8 CP Quantum Mechanics

by Lutz Jaitner, May, 2016 through March, 2019

8.1 Basic Assumptions

Modeling of CPs is based on the following basic assumptions:

(1) CPs contain ensembles of atomic nuclei densely lined up in a long and very narrow channel.

(2) The distances between the nuclei are so small, that all electrons bound to these nuclei are delocalized along the channel. In other words: Even in their electronic ground state CPs don't consist of individual atoms. CPs rather form a quasi-one-dimensional plasma (this could also be seen as a metal).

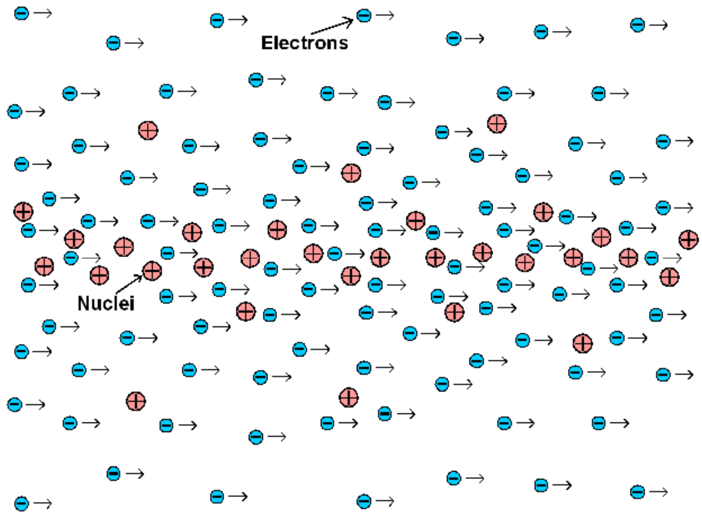

Figure 3 Basic model of a CP. The CP similarly extends to the left and to the right of this picture

8.2 The Cylindrical Model of CPs

The shape and quantum mechanical state of CPs can be very complicated. In order to obtain a simple quantum mechanical description of CPs, the following simplifications are used, which will subsequently be called "the cylindrical model of CPs":

(3) The CP is perfectly straight and cylindrically symmetric, i.e. it is not bent to rings, helices etc. The CP is oriented in parallel to and centered on the z-axis of the modeling cylindrical coordinate system.

(4) The CP has the length $\overline{L}$ and contains a total nuclear charge Q in its core.

(5) The electron wave functions of the CP are confined in the interval $0 \leq z < \overline{L}$. At $z = \overline{L}$ these wave functions are continuously extended to their value and gradient at $z = 0$, as if the CP were a ring. However, this is meant to describe only the *circular boundary condition* of the wave functions at $z = \overline{L}$, not the shape of the CP.

(6) No external field is applied to the CP.

(7) A *jellium* model is used for the spatial distribution of the nuclear charge. This means, for the purpose of computing the spatial distribution of the electrons, the positive charges of the nuclei are modeled as a uniform "positive jelly" background, rather than point charges with distances in between. The nucleic charge density is assumed to be constant in axial and azimuthal direction, but it depends on the radial distance.

(8) However, correction terms will be used for computing the long-range Coulomb interaction, which are taking care of the jellium's short-range granularity (i.e. its point charge quality).

(9) The nucleic charge distribution of the jellium is modeled by means of a two-dimensional normal distribution in radial direction (or alternatively, by a distribution function, which is more aligned with the computed electron charge distribution). The standard deviation (or the alternative distribution function) is to be determined by variation, such that the total energy of the CP is minimized.

(10) The core area of the CP (i.e. the space defined by the extend of its electron orbitals) is surrounded by a charge compensation layer ("halo") consisting of cations. The charge of the halo compensates the surplus negative charges of the electrons in the core. The halo is modeled as a cylindrical shell of positive charge. The halo radius has to be larger than the core radius.

(11) The CP is assumed to reside in a vacuum. Interaction of the CP with surrounding matter is thus neglected.

(12) Only stationary states are modeled, as the goal is to describe the ground state of a CP. Consequently, the model assumes there is no electron scattering, i.e. there is no momentum transfer between electrons and the nuclei.

(13) For computing the repulsion energy among the nuclei, short-range corrections to the jellium model have to be made, which account for the granularity of the nuclear charges. In case the CP contains a mixture of different sorts of atomic nuclei, only the mean nuclear charge is taken into account for the corrections, rather than the individual nuclear charges.

(14) The time-independent Klein-Gordon equation is used for modeling the electron wave functions, thereby neglecting the magnetic moments of electron spins. The Klein-Gordon equation is taking care of the sizable relativistic effects occurring in CPs. (Clearly, the Dirac equation would be more adequate for modeling CPs. However, the involved complexities of such approach are avoided here.). For comparing the formulas and simulation results with the ones obtained from a non-relativistic Hamiltonian, also the Schrödinger equation is used.

(15) The magnetic field of the azimuthal electron orbits is neglected.

(16) Magnetic field from nuclear spins is neglected.

(17) The electron wave functions are modeled in an inertial frame of reference, where no magnetic field is created by any collinear movements of the nuclei. This simplification amounts to an approximation in cases where the nucleic velocities are position dependent.

(18) The multi-electron system is approximated by computing a collection of one-electron orbitals, whereby each electron orbital is subjected to the mean electric potential and magnetic vector potential created by the total charge density and total current density of all other occupied orbitals and the nuclei (independent particle model). The Pauli exclusion principle is used for determining orbital occupations of the ground state. Exchange and correlation energies are neglected.

(19) Quantum field theory is not engaged. Particle count is conserved.

(20) Eigenstates are excluded from occupation, where the corresponding total energy eigenvalue (including the electron's rest energy) of the electron is negative. This shall ensure that the mass defect per electron doesn't exceed the electrons rest energy.

(21) The kinetic energy of the electrons is always positive, i.e. states with a negative kinetic energy are ignored.

8.3 The Klein-Gordon Equation of a CP

Initial calculations of a CP with the Schrödinger equation have shown, that the spectrum of the axial electron velocities can reach 80% of the speed of light. This provided a reason for engaging a relativistic Hamiltonian and a Lorentz-covariant quantum mechanical equation to model CPs.

Generally, the Dirac equation is regarded as the correct Lorentz-covariant equation for modeling fermions, especially when the effects resulting from the particle's spin is of concern. Unfortunately, the Dirac equation involves 4-component wave functions and the solution of four coupled differential equations, resulting in sizeable mathematical and computational efforts.

Assuming that the electron spins have only minor effects on the binding energy, charge density, current density and other observables, the Klein-Gordon equation provides a Lorentz-covariant alternative to the Dirac equation for modeling the electrons of CPs. At the non-relativistic limit the Klein-Gordon equation is equivalent to the Schrödinger equation, while both equations share the deficiency of not modeling the spin.

In relativistic electrodynamics with so-called minimal coupling the Hamiltonian (total energy) of a particle with charge q moving in the presence of a static (external) electromagnetic potential is:

(22) $\hat{H} = c\sqrt{\left(\vec{P} - q\vec{A}\right)^2 + m_e^2 c^2} + q\Phi$, where c is the speed of light, Φ is the electric potential, $\vec{A}$ is the magnetic vector potential, $\vec{P} = \gamma m_e \vec{v} + q\vec{A}$ is the electron's canonical momentum, m_e is the electron rest mass and γ is the Lorentz factor

By defining $\overline{E} \equiv \hat{H} - m_e c^2$ as being the total energy minus the rest energy and by using $q = -e$ as the charge of an electron, (22) is leading to the following equation for an electron in a static electromagnetic potential:

(23) $\overline{E} = c\sqrt{\left(\vec{P} + e\vec{A}\right)^2 + m_e^2 c^2} - m_e c^2 - e\Phi$, where e is the elementary charge

Therefore:

(24) $\left(\overline{E} + e\Phi + m_e c^2\right)^2 = \left(c\vec{P} + ec\vec{A}\right)^2 + m_e^2 c^4$

All formulas are written in SI units, unless otherwise noted. Throughout this document, energy symbols with a bar on top (e.g. $\overline{E}$) denote, that the energy is measured in Joule. Energy symbols without a bar on top denote, that the energy is measured in units of the Hartree energy (118), i.e. the energy is a dimensionless quantity in the respective formula. Likewise, other symbols with a bar (e.g. $\overline{\sigma}$, $\overline{J}_z$, $\overline{p}_z$, $\overline{P}_z$, $\overline{A}_z$) are in SI units, while its counterparts without the bar are in natural units (i.e. dimensionless).

By quantizing the canonical momentum via the del operator $\vec{P} \equiv -i\hbar\nabla$ and applying both sides to an electron wave function Ψ , equation (24) transforms to the **stationary Klein-Gordon equation of an electron in a static electromagnetic potential**:

(25) $\left(\overline{E} + e\Phi + m_e c^2\right)^2 \Psi = \left[\left(-i\hbar c\nabla + ec\vec{A}\right)^2 + m_e^2 c^4\right] \Psi$, where $\hbar$ is the reduced Planck constant and $i = \sqrt{-1}$

Due to simplification (19), Ψ is called here a "wave function", rather than a "quantum field".

The term $\overline{E} + m_e c^2$ represents the total energy of the electron. Usually the Klein-Gordon equation is written, such that the total energy is sought as the eigenvalue of this differential equation. However, this document deviates from the customary approach. Instead, the quantity $\overline{E}$ is sought here as the eigenvalue (both approaches are equivalent in their results).

Some authors prefer the term "relativistic Schrödinger equation" for (25), insisting that the Klein-Gordon equation is different. Here, these terms are used interchangeably.

In quantum mechanics a multi-electron system is correctly described by a single wave function $\Psi\left(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_N\right)$ depending on the positions of the N electrons. The multi-electron wave function is usually formed by a Slater determinant (or a linear combination of several Slater determinants) to ensure anti-symmetry and the Pauli exclusion principle.

However, the number of electrons in a CP can exceed 10^{12}, which renders a Slater determinant entirely impractical to compute, because a program cannot handle equations with e.g. 10^{12} positions and compute determinants of this size.

According to simplification (18) a rigorously simpler approach is used here for modeling CPs, requiring only moderate compute power:

So, instead of using a multi-electron Klein-Gordon equation describing the pair-wise interaction between N electrons, the cylindrical model uses ***N*** **single-electron Klein-Gordon equations with** ***N*** **wave functions** $\Psi\left(\vec{r}\right)$, each describing a single electron in the **mean potential** of all other electrons and the nuclei.

Of course, this is merely an independent particle approximation. For example, the approach doesn't account for the exchange energy and the correlation energy usually deemed important in quantum chemistry.

At first glance this looks still challenging to compute, because there are N Klein-Gordon equations to be solved. Fortunately, large numbers of these equations can be computed in groups, because they produce nearly the same charge density distributions and current density distributions.

Expanding the right side of (25) and using $\nabla \cdot \vec{A} = 0$ (Lorentz gauge in the static case) yields:

$$(26) \quad \left(\overline{E} + e\Phi + m_e c^2\right)^2 \Psi = \left(-\hbar^2 c^2 \nabla^2 - 2i\hbar e c^2 \vec{A} \cdot \nabla + e^2 c^2 \vec{A} \cdot \vec{A} + m_e{}^2 c^4\right)\Psi$$

A kinetic momentum operator is defined here as:

$$(27) \quad \hat{p} = -i\hbar\nabla + e\vec{A}$$

The expectation value of $\hat{p}$ equals $\langle\gamma\rangle m_e \langle\vec{v}\rangle$, hence the name "kinetic momentum" ($\langle\vec{v}\rangle$ is the expectation value of the electron's group velocity and $\langle\gamma\rangle = \left\langle 1 + \left(\overline{E} + e\Phi\right) / \left(m_e c^2\right)\right\rangle$ is the expectation value of the local Lorentz factor).

Using (27) in (26) yields:

$$(28) \quad \left(\overline{E} + e\Phi + m_e c^2\right)^2 \Psi = \left(c^2 \hat{p}^2 + m_e{}^2 c^4\right)\Psi \text{, where } c^2 \hat{p}^2 = -\hbar^2 c^2 \nabla^2 - 2i\hbar e c^2 \vec{A} \cdot \nabla + e^2 c^2 \vec{A} \cdot \vec{A}$$

According to simplification (14) and (15) the magnetic field of the electron spins and of the azimuthal movement of the electrons is neglected. Thus the only source of the magnetic field is the current carried by the electrons moving in z-direction. Therefore, the vector potential is everywhere oriented in z-direction:

$$(29) \quad \vec{A} = \overline{A}_z \vec{e}_z$$

The Laplace operator expands in cylindrical coordinates as following:

$$(30) \quad \nabla^2 = \frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial}{\partial\rho}\right) + \frac{1}{\rho^2}\frac{\partial^2}{\partial\varphi^2} + \frac{\partial^2}{\partial z^2}$$

, where ρ is the radial distance from the z-axis, φ is the azimuth and z is the coordinate of the z-axis

Inserting (29) and (30) into equation (26) and dividing both sides by $2m_e c^2$ is resulting in **the stationary Klein-Gordon equation of an electron in the mean potential of a CP's all other electrons and the nuclei**:

$$(31) \quad \left\{\frac{-\hbar^2}{2m_e}\left[\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial}{\partial\rho}\right) + \frac{1}{\rho^2}\frac{\partial^2}{\partial\varphi^2} + \frac{\partial^2}{\partial z^2} + 2\frac{e\overline{A}_z}{\hbar} i \frac{\partial}{\partial z} - \frac{e^2 \overline{A}_z{}^2}{\hbar^2}\right] - \frac{m_e c^2}{2}\left(\frac{\overline{E} + e\Phi}{m_e c^2} + 1\right)^2 + \frac{m_e c^2}{2}\right\}\Psi = 0$$

With simplification (6) the electric potential Φ is depending solely on the electron charge density $\overline{\sigma}_e(\rho)$ and the nuclear charge density $\overline{\sigma}_n(\rho)$. The magnetic vector potential $\overline{A}_z$ is solely depending on the electric current density $\overline{J}_z(\rho)$. The electron charge density and the electric current density are derived from the modulus square of the other electron's wave functions. This approach has **similarities with the density functional theory (DFT)** used in quantum chemistry modeling, except that the exchange and correlation energies are not accounted for. However, the influence of the magnetic field on the co-linear electron-electron interaction is maintained and the Pauli exclusion principle will be obeyed during orbital occupation.

8.4 Boundary Conditions for Solutions of the Klein-Gordon Equation

Care must be taken according to simplification (20), that **the total energy** $\overline{E} + m_e c^2$ **of an eigenstate is always positive**, therefore:

(32) $\overline{E} > -m_e c^2$

Requirement (32) can be fulfilled by **excluding eigenstates with a negative total energy during orbital occupation**.

The wave function amplitude must disappear at infinite radial distances:

(33) $\lim_{\rho \to \infty} \Psi(\rho) = 0$

As required by simplification (5) the wave function has to meet circular boundary conditions:

(34) $\Psi(z=0) = \Psi(z=\overline{L})$ and

(35) $\dfrac{\partial \Psi(z=0)}{\partial z} = \dfrac{\partial \Psi(z=\overline{L})}{\partial z}$

For computing observables the Klein-Gordon electron wave functions have to be **normalized** such that:

(36) $1 = \|\Psi\| = \iiint_{\mathbf{R}^3} |\Psi|^2 d\vec{r}$

8.5 Observables of the Klein-Gordon Electron Wave Function

The potential energy of an electron is solely stemming from the Coulomb field:

(37) $\overline{E}_{pot}(\vec{r}) = -e\Phi(\vec{r})$

The local kinetic energy of the electron is, what's left when the potential energy is subtracted from $\overline{E}$:

(38) $\overline{E}_{kin}(\vec{r}) = \overline{E} + e\Phi(\vec{r})$

The **volume charge density distribution of electron number** i in a static electromagnetic potential computes as following:

(39) $\overline{\sigma}_{e,i} = -e|\Psi_i|^2$

Summing this up for all N electrons of the CP and using modulus square factorization (71) is resulting in:

(40) $\overline{\sigma}_e = -e\sum_{i=1}^{N} |\Psi_i|^2 = -\dfrac{e}{2\pi \overline{L}} \sum_{i=1}^{N} |\Psi_{\rho,i}|^2$, where $\Psi_{\rho,i}$ is the radial wave function of electron number i

The **current density distribution of electron number** i in a static electromagnetic potential computes as following:

(41) $\vec{\overline{J}}_i = \dfrac{-e}{m_e}\left[-\dfrac{i\hbar}{2}\left(\Psi_i^* \nabla \Psi_i - \Psi_i \nabla \Psi_i^*\right) + e\vec{A}|\Psi_i|^2 \right]$

Summing (41) up for all N electrons of the CP provides:

(42) $\vec{\overline{J}} = \dfrac{-e}{m_e}\sum_{i=1}^{N}\left[-\dfrac{i\hbar}{2}\left(\Psi_i^* \nabla \Psi_i - \Psi_i \nabla \Psi_i^*\right) + e\vec{A}|\Psi_i|^2 \right]$

Using product ansatz (69), modulus square factorization (71) and Ψ_z-solution (75), the **z-component** (in cylindrical coordinates) **of the current density** (42) in a CP computes as:

$$(43)\quad \overline{J}_z = \frac{-e}{m_e}\sum_{i=1}^{N}\left[-\frac{i\hbar}{2}\left(\Psi_i^*\frac{\partial\Psi_i}{\partial z}-\Psi_i\frac{\partial\Psi_i^*}{\partial z}\right)+e\overline{A}_z\left|\Psi_i\right|^2\right]$$

$$=\frac{-e}{2\pi m_e\overline{L}}\sum_{i=1}^{N}\overline{p}_{z,i}\left|\Psi_{\rho,i}\right|^2 \text{, where}$$

$$(44)\quad \overline{p}_{z,i}=\overline{P}_{z,i}+e\overline{A}_z=\hbar k_i+e\overline{A}_z$$ is the **z-component of the electron's kinetic momentum** $\hat{p}$

When (40), (42) and (43) will be used for determining the electric and magnetic potentials in the Klein-Gordon equation (31), the electron number i is incorrectly exposed also to its own potential. However, this error is quite small, if the CP contains very many electrons.

The total **current** in z-direction carried by all electrons of the CP can be computed by integrating (43) over all radius values and azimuth values:

$$(45)\quad I_z=\int_{\varphi=0}^{2\pi}\int_{\rho=0}^{\infty}\overline{J}_z(\rho)\rho d\rho d\varphi=\frac{-e}{m_e\overline{L}}\int_0^{\infty}\sum_{i=1}^{N}\overline{p}_{z,i}\left|\Psi_{\rho,i}(\rho)\right|^2\rho d\rho$$

$$=\frac{-e}{m_e\overline{L}}\sum_{i=1}^{N}\int_0^{\infty}\left[\hbar k_i+e\overline{A}_z(\rho)\right]\left|\Psi_{\rho,i}(\rho)\right|^2\rho d\rho$$

The expectation value of the **electron group velocity's z-component** (averaged over all N electrons of the CP) can be computed from the z-component of the total current:

$$(46)\quad \langle v_z\rangle=\frac{I_z\overline{L}}{-Ne}$$

The **expectation value of the electron orbit radius** for eigenstates of equation (31) is:

$$(47)\quad \langle\rho\rangle=\int_0^{\infty}\left|\Psi\right|^2\rho^2 d\rho$$

One could naively assume, that the **total binding energy** $\overline{E}_B$ of a CP is the sum of the energy eigenvalues of all electrons plus the nuclear self-repulsion energy:

$$(48)\quad \overline{E}_B\neq\overline{E}_n+\sum_{i=1}^{N}\overline{E}_i$$, where $\overline{E}_i$ is the energy eigenvalue of electron number i and $\overline{E}_n$ is the nuclear self-repulsion energy defined in (84)

However, this approach would count the electron-electron interaction energies $\langle\overline{E}_{C,e}\rangle_i$ twice, because the electrons are interacting among themselves.

Instead, one needs to subtract half of $\langle\overline{E}_{C,e}\rangle_i$ from the eigenvalues $\overline{E}_i$ before summation:

$$(49)\quad \overline{E}_B=\overline{E}_n+\sum_{i=1}^{N}\left(\overline{E}_i-\frac{1}{2}\langle\overline{E}_{C,e}\rangle_i\right),$$

where $\langle\overline{E}_{C,e}\rangle_i=\langle-e\Phi_e\rangle_i$ is the expectation value of the electron-electron Coulomb energy for electron number i and Φ_e is the potential of all electrons

A CP resembles a microstrip, if it is attached to the surface of a dielectric plate, which has a conducting return plane attached at the other side. Therefore, microstrip formulas can be used for approximating the characteristic impedance, the capacitance and the inductance of a CP. For this purpose the following assumptions are made:

(50) $\langle\rho\rangle_{mean} << h << \overline{L}$, where $\langle\rho\rangle_{mean}$ is the expectation value of the electron radius averaged over all electrons, h is the thickness of the dielectric plate and $\overline{L}$ is the length of the CP

The **characteristic impedance of a CP** (in microstrip geometry) can be approximated by:

(51) $Z_0 \approx \frac{1}{2\pi}\sqrt{\frac{\mu_0}{\varepsilon_0\varepsilon_{eff}}}\ln\left(\frac{2h}{\langle\rho\rangle_{mean}}\right)$, where h is the thickness of the dielectric plate

The effective dielectric constant can be approximated as:

(52) $\varepsilon_{eff} \approx \frac{\varepsilon_r + 1}{2}$, where ε_r is the relative permittivity

The **capacitance of a CP** (in microstrip geometry) can be approximated by:

(53) $C \approx \frac{2\pi\varepsilon_0\varepsilon_{eff}\overline{L}}{\ln\left(2h/\langle\rho\rangle_{mean}\right)}$, where ,

The **inductance of a CP** (in microstrip geometry) can be approximated by:

(54) $\Lambda \approx Z_0{}^2 C \approx \frac{\mu_0\overline{L}}{2\pi}\ln\left(\frac{2h}{\langle\rho\rangle_{mean}}\right)$

8.6 The Electromagnetic Potential and Field of a CP

The electric potential of a CP splits as follows:

(55) $\Phi = \Phi_n + \Phi_e + \Phi_{G,e} + \Phi_h$, where Φ_n is the electric potential of the nuclear jellium in the core according to simplification (7) and (8), Φ_e is the electric potential of the electrons, $\Phi_{G,e}$ is the granularity correction of electron-nucleus interaction (94) and Φ_h is the electric potential of the halo (100).

As a tool for computing the electromagnetic potential the following geometry is analyzed:

A sample charge at distance ρ from the z-axis (origin) and azimuth φ shall act as the point of measurement for vector potential A_z and the electric potentials Φ.

The following figure illustrates this further:

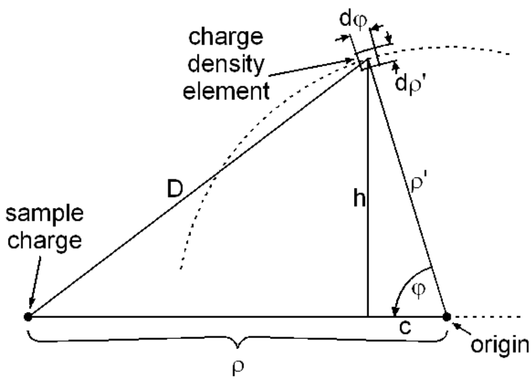

Figure 4 Scheme for computing the electromagnetic potential. This shows a cut perpendicular to the z-axis.

From the geometry of Figure 4 it can be concluded:

(56) $c = \rho' \cos\varphi$

(57) $h = \rho' \sin\varphi$

(58) $D = \sqrt{(\rho - c)^2 + h^2} = \sqrt{(\rho - \rho'\cos\varphi)^2 + \rho'^2 \sin^2\varphi} = \sqrt{\rho'^2 - 2\rho'\rho\cos\varphi + \rho^2}$

The following figure shall illustrate the geometry in z-direction:

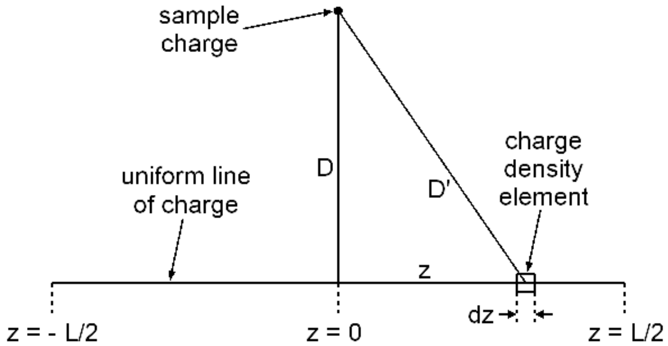

Figure 5 Scheme for computing the electromagnetic potential. This shows a cut in parallel to the z-axis.

From Figure 5 it can be concluded:

(59) $D' = \sqrt{z^2 + D^2}$

Figure 5 shows an infinitesimal thin line of charge extending from $z = -\overline{L}/2$ to $z = \overline{L}/2$. This line is in parallel to the z-axis. The volume charge density $\overline{\sigma}(\rho')$ is constant along the line.

An infinitesimal charge density element with a volume of $\rho' d\rho' d\varphi dz$ contains a charge of:

(60) $dQ = \overline{\sigma}(\rho')\rho' d\rho' d\varphi dz$, where

(61) $\overline{\sigma}(\rho') = \overline{\sigma}_n(\rho') + \overline{\sigma}_e(\rho') + \overline{\sigma}_h(\rho')$, i.e. the sum of the nuclear charge density in the core, the electron charge density and the charge density of the halo (99)

The electric potential at distance D from the infinitesimal line of charge and at axial position $z = 0$ computes as following:

(62) $$d\Phi(D) = \frac{1}{4\pi\varepsilon_0}\int_{-\overline{L}/2}^{\overline{L}/2}\frac{dQ}{D'} = \frac{1}{4\pi\varepsilon_0}\overline{\sigma}(\rho')\rho' d\rho' d\varphi 2\int_0^{\overline{L}/2}\frac{1}{\sqrt{z^2 + D^2}}dz$$
$$= \frac{1}{4\pi\varepsilon_0}\overline{\sigma}(\rho')\rho' d\rho' d\varphi 2\ln\frac{\overline{L}/2 + \sqrt{(\overline{L}/2)^2 + D^2}}{D}$$

Inserting (58) into (62) and integrating over ρ' and φ yields the contribution of the entire CP to the **electric potential** (in Lorentz gauge, static case):

(63) $\Phi(\rho) = \frac{1}{4\pi\varepsilon_0}\int_0^\infty \overline{\sigma}(\rho')G(\rho,\rho')\rho' d\rho'$, where

(64) $G(\rho,\rho') = 2\int_0^{2\pi}\ln\frac{\overline{L}/2 + \sqrt{(\overline{L}/2)^2 + \rho'^2 - 2\rho'\rho\cos\varphi + \rho^2}}{\sqrt{\rho'^2 - 2\rho'\rho\cos\varphi + \rho^2}}d\varphi$ is the geometry integral

The geometry integral can be solved by considering Gauss's law and by using the fact that the charge distribution is rotationally symmetric around the z-axis. For the case $\rho \le \rho'$ there is $G(\rho,\rho') = G(\rho',0)$. For the case $\rho > \rho'$ there is $G(\rho,\rho') = G(\rho,0)$:

(65) $$G(\rho,\rho') = \begin{cases} 4\pi\left[\ln\left(\overline{L}/2 + \sqrt{\overline{L}^2/4 + \rho'^2}\right) - \ln\rho'\right] & \text{for } \rho \le \rho' \\ 4\pi\left[\ln\left(\overline{L}/2 + \sqrt{\overline{L}^2/4 + \rho^2}\right) - \ln\rho\right] & \text{for } \rho > \rho' \end{cases}$$

Replacing $\overline{\sigma}(\rho')/\varepsilon_0$ with $\mu_0 \overline{J}_z(\rho')$ in (63) provides the z-component of the CP's **magnetic vector potential** (in Lorentz gauge, static case):

(66) $$\overline{A}_z(\rho) = \frac{\mu_0}{4\pi}\int_0^\infty \overline{J}_z(\rho')G(\rho,\rho')\rho' d\rho' = -\frac{e\mu_0}{8\pi^2 m_e \overline{L}}\int_0^\infty \sum_{i=1}^{N}\left[\overline{P}_{z,i} + e\overline{A}_z(\rho')\right]\left|\Psi_{\rho',i}\right|^2 G(\rho,\rho')\rho' d\rho',$$

where I_z is the total current of the electrons in z-direction, μ_0 is the vacuum permeability and $\overline{J}_z(\rho')$ is the z-component of the current density

Note, that $\overline{A}_z$ is depending on itself in equation (66). Therefore, the values of $\overline{A}_z$ and $\overline{J}_z$ need to be determined iteratively until self-consistency.

Based on the circular boundary condition (5) the electric potential (63) and the vector potential (66) are made to be constant in z-direction. This approximation is required for maintaining the full cylindrical symmetry of the model.

The radial and azimuthal (see simplification (15)) components of the vector potential and the current density is zero everywhere. Due to simplification (17) the nuclear jellium is not contributing to the current density.

Note, that $\lim_{\rho\to\infty}\Phi(\rho) = 0$ and $\lim_{\rho\to\infty}\overline{A}_z(\rho) = 0$. Equations (63) and (66) therefore can be used for determining the binding energy of electrons to a CP without engaging a non-zero reference potential.

The **radial electric field** of a CP computes as:

(67) $$\varepsilon_\rho = -\frac{\partial}{\partial\rho}\Phi(\rho)$$

The **azimuthal magnetic field** of a CP computes as:

(68) $$B_\varphi = -\frac{\partial}{\partial\rho}\overline{A}_z(\rho)$$

8.7 Product Ansatz

The following **product ansatz** is made to factorize the electron wave function:

(69) $\Psi(\rho,\varphi,z) = \Psi_\rho(\rho)\Psi_\varphi(\varphi)\Psi_z(z)$ or in short: $\Psi = \Psi_\rho\Psi_\varphi\Psi_z$

The wave function of a single electron is supposed to be normalized and it represents a stationary state. In azimuthal direction and in axial direction the electromagnetic potential is constant. Therefore the modulus square of Ψ_φ and Ψ_z is also constant:

(70) $\left|\Psi_\varphi\right|^2 = \Psi_\varphi^*\Psi_\varphi = \dfrac{1}{2\pi}$ and $\left|\Psi_z\right|^2 = \Psi_z^*\Psi_z = \dfrac{1}{\overline{L}}$

Hence the **modulus square** of the entire wave function factorizes as:

(71) $$\left|\Psi\right|^2 = \Psi_\rho^*(\rho)\Psi_\rho(\rho)\Psi_\varphi^*(\varphi)\Psi_\varphi(\varphi)\Psi_z^*(z)\Psi_z(z) = \frac{1}{2\pi\overline{L}}\left|\Psi_\rho(\rho)\right|^2$$

The **normalization criteria** (36) could then be carried out as:

$$(72)\quad 1=\|\Psi\|=\int_0^\infty \left|\Psi_\rho(\rho)\right|^2 \rho d\rho$$

8.8 Separation of the Klein-Gordon Equation

With product ansatz (69) the partial derivatives of the wave function are:

$$(73)\quad \frac{\partial\Psi}{\partial\rho}=\Psi_\varphi\Psi_z\frac{d\Psi_\rho}{d\rho} \text{ and } \frac{\partial\Psi}{\partial\varphi}=\Psi_\rho\Psi_z\frac{d\Psi_\varphi}{d\varphi} \text{ and } \frac{\partial\Psi}{\partial z}=\Psi_\rho\Psi_\varphi\frac{d\Psi_z}{dz}$$

Inserting this into the equation (31) and dividing both sides by Ψ yields:

$$(74)\quad -\frac{\hbar^2}{2m_e}\left[\frac{1}{\rho\Psi_\rho}\frac{d}{d\rho}\left(\rho\frac{d\Psi_\rho}{d\rho}\right)+\frac{1}{\rho^2\Psi_\varphi}\frac{d^2\Psi_\varphi}{d\varphi^2}+\frac{1}{\Psi_z}\frac{d^2\Psi_z}{dz^2}+2\frac{e\overline{A}_z}{\hbar\Psi_z}i\frac{d\Psi_z}{dz}-\frac{e^2\overline{A}_z^{\,2}}{\hbar^2}\right]$$
$$-\frac{m_ec^2}{2}\left(\frac{\overline{E}+e\Phi}{m_ec^2}+1\right)^2+\frac{m_ec^2}{2}=0$$

Remark for the mathematical purity: The division by Ψ is done here out of convenience. It could have been postponed to a later step without affecting the end result, such that wave functions (which can have zeros) never show up in the denominator.

The following **wave function is solving the z-dependent part** of (74):

$$(75)\quad \Psi_z=\sqrt{\frac{1}{L}}e^{ikz}\text{, where } k\in\mathbf{R}$$

Due to simplification (5) the energy eigenvalues are quantized to a discrete spectrum, because wave number k has to meet the following boundary condition:

$$(76)\quad k=l\frac{2\pi}{L}\text{, where } l\in\mathbf{Z}$$

Integer l acts as an **axial quantum number** here (This quantum number l should not be confused with the l in Laplace's spherical harmonic function $Y_l^m(\theta,\varphi)$ used for modeling the electrons of atoms).

The following **wave function is solving the φ-dependent part** of (74):

$$(77)\quad \Psi_\varphi=\sqrt{\frac{1}{2\pi}}e^{im\varphi}\text{, where } m\in\mathbf{Z}$$

Integer m is the **azimuthal quantum number**.

Inserting (44), (75) and (77) into (74) provides the **radial Klein-Gordon equation** of a CP:

$$(78)\quad \left\{\frac{\hbar^2}{2m_e}\left[-\frac{1}{\rho}\frac{d}{d\rho}\left(\rho\frac{d}{d\rho}\right)+\frac{m^2}{\rho^2}\right]+\frac{p_z^{\,2}}{2m_e}-\frac{m_ec^2}{2}\left(\frac{\overline{E}+e\Phi}{m_ec^2}+1\right)^2+\frac{m_ec^2}{2}\right\}\Psi_\rho=0$$

At the **non-relativistic limit** the term $x=(\overline{E}+e\Phi)/(m_ec^2)$ approaches zero. By using only the first two terms of the Taylor series of $(x+1)^2$ about $x=0$ one can approximate:

$$(79)\quad (x+1)^2\approx 1+2x$$

With this approximation equation (78) becomes the **radial Schrödinger equation** of a CP:

$$(80)\quad \left\{\frac{\hbar^2}{2m_e}\left[-\frac{1}{\rho}\frac{d}{d\rho}\left(\rho\frac{d}{d\rho}\right)+\frac{m^2}{\rho^2}\right]+\frac{p_z^{\ 2}}{2m_e}-\overline{E}-e\Phi\right\}\Psi_\rho=0$$

The radial Schrödinger equation (80) is based on the **non-relativistic Hamiltonian** for an electron in an electromagnetic field with minimal coupling:

$$(81)\quad \hat{H}=\frac{\left(-i\hbar\nabla+e\vec{A}\right)^2}{2m_e}-e\Phi=\frac{\left(\vec{P}+e\vec{A}\right)^2}{2m_e}-e\Phi$$

The eigenstates of differential equation (78) or (80) provide the radial wave functions Ψ_ρ. The eigenvalues $\overline{E}$ of bound states are discrete, i.e. they are countable by a principal quantum number n, the azimuthal quantum number m and the axial quantum number l. The **principal quantum number** $n = 1, 2, 3, \ldots$ is defined here analogous to the hydrogen atom: n equals one plus the number of node lines of $\Psi_\rho\Psi_\varphi$, therefore $n \geq |m|+1$ (In a stricter sense, Ψ_φ has no node lines. However, a standing wave of two superposed azimuthal wave functions, differing only in the sign of quantum number m, has m node lines.)

Principal quantum number n has no explicit representation in (78) or (80) or in any of the following formulas. It is useful however, as an ordering scheme for computational results.

One has to keep in mind, that the eigenvalues $\overline{E}$, the eigenstates Ψ_ρ, Ψ_φ and Ψ_z, as well as the quantum numbers n, m and l are generally distinct for each electron of the CP. In order to ease readability, the electron number as an index has been omitted from these symbols, unless the index is needed in a summation.

8.9 The Jellium Model of the Nuclear Charge Distribution

According to simplification (7) the charge of the nuclei is treated as if it were a uniform "positive jelly" background, rather than point charges with distances in between.

The nuclear charge density distribution $\overline{\sigma}_n(\rho)$ of the core jellium has cylindrical symmetry, i.e. it doesn't depend on φ and z. It is a function of the radial distance ρ.

According to equations (55), (61) and (63) the **electric potential of the core nuclear jellium** is:

$$(82)\quad \Phi_n(\rho)=\frac{1}{4\pi\varepsilon_0}\int_0^\infty \overline{\sigma}_n(\rho')G(\rho,\rho')\rho'd\rho'$$

An infinitesimal charge element $\overline{\sigma}_n(\rho')\rho'd\rho'd\varphi dz$ brought into potential Φ_n has the potential energy:

$$(83)\quad d\overline{E}_n=\overline{\sigma}_n(\rho)\Phi_n(\rho)\rho d\rho d\varphi dz$$

Integrating (83) over the entire space and dividing the result by two yields the **nuclear self-repulsion energy**:

$$(84)\quad \overline{E}_n=-\overline{E}_{G,n}+\overline{E}_{n,h}+\overline{E}_{h,h}+\frac{1}{2}\int_0^L\int_0^{2\pi}\int_0^\infty \overline{\sigma}_n(\rho)\Phi_n(\rho)\rho d\rho d\varphi dz$$

$$=-\overline{E}_{G,n}+\overline{E}_{n,h}+\overline{E}_{h,h}+\pi L\int_0^\infty \overline{\sigma}_n(\rho)\Phi_n(\rho)\rho d\rho\ ,$$

where $\overline{E}_{G,n}$ is the granularity correction (93), $\overline{E}_n>0$ and $\overline{E}_{G,n}>0$, $\overline{E}_{n,h}$ is the halo-core repulsion energy according to equation (102) and $\overline{E}_{h,h}$ is the halo self-repulsion energy according to equation (103)

The division by two in (84) takes care of the fact, that the jellium is interacting with itself and the repulsion energy must not be accounted twice during integration.

Treating the nuclear charges purely as a jellium is under-representing the electron-nucleus Coulomb interaction and is over-representing the nucleus-nucleus Coulomb interaction.

Therefore and according to simplification (8), a granularity correction $\Phi_{G,e}(\overline{\sigma}_n)$ of the total Coulomb potential (55) is needed for the electron-nucleus interaction (Also a granularity correction $\overline{E}_{G,n}$ of the nuclear self-repulsion energy is needed). In the following, these two corrections will be derived.

Regarding simplification (13) the nuclei are assumed to have a mean charge of Z_m. The mean charge is determined by the average of the nuclear charges Z_i of the atomic sort weighted by the fraction $0 < F_i < 1$ of the respective atomic sort:

(85) $Z_m = \sum_0^n F_i Z_i$, where $\sum_0^n F_i = 1$ and n is the number of different atomic sorts of the mixture

The **volume occupied by exactly one nucleus with a charge of** eZ_m would be:

(86) $$V_{1n} = \frac{eZ_m}{\overline{\sigma}_n} = \frac{4\pi}{3} R_{1n}^{\ 3}$$

Hence the **radius** R_{1n} **of a sphere with volume** V_{1n} would be:

(87) $R_{1n} = \sqrt[3]{\frac{3}{4\pi}\frac{eZ_m}{\overline{\sigma}_n}}$, therefore $\overline{\sigma}_n = \frac{3}{4\pi}\frac{eZ_m}{R_{1n}^{\ 3}}$

In the picture of nuclear point charges the **potential of a single nucleus** is as following:

(88) $\Phi_{1n}(r_n) = \frac{1}{4\pi\varepsilon_0}\frac{eZ_m}{r_n}$, where r_n is the distance to the nucleus

However, in the jellium model the potential of a single nucleus equates to the **potential of a homogeneously charged sphere** with radius R_{1n}:

(89) $\Phi'_{1n}(r_n) = \frac{eZ_m}{8\pi\varepsilon_0}\left(\frac{3}{R_{1n}} - \frac{r_n^{\ 2}}{R_{1n}^{\ 3}}\right)$, where $r_n \le R_{1n}$ and $\overline{\sigma}_n$ is assumed to be constant within V_{1n}

Using equation (89) the self-repulsion energy per nucleus of the jellium within sphere for case $r_n \le R_{1n}$ would be as following:

(90) $$\overline{E}_{1n}(\overline{\sigma}_n) = \frac{1}{2}\iiint_{V_{1n}} \Phi'_{1n}(r_n) dQ = \frac{1}{2}\int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi}\int_{r=0}^{R_{1n}} \overline{\sigma}_n \Phi'_{1n}(r_n) r_n^{\ 2} dr_n \sin\theta d\theta d\varphi = 2\pi\overline{\sigma}_n \int_0^{R_{1n}} \Phi'_{1n}(r_n) r_n^{\ 2} dr_n$$
$$= \frac{3}{16\pi\varepsilon_0}\frac{e^2 Z_m^{\ 2}}{R_{1n}^{\ 3}}\int_0^{R_{1n}}\left(\frac{3r_n^{\ 2}}{R_{1n}} - \frac{r_n^{\ 4}}{R_{1n}^{\ 3}}\right)dr_n = \frac{3}{20\pi\varepsilon_0}\frac{e^2 Z_m^{\ 2}}{R_{1n}} = \frac{1}{5\varepsilon_0}\sqrt[3]{\left(\frac{3}{4\pi}\right)^2 e^5 Z_m^{\ 5}\overline{\sigma}_n}$$

In reality, a single nucleus doesn't repel itself. Therefore, for each nucleus $\overline{E}_{1n}(\overline{\sigma}_n)$ needs to be subtracted from the jellium's self-repulsion energy.

An infinitesimal cylindrical zone of a CP with radius $\rho - \frac{1}{2}d\rho \le \rho' \le \rho + \frac{1}{2}d\rho$ has the volume:

(91) $$dV = 2\pi\overline{L}\rho d\rho$$

The number of nuclei residing in volume dV is:

(92) $$dN = \frac{dV}{V_{1n}} = 2\pi\overline{L}\frac{\overline{\sigma}_n(\rho)}{eZ_m}\rho d\rho$$

Multiplying (92) with $\overline{E}_{1n}$ and integrating over ρ yields the **granularity correction of the jellium's core self-repulsion energy**:

(93) $$\overline{E}_{G,n} = \int_{\rho=0}^{\infty} \overline{E}_{1n} dN = \frac{\overline{L}}{5\varepsilon_0} \sqrt[3]{\frac{9\pi}{2} e^2 Z_m{}^2} \int_{\rho=0}^{\infty} \overline{\sigma}_n{}^{4/3}(\rho) \rho d\rho$$

Within the volume V_{1n} there is also electron-electron interaction. No granularity correction applies to it, as this interaction is fully taken care of in (63).

Subtracting (89) from (88) and averaging over the volume V_{1n} provides the desired **granularity correction of the total potential (55) seen by the electrons** ($\overline{\sigma}_e$ is assumed to be constant within V_{1n}):

(94) $$\Phi_{G,e} = \frac{4\pi}{V_{1n}} \int_0^{R_{1n}} (\Phi_{1n} - \Phi'_{1n}) r_n{}^2 dr_n = \frac{eZ_m}{\varepsilon_0 V_{1n}} \int_0^{R_{1n}} \left(r_n - \frac{3r_n{}^2}{2R_{1n}} + \frac{r_n{}^4}{2R_{1n}{}^3} \right) dr_n$$
$$= \frac{eZ_m}{10\varepsilon_0 V_{1n}} R_{1n}{}^2 = \frac{\overline{\sigma}_n{}^{1/3}}{10\varepsilon_0} \left(\frac{3eZ_m}{4\pi} \right)^{2/3}$$

According to simplification (9) the **nucleic charge distribution in the core** is modeled by means of a two-dimensional normal distribution in radial direction:

(95) $$\overline{\sigma}_n(\rho) = \frac{Q}{\overline{L}} \frac{1}{2\pi\overline{s}^2} \exp\left(-\frac{\rho^2}{2\overline{s}^2} \right),$$

where $\overline{s}$ is the standard deviation in meter, Q is the nuclear charge of the CP core

The distribution function (95) is normalized, such that the integral over all space (in Cartesian coordinates) yields the nuclear charge Q:

(96) $$\iiint \overline{\sigma}_n(\rho) = \int_{x=-\infty}^{\infty} \int_{y=-\infty}^{\infty} \int_{z=0}^{\overline{L}} \frac{Q}{\overline{L}} \frac{1}{2\pi\overline{s}^2} \exp\left(-\frac{\rho^2}{2\overline{s}^2} \right) dzdydx = Q \text{, where } \rho^2 = x^2 + y^2$$

The standard deviation is to be determined iteratively (by variation), such that the total energy of the CP is minimized. During each computational iteration the electron eigenstates have to be recomputed, as they strongly depend on the nuclear charge distribution.

After studying the computational results of the radial electron density distribution, it became apparent, that equation (95) needs to be adjusted like this:

(97) $$\overline{\sigma}_n(\rho) = Height \cdot \exp\left(-\frac{\rho^2}{2\overline{s}^2} - \frac{\rho^5}{Slope^5} - \frac{\rho^{16}}{Cutoff^{16}} \right)$$

Parameter $Height$ has to be computed, such that the distribution function (97) is normalized to the core nuclear charge Q. Parameters $Slope$ and $Cutoff$ should be adjusted, such that the total energy of the CP is minimized.

8.10 The CP Halo (i.e. the Charge Compensation Layer)

The computational results achieved with the cylindrical model are showing, that the core of a CP can carry excess negative charge (for example, 2% more electrons than nuclear charges).

When a CP is in thermodynamic equilibrium with surrounding matter, the surplus negative charge of the CP has to be compensated by a surrounding layer of cations. This layer contains room charge, which terminates the electrical field around the CP core.

The charge compensation layer of cations will be called the "halo" of the CP, whereas the nuclei and the electrons comprising the CP (without the halo) will be called the "core" of the CP.

The halo can also be modeled as a jellium, like the core.

If the halo is fully compensating the charge of the core, the **linear charge density of the halo** is:

(98) $\overline{\lambda}_h \equiv \frac{Q_h}{\overline{L}} = -\overline{\lambda}_e - \overline{\lambda}_n$, where Q_h is the total charge of the halo, $\overline{\lambda}_n = Q/\overline{L}$ is the linear charge density of the nuclei in the core and $\overline{\lambda}_e$ is the linear charge density of the electrons in the core

For the purpose of computing the electric potential in the core, the easiest way is to assume a homogeneously charged cylindrical shell with a radius ρ_h, which is larger than the radial extent of the electron orbits and the extent of the nuclear charge distribution of the core (simplification (10)). The shell shall be concentric to the z-axis and have an infinitesimal wall thickness of $\delta\rho$. The **charge density of the halo** cations then is:

$$(99)\quad \overline{\sigma}_h = \frac{\overline{\lambda}_h}{2\pi\rho_h\delta\rho}$$

The potential summands sourced by the nuclei and the electrons had been specified in equation (55). The **contribution of the halo to the Coulomb potential** computes as:

$$(100)\quad \Phi_h = \frac{1}{4\pi\varepsilon_0}\int_0^\infty \overline{\sigma}_h(\rho')G(\rho,\rho')\rho' d\rho' = \frac{\overline{\lambda}_h}{8\pi^2\varepsilon_0}\int_{\rho_h}^{\rho_h+\delta\rho}\frac{1}{\rho'\delta\rho}G(\rho,\rho')\rho' d\rho' = \frac{\overline{\lambda}_h}{8\pi^2\varepsilon_0}G(\rho_h,\rho_h)$$

The **contribution of the halo to the Coulomb energy of a single electron** is:

$$(101)\quad \overline{E}_{C,h} \equiv -e\Phi_h = -\frac{e\overline{\lambda}_h}{8\pi^2\varepsilon_0}G(\rho_h,\rho_h)$$

The additional charge of the halo increases the self-repulsion energy between the nuclear charges, as mentioned in equation (84). In particular:

The **core-halo repulsion energy** can be computed via:

$$(102)\quad \overline{E}_{n,h} = Q\Phi_h$$

The **halo self-repulsion energy** is:

$$(103)\quad \overline{E}_{h,h} = \frac{1}{2}Q_h\Phi_h$$

The result in the above equation was divided by two, because the halo charges are interacting with themselves.

The halo is the part of the CP, which interchanges matter with the environment. It would therefore be interesting to model the properties (density distribution, electric field, pressure, etc.). Unfortunately, this is not trivial: The internal pressure of the halo is partially caused by electrostatic repulsion of the cations. It is also caused by the degeneracy pressure of the cation's core electron shells. The degeneracy pressure depends on how many electrons remain to be bound to the cations.

Depending on the electrical field strength, part of the cation's electron shells is ripped away. One can therefore expect, that the cations close to the CP core are carrying multiple positive charges, whereas the cations at the outer boundary of the halo are carrying only one positive charge. It was beyond the capacity of the author to model this reliably.

When a CP attaches itself to the surface of a dielectric (or metallic) substrate, some of the cationic charges are replaced by polarization charges induced in the substrate by the electric field of the CP. Per unit of charge it takes less energy to create polarization charge than it takes to create cationic charge. Therefore, a CP can lower its total energy by attaching to a surface and thereby neutralizing some of the halo cations.

8.11 A Plausibility Check on Pressures

Dividing equation (40) by the electron charge provides the **electron density** $d_e = -\overline{\sigma}_e / e = \sum_{i=1}^{N} |\Psi_i|^2$. By idealizing the electrons as a **free electron gas**, the electron density can be used for computing the **electron degeneracy pressure** (at the non-relativistic limit):

(104) $$P_d = \frac{(3\pi^2)^{2/3}\hbar^2}{5m_e} d_e^{\,5/3}$$

The degeneracy (outward) pressure is approximately balancing the (inward) pressure generated by the electrostatic and magnetic forces acting on the electrons:

(105) $P_d \approx P_e + P_m$, where P_e is the electrostatic pressure, P_m is the magnetic pressure

The above equation is useful as an **plausibility check** for any solutions produced by the Klein-Gordon equation.

The electric field $\varepsilon_\rho(\rho')$ from equation (67) creates a force $F_{\rho,e}(\rho')$ on the infinitesimal charge element $[\overline{\sigma}_n(\rho') + \overline{\sigma}_e(\rho')]\rho' d\rho' d\varphi dz$ of the plasma:

(106) $$F_{\rho,e}(\rho') = \varepsilon_\rho(\rho')[\overline{\sigma}_n(\rho') + \overline{\sigma}_e(\rho')]\rho' d\rho' d\varphi dz$$

Integrating (106) provides the **pressure** on the plasma **created by the electric field**:

(107) $P_e(\rho) = P_G + \int_\rho^\infty \frac{F_{\rho,e}(\rho')}{\rho' d\varphi dz} = P_G + \int_\rho^\infty \varepsilon_\rho(\rho')[\overline{\sigma}_n(\rho') + \overline{\sigma}_e(\rho')]d\rho'$, where P_G is the granularity correction of the electrostatic pressure specified in (117)

The magnetic field $B_\varphi(\rho')$ from equation (68) creates a inward force $F_{\rho,m}(\rho')$ on the infinitesimal current element $J_z(\rho')\rho' d\rho' d\varphi$ of the electron gas:

(108) $$F_{\rho,m,in}(\rho') = \overline{L} B_\varphi(\rho') J_z(\rho')\rho' d\rho' d\varphi$$

Integrating (108) provides the **inward pressure** on the moving electron gas **created by the magnetic field**:

(109) $$P_{m,in}(\rho) = -\int_\rho^\infty \frac{F_{\rho,m}(\rho')}{\overline{L}\rho' d\varphi} = -\int_\rho^\infty B_\varphi(\rho') J_z(\rho') d\rho'$$

An electron density element $2\pi\overline{L} d_e(\rho')\rho' d\rho'$ of the electron gas will also experience an outward force from the gradient of the diamagnetic energy:

(110) $$F_{\rho,m,out}(\rho') = 2\pi\overline{L} \frac{e^2}{2m_e}\left[\frac{\partial \overline{A}_z^{\,2}(\rho')}{\partial \rho'}\right] d_e(\rho')\rho' d\rho'$$

Integrating (110) provides the **outward pressure** on the electron gas **caused by the gradient of the diamagnetic energy**:

(111) $$P_{m,out}(\rho) = -\int_\rho^\infty \frac{F_{\rho,dm}(\rho')}{2\pi\rho'\overline{L}} = -\frac{e^2}{2m_e}\int_\rho^\infty \left[\frac{\partial \overline{A}_z^{\,2}(\rho')}{\partial \rho'}\right] d_e(\rho') d\rho'$$

The **total magnetic pressure** is resulting in:

(112) $$P_m(\rho) = P_{m,in} + P_{m,out}$$

The granularity correction P_G stems from electrostatic attraction of the electron gas to the nuclear point charges in the direct vicinity $r \leq R_{1n}$ of the nuclei. It can be computed as following:

(113) $P_G(\rho) = \frac{\partial}{\partial V_{1n}}\left(\overline{E}_{en} + \overline{E}_{ee}\right)$, where $\overline{E}_{en}$ is the electron-nucleus Coulomb energy and $\overline{E}_{ee}$ is the electron-electron Coulomb energy, respectively within a volume V_{1n} of the plasma

Using equation (88) and assuming the electron charge density is constant within V_{1n}, the electron-nucleus Coulomb energy computes as:

$$(114)\quad \overline{E}_{en} = 4\pi\overline{\sigma}_e \int_0^{R_{1n}} \Phi_{1n} r_n^{\,2} dr_n = \frac{eZ_m\overline{\sigma}_e}{\varepsilon_0}\int_0^{R_{1n}} r_n dr_n = \frac{eZ_m\overline{\sigma}_e}{2\varepsilon_0} R_{1n}^{\,2} = \left(\frac{3}{4\pi}\right)^{2/3} \frac{e^2 Z_m^{\,2}}{2\varepsilon_0}\frac{\overline{\sigma}_e}{\overline{\sigma}_n} V_{1n}^{\,-1/3}$$

Taking the idea from (89), the potential of the electrons within volume V_{1n} is:

$$(115)\quad \Phi_{ee}(r_n) = \frac{\overline{\sigma}_e V_{1n}}{8\pi\varepsilon_0}\left(\frac{3}{R_{1n}} - \frac{r_n^{\,2}}{R_{1n}^{\,3}}\right)$$

Using this potential, the electron-electron Coulomb energy within volume V_{1n} is:

$$(116)\quad \overline{E}_{ee} = 2\pi\overline{\sigma}_e \int_0^{R_{1n}} \Phi_{ee} r_n^{\,2} dr_n = \frac{\overline{\sigma}_e^{\,2} V_{1n}}{4\varepsilon_0}\int_0^{R_{1n}} \left(\frac{3r_n^{\,2}}{R_{1n}} - \frac{r_n^{\,4}}{R_{1n}^{\,3}}\right) dr_n = \frac{\overline{\sigma}_e^{\,2} V_{1n}}{5\varepsilon_0} R_{1n}^{\,2} = \left(\frac{3}{4\pi}\right)^{2/3} \frac{e^2 Z_m^{\,2}}{5\varepsilon_0}\frac{\overline{\sigma}_e^{\,2}}{\overline{\sigma}_n^{\,2}} V_{1n}^{\,-1/3}$$

Assuming that $\overline{\sigma}_e/\overline{\sigma}_n$ is constant at volume changes and putting together (86), (113), (114) and (116) yields:

$$(117)\quad P_G(\rho) = \left(\frac{3}{4\pi}\right)^{2/3} \frac{e^2 Z_m^{\,2}}{\varepsilon_0}\left(\frac{1}{2}\frac{\overline{\sigma}_e}{\overline{\sigma}_n} + \frac{1}{5}\frac{\overline{\sigma}_e^{\,2}}{\overline{\sigma}_n^{\,2}}\right)\frac{\partial}{\partial V_{1n}} V_{1n}^{\,-1/3} = -\left(\frac{3eZ_m}{4\pi}\right)^{2/3} \frac{\overline{\sigma}_n^{\,4/3}}{3\varepsilon_0}\left(\frac{1}{2}\frac{\overline{\sigma}_e}{\overline{\sigma}_n} + \frac{1}{5}\frac{\overline{\sigma}_e^{\,2}}{\overline{\sigma}_n^{\,2}}\right)$$

One has to keep in mind, though, that equation (105) is merely a coarse approximation:

- Polarization of the electron gas by the field of the nuclei has been neglected.
- At high densities, equation (104) overestimates the degeneracy pressure P_d, because a fraction of the electrons have a relativistic velocity. At the relativistic limit P_d is proportional to $d_e^{\,4/3}$, rather than $d_e^{\,5/3}$ suggested by (104).

8.12 Transformation to Natural Units

In the following text the **Hartree energy** will be used as a **unit of measure for energy**. It is defined as:

(118) $\overline{E}_h \equiv \frac{\hbar^2}{m_e a_0^{\,2}} = \frac{e^2}{4\pi\varepsilon_0 a_0} = m_e\left(\frac{e^2}{4\pi\varepsilon_0\hbar}\right)^2 = m_e c^2\alpha^2 \approx 27.211 eV$, where

(119) $a_0 \equiv \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} = \frac{\hbar}{m_e c\alpha} \approx 52.918\, pm$ is the **Bohr radius** and

(120) $\alpha \equiv \frac{1}{4\pi\varepsilon_0}\frac{e^2}{\hbar c} = \frac{\hbar}{m_e c a_0} \approx 7.2974 \cdot 10^{-3}$ is the **fine structure constant**.

The **electron rest energy** in units of $\overline{E}_h$ therefore becomes:

(121) $$\frac{m_e c^2}{\overline{E}_h} = \frac{1}{\alpha^2}$$

The following equation defines a **reference radius**:

(122) $\rho_0 \equiv \dfrac{a_0}{\sqrt{\lambda_n}}$, where

(123) $\lambda_n \equiv \dfrac{Q}{e}\dfrac{1}{L}$ is the **linear nuclear charge density of the core** in natural units,

(124) $L \equiv \dfrac{\overline{L}}{a_0}$ is the **CP length** in units of the Bohr radius.

The definition of the reference radius was crafted, such that the relative radial extent of the electron orbits at the non-relativistic limit becomes independent of the linear nuclear charge density.

The **relative radius** is defined as:

(125) $$r \equiv \frac{\rho}{\rho_0}$$

The **volume charge density** in natural units is defined here as:

(126) $$\sigma = \sigma_n + \sigma_e + \sigma_h \equiv \frac{a_0^3}{e}\overline{\sigma} = \frac{a_0^3}{e}\left(\overline{\sigma}_n + \overline{\sigma}_e + \overline{\sigma}_h\right)$$

The **current density** in natural units is defined here as:

(127) $$J_z \equiv \frac{a_0^3}{ec}\overline{J}_z$$

Additionally, the following quantities are defined here:

(128) $E \equiv \overline{E}/\overline{E}_h$, i.e. the **sum of the potential energy and the kinetic energy** of the electron, which is functioning as the **energy eigenvalue** of the Klein-Gordon equation

(129) $$E_C = E_{C,n} + E_{C,e} + E_{G,e} + E_{C,h} \equiv -e\Phi/\overline{E}_h$$
$$= -e\Phi_n/\overline{E}_h - e\Phi_e/\overline{E}_h - e\Phi_G/\overline{E}_h - e\Phi_h/\overline{E}_h ,$$
i.e. the **potential energy related to the Coulomb potential** of the electrons, the core nuclei and the halo as seen by an electron (negative sample charge)

(130) $E_{n,h} \equiv \overline{E}_{n,h}/\overline{E}_h = -\lambda_n L E_{C,h}$, i.e. the **core-halo repulsion energy in natural units**

(131) $E_{h,h} \equiv \overline{E}_{h,h}/\overline{E}_h = -\dfrac{1}{2}\lambda_h L E_{C,h}$, i.e. the **halo self-repulsion energy in natural units**

(132) $P_z \equiv a_0 \overline{P}_z/\hbar = 2\pi l/L$ is **the axial canonical momentum** of the electron in natural units

(133) $A_z \equiv -ea_0\overline{A}_z/\hbar$ is the **axial magnetic vector potential** in natural units. The related terms $-P_z A_z$ and $A_z^2/2$ are the **magnetic electron-electron interaction energy** and the so-called **diamagnetic energy**, respectively

(134) $p_z \equiv a_0 \overline{p}_z / \hbar = P_z - A_z = 2\pi l / L + e a_0 \overline{A}_z / \hbar$ is the **axial kinetic momentum** of the electron in natural units. The related term $p_z^{\,2}/2$ is **the axial kinetic energy** in natural units

(135) $E_n \equiv \overline{E}_n / \overline{E}_h$, i.e. the **nuclear self repulsion energy**

(136) $E_{G,n} \equiv \overline{E}_{G,n} / \overline{E}_h$, i.e. the **granularity correction** of the nuclear jellium's self-repulsion

The **radial wave function** in natural units is defined as:

(137) $R \equiv \rho_0 \Psi_\rho$

Dividing both sides of (78) by $\overline{E}_h$, using the product rule of calculus and substituting via (121), (124), (128), (129), (130) and (134) is resulting in:

$$\left\{ -\frac{a_0^{\,2}}{2}\frac{d^2}{d\rho^2} - \frac{a_0^{\,2}}{2\rho}\frac{d}{d\rho} + \frac{a_0^{\,2}}{2}\frac{m^2}{\rho^2} + \frac{p_z^{\,2}}{2} - \frac{\alpha^2}{2}\left(E - E_C + \frac{1}{\alpha^2} \right)^2 + \frac{1}{2\alpha^2} \right\} \Psi_\rho = 0 \tag{138}$$

Substituting (125) and (137) in (138), using the notation R' and R'' for the first and second derivative to r of radial wave function R and multiplying both sides of the equation by ρ_0 yields the **radial Klein-Gordon equation** in natural units:

$$-\frac{\lambda_n}{2} R'' - \frac{\lambda_n}{2r} R' + \left[\frac{\lambda_n m^2}{2r^2} + \frac{p_z^{\,2}}{2} - \frac{\alpha^2}{2}\left(E - E_C + \frac{1}{\alpha^2} \right)^2 + \frac{1}{2\alpha^2} \right] R = 0 \tag{139}$$

The **Schrödinger equation** (80) in natural units is:

$$-\frac{\lambda_n}{2} R'' - \frac{\lambda_n}{2r} R' + \left[\frac{\lambda_n m^2}{2r^2} + \frac{p_z^{\,2}}{2} + E_C - E \right] R = 0 \tag{140}$$

The **geometry integral** (65) can be expressed in natural units as:

$$G(r, r') = \begin{cases} 4\pi \left[\ln\left(\sqrt{\lambda_n} L/2 + \sqrt{\lambda_n L^2/4 + r'^2} \right) - \ln r' \right] & \text{for } r \le r' \\ 4\pi \left[\ln\left(\sqrt{\lambda_n} L/2 + \sqrt{\lambda_n L^2/4 + r^2} \right) - \ln r \right] & \text{for } r > r' \end{cases} \tag{141}$$

Multiplying (40) with $a_0^{\,3}/e$ and using (71) and (137) yields the **volume charge density in natural units**:

$$\sigma_e(r) = -\frac{\lambda_n}{2\pi L} \sum_{i=1}^{N} \left| R_i(r) \right|^2 \tag{142}$$

Multiplying (43) with $a_0^{\,3}/(ec)$ and using (76), (120), (124), (130) and (137) yields the **current density in natural units**:

$$J_z(r) = \frac{-\alpha \lambda_n}{2\pi L} \sum_{i=1}^{N} \left[P_{z,i} - A_z(r) \right] \left| R_i(r) \right|^2 \tag{143}$$

By using (120), (125), (130), (133), (137) in equation (45) the **total current** (averaged over all electrons, in amperes) can be computed from the quantities in natural units as following:

$$I_z = -\frac{e\alpha c}{a_0 L} \sum_{i=1}^{N} \int_0^\infty \left[P_{z,i} - A_z(r) \right] \left| R_i(r) \right|^2 r\,dr \tag{144}$$

Multiplying both sides of (63) by $-e/\overline{E}_h$ and substituting via (125), (126), (129) and (142) provides the **Coulomb energy** in natural units:

$$(145)\quad E_C(r) = E_{G,e} - \frac{1}{\lambda_n}\int_0^\infty \sigma(r')G(r,r')r'dr' = E_{G,e} + E_{C,h} - \frac{1}{\lambda_n}\int_0^\infty [\sigma_e(r') + \sigma_n(r')]G(r,r')r'dr'$$

The **contribution of the halo to the Coulomb energy of a single electron in natural units** is:

$$(146)\quad E_{C,h} = -\frac{\lambda_h}{2\pi}G(r_h, r_h),\ \text{where}\ \lambda_h = \frac{a_0\overline{\lambda}_h}{e}\ \text{and}\ r_h = \frac{\rho_h}{\rho_0}$$

Dividing both sides of equation (94) by $-e/\overline{E}_h$ and substituting via (118), (119) and (126) yields the **granularity correction of the electron-nucleus interaction energy** is**:**

$$(147)\quad E_{G,e} = -\frac{2\pi}{5}\sigma_n^{1/3}\left(\frac{3Z_m}{4\pi}\right)^{2/3}$$

Multiplying both sides of (66) by $-ea_0/\hbar$, substituting via (120), (122), (125), (127), (133) and (143) and using $\varepsilon_0\mu_0 = c^{-2}$ provides the **magnetic vector potential** in natural units:

$$(148)\quad A_z(r) = -\frac{\alpha}{\lambda_n}\int_0^\infty J_z(r')G(r,r')r'dr' = \frac{\alpha^2}{2\pi L}\int_0^\infty \left\{\sum_{i=1}^{N}[P_{z,i} - A_z(r')]\,|R_i(r')|^2\right\}G(r,r')r'dr'$$

By dividing (47) by ρ_0 and using (122), (125) and (137) the **expectation value of the electron orbit radius** in natural units becomes:

$$(149)\quad \langle r\rangle = \int_0^\infty |R|^2 r^2 dr$$

Dividing (84) by $\overline{E}_h$ and using (93), (118), (119), (122), (126), (129) and (136) and taking care of the fact, that the sample charges are positive, yields the **nuclear self-repulsion energy** in natural units:

$$(150)\quad E_n = -E_{G,n} + E_{n,h} + E_{h,h} - \frac{\pi L}{\lambda_n}\int_0^\infty \sigma_n(r)E_{C,n}(r)rdr\text{, where } E_n > 0 \text{ and}$$

$$E_{G,n} = \frac{4\pi}{5}\sqrt[3]{\frac{9\pi}{2}Z_m^{\ 2}}\,\frac{L}{\lambda_n}\int_{\rho=0}^\infty \sigma_n^{4/3}(r)rdr$$ is the **granularity error** in natural units, $E_{G,n} > 0$

Using (122), (137) and 0 the **normalization criteria** (72) in natural units becomes:

$$(151)\quad 1 = \|R\| = \int_0^\infty |R(r)|^2 rdr$$

The **standard deviation of the core nuclear charge distribution** in natural units is:

$$(152)\quad s \equiv \frac{\overline{s}}{\rho_0}$$

Multiplying both sides of (95) with a_0^3/e and substituting via (122), (124), (125) and (152) yields the **nuclear charge distribution of the core** in natural units:

$$(153)\quad \sigma_n(r) = \frac{Q\lambda_n}{2\pi eLs^2}\exp\left(-\frac{r^2}{2s^2}\right)$$

With the modifications made in (97) the nuclear charge distribution reads:

(154) $\sigma_n(r) = C_H \exp\left(-\frac{r^2}{2s^2} - \frac{r^5}{C_S^{\ 5}} - \frac{r^{16}}{C_C^{\ 16}}\right)$, where $C_H = \frac{a_0^{\ 3}}{e} Height$, $C_S = \frac{Slope}{\rho_0}$ and $C_C = \frac{Cutoff}{\rho_0}$

The **charge density of the halo** (derived from equation (99)) in natural units reads:

(155) $\sigma_h = \frac{\lambda_n \lambda_h}{2\pi r_h \delta r}$

8.13 Approximate Solution of the Radial Wave Function

The following **ansatz** will be used for approximating the **radial wave function**:

(156) $R(r) = f(r) \cdot \exp(-\zeta r)$, where
$f(r)$ is assumed to be a polynomial and $\zeta \in \mathbf{R}^+$ is a tunable scaling factor.

The radial Klein-Gordon equation (139) has a second solution, which is linear independent of the solution gained by ansatz (156). The second solution would be represented by the following ansatz:

(157) $R(r) = f(r) \cdot \exp(\zeta r)$, where $\zeta \in \mathbf{R}^+$

However, this second solution and all linear combinations with it were incompatible with boundary condition (33). Therefore, this second solution ansatz will not be used.

The first derivative of the radial wave functions (156) reads:

(158) $R' = (f' - \zeta f) \cdot \exp(-\zeta r)$

The second derivative of the radial wave functions is:

(159) $R'' = (f'' - 2\zeta f' + \zeta^2 f) \cdot \exp(-\zeta r)$

The value of ζ can be determined by analyzing the asymptotic behavior of the wave function R at $r \to \infty$:

The electromagnetic potential (and therefore the terms E_C and A_z) become zero, when the radius approaches infinity. Also, the terms proportional to $1/r$ and $1/r^2$ disappear at $r \to \infty$. The Klein-Gordon equation (139) then simplifies to:

(160) $-\lambda_n R'' + \left(P_z^{\ 2} - \alpha^2 E^2 - 2E\right) R = 0$

Inserting (157) and (159) into (160) leads to:

(161) $\lambda_n\left(-f'' + 2\zeta f' - \zeta^2 f\right) + \left(P_z^{\ 2} - \alpha^2 E^2 - 2E\right) f = 0$

Assuming function f can be approximated by a polynomial of finite degree, the function dominates over its derivatives at $r \to \infty$ and therefore the **exponential scaling factor** is:

(162) $\zeta = \sqrt{\frac{1}{\lambda_n}\left(P_z^{\ 2} - \alpha^2 E^2 - 2E\right)}$

Only the positive value of the square root is valid here, because of ansatz (156).

As a consequence of equation (162), there is an upper limit of the eigenvalues E:

(163) $E < \frac{1}{\alpha^2}\left(\sqrt{\alpha^2 P_z^{\ 2} + 1} - 1\right)$

Solving (162) for the energy provides:

$$(164)\quad E = \frac{1}{\alpha}\sqrt{P_z^2 - \lambda_n \zeta^2 + \frac{1}{\alpha^2}} - \frac{1}{\alpha^2}$$

Only the positive value of the square root is valid here, because of boundary condition (32).

Equation (164) in conjunction with boundary condition (32) has interesting consequences:

(165) $0 < \zeta < \sqrt{\frac{1}{\lambda_n}\left(P_z^2 + \frac{1}{\alpha^2}\right)}$, i.e. the scaling factor ζ is limited by means of the rest energy

At the **non-relativistic limit** the **exponential scaling factor** computes as:

(166) $\zeta = \sqrt{\frac{1}{\lambda_n}\left(P_z^2 - 2E\right)}$, thus $E = \frac{1}{2}\left(P_z^2 - \lambda_n \zeta^2\right)$, where $0 < \zeta < \sqrt{\frac{1}{\lambda_n}\left(P_z^2 + \frac{2}{\alpha^2}\right)}$ and $E < \frac{P_z^2}{2}$

Inserting (156), (158), (159) and (164) into radial Klein-Gordon equation (139) is leading to:

$$(167)\quad -\frac{\lambda_n}{2} f'' + \frac{\lambda_n}{2}\left(2\zeta - \frac{1}{r}\right) f'$$
$$+\left[\frac{\lambda_n \zeta}{2r} + \frac{\lambda_n m^2}{2r^2} + \frac{p_z^2}{2} - \frac{\alpha^2}{2}\left(\frac{1}{\alpha}\sqrt{P_z^2 - \lambda_n \zeta^2 + \frac{1}{\alpha^2}} - E_C\right)^2 + \frac{1}{2\alpha^2} - \frac{\lambda_n \zeta^2}{2}\right] f = 0$$

For the non-relativistic limit the Schrödinger equation (140) is leading to:

$$(168)\quad -\frac{\lambda_n}{2} f'' + \frac{\lambda_n}{2}\left(2\zeta - \frac{1}{r}\right) f' + \left(\frac{\lambda_n \zeta}{2r} + \frac{\lambda_n m^2}{2r^2} - P_z A_z + \frac{A_z^2}{2} + E_C\right) f = 0$$

Solutions to differential equation (167) or (168) consist of eigenvalues of ζ and eigenstates of polynomial f. These solutions can then be used to compute the eigenvalues of E and eigenstates of R of the radial Klein-Gordon equation (139) or Schrödinger equation (140).

Function $f(r)$ can be **approximated by a polynomial** of r as following:

(169) $f(r) \approx \sum_{j=0}^{J} c_j r^{\beta + j}$ for $\beta \in \mathbf{N}_0$ and $c_j \in \mathbf{R}$

The summation is running over a number $J+1$ of terms. The maximum index J is depending on the desired accuracy of the approximation. In practice, J needs to be 150 through 2500 with 80-bit floating point numbers for “reasonable” accuracy. The required J increases drastically with increasing axial current in the CP.

The (generally arbitrary) phase of the (generally complex) wave function R is chosen, such that the coefficients c_j become real numbers.

Generally, constants c_j and ζ are depending on quantum numbers n, m and l. For simplicity reasons, this dependency is not reflected in the respective indices of these constants.

The first derivative of (169) reads:

$$(170)\quad f'(r) \approx \sum_{j=0}^{J} (\beta + j) c_j r^{\beta + j - 1}$$

The second derivative of (169) is:

$$(171)\quad f''(r) \approx \sum_{j=0}^{J} (\beta + j)(\beta + j - 1) c_j r^{\beta + j - 2}$$

In equation (167) a number of terms can be approximated by a polynomial of degree P:

$$(172)\quad \frac{p_z^{\ 2}}{2} - \frac{\alpha^2}{2}\left(\frac{1}{\alpha}\sqrt{P_z^{\ 2} - \lambda_n \zeta^2 + \frac{1}{\alpha^2}} - E_C\right)^2 + \frac{1}{2\alpha^2} - \frac{\lambda_n \zeta^2}{2} \approx \sum_{p=0}^{P} b_p r^p \,,$$

where $P \le J - 1$ and $b_p \in \mathbf{R}$

At the non-relativistic limit (172) simplifies to:

$$(173)\quad -P_z A_z + \frac{A_z^{\ 2}}{2} + E_C \approx \sum_{p=0}^{P} b_p r^p \text{, where } P \le J - 1 \text{ and } b_p \in \mathbf{R}$$

Approximations (172) and (173) have a limited convergence radius, no matter how large P is made and how the coefficients are chosen. However, for a given closed interval of radius values the approximations can be made arbitrarily precise by choosing P and the coefficients appropriately. A good approximation accuracy has been achieved with $P = 8$.

A suitable approximation can be found by first determining the range $r_0 \le r \le r_P$ of relevant radius values reflecting the radial extent of the electron's wave function. For example, one can choose r_0 and r_P in such a way, that the electron resides with 99.9% probability between these radii and, at the same time, the range is made as small as possible.

Based on this range, additional nodes r_1 through r_{P-1} need to be determined between r_0 and r_P. The nodes should be chosen, such that the approximation error is minimized (e.g. via Chebyshev nodes). These nodes can then be used e.g. by Newton polynomials for interpolation.

Inserting (169), (170), (171) and (172) into (167) and multiplying both sides with $-2r^2/\lambda_n$ yields:

$$(174)\quad \sum_{j=0}^{J} (\beta + j)(\beta + j - 1) c_j r^{\beta + j} + (1 - 2\zeta r)\sum_{j=0}^{J} (\beta + j) c_j r^{\beta + j} - \left[\zeta r + m^2 + \frac{2}{\lambda_n}\sum_{p=0}^{P} b_p r^{p+2}\right]\sum_{j=0}^{J} c_j r^{\beta + j} = 0$$

By neglecting the terms with potencies of r higher than $\beta + J$ the result can be written as:

$$(175)\quad \sum_{j=0}^{J}\left\{\left[(\beta + j)^2 - m^2\right]c_j + \zeta(1 - 2\beta - 2j)c_{j-1} - \frac{2}{\lambda_n}\sum_{p=0}^{P} b_p c_{j-p-2}\right\} r^{\beta + j} + \varepsilon_{cut} = 0\,,$$

where $c_i = 0$ for $i < 0$

and ε_{cut} is the cut-off error produced by neglecting potencies of r higher than $\beta + J$

The cut-off error computes as:

$$(176)\quad \varepsilon_{cut} = \zeta(-1 - 2\beta - 2J)c_J r^{\beta + J + 1} - \frac{2}{\lambda_n}\sum_{p=0}^{P}\sum_{j=J+1}^{J+p+2} b_p c_{j-p-2} r^{\beta + j}$$

The left hand side of equation (175) equals zero for all values of r. This can only be true, if the coefficients of $r^{\beta + j}$ fulfill the following equation:

$$(177)\quad \left[(\beta + j)^2 - m^2\right]c_j + \zeta(1 - 2\beta - 2j)c_{j-1} - \frac{2}{\lambda_n}\sum_{p=0}^{P} b_p c_{j-p-2} = 0$$

Analyzing the case $j = 0$ gives:

(178) $\beta^2 - m^2 = 0$, therefore $\beta = |m|$

Inserting (178) into (177) yields the **iterative formula for computing the coefficients** from the value of c_0:

(179) $c_j = \frac{1}{\left(2|m|j + j^2\right)}\left\{\zeta\left(2|m| + 2j - 1\right)c_{j-1} + \frac{2}{\lambda_n}\sum_{p=0}^{P} b_p c_{j-p-2}\right\}$, where $c_i = 0$ for $i < 0$

Note, that the coefficients c_j are all proportional to each other. Formula (179) stays the same at the non-relativistic limit.

Equation (176) puts additional requirements on the coefficients c_{J-P} through c_J, which contradict the requirements of equation (179). Therefore, the polynomial approximation of the radial wave function cannot be made precise. Unfortunately, ε_{cut} diverges, if J is made too large. The latter effect is caused by rounding errors in conjunction with finite floating-point number precision.

The approximation error becomes minimal, when the last coefficient c_J is zero, which is the case only for the eigenvalues of ξ . Therefore, this defines a method for determining the eigenvalues.

Alternatively one could determine the eigenvalues by using the original Klein-Gordon equation (139) in conjunction with (164) as a measure of error:

$$
\begin{aligned}
(180)\quad \delta(r,\zeta) &= -\frac{\lambda_n}{2}R'' - \frac{\lambda_n}{2r}R' \\
&+ \left[\frac{\lambda_n m^2}{2r^2} + \frac{p_z^{\ 2}}{2} - \frac{\alpha^2}{2}\left(\frac{1}{\alpha}\sqrt{P_z^{\ 2} - \lambda_n\zeta^2 + \frac{1}{\alpha^2}} - E_C\right)^2 + \frac{1}{2\alpha^2}\right]R \\
&\approx -\frac{\lambda_n}{2}R'' - \frac{\lambda_n}{2r}R' + \left\{\frac{\lambda_n m^2}{2r^2} + \sum_{p=0}^{P} b_p r^p + \frac{\lambda_n\zeta^2}{2}\right\}R
\end{aligned}
$$

At the non-relativistic limit one would use the Schrödinger equation (140) in conjunction with (166) as a measure of error:

$$
\begin{aligned}
(181)\quad \delta(r,\zeta) &= -\frac{\lambda_n}{2}R'' - \frac{\lambda_n}{2r}R' + \left[\frac{\lambda_n m^2}{2r^2} - P_z A_z + \frac{A_z^{\ 2}}{2} + E_C + \frac{\lambda_n\zeta^2}{2}\right]R \\
&\approx -\frac{\lambda_n}{2}R'' - \frac{\lambda_n}{2r}R' + \left\{\frac{\lambda_n m^2}{2r^2} + \sum_{p=0}^{P} b_p r^p + \frac{\lambda_n\zeta^2}{2}\right\}R
\end{aligned}
$$

The function $\delta(r,\zeta)$ is approaching zero for all values of r only at the energy eigenvalues E or ζ .

The value of coefficient c_0 can be determined from ζ by normalization of the wave function R.

Combining (156), (169) and (178) leads to:

(182) $R \approx \sum_{j=0}^{J} c_j r^{|m|+j} \exp(-\zeta r)$

The normalization condition (151) requires:

(183) $1 = \|R\| = \int_0^\infty |R(r)|^2 r dr = \int_0^\infty \left(\sum_{j=0}^{J} c_j r^{|m|+j}\right)^2 \exp(-2\zeta r) r dr$

That means, one has to scale all c_j proportionally, such that (183) yields the value 1.

In many cases the cut-off error (176) is so small, that the radial wave function can be computed without having any noticeable distortion from it. Unfortunately, the cut-off error is not always small compared to the amplitude of the "real" wave function. The following plot shall illustrate this:

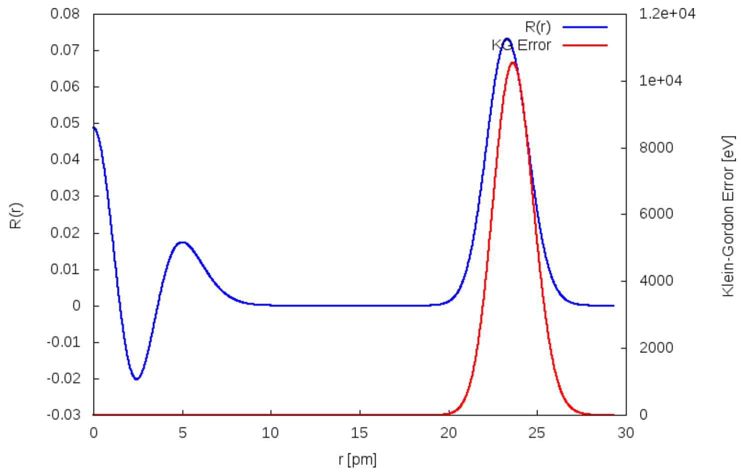

Figure 6 Example of a radial wave function (blue) with a large distortion from the cut-off error centered around $r \approx 23\,pm$. The distortion is leading to a large Klein-Gordon error (red).

Empirically, the Klein-Gordon error in Figure 6 as computed via (180) is closely correlated to the cut-off error computed via $\varepsilon_{cut} \cdot \exp(-\zeta r)$ for the same wave function:

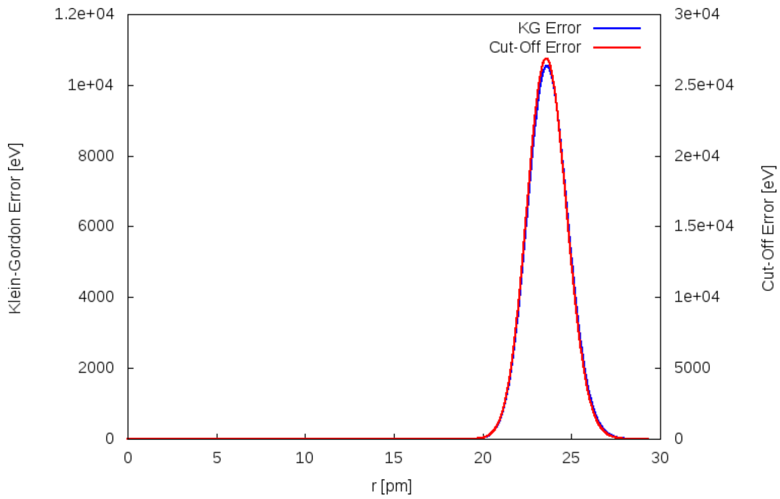

Figure 7 Correlation between the Klein-Gordon error (blue) and the cut-off error (red)

This correlation is a bit surprising, as the Klein-Gordon error is computed from different potencies of the radius than the cut-off error.

Distortions of the wave function and the related Klein-Gordon error are generally becoming smaller, if the upper limits of the summation index in (169) and (170) are adjusted, such that the highest potencies of the radius matches with (171):

(184) $f = \sum_{j=0}^{J-2} c_j r^{|m|+j}$ re-definition of (169)

(185) $f' = \sum_{j=0}^{J-1} (|m|+j) c_j r^{|m|+j-1}$ re-definition of (170)

(186) $f'' = \sum_{j=0}^{J} (|m|+j)(|m|+j-1) c_j r^{|m|+j-2}$ copy of (171)

The adjusted upper limits of j are changing the cut-off error (176) to:

$$\varepsilon_{cut} = \left[(|m| + J - 1)^2 c_{J-1} + \zeta(3 - 2|m| - 2J)c_{J-2}\right] r^{|m|+J-1} \tag{187}$$

$$+ (|m| + J - 1)\left[(|m| + J)c_J - 2\zeta c_{J-1}\right] r^{|m|+J} - \frac{2}{\lambda_n}\sum_{p=0}^{P}\sum_{j=J-1}^{J+p} b_p c_{j-p-2} r^{|m|+j} \quad \text{(Re-definition)}$$

8.14 Grouping, Orbital Occupation, Self-Consistent Field Iterations

The electron configuration of a CP consists of many orbitals, which are characterized by the quantum numbers n, m and l. According to the Pauli exclusion principle each orbital can only be occupied by a maximum of two electrons (one with spin up and one with spin down).

There are too many electrons in a CP for computing all occupied orbitals individually. Instead, ranges of orbitals with contiguous values for l are grouped together. Within a group all orbitals have the same quantum numbers n and m. These orbitals of such groups differ in quantum number l. The arithmetic mean of the quantum numbers l represents the group during computation.

The most simple approach is to let each group contain the same number of orbitals. On one hand the groups should be small enough to achieve a fine spacing in the electron energies (for accuracy). On the other hand the groups need to be coarse enough, such that computation time becomes affordable.

Equations (142) and (143) are computed by letting the summation run over the occupied number of groups. Each summand is multiplied by the number of electrons it represents.

For ground state computations the occupation should start with the lowest energy. It should progress to groups with successively higher energy until the targeted number of electrons "found their orbital".

Equations (142), (143) and (179), as well as the occupation process are depending on each other in a circular manner. Thus they can be computed only **iteratively** until reaching **self-consistency between eigenstates, potential and occupation**.

According to simplification (19) orbitals with eigenvalue energies below $-m_e c^2$ are "forbidden" to occupy. Care must be taken and appropriate numerical damping must be applied, such that fluctuations of orbitals between "forbidden" and "allowed" are not hindering convergence of the SCF algorithm.

Within each of these SCF-iterations (self-consistent field iterations) there is a need for sub-iterations:

According to (143) and (148) the axial current density J_z and the vector potential A_z are mutually depending on each other. Sub-iterations are required for making these quantities consistent with each other, while leaving the eigenstates unchanged.