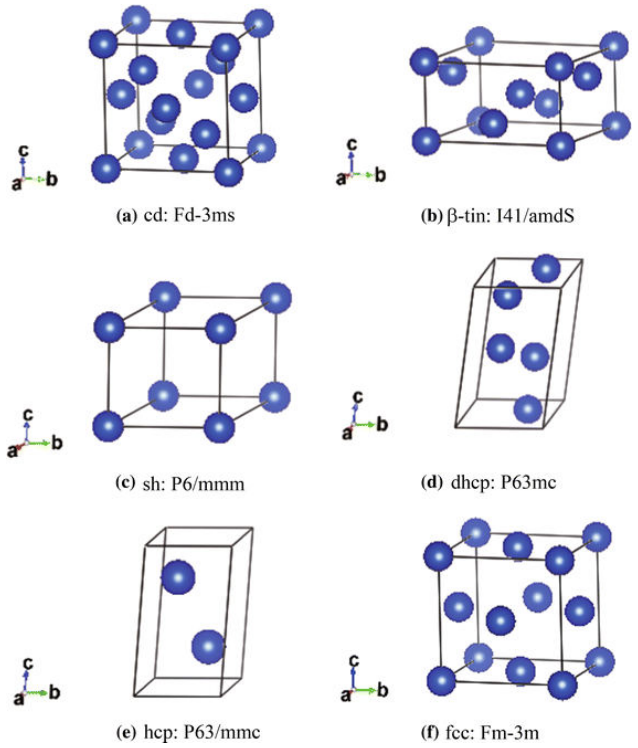
from msestudent.com

A few examples from modern research

Equilibrium crystal structure of silicon under pressure

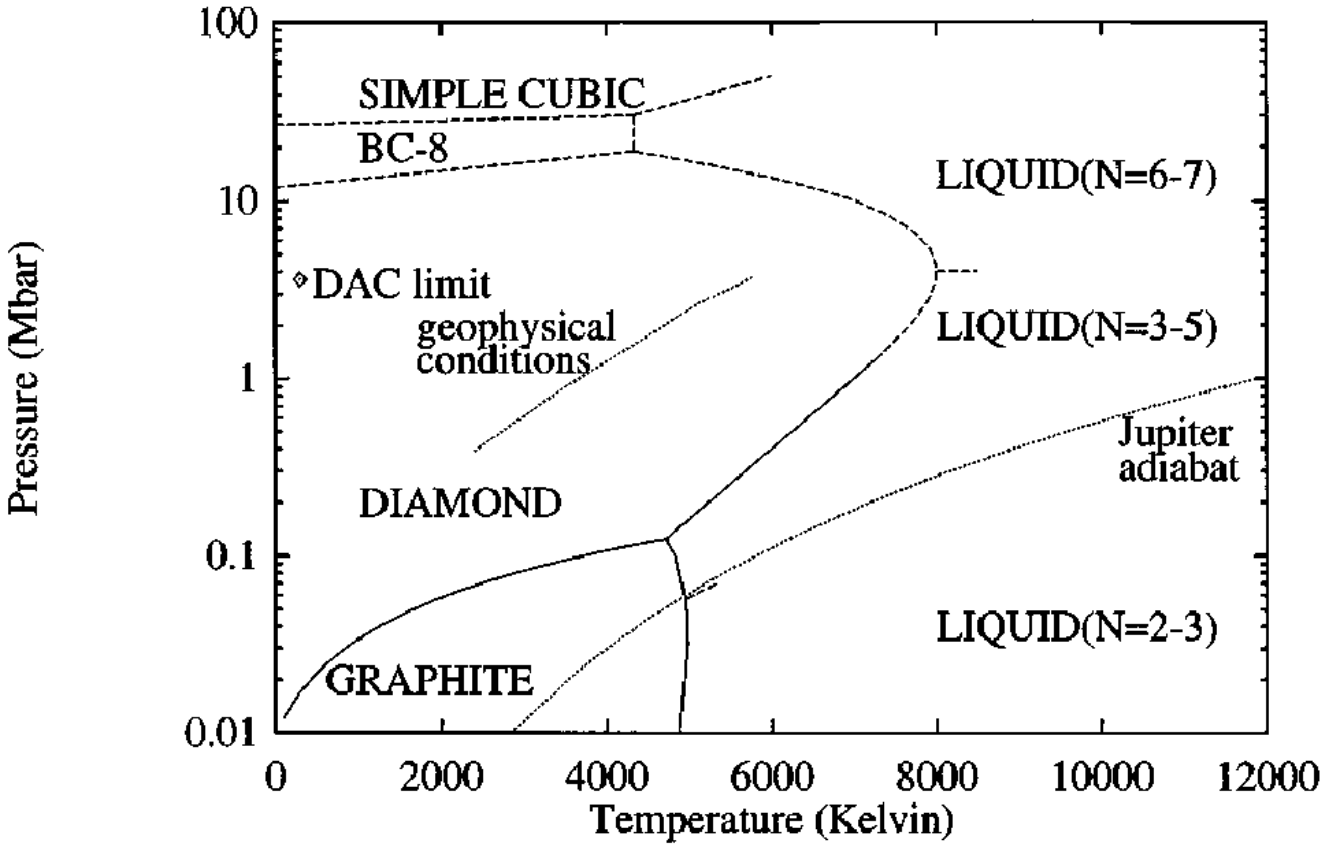


R. Martin, Electronic Structure, Cambridge University Press



Journal of materials science, 53, 7475 (2018)

Phase diagram of carbon



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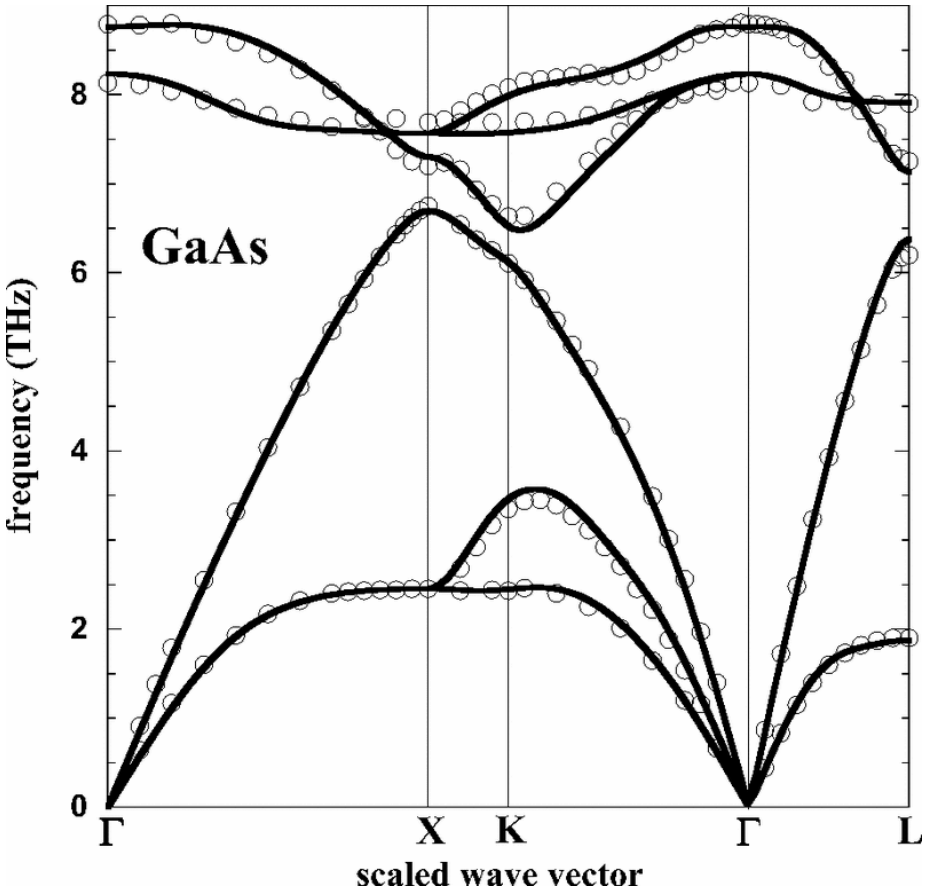
A few examples from modern research

Energy of the lattice vibrations in GaAs



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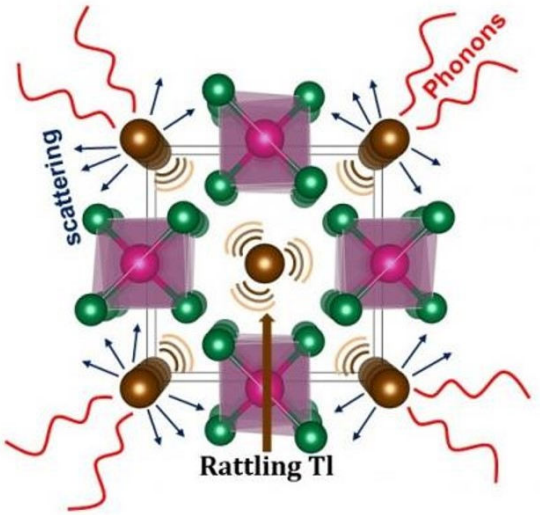


Angew. Chem. Int. Ed. **60**, 4259 (2021)

Prediction of novel 2-dimensional materials

TABLE II. List of two-dimensional dichalcogenides found by our search algorithm with the ICSD number of the corresponding bulk material and with our calculated band gap (in eV). The corresponding magnetic state (AFM refers to an antiferromagnetic ordering) is given in the last column to the right. (The cells of the table are left blank if the material is not magnetically ordered.)

2D chemical formula	3D ICSD number	Gap (eV)	Magnetism	2D chemical formula	3D ICSD number	Gap (eV)	Magnetism
YS_2	651404	Metal		$CrTe_2$	152836	Metal	FM
TiS_2	651178	0.02		MoS_2	644245	1.6	
$TiSe_2$	173923	Metal		$MoSe_2$	644334	1.4	
$TiTe_2$	653071	Metal		$MoTe_2$	015431	1.15	
ZrS_2	651465	1.1		WS_2	202366	1.8	
$ZrSe_2$	652236	0.4		WSe_2	040752	1.5	
$ZrTe_2$	653213	Metal		WTe_2	073323	Metal	
HfS_2	638847	1.3		TcS_2	081816	1.2	
$HfSe_2$	638899	0.6		ReS_2	075459	1.4	
$HfTe_2$	638959	Metal		$ReSe_2$	081813	1.3	
VS_2	651361	Metal	FM	$CoTe_2$	625401	Metal	
VSe_2	652158	Metal	FM	$RhTe_2$	650448	Metal	
VTe_2	603582	Metal	FM	$IrTe_2$	033934	Metal	
NbS_2	645307	Metal		$NiTe_2$	159382	Metal	
$NbSe_2$	645369	Metal		PdS_2	166276	1.1	
$NbTe_2$	645529	Metal		$PdSe_2$	170327	1.3	
TaS_2-*AB*	651089	Metal		$PdTe_2$	649016	0.2	
TaS_2-*AA*	651092	Metal		PtS_2	649534	1.8	
$TaSe_2$-*AB*	651948	Metal		$PtSe_2$	649589	1.4	
$TaSe_2$-*AA*	651950	Metal		$PtTe_2$	649747	0.8	
$TaTe_2$	014390	Metal		$SiTe_2$	652385	Metal	
CrS_2	075420	Metal	AFM	SnS_2	650992	1.6	
$CrSe_2$	626718	Metal	FM	$SnSe_2$	651910	0.8	

Phys. Rev. X 3, 031002 (2013)

Experimental confirmation after a decade

Table 1 Theoretical and experimental results of magnetic ground states (MGS), MAE and critical temperature T_c for various 2D magnetic crystals

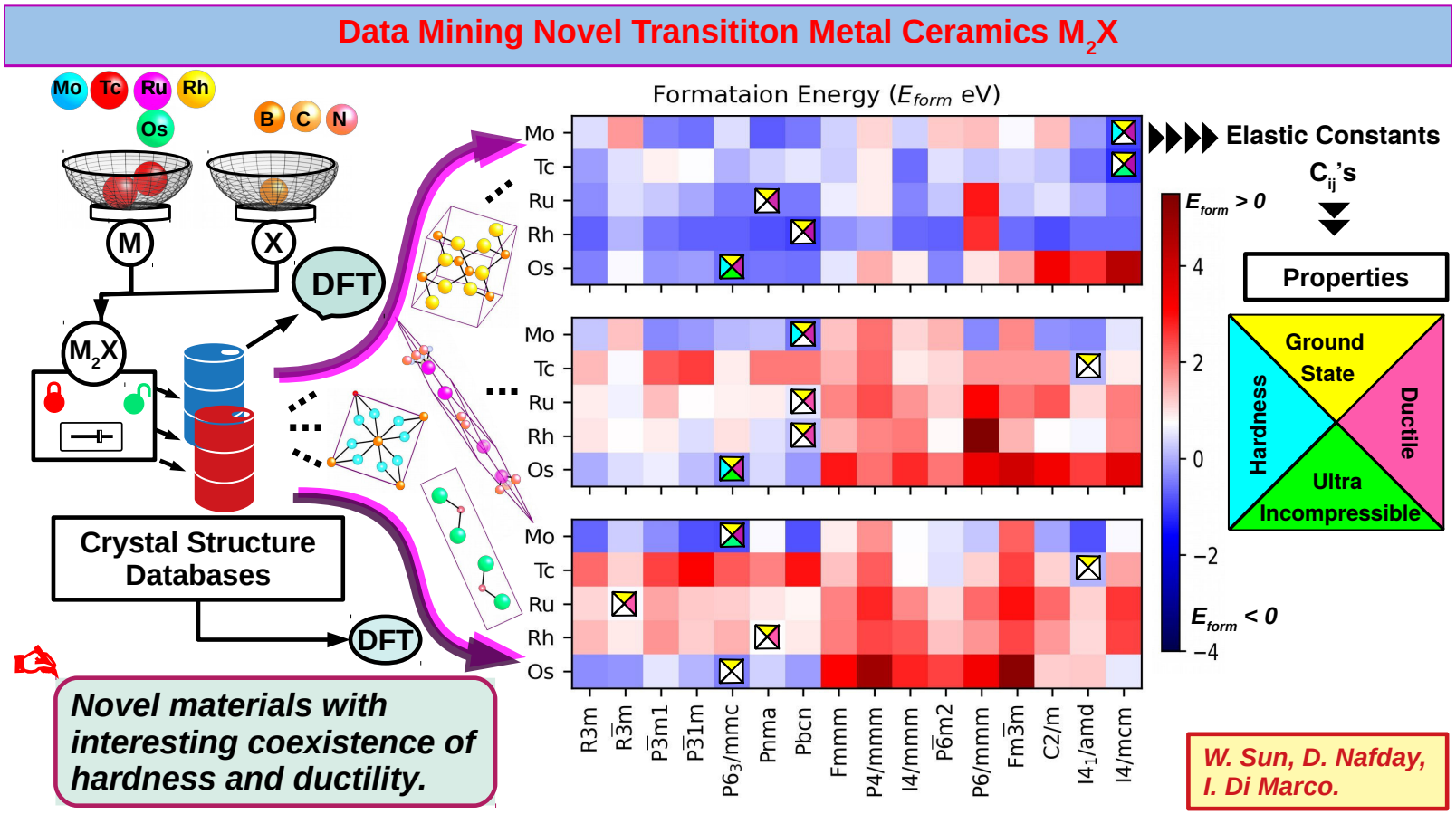
Sample	MGS	MAE [μeV]	T_c [K]	Sample	MGS	MAE [μeV]	T_c [K]
CrI_3[19,38]	FM	803.6 (Is)	46, 45[t1]	VS_2[92]	FM	~310 (XY)	90
$CrBr_3$[38,99]	FM	159.5 (Is)	41, 33[tf]	**VSe_2**[21]	FM	— (XY)	>300[t1]
$CrCl_3$[26,99]	FM	— (XY)	16.8, 15[tf]	MnS_2[100]	FM	—	225
VCl_3[101]	FM	—	80	**$MnSe_2$**[22,100]	FM	—	250, ~300[tf]
VI_3[101,102]	FM	—	98, 50[tf]	VCl_2[103]	AFM	40	—
VBr_3[48,104]	FM	450 (Is)	190, 27[tf]	VI_2[103]	AFM	60	—
$NiBr_3$[48]	FM	377 (Is)	100	VBr_2[103]	AFM	620	—
$PdBr_3$[48]	FM	659 (Is)	110	$FeCl_2$[89]	FM	~60 (XY)	165
$FeBr_3$[48]	nAFM	—	70	$FeBr_2$[89]	FM	— (XY)	210
$Cr_2Ge_2Te_6$[18]	FM	<1 (H)	28[t2]	FeI_2[89]	FM	— (XY)	122
$Cr_2Si_2Te_6$[50,105]	FM	419 (Is)	90, 31[tf]	**NiI_2**[25,106]	FM	1.12 (Is)	86, 35–55[tf]
$Cr_2Sn_2Te_6$[50]	FM	69 (Is)	170	$CoCl_2$[25]	FM	1.85 (Is)	25
Fe_3GeTe_2[20]	FM	2000 (Is)	68[t1]	$MnCl_2$[25]	AFM	111 (Is)	33
VPS_3[53]	nAFM	— (Is)	570	$MnBr_2$[25]	AFM	322 (Is)	40
$CrPS_3$[53]	FM	~160 (Is)	130	Fe_2C[65]	FM	22.8 (XY)	861
$MnPS_3$[53]	nAFM	~1000 (Is)	200, 79[tf]	$MnNO_2$[69]	FM	63 (Is)	67
$FePS_3$[53,169]	zAFM	— (Is)	260, 118[t1]	$CrNO_2$[69]	FM	22 (Is)	53
$CoPS_3$[53,107]	zAFM	>1000 (Is)	330	$MnNF_2$[69]	FM	2 (XY)	1128
$NiPS_3$[53,108]	zAFM	— (Is)	560, 130[t2]	Ti_2NO_2[69]	FM	0.78 (H)	—
$CrCuP_2S_6$[58,59]	FM	28 (XY)	64[tf]	$Hf_2VC_2F_2$[70]	AFM	—	313
$CrCuP_2Se_6$[58]	FM	242 (Is)	—	**$MnBi_2Te_4$**[109]	AFM	— (Is)	21[t7]
$CrOCl$[83]	FM	~110 (Is)	160	$CoGa_2S_4$[75]	FM	47 (XY)	195
$CrOBr$[83]	FM	~290 (Is)	129	$CoGa_2Se_4$[75]	FM	84 (XY)	516
$CrSCl$[84]	FM	20 (Is)	108	$CoGa_2Te_4$[75]	FM	634 (XY)	570
$CrSBr$[84]	FM	20 (Is-x)	127	**FeTe**[82]	AFM	—	45–70[tf]
$CrSI$[84]	FM	60 (Is-y)	146	$MnNCl$[84]	FM	70 (Is)	238
$CrSeCl$[84]	FM	10 (Is-y)	118	$MnNBr$[84]	FM	20 (Is)	261
$CrSeBr$[84]	FM	4 (Is-y)	135	$MnNI$[84]	FM	930 (Is-x)	492
$CrSeI$[84]	FM	20 (Is-y)	164	$CrTeBr$[84]	FM	750 (Is)	187
$CrTeCl$[84]	FM	150 (Is-x)	248	$CrTeI$[84]	FM	550 (Is)	139

The synthesized 2D magnets are marked with bold sample names. In the T_c column, numbers without superscripts are theoretical results for monolayer samples. Superscripts 'tf' and 'tn' denote results of thin flakes and n-layer (n = 1, 2, 3...) experimental samples, respectively. Is, XY and H in the MAE column represent Ising, XY, and Heisenberg magnets, respectively, and Is-x and Is-y refer to the easy axis lying in the x or y directions in the plane of 2D anisotropic MXY magnets.

Nanoscale **13**, 1398 (2021)

A few examples from modern research

Big data studies and perspective for machine learning



Applications for renewable energy

Photovoltaic Materials

→ to improve efficiency in energy conversion and stability to degradation

Thermoelectric Materials

→ to predict novel materials and optimize for carrier concentration

Hydrogen Storage Materials

→ to identify and optimize materials with better hydrogen interaction

Catalysts for Renewable Energy

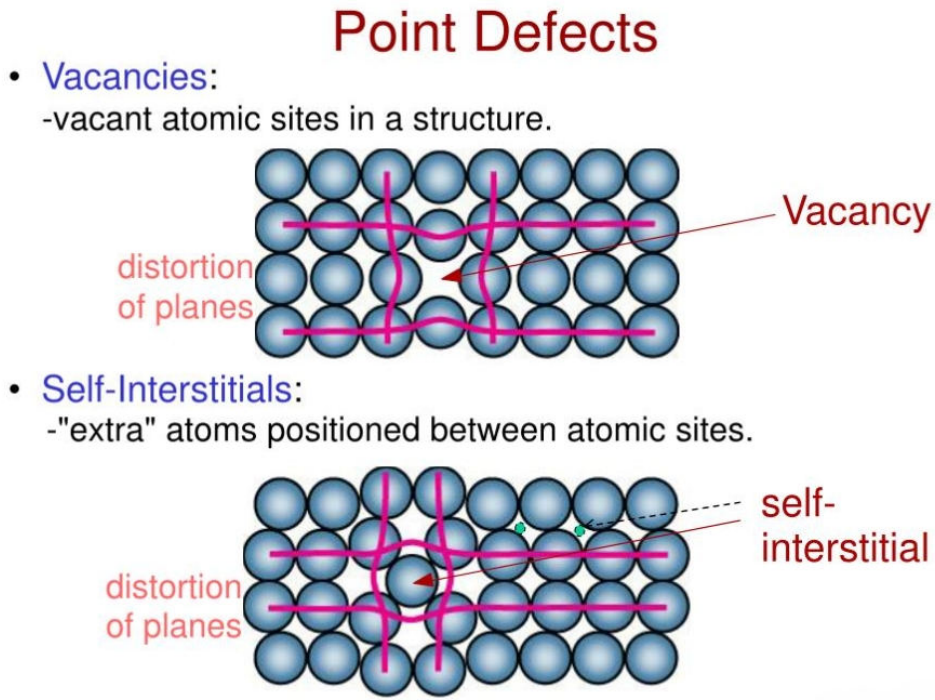
→ to design catalysts for processes like water splitting and CO_2 reduction

Battery Materials

→ to discover materials with a higher energy density and a longer lifespan

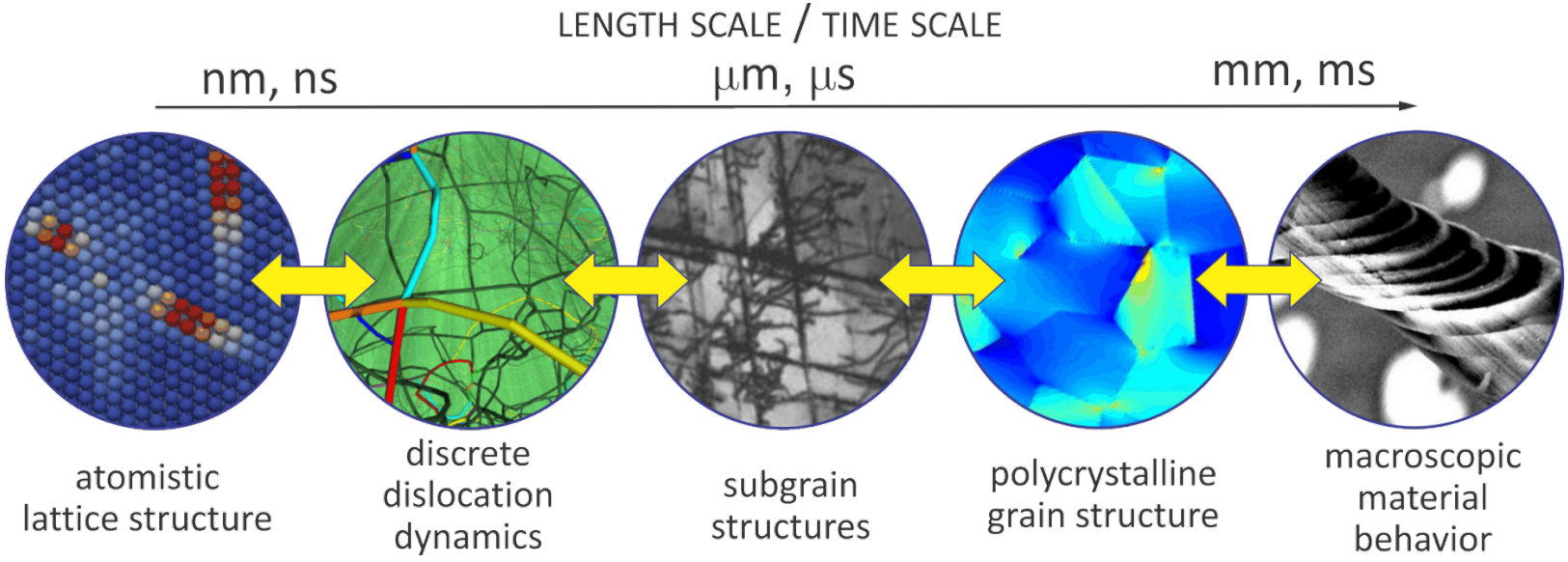
The role of defects and other imperfections

Perfect crystals do not represent reality very well…



from docs.neu.edu.tr

Multi scale simulations are the next big step?



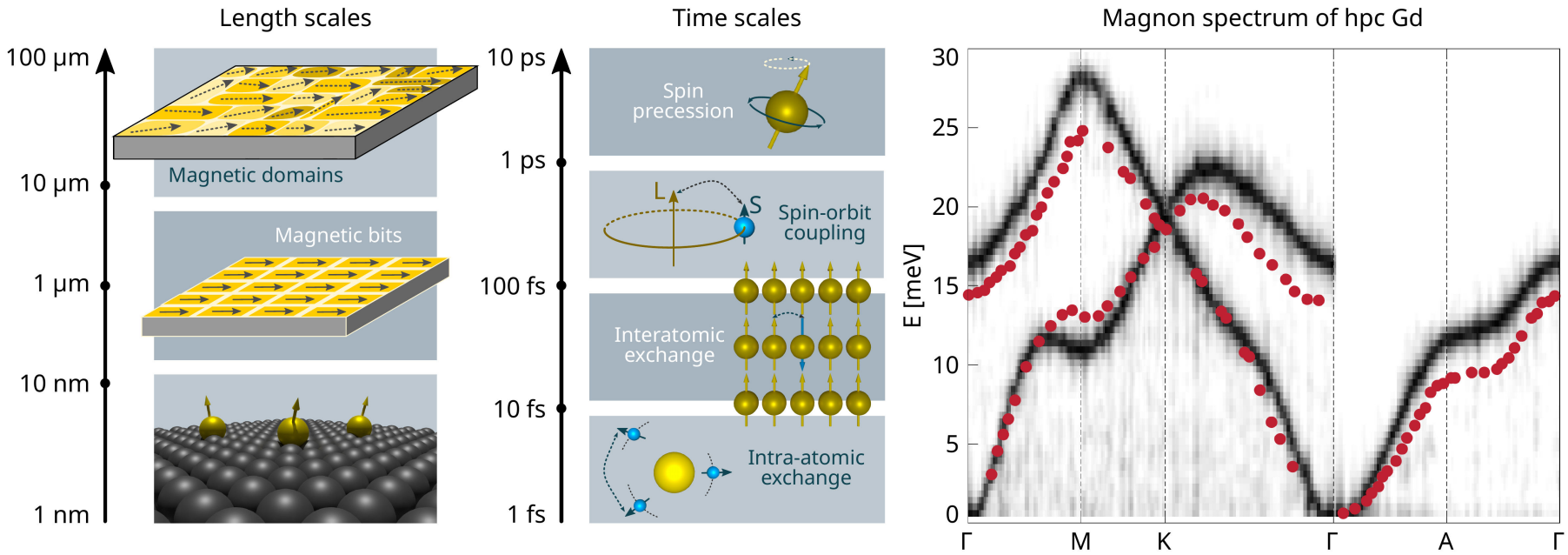
Computer-Aided Design **77**, 73 (2016)

A few examples from modern research

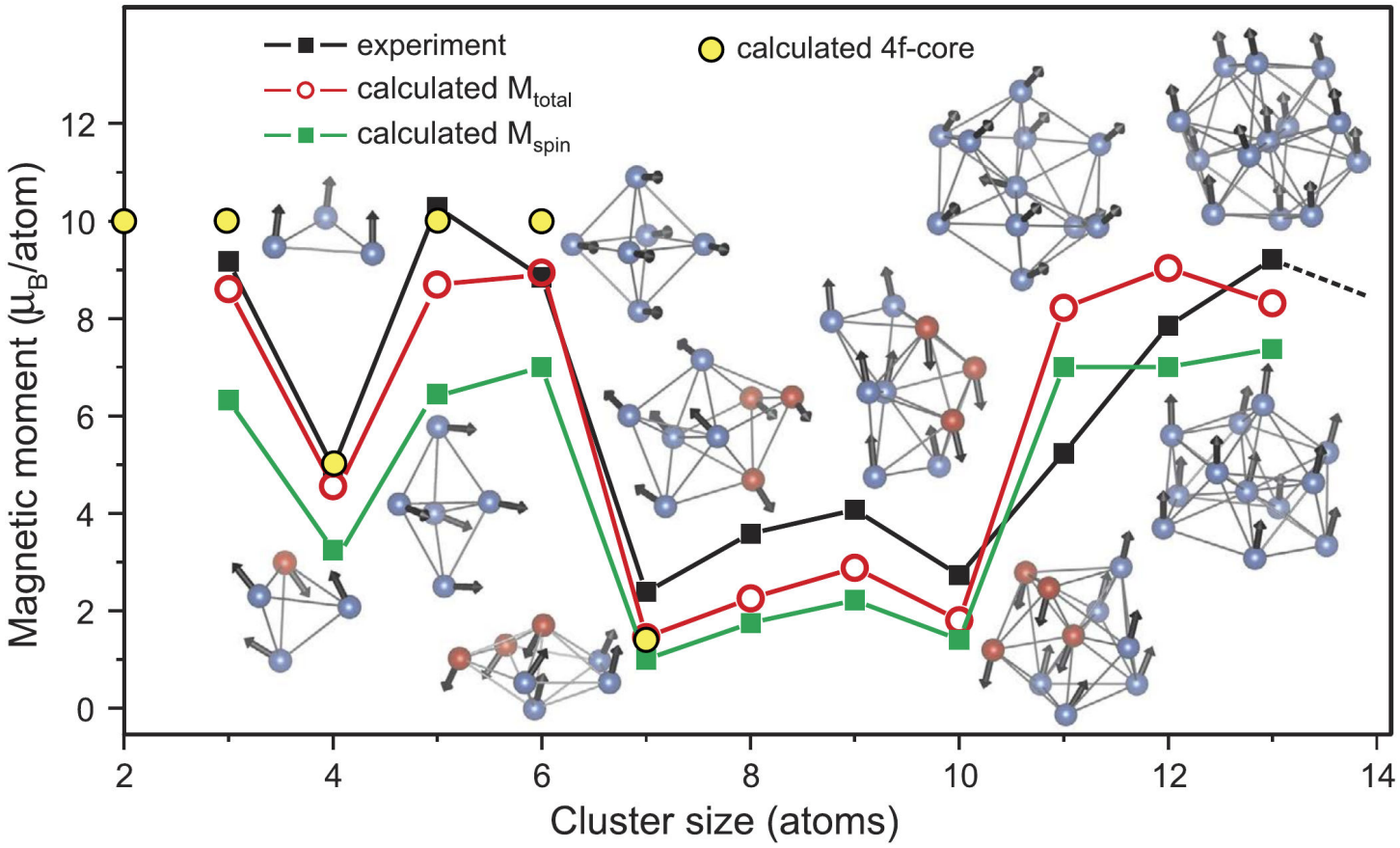
Multi scale simulations are the next big step?

Multi-scale approaches are the frontier in magnetic simulations

These problems have a very high relevance for industrial applications



Magnetism of small Tb clusters

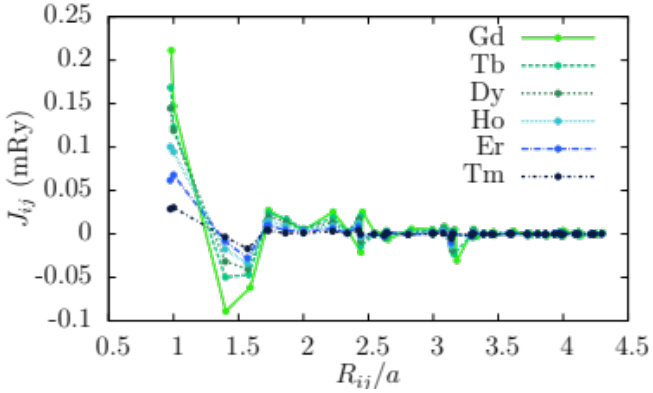


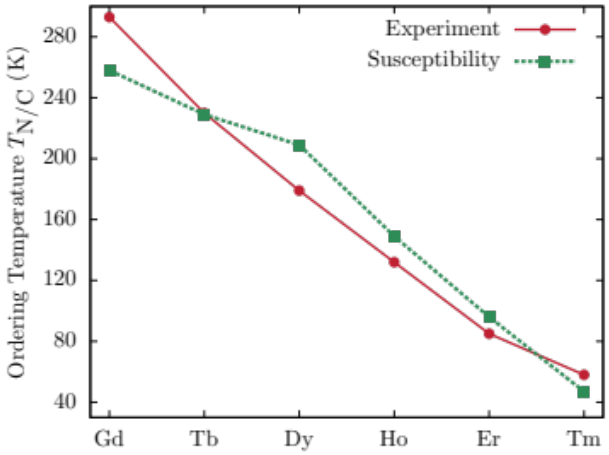
Scientific Reports **6**, 19676 (2016)

Magnetism in rare-earth elements

Multi-scale approaches are the frontier in magnetic simulations

- Atomic-scale description in DFT
- Effective magnetic coupling
- Coupling used for spin dynamics
- Domain walls in micromagnetics

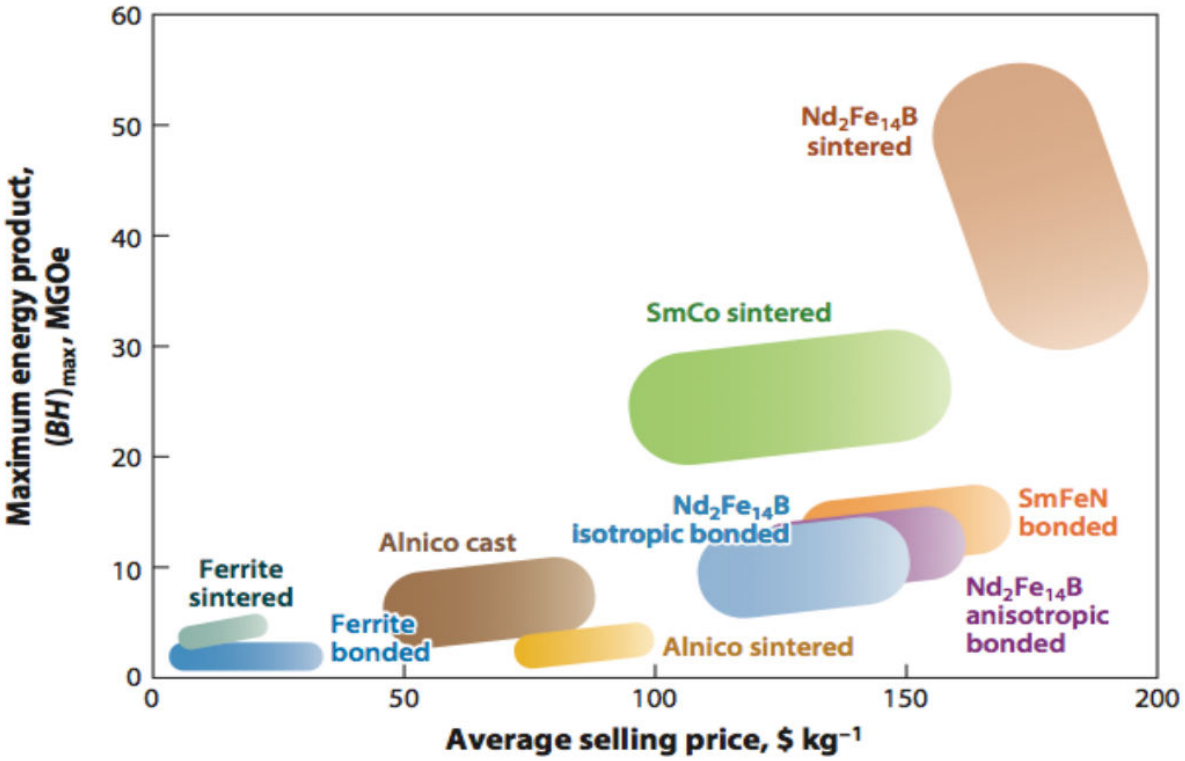




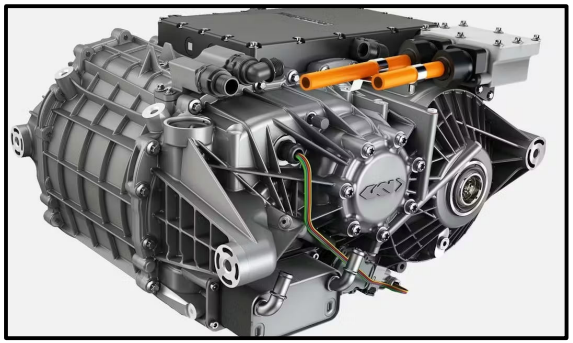
A few examples from modern research

Magnetism in rare-earth elements

Multi-scale approaches are the frontier in magnetic simulations



from businessinsider.com.pl



from www.sw.siemens.com

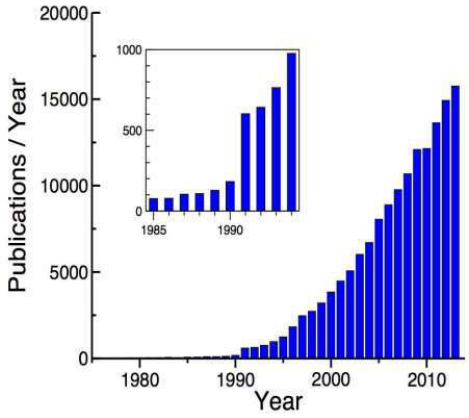
Solving the many-electron problem in solids

Density-functional theory (DFT) is the most used electronic structure theory

It is a very general approach, from atoms, molecules and clusters to solids

Provides access to a variety of properties

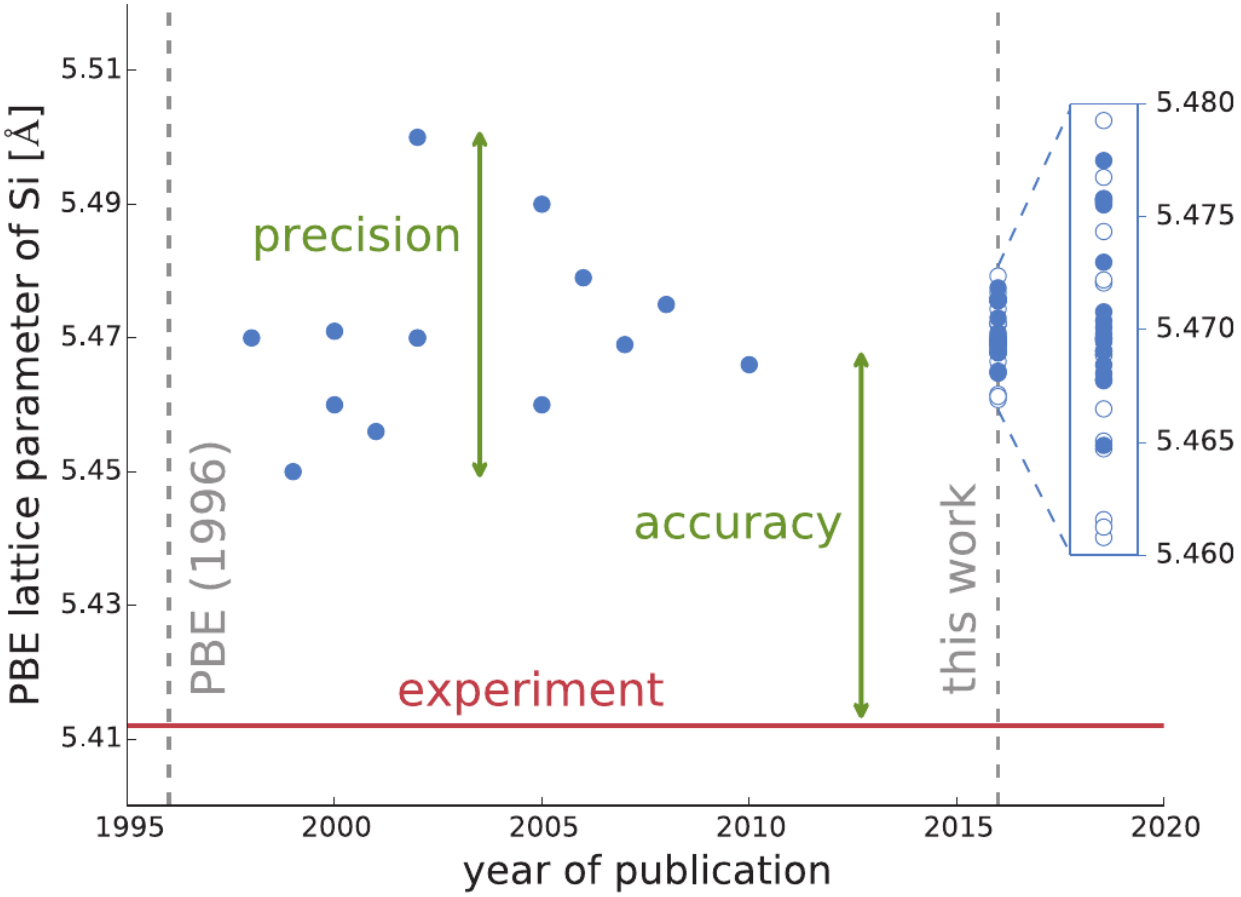
- equilibrium crystal structure
- elastic properties
- magnetic properties
- optical properties
- thermoelectric properties
- ...



A high accuracy and a high computational efficiency

But what are exactly the limitations of modeling based on DFT?

Lattice parameter of silicon and DFT accuracy

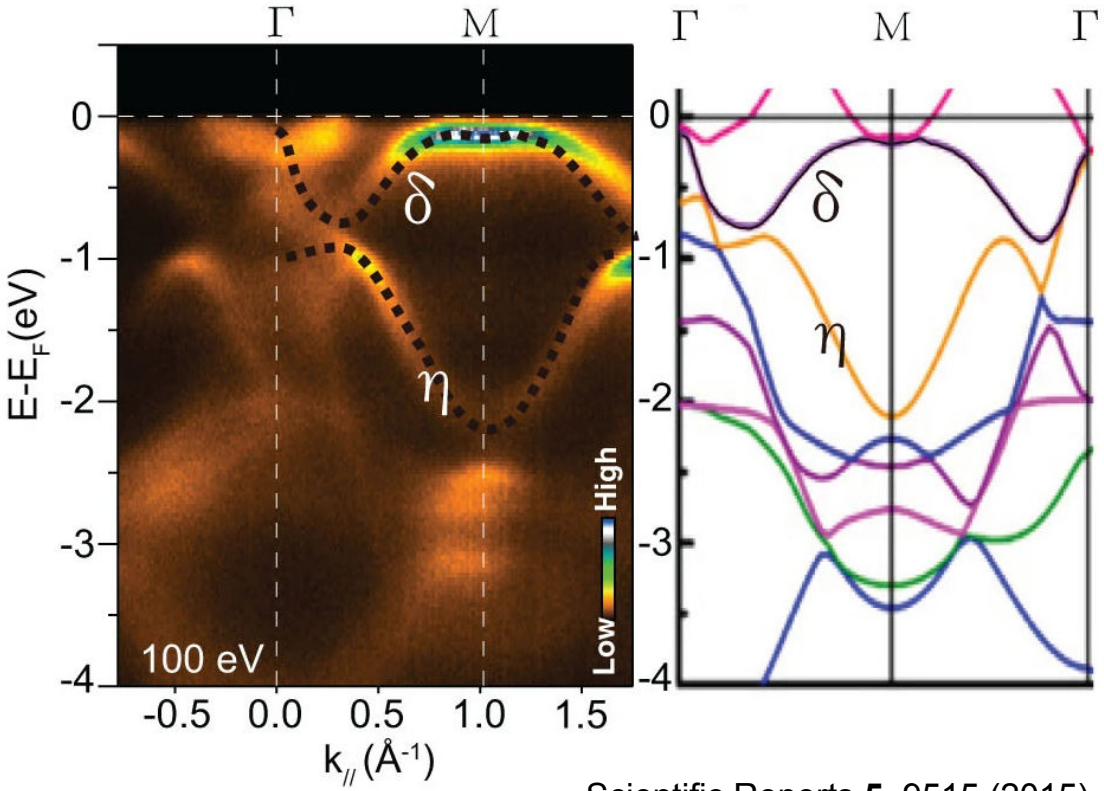


Science **351**, 6280 (2016)

Excited-state properties

How does DFT results compare with ARPES?

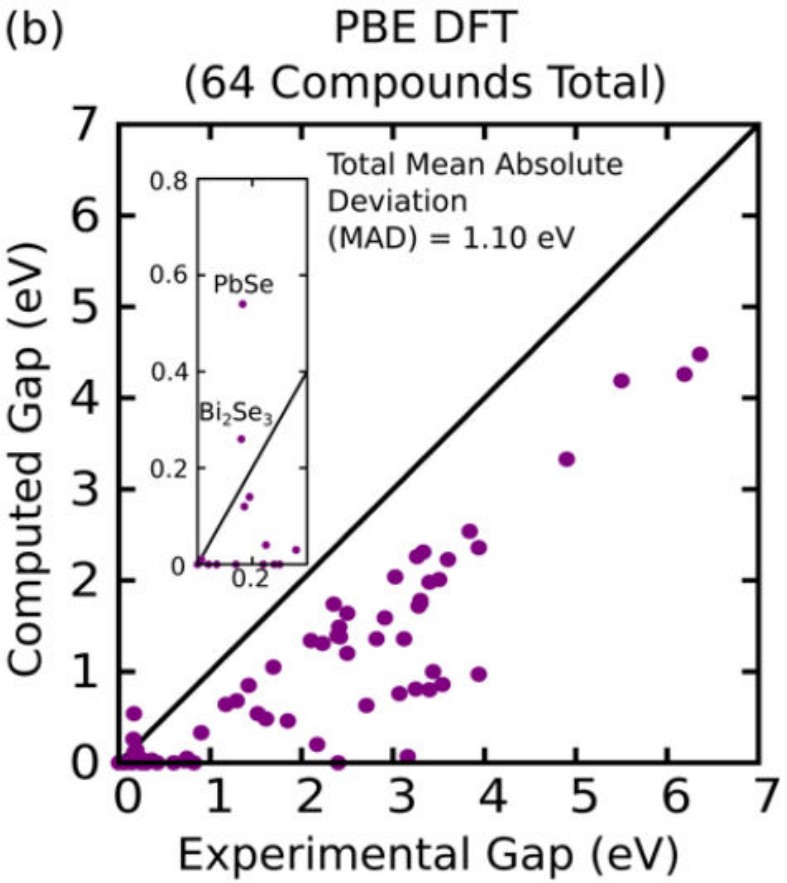
Let us see the charge-density wave state in $Na_2Ti_2Sb_2O$



Scientific Reports **5**, 9515 (2015)

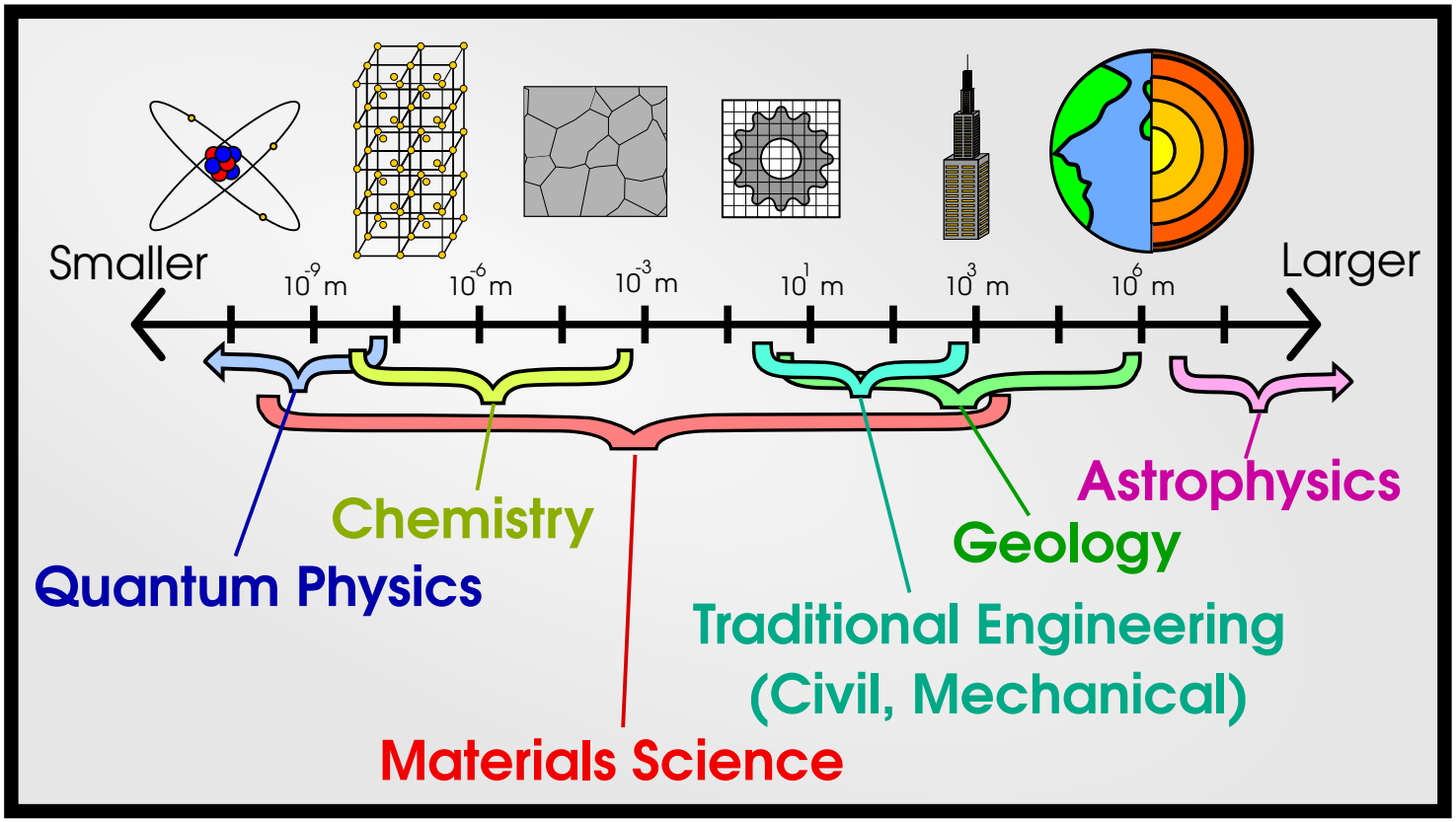
Excited-state properties

The band-gap problem in the modeling of insulators



Can we go from small to big length scales?

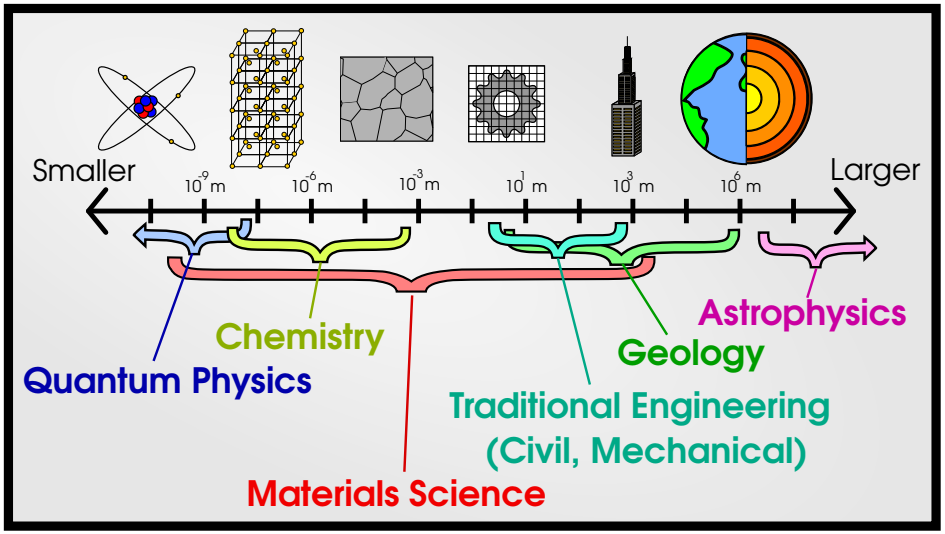
What if had infinite mathematical or computational power?



from msestudent.com

A final question

How far can I go with a finite computational power?



Thank you for listening!