COHERENCE 2024

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Analytical Chemistry Group

SCIENCE FOR the PLANET

Catalytic Phenomena and Quantum Chemistry Puzzles

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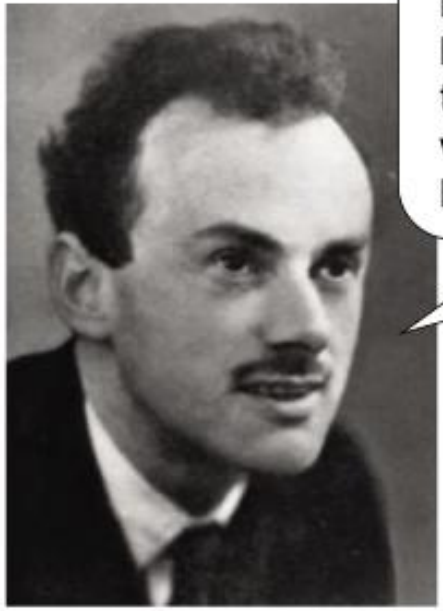
Quantum Chemistry



Paul Dirac

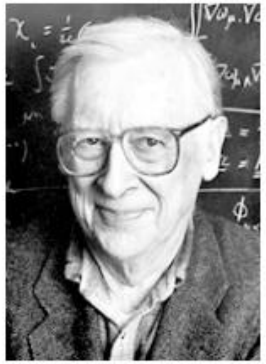
The general theory of quantum mechanics is now complete... The underlying physical laws necessary for the mathematical theory of a large part of physics and **the whole of chemistry** are thus completely known – Paul Dirac, 1929.

Right: QM is the foundation of Chemistry

Wrong: Not so fast - complexities necessitate approximations

Nowadays we have powerful computers!!

The Nobel Prize in Chemistry 1998



John A. Pople

"for his development of computational methods in quantum chemistry"

Walter Kohn

"for his development of the density-functional theory”

The Nobel Prize in Chemistry 2013

2013 Nobel Chemistry Prize jointly to Martin Karplus, Michael Levitt and Arieh Warshel *"for the development of multiscale models for complex chemical systems"*.

Martin Karplus

Michael Levitt

Arieh Warshel

WHAT IS QUANTUM CHEMISTRY?

- In the late seventeenth century, Isaac Newton discovered **classical mechanics**, the *laws of motion of macroscopic objects*.
- In the early twentieth century, physicists found that classical mechanics does not correctly describe the behavior of very small particles such as the electrons and nuclei of atoms and molecules.
- The behavior of such particles is described by a set of appropriate concepts and equations, which is called **quantum mechanics**.
- **Quantum chemistry applies quantum mechanics to problems in chemistry**.

Classical Mechanics

Do the electrons in atoms and molecules obey Newton's classical laws of motion?

We discovered that the answer to this question was "No".

This has led to the development of Quantum Mechanics

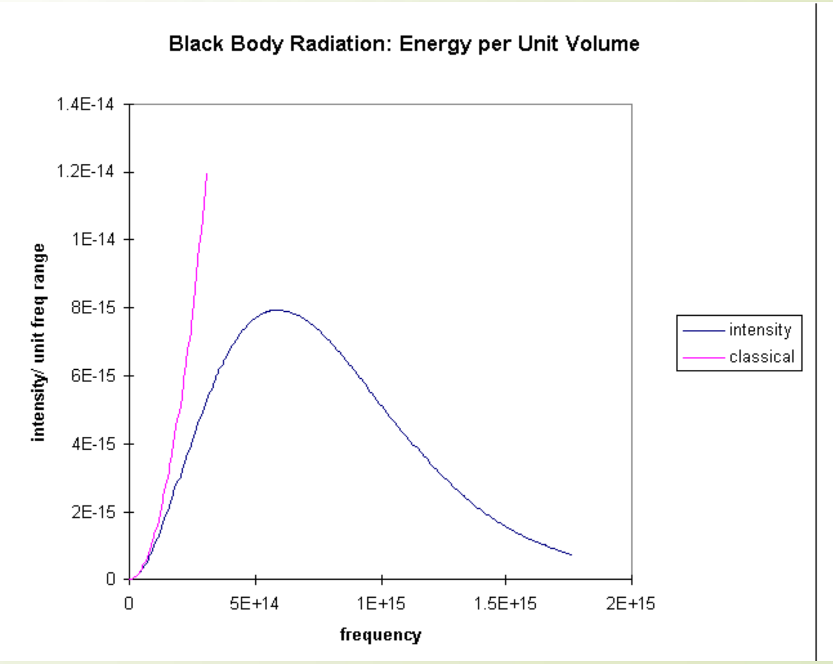
We will contrast classical and quantum mechanics.

Crises in physics that demanded Q.M.

- Why don't atoms disintegrate in nanoseconds?
  - if electron is "orbiting", it's accelerating (wiggling)
  - wiggling charges emit electromagnetic radiation (energy)
  - loss of energy would cause prompt decay of orbit

Why don't hot objects emit more ultraviolet light than they do?

- classical theory suggested a "UV catastrophe," leading to obviously nonsensical infinite energy radiating from hot body
- Max Planck solved this problem by postulating light quanta (now often called the father of quantum mechanics)



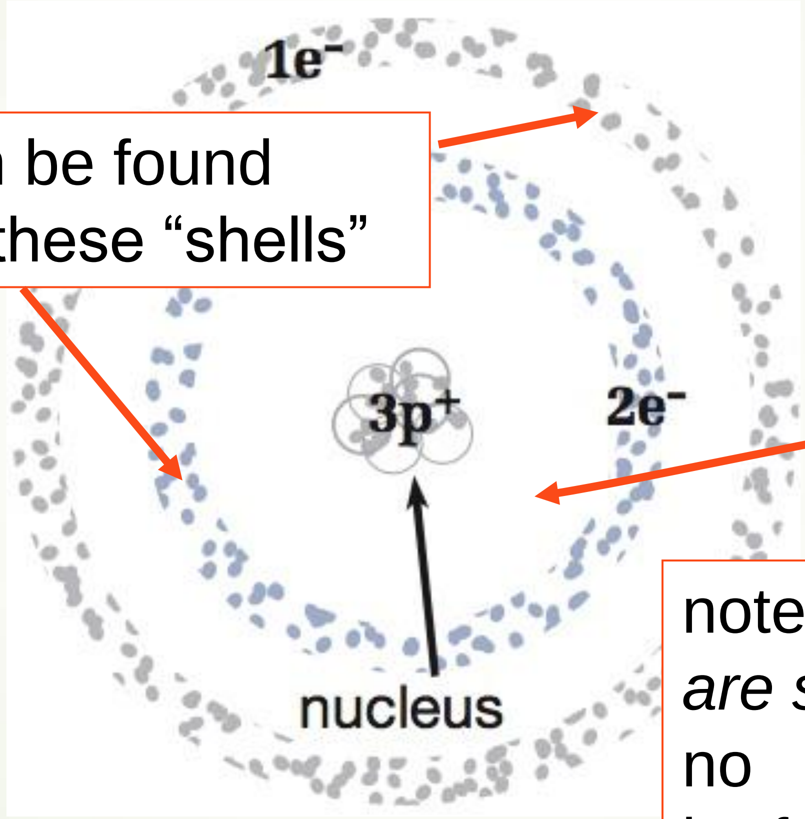
The Quantum Mechanics View

- All matter (particles) has wave-like properties
  - so-called particle-wave *duality*
- Particle-waves are described in a probabilistic manner
  - electron doesn't whiz around the nucleus, it has a probability distribution describing where it might be found
  - allows for seemingly impossible "quantum tunneling"
- Some properties come in dual packages: can't know both simultaneously to arbitrary precision
  - called the Heisenberg Uncertainty Principle
  - not simply a matter of measurement precision
  - position/momentum and energy/time are example pairs
- The act of "measurement" fundamentally alters the system
  - called entanglement: information exchange alters a particle's state

Quantum Mechanical Model

- The ***current*** understanding of the atom is based on Quantum Mechanics
- This model sees the electrons not as individual particles, but as behaving like a cloud - the electron can be “anywhere” in a certain energy level
- Remember back to CPE with electrons behaving like bees in a beehive

Quantum Mechanical Model



electrons can be found anywhere in these "shells"

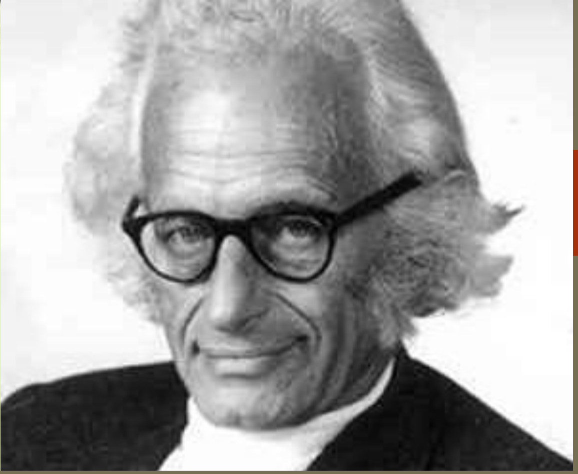
note: *the electrons are still quantized*
no electrons can be found here

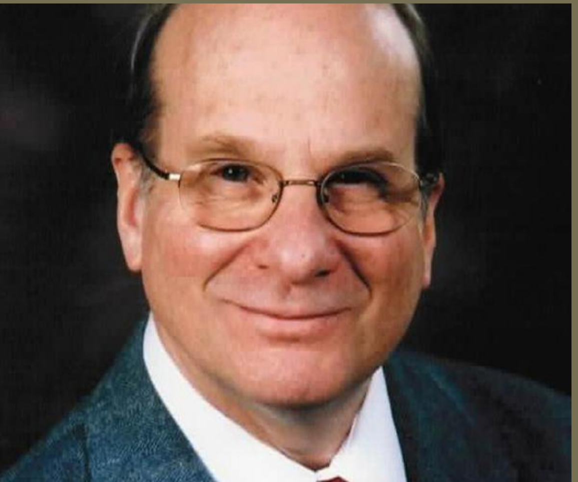
Wave or Particle?
Neither; Both; take your pick

- Non-intuitive combination of wavelike *and* particle-like
- Appears to behave in wavelike manner. But with low intensity, see the interference pattern build up out of individual photons, arriving one at a time.
- How does the photon *know* about "the other" slit?
  - Actually, it's impossible to simultaneously observe interference *and* know which slit the photon came through
  - Photon "sees", or "feels-out" *both* paths simultaneously!
- Speak of wave-part describing *probability distribution* of where individual photons may land

The victory of the weird theory

- Without Quantum Mechanics, we could never have designed and built:
  - semiconductor devices
    - computers, cell phones, etc.
  - lasers
    - CD/DVD players, bar-code scanners, surgical applications
  - MRI (magnetic resonance imaging) technology
  - nuclear reactors
  - atomic clocks (e.g., GPS navigation)
- Physicists didn’t embrace quantum mechanics because it was gnarly, novel, or weird
  - it’s simply that the #$!&@ thing worked so well





- 1937: Herbert Fröhlich was the first to hypothesize that the properties of a material could depend on the size of the particles. Fröhlich pointed out that the free electron model yielded different results depending on whether very small particles or large materials were considered, and that these changes manifested in the form of visible effects.
- 1960s: Quantum effects were observed in microfilms, so much so that by the 1980s the experimental observations of these phenomena had become a scientific fact.
- 1979: Alexei Ekimov began working on doped glasses to study their structure in depth, particularly the colloidal structure characteristic of colored glasses, as well as the growth mechanism of these particles. He noticed that the optical properties of these silica glasses, doped with copper and chlorine, varied based on temperature due to the formation of thin films of copper chloride. Ekimov attributed these properties to the quantum effects that had been theorized in previous decades.
- 1983: Louis Brus demonstrated the same behavior in colloidal nanoparticles outside of colored glasses. This marked his entry into the history of quantum dots, adding redox potential to the list of quantum effects, along with color.

- Today, quantum theory and nanotechnology have integrated to such an extent that an important application of quantum chemistry is certainly directed towards nanotechnologies. But what happens if we shift to a cellular system with a rogue cell that triggers a degenerative process? Every possibility of prevention based on that single cell falls apart, unless we can employ interpretative technologies that allow us to identify it.
- Still referring to medicine, we are talking about nanotechnologies, in the case of drug delivery. Other potential applications of graphene-based quantum dots can be found in therapies against diabetes mellitus, in radiotherapy, in the fight against multidrug resistance, and many others.
- Their potential for electrochemical energy accumulation has also paved the way for the possible use of nanodots in the field of renewable energy, particularly in energy storage and solar energy conversion.
- The ability to store large amounts of charge makes them interesting for use in supercapacitors or even in the photocatalytic process of converting water into hydrogen using solar energy.

Physical chemists use quantum mechanics to:

- calculate (with the aid of statistical mechanics) thermodynamic properties (for example, entropy, heat capacity) of gases;
- to interpret molecular spectra, thereby allowing experimental determination of molecular properties (for example, bond lengths and bond angles, dipole moments, barriers to internal rotation, energy differences between conformational isomers);
- to calculate molecular properties theoretically;
- to calculate properties of transition states in chemical reactions, thereby allowing estimation of rate constants ;
- to understand intermolecular forces and to deal with bonding in solids.
- **Inorganic chemists** use ligand field theory, an approximate quantum-mechanical method, to predict and explain the properties of transition-metal complex ions.

Organic chemists use quantum mechanics to:

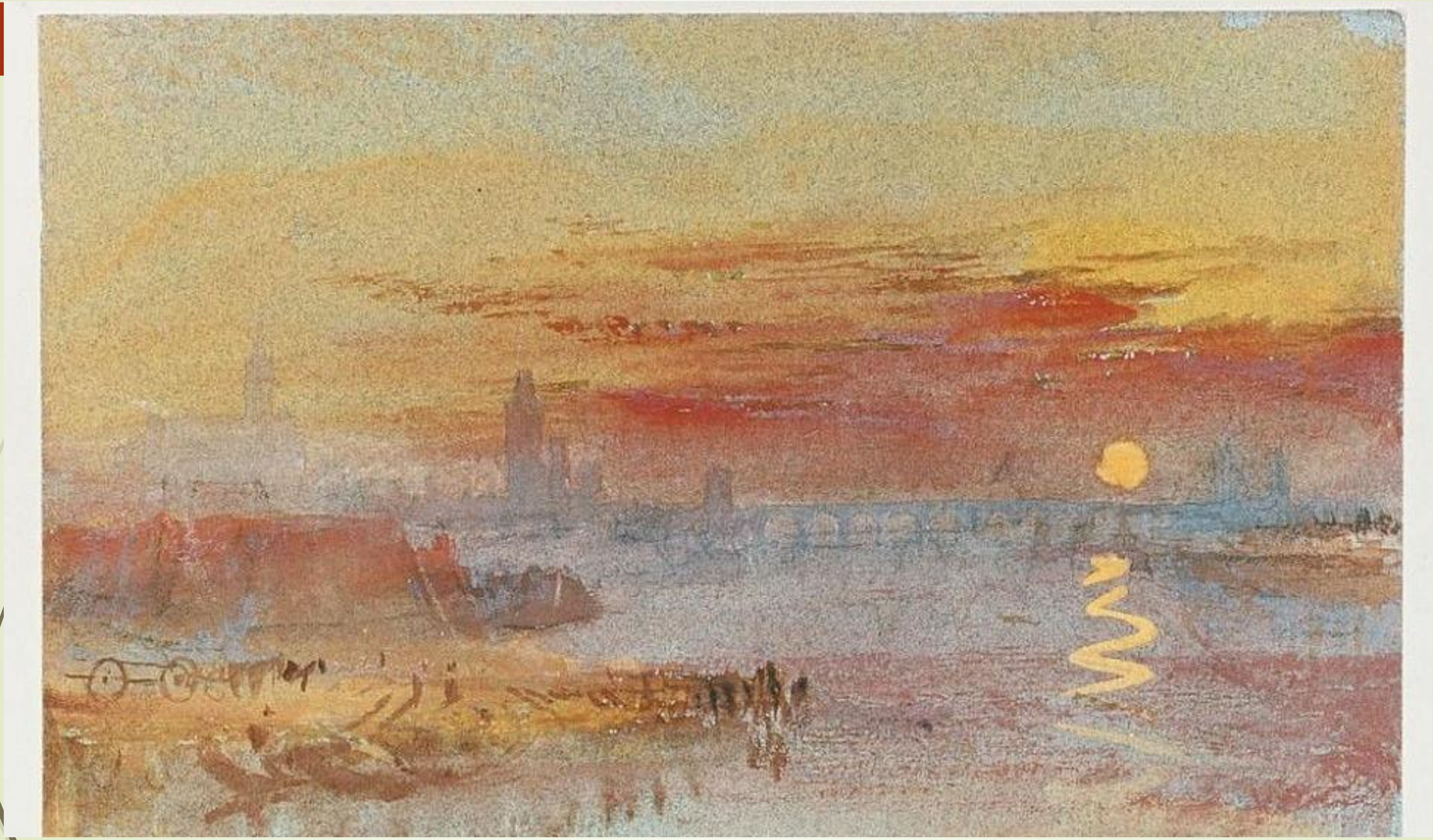
- estimate the relative stabilities of molecules;
- to calculate properties of reaction intermediates;
- to investigate the mechanisms of chemical reactions;
- to analyze NMR spectra.
- **Biochemists** are beginning to benefit from quantum-mechanical studies of conformations of biological molecules, enzyme-substrate binding, and solvation of biological molecules.
- Several companies sell quantum-chemistry software for doing molecular quantum-chemistry calculations. These programs are designed to be used by all kinds of chemists, not just quantum chemists.

In short, the applications of quantum dots - both present and future, already established or potentially possible - are numerous and span across very different fields, from pure medicine to the devices we use daily to watch a TV series or a movie. When discussing quantum mechanics, practical aspects are often overlooked in favor of theoretical or even philosophical considerations. However, quantum dots demonstrate that even aspects of science that seem to have no practical purpose can be crucial in the development of cutting-edge new technologies.

And they may even be worthy of a Nobel Prize.

Thank you for your kind attention

The Scarlet Sunset



by Joseph Mallord William Turner (183