MSE 468 Week 2

It’s a quantum world!

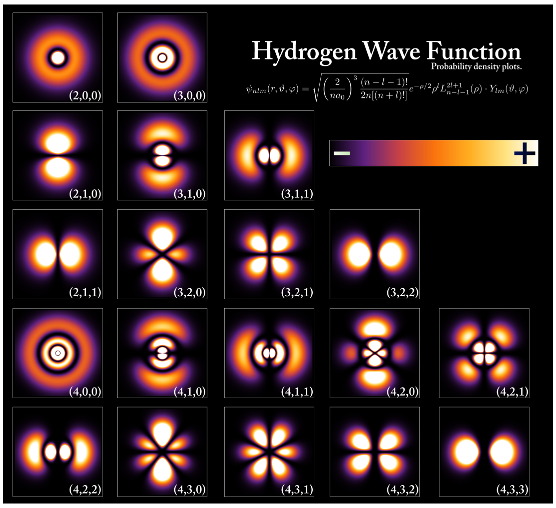


Image from Wikipedia

Usage of the VM (and new form this week)

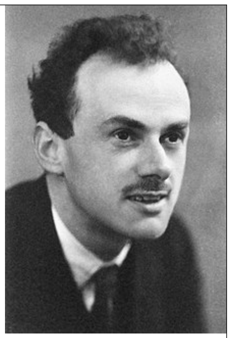
- **Did everybody manage to run in the VM?**

- **Second form for this week (by next Thursday 6th March)** - last form hopefully!
  - Test access to **VPN** (in case you need to work from outside the campus)
  - Test running on the **Helvetios supercomputer** at EPFL (useful for lab 2/3/4)

AROSA, CANTON DES GRISONS, 27 DÉCEMBRE 1925

At the moment I am struggling with a new atomic theory. I am very optimistic about this thing and expect that if I can only… solve it, it will be very beautiful.

Erwin Schrödinger

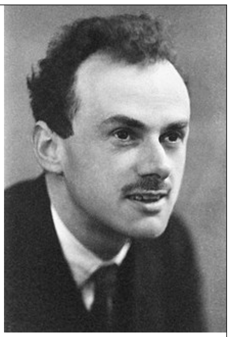


MOVE TO 1929…

the underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

it therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

P.A.M. DIRAC, PROC. ROY. SOC. 123, 714 (1929)



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P.A.M. DIRAC, PROC. ROY. SOC. 123, 714 (1929)

…AND 1963

It is more important to have beauty in one's equations than to have them fit experiment... [...]

if there is no complete agreement between the results of one’s work and the experiment, one should not allow oneself to be too discouraged, because the discrepancy may well be due to minor features that are not properly taken into account and that will get cleared up with further development of the theory.

P.A.M. DIRAC, SCIENTIFIC AMERICAN 1963

Physical Review **Focus**

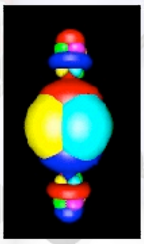
Inhomogeneous Electron Gas
P. Hohenberg and W. Kohn
Phys. Rev. **136**, B864 (9 November 1964)

Self-Consistent Equations Including Exchange and Correlation Effects
W. Kohn and L. J. Sham
Phys. Rev. **140**, A1133 (15 November 1965)

Nobel Focus: Chemistry by Computer

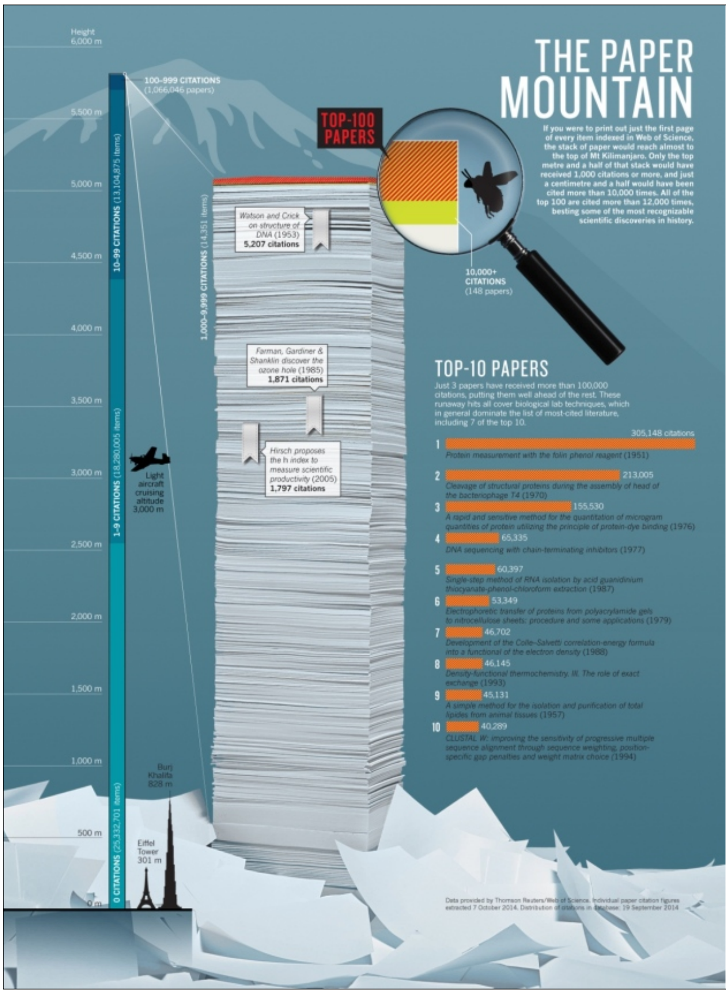
21 October 1998

The 1998 Nobel Prize in chemistry recognizes two researchers whose work has allowed chemists to calculate the properties of molecules and solids on computers, without performing experiments in the lab. The basic principles of the calculation scheme were first described in *Physical Review* in the 1960s, and solid state physicists used them for decades before they became important in the chemistry world. The scheme drastically simplifies the solution of the quantum mechanical equations for a system of many electrons, and although approximate, the solutions are accurate enough that chemists can learn about large molecules without getting their hands wet.



Calculations made easy. Localized orbitals in the electronic structure of the $BaTiO_3$ crystal, calculated using density functional theory, which was invented by 1998 Nobel Laureate Walter Kohn.

Nicola Marzari and David Vanderbilt/Rutgers University



NATURE, OCT 2014

THE TOP 100 PAPERS:
12 papers on density-functional theory in the top-100 most cited papers in the entire scientific literature, ever.

The challenges

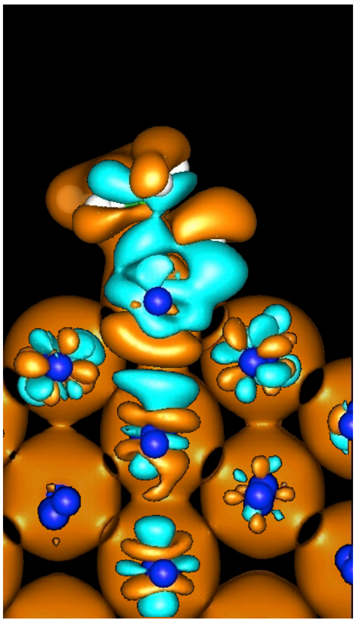
- Accuracy
- Size
- Time

Why do we need quantum mechanics?

- Potential models: **limited transferability** (not universal)
- They do not describe bond breaking
- **Explicit treatment of electrons needed** for electronic, optical, magnetic properties

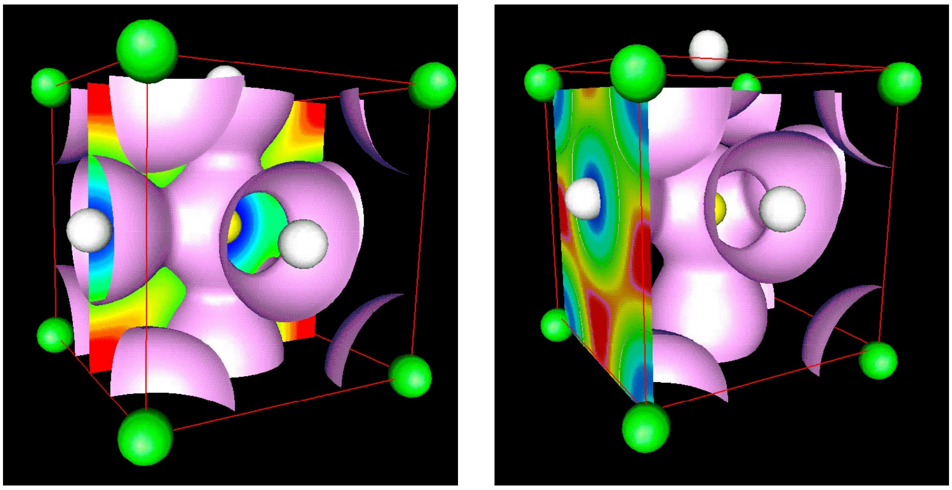
(Quantum) electrons hold matter together

- Atoms are made by massive, point-like nuclei (protons+neutrons)
- Surrounded by tightly bound, rigid shells of core electrons
- Bound together by a glue of valence electrons



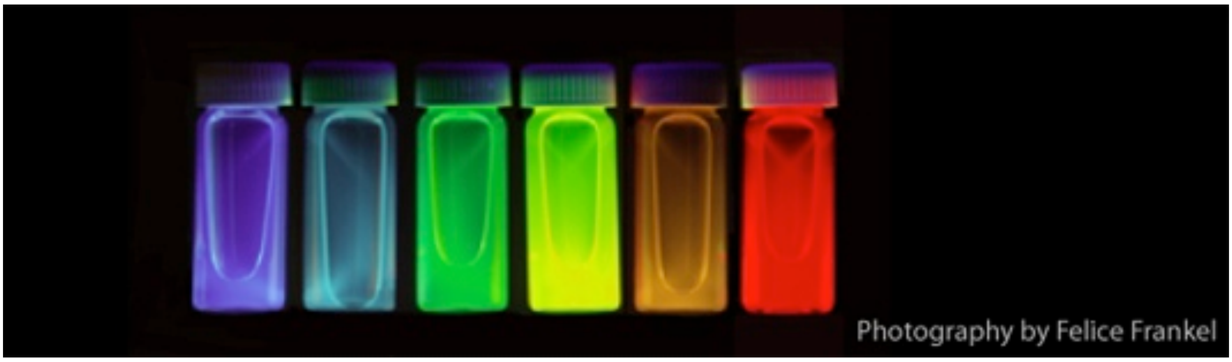
Simulation of methane on a Pt surface

Why do we need quantum mechanics? 1) Bonding and Structure



Paraelectric (cubic) and ferroelectric (tetragonal) phases of $PbTiO_3$

Why do we need quantum mechanics?
2) Electronic, optical, magnetic properties



Particle size tunes the emission wavelength of CdSe quantum dots

Why do we need quantum mechanics?
3) Dynamics, chemistry

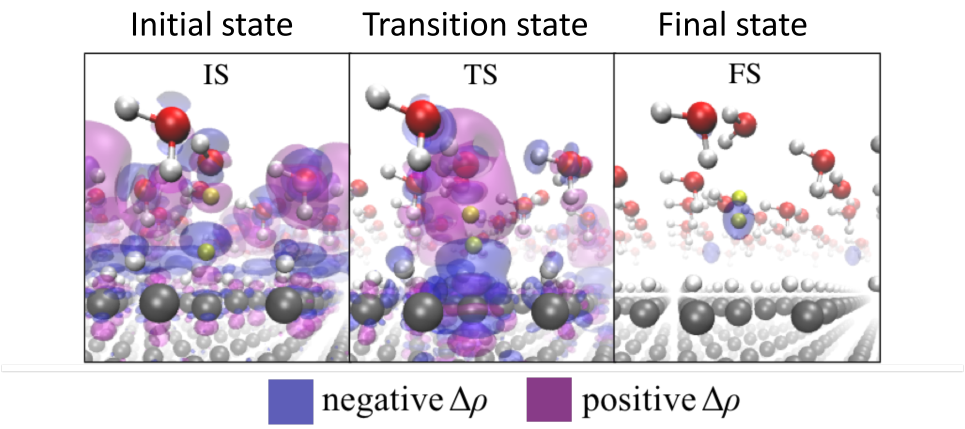
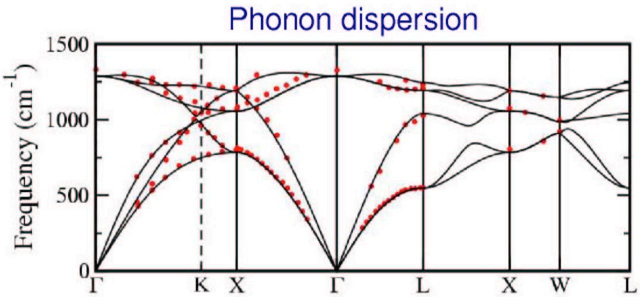
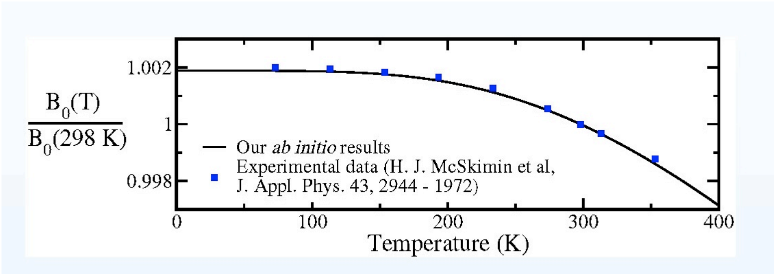


Figure from https://suncat.stanford.edu/
Charge density difference isosurfaces for the Heyrovsky reaction.
(See also Chen, Nørskov, J.Phys.Chem.Lett. 7, 1686−1690 (2016))

Example: Diamond from First Principles

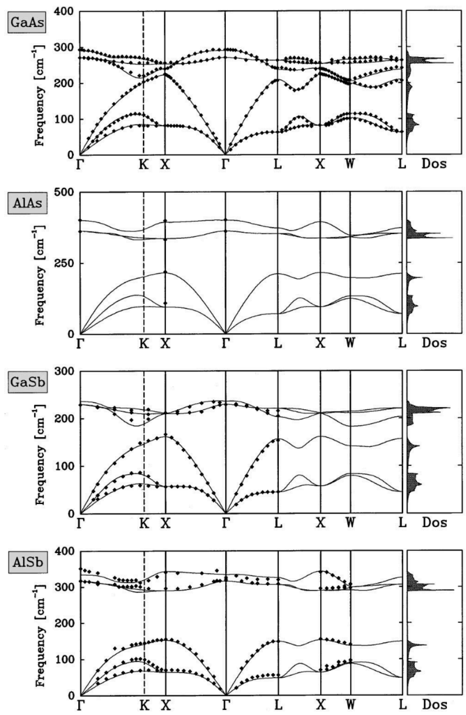
	GGA	Exp. (300 K)
a_0 (a.u.)	6.743 (0 k) 6.769 (300 K)	6.740
B (GPa)	432 (0 K) 422 (300 K)	442





Some more examples

Phonons of semiconductors computed by DFT, compared with experiments



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

The total energy bias

"If the only tool if you have is a hammer,

every problem starts looking like a nail"

Ab-initio spectroscopies and microscopies

- Vibrations and phonons
- Infrared
- Raman
- Thermal conductance
- Superconductivity
- Nuclear magnetic resonance
- Core level shifts
- Scanning tunnelling microscopy
- ...

What can first-principles do for me ?

- **Fairly straightforward, but fundamental:** equilibrium structures, thermodynamic stability, thermomechanic properties, electronic structure, energetics and reactions...
- **Harder:** vibrational and magnetic spectroscopies (IR, Raman, NMR, EPR), XPS/XANES, BCS superconductivity, basic optical properties (TDDFT), phase diagrams
- **Jedi master:** thermal and electrical conductivities, complex optical properties (GW+BSE).

Predictive accuracy is a key challenge

Material Properties From First-Principles

- Energy scale at our living conditions ($k_B T$, for T=300 K): **0.025 eV** (kinetic energy of an atom in an ideal gas: 3/2 $k_B T$).
- Differences in bonding energies are within one order of magnitude of **~0.3 eV** (hydrogen bond).
- Binding energy of an electron to a proton (hydrogen):
  13.606 eV = 1 Rydberg (Ry) = 0.5 Hartree (Ha) = 0.5 a.u.
- Energy of 1s electrons in a Pt atom (Z=78): **~80,000 eV (energy $\propto Z^2$)**
  (https://xdb.lbl.gov/Section1/Table_1-1.pdf)

Wave-particle Duality

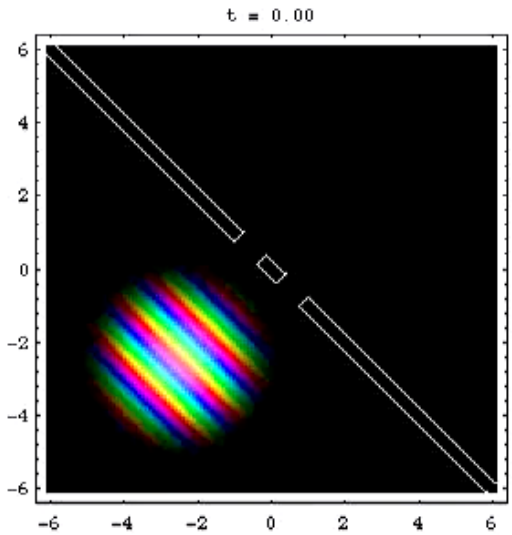
- ***Waves have particle-like properties:***
  - Photoelectric effect: quanta (photons) are exchanged discretely
  - Energy spectrum of an incandescent body looks like a gas of very hot particles
- **Particles have wave-like properties:**
  - Electrons in an atom are like standing waves (harmonics) in an organ pipe
  - Electrons beams can be diffracted, and we can see the fringes

Wave-particle Duality

- Position and momentum of a particle cannot be simultaneously measured with arbitrarily high precision
- Minimum for the product of the uncertainties:

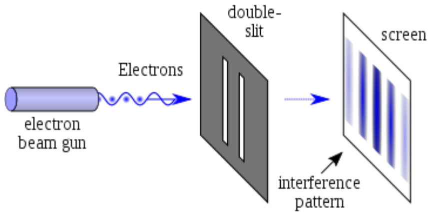
$$\Delta x \Delta p \geq \frac{\hbar}{2} \qquad \hbar \approx 1.05 \cdot 10^{-34} Js$$

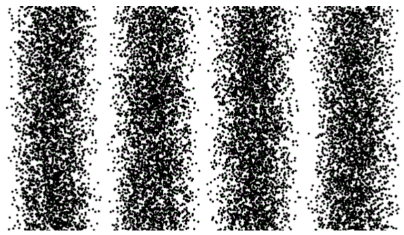
When is a particle like a wave ?



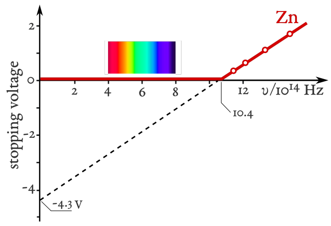
From https://vqm.uni-graz.at

When is a particle like a wave ?





- Einstein (1905): light is emitted and absorbed discretely (photons; photoelectric effect)



- De Broglie (1924): all matter is a wave
  The smaller the dimension, the more wave-like the behaviour

$$\lambda = \frac{h}{p}$$

Images from Wikipedia

Typical length scales

$$E = pc$$

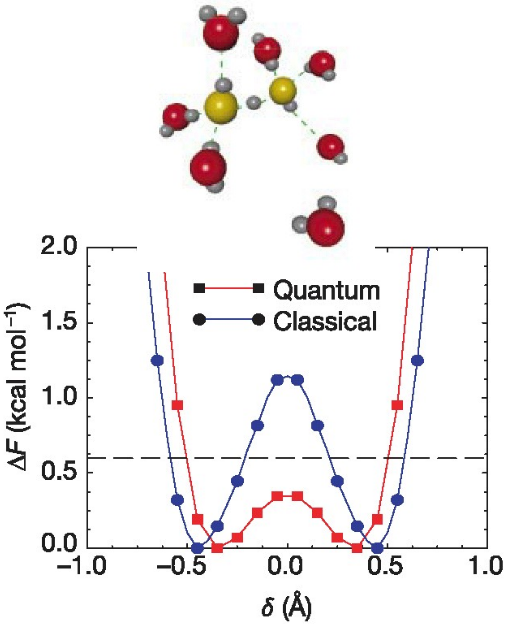
Massless particles (photons)

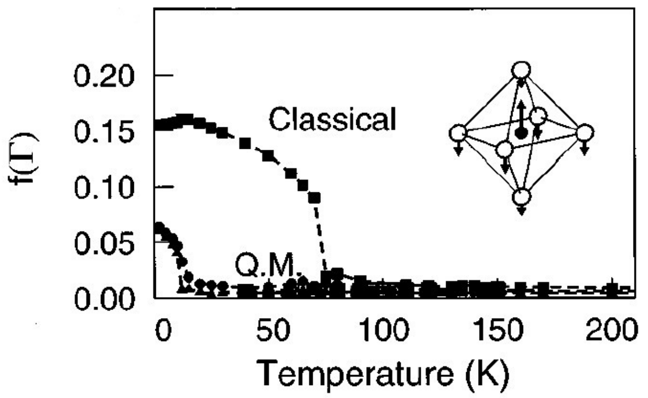
$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} \Rightarrow p = \sqrt{2mE}$$

Massive *non-relativistic* particles

- Atomic diameter?
  - *0.1 nm* (1 angstrom)
- Electron accelerated through 100V: *0.12 nm*
  - *See: electron microscope*
- Nitrogen molecule at 300K: *0.03 nm*
- Baseball at 150 km/h: 10^{-25} nm
  - **Wavelength of heavy objects not relevant for bonding**

There can be quantum effects in the nuclear motion

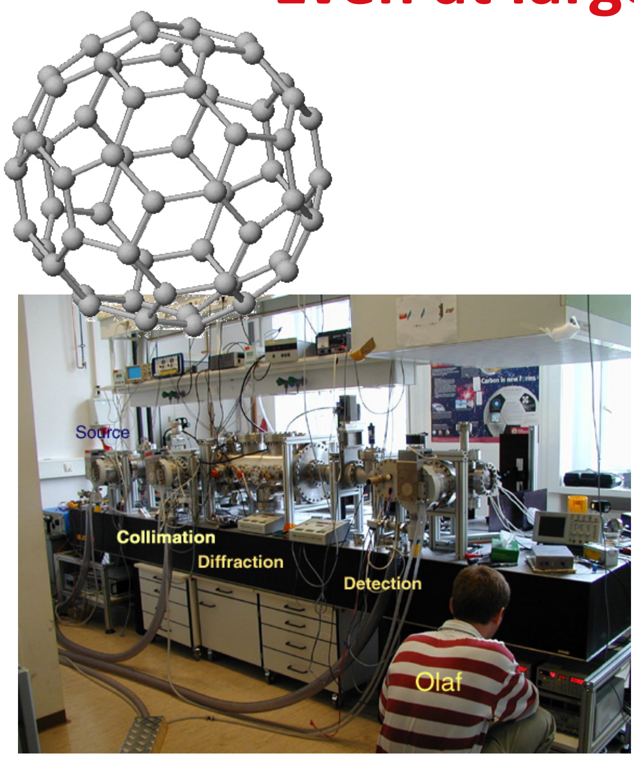


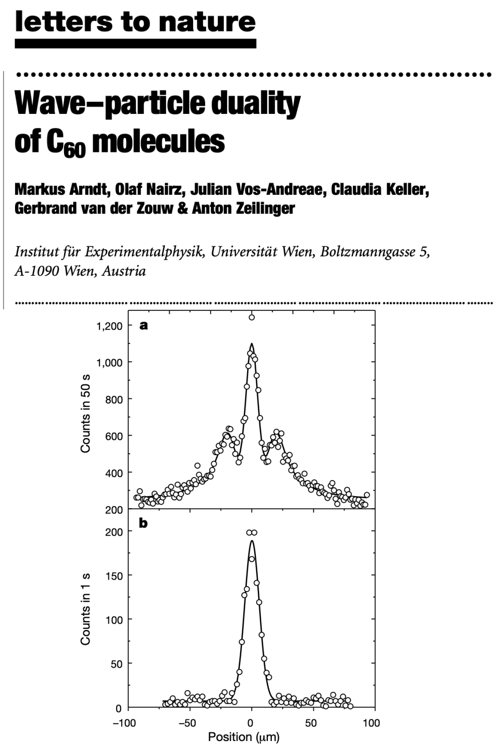


Hydrated hydroxide diffusion (Tuckerman, Marx, and Parrinello)

Quantum paraelectricity in $SrTiO_3$ (Vanderbilt)

Even at large scales!




letters to nature

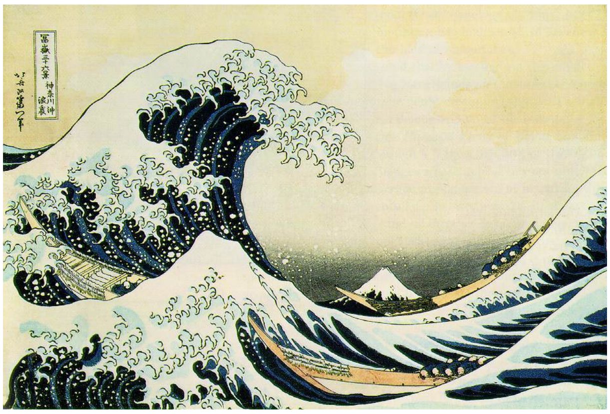
Wave–particle duality of C_{60} molecules

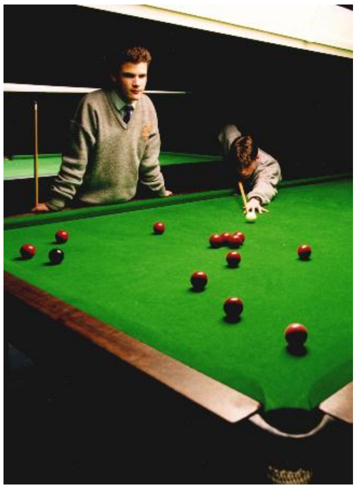
Markus Arndt, Olaf Nairz, Julian Vos-Andreae, Claudia Keller, Gerbrand van der Zouw & Anton Zeilinger

Institut für Experimentalphysik, Universität Wien, Boltzmanngasse 5, A-1090 Wien, Austria

So, What Is It?

It's the mechanics of waves, instead of classical particles



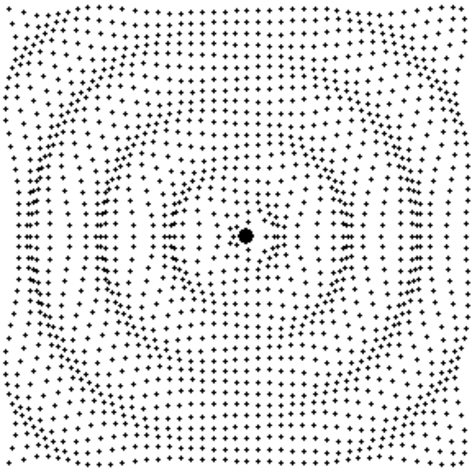


Mechanics of a Particle

$$m\frac{d^2\vec{r}}{dt^2} = \vec{F}(\vec{r}) = -\vec{\nabla}V(\vec{r}) \longrightarrow \vec{r}(t),\ \vec{v}(t)$$

The sum of the kinetic and potential energy is conserved

Description of a Wave



The wave is an excitation (a vibration): we need to know the amplitude of the excitation at every point and at every instant

$$\psi = \psi(\vec{r}, t)$$

Stationary Schrödinger's equation

(Newton's 2nd law for quantum objects)

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r})$$

1925-onwards: E. Schrödinger (wave equation), W. Heisenberg (matrix formulation), P.A.M. Dirac (relativistic)

Interpretation of the Quantum Wavefunction (Copenhagen)

$$||\psi_i(\vec{r})||^2$$

is the probability of finding an electron in *r*, when its wavefunction is ψ_i

$$\int \psi_i^*(\vec{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi_i(\vec{r}) d\vec{r} = E_i$$

is the value of the energy for the electron, when its wavefunction is ψ_i

From classical mechanics to operators

- classical momentum $\vec{p}$ →
  → gradient operator $-i\hbar\vec{\nabla}$
- classical position $\vec{r}$ →
  → multiplicative operator $\hat{r}$

Orthogonality, Expectation Values, and Dirac's <bra|kets>

Ket $\psi = \psi(\vec{r}) = |\psi\rangle$

Orthonormal wavefunctions $\int \psi_i^*(\vec{r})\psi_j(\vec{r})d\vec{r} = \langle\psi_i|\psi_j\rangle = \delta_{ij}$

Expectation value of an operator (here: Hamiltonian *H*)

$$\int \psi_i^*(\vec{r})\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi_i(\vec{r})d\vec{r} = \langle\psi_i|\hat{H}|\psi_i\rangle = E_i$$

$$p \rightarrow -i\hbar\vec{\nabla} \Rightarrow \frac{p^2}{2m} \rightarrow -\frac{\hbar^2}{2m}\nabla^2$$

For Hermitian operators $\hat{O} = \hat{O}^\dagger$: expectation values are real numbers

Eigenvectors with different eigenvalues are orthogonal

$$H\,|\psi_1\rangle = E_1\,|\psi_1\rangle$$
$$H\,|\psi_2\rangle = E_2\,|\psi_2\rangle$$

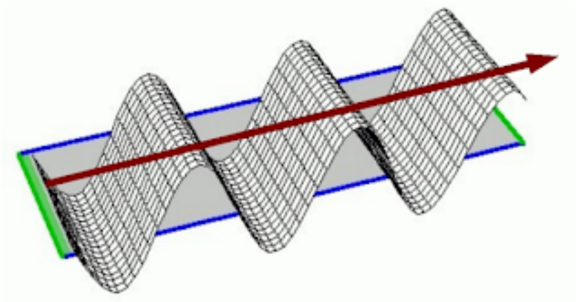
$$\downarrow$$

$$(E_2 - E_1)\,\langle\psi_2|\psi_1\rangle = 0$$

If instead they have the same eigenvalue, they are *not required* to be orthogonal, but can always *chosen to be orthogonal*

Free electron ψ(x)

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x) = E\psi(x)$$



A plane wave

Free electron ψ(x)

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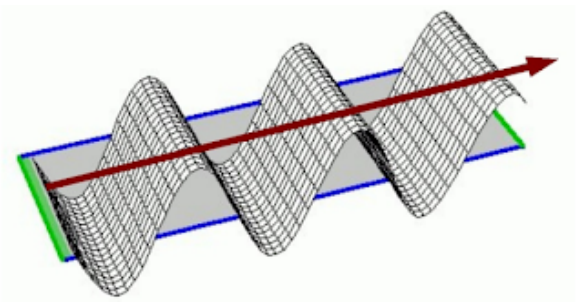


$$\psi_k(x) = Ae^{ikx}$$

$$p \rightarrow -i\hbar\frac{\partial}{\partial x} \Rightarrow \frac{\langle\psi_k|p|\psi_k\rangle}{\langle\psi_k|\psi_k\rangle} = \hbar k$$

$$E = \frac{\langle\psi_k|H|\psi_k\rangle}{\langle\psi_k|\psi_k\rangle} = \frac{\hbar^2 k^2}{2m}$$

A plane wave

In more than 1D (in 3D)

$$\vec{\nabla} f = \left(\frac{\partial f}{\partial x}, \frac{\partial f}{\partial y}, \frac{\partial f}{\partial z} \right)$$

$$\nabla^2 f = \vec{\nabla} \cdot (\vec{\nabla} f) = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2}$$

For a free electron, V=0, and we can separate variables writing

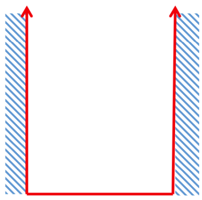
$$\psi(x, y, z) = \phi_x(x)\phi_y(y)\phi_z(z)$$

$$\phi_x(x) = A_x e^{ik_x x}, \ \ldots \quad \Rightarrow \quad \psi_{\vec{k}}(\vec{r}) = A' e^{i\vec{k}\cdot\vec{r}}$$

$$\frac{\langle \psi_{\vec{k}} | \vec{p} | \psi_{\vec{k}} \rangle}{\langle \psi_{\vec{k}} | \psi_{\vec{k}} \rangle} = \hbar \vec{k} \qquad E = \frac{\langle \psi_{\vec{k}} | H | \psi_{\vec{k}} \rangle}{\langle \psi_{\vec{k}} | \psi_{\vec{k}} \rangle} = \frac{\hbar^2 |\vec{k}|^2}{2m}$$

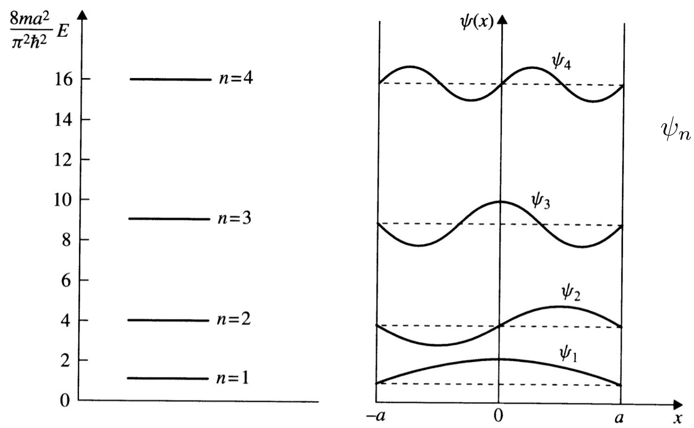
Infinite Square Well

Find plane-wave solutions subject to boundary conditions



$$\psi(0) = \psi(a) = 0$$

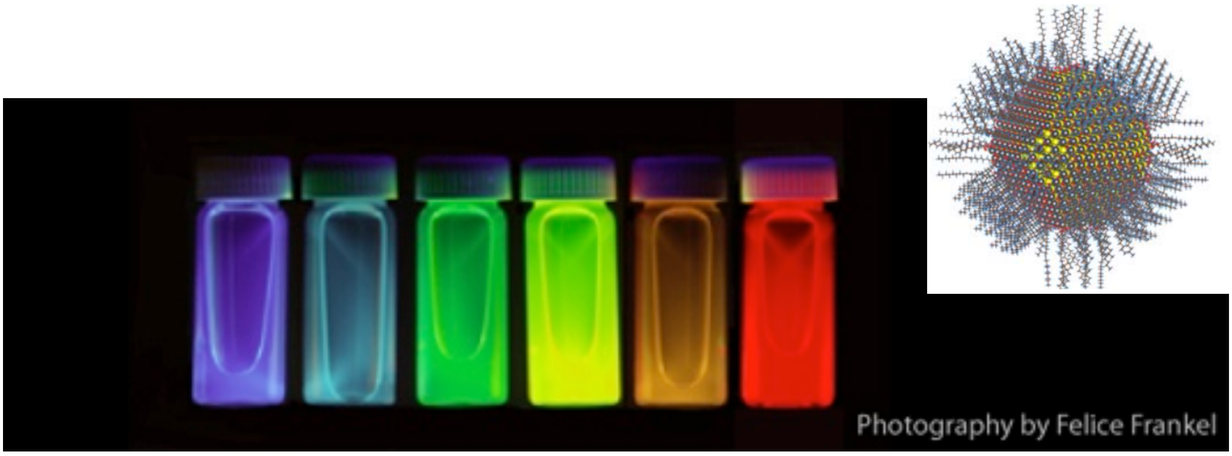
$$\hat{H} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2}$$



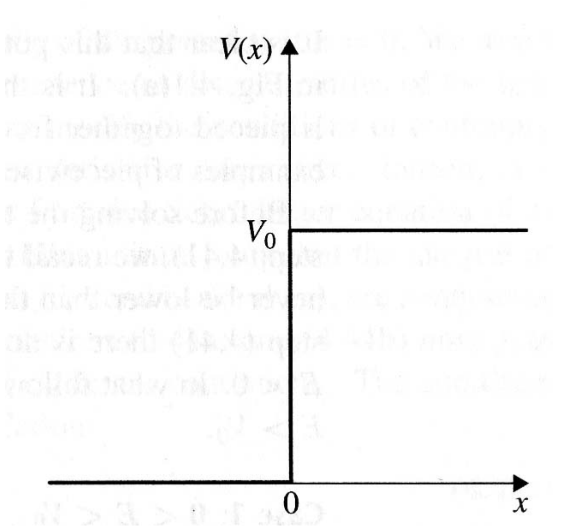
$$\psi_n(x) = A' \sin\left(\frac{n\pi x}{a}\right)$$

$$E_n = \frac{\hbar^2 \pi^2}{2ma^2} n^2$$

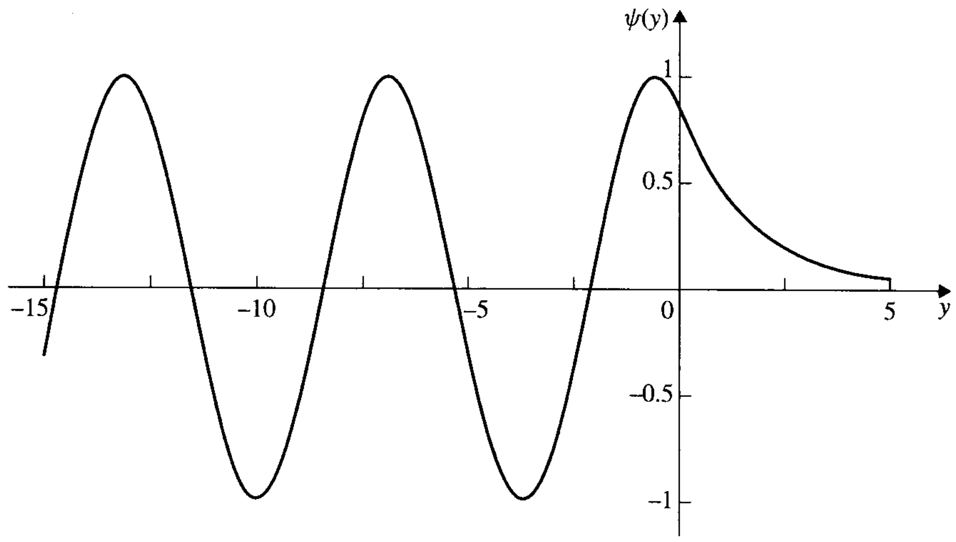
Quantum confinement in quantum dots



Metal Surfaces (I)



Metal Surfaces (II)

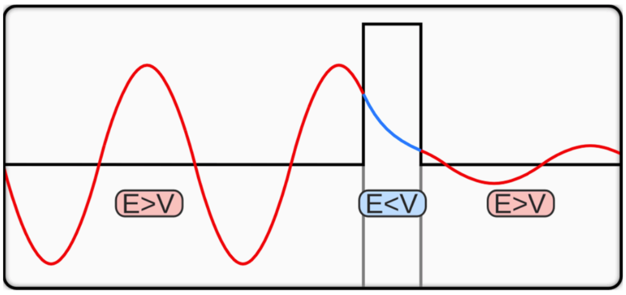


Metal Surfaces (III)

From http://www.quantum-physics.polytechnique.fr

Quantum tunneling

- Energy of the tunnelled particle is the same
- Probability amplitude is decreased



STM image of graphite surface

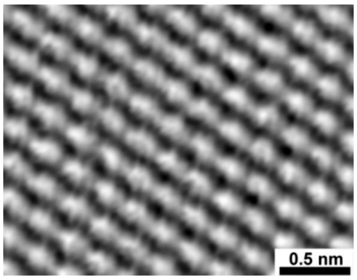
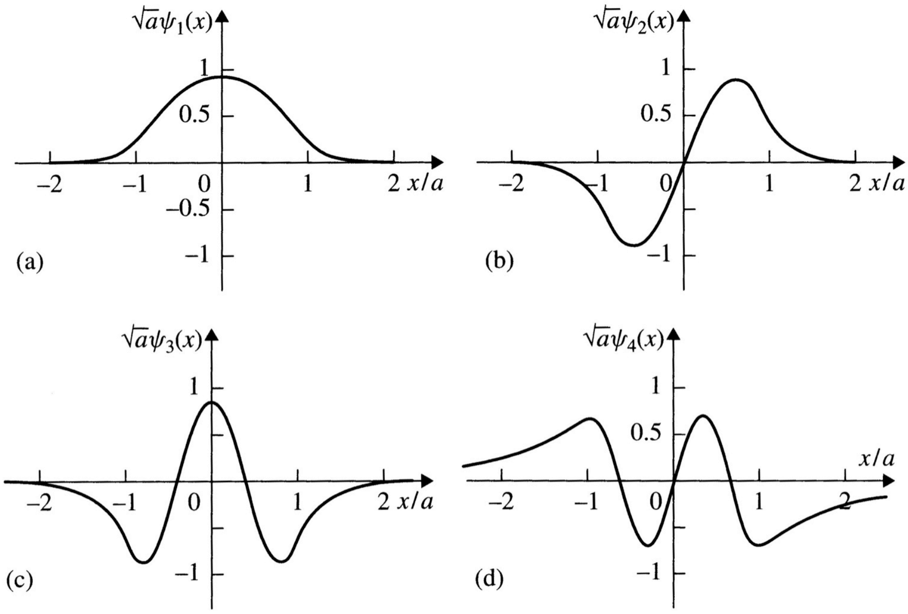


Figure from Wikipedia

Finite Square Well



Quantum Applets

http://www.quantum-physics.polytechnique.fr

- Used to be in Java, now just some videos left (and some new Javascript animations)

Quantum Applets

OSSCAR

http://www.osscar.org

Open Software Services for Classrooms and Research – An Open Science Educational Hub

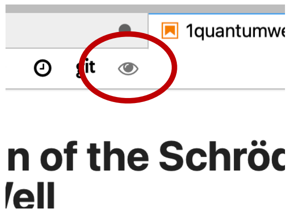
HOME THE PROJECT TOOLS COURSES TEAM ACKNOWLEDGEMENTS GITHUB

https://osscar-quantum-mechanics.materialscloud.io

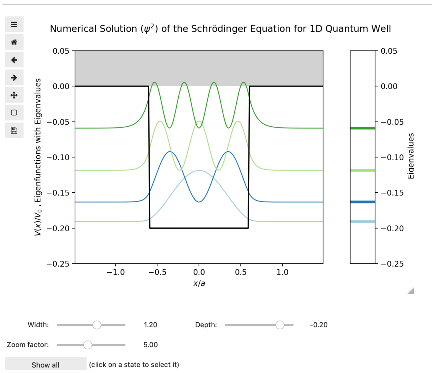
Try and modify them interactively on noto.epfl.ch

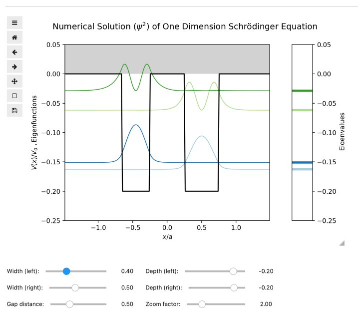
https://noto.epfl.ch/hub/user-redirect/git-pull?repo=https%3A%2F%2Fgithub.com%2Fosscar-org%2Fquantum-mechanics&urlpath=lab%2Ftree%2Fquantum-mechanics%2Fnotebook%2Findex.ipynb&branch=master

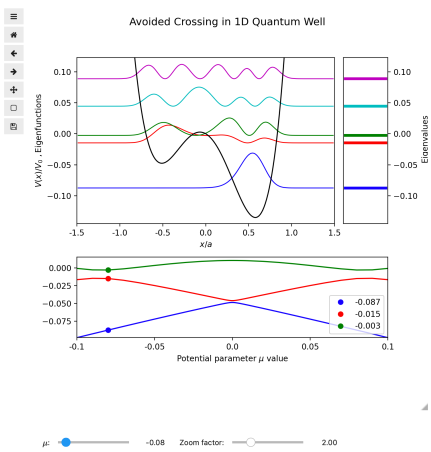
- noto.epfl.ch: JupyterLab instance provided by EPFL
- Login with your EPFL credentials
- Press eye icon on the bar
  to hide code and just see outputs

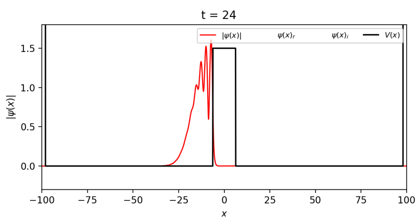


Some of the available apps on OSSCAR









Quantum atoms

Coulomb interaction between point-like nucleus and electron:

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r} \qquad \hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

We can write the Laplacian operator in spherical coordinates

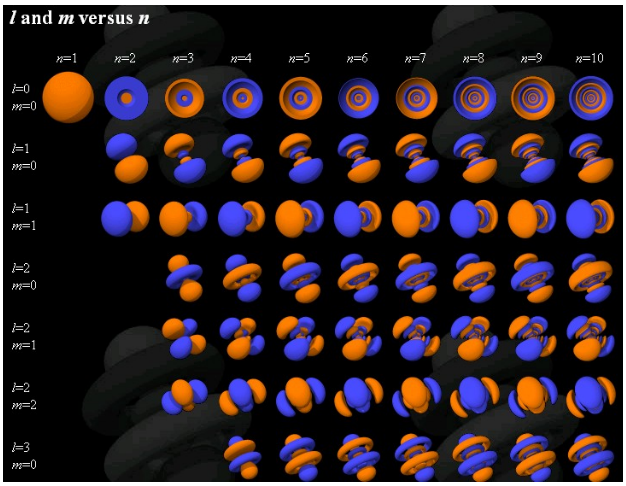
$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

We can separate variables and solve independently the radial part, while having always **the same angular part for any radial V:**

$$\Psi_{nlm}(\vec{r}) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

Solutions in a Coulomb Potential: the Periodic Table

http://www.orbitals.com/orb/orbtable.htm



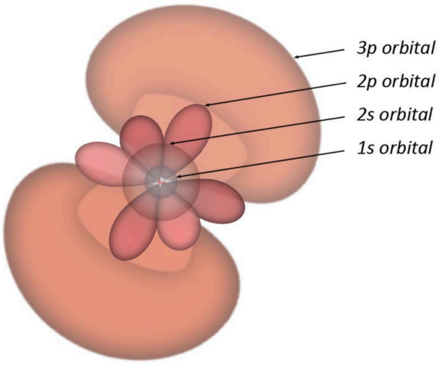
$$\Psi_{nlm}(\vec{r}) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

n: principal quantum number: 1, 2, 3, ...
l: azimuthal quantum number: 0, 1, ..., *n*-1
m: magnetic quantum number:
-*l*, -(*l*-1), ..., 0., ..., (*l*-1), *l*

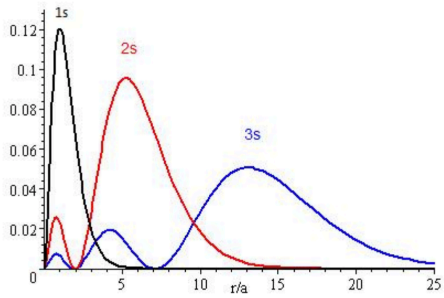
Hydrogen atom orbitals

angular part of the orbital wavefunctions

$$\psi_l^m(\theta,\phi) = \left[\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|!)}\right]^{1/2} P_l^{|m|}(\cos\theta)e^{im\phi}$$



radial probability densities



Two-electron atom

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|}\right]\psi(\vec{r}_1,\vec{r}_2) = E_{el}\psi(\vec{r}_1,\vec{r}_2)$$

Many-electron atom

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_i \sum_{j>i} \frac{1}{|\vec{r}_i - \vec{r}_j|}\right]\psi(\vec{r}_1,\ldots,\vec{r}_n) = E_{el}\psi(\vec{r}_1,\ldots,\vec{r}_n)$$

Complexity of the many-body Ψ

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_i \sum_{j>i} \frac{1}{|\vec{r}_i - \vec{r}_j|}\right]\psi(\vec{r}_1,\ldots,\vec{r}_n) = E_{el}\psi(\vec{r}_1,\ldots,\vec{r}_n)$$

"...Some form of approximation is essential, and this would mean the construction of tables. The tabulation function of **one** variable requires a **page**, of **two** variables a **volume** and of **three** variables a **library**; but the full specification of a single wave function of **neutral iron (Z=26) is a function of 78 variables**. It would be rather crude to restrict to 10 the number of values of each variable at which to tabulate this function, but even so, full tabulation would require **10^{78} entries**."

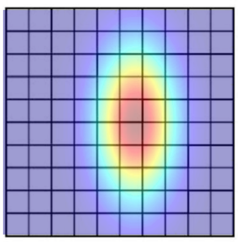
Douglas R Hartree

Charles G. Darwin, *Biographical Memoirs of Fellows of the Royal Society*, 4, 102 (1958)

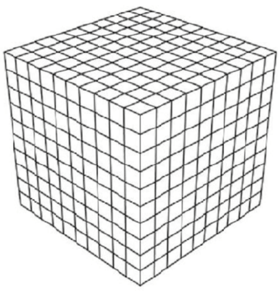
Complexity of the many-body Ψ

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_i \sum_{j>i} \frac{1}{|\vec{r}_i - \vec{r}_j|}\right]\psi(\vec{r}_1,\ldots,\vec{r}_n) = E_{el}\psi(\vec{r}_1,\ldots,\vec{r}_n)$$

Example: "loose" grid with only 10 points per direction



2 variables:
10^2 numbers: ~2kB



3 variables:
10^3 numbers: ~16kB

Not a problem only in the '60s!

10^{78} entries: would need to store 1 entry on each atom in the universe!

Energy of a collection of atoms

$$\hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{e-e} + \hat{V}_{N-N} + \hat{V}_{e-N}$$

- T_e: quantum kinetic energy of the electrons
- V_{e-e}: electron-electron interactions
- V_{N-N}: electrostatic nucleus-nucleus repulsion
- V_{e-N}: electrostatic electron-nucleus attraction (electrons in the field of all the nuclei)

$$\hat{T}_e = -\frac{1}{2}\sum_i \nabla_i^2 \qquad \hat{V}_{e-N} = \sum_i \left[\sum_I V\left(\vec{R}_I - \vec{r}_i\right) \right] \qquad \hat{V}_{e-e} = \sum_i \sum_{j>i} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

Electrons and Nuclei

- We treat only the electrons as quantum particles, in the field of the fixed (or slowly varying) nuclei
- This is generically called the adiabatic or Born-Oppenheimer approximation
- Adiabatic means that there is no coupling between different electronic surfaces; B-O no influence of the ionic motion on one electronic surface.

Matrix Formulation (I)

$$\hat{H}\left|\psi\right\rangle = E\left|\psi\right\rangle$$

$$\left|\psi\right\rangle = \sum_{n=1,k} c_n \left|\phi_n\right\rangle \qquad \left\{\left|\phi_n\right\rangle\right\} \text{ orthogonal}$$

$$\left\langle\phi_m\right|\hat{H}\left|\psi\right\rangle = E\left\langle\phi_m\middle|\psi\right\rangle$$

$$\sum_{n=1,k} c_n \left\langle\phi_m\right|\hat{H}\left|\phi_n\right\rangle = E c_m$$

Matrix Formulation (II)

$$\sum_{n=1,k} H_{mn} c_n = E c_m$$

$$\begin{pmatrix} H_{11} & \ldots\ldots & H_{1k} \\ . & & . \\ . & & . \\ . & & . \\ H_{k1} & \ldots\ldots & H_{kk} \end{pmatrix} \cdot \begin{pmatrix} c_1 \\ . \\ . \\ . \\ c_k \end{pmatrix} = E \begin{pmatrix} c_1 \\ . \\ . \\ . \\ c_k \end{pmatrix}$$

Matrix Formulation (III)

$$\det\begin{pmatrix} H_{11}-E & \ldots\ldots & & H_{1k} \\ . & H_{22}-E & & . \\ . & & & . \\ . & & & . \\ H_{k1} & \ldots\ldots & & H_{kk}-E \end{pmatrix}=0$$

Variational Principle

$$E\left[\Psi\right]=\frac{\left\langle\Psi\middle|\hat{H}\middle|\Psi\right\rangle}{\left\langle\Psi\middle|\Psi\right\rangle}$$

Variational Principle

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

$$E[\Psi] \geq E_0$$

If $E[\Psi] = E_0$, then Ψ is the ground state wavefunction, and viceversa

Variational principle (proof)

$$\phi = \sum_n c_n \psi_n \qquad \sum_n |c_n|^2 = 1 \qquad \langle \psi_n | \psi_m \rangle = \delta_{nm}$$

$$E[\phi] = \langle \phi | \hat{H} | \phi \rangle = \left\langle \sum_n c_n \psi_n \middle| \hat{H} \middle| \sum_m c_m \psi_m \right\rangle$$

$$= \sum_{n,m} \langle c_n \psi_n | E_m | c_m \psi_m \rangle = \sum_{n,m} c_n^* c_m E_m \langle \psi_n | \psi_m \rangle$$

$$= \sum_n |c_n|^2 E_n \geqslant E_0 \sum_n |c_n|^2 = E_0$$

Equality holds **only** if we guessed the **exact** ground state wave function

Energy of an Hydrogen Atom

$$E_\alpha = \frac{\left\langle \Psi_\alpha \middle| \hat{H} \middle| \Psi_\alpha \right\rangle}{\left\langle \Psi_\alpha \middle| \Psi_\alpha \right\rangle}$$

$$\Psi_\alpha = C \exp(-\alpha r)$$

$$\left\langle \Psi_\alpha \middle| \Psi_\alpha \right\rangle = \pi \frac{C^2}{\alpha^3}, \qquad \left\langle \Psi_\alpha \middle| -\frac{1}{2}\nabla^2 \middle| \Psi_\alpha \right\rangle = \pi \frac{C^2}{2\alpha} \qquad \left\langle \Psi_\alpha \middle| -\frac{1}{r} \middle| \Psi_\alpha \right\rangle = -\pi \frac{C^2}{\alpha^2}$$

$$\alpha_{\min} = \frac{1}{a_{\text{Bohr}}} \approx \frac{1}{0.529\ \text{Å}}, \qquad E_{\alpha_{\min}} = -1\ \text{Rydberg} \approx -13.6\ \text{eV}$$

Mean-field approach

- Independent particle model (Hartree): each electron moves in an effective potential, representing the attraction of the nuclei and the average effect of the repulsive interactions of the other electrons
- This average repulsion is the electrostatic repulsion of the average charge density of all other electrons

Hartree Equations

The Hartree equations can be obtained directly from the variational principle, once the search is restricted to the many-body wavefunctions that are written as the product of single orbitals (i.e. we are working with independent electrons)

$$\psi(\vec{r}_1,\ldots,\vec{r}_n)=\phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\cdots\phi_n(\vec{r}_n)$$

$$\left[-\frac{1}{2}\nabla_i^2+\sum_I V(\vec{R}_I-\vec{r}_i)+\sum_{j\neq i}\int|\phi_j(\vec{r}_j)|^2\frac{1}{|\vec{r}_j-\vec{r}_i|}d\vec{r}_j\right]\phi_i(\vec{r}_i)=\varepsilon\phi_i(\vec{r}_i)$$

The self-consistent field

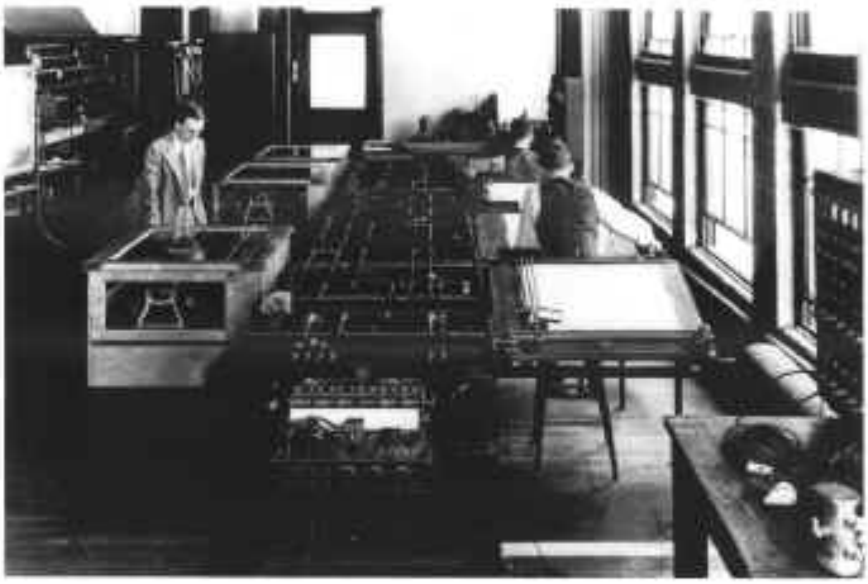
- The single-particle Hartree operator is self-consistent! It depends on the orbitals that are the solution of all other Hartree equations
- We have *n* simultaneous integro-differential equations for the *n* orbitals
- Solution is achieved iteratively

$$\left[-\frac{1}{2}\nabla_i^2+\sum_I V(\vec{R}_I-\vec{r}_i)+\sum_{j\neq i}\int|\varphi_j(\vec{r}_j)|^2\frac{1}{|\vec{r}_j-\vec{r}_i|}d\vec{r}_j\right]\varphi_i(\vec{r}_i)=\varepsilon\varphi_i(\vec{r}_i)$$

Iterations to self-consistency

- Initial guess at the orbitals
- Construction of all the operators
- Solution of the single-particle pseudo-Schrödinger equations
- With this new set of orbitals, construct the Hartree operators again
- Iterate the procedure until it (hopefully) converges

Bush Differential Analyzer



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