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The Birth of Computational Chemistry

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Dedicated to famma(aunt) Khuki, fupa(uncle) Sadi and sister samara

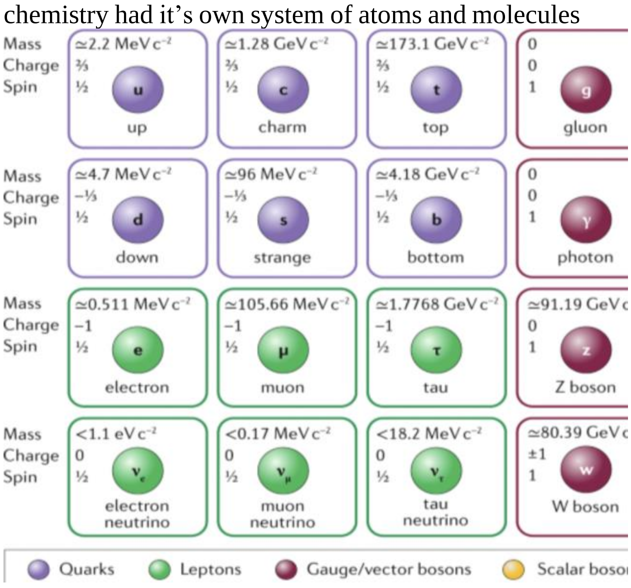
Abstract: Chemistry the central of Science Combination of physics ,biology and mathematics and economics also . When Computer science and hard core Mathematics added to it ,it is named as computational Chemistry . In fact , Quantum Physicist has created this field to make the relation strong between physical sciences . Theoretical inorganic chemistry is the subfield where Mathematical methods are combined with fundamental laws of physics to study the process of chemical relevance . Given a set of nuclei and electrons theoretical chemistry can attempts to calculate things such as, Geometrical arrangement of nuclei?? relative energies, Their properties, Rate of transformation of stable molecules, Time dependence's of molecular structures and their properties, interaction between molecules

Keywords: Describing the System, Fundamental forces, The Dynamical Equation;Variable Separation(Space and Time var.) Separating Nuclear and Electronics Variables, Classical Mechanics, Hydrogen and Helium Atom

Describing The System

- System description -What are the fundamental units of particles ,and how many are there ?
- Starting condition : Particles and there velocities
- Interaction : mathematical form of acting two forces the particles
- Dynamical Equation : Mathematical form for evolving the system in time

Just like the classification of animals in biology; chemistry had it's own system of atoms and molecules



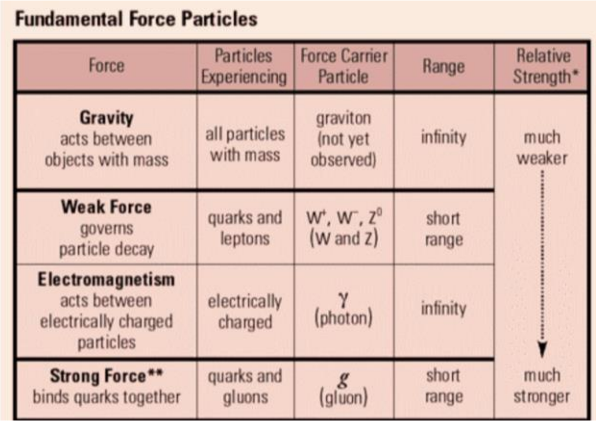
Src:https://www.nature.com/articles/s41570-020-0195-y

The integration between particles in combination with the dynamical equation determines how the system evolves in time. At the fundamental level ,the only important force at the atomic level is the electromagnetic interaction.Depending on the particles ;the force fields method can be different .the interactions are parameterised ad stretch ,bend ,torsional,Van dar walls etc .For the short-lived transactinides, the nuclear stability becomes an important factor in chemical studies. Nuclear stability, decay rates, spectra and reaction cross sections are also important for predicting the astrophysical origin of the elements, including the production of the heavy elements beyond iron in supernova explosions or neutron-star mergers. In this Perspective, we critically analyse the periodic table of elements and the current status of theoretical predictions and origins for the heaviest elements, which combine both quantum chemistry and physics.

Fundamental Forces

The interaction between particles can be described in terms of either a force (F) or a potential (V). These are equivalent ,As the

$$F(r) = -\Delta V/\Delta r$$



Fundamental Force Particles

Force	Particles Experiencing	Force Carrier Particle	Range	Relative Strength*
Gravity acts between objects with mass	all particles with mass	graviton (not yet observed)	infinity	much weaker
Weak Force governs particle decay	quarks and leptons	W⁺, W⁻, Z⁰ (W and Z)	short range	
Electromagnetism acts between electrically charged particles	electrically charged	γ (photon)	infinity	
Strong Force** binds quarks together	quarks and gluons	g (gluon)	short range	much stronger

Src: https://www.clearias.com/four-fundamental-forces-of-nature/

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Same process it can be found the electronic potential and gravitational force is

$$Velec(rij) = (Celec * qiqj)/rij$$

$$Vgrav(rij) = -Cgrav(mimj)/rij$$

Within QED or Quantum Electrodynamics

The modified equation will be

$$Velec(r12) = 1/r12[1/r12 - 1/2(\alpha1\alpha2 + (\alpha1r1)(\alpha2r2)/r12^2)]$$

The dynamics Equation :

Quantum (velocity unto 1/3 c-10^8m/s	Classical	Type of interaction	
Dirac $H'\Psi = id'\Psi/dt$	Einstein f=ma	relativistic	
Schrodinger $H'\Psi = id'\Psi/dt >> H = T + V$	newton $F = ma$	Non -relativistic	

Here

$$Hdirac = (c * ap + bmc^2) + V$$

The alpha and beta are 4*4 matrices and this relativistic wave function has 4 components . Traditionally these are labelled as large and small components .,such have alpha and beta spin function .The large component describe the electronic part and small components describe positron (electron antiparticle of wave function) and the alpha and beta matrices couple these components in the limit of c->∞.

The two large components of the wave function reduce to the alpha and beta spin orbitals in schrodinger equation .

The Hamiltonian operators can be represented as

$$H = -0.5 * dxyz^2 - 1/2meu - z/(x^2 + y^2 + z^2)^0.5$$

The atomic orbitals of hydrogen-like atoms are solutions to the Schrödinger equation in a spherically symmetric potential. In this case, the potential term is the potential given by Coulomb's law:

$$V(r) = -\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}$$

where

- ε_0 is the permittivity of the vacuum,
- *Z* is the atomic number (charge of the nucleus),
- *e* is the elementary charge (charge of an electron),
- *r* is the distance of the electron from the nucleus.

After writing the wave function as a product of functions:

$$\psi(r,\theta,\phi) = R(r)Y_{lm}(\theta,\phi)$$

(in spherical coordinates), where Y_{lm} are spherical harmonics, we arrive at the following Schrödinger equation:

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right) + \frac{l(l+1)R}{r^2}\right) + V(r)R(r)\right] = ER(r),$$

where μ is, approximately, the mass of the electron. More accurately, it is the reduced mass of the system consisting of the electron and the nucleus.

Different values of *l* give solutions with different angular momentum, where *l* (a non-negative integer) is the quantum number of the orbital angular momentum. The magnetic quantum number *m* (satisfying $-l \leq m \leq l$) is the (quantized) projection of the orbital angular momentum on the *z*-axis. See here for the steps leading to the solution of this equation.

Non-relativistic Wave function and energy

In addition to *l* and *m*, a third integer *n* > 0, emerges from the boundary conditions placed on *R*. The functions *R* and *Y* that solve the equations above depend on the values of these integers, called *quantum numbers*. It is customary to subscript the wave functions with the values of the quantum numbers they

The first order correction is known as Brett term and α1 and α2 represents velocity operators . Brett corrections corresponds to magnetic interaction between two electrons. While second terms describes “retardation effect “ since the interaction between distance particles is”delayed”relative to interactions between close particles .owing to finite value of c (in atomic units (c ~137) depend on. The final expression for the normalized wave function is:

$$\psi_{nlm} = R_{nl}(r)\, Y_{lm}(\theta,\phi)$$
$$R_{nl}(r) = \sqrt{\left(\frac{2Z}{na_\mu}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]}}\, e^{-Zr/na_\mu} \left(\frac{2Zr}{na_\mu}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_\mu}\right)$$

where:

- L_{n-l-1}^{2l+1} are the generalized Laguerre polynomials in the definition given here.
- $a_\mu = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$

Note that a_μ is approximately equal to a_0 (the Bohr radius). If the mass of the nucleus is infinite then $\mu = m_e$ and $a_\mu = a_0$.

- $E_n = -\left(\frac{Z^2\mu e^4}{32\pi^2\epsilon_0^2\hbar^2}\right)\frac{1}{n^2}$.
- $Y_{lm}(\theta,\phi)$ function is a spherical harmonic.

Relativistic Wave function and energy

Quantum relativistic treatment of electrons uses Dirac equation. In this approach energy levels depends on *n* (principal quantum number) and *m* (magnetic quantum number)[3], energies allowed are:

$$E_n = m_e c^2 \sqrt{1 + \left(\frac{Z\alpha}{n - |m| + \sqrt{m^2 + (Z\alpha)^2}}\right)^2}$$

Where:

m_e, is the mass of electron.
$c\ \alpha$, are speed of light and fine structure constant.
Z, n, m, are the number of protons of the nucleus, principal quantum number and magnetic quantum number.
If we discount energy associated with rest mass of electron levels can be written as:

$$E_n - m_e c^2 \approx \frac{m_e c^2}{2}\left(\frac{Z\alpha}{n - |m| + \sqrt{m^2 + (Z\alpha)^2}}\right)^2$$

Quantum numbers

The quantum numbers *n*, *l* and *m* are integers and can have the following values:

$$n = 1, 2, 3, 4, \ldots$$
$$l = 0, 1, 2, \ldots, n-1$$
$$m = -l, -l+1, \ldots, 0, \ldots, l-1, l$$

See for a group theoretical interpretation of these quantum numbers this article. Among other things, this article gives group theoretical reasons why $l < n$ and $-l \leq m \leq l$.

Angular momentum

Each atomic orbital is associated with an angular momentum **l**. It is a vector operator, and the eigenvalues of its square $l^2 \equiv l_x^2 + l_y^2 + l_z^2$ are given by:

$$l^2 Y_{lm} = \hbar^2 l(l+1) Y_{lm}$$

The projection of this vector onto an arbitrary direction is quantized. If the arbitrary direction is called *z*, the quantization is given by:

$$l_z Y_{lm} = \hbar m Y_{lm},$$

where *m* is restricted as described above. Note that l^2 and l_z commute and have a common eigenstate, which is in accordance with Heisenberg's uncertainty principle. Since l_x and l_y do not commute with l_z, it is not possible to find a state which is an eigenstate of all three components simultaneously. Hence the values of the *x* and *y* components are not sharp, but are given by a probability function of finite width. The fact that the *x* and *y* components are not well-determined, implies that the direction of the angular momentum vector is not well determined either, although its component along the *z*-axis is sharp.

These relations do not give the total angular momentum of the electron. For that, electron spin must be included.

This quantization of angular momentum closely parallels that proposed by Niels Bohr (see Bohr model) in 1913, with no knowledge of wavefunctions.

Including spin-orbit interaction

For more details on this topic, see Azimuthal quantum number#Addition of quantized angular momenta.

In a real atom the spin interacts with the magnetic field created by the electron movement around the nucleus, a phenomenon known as spin-orbit interaction. When one takes this into account, the spin and angular momentum are no longer conserved, which can be pictured by the electron precessing. Therefore one has to replace the quantum numbers *l*, *m* and the projection of the spin m_s by quantum numbers which represent the total angular momentum (including spin), *j* and m_j, as well as the quantum number of parity.

Gravitational **N-body simulations**, that is numerical solutions of the equations of motions for N particles interacting gravitationally, are widely used tools in astrophysics, with applications from few body or solar system like systems all the way up to galactic and cosmological scales. In this article we present a summary review of the field highlighting the main methods for N-body simulations and the astrophysical context in which they are usually applied.

$$meu = Mstar * mplanet / Mstar + mpalnet$$

Electron	Atom	Molecules	Macro Molecules
Boson Quarks ->Protons Neutrons -> Nuclei|^ Positron Neutrino Antinutrino Fermion			

The Choice Of particles starting condition effectively determines what we are trying to describe . The complete phase space is huge and we will only be able to describe a small part of it . There are many structural isomers with molecular formula $C6H6$.

Conclusion:

This paper is written to introduce what computational chemistry is . Computational Chemistry Is Important in **Predicting Reaction Mechanisms of New Experiments**. Since there are so many experiments that have been studied thoroughly, various algorithms and computer programs have enough data to predict the reaction mechanisms of new experiments. I will write a series of articles on it in future .

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