Advanced Quantum Chemistry

Lecture Summary
(Autumn Semester 2015)

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Disclaimer

This is a summary of the *Advanced Quantum Chemistry* lecture taught by Prof. Reiher during the autumn semester 2015 at the ETH Zürich and was written by me as a preparation for the oral exam. All of the equations presented in this summary have been presented during the lecture [4], which is based on [5]; equations taken from other sources are appropriately referenced in the text.

Lecture 1(a): Standard Quantum Chemistry

- The goal of quantum chemistry is to retrieve molecular properties of interest like reaction energies, excitation energies, bond lengths and angles, vibrational frequencies, dipole moments, etc.
  - All quantities can be derived from the electronic energy E_{el}, either as differences or derivatives of E_{el}
- The non-relativistic Hamiltonian operator of a molecule of N electrons and M atomic nuclei is given by

$$\hat{H} = \hat{T} + \hat{V} = \hat{T}_{\mathrm{e}} + \hat{T}_{\mathrm{n}} + \hat{V}_{\mathrm{ee}} + \hat{V}_{\mathrm{en}} + \hat{V}_{\mathrm{nn}} \quad , \tag{1}$$

with

$$\hat{T}_{\mathrm{e}} = \sum_{i=1}^{N} \left(-\frac{1}{2} \nabla_i^2 \right) \quad , \tag{2}$$

$$\hat{T}_{n} = \sum_{I=1}^{M} \left(-\frac{1}{2M_I} \right) \quad , \tag{3}$$

$$\hat{V}_{\mathrm{ee}} = \sum_{i=1}^{N} \sum_{j>i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad , \tag{4}$$

$$\hat{V}_{\mathrm{en}} = -\sum_{i=1}^{N} \sum_{I=1}^{M} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \quad , \tag{5}$$

$$\hat{V}_{\mathrm{en}} = \sum_{I=1}^{M} \sum_{J>I}^{M} \frac{Z_I \, Z_J}{|\mathbf{R}_I - \mathbf{R}_I|} \quad , \tag{6}$$

where $\hat{T}_{\mathrm{n}}$ consists of the kinetic energy operators for each nucleus in the system, $\hat{T}_{\mathrm{e}}$ consists of the kinetic energy operators for each electron in the system, $\hat{V}_{\mathrm{ee}}$ is the potential energy arising from Coulombic electron-electron repulsions, $\hat{V}_{\mathrm{en}}$ is the total electron-nucleus Coulombic attraction in the system, and V_{nn} is the potential energy arising from the Coulombic nuclei-nuclei repulsion [1]

- The electronic Schrödinger equation is defined as

$$\hat{H}_{\mathrm{el}} \Psi_{\mathrm{el},n}^{\{\mathbf{R}_I\}}(\{\mathbf{r}_i\}) = E_{\mathrm{el}} \Psi_{\mathrm{el},n}^{\{\mathbf{R}_I\}}(\{\mathbf{r}_i\}) \quad , \tag{7}$$

  with the superscript implying that the electronic Schrödinger equation is solved for a given set of nuclear coordinates $\{\mathbf{R}_I\}$, which reduces then the number of dynamical coordinates over which one has to integrate

  - The Hamiltonian $\hat{H}_{\mathrm{el}}$ is defined as (see Eq. (1))

$$\hat{H}_{\mathrm{el}} = \hat{H} - \hat{T}_{\mathrm{n}} \tag{8}$$

- Separation of electronic and nuclear motion: The Schrödinger equation depends on both nuclear and electronic coordinates, and is defined as

$$\hat{H} \psi_k(\{\mathbf{r}_i\}, \mathbf{R}_I) = E_k \psi_k(\{\mathbf{r}_i\}, \mathbf{R}_I) \tag{9}$$

  - Exact ansatz: The total wave function Ψ_k may be expanded from a complete basis set consisting of the electronic wave functions $\Psi_{\mathrm{el,n}}$, i.e.,

$$\psi_k(\{\mathbf{r}_i\}, \mathbf{R}_I) = \sum_n \chi_{k,n}(\{\mathbf{R}_I\}) \cdot \Psi_{\mathrm{el},n}(\{\mathbf{r}_i\}, \mathbf{R}_I) \tag{10}$$

  - Born-Oppenheimer approximation: The total wave function Ψ_k is expressed as a product of a single electronic and nuclear wave function, i.e.,

$$\psi_k(\{\mathbf{r}_i\}, \mathbf{R}_I) \approx \chi_{k,n}(\{\mathbf{R}_I\}) \cdot \Psi_{\text{el,n}}^{\{\mathbf{R}_I\}} \mathbf{R}_I(\{\mathbf{r}_i\}) \tag{11}$$

- The electronic wave function Ψ_{el} can be approximated using one-electron functions ϕ_i. The Slater determinant is the general ansatz for an antisymmetrized and normalized N-electron wave function and is given by

$$\Psi_{\text{el}}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{x}_1) & \ldots & \phi_N(\mathbf{x}_1) \\ \vdots & \ddots & \vdots \\ \phi_1(\mathbf{x}_N) & \ldots & \phi_N(\mathbf{x}_N) \end{vmatrix} \tag{12}$$

- Hartree-Fock theory uses a single Slater determinant to approximate the exact ground-state energy $E_{\text{el},0}$. Since the Hartree-Fock approach does not consider electron correlation effects, i.e. effects arising from the interaction between electrons, even by using a complete basis set (Hartree-Fock limit) a Hartree-Fock error is introduced, which is called the correlation energy $E_{\text{el,corr}}$. The correlation energy is defined as the difference between the Hartree-Fock energy calculated at the Hartree-Fock limit $E_{\text{el}}^{\text{HF}}$ and the exact ground-state energy $E_{\text{el},0}$, i.e.,

$$E_{\text{el,corr}} = E_{\text{el}}^{\text{HF}} - E_{\text{el},0} \tag{13}$$

  - Møller-Plesset perturbation theory, configuration interaction, multi-configuration self-consistent-field methods, and density functional theory consider the electron correlation effects

Lecture 1(b): Newtonian Mechanics and Maxwell's Electrodynamics

- An inertial frame IS has a constant velocity
- Relativity principle of Galilei:
  1. All inertial frames are equivalent; none can be favored over another
  2. Newton's laws of motion have the same form in all inertial frames of reference; this is called *invariance in form* or *covariance*
     - General covariance: invariance of the form of physical laws under arbitrary differentiable coordinate transformations
     - Newton's laws of motion are also called *Gallilean-covariant*, since they are invariant under Galilean transformations
- Lagrange Formalism: Any mechanical system of N particles in $\mathbb{R}^3$, which is subject to R constraints, features in general $f = 3N - R$ degrees of freedom represented by generalized coordinates $q_1, \ldots, q_f$ independent of each other and compatible with all constraints. The Lagrangian is thus defined as

$$L(q, \dot{q}, t) = T(q, \dot{q}, t) - V(q, \dot{q}, t) \tag{14}$$

- The Poisson bracket between two arbitrary phase space functions $u = u(q, p, t)$ and $v = v(q, p, t)$ is defined as

$$\{u, v\} = \{u, v\}_{q,p} = \sum_{i=1}^{f} \left(\frac{\partial u}{\partial q_i} \frac{\partial v}{\partial p_i} - \frac{\partial u}{\partial p_i} \frac{\partial v}{\partial q_i} \right) \tag{15}$$

Electrodynamics

- Maxwell's equations describe the classical behaviour of electric and magnetic fields and their interation with charged particles and currents. The Maxwell equations consist of the following equations (Gaussian units are used, i.e., $4\pi\epsilon_0 = 1$):
  1. Gauss's law for electric fields states that the electric flux out of any closed surface is proportional to the total charge enclosed within the surface [3]:

$$\operatorname{div} \mathbf{E}(\mathbf{r}, t) = 4\pi\rho(\mathbf{r}, t) \tag{16}$$

  2. Ampères' law states that a current density $\mathbf{j}$ and a time-varying electric field $\mathbf{E}$ give rise to a magnetic vortex field $\mathbf{B}$:

$$\operatorname{curl} \mathbf{B}(\mathbf{r}, t) - \frac{1}{c} \frac{\partial \mathbf{E}(\mathbf{r}, t)}{\partial t} = \frac{4\pi}{c} \mathbf{j}(\mathbf{r}, t) \tag{17}$$

3. Faraday's law of induction states that a time-varying magnetic field causes an electric vortex field:

$$\operatorname{curl}\mathbf{E}(\mathbf{r},t)+\frac{1}{c}\frac{\partial\mathbf{B}(\mathbf{r},t)}{\partial t}=0 \tag{18}$$

4. Gauss's law for magnetism states that magnetic monopoles, i.e., *magnetic charges*, do not exist:

$$\operatorname{div}\mathbf{B}(\mathbf{r},t)=0 \tag{19}$$

- The continuity equation describes the transport of some quantity and is a direct result of Eqs. (16) and (17), and is given by

$$\frac{\partial\rho}{\partial t}+\operatorname{div}\mathbf{j}=0 \tag{20}$$

- Electric and magnetic fields are completely determined by a set of only four fields - the *scalar potential* $\phi=\phi(\mathbf{r},t)$ and the *vector potential* $\mathbf{A}=\mathbf{A}(\mathbf{r},t)$:

$$\mathbf{E}=-\operatorname{grad}\phi-\frac{1}{c}\frac{\partial\mathbf{A}}{\partial t} \tag{21}$$

$$\mathbf{B}=\operatorname{curl}\mathbf{A} \tag{22}$$

  - A vector potential is a function $\mathbf{A}$ such that [6]

$$\mathbf{B}\equiv\operatorname{curl}\mathbf{A} \tag{23}$$

  - From Eqs. (21) and (22) we find that ϕ and $\mathbf{A}$ are not unique, since both are defined in terms of derivatives of the potentials, meaning there is an infinite family of possible potentials that will alll lead to the same fields [2]:

$$\phi\rightarrow\phi'=\phi-\frac{1}{c}\frac{\partial\chi(\mathbf{r},t)}{\partial t} \tag{24}$$

$$\mathbf{A}\rightarrow\mathbf{A}'=\mathbf{A}+\operatorname{grad}\chi(\mathbf{r},t) \tag{25}$$

    * The freedom to add a constant potential is called *gauge freedom* [2].
    * The different potentials one can obtain from Eqs. (24) and (25) that lead to the same physical field are generated by means of a gauge transformation [2].
      · In our case, a gauge transformation is any formal, systematic transformation of the potentials ϕ and $\mathbf{A}$ that leaves the fields $\mathbf{E}$ and $\mathbf{B}$ invariant.[2]. Any observable, e.g. $\mathbf{E}$ and $\mathbf{B}$ must be gauge invariant.

- The Lagrangian that yields empirically confirmed equations of motions is given by

$$L(\mathbf{r},\dot{\mathbf{r}},t)=\underbrace{\frac{1}{2}m\dot{\mathbf{r}}^2}_{\equiv T(\dot{\mathbf{r}})}-\underbrace{q\,\phi(\mathbf{r},t)+\frac{q}{c}\dot{\mathbf{r}}\cdot\mathbf{A}(\mathbf{r},t)}_{\equiv U(\mathbf{r},\dot{\mathbf{r}},t)} \tag{26}$$

- The Hamiltonian for a charged particle moving in electromagnetic fields is defined as

$$H(\mathbf{r},\mathbf{p},t) = \frac{1}{2m}\left[\mathbf{p} - \frac{q}{c}\mathbf{A}(\mathbf{r},t)\right]^2 + q\,\phi(\mathbf{r},t) \tag{27}$$

Lecture 2: Einsteinean Mechanics

- Galilei transformations permit velocities larger than the speed of light in vacuum c, but it has been verified in numerous experiments that all observers in all inertial frames, independently of their state of motion, always measure the same speed of light,

$$c \approx 299792 \frac{\text{km}}{\text{s}} = \text{const} \quad , \forall \text{IS} \quad . \tag{28}$$

- Maxwell's equations directly yield a wave equation, which states that the propagation of electromagnetic fields in vacuum occurs with the speed c.
  - Experimentally one finds that the Maxwell equations are valid for any inertial system.

- Consider two events E_1, E_2 connected by a light signal. An observer in IS will describe this process by the two events

$$E_1 : (t_1, \mathbf{r}_1) \quad \text{and} \quad E_2 : (t_2, \mathbf{r}_2) \tag{29}$$

$$\frac{|\mathbf{r}_2 - \mathbf{r}_1|}{t_2 - t_1} = c \Leftrightarrow c^2(t_2 - t_1)^2 - (\mathbf{r}_2 - \mathbf{r}_1)^2 = 0 \quad . \tag{30}$$

  - The four-dimensional distance or *space-time* interval s_{12} between any two events is defined as

$$s_{12}^2 \equiv c^2(t_2 - t_1)^2 - r_{12}^2 \quad . \tag{31}$$

Lorentz Transformations*

- Four-dimensional space-time vector:

$$x = x^\mu = \begin{pmatrix} x^0 \\ x^1 \\ x^2 \\ x^3 \end{pmatrix} = \begin{pmatrix} ct \\ x \\ y \\ z \end{pmatrix} = \begin{pmatrix} ct \\ \mathbf{r} \end{pmatrix} \quad . \tag{32}$$

- Metric tensor (Minkowski tensor):

$$g = g_{\mu\nu} = \text{diag}(1, -1, -1, -1) \quad . \tag{33}$$

  - Express the squared four-dimensional distance s_{12}^2 between two events (Eq. (31)) as

$$s_{12}^2 = g_{\mu\nu}(x_2^\mu - x_1^\mu)(x_2^\nu - x_1^\nu) = c^2(t_2 - t_1)^2 - r_{12}^2 \tag{34}$$

* Einstein's summation convention is used, i.e.,

$$y = \sum_{i=1}^{3} c_i x^i = c_1 x^1 + c_2 x^2 + c_3 x^3 = c_i x^i \tag{35}$$

- The flat four-dimensional space described by space-time vectors x and equipped with the metric g is called *Minkowski space*.
- The *covariant* four-dimensional space-time vector x_μ is defined as

$$x_\mu = \begin{pmatrix} x^0 \\ x^1 \\ x^2 \\ x^3 \end{pmatrix} = \begin{pmatrix} ct \\ -x \\ -y \\ -z \end{pmatrix} = \begin{pmatrix} ct \\ -\mathbf{r} \end{pmatrix} \quad . \tag{36}$$

  - The *contravariant* four-dimensional space-time vector x^μ is defined in Eq. (32).

- The metric g can be employed to lower (or raise) indices of any vector according to

$$x_\mu = g_{\mu\nu} x^\nu \Leftrightarrow x^\mu = g_{\mu\nu} x_\nu \quad . \tag{37}$$

- The *four-dimensional scalar product* between two 4-vectors a and b is defined by

$$a\dot{b} = a^T g b = a^\mu b_\mu = a^0 b^0 - \mathbf{a} \cdot \mathbf{b} \quad . \tag{38}$$

- Transformations that leave the space-time interval s_{12}^2 for any two events invariant are called *Lortentz transformations* and are given by

$$x' = \Lambda x + b \Leftrightarrow x'^\mu = \Lambda^\mu{}_\nu x^\nu + b^\mu \quad . \tag{39}$$

  - The fundamental property of the Lorentz transformations is

$$\Lambda^T g \Lambda = g \Leftrightarrow \Lambda^\alpha{}_\mu g_{\alpha\beta} \Lambda^\beta{}_\nu = g_{\mu\nu} \quad . \tag{40}$$

  - Shorthand notations:

$$\overline{\Lambda} = \Lambda^{-1} = \overline{\Lambda}^\mu{}_\nu \equiv \Lambda_\nu{}^\mu \quad , \tag{41}$$

$$\Lambda_\nu{}^\mu \equiv g_{\nu\alpha} g^{\mu\beta} \Lambda^\alpha{}\beta \quad . \tag{42}$$

- Contravariant Lorentz 4-vector:

$$A'^\mu = \Lambda^\mu{}_\nu A^\nu \quad . \tag{43}$$

- Covariant Lorentz 4-vector:

$$B'_\mu = \overline{\Lambda}^\mu{}_\nu B_\nu = \Lambda_\mu{}^\nu B_\nu \quad . \tag{44}$$

- 4-gradient:

$$\partial_\mu = \frac{\partial}{\partial x^\mu} = \left(\frac{1}{c}\frac{\partial}{\partial t}, \nabla\right) \quad . \tag{45}$$

The d'Alembert Operator (Eq. (75))

The d'Alembert operator is defined as

$$\Box \equiv \partial_\mu \partial^\mu = \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \Delta \tag{46}$$

and is the Laplace operator of the Minkowski space.

The Lorentz Factor γ (Eq. (87))

$$\gamma = \frac{1}{\sqrt{1 - v^2/c^2}} \tag{47}$$

Derivation

1. For the sake of simplicity a Lortenz boost in x-direction is considered, i.e.,

$$\begin{pmatrix} ct' \\ x' \end{pmatrix} = \begin{pmatrix} \Lambda^0{}_0 & \Lambda^0{}_1 \\ \Lambda^1{}_0 & \Lambda^1{}_1 \end{pmatrix} \begin{pmatrix} ct \\ x \end{pmatrix} \quad . \tag{48}$$

2. By considering the emission of two light signals at $t = t' = 0$ from the origin, one in negative x-direction and one in positive x-direction we find that $\Lambda^0{}_0 = \Lambda^1{}_1$ and $\Lambda^1{}_0 = \Lambda^1{}_0$, such that only two parameters of Λ remain to be determined. With further considerations, we finally find that

$$\Lambda^1{}_0 = -(v/c)\Lambda^0{}_0 \quad . \tag{49}$$

3. The Lorentz back transfromation from IS' to IS is given by replacing v with $-v$.

4. Considering the Lorentz back and forth transformations for the x-coordinate we find

$$x = \Lambda^0{}_0(x' + vt') = (\Lambda^0{}_0)^2 \left(1 - \frac{v^2}{c^2}\right) x \Leftrightarrow \Lambda^0{}_0 = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} \equiv \gamma = \gamma(v) \quad . \tag{50}$$

General

- The Lorentz factor is the factor by which time, length and relativistic mass change for an object while that object is moving.
  - Length contraction:
    1. An object of length l_0 is at rest in IS'. An observer in IS' will measure the length of this stick to be l_0. This length of an object is denoted as its *proper length* l_0.
    2. The length of this object in IS must be measured at the same time t, i.e. $t_1 = t_2 = 0$.
    3. By applying the Lorentz boost, one finds that the length of this object in IS is defined as

$$l = \frac{l_0}{\gamma} \quad , \tag{51}$$

       thus meaning that the length of moving bodies is smaller than their proper length. This phenomenon is called *length contraction of moving bodies*.
  - Time delation:
    1. Place a clock at the origin of IS' which shall be at rest in IS'.
    2. Two measurements are in IS for position x_1, x_2, where x_1 is assumed to be 0.
    3. Define two events E_1, E_2 by the passing of the IS'-clock at positions x_1, x_2, which are at rest in IS:

$$E_1 : (t_1 = 0, x_1 = 0) \quad \text{in IS} \quad \rightarrow (t_1' = 0, x_1' = 0) \quad \text{in IS'} \tag{52}$$
$$E_1 : (t_2, x_2 = vt_2) \quad \text{in IS} \quad \rightarrow (t_2', x_2' = x_1' = 0) \quad \text{in IS'} \tag{53}$$
$$\tag{54}$$

    4. The time difference of these two events for an observer in IS' is

$$\tau \equiv t_2' - t_1' \tag{55}$$

       and it's called the *proper time* of the clock.
    5. With $t \equiv t_2 - t_1$ denoting the time difference in IS, the relation between the time differences in IS and IS' is

$$t = \gamma\tau \quad , \tag{56}$$

       meaning that the time difference t in IS is thus always larger than the time difference τ in IS', where the clock is at rest. This is called *time delation*, meaning that moving clocks show different times as compared to those at rest.

- For small velocities $v \ll c$, the Lorentz factor might be approximated by the first terms of its series expansion, i.e.,

$$\gamma(v) \approx 1 + \frac{1}{2}\frac{v^2}{c^2} + \frac{3}{8}\frac{v^4}{c^4} + \dots \quad . \tag{57}$$

The Covariant Continuity Equation (Eq. (125))

The covariant continuity equation is given by

$$\underbrace{\partial_\mu j^\mu}_{\text{Lorentz scalar}} = 0 \Leftrightarrow \frac{\partial \rho}{\partial t} + \operatorname{div} \mathbf{j} = 0 \quad , \tag{58}$$

where

$$(j^\mu(x)) = (c\rho(\mathbf{r}, t), \mathbf{j}(\mathbf{r}, t)) \tag{59}$$

combines the charge density ρ and the current density $\mathbf{j}$ to give a four-component quantity. Further, a Lorentz scalar is a scalar which is invariant under Lorentz transformation.

The General Lorentz Boost (Eq. (90))

A rotation-free Lorentz transformation is called a *Lorentz boost*. The general Lorentz boost is defined as

$$\Lambda(\mathbf{v}) = \begin{pmatrix} \gamma & -\gamma v_1/c & -\gamma v_2/c & -\gamma v_3/c \\ -\gamma v_1/c & & & \\ -\gamma v_2/c & & \delta_{ij} + \frac{v_i v_j(\gamma-1)}{v^2} & \\ -\gamma v_3/c & & & \end{pmatrix} \quad , \tag{60}$$

which describes the general boost from IS to IS', which moves with constant velocity $\mathbf{v} = \sum v_i \mathbf{e}_i$ relative to IS and where

$$\gamma = \frac{1}{\sqrt{1 - v^2/c^2}} \quad . \tag{61}$$

The Energy-Momentum Dispersion Relation (Eq. (108))

$$E^2 = c^2\mathbf{p}^2 + m^2c^4 \tag{62}$$

Derivation

1. Generalize the nonrelativistic three-dimensional definition of velocity by the so-called *4-velocity* u^μ, i.e.,

$$u^\mu = \frac{\mathrm{d}x^\mu}{\mathrm{d}\tau} = \gamma(c, \mathbf{v}) \quad . \tag{63}$$

- Since the proper time τ is a Lorentz scalar and the space-time x^μ is a Lorentz vector, u^μ is also a Lorentz vector.

2. The *4-momentum* p^μ is defined analogously to the nonrelativistic set-up, i.e.,

$$p^\mu = \left(\frac{E}{c}, \mathbf{p}\right) \quad . \tag{64}$$

- The relativistic 3-momentum $\mathbf{p}$ is defined as

$$\mathbf{p} = \gamma m \mathbf{v} \quad . \tag{65}$$

- E and $\mathbf{p}$ are called relativistic energy and momentum, respectively.

3. According to Einstein's famous equation $E = \gamma m \mathbf{c}^2$, by rewriting the squared relativistic energy expression E^2 we arrive at the energy-momentum dispersion relation given in Eq. (62).

4. Eq. (62) actually gives raise to anti-particles with negative energy, since

$$E = \begin{cases} \gamma m c^2 & E > 0 \\ -\gamma m c^2 & E < 0 \end{cases} \tag{66}$$

The Covariant Form of the Lagrangian (Eq. (119))

Since the electromagnetic force $\mathbf{F}_L = q(\mathbf{E} + \mathbf{v} \times \mathbf{B})$ (Lorentz force) has a velocity-dependent component, the simplest choice for interaction term is proportional to $A_\mu u^\mu$, which gives

$$L_2(x, u) = -mc\sqrt{u^\mu u_\mu} - \frac{q}{c} A_\mu(x) u^\mu \quad . \tag{67}$$

Derivation

1. The relativistic Lagrangian might be expressed in terms of $x(\tau)$:

$$L_2 = L_2(x, u) \quad . \tag{68}$$

2. The Euler-Lagrange equations are derived from the Hamiltonian principle, $\delta S = 0$.

3. The Lagrangian for a free particle is derived in the exercises and is given by

$$L_2(u) = -mc\sqrt{u^\mu u_\mu} \quad . \tag{69}$$

4. The Lagrangian for a particle in an external electromagnetic field has to be a linear function of the 4-potential $A^\mu = (\phi, \mathbf{A})$, since the electromagnetic force $\mathbf{F}_L = q(\mathbf{E} + \mathbf{v} \times \mathbf{B})$ (Lorentz force) is linear in the field strengths $\mathbf{E}$ and $\mathbf{B}$

5. Since the Lorentz force $\mathbf{F}_L$ has a velocity-dependent component, the simplest choice for the interaction term is proportional to $A_\mu u^\mu$, thus resulting in the form shown in Eq. (67).

Lecture 3: Two Moving Classical Charges

Symmetrized Darwin Interaction for Velocities Small Compared to The speed of Light (Eq. (168))

$$V_{12} = \frac{q_1 q_2}{r_{12}} - \frac{q_1 q_2}{2c^2}\left[\frac{\dot{\mathbf{r}}_1 \cdot \dot{\mathbf{r}}_2}{r_{12}} + \frac{(\mathbf{r}_{12} \cdot \dot{\mathbf{r}}_1)(\mathbf{r}_{12} \cdot \dot{\mathbf{r}}_2)}{r_{12}^3}\right] + O(c^{-3}) \tag{70}$$

Derivation

1. Particle 2 produces ϕ_2 and $\mathbf{A}_2$ and are exerted on particle 1
   - Particle 2's position is called the *retardation position*.
2. Potential energy of particle 1 in the field of particle 2 at time t in IS is given by

$$V_{12}(t) = q_1 \phi_2(\mathbf{r}_1, t) - \frac{q_1}{c}\dot{\mathbf{r}}_1(t) \cdot \mathbf{A}_2(\mathbf{r}_1, t) \quad . \tag{71}$$

3. IS' is moving with the same velocity as particle 2, i.e.,

$$\mathbf{v} = \dot{\mathbf{r}}_2 \quad . \tag{72}$$

   a) Particle 2 is observed at rest in IS', this means that

$$\mathbf{A}_2'(\mathbf{r}', t') = 0 \quad \forall \mathbf{r}' \quad , \tag{73}$$

   since a charge at rest does not produce magnetic fields.

   b) Only the scalar potential, i.e., the standard Coulomb potential of a point charge, contributes to the interaction energy:

$$\phi_2'(\mathbf{r}', t') = \frac{q_2}{|\mathbf{r}' - \mathbf{r}_2'|} \tag{74}$$

4. Perform a Lorentz transformation using $\Lambda(\mathbf{v})$ to obtain the space-like coordinate $\mathbf{r}'$ from the space-time coordinate $(ct, \mathbf{r})$ in IS.

   a) ϕ_2' is then expressed at the position of particle 1, i.e.,

$$\phi_2'(\mathbf{r}_1', t_1') = \frac{q_2}{|\mathbf{r}_1 - \mathbf{r}_2 + \ldots|} \tag{75}$$

5. Perform an inverse Lorentz transformation using $\Lambda(\mathbf{v})^{-1} = \Lambda(-\mathbf{v})$ to include the portential terms.
   - Since two different times t_1 and t_2 would create insurmountable difficulties upon a later transition to quantum mechanics, it is desirable to calculate the interaction energy solely from quantities defined at an absolute time, say, t_1.

6. The resulting general Darwin interaction energy is not symmetric with respect to the particle labels. The symmetrized version is derived by introducing a gauge transformation of the Lagrangian, i.e., by adding a total time derivative of

$$F(\dot{\mathbf{r}}_2, \mathbf{r}_{12}, r_{12}) = \frac{q_1 q_2}{2c^2} \frac{\mathbf{r}_{12} \cdot \dot{\mathbf{r}}_2}{r_{12}} \tag{76}$$

to the potential energy V_{12}.

Lecture 4:
Some Important Elements of Quantum Theory

Unitary Transformations (Eq. (176))

The hermitean operator $\hat{O}$ and $U\hat{O}U^\dagger$ with U being unitary possess the same set of eigenvalues, i.e.,

$$\hat{O}\Psi = a\Psi \quad \textit{and} \quad (U\hat{O}U^\dagger) = a(U\Psi) \quad . \tag{77}$$

- An operator U on Hilber space $\mathcal{H}$ is *unitary* if

$$UU^\dagger = U^\dagger U = \underline{\mathbf{1}} \quad . \tag{78}$$

- A unitary operator U changes the state, but not the physics. It also preserves length, i.e.,

$$\langle U\Psi_n | U\Psi_m \rangle = \langle \Psi_n | \Psi_m \rangle \quad \forall \Psi_n, \Psi_m \in \mathcal{H} \quad . \tag{79}$$

Heisenberg's Equation of Motion (Eq. (189))

$$\frac{\mathrm{d}\hat{O}^{(\mathrm{H})}}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar} \left[\hat{H}, \hat{O}^{(\mathrm{H})} \right] \tag{80}$$

Derivation

1. Introduce the unitary transformation

$$U(t) = \exp\{-\frac{\mathrm{i}}{\hbar} \hat{H}^{(\mathrm{S})} t\} \quad . \tag{81}$$

2. $U(t)$ allows to describe the propagation of any state $\Psi(t)$ in time, i.e.,

$$\Psi(t) = U(t)\Psi(t_0) \quad , \tag{82}$$

where $\Psi(t_0) = \Psi(t = 0)$ is time-independent.

3. The unitary transformation $U(t)$ allows us to switch from an operator in the Schrödinger picture to the corresponding one in the Heisenberg picture, i.e.,

$$\hat{O}^{(\mathrm{H})} = U^{\dagger}(t) O^{(\mathrm{S})} U(t) \tag{83}$$

4. Differentiate Eq. (83) and we obtain the Heisenberg equation of motion shown in Eq. (80).

General

Schrödinger Picture : The equation of motion

$$\mathring{i}\hbar \frac{\partial}{\partial t} \Psi_n(\mathbf{r}, t) = \hat{H} \Psi_n(\mathbf{r}, t) \quad . \tag{84}$$

defines the Schrödinger picture, where the state Ψ is propagated in time while the observables are stationary, i.e., $\hat{H} \rightarrow \hat{H}^{(\mathrm{S})}$.

- The Schrödinger picture holds for *ordinary* observables like energy, momentum and position rather than for a system interacting with a time-dependent external potential (like an electromagnetic light wave).

Heisenberg Equation of Motion : The Heisenberg picture rests on stationary states but time-propagated operators.

Schrödinger Velocity Operator (Eq. (198))

$$\dot{\hat{\mathbf{r}}} = \frac{\hat{\mathbf{p}}}{m} \tag{85}$$

Derivation

1. Heisenberg's equation of motion, Eq. (80), can be utilized to define the velocity operator $\dot{\hat{\mathbf{r}}}$,

$$\hat{\mathbf{v}} \equiv \dot{\hat{\mathbf{r}}} = \frac{\mathrm{d}\hat{\mathbf{r}}}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}[\hat{H}, \hat{\mathbf{r}}] \quad . \tag{86}$$

2. By inserting the Schrödinger Hamiltonian $\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + \hat{V}(\hat{\mathbf{r}})$ in Eq. (86) we get the Schrödinger velocity operator shown in Eq. (85).

General Formulation of the Ehrenfest Theorem (Eq. (199))

If we consider the expectation value of an observable O for a normalized state Ψ, then its time derivative is given by

$$\frac{\mathrm{d}}{\mathrm{d}t} \left\langle \hat{O} \right\rangle_{\Psi} = \frac{\mathrm{i}}{\hbar} \left\langle [\hat{H}, \hat{O}] \right\rangle_{\Psi} + \left\langle \frac{\partial \hat{O}}{\partial t} \right\rangle_{\Psi} \quad . \tag{87}$$

- If Ψ is an eigenfunction of $\hat{H}$ or if $\hat{O}$ commutes with $\hat{H}$, then we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\langle \hat{O} \right\rangle_{\Psi} = \left\langle \frac{\partial \hat{O}}{\partial t} \right\rangle_{\Psi} \quad . \tag{88}$$

Hellmann-Feynman Theorem (Eq. (202))

For the special choice that $\hat{O}$ is the Hamiltonian $\hat{H}$ in Eq. (87), we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\langle \hat{H} \right\rangle_{\Psi} = \left\langle \frac{\partial \hat{H}}{\partial t} \right\rangle_{\Psi} \quad . \tag{89}$$

The Hellmann-Feynman theorem generalizes this for first derivatives of any parameter λ, on which the wave function may depend, i.e.,

$$\frac{\mathrm{d}}{\mathrm{d}\lambda}\left\langle \hat{H} \right\rangle_{\Psi} = \left\langle \frac{\mathrm{d}\hat{H}}{\mathrm{d}\lambda} \right\rangle_{\Psi} \quad . \tag{90}$$

Density Operator (Eq. (205))

$$\hat{\rho}\mathbf{r} = \sum_{i=1}^{N} \delta^{(3)}(\mathbf{r}_i - \mathbf{r}) \tag{91}$$

Derivation

1. Relate

$$\langle \hat{\rho}\mathbf{r} \rangle \equiv \int_{-\infty}^{\infty} \mathrm{d}^3 r_1 \ldots \int_{-\infty}^{\infty} \mathrm{d}^3 r_N \, \Psi^{\dagger}(\mathbf{r}_1, \ldots, \mathbf{r}_N, t) \, \hat{\rho}\mathbf{r} \, \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N, t) \tag{92}$$

to the Born interpretation so that we must fulfill

$$\langle \hat{\rho}\mathbf{r} \rangle = N \int_{-\infty}^{\infty} \mathrm{d}^3 r_1 \ldots \int_{-\infty}^{\infty} \mathrm{d}^3 r_N \, \Psi^{\dagger}(\mathbf{r}_1, \ldots, \mathbf{r}_N, t) \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N, t) \quad , \tag{93}$$

i.e.,

$$\hat{\rho}\mathbf{r} = N \quad . \tag{94}$$

This is achieved by defining $\hat{\rho}\mathbf{r}$ as shown in Eq. (91), since

$$\int_{-\infty}^{\infty} \mathrm{d}^3 x \, \delta^{(3)}(\mathbf{x}) = 1 \quad , \tag{95}$$

thus resulting in

$$\int_{-\infty}^{\infty} \mathrm{d}^3 r_1 \ldots \int_{-\infty}^{\infty} \mathrm{d}^3 r_N \sum_{i=1}^{N} \delta^{(3)}(\mathbf{r}_i - \mathbf{r}) = N \quad . \tag{96}$$

Schrödinger Current Density and Continuity Equation (Eq. (210))

The Schrödinger current density and continuity equation is defined as

$$\frac{\partial}{\partial t}(\Psi^\star\Psi) = -\nabla \cdot \underbrace{\frac{\hbar^2}{2m\mathrm{i}}\{\Psi^\star\nabla\Psi - (\nabla\Psi)^\star\Psi\}}_{\equiv \mathbf{j}} \quad , \tag{97}$$

where $\mathbf{j}$ is the nonrelativistic current density for the time-dependent state $\Psi(\mathbf{r}, t)$.

Derivation

1. Use Ehrenfest's theorem to calculate the time evolution of the density, i.e.,

$$\frac{\mathrm{d}\rho(\mathbf{r}, t)}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{\rho}\mathbf{r}\rangle \quad . \tag{98}$$

2. Assume that all particles are electrons and hence physically indistinguishable.
3. In the most simple case of a single particle this reduces to Eq. (97).

Klein-Gordon Equation for a Free Particle (Eq. (215))

$$-\hbar^2\frac{\partial^2}{\partial t^2}\Psi = (-\hbar^2c^2\nabla^2 + m_e^2c^4)\Psi \tag{99}$$

Derivation

1. Schrödinger quantum mechanics is not Lorentz covariant; time and spacial coordinates occure to different orders in the derivatives.
2. Correspondence Principle: Apply substitutions to the relativistic energy of the freely moving particle $E = \sqrt{\mathbf{p}^2c^2 + m_e^2c^4}$, i.e.,

$$E \to \mathrm{i}\hbar\frac{\partial}{\partial t} \quad \text{and} \quad \mathbf{p} \to -\mathrm{i}\hbar\nabla \quad . \tag{100}$$

3. Since it would be difficult to evaluate the square root ∇^2 in position space, start again from the squared energy expression $E^2 = \mathbf{p}^2c^2 + m_e^2c^4$. By applying again the substitutions in Eq. (100) we get the Klein-Gordon equation shown in Eq. (99).

Klein-Gordon Equation in Covariant Form (Eq. (216))

In covariant form the Klein-Gordon equation shown in Eq. (99) reads

$$[\Box + \left(\frac{m_ec}{\hbar}\right)^2]\Psi = 0 \quad . \tag{101}$$

Klein-Gordon Eigenvalue for Free Particles (Eq. (218))

$$E = \pm\sqrt{\mathbf{p}^2c^2 + m_e^2c^4} \tag{102}$$

Rejection of the Klein-Gordon Equation

Since the Klein-Gordon equation is a second-order differential equation in t, two integration constants arise which allow one to choose the initial values of Ψ and $\partial\Psi/\partial t$ independently of one another in such a way that ρ may take positive or negative values. Consequently, ρ is not positive definite and, hence, does not represent a probability density distribution, which must take strictly positive values for any coordinates t and x_k. The Klein-Gordon equation is thus rejected as fundamental quantum mechanical equation.

Lecture 5: Dirac's Theory of the Electron

Dirac Equation for a Free Particle (Eq. (270))

$$[c\boldsymbol{\alpha}\cdot\hat{\mathbf{p}} + \beta m_e c^2]\Psi = \mathrm{i}\hbar\frac{\partial}{\partial t}\Psi \tag{103}$$

Derivation

1. The correct relativistic equation for the electron requires that it does not contain second order derivatives w.r.t. time, which would result in a negative Klein-Gordon density.

2. The Klein-Gordon equation features the correct free-particle energies, meaning that we must be able to turn the Dirac equation into a Klein-Gordon equation so that the correct eigenvalues are obtained.

3. The standard representation is given by the 4×4 matrices

$$\alpha^i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} \mathbf{1}_2 & 0 \\ 0 & -\mathbf{1}_2 \end{pmatrix} \quad . \tag{104}$$

   - The choice of the 4×4 matrices is not unique (and also higher dimensions are possible): For example, the Weyl representation

$$\alpha^i_{\text{Weyl}} = \begin{pmatrix} \sigma_i & 0 \\ 0 & -\sigma_i \end{pmatrix} \quad \text{and} \quad \beta_{\text{Weyl}} = \begin{pmatrix} 0 & \mathbf{1}_2 \\ \mathbf{1}_2 & 0 \end{pmatrix} \tag{105}$$

     is also a working representation.

Dirac Equation for a Free Particle with Electromagnetic Fields (Eq. (305))

The equation for a free particle with electromagnetic fields is defined as

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi = \left[c\boldsymbol{\alpha}\cdot\left(\mathbf{p}-\frac{q_e}{c}\mathbf{A}\right)+\beta m_e c^2+q_e\phi\right]\Psi \quad , \tag{106}$$

where $\mathbf{A} = (A^1, A^2, A^3)$ contains the contravariant components of the vector potential $A^i = -A_i$.

Derivation

1. The most important requirement for truly fundamental physical equations is their invariance in form under Lorentz transformations, i.e., Lorentz covariance.

2. The only guiding principle for the derivation of the field-dependent Dirac equation for a single electron interacting with external electromagnetic fields is Lorentz covariance.

Dirac Equation for a Free Particle in Split Notation (Eqs. (272) and (273))

$$c\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}\Psi^S + m_e c^2\Psi^L = \mathrm{i}\hbar\frac{\partial}{\partial t}\Psi^L \tag{107}$$

$$c\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}\Psi^L - m_e c^2\Psi^S = \mathrm{i}\hbar\frac{\partial}{\partial t}\Psi^S \tag{108}$$

Derivation

1. Due to the block structure of the matrices α^i in Eq. (104), the spinor Ψ is often split into an upper and lower 2-spinor, Ψ^L and Ψ^S,

$$\Psi = \begin{pmatrix}\Psi_1\\ \Psi_2\\ \Psi_3\\ \Psi_4\end{pmatrix} = \begin{pmatrix}\Psi^L\\ \Psi^S\end{pmatrix} \quad . \tag{109}$$

2. Using the new definition of the spinor Ψ, Eq. (104) can be cast in split notation, as displayed in Eqs. (107) and (108).

Dirac Density and Current Density (Eqs. (250) and (251))

The Dirac current density is defined as

$$\mathbf{j} \equiv c\Psi^\dagger\boldsymbol{\alpha}\Psi, \quad \text{i.e.,} \quad j^k \equiv c\Psi^\dagger\alpha^k\Psi \quad . \tag{110}$$

The 4-current is then given by

$$j^{\mu} = (j^0, j^k) \quad , \tag{111}$$

with

$$j^0 \equiv c\rho \tag{112}$$

Energy of a Free Dirac Electron (Eq. (291))

$$E = \pm\sqrt{\mathbf{p}^2c^2 + m_e^2c^4} \quad .. \tag{113}$$

Derivation

1. The energy of a free Dirac electron results from the derivation of the solution of the free-electron Dirac equation, by arriving at the equation

$$u^S = \left[\frac{c\boldsymbol{\sigma}\cdot\mathbf{p}}{E+m_ec^2}\right]\left[\frac{c\boldsymbol{\sigma}\cdot\mathbf{p}}{E-m_ec^2}\right] u^S \tag{114}$$

   and thus postulating that

$$\left[\frac{c\boldsymbol{\sigma}\cdot\mathbf{p}}{E+m_ec^2}\right]\left[\frac{c\boldsymbol{\sigma}\cdot\mathbf{p}}{E-m_ec^2}\right] = 1 \tag{115}$$

   in order to guarantee consistancy. The latter equation allows us then to determine the energy E, which is shown in Eq. (113).

Dirac Velocity Operator (Eq. (298))

$$\dot{\mathbf{x}}^k = c\alpha^k \tag{116}$$

Derivation

1. The Dirac velocity operator is defined from the Heisenberg equation of motion

$$\dot{\mathbf{x}}^k = \frac{\mathrm{i}}{\hbar}\left[H^D, x^k\right] \quad . \tag{117}$$

Kinematic Momentum (Eq. (306))

The connection of the canonical momentum operator $\mathbf{p}$ with the effect of external vector potentials $\mathbf{A}$ on a moving electron with charge $q_e = -e$ is often simply written as

$$\mathbf{p} \to \mathbf{p} - \frac{q_e}{c}\mathbf{A} = \mathbf{p} + \frac{e}{c}\mathbf{A} \equiv \boldsymbol{\pi} \quad . \tag{118}$$

$\boldsymbol{\pi}$ is called the *mechanical-momentum operator*.

Electromagnetic Interaction Operator (Eq. (308))

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi = [c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta m_e c^2 + \underbrace{q_e\phi - q_e\boldsymbol{\alpha}\cdot\boldsymbol{A}}_{\equiv\hat{V}}]\Psi \quad . \tag{119}$$

Pauli Equation (Schrödinger Equation with Electromagnetic Fields) (Eq. (317))

$$\frac{1}{2m_e}\left(\mathbf{p} - \frac{q_e}{c}\mathbf{A}\right)^2\Psi^L - \frac{q_e\hbar}{2m_e c}(\boldsymbol{\sigma}\cdot\mathbf{B})\Psi^L + V\Psi^L = \mathrm{i}\hbar\frac{\partial}{\partial t}\Psi^L \tag{120}$$

Derivation

1. Rewrite the notation for the Dirac electron in an external electromagnetic field by using the split notation (Eq. (312) in the script).
2. Since the lowest possible nonrelativistic energy of a free particle is zero instead of $m_e c^2$ in Schrödinger quantum mechanics, the origin of the energy scale needs to be shifted by $-m_e c^2$.
3. Retrive the kinetic-balance condition by first working with the lower part of the equation in split notation.
4. Inserting the kinetic-balance condition in the upper part and utilizing Dirac's relation

$$(\boldsymbol{\sigma}\cdot\mathbf{B})(\boldsymbol{\sigma}\cdot\mathbf{B}) = \boldsymbol{\pi}^2 - \frac{q_e\hbar}{c}\boldsymbol{\sigma}\cdot\mathbf{B} \tag{121}$$

yields the Pauli equation.

Kinetic-Balance Condition (Eq. (314))

$$\Psi^S \approx \frac{\boldsymbol{\sigma}\cdot\boldsymbol{\pi}}{2m_e c}\Psi^L \tag{122}$$

Derivation

1. Rewrite the notation for the Dirac electron in an external electromagnetic field by using the split notation (Eq. (312) in the script).
2. The lower part of this equation can be written as

$$\left(\mathrm{i}\hbar\frac{\partial}{\partial t} + 2m_e c^2 - V\right)\Psi^S = c(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})\Psi^L \quad . \tag{123}$$

3. For nonrelativistic energies, the energy $E \to \mathrm{i}\hbar\frac{\partial}{\partial t}$ and the potential V are small compared to the rest energy $m_e c^2$, giving the kinetic-balance condition shown in Eq. (122).

Lecture 6: The Dirac Hydrogen Atom

Pauli Bispinors (Eqs. (337) and (338))

$$\chi^{(+)}_{jm_j} = \sqrt{\frac{l+m_j+1/2}{2l+1}}\Phi_l(m_j-1/2) + \sqrt{\frac{l-m_j+1/2}{2l+1}}\Phi_l(m_j+1/2) \tag{124}$$

$$\chi^{(-)}_{jm_j} = -\sqrt{\frac{l-m_j+1/2}{2l+1}}\Phi_l(m_j-1/2) + \sqrt{\frac{l+m_j+1/2}{2l+1}}\Phi_l(m_j+1/2) \tag{125}$$

Derivation

1. The Dirac Hamiltonian for the fermions electron e and proton p plus the interaction operator V_{ep} yield the total Hamiltonian
$$H = h^d_e \otimes \mathbf{1} + \mathbf{1} \otimes h^D_p + V_e p \quad . \tag{126}$$
2. Transform the operator
$$h_D = \begin{pmatrix} m_e c^2 + V(r) & c\boldsymbol{\sigma}\cdot\mathbf{p} \\ c\boldsymbol{\sigma}\cdot\mathbf{p} & -m_e c^2 + V(r) \end{pmatrix} \quad . \tag{127}$$
to spherical coordinates (the diagonal is alread in spherical coordinates).
3. $\boldsymbol{\sigma}\cdot\mathbf{p}$ is expanded by exploiting Dirac's relation, resulting in an expression containing $\mathbf{r}\cdot\mathbf{p}$ and $\boldsymbol{\sigma}\cdot\mathbf{l}$.
4. All angular variables are contained in $(\boldsymbol{\sigma}\cdot\mathbf{l})$, which is essential the spin-orbit coupling paramater known from the Pauli equation.
5. We will require the eigenstates and eigenvalues of the spin-orbit coupling operator $(\boldsymbol{\sigma}\cdot\mathbf{l})$.

Ansatz for the Spinor (Eq. (367))

$$\Psi_i(\mathbf{r}) \to \Psi_{n_i\,\kappa_i\,m_{j(i)}}(\mathbf{r}) = \begin{pmatrix} \frac{P_{n_i\,\kappa_i}(r)}{r}\chi_{\kappa_i\,m_{j(i)}}(\vartheta,\phi) \\ \frac{Q_{n_i\,\kappa_i}(r)}{r}\chi_{-\kappa_i\,m_{j(i)}}(\vartheta,\phi) \end{pmatrix} \tag{128}$$

Derivation

1. Because of the general 2×2 block structure of the Hamiltonian h^D, a suitable ansatz for $\Psi(\mathbf{r})$ is
$$\Psi(\mathbf{r}) = \begin{pmatrix} F_i(r)\chi_{jm_j}(\vartheta,\gamma) \\ \mathrm{i}G_i(r)\chi'_{jm_j}(\vartheta,\gamma) \end{pmatrix} \quad , \tag{129}$$
with G_i, F_i being the radial and $\chi_{\ldots}$ being the angular components.
2. *Equivalence restriction*: assign a single pair of radial functions $F_{n\kappa}(r)$ and $G_{n\kappa}(r)$ to a given set of $(2j+1)$-degenerate spherical spinors $\chi^{(\pm)}_{jm_j}(\vartheta,\gamma)$

Radial Density (Eq. (434))

$$\rho_i(r) = P^2_{n_i\,\kappa_i}(r) + Q^2_{n_i\kappa_i}(r) \tag{130}$$

Dirac Radial Equation (Eqs. (377) and (378))

$$[V(r) + m_e c^2]P_i(r) + c\hbar\left[-\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\kappa_i}{r}\right]Q_i(r) = E_i P_i(r) \tag{131}$$

$$c\hbar\left[\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\kappa_i}{r}\right]P_i(r) + [V(r) - m_e c^2]Q_i(r) = E_i Q_i(r) \tag{132}$$

Derivation

1. Rewrite the Dirac equation using the ansatz for the spinor shown in Eq. (129), where we utilized the fact that Pauli spinors are eigenfunctions of $\mathbf{k}$.

2. When $(\boldsymbol{\sigma}\cdot\hat{\mathbf{r}})$ operates on Pauli spinors $\chi_{\kappa m_j}(\vartheta,\gamma)$, this results in

$$(\boldsymbol{\sigma}\cdot\hat{\mathbf{r}})\chi_{\kappa m_j}(\vartheta,\gamma) = -\chi_{-\kappa m_j}(\vartheta,\gamma) \quad . \tag{133}$$

   Multiplying this equation from the left with $(\boldsymbol{\sigma}\cdot\hat{\mathbf{r}})$ and recalling Dirac's relation yields after multiplication by (-1)

$$-\chi_{\kappa m_j}(\vartheta,\gamma) = (\boldsymbol{\sigma}\cdot\hat{\mathbf{r}})\chi_{-\kappa m_j}(\vartheta,\gamma) \quad . \tag{134}$$

3. The Dirac equation can now be written as

$$h^D\Psi_i = \begin{pmatrix} \left\{(V + m_e e^2)F_i - c\hbar\left[\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}r - \frac{\kappa_i}{r}\right]G_i\right\}\chi_{\kappa_i m_j(i)} \\ \left\{c\hbar\left[\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}r + \frac{\kappa_i}{r}\right]F_i + (V - m_e e^2)G_i\right\}\mathrm{i}\chi_{-\kappa_i m_j(i)} \end{pmatrix} \stackrel{!}{=} E_i\Psi_i \tag{135}$$

4. Using the radial functions defined in Eq. (128) the equations take the simple form shown in Eq. (132). As ordinary differential equations, they can be solved analytically.

Ground State Energy of the Dirac Hydrogen Atom (Eq. (431))

$$E_0 = c^2\sqrt{1 - Z^2/c^2} \tag{136}$$

Derivation

1. The expression for the energy eigenvalue is given by

$$E^2 \frac{Z^2 e^4}{c^2 \hbar^2} = \left[m_e^2 c^4 - E^2 \right] (\alpha + n_r)^2 \tag{137}$$

$$\implies E^{\pm} = \pm m_e c^2 \left[1 + \frac{Z^2 e^4}{c^2 \hbar^2 (\alpha + n_r)^2} \right]^{-1/2} \tag{138}$$

   with $n_r = 0, 1, 2, 3, \cdots \in \mathcal{N}_0$ being the radial quantum number

2. The principal quantum number n can be defined as

$$n = n_r + |\kappa| = n_r + j + 1/2 \tag{139}$$

3. The energy eigenvalue in Eq. (138) for the electronic bound states in Dirac hydrogen-like atom reads in Hartree atomic units

$$E_{n|k|} \equiv E^{+} = c^2 \left\{ 1 + \left(\frac{Z/c}{\sqrt{\kappa^2 - Z^2/c^2} + n - |\kappa|} \right)^2 \right\}^{-1/2} \tag{140}$$

4. For the pair $(n, \kappa) = (1, -1)$ we get Eq. (136)

Lowest Exponent of the Series Expansion for Radial Functions (Eq. (452))

$$\alpha = \sqrt{\kappa^2 - v_{-1}^2/(\hbar^2 c^2)} = \begin{cases} \sqrt{\kappa^2 - Z^2 e^4/(\hbar^2 c^2)} & \text{for a point-like nuclei} \\ |\kappa| & \text{for finite-size nuclei} \end{cases} \tag{141}$$

Derivation

- The finite nucleus is usually approximated by some spherical distribution of the positive charges (e.g. the homogeneously or uniformly charged sphere is a simple model for the finite size of the nucleus)

1. The homogeneous electron-nucleaus potential energy operator is given by

$$V_{\text{hom}}(r) = \begin{cases} -\frac{Ze^2}{2R} \left[3 - \frac{r^2}{R^2} \right] & ; r \leq R \\ -Ze^2/r & ; r > R \end{cases} , \tag{142}$$

   where R may be understood as the *size* of the nucleus and outside of the nucleus the ordinary Coulomb attraction governs the electron-nucleus interaction where erf denotes the error function.

2. The series expansion for the general electron-nucleus potential is defined as

$$V_{\text{nuc}}(r) = v_{-1}r^{-1} + v_0 + O(r) \tag{143}$$

with

$$v_{-1} = \begin{cases} -Ze^2 & \text{for point-like nuclear charges} \\ 0 & \text{for finite-size nuclei} \end{cases} . \tag{144}$$

3. The coefficients of the $r^{\alpha-1}$ term of the radial equation give

$$\frac{v_{-1}}{\hbar c}a_0 + (\kappa_i - \alpha)b_0 = 0 \tag{145}$$

$$\frac{v_{-1}}{\hbar c}b_0 + (\kappa_i + \alpha)a_0 = 0 \tag{146}$$

$$\tag{147}$$

which finally yields Eq. (141).

Lecture 7: The Interaction of Two Electrons

The Gaunt Operator for Unretarded Interactions (Eq. (465))

$$G_0(1,2) = -q_1q_2\frac{\boldsymbol{\alpha}_1\boldsymbol{\alpha}_2}{r_{12}} = -\frac{q_1q_2}{r_{12}}\frac{4}{\hbar^2}\begin{pmatrix} 0 & \boldsymbol{s}_1\boldsymbol{s}_2 \\ \boldsymbol{s}_1\boldsymbol{s}_2 & 0 \end{pmatrix} \tag{148}$$

Derivation

1. According to the Dirac equation for an electron in external electromagnetic fields (Eq. (106)) we should make an ansatz for the two-electron system including the external potential energy, V_{nuc}, of resting nuclei with the vector and scalar potential felt by one electron and generated by the other, respectively.

2. The exact total wave function Ψ is a 16×16 matrix defined as

$$\Psi(ct_1, \mathbf{r}_1, ct_2, \mathbf{r}_2) = \psi_1(ct_1, \mathbf{r}_1) \otimes \psi_2(ct_2, \mathbf{r}_2) \quad . \tag{149}$$

3. *First issue:* What to do with the two different time derivatives?
   a) *Solution:* Adopt a single absolute time frame $t_1, t_2 \to t$ to remove the two different time derivatives

4. *Second issue:* How are the scalar and vector potentials of the electrons to be chosen?
   - *Solution:*

a) Study the unretarded classical scalar potential created by electron 2,

$$\phi_{2,\text{unret.}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{q_2}{r_{12}} \quad , \tag{150}$$

which is in accord with the standard Coulomb law.

b) The unretarded expression for the corresponding vector potential of the moving electron 2 is then given by

$$\mathbf{A}_{2,\text{unret.}}(\mathbf{r}_1, \mathbf{r}_2, \dot{\mathbf{r}}_\mathbf{2}) = \frac{\dot{\mathbf{r}}_\mathbf{2}}{c}\phi_{2,\text{unret.}} \quad . \tag{151}$$

c) According to the correspondence principle, the velocities $\dot{\mathbf{r}}_1$ and $\dot{\mathbf{r}}_2$ are substituted by the Dirac velocity operators $c\boldsymbol{\alpha}_1$ and $c\boldsymbol{\alpha}_2$. The unretarded electromagnetic potential operator then become

$$\hat{\phi}_{2,\text{unret.}}(\mathbf{r}_i, \mathbf{r}_j) \quad \text{and} \quad \hat{\mathbf{A}}_{2,\text{unret.}}(\mathbf{r}_i, \mathbf{r}_j) = \boldsymbol{\alpha}_i \frac{q_i}{r_{ij}} \tag{152}$$

d) Since the electromagnetic fields are no longer retarded, their effect is felt instantaneously by both electrons at the same time, and we would count the interaction twice for any instant of time in our absolute time frame. Therefore, it is important to avoid double counting by dividing the terms that carry the potentials by two.

e) The unretarded classical interaction energy is given by

$$V_{12} = \frac{q_1}{q_2}\left(1 - \frac{\dot{\mathbf{r}}_\mathbf{1} \cdot \dot{\mathbf{r}}_\mathbf{2}}{c^2}\right) \quad . \tag{153}$$

If we now substitute the velocities by their quantum analogs we get

$$\hat{V}_{12} = \frac{q_1 q_2}{r_{12}}(1 - \boldsymbol{\alpha}_1\boldsymbol{\alpha}_2) \quad , \tag{154}$$

where the first term is the Coulomb operator and then the so-called Gaunt operator as defined in Eq. (148).

The Breit Operator for Retarded Interactions (Eq. (467))

$$B_0(1,2) = -\frac{q_1 q_2}{2}\left[\frac{\boldsymbol{\alpha}_1\boldsymbol{\alpha}_2}{r_{12}} + \frac{(\mathbf{r}_{12} \cdot \boldsymbol{\alpha}_1)(\mathbf{r}_{12} \cdot \boldsymbol{\alpha}_2)}{r_{12}^3}\right] \tag{155}$$

Derivation

1. The operator for the classical potential energy of the retarded interaction of the two electrons can be obtained from the correspondence principle applied to Darwin's approximation shown in Eq. (70), i.e., we choose the velocity operator expression $\dot{\mathbf{r}} \to c\boldsymbol{\alpha}$ and optain the Breit operator shown in Eq. (155).

Lecture 8: First-Quantized Semi-Classical Relativistic Many-Electron Theory

First-Quantized Electron Hamiltonian (Eq. (503))

$$H'_{\text{el}} = \sum_{i}^{N} h^D(i) + \sum_{i<j}^{N} g(i,j) + V_0 \quad , \tag{156}$$

with the single one-electron external-field-free Hamiltonian $h^D(i)$ defined as

$$h^D(i) = c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + (\beta_i - 1)m_e c^2 + V_{\text{nuc}}(\mathbf{r}_i) \tag{157}$$

and

$$V_0 \equiv \sum_{J<I}^{M} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} \quad . \tag{158}$$

Further, $g(i,j)$ is the electron-electron repulsion operator. For the Dirac-Coulomb many-electron Hamiltonian, it is defined as

$$g(i,j) \rightarrow V_C(i,j) = \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad . \tag{159}$$

Instead, for the Dirac-Coulomb-Breit many-electron Hamiltonian it is given by

$$g(i,j) \rightarrow V_C(i,j) + B_0(i,j) = \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + B_0(i,j) \quad , \tag{160}$$

where B_0 is the Breit operator (the unretarded Gaunt interaction may be deployed instead of $B_0(i,j)$).

N-electron current density (Eq. (517))

$$\mathbf{j} \equiv \langle \Psi | c\boldsymbol{\alpha} \hat{\rho} \mathbf{r} | \Psi \rangle \tag{161}$$

Derivation

1. Derive the current-density expression for the many-electron system according to Ehrenfest's theorem employing the many-electron Dirac-Coulomb-(Breit) Hamiltonian

$$\frac{\partial}{\partial t} \langle \hat{\rho} \mathbf{r} \rangle = \frac{\mathrm{i}}{\hbar} \left\langle \left[\sum_{i=1}^{N} (c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i), \hat{\rho} \mathbf{r} \right] \right\rangle \tag{162}$$

2. By using the definition of the density operator $\hat{\rho}\mathbf{r}$ shown in Eq. (91) and the fact that the electrons are phyiscally indistinguishable, we may write

$$\frac{\partial}{\partial t}\langle\hat{\rho}\mathbf{r}\rangle = \frac{\mathrm{i}}{\hbar}N\left\langle\Big[c\boldsymbol{\alpha}_1\cdot\mathbf{p}_1),\delta^{(3)}(\mathbf{r}_1-\mathbf{r})\Big]\right\rangle \quad . \tag{163}$$

3. By substituting $\mathbf{p}_i = -\mathrm{i}\hbar\nabla_i$, we may write the Ehrenfest equation now as

$$\frac{\partial}{\partial t}\langle\hat{\rho}\mathbf{r}\rangle = -\nabla\cdot cN\left\langle\Psi|\boldsymbol{\alpha}_1\delta^{(3)}(\mathbf{r}_1-\mathbf{r})|\Psi\right\rangle \quad . \tag{164}$$

4. From the last equation we now obtain the most general form of a continuity equation for an N-electron system,

$$\frac{\partial}{\partial t}\langle\hat{\rho}\mathbf{r}\rangle = -\nabla\cdot\langle\Psi|(c\boldsymbol{\alpha})\hat{\rho}\mathbf{r}|\Psi\rangle \tag{165}$$

   and thus define the N-electron current-density as shown in Eq. (161).

Energy Density Functional of the 4-Current (Eq. (509))

$$E_{\mathrm{el}}[j^\mu] = T[j^\mu] + V_{\mathrm{nuc}}[j^\mu] + J[j^\mu] + E_{\mathrm{xc}}[j^\mu] \tag{166}$$

where $T[j^\mu]$ is the kinetic energy functional, $V_{\mathrm{nuc}}[j^\mu]$ is the external potential energy of the interaction of the electronic 4-current j^μ with all nuclei, and $J[j^\mu]$ is the classical repulsion energy of the electrons, while $E_{\mathrm{xc}}[j^\mu]$ denotes the exchange-correlation current-density function, which contains all quantum, i.e., exchange and correlation effects.

Four-Component Single-Determinant Density and Current Density (Eqs. (518) and (519))

$$\rho^{\mathrm{SD}}(\mathbf{r}) = \sum_i \psi_i^\dagger(\mathbf{r})\cdot\psi_i(\mathbf{r}) \tag{167}$$

$$\mathbf{j}^{\mathrm{SD}}(\mathbf{r}) = c\sum_i \psi_i^\dagger(\mathbf{r})\cdot\alpha\cdot\psi_i(\mathbf{r}) \quad , \tag{168}$$

where SD denotes the case of a single Slater Determinant.

Four-Component Kohn-Sham Equation (Eq. (520))

$$\Big[c\boldsymbol{\alpha}\cdot\Big(\mathbf{p}-\frac{q_e}{c}\mathbf{A}_{\mathrm{eff}}(\mathbf{r})\Big)]+\beta m_e c^2 + q_e\phi_{\mathrm{eff}}(\mathbf{r})\Big]\,\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}) \tag{169}$$

Lecture 9: Atoms and Molecules (Summary Based on Exercise 8)

Dirac-Hartree-Fock Equations

- The analog to the Hartree–Fock method in relativistic quantum chemistry is the Dirac-Hartree-Fock (or Dirac–Fock) method.
- As in the nonrelativistic case, the many-electron Hamiltonian is a sum of one- and two-electron operators and is given by

$$H = \sum_{i=1}^{N} h_D(i) + \sum_{i=1}^{N} \sum_{j=1}^{i-1} g(i,j) \quad , \tag{170}$$

  where N denotes the number of electrons and $h_D(i)$ is the Dirac operator

$$h^D(i) = c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + (\beta_i - \mathbf{1}_4)mc^2 - \sum_{A=1}^{M} \frac{Z_A}{R_{iA}} \mathbf{1}_4 \quad , \tag{171}$$

  in which the sum runs over all M nuclei.
- The Dirac operator $h_D(i)$ requires the wave function to be a spinor with four components.
- Within the Dirac-Hartree-Fock method, the wave function Ψ is approximated by a slater determinant

$$\Psi = \mathcal{A}(\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \cdot \cdots \cdot \psi_1(\mathbf{r}_N)) \quad , \tag{172}$$

  where $\mathcal{A}$ is the antisymmetrizer, and the orbitals $\psi_i(\mathbf{r}_i)$ are four-spinors.

Dirac-Hartree-Fock Equations in Two-Component Notation

- The Dirac Hamiltonian can be rewritten as

$$h_D(i) = \begin{pmatrix} V & c\boldsymbol{\sigma}_i \cdot \mathbf{p}_i \\ c\boldsymbol{\sigma}_i \cdot \mathbf{p}_i & (V - 2m_e c^2) \end{pmatrix} \quad . \tag{173}$$

- It is now reasonable to summerize the two upper scalar entries in the wave function in terms of a two-spinor called *large component* ψ^L, and the two lower entries as a two-spinor called *small component* ψ^S. Accordingly, the orbitals can be written as

$$\psi_i(\mathbf{r}_i) = \begin{pmatrix} \psi_i^L(\mathbf{r}_i) \\ \psi_i^S(\mathbf{r}_i) \end{pmatrix} \quad . \tag{174}$$

Dirac-Hartree-Fock-Roothaan Equations: Relativistic Equivalent to the Roothan-Hall Equations

- The orbitals $\psi_i(\mathbf{r}_i)$ can be expanded in the one-electron basis sets $\{\phi_a^L\}$ and $\{\phi_a^S\}$ of the dimensions K_L and K_S, and with corresponding expansion coefficients c_{ia}^L and c_{ib}^S,

$$\psi_i(\mathbf{r}_i) = \begin{pmatrix} \psi_i^L(\mathbf{r}_i) \\ \psi_i^S(\mathbf{r}_i) \end{pmatrix} = \begin{pmatrix} \sum_{a=1}^{K_L} c_{ia}^L \phi_a^L(\mathbf{r}_i) \\ \sum_{a=1}^{K_S} c_{ib}^L \phi_b^L(\mathbf{r}_i) \end{pmatrix} \quad . \tag{175}$$

- The Dirac-Hartree-Fock-Roothaan equations are given by

$$\underbrace{\begin{pmatrix} \mathbf{F}^{LL} & \mathbf{F}^{SL} \\ \mathbf{F}^{LS} & \mathbf{F}^{SS} \end{pmatrix}}_{\text{Fock matrix}} \begin{pmatrix} \mathbf{c}_i^L \\ \mathbf{c}_i^S \end{pmatrix} = \epsilon_i \underbrace{\begin{pmatrix} \mathbf{S}^{LL} & 0 \\ 0 & \mathbf{S}^{SS} \end{pmatrix}}_{\text{Overlap matrix}} \begin{pmatrix} \mathbf{c}_i^L \\ c_i^S \end{pmatrix} \tag{176}$$

$$\Longleftrightarrow \mathbf{Fc} = \mathbf{Sc}\boldsymbol{\epsilon} \tag{177}$$

Lecture 10: Decoupling Negative-Energy States: Foldy-Wouthuysen and Douglas-Kroll-Hess (Summary Based on Exercise 9)

Closed-form unitary transformation of the Dirac Hamiltonian

- The small components of the spinor are the reason for:
  1. Unboundedness of the Dirac Hamiltonian, which leads to variational instability.
  2. Increased computational cost due to the increased basis-set size.
     - Small-component basis can become almost twice as large as the large-component basis.

- *Solution:* Block-diagonalize the Dirac Hamiltonian by a unitary transformation U,

$$f_{bd} = UfU^\dagger = \begin{pmatrix} f_+ & 0 \\ 0 & f_- \end{pmatrix} \quad , \tag{178}$$

  where $f = h^D + V$ and V represents any potential energy operator. Further, the operators f_+ and f_- reproduce the entire energy spectrum without coupling the large and small components.
  - The spinor is also reduced by the unitary transformation, i.e.,

$$\tilde{\psi} = U\psi = \begin{pmatrix} \tilde{\psi}^L \\ \tilde{\psi}^S \end{pmatrix} \quad , \tag{179}$$

with $\tilde{\psi}^S = \mathbf{0}$ for class-I solutions and $\tilde{\psi}^L = \mathbf{0}$ for class-II solutions, i.e., solutions corresponding to positive-energy and negative-energy spinors, respectively.

* The relation

$$\psi^S = X\psi^L \tag{180}$$

holds between the lower and upper components of the 4-spinor.

The Free-Particle Foldy-Wouthuysen Transformation

- Historically first attempt to achieve the block-diagonalization of the Dirac Hamiltonian h^D is due to Foldy and Wouthuysen
- They derived a closed-form expression for both the unitary transformations and the decoupled Hamiltonian for the case of a free particle
- The unitary operator of interest is given by

$$U_0 = \begin{pmatrix} 1 & \boldsymbol{\sigma}\cdot\mathbf{P}_p \\ -\boldsymbol{\sigma}\cdot\mathbf{P}_p & 1 \end{pmatrix} \tag{181}$$

with

$$A_p = \sqrt{\frac{E_p + m_e c^2}{2E_p}}, \quad \mathbf{P}_p = \frac{c\mathbf{p}}{E_p + m_e c^2}, \quad R_p \equiv \boldsymbol{\alpha}\mathbf{P}_p \quad . \tag{182}$$

- In the literature, many forms of this transformation can be found. An often employed representation of U_0 is the exponential form given by

$$U_0 = \exp\left\{\beta\frac{\boldsymbol{\alpha}\cdot\mathbf{p}}{p}\omega(p)\right\} \tag{183}$$

with

$$U_0^\dagger = \exp\left\{-\beta\frac{\boldsymbol{\alpha}\cdot\mathbf{p}}{p}\omega(p)\right\} \tag{184}$$

Foldy-Wouthuysen Expansion in Powers of $1/c$

- The free-particle Foldy-Wouthuysen transformation can be performed in closed form even in the presence of a scalar potential V of any form,

$$f_1 = U_0(h^D + V)U_0^\dagger = \mathcal{E}_0 + \mathcal{E}_1 + \mathcal{O}_1 \quad , \tag{185}$$

with

$$\mathcal{E}_0 = \beta E_p - m_e c^2 \tag{186}$$
$$\mathcal{E}_1 = A_p V A_p + A_p R_p V R_p A_p \tag{187}$$
$$\mathcal{O}_1 = \beta A_p [R_p, V] A_p \tag{188}$$

where $\mathcal{E}$ denotes a block-diagonal operator with LL and SS blocks, which is called *even*, while $\mathcal{O}$ denotes an operator with entries on two off-diagonal LS and SL blocks, which is called *odd*. Further, the subscripts denote the order in the scalar potential of the corresponding term (e.g. $\mathcal{E}_0$ does not contain a scalar potential).

- The odd operator $\mathcal{O}_1$ hinders the exact decoupling.
- Though the Foldy-Wouthuysen procedure may formally be repeated until exact decoupling seems to be achieved, the resulting even terms are highly singular and ill-defined, and are not related to the original Dirac Hamiltonian at all.
- Failure of the higher-order Foldy-Wouthuysen transformation is that it relies on an illegal $1/c$ expansion of all terms occuring in the free-particle Foldy-Wouthuysen Hamiltonian f_1 defined by Eq. (185).
  - This step also requires to expand E_p, but such a power series expansion is, however, only permitted for analytic functions and must never be extended beyond a singular point.l
  - For larger momenta, which arise in the vicinity of the nucleus and in a complete basis set expansion, the series expansion up to any arbitrary or even infinite order in $p/m_e c$ does not represent the original function E_p, i.e. the series does not even converge for these momenta.
  - The singular behaviour of the series expansions of E_p becomes worse the more terms of the expansion are taken into account.
- It follows that all $1/c$-expansions are ill-defined and thus only Douglas-Kroll-Hess expansions are possible for Dirac electrons in external fields!

Douglas-Kroll-Hess Transformation in V

- We need to remove the odd term $\mathcal{O}$, since the free-particle transformation cannot decouple potential-affected one-electron operators, which poses a problem molecular quantum mechanics.
- Since the expansion in powers of $1/c$ (Foldy-Wouthuysen) is ill-defined, only the expansion in the external potential V remains, which leads to the Douglas-Kroll-Hess (DKH) transformation.
- Recall the result of the free-particle Foldy-Wouthuysen transformation:

$$f_1 = U_0 (h^D + V) U_0^\dagger = \mathcal{E}_0 + \mathcal{E}_1 + \mathcal{O}_1 \quad , \tag{189}$$

with

$$\mathcal{E}_0 = \beta E_p - m_e c^2 \tag{190}$$
$$\mathcal{E}_1 = A_p V A_p + A_p R_p V R_p A_p \tag{191}$$
$$\mathcal{O}_1 = \beta A_p [R_p, V] A_p \tag{192}$$

- After the initial transformation U_0, the new odd part $\mathcal{O}_1$ in f_1 needs to be deleted by the next transformation U_1, which can be done by introducing new odd terms of higher order in the scalar potential V.
- The general DKH approximation is given by

$$h_{\mathrm{HDK1}} = \sum_{k=0}^{\infty} \begin{pmatrix} \mathcal{E}_k & 0 \\ 0 & \mathcal{E}_k \end{pmatrix} \tag{193}$$

- The following DKH approximations have been presented during the lecture:

$$h_{\mathrm{HDK1}} = \mathcal{E}_0 + \mathcal{E}_1 \tag{194}$$
$$\dots \tag{195}$$
$$h_{\mathrm{HDK5ichha}} = \sum_{i=1}^{5} \mathcal{E}_i \tag{196}$$

  - DKH1 is no reliable approximation, but DKH2 is very accurate already

Lecture 11: Elimination Techniques: Pauli, Breit-Pauli, and Zora (Based on Exercises 10 and 11)

- The goal of elimination techniques is a straightforward and easy reduction of the four-component one-electron equations to two-component form by elimination of the two small components. This is achieved by exploiting the kinetic-balance condition $\Psi^S = X\Psi^L$.

Pauli Elimination

- A widely used operator to take into account relativistic effects is the Pauli Hamiltonian

$$h_{\mathrm{Pauli}} = \underbrace{\frac{\mathbf{p}^2}{2m_e} + V}_{\text{Non-relativistic Hamiltonian } h_{\mathrm{nr}}} - \underbrace{\frac{\mathbf{p}^4}{8m_e^3 c^2}}_{\text{Mass-velocity operator } h_{\mathrm{mv}}} \tag{197}$$

$$+ \underbrace{\frac{\hbar^2}{8m_e^2 c^2}(\Delta V)}_{\text{Darwin term } h_{\mathrm{Dar}}} + \underbrace{\frac{\hbar}{4m_e^2 c^2}\boldsymbol{\sigma} \cdot [(\nabla V) \times \mathbf{p}]}_{\text{Spin-orbit coupling term } h_{\mathrm{SO}}} \tag{198}$$

  - The spin-orbit term can be cast in a more convenient form for a hydrogen-like atom with a point-like nucleus so that the spin-orbit term h_{SO} reads

$$h_{\mathrm{SO}} = \frac{\hbar}{4m_e^2c^2}\boldsymbol{\sigma}\cdot[(\nabla V)\times\mathbf{p}] = \frac{Ze^2}{2m_e^2c^2}\frac{\mathbf{s}\cdot\mathbf{l}}{r^3} \tag{199}$$

- **Problem:** The Pauli Hamiltonian is again a $1/c$-expansion (see Eq. (205)), and therefore cannot be used in variational procedures. This is due to the mass-velocity term which leads to a strongly attractive potential for states with high moentum, and would thus lead to variational collapse, since it is not bound from below.
  - The problem cannot be remedied by going to higher orders, since the geometric series expansion of ω given by Eq. (205) is only valid for

$$1 - \frac{V-\epsilon}{2m_ec^2} > 0 \Longleftrightarrow |V-\epsilon| < 2m_ec^2 \tag{200}$$

    which is violated in regions close to the nucleus contributing.
  - Also, the Darwin term produces difficulties as it degenerates to the singular Delta distribution term in the case of a point-like nucleus.

Rough Derivation

- By exploiting the kinetic-balance condition $\psi^S = X\psi^L$ for the substitution of ψ^S, we get the two-component eigenvalue equation

$$(V + c\boldsymbol{\sigma}\cdot\mathbf{p}X)\psi^L = \epsilon\psi^L \quad . \tag{201}$$

- The energy-dependent X-operator

$$X = \frac{c\boldsymbol{\sigma}\cdot\mathbf{p}}{2m_ec^2 - V + \epsilon} \tag{202}$$

  which yields the two component equation

$$(V-\epsilon)\psi^L + \frac{1}{2m_ec^2}[(c\boldsymbol{\sigma}\cdot\mathbf{p})\omega(c\boldsymbol{\sigma}\cdot\mathbf{p})]\psi^L = 0 \quad , \tag{203}$$

  with

$$\omega = \left[1 - \frac{V-\epsilon}{2m_ec^2}\right] \quad . \tag{204}$$

- For ω, the Pauli approximation is used (which is the first approximation used in this approach; Eq. (203) still yields the exact Diract eigenvalues and large components), which utilizes the properties of the geometric series

$$\omega = \sum_{k=0}^{\infty}\frac{V-\epsilon}{2m_ec^2}^k \tag{205}$$

  that is truncated after the first two terms ($k = 0, 1$).

- After applying some more changes and substitutions (e.g. using Dirac's relation and using the nonrelativistic Schrödinger equation to find an expression for a specific commutator; see lecture notes for more details), the nonrelativistic Hamiltonian $\mathbf{p}^2/2m_e + V$ is recovered, and we find as correction terms the ones shown in Eq. (198), i.e., the mass-velocity operator, the Darwin term, and the spin-orbit coupling term.

Derivation of the spin-orbit term h_{SO}:

1. For hydrogen-like atoms, the potential energy is given by

$$V = \frac{-Ze^2}{r} \quad . \tag{206}$$

2. The gradient of V is then

$$\nabla V = -Ze^2 \left(\nabla \frac{1}{r}\right) = -Ze^2 \left(\nabla \frac{1}{\sqrt{x^2+y^2+z^2}}\right) \tag{207}$$

$$= Ze^2 \begin{pmatrix} x \\ y \\ z \end{pmatrix} \frac{1}{(x^2+y^2+z^2)^{3/2}} = Ze^2 \frac{\mathbf{r}}{r^3} \quad . \tag{208}$$

3. Following from this, we can write

$$h_{\mathrm{SO}} = \frac{\hbar}{4m_e^2c^2} \boldsymbol{\sigma} \cdot [(\nabla V) \times \mathbf{p}] = \frac{Ze^2\hbar}{4m_e^2c^2} \frac{\boldsymbol{\sigma} \cdot [\mathbf{r} \times \mathbf{p}]}{r^3} \tag{209}$$

$$= \frac{Ze^2\hbar}{4m_e^2c^2} \frac{\boldsymbol{\sigma} \cdot \mathbf{l}}{r^3} \overset{\text{Def. angul. mom.}}{=} \underline{\underline{\frac{Ze^2}{2m_e^2c^2} \frac{\mathbf{s} \cdot \mathbf{l}}{r^3}}} \tag{210}$$

Lecture 15: Spin-DFT (Based on Exercise 12)

- In the four-component DFT no spin is visible in the equations.
- The definition of the current density (Eq. (110)) involves a velocity operator (Eq. (116)). The velocity operator turns out to be $c\boldsymbol{\alpha}$. Hence, as the Dirac $\boldsymbol{\alpha}$ matrices contain the Pauli spin matrices $\boldsymbol{\sigma}$, it can be seen that the current density $\mathbf{j}$ carries the spin information.
- The Gordon decomposition separates the current density into a charge- and spin-related current.

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