Sected Topics of Quantum Mechanics

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SELECTED TOPICS OF QUANTUM MECHANICS

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BRIEF HISTORY

- Max Karl Ernst Ludwig Planck 1858-1947 – Black body radiation, quanta of energy 1900, the Nobel Prize 1918.
- Albert Einstein 1879-1955 – Photoelectric effect $\Rightarrow$ quantum structure of radiation 1905, Nobel Prize 1921
- Sir Ernest Rutherford 1871-1937 – Atomic nucleus 1911, Nobel Prize 1908 (for his investigations for the chemistry of radioactive substances)
- Niels Hendrik Bohr 1885-1962 – "Old quantum theory" 1913, Nobel Prize 1922 (for his investigations of the structure of atoms, and of the radiation emanating from them)
- Arnold Sommerfed 1868-1951 – The unification of the quantum theory of Bohr with the special theory of relativity 1916.

- Louis-Victor Pierre Raymond Prince de Broglie 1892-1987 – for his discovery of the wave nature of electrons awarded the nobel Prize in 1929.
- Werner Karl Heisenberg 1901-1976 – Quantum mechanics 1925, the uncertainty principle, Nobel Prize (for the creation of quantum mechanics) 1932
- Erwin Schrödinger 1887-1961 – Wave equation 1926, Nobel Prize (for the discovery of new productive forms of atomic theory) 1933
- Wolfgang Pauli 1900-1958 – Quantum theory of many-particle systems, the Pauli principle 1925, Nobel Prize (for the discovery of the Exclusion Principle, also called the Pauli Principle) 1945
- Paul Adrien Maurice Dirac 1902-1984 – The unification of quantum mechanics and special theory of relativity 1928, Nobel Prize 1933 (shared with Schrödinger)

- Enrico Fermi 1901-1954 – Statistics of identical particles 1934, solid state physics, artificial radioactivity, Nobel Prize (for his demonstration of the existence of new radioactive elements produced by neutron irradiation, and for his related discovery of nuclear reactions brought about by slow neutrons) 1938
- Richard Feynman 1918-1988, Julian Schwinger 1918-1994, Shinichiro Tomonaga 1906-1979 – Quantum electrodynamics 1949, Nobel Prize (for their fundamental work in quantum electrodynamics, with deep ploughing consequences for the physics of elementary particles) 1965.
- Tsung Dao Lee 1926, Chen Ning Yang 1922 – the violation of the parity conservation law in weak interactions, Nobel Prize 1957 (for their penetrating investigation of the so-called parity laws, which has led to important discoveries regarding the elementary particles).

- Hans Albrech Bethe 1906 – Nucleosythesis, Nobel Prize 1967 (for his discoveries concerning the energy production in stars)
- Murray Gell-Mann (Czerniowce) 1929 – The classification of elementary particles, quark model, quantum chromodynamics, Nobel Prize 1969
- Sheldon Lee Glashow (Bobrujsk) 1932, Abdus Salam 1926-1996, Steven Weinberg 1933 – unified theory of the electromagnetic and weak interactions, Nobel Prize 1979
- John Henry Schwarz 1941, Michael Green 1946, Edward Witten 1951 – quantum theory of gravitation, string theory, grand unification (TOE)

- John Stewart Bell 1928-1990 - Bell inequalities; Alain Aspect 1947 – the experimental proof of the completeness of quantum mechanics 1981
- Robert Floyd Curl 1933, Sir Harold Walter Kroto (Krotoschiner, Bojanowo) 1939, Richard Errett Smalley 1943-2005 - the discovery of fullerenes, nanostructures, Nobel Prize 1996 (chemistry)
- Eric Allin Cornell 1961, Carl Edwin Wieman 1951, Wolfgang Ketterle 1957 - Bose-Einstein condensation (the phenomenon predicted by Satyendra Nath Bose 1894-1974 and Albert Einstein in 1924), the Nobel Prize 2001
- Quantum features of the Hall effect: Klaus von Klitzing 1943 – quantum Hall effect Nobel Prize 1985; Robert Betts Laughlin 1950, Horst Ludwig Störmer 1949, Daniel Chee Tsui 1939 – fractional Hall effect, Nobel Prize (for their discovery of a new form of quantum fluid with fractionally charged excitations) 1998.

THE POSTULATES

POSTULATE I

A quantum system is associated with a linear vector space $\mathcal{H}$.

- The elements of $\mathcal{H}$: *kets* $|\rangle$. (e. g. $|A_1\rangle$, $|A_2\rangle$).
- The basis: orthonormal, in general infinite.
  May be discrete or continuous or both.
  An arbitrary vector in $\mathcal{H}$ may be represented as

$$|A\rangle = \sum_n A_n |n\rangle + \int_C A(\xi)|\xi\rangle d\xi,$$

- Vectors dual to the kets: *bras* $\langle|$ (e.g $\langle A_1|$, $\langle A_2|$)

$$\langle A| = \sum_n A_n^* \langle n| + \int_C A^*(\xi)\langle\xi| d\xi.$$

- The scalar product of A by B is the complex conjugate of the scalar product of B by A: $\langle A|B\rangle = \langle B|A\rangle^*$.
- The orthonormality of the basis:

$$\langle n|n'\rangle = \delta_{mn'}, \qquad \langle \xi|\xi'\rangle = \delta(\xi - \xi').$$

- The completeness of the basis: the closure relation:

$$\hat{I} = \sum_n |n\rangle\langle n| + \int_C |\xi\rangle d\xi\langle\xi|,$$

Note: $|n\rangle\langle n| \equiv \hat{P}_n$
is a projector on the one dimensional space of vector $|n\rangle$.

POSTULATE II

Each state of the quantum system is described by a normalized ket in $\mathcal{H}$.

A quantum state may be identified with a point on a unit sphere in $\mathcal{H}$ or, alternatively, with a direction in $\mathcal{H}$

The linearity of $\mathcal{H}$ implies that a superposition of two different states is also a state of the quantum system, i.e., if $|\psi_1\rangle$ and $|\psi_2\rangle$ describe quantum states, then also

$$|\psi\rangle = c_1|\psi_1\rangle + c_2|\psi_2\rangle$$

is a state of this system.

Conclusion:
equations which determine the evolution of a quantum system are linear.

POSTULATE III

Each dynamical variable Ω is represented in $\mathcal{H}$ by a Hermitian operator $\hat{\Omega}$.

- The correspondence principle: The relationship between the operator (observable) and the dynamical variable is the same as in the classical mechanics.
  Example: if $x \Rightarrow \hat{x}$, $p_x \Rightarrow \hat{p}_x$ then

$$T \Rightarrow \hat{T} = \frac{\hat{p}^2}{2m}, \quad kx^2 \Rightarrow k\hat{x}^2$$

$$\hat{\boldsymbol{r}} = (\hat{x}_1, \hat{x}_2, \hat{x}_3), \quad \hat{\boldsymbol{p}} = (\hat{p}_1, \hat{p}_2, \hat{p}_3)$$

$$\boldsymbol{L} \Rightarrow \hat{\boldsymbol{L}} = [\hat{\boldsymbol{r}} \times \hat{\boldsymbol{p}}]$$

- Each observable has a complete set of eigenvectors and real eigenvalues. Its eigenvalue problem

$$\hat{\Omega}|\omega_n\rangle = \omega_n|\omega_n\rangle,$$

  defines a complete basis $|\omega_n\rangle$.

- If the eigenvectors of $\hat{\Omega}$ are taken as the basis in $\mathcal{H}$ we say that we have the $\{\Omega\}$ representation.

- A vector space $\mathcal{H}$ spanned by the basis of the representation $\{\Omega\}$ is referred to as *the* Ω *space*, e.g. the *coordinate space*, the *momentum space*, etc.

- The closure relation gives the resolution of the identity

$$\hat{I} = \sum_n |\omega_n\rangle\langle\omega_n|,$$

Therefore for a vector $|A\rangle = \sum_n |\omega_n\rangle \langle\omega_n|A\rangle$

and for an observable $\hat{\Xi} = \sum_{mn} |\omega_m\rangle\langle\omega_n|\hat{\Xi}|\omega_m\rangle\langle\omega_n|.$

- Matrix element of the operator $\hat{\Xi}$:

$$\Xi_{mn} = \langle\omega_n|\hat{\Xi}|\omega_m\rangle$$

- Spectral decomposition of $\hat{\Omega}$ in its own representation:

$$\hat{\Omega} = \sum_n |\omega_n\rangle\omega_n\langle\omega_n|.$$

Conclusions:

- In a given representation $\{\Omega\}$, a vector $|A\rangle$ is represented by a set of numbers $A_n = \langle\omega_n|A\rangle$ labeled by one index, i.e. a column matrix composed of the numbers A_n, $n = 1, 2, \ldots$, is the representative of $|A\rangle$.
- An operator $\hat{\Xi}$ is represented by a set of numbers $\Xi_{mn} = \langle\omega_m|\hat{\Xi}|\omega_n\rangle$ labeled by two indices, i.e. a square matrix composed of elements Ξ_{mn}, $m, n = 1, 2, \ldots$ is the representative of $\hat{\Xi}$.
- A transition from one representation to another is equivalent to a transition from one orthonormal basis to another orthonormal basis in the same space; it is described by a unitary transformation performed on all the representatives of vectors and operators. Such a transformation changes the numerical values of the matrix elements, however it does not change the physical content of the theory.

"Measurement postulates" defining links between the formalism and the physical reality modeled by this formalism.

POSTULATE IV

Each result of a measurement of Ω is equal to one of the eigenvalues of $\hat{\Omega}$.

POSTULATE V

The probability $P(\omega_n)$ that ω_n is the result of a measurement of Ω performed on a quantum system in a state $|A\rangle$ is equal to

$$P(\omega_n) = \langle A|\hat{P}_n|A\rangle = \langle A|\omega_n\rangle\langle\omega_n|A\rangle.$$

Conclusions:

- An observable $\{\Omega\}$ has a precisely defined value in its eigenstate only: $P(\omega_n) = \delta_{kn}$ only if $|A\rangle = |\omega_k\rangle$.
- Two different dynamical variables may have precisely defined values in a given state, only if this state is simultaneously an eigenstate of the corresponding observables. This is possible if these two operators commute.

THE EQUATIONS OF MOTION

THE SCHRÖDINGER PICTURE

$|\psi, t\rangle$ – a time-dependent state vector

The *evolution operator* $\hat{T}(t, t_0)$:

$$|\psi, t\rangle = \hat{T}(t, t_0)|\psi, t_0\rangle$$

moves the state vector from t_0 to t.

For an infinitesimal displacement in time:

$$\hat{T} \equiv \hat{T}(t_0 + \delta t, t_0) = \hat{I} - \frac{i}{\hbar}\hat{H}\delta t,$$

Thus, $\hat{H}$ is the generator of the infinitesimal displacement in time.

If $\hat{T}$ is unitary then $\hat{H}$ is Hermitian.

By analogy to the classical mechanics it is identified with the Hamiltonian of the quantum system.

The Schrödinger equation

From the definition of $\hat{H}$:

$$\frac{|\psi, t_0 + \delta t\rangle - |\psi, t_0\rangle}{\delta t} = -\frac{i}{\hbar}\hat{H}|\psi, t_0\rangle.$$

If $\delta t \to 0$ then

$$i\hbar\frac{d|\psi\rangle}{dt} = \hat{H}|\psi\rangle.$$

This is the Schrödinger equation in the representation-independent form.

The initial state $|\psi, t_0\rangle$ is an arbitrary normalized vector in $\mathcal{H}$
Therefore

$$i\hbar \frac{d\hat{T}}{dt} = \hat{H}\hat{T}.$$

If $\hat{H}$ is time-independent then

$$\hat{T}(t, t_0) = \mathrm{e}^{-\frac{i}{\hbar}\hat{H}(t-t_0)}.$$

If we select the representation in which $\hat{H}$ is diagonal, i.e. if

$$\hat{H}|E_n\rangle = E_n|E_n\rangle,$$

then

$$\hat{T}|E_n\rangle = \mathrm{e}^{-\frac{i}{\hbar}E_n(t-t_0)}|E_n\rangle,$$

Conclusions:

- If $\hat{H}$ is time-independent, the quantum system would remain permanently in its eigenstate.
- Transitions between different eigenstates of the Hamiltonian are possible as a consequence of time-dependent perturbations (e.g. due to an external electromagnetic field).

For an arbitrary state:

$$|\psi, t_0\rangle = \sum_n c_n(0)|E_n\rangle.$$

The time evolution:

$$|\psi, t\rangle = \sum_n c_n(t)|E_n\rangle = \hat{T}|\psi, t_0\rangle$$

with

$$c_n(t) = c_n(0)\mathrm{e}^{-\frac{i}{\hbar}E_n(t-t_0)}.$$

This is a general solution of the Schrödinger equation in the case of a time-independent Hamiltonian.

The state vector changes in time, but the distribution of the $P(E_n)$ probabilities remains constant since $|c_n(t)|^2 = |c_n(0)|^2$.

THE HEISENBERG PICTURE

One may obtain another, equivalent, mode of description of the evolution of a quantum system by performing a time dependent unitary transformation on the vectors and operators of the Schrödinger picture.

Transformation $\hat{T}^\dagger$ defines the *Heisenberg picture*:

$$|\psi_H\rangle = \hat{T}^\dagger |\psi_S\rangle = \hat{T}^{-1}|\psi_S\rangle$$
$$\hat{\Xi}_H = \hat{T}^\dagger \hat{\Xi}_S \hat{T},$$

One can see that $|\psi_H\rangle = |\psi, t_0\rangle$ is time-independent.

Operators in the Schrödinger picture are time-independent.
In the Heisenberg picture the operators are time-dependent.

The Heisenberg equation of the motion:

$$i\hbar \frac{d\hat{\Xi}_H}{dt} = [\hat{\Xi}_H, \hat{H}] + i\hbar \frac{\partial \hat{\Xi}_H}{\partial t}.$$

Conclusion:
If the quantum system is isolated then an observable is time-independent (i.e. it describes a constant of the motion) if it commutes with the Hamiltonian.

COORDINATE AND MOMENTUM REPRESENTATIONS

The coordinate operator

The basis vectors of the coordinate representation:

$$\hat{\mathbf{r}}|\mathbf{r}\rangle = \mathbf{r}|\mathbf{r}\rangle,$$

The spectrum is continuous and extends from $-\infty$ to $+\infty$ in each dimension.

The orthonormality condition:

$$\langle \mathbf{r}|\mathbf{r}'\rangle = \delta(\mathbf{r} - \mathbf{r}').$$

The closure relation:

$$\hat{I} = \int_{R_3} |\mathbf{r}\rangle d^3\mathbf{r}\langle \mathbf{r}|.$$

The representative of a state vector $|\boldsymbol{\psi}, \boldsymbol{t}\rangle$ depends upon the basis vector $\mathbf{r}$, i.e. it is a function of $\mathbf{r}$. It is called the **wavefunction**:

$$\boldsymbol{\psi}(\mathbf{r}, \boldsymbol{t}) \equiv \langle \mathbf{r} | \boldsymbol{\psi}, \boldsymbol{t} \rangle.$$

Similarly,

$$\psi(\mathbf{r}, t)^* = \langle \psi, t | \mathbf{r} \rangle.$$

The normalization condition:

$$1 = \langle \psi, t | \psi, t \rangle = \int_{R_3} \langle \psi, t | \mathbf{r} \rangle d^3\mathbf{r} \langle \mathbf{r} | \psi, t \rangle = \int_{R_3} |\psi(\mathbf{r}, t)|^2 d^3\mathbf{r}.$$

The momentum operator

Electron diffraction experiments and the de Broglie hypothesis say that the coordinate representative of an eigenvector of the momentum operator is a plane wave:

$$\langle \mathbf{r}|\mathbf{p}\rangle = \frac{1}{\sqrt{(2\pi\hbar)^3}} \mathrm{e}^{\frac{i}{\hbar}\mathbf{r}\cdot\mathbf{p}},$$

where

$$\hat{\mathbf{p}}|\mathbf{p}\rangle = \mathbf{p}|\mathbf{p}\rangle$$

By differentiating with respect to $\mathbf{r}$ one gets

$$-\frac{\hbar}{i}\nabla_{\mathbf{r}}\langle \mathbf{p}|\mathbf{r}\rangle = \mathbf{p}\langle \mathbf{p}|\mathbf{r}\rangle.$$

An observable which depends upon the coordinate operator only is diagonal in the coordinate representation:

$$\langle \mathbf{r}|f(\hat{\mathbf{r}})|\mathbf{r}'\rangle = f(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}').$$

Also:

$$\begin{aligned}\langle \mathbf{r}|\hat{\mathbf{p}}|\mathbf{r}'\rangle &= \int \langle \mathbf{r}|\hat{\mathbf{p}}|\mathbf{p}\rangle\langle \mathbf{p}|\mathbf{r}'\rangle d^3\mathbf{p} = \int \mathbf{p}\langle \mathbf{r}|\mathbf{p}\rangle\langle \mathbf{p}|\mathbf{r}'\rangle d^3\mathbf{p} \\ &= -i\hbar\nabla_{\mathbf{r}}\int \langle \mathbf{r}|\mathbf{p}\rangle\langle \mathbf{p}|\mathbf{r}'\rangle d^3\mathbf{p} = -i\hbar\nabla_{\mathbf{r}}\delta(\mathbf{r}-\mathbf{r}'),\end{aligned}$$

and similarly $\langle \mathbf{r}|\hat{\mathbf{p}}|\psi,t\rangle = -i\hbar\nabla_{\mathbf{r}}\psi(\mathbf{r},t)$.

In this way we have derived the well known formula for the momentum operator in the coordinate representation:

$$\hat{\mathbf{p}} = -i\hbar\,\nabla_{\mathbf{r}},$$

The Schrödinger equation

By multiplying the representation-independent Schrödinger equation by $\langle \mathbf{r}|$ from the left and inserting the resolution of identity between $\hat{H}$ and $|\psi, t\rangle$, we get

$$i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} = \int H(\mathbf{r}, \mathbf{r}')\psi(\mathbf{r}', t)d\mathbf{r}',$$

where

$$H(\mathbf{r}, \mathbf{r}') = \langle \mathbf{r}|\hat{H}|\mathbf{r}'\rangle.$$

If

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{r}}),$$

then

$$\langle \mathbf{r}|\hat{H}|\mathbf{r}'\rangle = \left[-\frac{\hbar^2}{2m}\triangle_{\mathbf{r}'} + V(\mathbf{r}')\right]\delta(\mathbf{r}-\mathbf{r}').$$

In consequence

$$i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\triangle_{\mathbf{r}} + V(\mathbf{r})\right]\psi(\mathbf{r},t).$$

The momentum representation:

The basis in $\mathcal{H}$ is formed by the eigenvectors of the momentum operator.

The state vector in the momentum representation:

$$\chi(\mathbf{p}, t) \equiv \langle \mathbf{p} | \psi, t \rangle.$$

The coordinate and the momentum representatives of the state vector are related by a Fourier transformation:

$$\psi(\mathbf{r}, t) = \langle \mathbf{r} | \psi, t \rangle = \int_{R_3} \langle \mathbf{r} | \mathbf{p} \rangle \chi(\mathbf{p}, t) d^3\mathbf{p} = \frac{1}{\sqrt{(2\pi\hbar)^3}} \int_{R_3} \mathrm{e}^{\frac{i}{\hbar}\mathbf{r}\cdot\mathbf{p}} \chi(\mathbf{p}, t) d^3\mathbf{p}.$$

Similarly:

$$\langle \mathbf{p} | f(\hat{\mathbf{p}}) | \mathbf{p}' \rangle = f(\mathbf{p}) \delta(\mathbf{p} - \mathbf{p}')$$

and

$$\langle \mathbf{p} | \hat{\mathbf{r}} | \mathbf{p}' \rangle = -i\hbar \nabla_p \delta(\mathbf{p} - \mathbf{p}').$$

The Schrödinger equation in momentum representation

$$i\hbar\frac{\partial\chi(\mathbf{p},t)}{\partial t}=\int_{R_3}H(\mathbf{p},\mathbf{p}')\chi(\mathbf{p}',t)d^3\mathbf{p}',$$

where

$$H(\mathbf{p},\mathbf{p}')=\langle\mathbf{p}|\hat{H}|\mathbf{p}'\rangle.$$

If

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{r}}),$$

then

$$i\hbar \frac{\partial \chi(\mathbf{p}, t)}{\partial t} = \frac{\mathbf{p}^2}{2m}\chi(\mathbf{p}, t) + \int V(\mathbf{p}, \mathbf{p}')\chi(\mathbf{p}', t)d\mathbf{p}',$$

where

$$\begin{aligned} V(\mathbf{p}, \mathbf{p}') &= \langle \mathbf{p}|V(\hat{\mathbf{r}})|\mathbf{p}'\rangle \\ &= \int \langle \mathbf{p}|\mathbf{r}\rangle\langle \mathbf{r}|V(\hat{\mathbf{r}})|\mathbf{r}'\rangle\langle \mathbf{r}'|\mathbf{p}'\rangle d^3\mathbf{r}\; d^3\mathbf{r}' \\ &= \frac{1}{(2\pi\hbar)^3}\int V(\mathbf{r})e^{\frac{i}{\hbar}(\mathbf{p}-\mathbf{p}')\mathbf{r}}d^3\mathbf{r}. \end{aligned}$$

Note:

In the case of the harmonic oscillator with

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + \frac{m\omega^2}{2}\hat{\mathbf{r}}^2$$

the Schrödinger equation in the coordinate and in the momentum representation has the same mathematical structure.

In most of other cases, the Schrödinger equation in the momentum representation is an integral equation in which the potential function is the kernel of the integral.

THE SCHRÖDINGER
AND
THE DIRAC EQUATIONS

Invariance properties

Given an equation

$$\hat{\Omega}\Psi = 0$$

and a transformation S. The transformed equation reads

$$\hat{\Omega}'\Psi' = 0$$

where

$$\hat{\Omega}' = S\hat{\Omega}S^{-1}$$

and

$$\Psi' = S\Psi.$$

The results given by a model described by this equation are independent of the transformation if $\hat{\Omega}$ is invariant with respect to S:

$$S\hat{\Omega}S^{-1} = \hat{\Omega}$$

i.e. if

$$\left[S, \hat{\Omega}\right] = 0.$$

In such a case S is called *a symmetry transformation*.

The transformation S is a symmetry transformation if one cannot design an experiment which would allow to detect whether this transformation has been performed or not.

For example, a translation in three-dimensional space of a free particle or a rotation of a free atom belong the symmetry operations of these systems.

The most universal symmetry is related to transformations between two inertial (i.e. moving with a constant velocity relative to each other) reference frames.

Newton: *"The motions of bodies included in a given space are the same among themselves, whether that space is at rest or moves uniformly forward in a straight line"*.

Poincaré (principle of relativity): *"The laws of physical phenomena must be the same for a fixed observer as for an observer who has a uniform motion of translation relative to him, so that we have not, nor can we possibly have, any means of discerning whether or not we are carried along in such a motion"*.

Conclusion:

All physical theories, including quantum mechanics, should be formulated in such a way that the results of all measurements are the same independent of whether they are taken by an observer in rest or by an observer moving in uniform translation.

This implies that the equation of the motion must be invariant with respect to a transformation from one inertial frame to another. In the non-relativistic case this implies the invariance of the Hamiltonian.

Transformations of the reference frames:

Newtonian mechanics is invariant with respect to the Galilean transformations:

$$\begin{aligned} x_1' &= x_1 - ut, \\ x_2' &= x_2, \quad x_3' = x_3, \\ t' &= t, \end{aligned}$$

The axes of both frames are parallel,
The unprimed quantities: the frame is "in rest"
The primed quantities:
the frame is moving with a constant velocity u along the x_1 axis.

Michelson and Morley experiment (1887):

The velocity of light measured from different inertial reference frames is always the same.

Inconsistent with the Galilean transformation.

Einstein (1905): The transformation between two inertial frames which leads to the conclusion that the velocity of light is a universal constant is the Lorentz transformation

$$x_1' = \frac{x_1 - ut}{\sqrt{1 - u^2/c^2}}, \quad x_2' = x_2, \quad x_3' = x_3, \quad t' = \frac{t - ux_1/c^2}{\sqrt{1 - u^2/c^2}}$$

with respect to which the Maxwell equations are invariant. Mechanics has to be formulated in such a way that it is also invariant with respect to this transformation.

Result: the special theory of relativity.

The *causality principle*: In a Lorentz-invariant theory no signal can travel with a velocity larger than that of light.

A requirement of invariance with respect to either Galilean or Lorentzian transformation imposes very strong restrictions on the structure of a theory and on the form of the basic equations.

A model which is Galileo-invariant is called NON-RELATIVISTIC.

In a non-relativistic model three coordinates of a point, momentum, velocity, are three-component vectors, while time or energy are invariants (scalars). Therefore the equation of motion (the Schrödinger equation) is invariant with respect to the Galilean transformation if the Hamiltonian is Galileo-invariant.

The non-relativistic (Galileo-invariant) Hamilton function of a free particle:

$$H_0 = \frac{p^2}{2m}.$$

If the particle moves in an external field characterized by

- Scalar potential V and
- Vector potential $\mathbf{A}$,

the non-relativistic Hamilton function is

$$H = \frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right)^2 + V.$$

The correspondence principle applied to the nonrelativistic Hamilton function leads to the nonrelativistic Hamiltonian operator and opens a way to formulation of the nonrelativistic (Schrödinger) quantum mechanics.

Models which are Lorentz-invariant, are called RELATIVISTIC

In a relativistic model three coordinates: x_1, x_2, x_3 and time, $x_4 = ict$, form a four-component vector.

Also momentum and energy, current and density, are components of the same four-vector.

Conclusion: In a Lorentz-invariant model, the space coordinates of a particle and the time corresponding to this particle should appear on an equal footing, contrary to a non-relativistic model, where time is an absolute quantity, the same for all particles.

In particular, if an equation is of the first-order in time, it must be of the first-order in all coordinates.

In the general equation of motion

$$i\hbar\frac{d|\psi\rangle}{dt} = \hat{H}|\psi\rangle.$$

time plays a special role.

We say that this equation is written in a non-covariant form, i.e. its possible Lorentz-invariance is hidden and may be discovered only after analyzing simultaneously the form of the Hamiltonian and the structure of the equation.

A Lorentz-invariant quantum mechanical equation (the Dirac equation) results from the general equation of motion if the Hamilton operator is derived, through the correspondence principle, from the relativistic Hamilton function.

The relativistic Hamilton function of a free particle:

$$H_0 \equiv E_p = mc^2 \sqrt{1 + \left(\frac{p}{mc}\right)^2}.$$

Its resolution into a power series of $\left(\frac{p}{mc}\right)^2$:

$$H_0 = mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + mc^2\, O\left[(p/mc)^6\right],$$

The Hamilton function of a particle in an external field:

$$H = mc^2 \sqrt{1 + \frac{1}{m^2c^2}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right)^2} + V.$$

Note:

No Lorentz-invariant equation describing more than one particle can be written in the form

$$i\hbar \frac{d|\psi\rangle}{dt} = \hat{H}|\psi\rangle.$$

In the case of N particles such an equation would have to depend on N independent time coordinates.

The relativistic quantum mechanics

The first Lorentz-invariant equation describing the evolution of a quantum state was obtained by Schrödinger, Klein and Gordon.

They took a square of the operators on both sides of

$$i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t} = \hat{H}\psi(\mathbf{r},t).$$

For the free-particle relativistic Hamiltonian they got:

$$-\hbar^2\frac{\partial^2\psi(\mathbf{r},t)}{\partial\, t^2} = (m^2c^4 + c^2\hat{p}^2)\psi(\mathbf{r},t).$$

Putting

$$\hat{p}^2\psi = -\hbar^2 \triangle \psi$$

we get

$$(\Box - \kappa^2)\psi = 0,$$

where

$$\Box = \triangle - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}$$

and

$$\kappa = \frac{mc}{\hbar}.$$

This equation is known as the Klein-Gordon equation. It

- Is relativistically invariant,
- May be generalized to account for an external field,
- **Does not describe electrons**,
- Describes spinless particles.

In order to derive a relativistic equation describing an electron, let us consider the non-relativistic free-particle Hamiltonian

$$\hat{H}_0^{\rm a} = \frac{\hat{\mathbf{p}}^2}{2m}.$$

For a spin-$\frac{1}{2}$ particle one may take

$$\hat{H}_0^{\rm b} = \frac{(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})^2}{2m},$$

instead, where $\boldsymbol{\sigma}$ are the Pauli spin matrices.

Due to the identity

$$(\boldsymbol{\sigma}\hat{\mathbf{a}})(\boldsymbol{\sigma}\hat{\mathbf{b}}) = (\hat{\mathbf{a}}\cdot\hat{\mathbf{b}}) + i\boldsymbol{\sigma}\cdot[\hat{\mathbf{a}}\times\hat{\mathbf{b}}],$$

both equations are consistent with the correspondence principle.

However, in equation

$$H_0^{\mathrm{a}}\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

Ψ is a scalar function while in equation

$$H_0^{\mathrm{b}}\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

Ψ is a two-component function.

If the particle moves in an external field the difference between these two equations becomes even larger.

After the substitution

$$\hat{\mathbf{p}} \to \hat{\mathbf{p}} - \frac{e}{c}\hat{\mathbf{A}}$$

one gets

$$\hat{H}^{\mathrm{a}} = \frac{1}{2m}\left(\hat{\mathbf{p}} - \frac{e}{c}\hat{\mathbf{A}}\right)^2$$

and

$$\hat{H}^{\mathrm{b}} = \frac{1}{2m}\left(\hat{\mathbf{p}} - \frac{e}{c}\hat{\mathbf{A}}\right)^2 - \frac{e\hbar}{2mc}\left(\boldsymbol{\sigma}\cdot\hat{\mathbf{B}}\right),$$

where $\hat{\mathbf{B}} = \nabla \times \hat{\mathbf{A}}$ is the magnetic field operator.

The $\boldsymbol{\sigma}$-dependent term was introduced to the Schrödinger equation by Pauli on a purely phenomenological basis in order to account for the interaction of the electron spin magnetic moment with the external magnetic field.

Spin-$\frac{1}{2}$ particle.

The correspondence principle applied in the same way as in $\hat{H}_{\rm b}$ to

$$E_p^2 - c^2\mathbf{p}^2 = m^2c^4$$

gives the following quantum equation:

$$[\hat{E} - c\,(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})][\hat{E} + c\,(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})]\Psi = m^2c^4\Psi,$$

where Ψ is a two-component function.
One may rewrite this equation in the form

$$\hat{\Omega}_-\hat{\Omega}_+\Psi = m^2c^4\Psi,$$

where

$$\hat{\Omega}_\pm = \hat{E} \pm c\,(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}).$$

Dirac equation in the representation of Weyl

Defining

$$\begin{aligned} \Psi^{\mathrm{r}} &\equiv \frac{1}{mc^2}\hat{\Omega}_+\Psi \\ \Psi^{\mathrm{l}} &\equiv \Psi \end{aligned}$$

we get

$$\begin{aligned} \hat{\Omega}_+\Psi^{\mathrm{l}} &= mc^2\Psi^{\mathrm{r}}, \\ \hat{\Omega}_-\Psi^{\mathrm{r}} &= mc^2\Psi^{\mathrm{l}}, \end{aligned}$$

i.e.

$$\begin{pmatrix} \hat{E} - c\,(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}), & -mc^2 \\ -mc^2, & \hat{E} + c\,(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}) \end{pmatrix} \begin{pmatrix} \Psi^{\mathrm{l}} \\ \Psi^{\mathrm{r}} \end{pmatrix} = 0.$$

Taking

$$\hat{E} = i\hbar \frac{\partial}{\partial t}$$

This pair of equations may be rewritten as

$$i\hbar \frac{\partial \boldsymbol{\Psi}_{\mathrm{w}}}{\partial t} = \hat{H}_{\mathrm{w}} \boldsymbol{\Psi}_{\mathrm{w}}$$

where

$$\boldsymbol{\Psi}_{\mathrm{w}} = \begin{pmatrix} \Psi^{\mathrm{r}} \\ \Psi^{\mathrm{l}} \end{pmatrix}$$

is a four-component wavefunction and

$$\hat{H}_{\mathrm{w}} = \begin{pmatrix} c\,(\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}), & mc^2 \\ mc^2, & -c\,(\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}) \end{pmatrix}$$

We derived **Dirac equation in the representation of Weyl**.

Representations in the spinor space

Let A be non-singular 4×4 matrix. Then the equation

$$i\hbar \frac{\partial \mathbf{\Psi}}{\partial t} = \hat{H}\,\mathbf{\Psi}$$

where

$$\hat{H} = A\,\hat{H}_{\mathrm{w}}\,A^{-1}$$

and

$$\mathbf{\Psi} = A\,\mathbf{\Psi}_{\mathrm{w}}.$$

is equivalent to the original equation.

The standard (Dirac-Pauli) representation is obtained if

$$A = \frac{1}{\sqrt{2}} \begin{pmatrix} I, & I \\ I, & -I \end{pmatrix} = A^{-1}.$$

Dirac-Pauli representation

In this representation

$$i\hbar\frac{\partial \mathbf{\Psi}_{\rm D}}{\partial t} = \hat{H}_{\rm D}\,\mathbf{\Psi}_{\rm D}$$

where

$$\mathbf{\Psi}_{\rm D} = \begin{pmatrix} \Psi^{\rm L} \\ \Psi^{\rm S} \end{pmatrix}$$

is the Dirac wavefunction [$\Psi^{\rm L}$ / $\Psi^{\rm S}$ are its large / small components] and

$$\hat{H}_{\rm D} = \begin{pmatrix} mc^2, & c\,(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}) \\ c\,(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}), & -mc^2 \end{pmatrix} = c\,\boldsymbol{\alpha}\cdot\mathbf{p} + \beta\,mc^2$$

with

$$\boldsymbol{\alpha} = \begin{pmatrix} 0, & \boldsymbol{\sigma} \\ \boldsymbol{\sigma}, & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} I, & 0 \\ 0, & -I \end{pmatrix}$$

External fields

In the presence of an external electromagnetic field the free-particle Dirac Hamiltonian has to be replaced by

$$\hat{H}_{\mathrm{D}} = c\,\boldsymbol{\alpha}\cdot\left(\hat{\mathbf{p}} - \frac{e}{c}\hat{\mathbf{A}}\right) + \beta\, mc^2 + \hat{V}.$$

It is important to note that equations:

$$i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t}=\frac{\hat{\mathbf{p}}^2}{2m}\Psi(\mathbf{r},t)$$

and

$$i\hbar\frac{\partial\boldsymbol{\Psi}(\mathbf{r},t)}{\partial t}=\left[c\,\boldsymbol{\alpha}\cdot\hat{\mathbf{p}}+\beta\,mc^2\right]\boldsymbol{\Psi}(\mathbf{r},t)$$

are defined in different Hilbert spaces.

The Hilbert space of the first equation is $\mathcal{H}$. In this case it is spanned by the set of eigenvectors of the coordinate operator. The second equation is represented in a space $\mathcal{H}_{\mathrm{D}}$ which is a tensor product of $\mathcal{H}$ and a 4-dimensional spin-space $\mathcal{H}_\Sigma$ in which operators $\boldsymbol{\alpha}$ and β are represented as 4×4 matrices:

$$\mathcal{H}_D=\mathcal{H}\otimes\mathcal{H}_\Sigma.$$

Non-relativistic limit

The non-relativistic Schrödinger equation may also be written as a first-order, four-component equation.

For a stationary state, after shifting the energy scale by mc^2, i.e. $E - mc^2 \to E$, the Dirac equation may be rewritten as

$$\begin{pmatrix} -E, & c(\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}) \\ c\,(\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}), & -E - 2mc^2 \end{pmatrix} \begin{pmatrix} \Psi^{\mathrm{L}} \\ \Psi^{\mathrm{S}} \end{pmatrix} = 0.$$

From here

$$\begin{pmatrix} -E, & (\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}) \\ (\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}), & -2m - Ec^{-2} \end{pmatrix} \begin{pmatrix} \Psi^{\mathrm{L}} \\ c\Psi^{\mathrm{S}} \end{pmatrix} = 0.$$

Lévy-Leblond equation

In the non-relativistic approximation $Ec^{-2} = 0$ and

$$\begin{pmatrix} -E, & (\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}) \\ (\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}), & -2m \end{pmatrix} \begin{pmatrix} \Psi^{\mathrm{L}} \\ c\Psi^{\mathrm{S}} \end{pmatrix} = 0.$$

This is Lévy-Leblond equation. It is defined in the same space as the Dirac equation.

The elimination of $c\Psi^{\mathrm{S}}$ gives

$$\frac{(\boldsymbol{\sigma} \cdot \mathbf{p})^2}{2m} \Psi^{\mathrm{L}} = E\Psi^{\mathrm{L}}$$

SIMPLE SOLUTIONS

A free particle

Both Schrödinger and Dirac Hamiltonians commute with the momentum operator. Then, in both cases the eigenstates of the Hamiltonian may be chosen to be eigenfunctions of the momentum and represented by the plane waves. The eigenfunction of the free-particle Dirac equation, corresponding to the momentum $\mathbf{p}$, may be expressed as

$$\psi(\mathbf{r}) = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} \frac{\mathrm{e}^{\frac{i}{\hbar}(\mathbf{r}\cdot\mathbf{p})}}{\sqrt{2\pi\hbar}^3},$$

where $\mathbf{r}$-independent ψ_k, $k = 1, 2, 3, 4$ form a four-component *spinor*.

The components of the spinor may be obtained from the Dirac equation:

$$\begin{aligned}(mc^2 - E)\psi^{\mathrm{L}} + c\,(\boldsymbol{\sigma}\cdot\mathbf{p})\psi^{\mathrm{S}} &= 0,\\ c\,(\boldsymbol{\sigma}\cdot\mathbf{p})\psi^{\mathrm{L}} - (mc^2 + E)\psi^{\mathrm{S}} &= 0,\end{aligned}$$

where $\mathbf{p}$ are eigenvalues of $\hat{\mathbf{p}}$ and

$$\psi^{\mathrm{L}} = \begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}, \quad \psi^{\mathrm{S}} = \begin{pmatrix}\psi_3\\ \psi_4\end{pmatrix}$$

If $|E - mc^2| = |\varepsilon| << mc^2$ (non-relativistic approximation) then

$$|\psi^{\mathrm{S}}| \approx \left|\frac{(\boldsymbol{\sigma}\cdot\mathbf{p})}{2mc}\psi^{\mathrm{L}}\right| << |\psi^{\mathrm{L}}|.$$

Therefore ψ^{L} and ψ^{S} are, respectively, referred to as the *large* and the *small* components of the Dirac wavefunction.

The free-particle Schrödinger Hamiltonian commutes with the orbital angular momentum operator $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$, but the Dirac one does not.

For a free particle, $\hat{\mathbf{L}}$ is a constant of the motion for the Schrödinger electron but not for the Dirac one.

The free-particle Dirac Hamiltonian commutes with

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \frac{\hbar}{2}\boldsymbol{\Sigma},$$

where

$$\boldsymbol{\Sigma} = \begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix}$$

It is defined as the total angular momentum operator of the electron, composed of the orbital part $\hat{\mathbf{J}}$ and the spin part $\frac{\hbar}{2}\,\boldsymbol{\Sigma}$.

The eigenvalues of the Dirac Hamiltonian are:

$$E = \pm mc^2 \sqrt{1 + \left(\frac{p}{mc}\right)^2}.$$

Then, the spectrum of the Dirac Hamiltonian is not limited from below.

One should expect that an electron in a positive energy state should fall into a negative energy state and emit a photon with an energy which may be infinite, since the spectrum is unlimited. In order to solve this difficulty Dirac proposed that all the negative-energy states are filled under normal conditions and the Pauli exclusion principle prevents transitions to these states. An excitation of one negative-energy electron results in creation of a hole in the "Dirac vacuum" and of one positive-energy electron and corresponds to the creation of an electron-positron pair. This interpretation contains a self-contradiction: the Dirac model describes a single electron. At the same time, it is unable even to explain the behaviour of a free particle without assuming that it is surrounded by an infinite number of particles occupying the negative-energy states.

Dirac velocity

In the Schrödinger case:

$$\left(\frac{d\hat{\mathbf{r}}}{dt}\right)_{\mathrm{S}} = \frac{i}{\hbar}[\hat{H}_{\mathrm{S}}, \hat{\mathbf{r}}] = \frac{\hat{\mathbf{p}}}{m}.$$

In the Dirac case:

$$\left(\frac{d\hat{\mathbf{r}}}{dt}\right)_{\mathrm{D}} = \frac{i}{\hbar}[\hat{H}_{\mathrm{D}}, \hat{\mathbf{r}}] = c\,\boldsymbol{\alpha}.$$

This result is very strange in many aspects. First, the eigenvalues of α_k are ± 1. Therefore the eigenvalues of $\left(\frac{d\hat{\mathbf{r}}}{dt}\right)_{\mathrm{D}}$ are equal to $\pm c$.

Besides, different components of $\left(\frac{d\hat{\mathbf{r}}}{dt}\right)_{\mathrm{D}}$ do not commute. Then, a measurement of one component of the Dirac velocity is incompatible with a measurement of another one. This is also strange since different components of the momentum operator do commute. Moreover, $\left(\frac{d\hat{\mathbf{r}}}{dt}\right)_{\mathrm{D}}$ does not commute with $\hat{H}_{\mathrm{D}}$ and therefore the velocity is not a constant of the motion despite the fact that the particle is free.

An explanation of this fact involves an analysis of the time-dependence of $\boldsymbol{\alpha}$ and of the coordinate operator $\hat{\mathbf{r}}$. It results that both of them execute very rapid oscillations with an angular frequency $(2mc^2)/\hbar = 1.5 \cdot 10^{21}\mathrm{sec}^{-1}$. This motion, named by Schrödinger *Zitterbewegung*, is due to an interference between the positive- and negative-energy components of the wavepacket describing the electron. Intuitively it may be interpreted as a consequence of a permanent creation and annihilation of the so called *virtual* electron-positron pairs.

In order to explore this problem in more detail it is convenient to introduce the *even* and *odd* operators. An even operator acting on a function which belongs to the positive (negative) energy subspace of a free electron transforms it into a function which belongs to the same subspace. An odd operator transforms a positive (negative)-energy-subspace function into a function which belongs to the complementary subspace.
Operators

$$\hat{\Pi}_{\pm} = \frac{1}{2}(\hat{I} \pm \hat{\Lambda}),$$

where

$$\hat{\Lambda} = \frac{\hat{H}_{\mathrm{D}}}{E_p} = \frac{c\,(\boldsymbol{\alpha} \cdot \hat{\mathbf{p}}) + \beta\, mc^2}{\sqrt{m^2c^4 + c^2p^2}}$$

is the operator of the sign of energy (its eigenvalues are $+1$ for the positive- and -1 for the negative-energy states), are projection operators to the positive $(\hat{\Pi}_+)$ and to the negative $(\hat{\Pi}_-)$ energy subspace.

For example, the operator $\hat{\Pi}_+\hat{\Omega}\hat{\Pi}_+$ acts in the free-electron positive-energy space only. In the free particle space each operator, say $\hat{\Omega}$, may be decomposed into its even part $[\hat{\Omega}]$ and its odd part $\{\hat{\Omega}\}$:

$$\hat{\Omega} = [\hat{\Omega}] + \{\hat{\Omega}\},$$

where

$$\begin{aligned} [\hat{\Omega}] &= \frac{1}{2}(\hat{\Omega} + \hat{\Lambda}\hat{\Omega}\hat{\Lambda}), \\ \{\hat{\Omega}\} &= \frac{1}{2}(\hat{\Omega} - \hat{\Lambda}\hat{\Omega}\hat{\Lambda}). \end{aligned}$$

After some algebra one can see that

$$\left[\left(\frac{d\hat{\mathbf{r}}}{dt}\right)_{\mathrm{D}}\right] = c\,[\boldsymbol{\alpha}] = \frac{c^2\mathbf{p}}{E_p}\hat{\Lambda},$$

i.e. the result corresponding to the standard definition of velocity.

One-electron atom

An exact quantum-mechanical treatment of a hydrogen-like atom is equivalent to solving a two-body problem with a Coulomb interaction. In the nonrelativistic case it may be solved exactly. By the separation of the center of mass the six-dimensional Schrödinger equation is split into two three-dimensional equations. One of them describes a free motion of the center of mass and the other one – the relative motion of the electron and the nucleus.

The Hamiltonian which governs the relative motion:

$$\hat{H}_{\mathrm{S}} = \frac{\hat{\mathbf{p}}^2}{2\mu} - \frac{Ze^2}{r},$$

where Ze is the nuclear charge,

$$\mu = \frac{mM}{m+M}$$

is the reduced mass; m – mass of electron and M – mass of the nucleus.

The Hamiltonian and the orbital angular momentum operators $\hat{L}^2$ and $\hat{L}_z$ form a set of mutually commuting operators.

The eigenvalue spectrum of $\hat{H}_{\rm S}$ consists of the discrete part (describing the bound states) and the continuous part (describing the ionized states). The discrete part of the eigenvalue problem may be written as

$$\hat{H}_{\rm S}\psi_{nlm}(r,\theta,\phi) = E_n^{\rm S}\psi_{nlm}(r,\theta,\phi)$$

where r, θ and ϕ are the spherical coordinate system variables and

$$n = 1, 2, \ldots,$$

$$l = 0, 1, \ldots, n-1,$$

$$m = -l, -l+1, \ldots, l$$

are the quantum numbers describing, respectively, the energy (the principal quantum number), the orbital angular momentum and its projection.

The eigenvalues (the energies of the bound states) in the Hartree atomic units (a.u.: $m = 1$, $e = 1$, $\hbar = 1$) are given by

$$E_n^{\mathrm{S}} = -\frac{Z^2}{2n^2}\frac{\mu}{m}\ \text{a.u.} = -\left(\frac{Z}{n}\right)^2 R_M,$$

where

$$R_M = \frac{\mu}{m} R_\infty$$

and

$$R_\infty = \frac{mc^2}{2}\,\alpha^2$$

are the Rydberg constants for the finite and infinite nuclear mass, respectively, and

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$$

is the fine structure constant.

The eigenfunctions are labeled by three quantum numbers and the degree of degeneracy is equal to n^2. There are two origins for this degeneracy. One, with respect to the quantum number m, is a consequence of the spherical symmetry of the problem (in all spherically symmetric one-electron systems this kind of degeneracy would appear). The second one, with respect to the quantum number l, is a consequence of a *dynamical symmetry* connected with some specific properties of the interaction potential. In the case of the non-relativistic one-electron atom there is an additional constant of the motion arising from the commutation of the so called *Runge-Lenz* vector with the Hamiltonian. The l-degeneracy is related to the existence of this constant of the motion and is removed if the potential is deformed so that it loses its Coulomb character.

The eigenfunctions of the hydrogen-like Hamiltonian are prototypes for most of approximate one-electron functions (orbitals) used in quantum chemical calculations. They may be expressed as

$$\psi_{nlm}(r,\theta,\phi) = \frac{1}{r} R_{nl}(r) Y_{lm}(\theta,\phi),$$

where Y_{lm} (the spherical harmonics) are the eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$ and R_{nl} are the radial functions.
The radial functions are of the form

$$R_{nl}(r) = W_n^l(r) e^{-Zr/n},$$

where W_n^l is a polynomial of the degree n with l-dependent coefficients.
The number of nodes of this polynomial is equal to $n - l$.
At the origin the radial part of the wavefunction $r^{-1}R_{nl}$ behaves as r^l, i.e. it vanishes for $r = 0$ if $l \neq 0$.

The spherical harmonics are, for $m \neq 0$, complex and:

$$Y_{l,-m} = (-1)^m Y^*_{lm}.$$

Their real combinations;

$$Y_{lm} + (-1)^m Y_{l,-m} \quad \text{and} \quad i\left[Y_{lm} - (-1)^m Y_{l,-m}\right]$$

may be expressed as

$$\frac{1}{r^l} \sum_{abc} C_{abc} x^a y^b z^c,$$

where $a + b + c = l$.

For $l = 0, 1, 2, 3, \ldots$ they are referred to as s,p,d,f,. . .-type functions, respectively.

The consecutive discrete states of the hydrogen-like atom are labeled by the quantum numbers n and l as $1s$, $2s$, $2p$, $3s$, $3p$, $3d$, ...

The standard Schrödinger model of a hydrogen-like atom does not contain spin. Spin may be introduced by using the phenomenological Pauli model. Then the wavefunction ψ_{nlm} has to be multiplied by a two-component spin function α or β corresponding, respectively, to the eigenvalues $+\frac{\hbar}{2}$ and $-\frac{\hbar}{2}$ of a projection $\hat{S}_z$ of the spin operator. These functions are referred to as *spinorbitals*. The spinorbitals may be combined according to the rules of coupling the angular momenta to form eigenfunctions of the total angular momentum operator which, of course, also commutes with the Hamiltonian. However introducing spin at this level does not influence the energy of the atom, unless the atom is placed into an external magnetic field when the Pauli term influences the energy (do not confuse with the Pauli relativistic corrections which result from a reduction of the Dirac equation).

In the relativistic case a two-body Coulomb problem cannot be solved exactly. Therefore the hydrogen-like atom in the Dirac theory is modeled by an electron moving in an external Coulomb field. We solve the corresponding Dirac equation in the reference frame in which the singularity of the potential is placed at the origin, i.e. with

$$V(r) = -\frac{Ze^2}{r}$$

Neither the square nor the projection of $\hat{\boldsymbol{L}}$ commutes with the Dirac Hamiltonian. Therefore the Dirac wavefunction can be an eigenfunction of neither $\hat{L}^2$ nor $\hat{L}_z$. However, in the standard representation, the large and small components are eigenfunctions of $\hat{L}^2$, to the eigenvalues $l(l+1)$ and $l'(l'+1)$ respectively, where $l' = l \pm 1$. We introduce, apart of the total angular momentum quantum number $j = l \pm 1/2$ and its projection $m_j = -j, -j+1, \ldots, j$, the relativistic angular momentum quantum number

$$\kappa = \pm(j+1/2) = \begin{cases} l & \text{if } j = l - 1/2 \\ -(l+1) & \text{if } j = l + 1/2. \end{cases}$$

The energy spectrum consists of two continua (one extending from $+mc^2$ up and another one extending from $-mc^2$ down) and the discrete spectrum located below the ionization threshold $+mc^2$ and depending on two quantum numbers: n and j (or, equivalently, on n and κ).

The eigenvalue equation:

$$\hat{H}_{\mathrm{D}}\psi_{nljm_j} = E^{\mathrm{D}}_{nj}\psi_{nljm_j},$$

where

$$E^{\mathrm{D}}_{nj} - mc^2 = -\frac{Z^2}{N(N+\tilde{n})}\cdot 2R_\infty$$

with

$$N = \sqrt{\alpha^2 Z^2 + \tilde{n}^2},$$

$$\tilde{n} = n + s - |\kappa|,$$

and

$$s = \sqrt{\kappa^2 - \alpha^2 Z^2}.$$

The Dirac states are labeled by n, l and j (l corresponds to the $\hat{L}^2$ eigenvalue for the large component of the pertinent wavefunction).

The consecutive discrete states of the Dirac atom are:
$1s_{1/2}$, $2s_{1/2}$, $2p_{1/2}$, $2p_{3/2}$, $3s_{1/2}$, $3p_{1/2}$, $3p_{3/2}$, $3d_{3/2}$, $3d_{5/2}$, ...
For $\alpha \to 0$, i.e. in the nonrelativistic limit,

$$s \to \kappa,$$

$$\tilde{n} \to n,$$

$$N \to n,$$

$$(E_{nj}^{\mathrm{D}} - mc^2) \to E_n^{\mathrm{S}}.$$

By expanding the Dirac energy into a power series of $(\alpha Z)^2$ one gets

$$E_{nj}^{\mathrm{D}} = mc^2 \left[1 - \frac{(\alpha Z)^2}{2n^2} - \frac{(\alpha Z)^4}{2n^3}\left(\frac{1}{|\kappa|} - \frac{3}{4n}\right) + O\left((\alpha Z)^6\right)\right],$$

where the first term is the rest energy of the electron, the second one is the non-relativistic (Schrödinger) energy and the third one is the relativistic (Pauli) correction.

In the Dirac spectrum, apart of shifting the energy levels relative to the Schrödinger ones, some of the degeneracies have been removed. Now the energy levels depend upon the total angular momentum quantum number j but, also in the Dirac theory, they do not depend upon l. Then, the energy of the states $2p_{1/2}$ and $2p_{3/2}$ are different while the energies of $2p_{1/2}$ is the same as that of $2s_{1/2}$. The splitting of the energy levels due to j is called the *fine structure splitting*. It is relatively small for small Z but it grows very fast with increasing nuclear charge (it is proportional to Z^4).

Experimental measurements show that the energies of a real hydrogen-like atom depend upon l. In particular the energies of $2s_{1/2}$ and $2p_{1/2}$ are different. For the first time this splitting was measured for the hydrogen atom by Lamb and Retherford. The effect is called the *Lamb shift*. It may be explained on the ground of quantum electrodynamics. Its value grows rapidly with increasing Z. For the hydrogen atom it is equal 1060 Mc = $4{\cdot}10^{-6}$ eV; for the uranium like atoms it is about 70 eV, i.e. by 7 orders of magnitude larger than in hydrogen!

The eigenfunctions of a spherically-symmetric Dirac Hamiltonian may be represented as

$$\psi_{nl\kappa m_j} = \frac{1}{r} \begin{pmatrix} G_{n\kappa}(r)\, \Phi(\theta,\phi)_{nl\kappa m_j} \\ i\, F_{n\kappa}(r)\, \Phi(\theta,\phi)_{nl'-\kappa m_j}\,, \end{pmatrix}$$

where $l' = l - \kappa/|\kappa|$ and $\Phi(\theta,\phi)$ are combinations of products of the spherical harmonics and the two-component spin functions constructed according to the rules of coupling the angular momenta.
The radial functions fulfill the following eigenvalue equation:

$$\begin{aligned} \left[mc^2 - E + V(r)\right] G(r) - c \left[\frac{d}{dr} - \frac{\kappa}{r}\right] F(r) &= 0, \\ c \left[\frac{d}{dr} + \frac{\kappa}{r}\right] G(r) - \left[mc^2 + E - V(r)\right] F(r) &= 0, \end{aligned}$$

where, in the case of a hydrogen-like atom, $V(r) = -Ze^2/r$.

Then, the small component is related to the large one:

$$F(r) = c\left[mc^2 + E - V(r)\right]^{-1}\left(\frac{d}{dr} + \frac{\kappa}{r}\right)G(r).$$

Both large and small radial components may be expressed as products of $\mathrm{e}^{-\zeta r}$ and a polynomial, where $\zeta = \sqrt{m^2c^2 - E^2/c^2}$. At the origin $R(r)$ behaves as r^s. Then, for $|\kappa| > 1$ it vanishes for $r = 0$. However, for $\kappa = \pm 1$, $s < 1$ and $r^{-1}R(r)$ is singular. This singularity is weak and for $Z\alpha < 1$ does not obstruct the normalizability of the wavefunctions. The relativistic radial electron density is contracted relative to the non-relativistic one (the Dirac hydrogen atom is "smaller" than the Schrödinger one) . Besides, it is nodeless since the nodes of the large and small radial components (except the $r = 0$ node) never coincide.

Singularity of the Dirac wavefunctions at the origin is a consequence of the Coulomb singularity in the potential. A more general potential may be taken in the form

$$V(r) = -Z(r)\frac{e^2}{r}.$$

If $Z(r)$ is constant, then we have a point nucleus and singular potential. One of the simplest and most common is a model in which a uniform nuclear charge distribution is assumed. In this case

$$V(r) = \begin{cases} -\frac{3Z}{2A}\left(1 - \frac{r^2}{3A^2}\right)e^2, & \text{if } 0 \le r \le A \\ -\frac{Ze^2}{r} & \text{if } r > A. \end{cases}$$

Taking the finite nuclear model we get the wavefunction without any singularity: $r^{-1}G(r)$ behaves as r^l and $r^{-1}F(r)$ – as r^{l+1}.

RELATIVISTIC COVARIANCE OF THE DIRAC EQUATION

Notations and basic properties

$$
\begin{aligned}
x_\mu &= (\mathbf{r}, ict) \\
p_\mu &= -i\hbar \frac{\partial}{\partial\, x_\mu} = \left(\mathbf{p}, -\frac{\hbar}{c}\frac{\partial}{\partial\, t}\right) \\
\gamma_\mu &= (-i\beta\boldsymbol{\alpha}, \beta) = (\boldsymbol{\gamma}, \beta)
\end{aligned}
$$

$$
\boldsymbol{\gamma} = \begin{pmatrix} 0 & -i\boldsymbol{\sigma} \\ i\boldsymbol{\sigma} & 0 \end{pmatrix}, \qquad \gamma_4 = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}
$$

$$
\gamma_\mu = \gamma_\mu^\dagger
$$

$$
\gamma_\mu\gamma_\nu + \gamma_\nu\gamma_\mu = 2\delta_{\mu\nu}
$$

Dirac equation

$$i\hbar\frac{\partial\Psi}{\partial\, t} = \left(c\,\boldsymbol{\alpha}\cdot\boldsymbol{p} + \beta\, mc^2\right)\Psi$$

$$\Psi = \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix}, \qquad \Psi^\dagger = [\psi_1^*, \psi_2^*, \psi_3^*, \psi_4^*]$$

$$\overline{\Psi} = \Psi^\dagger\beta = [\psi_1^*, \psi_2^*, -\psi_3^*, -\psi_4^*] = \Psi^\dagger\gamma_4$$

$$\gamma_\mu\frac{\partial\Psi}{\partial\, x_\mu} + \kappa\Psi = 0, \qquad \frac{\partial\overline{\Psi}}{\partial\, x_\mu}\gamma_\mu - \kappa\overline{\Psi} = 0, \qquad \kappa = \frac{mc}{\hbar}$$

Continuity equation: $$\frac{\partial j_\mu}{\partial x_\mu} = 0$$

$$j_\mu = ice\overline{\Psi}\gamma_\mu\Psi = (\boldsymbol{j}, ic\rho), \quad \Rightarrow \quad \boldsymbol{j} = ce\Psi^\dagger\boldsymbol{\alpha}\Psi, \quad \rho = e\Psi^\dagger\Psi$$

Pauli fundamental theorem

Given two sets of 4×4 matrices satisfying

$$\{\gamma_\mu, \gamma_\nu\} = 2\delta_{\mu\nu} \quad \text{and} \quad \{\gamma'_\mu, \gamma'_\nu\} = 2\delta_{\mu\nu}$$

with $\mu, \nu = 1, 2, 3, 4$, there exists a nonsingular 4×4 matrix S such that

$$S\gamma_\mu S^{-1} = \gamma'_\mu.$$

Moreover, S is unique up to a multiplicative constant.

Most commonly used representations: Dirac-Pauli (standard), Weyl, Majorana (γ_k are purely real, γ_4 is purely imaginary)

Lorentz transformation – a rotation in the Minkowski space

$$x'_\mu = a_{\mu\nu} x_\nu$$

$$a_{\mu\nu} a_{\lambda\nu} = \delta_{\mu\lambda}, \quad \det |a_{\mu\nu}| = 1, \quad a_{44} > 0.$$

Special cases

- Rotation in the usual three-dimensional space

$$\begin{pmatrix} x'_1 \\ x'_2 \end{pmatrix} = \begin{pmatrix} \cos\omega & \sin\omega \\ -\sin\omega & \cos\omega \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}$$

- "Pure" Lorentz transformation – rotation in $1-4$ plane by angle $i\chi$

$$\begin{pmatrix} x'_1 \\ x'_2 \end{pmatrix} = \begin{pmatrix} \cosh\chi & i\sinh\chi \\ -\sinh\chi & \cosh\chi \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}, \quad \tanh\chi = \frac{v}{c}$$

Covariance of the Dirac equation

$$A'_\mu(x') = a_{\mu\nu} A_\nu(x),$$

$$\frac{\partial}{\partial x'_\mu} = a_{\mu\nu} \frac{\partial}{\partial x_\nu}$$

$$\gamma_\mu \frac{\partial \Psi(x)}{\partial x_\mu} + \kappa \Psi(x) = 0 \quad \Rightarrow \quad \gamma_\mu \frac{\partial \Psi'(x')}{\partial x'_\mu} + \kappa \Psi'(x') = 0$$

Assumption: $\Psi'(x') = S\Psi(x)$, S – 4×4 matrix independent of x_μ

$$S^{-1} \gamma_\mu S a_{\mu\nu} = \gamma_\nu \quad \Rightarrow \quad S^{-1} \gamma_\lambda S = a_{\lambda\nu} \gamma_\nu$$

The non-relativistic Pauli model

$$R^z_\omega |lm\rangle = \mathrm{e}^{im\omega}|lm\rangle, \quad m = -l, -l+1, \ldots, l$$

$$R^z_\omega \left|\tfrac{1}{2} \pm \tfrac{1}{2}\right\rangle = \mathrm{e}^{\pm i\omega/2} \left|\tfrac{1}{2} \pm \tfrac{1}{2}\right\rangle \;\Rightarrow\; R^z_\omega \begin{pmatrix} U_+ \\ U_- \end{pmatrix} = \begin{pmatrix} \mathrm{e}^{i\omega/2} & 0 \\ 0 & \mathrm{e}^{-i\omega/2} \end{pmatrix} \begin{pmatrix} U_+ \\ U_- \end{pmatrix}$$

$$S_{\mathrm{Pauli}}\, U(x) = U'(x')$$

$$\begin{aligned} S_{\mathrm{Pauli}} &= \begin{pmatrix} \cos\frac{\omega}{2} + i\sin\frac{\omega}{2} & 0 \\ 0 & \cos\frac{\omega}{2} - i\sin\frac{\omega}{2} \end{pmatrix} \\ &= I\,\cos\tfrac{\omega}{2} + i\sigma_3\,\sin\tfrac{\omega}{2} \end{aligned}$$

Several formulas

$$\boldsymbol{\sigma} \times \boldsymbol{\sigma} = 2i\boldsymbol{\sigma}$$

$$\sigma_j \sigma_k - \sigma_k \sigma_j = 2i\sigma_l$$

$$\sigma_j \sigma_k + \sigma_k \sigma_j = 0$$

$$\sigma_j \sigma_k = i\sigma_l, \quad \text{(cyclic)}$$

$$\Sigma_3 = \begin{pmatrix} \sigma_3 & 0 \\ 0 & \sigma_3 \end{pmatrix}$$

$$\gamma_1\gamma_2 = \begin{pmatrix} 0 & -i\sigma_1 \\ i\sigma_1 & 0 \end{pmatrix} \begin{pmatrix} 0 & -i\sigma_2 \\ i\sigma_2 & 0 \end{pmatrix} = i \begin{pmatrix} \sigma_3 & 0 \\ 0 & \sigma_3 \end{pmatrix} = i\Sigma_3,$$

$$(\gamma_1\gamma_2)^2 = -I_4$$

The Dirac model - rotation in $1-2$ plane

$$S_{\rm rot} = I_4 \cos\tfrac{\omega}{2} + i\Sigma_3 \sin\tfrac{\omega}{2} = I_4 \cos\tfrac{\omega}{2} + \gamma_1\gamma_2 \sin\tfrac{\omega}{2}$$

$$S_{\rm rot}^{-1} = I_4 \cos\tfrac{\omega}{2} - i\Sigma_3 \sin\tfrac{\omega}{2} = I_4 \cos\tfrac{\omega}{2} - \gamma_1\gamma_2 \sin\tfrac{\omega}{2}$$

Theorem: $$S_{\rm rot}^{-1}\gamma_\lambda\, S_{\rm rot} = a_{\lambda\mu}\gamma_\nu$$

$$a = \begin{pmatrix} \cos\omega & \sin\omega & 0 & 0 \\ -\sin\omega & \cos\omega & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

where a – matrix with elements $a_{\lambda\mu}$, $\lambda, \mu = 1, 2, 3, 4$.

The Dirac model - rotation in $1-4$ plane

$$\omega \to i\chi, \quad \cos\omega \to \cosh\chi, \quad \sin\omega \to i\sinh\chi, \quad \gamma_2 \to \gamma_4.$$

$$S_{\rm Lor} = I_4 \cosh\tfrac{\chi}{2} + i\gamma_1\gamma_4 \sinh\tfrac{\chi}{2}$$

$$S_{\rm Lor}^{-1} = I_4 \cosh\tfrac{\chi}{2} - i\gamma_1\gamma_4 \sinh\tfrac{\chi}{2}$$

Theorem: $$S_{\rm Lor}^{-1}\gamma_\lambda\, S_{\rm Lor} = a_{\lambda\mu}\gamma_\nu$$

$$a = \begin{pmatrix} \cosh\chi & 0 & 0 & i\sinh\chi \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ -i\sinh\chi & 0 & 0 & \cosh\chi \end{pmatrix}$$

More definitions and formulas

$$\sigma_{\mu\nu} \equiv \frac{1}{2i}\left[\gamma_\mu, \gamma_\nu\right].$$

$$\sigma_{\mu\nu} = -i\,\gamma_\mu\gamma_\nu,\ \mu \neq \nu$$

$$\sigma_{ij} = -\sigma_{ji} = \Sigma_k = \begin{pmatrix} \sigma_k & 0 \\ 0 & \sigma_k \end{pmatrix}$$

$$\sigma_{k4} = -\sigma_{4k} = \alpha_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix}$$

$$[\gamma_4, \sigma_{ij}] = 0, \quad \{\gamma_4, \sigma_{k4}\} = 0$$

$$\gamma_5 \equiv \gamma_1\gamma_2\gamma_3\gamma_4 = \begin{pmatrix} 0 & -I \\ -I & 0 \end{pmatrix}$$

$$\{\gamma_\mu, \gamma_5\} = 0, \quad \gamma_5^2 = I_4 \quad [\gamma_5, \sigma_{\mu\nu}] = 0$$

Summary

$$S^{ij}_{\rm rot} = I_4 \cos\tfrac{\omega}{2} + i\sigma_{ij} \sin\tfrac{\omega}{2}$$

$$S^{k4}_{\rm Lor} = I_4 \cosh\tfrac{\chi}{2} - \sigma_{k4} \sinh\tfrac{\chi}{2}$$

$$S^{\dagger}_{\rm rot} = S^{-1}_{\rm rot}$$

$$S^{\dagger}_{\rm Lor} = S_{\rm Lor} \neq S^{-1}_{\rm Lor}$$

Conclusion: $S_{\rm Lor}$ **is not unitary!**.

But

$$S^{-1} = \gamma_4 \, S^{\dagger} \gamma_4 \quad \text{and} \quad S^{\dagger} = \gamma_4 \, S^{-1} \gamma_4$$

It is consistent with $\overline{\Psi} = \Psi^{\dagger}\gamma_4$.

Also $S^{-1}\gamma_5 \, S = \gamma_5$

Space inversion

$$\mathbf{r}' = -\mathbf{r}, \quad t' = t$$

$$a = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$S_{\text{inv}}^{-1}\,\gamma_\lambda\,S_{\text{inv}} = a_{\lambda\nu}\gamma_\nu \quad \Rightarrow \quad \begin{cases} S_{\text{inv}}^{-1}\,\gamma_k\,S_{\text{inv}} = -\gamma_k \\ S_{\text{inv}}^{-1}\,\gamma_4\,S_{\text{inv}} = \gamma_4 \end{cases} \quad \Rightarrow \quad S_{\text{inv}} = \gamma_4 = S_{\text{inv}}^{-1}$$

Transformation of the wavefunction under space inversion: $\Psi' = \gamma_4\Psi = \overline{\Psi}^\dagger$

$$S_{\text{inv}}\gamma_5\,S_{\text{inv}} = \gamma_4\gamma_5\gamma_4 = -\gamma_5$$

Infinitesimal rotation

$$\omega \to \delta\omega << 1 \quad \Rightarrow \quad \cos\omega \to 1, \;\; \sin\omega \to \delta\omega.$$

$$S_{\mathbf{rot}} = 1 + \frac{i}{2}\Sigma_3\,\delta\omega$$

$$\mathbf{r}' = \mathbf{r} + \delta\mathbf{r} \quad \Rightarrow \quad \begin{cases} x_1' = x_1 + x_2\delta\omega \\ x_2' = x_2 - x_1\delta\omega \\ x_3' = x_3 \end{cases}$$

$$
\begin{aligned}
\Psi'(\mathbf{r}') &= \Psi'(\mathbf{r}+\delta\mathbf{r}) \\
&= \Psi'(\mathbf{r}) + \frac{\partial\,\Psi'}{\partial\,x_1}\delta x_1 + \frac{\partial\,\Psi'}{\partial\,x_2}\delta x_2 + \frac{\partial\,\Psi'}{\partial\,x_3}\delta x_3 \\
&= \Psi'(\mathbf{r}) + \left(\frac{\partial\,\Psi'}{\partial\,x_1}\,x_2 - \frac{\partial\,\Psi'}{\partial\,x_2}\,x_1\right)\delta\,\omega \\
&= S_{\rm rot}\Psi(\mathbf{r}) = \left(1 + \frac{i}{2}\Sigma_3\,\delta\omega\right)\Psi(\mathbf{r})
\end{aligned}
$$

$$
\begin{aligned}
\Psi'(\mathbf{r}) &= \left[1 + \frac{i}{2}\Sigma_3\,\delta\omega - \left(x_2\frac{\partial}{\partial\,x_1} - x_1\frac{\partial}{\partial\,x_2}\right)\delta\omega\right]\Psi(\mathbf{r}) \\
&= \left[1 + \left(\frac{1}{2}\Sigma_3 + \hat{L}_3\right)\,i\,\delta\omega\right]\,\Psi(\mathbf{r}) = \left(1 + i\,\delta\omega\,\hat{J}_3\right)\,\Psi(\mathbf{r})
\end{aligned}
$$

$$
\hat{L}_3 = i\,\left(x_2\frac{\partial}{\partial\,x_1} - x_1\frac{\partial}{\partial\,x_2}\right), \quad \hat{J}_3 = \frac{1}{2}\Sigma_3 + \hat{L}_3.
$$

Infinitesimal rotation – conclusions

$$\Psi'(\mathbf{r}) = \left(1 + i\,\delta\omega\,\hat{J}_3\right)\,\Psi(\mathbf{r})$$

$$\hat{J}_3 = \frac{1}{2}\Sigma_3 + \hat{L}_3$$

The change in the *functional form* of Ψ induced by the infinitesimal rotation consists of two parts: the space-time independent one (associated with the operator Σ_3) and the one corresponding to the rotation in three-dimensional space (associated with $\hat{L}_3$). The total angular momentum operator $\hat{J}_3$ is the generator of an infinitesimal rotation around the third axis.

Bilinear covariants: $\overline{\Psi}\Gamma\Psi$

$$\Psi'(x') = S\Psi(x),$$

$$\Psi'(x')^\dagger = \Psi(x)^\dagger\, S^\dagger = \Psi(x)^\dagger\gamma_4 S^{-1}\gamma_4 = \overline{\Psi}(x)S^{-1}\gamma_4$$

$$\Psi'(x')^\dagger\gamma_4 = \overline{\Psi}(x)S^{-1}, \quad \overline{\Psi}'(x') = \overline{\Psi}(x)S^{-1}$$

$$S^{-1}\gamma_\mu\, S = a_{\mu\nu}\gamma_\nu$$

1. $\overline{\Psi}'(x')\Psi'(x') = \overline{\Psi}(x)S^{-1}S\Psi(x) = \overline{\Psi}(x)\Psi(x), \quad -$ scalar
2. $\overline{\Psi}'(x')\gamma_\mu\Psi'(x') = \overline{\Psi}(x)S^{-1}\gamma_\mu\, S\Psi(x) = a_{\mu\nu}\overline{\Psi}(x)\gamma_\nu\Psi(x)$

   $\left(\overline{\Psi}\gamma_\mu\Psi\right)' = a_{\mu\nu}\left(\overline{\Psi}\gamma_\nu\Psi\right), \quad -$ vector
3. $\overline{\Psi}'(x')\gamma_5\Psi'(x') = \overline{\Psi}(x)S^{-1}\gamma_5\, S\Psi(x) = \begin{cases} \overline{\Psi}\gamma_5\Psi & \text{Lor tr} \\ -\overline{\Psi}\gamma_5\Psi & \text{rot} \end{cases}$

   pseudoscalar

Bilinear covariants – summary

Scalar	$\overline{\Psi}\Psi$
Vector	$\overline{\Psi}\gamma_\mu\Psi$
Antisymmetric tensor	$\overline{\Psi}\sigma_{\mu\nu}\Psi$
Pseudovector	$i\,\overline{\Psi}\gamma_5\gamma_\mu\Psi$
Pseudoscalar	$\overline{\Psi}\gamma_5\Psi$

Large and small covariants

$$\overline{\Psi}\Gamma\Psi = \begin{cases} \left(\Psi^{\mathrm{L}\dagger} - \Psi^{\mathrm{S}\dagger}\right) \begin{pmatrix} A & 0 \\ 0 & -B \end{pmatrix} \begin{pmatrix} \Psi^{\mathrm{L}} \\ \Psi^{\mathrm{S}} \end{pmatrix} = \Psi^{\mathrm{L}\dagger} A \Psi^{\mathrm{L}} + \Psi^{\mathrm{S}\dagger} B \Psi^{\mathrm{S}} \; - \; \text{large} \\ \left(\Psi^{\mathrm{L}\dagger} - \Psi^{\mathrm{S}\dagger}\right) \begin{pmatrix} 0 & A \\ A^{\dagger} & 0 \end{pmatrix} \begin{pmatrix} \Psi^{\mathrm{L}} \\ \Psi^{\mathrm{S}} \end{pmatrix} = \Psi^{\mathrm{L}\dagger} A \Psi^{\mathrm{S}} - \Psi^{\mathrm{S}\dagger} B \Psi^{\mathrm{L}} \; - \; \text{small} \end{cases}$$

Large: I, γ_4, $i\gamma_5\gamma_k$, σ_{ij}

Small: γ_k, $i\gamma_5\gamma_4$, γ_5, σ_{k4}

Clifford algebra

Generalized quaternions - William K. Clifford (1845-1879)

Questions: Can we generate more bilinear covariants of the form $\overline{\Psi}\Gamma\Psi$?

1. $\gamma_\mu, \gamma_\mu^2 = 1$
2. $\gamma_\mu\gamma_\nu = -\gamma_\nu\gamma_\mu = i\,\sigma_{\mu\nu}$
3. $\gamma_\mu\gamma_\nu\gamma_\lambda = \gamma_5\gamma_\sigma,\ \mu \neq \nu \neq \lambda \neq \sigma$
   $\gamma_\mu\gamma_\nu\gamma_\mu = -\gamma_\nu$
4. $\gamma_5 = \gamma_1\gamma_2\gamma_3\gamma_4$

Products of more than 4 matrices can be reduced to products of at most 4

$p, q = 1, 2, 3, 4, 5:$ $\quad 1$ matrix I, $\quad 5$ matrices γ_q, $\quad 10$ matrices σ_{pq}

$-$ together 16 matrices Γ

$$\Gamma^2 = I \quad \Rightarrow \quad \Gamma = \Gamma^{-1}$$

If $\Gamma_{\rm A} \neq \Gamma_{\rm B}$ and $\Gamma_{\rm A}, \Gamma_{\rm B} \neq I$ then

1. $\mathrm{Tr}\left(\Gamma_{\rm A}\,\Gamma_{\rm B}\right) = -\mathrm{Tr}\left(\Gamma_{\rm B}\,\Gamma_{\rm A}\right) = 0,$
2. $\mathrm{Tr}\left(\Gamma_{\rm A}^2\right) = 4,$
3. $\mathrm{Tr}\left(\Gamma_{\rm A}\right) = 0,$

$$\mathrm{Tr}\left(\Gamma_{\rm A}\right) = \mathrm{Tr}\left(\Gamma_{\rm B}^2\Gamma_{\rm A}\right) = -\mathrm{Tr}\left(\Gamma_{\rm B}\Gamma_{\rm A}\Gamma_{\rm B}\right) = -\mathrm{Tr}\left(\Gamma_{\rm B}^{-1}\Gamma_{\rm A}\Gamma_{\rm B}\right) = -\mathrm{Tr}\left(\Gamma_{\rm A}\right)$$

Let $$\Lambda = \sum_{\rm A=1}^{16} \lambda_{\rm A}\Gamma_{\rm A}$$

then $$\lambda_{\rm A} = \frac{1}{4}\mathrm{Tr}\left(\Lambda\Gamma_{\rm A}\right).$$

APPROXIMATIONS

APPROXIMATE SOLVING EIGENVALUE PROBLEMS

It is customary to divide the most commonly used approximate methods of solving eigenvalue problems to two classes:

- **Variational methods**,
- **Perturbational methods**.

VARIATIONAL METHOD

The variational methods are most appropriate if we have a discrete eigenvalue problem:

$$\hat{H}|\psi_k\rangle = E_k|\psi_k\rangle, \quad k = 1, 2, \ldots$$

with

$$E_1 \leq E_2 \leq E_3 \leq \cdots .$$

The variational methods result from a very simple property of the eigenvalue problem known as the variational principle.

The basic theorem:
For a $|\Phi\rangle$ which belongs to the space spanned by the eigenvectors of $\hat{H}$,

$$\mathcal{K}[\Phi] \equiv \frac{\langle\Phi|\hat{H}|\Phi\rangle}{\langle\Phi|\Phi\rangle} \geq E_1.$$

The equality can be achieved only if

$$|\Phi\rangle = |\psi_1\rangle.$$

The functional $\mathcal{K}[\Phi]$ is called the *Rayleigh quotient*.

Conclusion: $$\frac{\langle\Phi^{(q)}|\hat{H}|\Phi^{(q)}\rangle}{\langle\Phi^{(q)}|\Phi^{(q)}\rangle} \geq E_q$$

if $|\Phi^{(q)}\rangle$ is orthogonal to $|\psi_i\rangle$ for $i = 1, 2, \ldots, q-1$.
Applications of the variational principle result in modifying a trial function Φ so that the value of $\mathcal{K}[\Phi]$ becomes as small as it is possible within the constraints imposed upon Φ.

Different trial functions $\Rightarrow$ different variational models.

A precondition for applicability of the variational method is that the eigenvalue problem we are dealing with is bounded from below.

Fulfilled in the case of a Schrödinger equation

Not fulfilled in the case of the Dirac equation.

In the case of the Dirac equation some preliminary steps are necessary

- Restriction of the space of the trial functions by imposing the boundary conditions which would force them to be orthogonal to the negative-energy solutions. In such a space the Dirac eigenvalue problem is limited from below.
- Modification of the Dirac Hamiltonian so that it is bounded from below for all square-integrable trial functions and retains the interesting part of its spectrum unchanged.

In order to accomplish this one can

- project the Hamiltonian onto the space of the positive-energy states,
- transform it in such a way that the negative-energy continuum would overlap with the positive-energy continuum,
- transform the Hamiltonian so that the large and small components are decoupled.

SCHRÖDIGER EQUATION: ALGEBRAIC REPRESENTATION

Schrödinger Hamiltonian eigenvalue problem ("time-independent Schrödinger equation"):

$$\hat{H}\psi_k = E_k\psi_k$$

A basis set expansion of the trial function

$$\Phi = \sum_{n=1}^{K} C_n\ \phi_n, \quad \langle\phi_n|\phi_m\rangle = \delta_{mn},$$

leads to the algebraic approximation to the Schrödinger equation.

$$\sum_{n=1}^{K} (H_{mn} - E_k\delta_{mn})\, C_{kn} = 0, \qquad k = 1, 2, \ldots, n$$

The K-dimensional space $\mathcal{H}_K$ spanned by $\{\phi_n\}_{n=1}^{K}$ is referred to as the *model space*

McDonald theorem

Let the model space be spanned by K basis functions and let the Hamiltonian matrix eigenvalues be

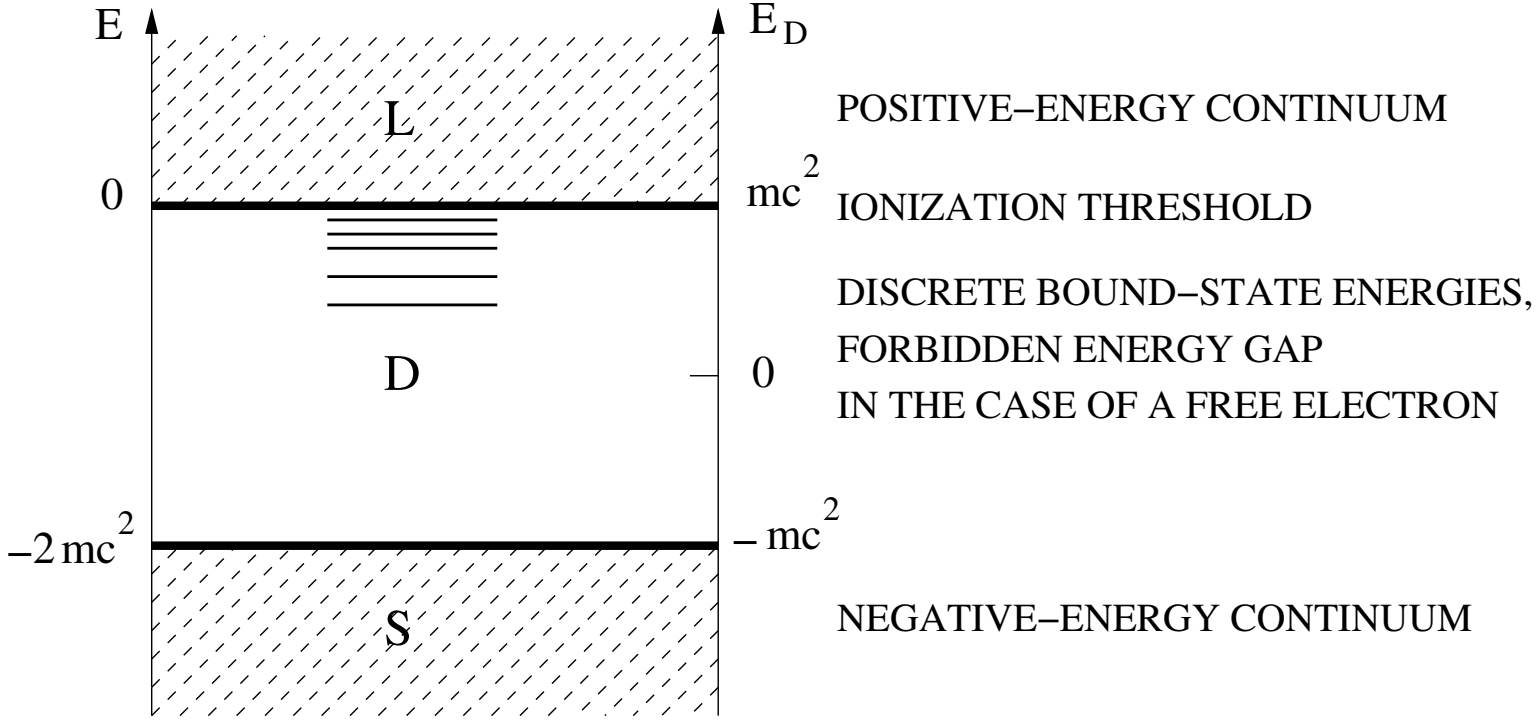
$$E_1^{(K)} \leq E_2^{(K)} \leq \cdots \leq E_K^{(K)};$$

as the dimension of the model space is increased by adding an additional basis function, eigenvalues $E_p^{(K+1)}$ of the $(K+1)$-dimensional problem satisfy the inequalities:

$$E_{p-1}^{(K)} \leq E_p^{(K+1)} \leq E_p^{(K)}$$

and as the model space approaches completeness, the algebraic solutions approach the exact solutions of the Hamiltonian eigenvalue equation.
Conclusion: each eigenvalue of the algebraic eigenvalue problem is an upper bound to the corresponding eigenvalue of the Hamiltonian.

SPECTRUM OF ONE-ELECTRON DIRAC HAMILTONIAN



ENERGY FUNCTIONAL

Rayleigh quotient: $$\mathcal{K}[\Phi] = \frac{\langle\Phi|\hat{H}|\Phi\rangle}{\langle\Phi|\Phi\rangle}, \quad \Phi = \begin{bmatrix} c_a\Phi^{\mathrm{L}} \\ c_b\Phi^{\mathrm{S}} \end{bmatrix}$$

Dirac: $$\mathcal{K}[\Phi]_D = W_+ + \sqrt{{W_-}^2 + 2mc^2T}$$

Lévy-Leblond: $$\mathcal{K}[\Phi]_L = T + (W_+ + W_-)$$

$$W_\pm = \frac{1}{2}\left(\frac{\langle\Phi^{\mathrm{L}}|V|\Phi^{\mathrm{L}}\rangle}{\langle\Phi^{\mathrm{L}}|\Phi^{\mathrm{L}}\rangle} \pm \frac{\langle\Phi^{\mathrm{S}}|V|\Phi^{\mathrm{S}}\rangle}{\langle\Phi^{\mathrm{S}}|\Phi^{\mathrm{S}}\rangle}\right) \mp mc^2,$$

$$T = \frac{1}{2m}\frac{\langle\Phi^{\mathrm{L}}|\boldsymbol{\sigma}\cdot\mathbf{p}|\Phi^{\mathrm{S}}\rangle\langle\Phi^{\mathrm{S}}|\boldsymbol{\sigma}\cdot\mathbf{p}|\Phi^{\mathrm{L}}\rangle}{\langle\Phi^{\mathrm{L}}|\Phi^{\mathrm{L}}\rangle\langle\Phi^{\mathrm{S}}|\Phi^{\mathrm{S}}\rangle}.$$

KINETIC BALANCE

LL energy functional: $\mathcal{K}[\Phi]_L = T + \dfrac{\langle \Phi^{\rm L}|V|\Phi^{\rm L}\rangle}{\langle \Phi^{\rm L}|\Phi^{\rm L}\rangle}$

$$T = \frac{1}{2m}\frac{\langle \Phi^{\rm L}|\boldsymbol{\sigma}\cdot\mathbf{p}|\Phi^{\rm S}\rangle\langle \Phi^{\rm S}|\boldsymbol{\sigma}\cdot\mathbf{p}|\Phi^{\rm L}\rangle}{\langle \Phi^{\rm L}|\Phi^{\rm L}\rangle\langle \Phi^{\rm S}|\Phi^{\rm S}\rangle}.$$

Kinetic balance condition: $\Phi^{\rm S} \sim (\boldsymbol{\sigma}\cdot\mathbf{p})\Phi^{\rm L} \quad \Rightarrow$

$$T = \frac{1}{2m}\frac{\langle \Phi^{\rm L}|(\boldsymbol{\sigma}\cdot\mathbf{p})^2|\Phi^{\rm L}\rangle}{\langle \Phi^{\rm L}|\Phi^{\rm L}\rangle}$$

Kinetic balance condition $\Rightarrow$ { variational LL and Schrödinger eigenvalue problems are equivalent.

ALGEBRAIC REPRESENTATION: MODEL SPACE

Basis set expansion of the components of the trial function

$$\Phi^{\mathrm{L}} = \sum_{k=1}^{K_{\mathrm{L}}} C_k^{\mathrm{L}}\ \phi^{\mathrm{L}}, \quad \Phi^{\mathrm{S}} = \sum_{k=1}^{K_{\mathrm{S}}} C_k^{\mathrm{S}}\ \phi^{\mathrm{S}}$$

leads to the algebraic approximation to the Dirac equation.

The kinetic balance condition implies

$$\mathcal{H}\{\Phi^{\mathrm{S}}\} \supseteq (\boldsymbol{\sigma}\cdot\boldsymbol{p})\mathcal{H}\{\Phi^{\mathrm{L}}\}$$

where $\mathcal{H}\{\Phi\}$ – space in which Φ is expanded.
This condition is necessary for the correct behaviour of the variational procedure applied to the Dirac equation.

ALGEBRAIC REPRESENTATION

Dirac equation: variation of $\mathcal{K}[\Phi]$ leads to an algebraic $(K_{\rm L}+K_{\rm S})\times(K_{\rm L}+K_{\rm S})$ eigenvalue problem:

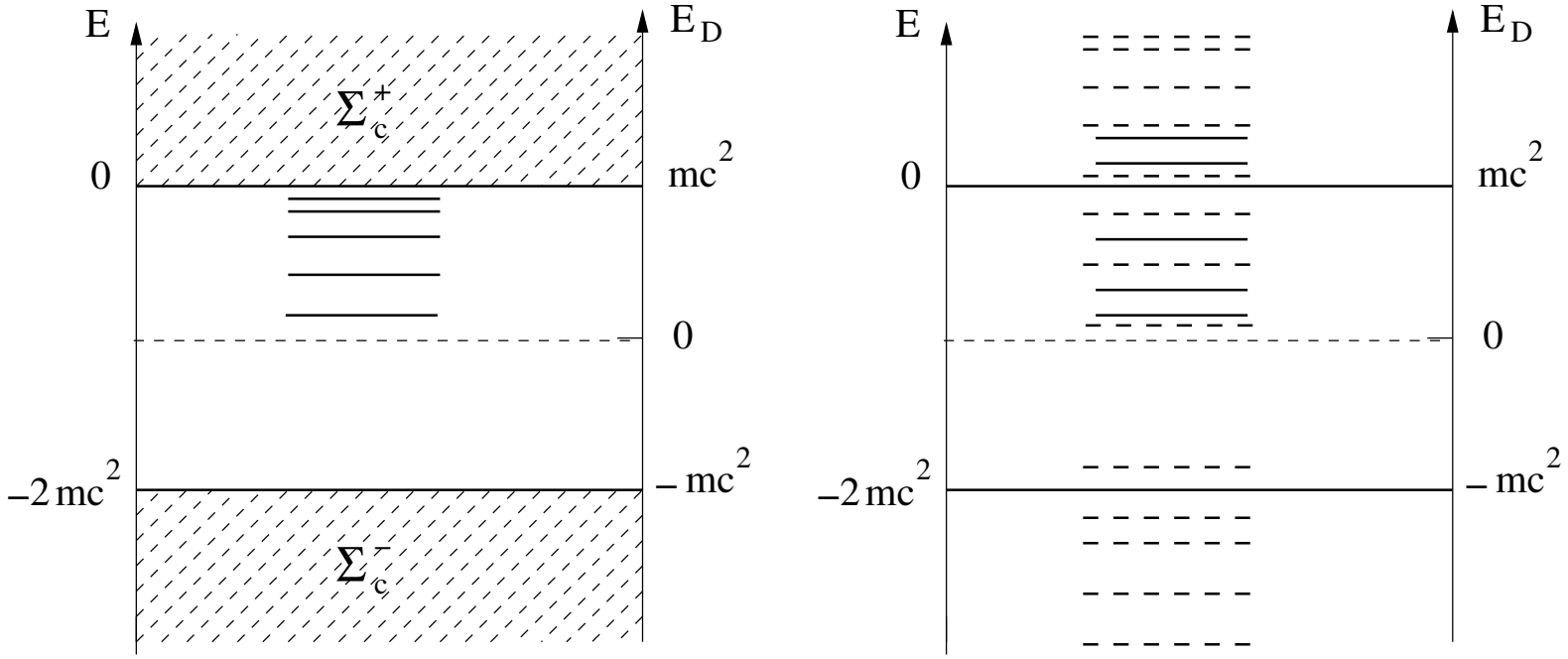
$$\begin{pmatrix} \boldsymbol{H}_{\rm LL}-E\boldsymbol{S}_{\rm LL} & c\,\boldsymbol{H}_{\rm LS} \\ c\,\boldsymbol{H}_{\rm SL} & \boldsymbol{H}_{\rm SS}-E\boldsymbol{S}_{\rm SS} \end{pmatrix} \begin{pmatrix} \boldsymbol{C}^{\rm L} \\ \boldsymbol{C}^{\rm S} \end{pmatrix} = 0,$$

Lévy-Leblond equation: $K_{\rm L}\times K_{\rm L}$ matrix eigenvalue equation:

$$(\boldsymbol{H}-E\boldsymbol{S}_{\rm LL})\,\boldsymbol{C}^{\rm L}=0,$$

$$\boldsymbol{H}=\boldsymbol{H}_{\rm LL}+\frac{1}{2m}\boldsymbol{H}_{\rm LS}\boldsymbol{S}_{\rm SS}^{-1}\boldsymbol{H}_{\rm SL}.$$

ALGEBRAIC REPRESENTATION: SPECTRUM



EXACT SPECTRUM

ALGEBRAIC REPRESENTATION

EXAMPLE: SPHERICAL SYMMETRY

Symmetry-adapted basis functions:

$$\Phi^{\mathrm{L}}(\mathbf{r}) = \frac{\varphi^{\mathrm{L}}(r)}{r} A^{\mathrm{L}}(\Omega), \quad \Phi^{\mathrm{S}}(\mathbf{r}) = \frac{\varphi^{\mathrm{S}}(r)}{r} A^{\mathrm{S}}(\Omega)$$

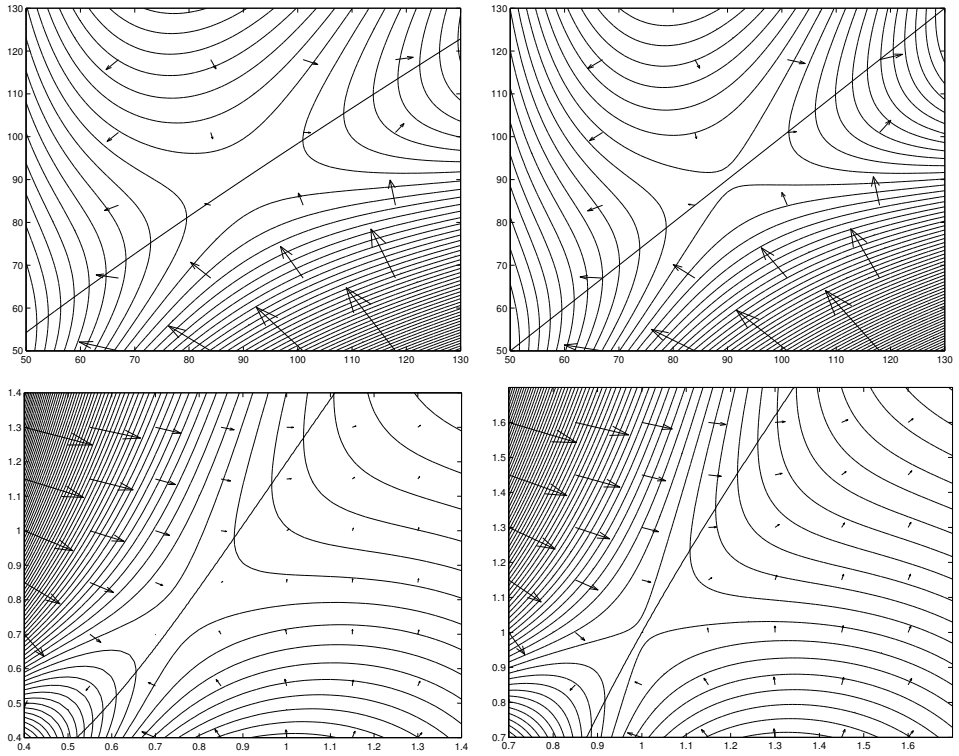
$A(\Omega)$ – exact spin-angular functions

$$\varphi^{\mathrm{L}}(r) = \sum_{k=1}^{N} C_k^{\mathrm{L}}\, r^{l_k} \mathrm{e}^{-\alpha_k r}, \quad \varphi^{\mathrm{S}}(r) = \sum_{k=1}^{N} C_k^{\mathrm{S}}\, r^{s_k} \mathrm{e}^{-\beta_k r}$$

STRUCTURE OF THE SADDLE POINT

Ground state of $Z = 90$ H-like atom, $K = 1$, Dirac (left), LL (right)

$E = E(\alpha_1, \beta_1)|_{l_1 = s_1 = \text{exact}}$ (up), $E = E(l_1, s_1)|_{\alpha_1 = \beta_1 = \text{exact}}$ (down)



BOUNDS TO EIGENVALUES: MINIMAX PRINCIPLE

A relativistic variational principle formulated as a recipe for reaching the saddle point on the energy hypersurface in the space of variational parameters.

$$E = \min_{\{\mathrm{L}\}} \left[\max_{\{\mathrm{S}\}} \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \right].$$

TWO-ELECTRON DIRAC-COULOMB EQUATION

$$H_{\mathrm{DC}}(1,2)\Psi(1,2) = E_{\mathrm{DC}}\Psi(1,2)$$

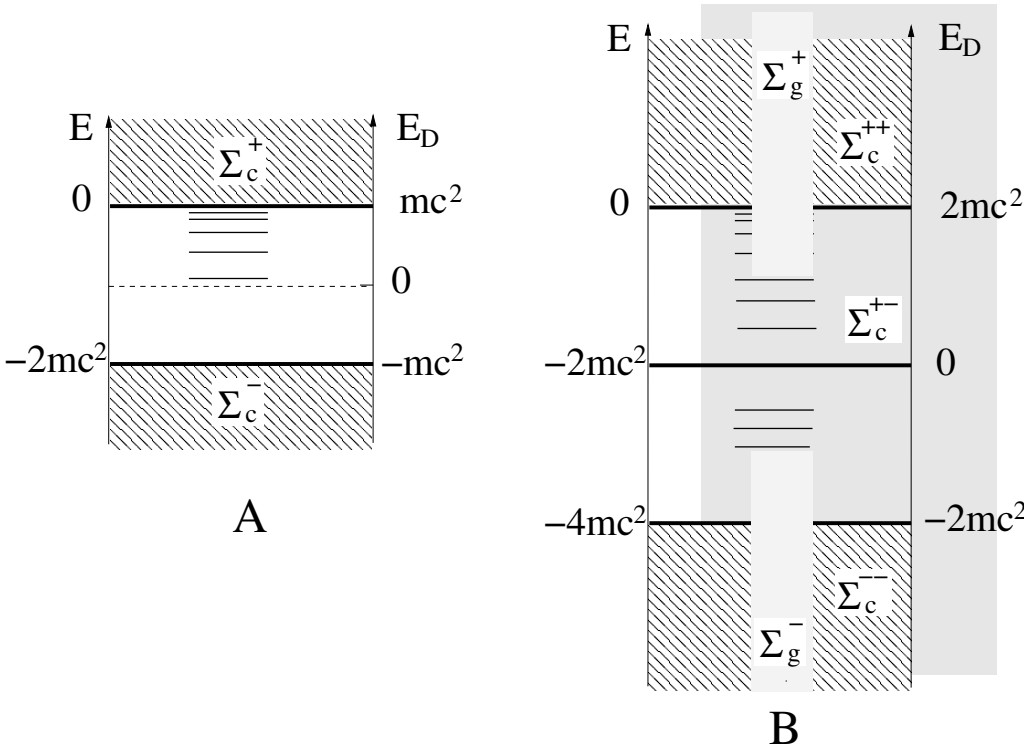
Dirac-Coulomb Hamiltonian:

$$\hat{H}_{\mathrm{DC}}(1,2) = \hat{H}_{\mathrm{D}}(1) + \hat{H}_{\mathrm{D}}(2) + \frac{1}{r_{12}}$$

A hybrid composed of a relativistic one-electron part and a non relativistic two-electron term. Its eigenvalues corresponding to the bound-state solutions are embedded in a continuum spreading from $-\infty$ to $+\infty$ and that the discrete and the continuum spectra are coupled by the electron-electron interaction. This effect is known as the Brown-Ravenhall disease and the continuum is referred to as the Brown-Ravenhall continuum.

SPECTRUM OF DIRAC-COULOMB HAMILTONIAN

Spectra of one-electron (A) and two-electron (B) Dirac Hamiltonian.



Two-electron discrete and continuous spectra overlap.

ARTIFACTS OF DIRAC-COULOMB EQUATION

- Electron-electron interaction couples discrete and continuum states. Consequently, all eigenvalues of the Dirac-Coulomb Hamiltonian corresponding to physically bound states (including, for example, the ground state of helium atom) are autoionizing.
- Dirac-Coulomb Hamiltonian does not have normalizable eigenfunctions.
- Removing the ‘unphysical” continuum by a projection results in an incomplete model space.
- The Dirac-Coulomb Hamiltonian is unbounded from below.

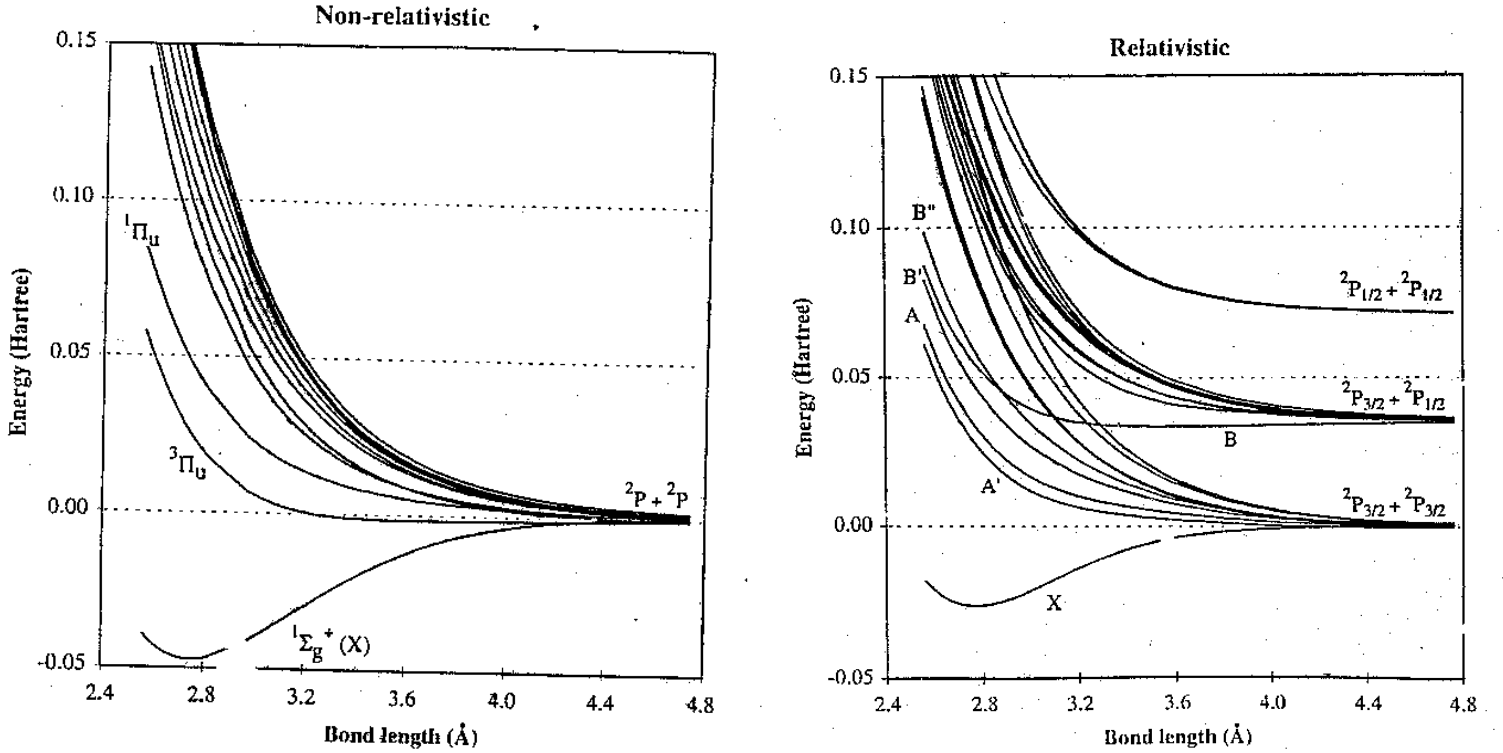
IMPLEMENTATIONS

The Dirac-Coulomb equation is a basis for relativistic Hartree-Fock-type methods referred to as *Dirac-Fock* or *Dirac-Hartree-Fock methods*.

In these methods the trial functions are represented by antisymmetrized products of Dirac spinors.

The influence of the artifacts is usually removed by appropriate selection of the model space corresponding to a projection of the Dirac-Coulomb Hamiltonian to the positive energy space.

EXAMPLE: POTENTIAL ENERGY CURVES



Non-relativistic (left panel) and relativistic (right panel) potential energy curves for the excited state of I_2. States dissociating in two $5p^5$, ^2P iodine atoms are shown [L. Vissher *et al.* JCP 1995]

EXAMPLE: X-RAY SPECTRA

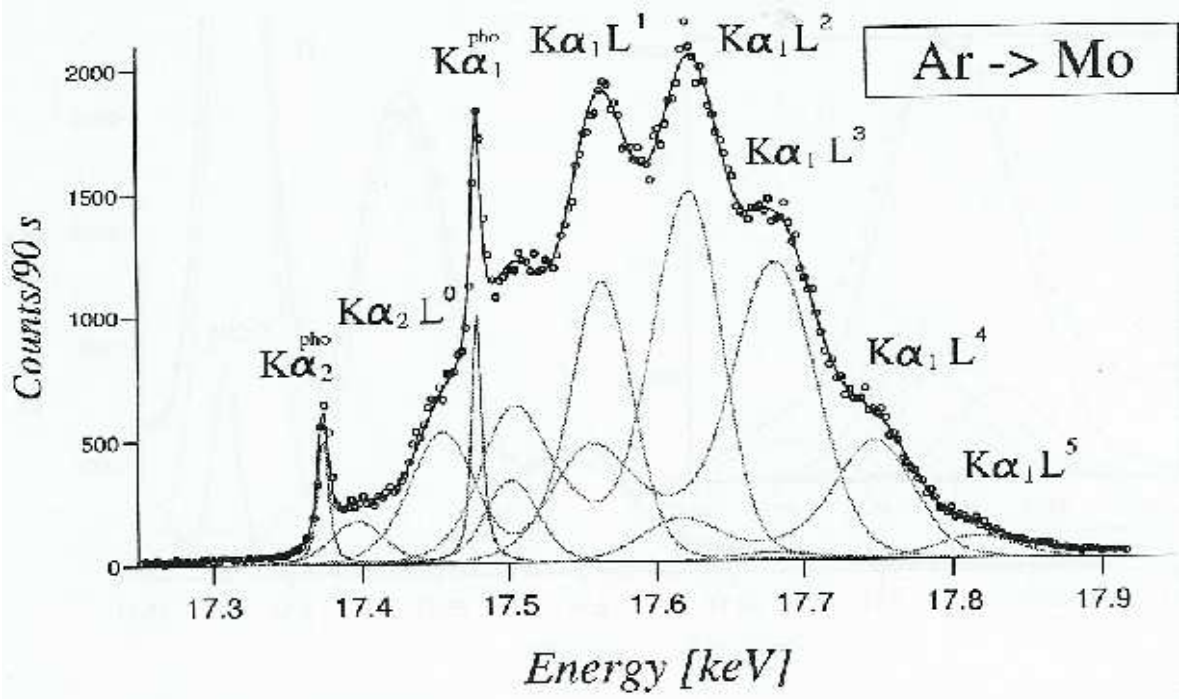


Figure 1: High-resolution crystal spectrometer spectrum of molybdenum $K\alpha$ x-rays. The metallic target was bombarded by Argon ions, accelerated by the cyclotron to an energy of 280 MeV. The dots correspond to the experimental points and the curve to the fit. The figure shows the $K\alpha L$ satellite groups (dotted lines) and the total fit (solid line) of the spectrum. One can notice that, in the case of the ^{40}Ar beam, the shifts of the satellites are sufficiently large for permitting the separation of the photoinduced $K\alpha_{1,2}$ diagram lines labelled "pho".

[B. Galley *et al.*, PRA 1999]

COMPLEX SCALING

The method known as complex coordinate rotation (CCR) has been developed to study the autoionizing states also referred to as *resonances*. These are the states whose discrete energies are embedded in a continuum.

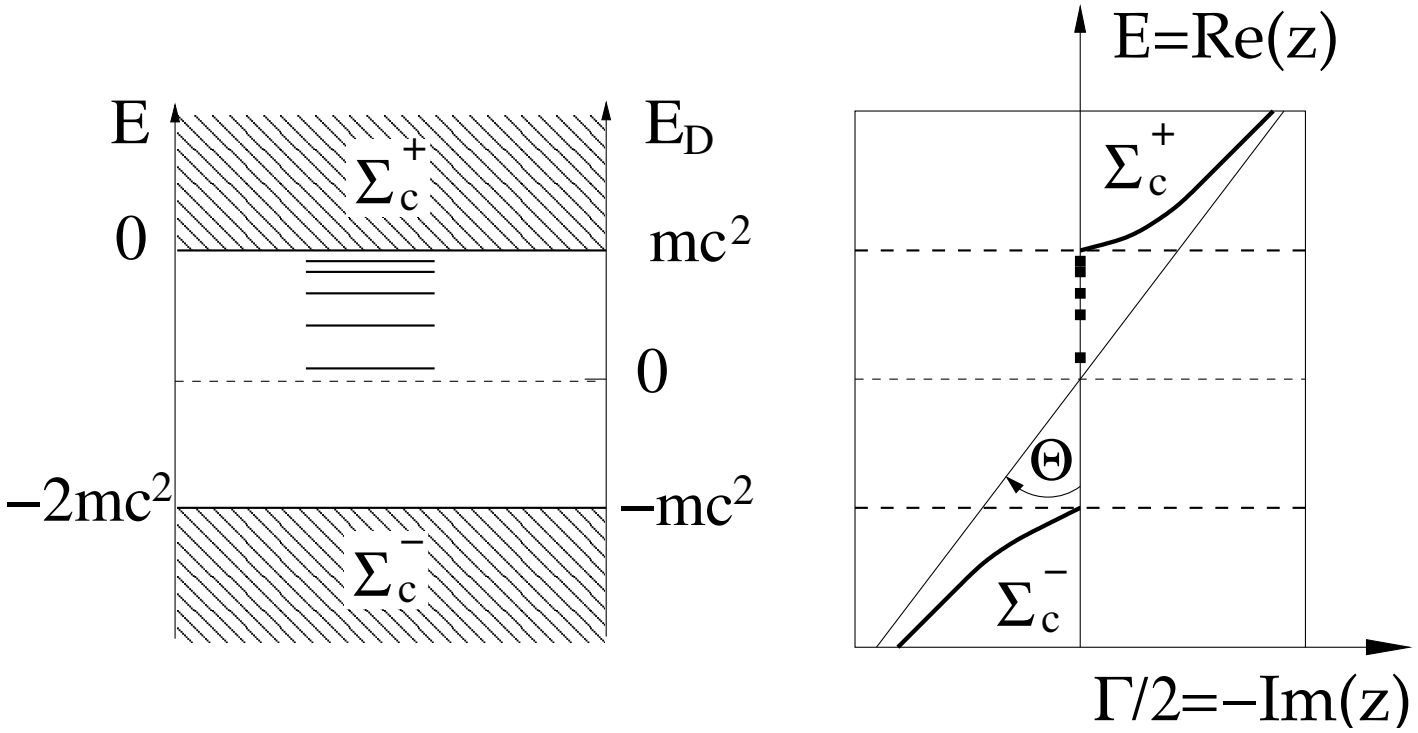
Basic theorem: *Bound state energies of a Hamiltonian do not change under the complex rotation of coordinates*,

$$\boldsymbol{r} \rightarrow \boldsymbol{r} e^{i\Theta},$$

whereas the continua move to the complex plane.

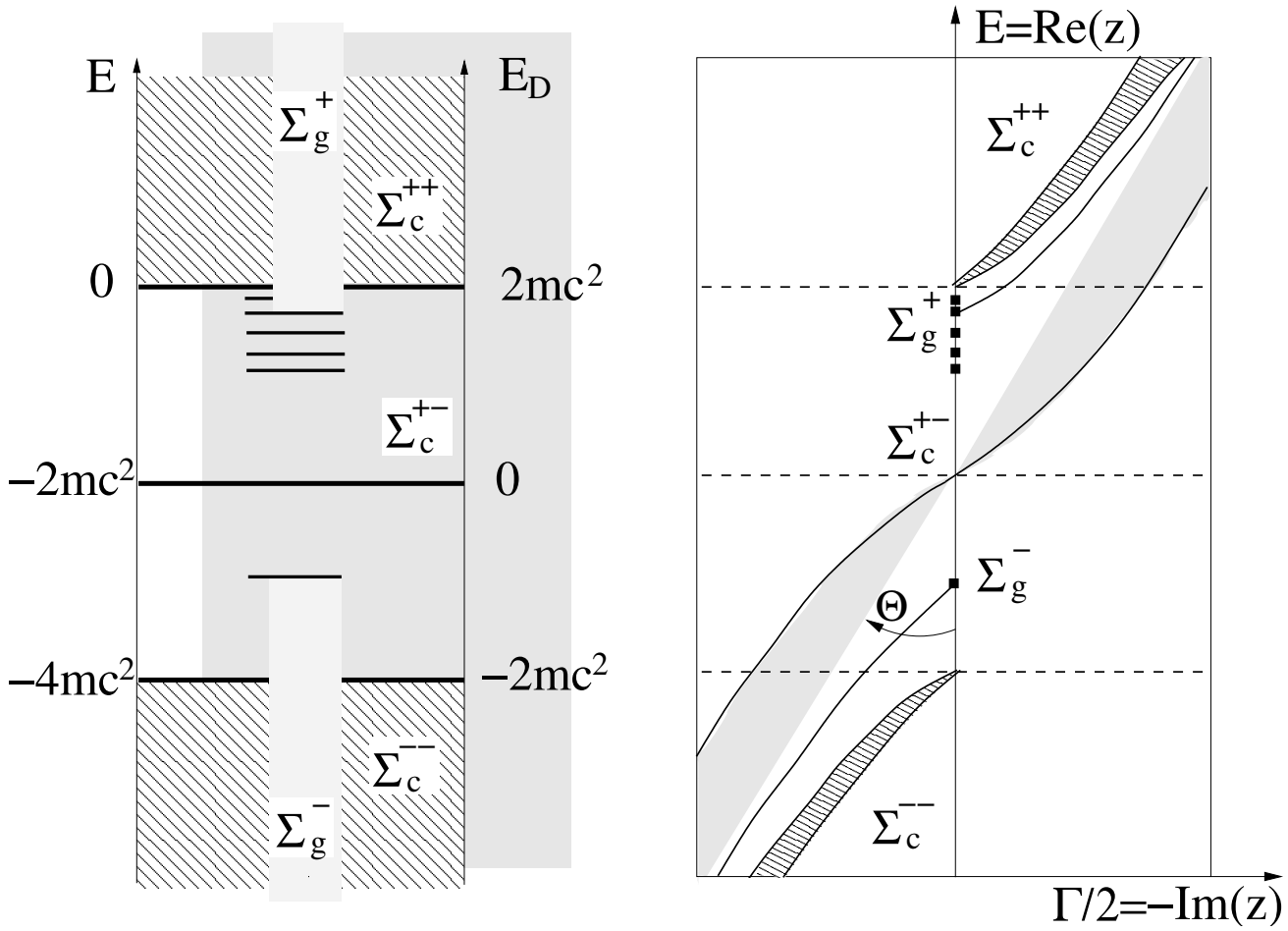
From the formal point of view discrete eigenvalues of a many-electron Dirac Coulomb Hamiltonian are resonances. Therefore the complex scaling method may also be applied to analyzing the Dirac-Coulomb spectrum.

EFFECT OF COMPLEX COORDINATE ROTATION



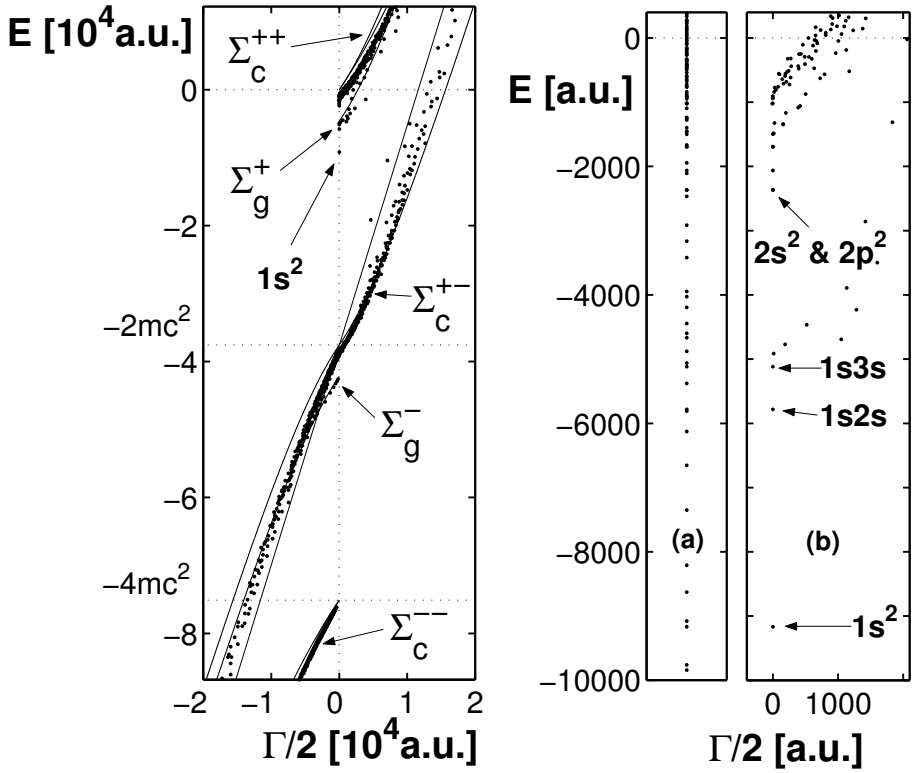
Standard (left) and CCR (right) spectrum of a one-electron Dirac Hamiltonian. Solid lines represent the positive, Σ_c^+, and the negative, Σ_c^-, continua. The points in the real axis represent bound-state energies.

SPECTRUM OF A TWO-ELECTRON DC HAMILTONIAN



The same as before but for a two-electron system.

ALGEBRAIC CCR SPECTRUM OF Z=90 He-LIKE ATOM



Right panel: Enlargement of the bound-state region.

(a) No complex rotation: The discrete and the continuum energies are mixed together.

(b) The rotated spectrum: The continuum eigenvalues are moved to the complex plane.

Basis set: 1826 Dirac spinors

Dots – the computed eigenvalues; Lines – limits of continua

PERTURBATIONAL METHODS

CLASSICAL METHODS

Perturbational methods are applicable if the Hamiltonian may be split onto the unperturbed part $\hat{H}_0$ and a perturbation $\hat{H}'$:

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

so that solutions of the eigenvalue problem of $\hat{H}_0$ are known.
Solutions of the eigenvalue problem of $\hat{H}$ may then be expanded into a power series of the perturbation using the solutions of the unperturbed problem.

- Non-relativistic:
  - Brillouin-Wigner
  - Rayleigh-Schrödinger
- Relativistic
  - Direct perturbation method

Brillouin-Wigner theory

Let

$$(\hat{H}_0 + \hat{H}')|\Psi\rangle = E|\Psi\rangle,$$

$$\hat{H}_0|\Psi^0\rangle = E^0|\Psi^0\rangle.$$

and

$$\langle\Psi^0|\Psi^0\rangle = 1, \quad \langle\Psi|\Psi^0\rangle = 1$$

(the intermediate normalization).

Then $$E = E^0 + \langle\Psi^0|\hat{H}'|\Psi\rangle$$

and

$$|\Psi\rangle = |\Psi^0\rangle + \frac{1}{E - \hat{H}_0}\hat{P}\hat{H}'|\Psi\rangle,$$

where $$\hat{P} = \hat{I} - |\Psi^0\rangle\langle\Psi^0|$$

projects onto the space orthogonal to $|\Psi^0\rangle$.

The last two equations may be iterated.

The result:

$$E = E^0 + \langle \Psi^0 | \hat{H}' | \Psi^0 \rangle + \langle \Psi^0 | \hat{H}' \frac{\hat{P}}{E - \hat{H}_0} \hat{H}' | \Psi^0 \rangle + \cdots .$$

is known as the Brillouin-Wigner expansion.

Note:

On both left- and right-hand-side of the perturbational expansion appears the exact energy E.

Therefore neither E nor $|\Psi\rangle$ is here expanded terms of powers of the perturbation operator.

The method, when restricted to a given order and applied to an N-electron problem, is not *size extensive*, i.e. its N-behaviour is incorrect.

Rayleigh-Schrödinger theory

Let

$$(\hat{H}_0 + \hat{H}')|\Psi\rangle = E|\Psi\rangle,$$

$$\hat{H}_0|\Psi^0\rangle = E^0|\Psi^0\rangle.$$

and

$$\langle\Psi^0|\Psi^0\rangle = 1, \quad \langle\Psi|\Psi^0\rangle = 1$$

(the intermediate normalization).

Then

$$E = E^0 + \langle\Psi^0|\hat{H}'|\Psi\rangle$$

and

$$|\Psi\rangle = |\Psi^0\rangle + \frac{1}{E^0 - \hat{H}_0}\hat{P}(\hat{H}' - E + E^0)|\Psi\rangle.$$

The energy expansion:

$$E = E^0 + \langle \Psi^0 | \hat{H}' | \Psi^0 \rangle + \langle \Psi^0 | \hat{H}' \frac{\hat{P}}{E_0 - \hat{H}_0} \hat{H}' | \Psi^0 \rangle + \cdots .$$

The operator

$$\hat{R}_0 = \frac{\hat{P}}{E^0 - \hat{H}_0}$$

is called the *reduced resolvent*.

In the basis of eigenvectors of $\hat{H}_0$ it may be represented as

$$\hat{R}_0 = \sum_{i \neq 1} \frac{|\Psi_i^0\rangle\langle\Psi_i^0|}{E_0^{(i)} - E_1^0},$$

where $\Psi_1^0 \equiv \Psi^0$ and $E_1^0 \equiv E^0$.

In the third term of the Rayleigh-Schrödinger expansion appears the unperturbed energy E^0, while in the corresponding term of the Brillouin-Wigner expansion - the exact one, E. The higher terms of the Rayleigh-Schrödinger expansion are entirely different from the ones of the Brillouin-Wigner ones. Their classification may be conveniently performed by means of diagrammatic techniques (the Goldstone and the Hugenholtz diagrams are the most commonly used).

In the case of N electron system the Rayleigh-Schrödinger approach may be formulated in such a way that its N-dependence is correct in every order of approximation (the formulation is size-consistent).

The size-consistent version of the Rayleigh-Schrödinger perturbation method is referred to as the *many-body perturbation theory* (MBPT).

Direct perturbation theory

The Dirac equation for a stationary state of an electron in an external potential V (the energy scale is shifted by by mc^2, i.e. $E - mc^2 \to E$):

$$\begin{pmatrix} V-E, & c(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}) \\ c\,(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}), & V-E-2mc^2 \end{pmatrix} \begin{pmatrix} \Psi^{\mathrm{L}} \\ \Psi^{\mathrm{S}} \end{pmatrix} = 0.$$

The unperturbed problem:

$$\begin{pmatrix} V-E, & c(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}) \\ c\,(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}), & -2mc^2 \end{pmatrix} \begin{pmatrix} \Psi^{\mathrm{L}} \\ \Psi^{\mathrm{S}} \end{pmatrix} = 0.$$

From here $\Psi^{\mathrm{S}} = \dfrac{(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})}{2mc}\Psi^{\mathrm{L}}$ and $\left[\dfrac{(\boldsymbol{\sigma}\cdot\mathbf{p})^2}{2m} + V\right]\Psi^{\mathrm{L}} = E\Psi^{\mathrm{L}}$

Dirac equation: $$\left[\hat{H}_0 - \beta^+ E + \beta^- (V - E)\right] \psi = 0,$$

$$\beta^+ = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \quad \beta^- = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix},$$

$$\psi = \begin{pmatrix} \psi^{\mathrm{L}} \\ \psi^{\mathrm{S}} \end{pmatrix} = \begin{pmatrix} \psi^{\mathrm{L}} \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ \psi^{\mathrm{S}} \end{pmatrix} = \psi^+ + \psi^-$$

$$\hat{H}_0 = c\,(\boldsymbol{\alpha} \cdot \hat{\mathbf{p}}) + \beta^+ V - 2\beta^- mc^2,$$

four-component spinors ψ^+ and ψ^- are projections of ψ:

$$\psi^+ = \beta^+ \psi, \quad \psi^- = \beta^- \psi.$$

$$(\hat{H}_0 - \beta^+ E)\psi = 0 \quad - \quad \text{the unperturbed problem,}$$

$$\hat{H}' = \beta^- (V - E) \quad - \quad \text{the perturbation.}$$

The direct perturbation method is appropriate for relativistic perturbational calculations.

It is based on the partition of the Dirac equation which defines the unperturbed problem in the same Hilbert space as the exact one.

The perturbation parameter is equal to the square of the fine-structure constant α. Therefore the k-th order of the perturbation corresponds to a term proportional to α^{2k}.

RELATIVISTIC TWO-COMPONENT METHODS

THE ELIMINATION OF THE SMALL COMPONENTS

The simplest and the most commonly used approach to an approximate describing relativistic effects is the method in which the small components of the wavefunctions are expressed by the large ones using the Dirac equation and then eliminated. As a result a relativistic description based on a two-component wavefunction is obtained. By expanding the resulting equation into a power series of $(E-V)/mc^2$ one obtains the well known Pauli approximation. The resulting Hamiltonian is strongly singular and the relativistic terms can only be used as the first order perturbations. Works directed towards development of a two-component relativistic theory free of the deficiencies of the Pauli approach resulted in formulation of numerous quasirelativistic theories.

THE PAULI METHOD

The Dirac equation

$$V\psi^{\mathrm{L}} + c\,(\boldsymbol{\sigma}\cdot\hat{\boldsymbol{p}})\psi^{\mathrm{S}} = E\,\psi^{\mathrm{L}}$$
$$c\,(\boldsymbol{\sigma}\cdot\hat{\mathrm{p}})\psi^{\mathrm{L}} + (V - 2mc^2)\psi^{\mathrm{S}} = E\,\psi^{\mathrm{S}},$$

Eliminating the small component gives

$$\psi^{\mathrm{S}} = \frac{1}{2mc}\left(1 + \frac{E-V}{2mc^2}\right)^{-1}(\boldsymbol{\sigma}\cdot\hat{\mathrm{p}})\,\psi^{\mathrm{L}} \equiv \hat{X}\psi^{\mathrm{L}},$$

and

$$\hat{H}^{\mathrm{lc}}\psi^{\mathrm{L}} = E\,\psi^{\mathrm{L}}.$$
$$\hat{H}^{\mathrm{lc}} = \frac{1}{2m}(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})\left(1 + \frac{E-V}{2mc^2}\right)^{-1}(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}) + V$$

QUASIRELATIVISTIC FORMULATION

In order to convert this formalism into a quasirelativistic one in which only two-component wavefunctions appear one has to renormalize ψ^{L}:

$$1 = \langle\psi|\psi\rangle = \langle\psi^{\mathrm{L}}|\psi^{\mathrm{L}}\rangle + \langle\psi^{\mathrm{S}}|\psi^{\mathrm{S}}\rangle = \langle\psi^{\mathrm{L}}|\hat{I} + \hat{X}^{\dagger}\hat{X}|\psi^{\mathrm{L}}\rangle = \langle\psi^{\mathrm{qr}}|\psi^{\mathrm{qr}}\rangle,$$

where the quasirelativistic wavefunction and Hamiltonian are defined as

$$\psi^{\mathrm{qr}} = \hat{\mathcal{O}}\psi^{\mathrm{L}},$$

$$\hat{H}^{\mathrm{qr}} = \hat{\mathcal{O}}\hat{H}^{\mathrm{lc}}\hat{\mathcal{O}}^{-1}.$$

with

$$\hat{\mathcal{O}} = \left(\hat{I} + \hat{X}^{\dagger}\hat{X}\right)^{\frac{1}{2}}$$

PAULI HAMILTONIAN

Expanding $\hat{H}^{\mathrm{lc}}$ and $\hat{\mathcal{O}}$ in $(E-V)/mc^2$ on obtains the Pauli Hamiltonian:

$$\hat{H}^{\mathrm{P}} = \frac{\hat{\mathbf{p}}^2}{2m} + V - \frac{\hat{\mathbf{p}}^4}{8m^3c^2} - \frac{\mathbf{s}\cdot(\nabla V \times \hat{\mathbf{p}})}{2m^2c^2} - \frac{\hbar^2}{8m^2c^2}\triangle V.$$

The first two terms give the Schrödinger Hamiltonian. The next terms: the effect of change of the electron mass with velocity, the spin-orbit interaction, a correction due to *Zitterbewegung* (the Darwin correction). All these terms are highly singular and the eigenvalue problem of $\hat{H}^{\mathrm{P}}$ does not have any square-integrable solutions. However this operator may be (and has been) used to estimate the relativistic corrections as the first-order perturbations. By properly restricting its domain one can also use this operator in some variational approaches. However one should remember that for a Coulomb potential there exists an area around the nucleus in which the expansion is invalid, because $\left|(E-V)/mc^2\right| > 1$. On the other hand, in this very area the relativistic effects are the most important.

REGULAR APPROXIMATIONS: ZORA, FORA, etc

There exist many other ways of reducing the Dirac equation to a two-component form. A special attention deserves a recent approach by van Lenthe. If we write

$$\hat{H}^{\rm lc} = (\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})\frac{c^2}{2mc^2-V}\left(1+\frac{E}{2mc^2-V}\right)^{-1}(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})+V,$$

then $\hat{H}^{\rm lc}$ may be expanded in $E/(2mc^2-V)$. This expansion is justified for Coulomb-type potentials also near the singularity. One gets

$$\begin{aligned}\hat{H}^{\rm lc} &= V+(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})\frac{c^2}{2mc^2-V}(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})\\ &- (\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})\left(\frac{c^2}{2mc^2-V}\right)\left(\frac{E}{2mc^2-V}\right)(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})+\cdots\end{aligned}$$

In a similar way one can expand the normalization operator $\hat{\mathcal{O}}$. In effect, in the lowest order of the expansion, one obtains the so called *zeroth-order regular approximated* (ZORA) Hamiltonian:

$$\hat{H}^{\mathrm{zora}} = (\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}) \frac{c^2}{2mc^2 - V} (\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}) + V.$$

ZORA Hamiltonian is regular, bounded from below and can be used in variational calculations without any special restrictions.

In the higher order one gets the Hamiltonian in the *first-order regular approximation* (FORA):

$$\hat{H}^{\mathrm{fora}} = \hat{H}^{\mathrm{zora}} - \frac{1}{2}\left\{(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})\frac{c^2}{2mc^2 - V}(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}),\ \hat{H}^{\mathrm{zora}}\right\}$$

This Hamiltonian, similarly as the Pauli one, does not have square-integrable eigenfunctions and in not limited from below. Therefore it cannot be used in variational calculations, unless the space of the trial function is properly constrained.

FOLDY-WOUTHUYSEN TRANSFORMATION

A large family of two-component relativistic equations may be obtained by using different modifications of unitary transformations which decouple the large and small components in the Dirac equation. The best known are the Foldy-Wouthuysen and Douglas-Kroll transformations.

Foldy and Wouthuysen transformation: a systematic procedure for decoupling the large and the small component parts of the Dirac equation to any fixed order in the fine structure constant.

Let us consider a unitary transformation

$$\hat{H}^{\mathrm{fw}} = U\,\hat{H}_{\mathrm{D}}\,U^{\dagger}$$

with

$$U = \left(\hat{I} + \hat{W}^{\dagger}\hat{W}\right)^{-1/2} \begin{pmatrix} \hat{I} & \hat{W}^{\dagger} \\ -\hat{W} & \hat{I} \end{pmatrix}$$

This transformation brings the Dirac Hamiltonian to a block-diagonal form (I.E. decouples the large and the small components) if $\hat{W}$ fulfills the following condition:

$$\hat{W} = \frac{1}{2mc}\left[(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}) - \hat{W}(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})\hat{W}\right] + \frac{1}{2mc^2}\left[V,\hat{W}\right].$$

If this equation is solved iteratively then consecutive iterations give corrections of consecutive orders in α. One can also represent this equation algebraically in a model space and find matrix elements of $\hat{W}$.

The "large component" part of the transformed equation:

$$\hat{H}^{\mathrm{fw}}\psi^{\mathrm{fw}} = E\psi^{\mathrm{fw}},$$

where

$$\hat{H}^{\mathrm{fw}} = \hat{W}^{\dagger}\, V\, \hat{W} - V + c\left[(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})\hat{W} + \hat{W}^{\dagger}(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})\right] - 2mc^2$$

is bounded from below and its spectrum is the same as the positive-energy spectrum of $\hat{H}_D$.

The expansion of $\hat{W}$ into a power series of α in the lowest order leads to the Pauli Hamiltonian.

DOUGLAS-KROLL TRANSFORMATION

In the case of a free particle ($V = 0$) the Foldy-Wouthuysen transformation may be expressed in a finite form:

$$\hat{W}_0 = \frac{(\boldsymbol{\sigma} \cdot \hat{\mathbf{p}})}{mc} \left[1 + \sqrt{1 + \frac{(\boldsymbol{\sigma} \cdot \hat{\mathbf{p}})^2}{(mc)^2}} \right]^{-1}$$

If $V \neq 0$ then in the $\hat{W}_0$ transformed Dirac Hamiltonian the term coupling large and small components is proportional to $\left[V, \hat{W} \right]$. From here one can design a decoupling procedure in which consecutive orders are proportional to powers of V. This procedure is known as the Douglas-Kroll transformation.

ONE-ELECTRON PAULI HAMILTONIAN

$$\hat{\boldsymbol{\pi}} = \left(\hat{\mathbf{p}} - \frac{e}{c}\hat{\mathbf{A}}\right)$$

$$\mathbf{s} = \frac{\hbar}{2}\boldsymbol{\sigma}$$

$$\hat{H}^{\mathrm{P}}(1) = \hat{H}^{\mathrm{Sch}}(1) + \hat{h}^{\mathrm{P}}(1)$$

Unperturbed Hamiltonian – non-relativistic (Schrödinger):

$$\hat{H}^{\mathrm{Sch}} = \frac{\hat{\boldsymbol{\pi}}^2}{2m} + V,$$

Perturbation – Pauli corrections:

$$\hat{h}^{\mathrm{P}} = -\frac{e}{mc}\left(\mathbf{s}\cdot\hat{\mathbf{B}}\right) - \frac{\hat{\boldsymbol{\pi}}^4}{8m^3c^2} - \frac{\mathbf{s}\cdot(\nabla V\times\hat{\boldsymbol{\pi}})}{2m^2c^2} - \frac{\hbar^2}{8m^2c^2}\nabla(\nabla V).$$

Two-electron Pauli-Breit Hamiltonian:

$$\hat{H}^{\mathrm{BP}}(1,2) = \hat{H}^{\mathrm{Sch}}(1,2) + \hat{h}^{\mathrm{P}}(1) + \hat{h}^{\mathrm{P}}(2) + V_{12}^{\mathrm{B}}(1,2)$$

LIÉNARD-WIECHERT POTENTIALS

Potentials generated at $\mathbf{r}_1$ by a charge e located at $\mathbf{r}_2$ and moving with velocity $\mathbf{v}_2$ (Alfred-Marie Liénard 1898, Emil Wiechert 1900)

$$\begin{aligned} V_2^{\mathrm{lw}}(\mathbf{r}_1) &= \frac{e}{r_{12}}\left[1+\frac{(\mathbf{v}_2\cdot\mathbf{r}_{12})}{cr_{12}}\right]^{-1} \\ &= \frac{e}{r_{12}}\left[1-\frac{(\mathbf{v}_2\cdot\mathbf{r}_{12})}{cr_{12}}\right]+O\left[\left(\frac{v}{c}\right)^2\right] \end{aligned}$$

and

$$\mathbf{A}_2^{\mathrm{lw}}(\mathbf{r}_1)=\frac{\mathbf{v}_2}{c^2}\,V_2^{\mathrm{lw}}(\mathbf{r}_1)=\frac{e}{r_{12}}\frac{\mathbf{v}_2}{c^2}+O\left[\left(\frac{v}{c}\right)^2\right]$$

Assuming that in a two-electron system V and $\mathbf{A}$ are due to the nucleus *and* the second electron we get the classical (non-quantum) interaction energy of two electrons:

$$V_{12} = \frac{e^2}{r_{12}} \left[1 - \frac{\mathbf{v}_1 \cdot \mathbf{v}_2}{2c^2} - \frac{(\mathbf{v}_1 \cdot \mathbf{r}_{12})(\mathbf{v}_2 \cdot \mathbf{r}_{12})}{2c^2 {r_{12}}^2} \right] + O\left[\left(\frac{v}{c} \right)^4 \right],$$

According to the correspondence principle, we substitute:

$$\mathbf{v} \Rightarrow c\,\alpha.$$

The resulting quaantum-mechanical interacion operator (Breit correction):

$$V_{12}^{\mathrm{B}} = \frac{e^2}{r_{12}} \left[1 - \frac{(\alpha_1 \cdot \alpha_2)}{2} - \frac{(\alpha_1 \cdot \mathbf{r}_{12})(\alpha_2 \cdot \mathbf{r}_{12})}{2 {r_{12}}^2} \right].$$

The cosecutive term describe, respectively, the instantenous (non-relativistic) interaction, correction due to two-electron magnetic interaction and correction due to retardation resulting from the finite velocity of propagation of the interaction.

A relativistic Hamiltonian in which the two-electron terms are approximated by e^2/r_{12} is known as the *Dirac-Coulomb Hamiltonian*. If the magnetic and retardation corrections (*Breit interactions*) are included, then the Hamiltonian is called the *Dirac-Breit Hamiltonian*.

Since the interaction potential is correct up to $(v/c)^2$ terms, the formulation based on this Hamiltonian is only approximately Lorentz invariant.

The elimination of the small components from the Dirac-Breit equation leads to two-electron relativistic Breit-Pauli corrections:

- orbit-orbit interaction,
- spin-spin interaction,
- spin-other orbit interaction,
- two-electron Darwin correction.

BREIT-PAULI HAMILTONIAN

$$\begin{aligned} \hat{H}^{\rm BP}(1,2) &= \hat{H}^{\rm Sch}(1,2) + \hat{h}^{\rm P}(1) + \hat{h}^{\rm P}(2) \\ &+ \hat{h}^{\rm oo}(1,2) + \hat{h}^{\rm d2}(1,2) + \hat{h}^{\rm so}(1,2) + \hat{h}^{\rm ss}(1,2) \end{aligned}$$

where

- $\hat{H}^{\rm Sch}(1,2)$ is the two-electron Schrödinger Hamiltonian,
- $\hat{h}^{\rm P}(j) = \dfrac{\hat{\boldsymbol{p}}_j^4}{8m^3c^2} - \dfrac{\mathbf{s}_j \cdot (\nabla V_j \times \hat{\boldsymbol{p}}_j)}{2m^2c^2} - \dfrac{\hbar^2}{8m^2c^2}\triangle V_j,\ j = 1,2$

  where $V_j \equiv V(j)$, $\hat{\boldsymbol{p}}_j \equiv \hat{\boldsymbol{p}}(j)$, etc, are one-electron Pauli corrections,
- The remaining two-electron terms – Breit-Pauli corrections

BREIT-PAULI CORRECTIONS

- Orbit-orbit interaction:

$$\hat{h}^{\mathrm{oo}}(1,2) = -\frac{1}{2m^2c^2}\left[\frac{(\hat{\boldsymbol{p}}_1 \cdot \hat{\boldsymbol{p}}_2)}{r_{12}} + \frac{\mathbf{r}_{12} \cdot (\mathbf{r}_{12} \cdot \hat{\boldsymbol{p}}_1)\,\hat{\boldsymbol{p}}_2}{r_{12}^3}\right]$$

- Two-electron Darwin correction:

$$\hat{h}^{\mathrm{d2}}(1,2) = \frac{1}{4m^2c^2}\,(\triangle_1 + \triangle_2)\,\frac{1}{r_{12}}$$

- Two-electron spin-orbit coupling:

$$\hat{h}^{\mathrm{so}}(1,2) = \frac{1}{m^2c^2}\left(\frac{[\mathbf{r}_{12} \times \hat{\boldsymbol{p}}_2] \cdot \mathbf{s}_1}{r_{12}^3} + \frac{[\mathbf{r}_{21} \times \hat{\boldsymbol{p}}_1] \cdot \mathbf{s}_2}{r_{12}^3}\right)$$

- Spin-spin interaction:

$$\hat{h}^{\mathrm{ss}}(1,2) = \frac{1}{m^2c^2}\left[\frac{(\mathbf{s}_1 \cdot \mathbf{s}_2)}{r_{12}^3} - \frac{(\mathbf{s}_1 \cdot \mathbf{r}_{12})(\mathbf{s}_2 \cdot \mathbf{r}_{12})}{r_{12}^5} - \frac{8\pi}{3}(\mathbf{s}_1 \cdot \mathbf{s}_2)\delta(\mathbf{r}_{12})\right]$$