Quasirelativistic theory.
(Relativistic theory in terms of two-component spinors)

Werner Kutzelnigg\textsuperscript{a,*} and Wenjian Liu\textsuperscript{b,*}

\textsuperscript{a}Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum
D-44780 Bochum, Germany

\textsuperscript{b}Institute of Theoretical and Computational Chemistry,
College of Chemistry and Molecular Engineering, Peking University
Beijing, P. R. China, 100871

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Abstract

A quasirelativistic theory is a relativistic theory for electrons only, in terms of two-component spinors. The first part of this lecture deals with the theory in terms of operators and wave functions. We start with a simple derivation of the key relation between the upper ($\phi$) and lower ($\chi$) components of the Dirac bispinor ($\psi$) for both electrons and positrons. The three possible choices of a nonhermitian quasirelativistic Hamiltonian $L$, a hermitian one $\tilde{L}$ with non-unit metric, and a hermitian one $L^+$ with unit metric are compared. The eigenfunctions of the first two are the upper components $\phi$ of $\psi$, while those of $L^+$ are the Foldy-Wouthuysen-type spinors $\phi$. Some general properties of quasirelativistic Hamiltonians and their eigenfunctions are discussed, especially the behavior near the position of a nucleus. Exact solutions, and even variational ones are only obtained if the orbital basis describes the weak singularities at the positions of the nuclei correctly. The problems that arise for a Douglas-Kroll transformation or the regular approximation at operator level are studied in detail.
The second part deals with the theory in terms of matrices and vectors. In fact, everything becomes much simpler, and most problems disappear, if one performs the transformation from relativistic to quasirelativistic theory at matrix level. The Dirac operator in a matrix representation in a kinetically balanced basis is transformed to the matrix representation of a quasi-relativistic Hamiltonian that has the same electronic eigenstates as the original Dirac matrix (but no positronic eigenstates). This transformation involves a matrix $X$, for which an exact identity is derived, and which can be constructed either in a non-iterative way or by various iteration schemes, not requiring an expansion parameter. Both linearly convergent and quadratically convergent iteration schemes are discussed and compared numerically. We present three rather different schemes, for each of which even in unfavorable cases convergence is reached within 3 or 4 iterations, for all electronic eigenstates of the Dirac operator. We formulate the theory both in terms of a non-hermitian and a hermitian quasirelativistic Hamiltonian. Quasi-relativistic approaches at matrix level known from the literature are critically analyzed in the frame of the general theory.
References


# General introduction

**Table 1: Motion of a particle under the influence of a force**

<table>
<thead>
<tr>
<th>velocity/dimension</th>
<th>macroscopic</th>
</tr>
</thead>
<tbody>
<tr>
<td>low velocity</td>
<td>Classical Mechanics</td>
</tr>
<tr>
<td>velocities additive Galilei transformation</td>
<td>Galilei, Newton</td>
</tr>
<tr>
<td>high velocity</td>
<td>Special Relativity</td>
</tr>
<tr>
<td>maximum velocity $c$ (E = mc^2) Lorentz transformation</td>
<td>Einstein</td>
</tr>
<tr>
<td></td>
<td>4-vectors ((t, x, y, z))</td>
</tr>
</tbody>
</table>
Non-relativistic quantum mechanics

**H-atom**: One electron moving in the Coulomb field of a proton.

Stationary (bound) states, specified by *quantum numbers* $n, l, m$

\[
\Psi_{n,l,m}(\vec{r}, t) = \psi_{n,l,m}(\vec{r}) f(t)
\]  

(1)

$f(t)$ a periodic function of time. $\psi$ normalizable.

$\psi(\vec{r})$ satisfies the Schrödinger equation

\[
\hat{H}\psi_{n,l,m}(\vec{r}) = E_n\psi_{n,l,m}(\vec{r})
\]  

(2)

\[
E_n = -\frac{1}{n^2}; \quad n = 1, 2, 3, ...
\]  

(3)

Eigenvalue problem. Stationary states have discrete energies.

The lowest energy is that of the ground state.
The energy depends only on the principal quantum number $n$.

Lowest eigenstates of the H atom:

<table>
<thead>
<tr>
<th>$n$</th>
<th>$l$</th>
<th>$m$</th>
<th>$E$ [Hartree]</th>
</tr>
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<tr>
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</tr>
<tr>
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<tr>
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<tr>
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<td>1</td>
<td>-0.125</td>
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<tr>
<td>...</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\infty$</td>
<td>$l$</td>
<td>$m$</td>
<td>0.0</td>
</tr>
</tbody>
</table>

A state is called $d$-fold degenerate, if there are $d$ linear independent eigenfunctions with the same energy eigenvalue $E$.

Above the ionization limit ($E = 0$) there is a continuum of unbound (scattering) states.

Variation principle:

$$E(\tilde{\psi}) \geq E_{100} \quad (4)$$
There are again bound states, but these are described by a 4-component wave function (bispinor)

\[
\psi(\vec{r}) = \begin{pmatrix}
\psi_1(\vec{r}) \\
\psi_2(\vec{r}) \\
\psi_3(\vec{r}) \\
\psi_4(\vec{r})
\end{pmatrix} = \begin{pmatrix}
\varphi(\vec{r}) \\
\chi(\vec{r})
\end{pmatrix} ; \quad \varphi(\vec{r}) = \begin{pmatrix}
\psi_1(\vec{r}) \\
\psi_2(\vec{r})
\end{pmatrix} ; \quad \chi(\vec{r}) = \begin{pmatrix}
\psi_3(\vec{r}) \\
\psi_4(\vec{r})
\end{pmatrix}
\]

(5)

\(\psi(\vec{r})\) is solution of the Dirac equation

\[
\hat{D}\psi_{n,\kappa,m} = W_{n\kappa}\psi_{n,\kappa,m}
\]

(6)

Lowest relativistic bound eigenstates of the H atom:
\[
E = W - mc^2 [\text{Hartree}]
\]

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \kappa )</th>
<th>( m_j )</th>
<th>( Z=1 )</th>
<th>( Z=10 )</th>
<th>( Z=100 )</th>
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<td>-0.125000</td>
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</tr>
</tbody>
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...
Why do we need a 4-component wave function?

2 components for spin.

2 components for the antiparticle of the electron, the positron.

What is spin? An intrinsic angular momentum and magnetic moment.

Is spin a relativistic effect? No!

In nonrelativistic theory we must consider an extra quantum number \( m_s \), which can take the values \( \frac{1}{2} \) or \( -\frac{1}{2} \). It affects the energy only in the presence of a magnetic field.

It is important for the formulation of the Pauli principle.
The Dirac equation has eigenstates with positive and negative energy. Only those with positive energy have a direct physical meaning. Those with negative $W$ can, after change of sign, be interpreted as positronic states.

Note that the Dirac eigenvalue $W$ contains the rest energy $mc^2$. To compare with the nonrelativistic case we must substract $mc^2$ and consider

$$E = W - mc^2$$

The presence of negative-energy states is very inconvenient. No upper-bound property and no variation principle. Variational collapse: One may arrive at physically meaningless states in the forbidden region between lowest bound state and onset of the negative-energy continuum.

A remedy: use of a kinetically balanced basis.

Try to construct an eigenvalue equation for electrons only, in terms of 2-component spinors, without negative energy states: A quasi-relativistic theory.
\[ 0 \quad E_0 \quad mc^2 \quad W_0 \quad 0 \quad mc^2 \quad -mc^2 \]

non-rel. rel.
Why worry about relativistic Quantum Chemistry?

If we replace an H-atom by an H-like ion, with nuclear charge $Z$, such as He$^+$, Li$^{2+}$, the nonrelativistic energy eigenvalues are multiplied by $Z^2$, the leading relativistic corrections by $Z^4$. Relativistic effects are very small for light atoms, mainly for H, but appreciable for heavy and essential for superheavy elements.

Relativistic effects in chemistry have long been ignored, with the following argument going essentially back to Dirac.

*Inner shell electrons* move in the neighborhood of the high nuclear charges and get velocities comparable to $c$. They experience strong relativistic effects. The chemistry is, however, determined by the valence electrons, which only feel the effective nuclear charge $Z_{\text{eff}}$ *screened* by the inner electrons. The effective nuclear charge $Z_{\text{eff}}$ is nearly the same, e.g. for all alkali atoms Li, Na, K, etc. and the heavier alkali atoms should therefore not be more strongly affected by relativity than the lighter ones.
This argument is false. Even the valence electrons of \( s \) and \( p \) type have a high probability to be near the nucleus and feel there the full \( Z \). Relativistic effects go hence with \( Z^4 \) rather than \( Z_{\text{eff}}^4 \). \( s \) and \( p \) electrons experience a strong relativistic contraction. The situation is different for \( d \) and \( f \) electrons, that cannot come close to the nucleus (due to the high centrifugal force). As a consequence of the strong contraction of \( s \) and \( p \) electrons the \( d \) and \( f \) electrons see a more strongly shielded nuclear field, and are therefore expanded.

In addition to these scalar relativistic effects, the spin-orbit interaction (absent in the nonrelativistic limit) plays a big role.

Relativistic effects are very important in chemistry, especially for gold and the elements close to gold in the periodic system. The entire chemistry of gold can only be understood within relativistic theory. Even the yellow colour of gold is a relativistic effect. So is the low boiling point of mercury.
Introduction

A relativistic formalism in terms of bispinors (4-component spinors) is necessary if one wants to describe electrons and positrons simultaneously. For electrons only, a theory in terms of (2-component) spinors, called quasi-relativistic, is sufficient. Let $\psi$ satisfy the Dirac equation.

\[
(D - mc^2)\psi = E\psi
\]  

**Equation (8)**

\[
D = \begin{pmatrix}
mc^2 + V & c\vec{\sigma} \cdot \vec{p} \\
\vec{c}\vec{\sigma} \cdot \vec{p} & -mc^2 + V
\end{pmatrix}; \quad \psi = \begin{pmatrix}
\varphi \\
\chi
\end{pmatrix}
\]  

**Equation (9)**

\[
\vec{\sigma} \cdot \vec{p} = \sigma_x p_x + \sigma_y p_y + \sigma_z p_z
\]  

**Equation (10)**

$V$ is the potential, $p_x, p_y, p_z$ are the cartesian components of the momentum $\vec{p}$, and $\sigma_x, \sigma_y, \sigma_z$ the 3 $(2 \times 2)$ Pauli matrices.
Then, for an electronic eigenstate it is necessary that the upper and lower components \( \varphi \) and \( \chi \) satisfy the key relation

\[
\chi = X \varphi
\]  

(11)

with \( X \) solution of the implicit equation

\[
2mc^2 X = c\vec{\sigma}\vec{p} - [X, V] - cX\vec{\sigma}\vec{p}X
\]  

(12)

If we know \( X \), we can eliminate \( \chi \) and arrive at a quasirelativistic theory.

Don’t confuse with the traditional ESC (elimination of the small component) method, in which one considers a single eigenstate!
The textbook type of a quasi-relativistic theory is based on the application of the Foldy-Wouthuysen (FW) transformation to the Dirac operator $D$.

$$D \rightarrow L_{FW} = W^\dagger DW = \begin{pmatrix} L^+ & 0 \\ 0 & L^- \end{pmatrix}; \quad W^\dagger W = 1 \quad (13)$$

$W$ can be expressed in terms of $X$, but a theory that avoids $W$ is preferable.

If we were able to construct this transformation, we would have achieved two important goals. On one hand we would have to worry only about the eigenvalue equation

$$(L^+ - mc^2)\phi = E\phi \quad (14)$$

in terms of the 2-component spinor $\phi$, which has only electronic eigenstates.

On the other hand we would have an operator $L^+$ that is bounded from below by the lowest electronic eigenvalue, and that would allow a genuine variational calculation, providing rigorous upper bounds like in non-relativistic energy.
Questions at the beginning

1. Does one want a theory at *operator level* or one at *matrix level*?

2. Does one care for the upper-component spinor $\varphi$ of the Dirac bispinor $\psi$ or the FW spinor $\phi$, which satisfies (14). The two spinors are related as

$$\phi = (1 + X^\dagger X)^{\frac{1}{2}} \varphi \quad (15)$$

and the switch between them has to do with what is commonly called *picture change*. $\varphi$ and $\phi$ have very different analytical properties.

3. Does one want a theory that is exactly *equivalent* to the original Dirac theory or rather an approximate, but sufficiently simple theory?

4. Does one want an expansion in terms of a *perturbation parameter*, and if so, in terms of which one? The classical expansion is, of course that in powers of $c^{-1}$, with the nonrelativistic limit (nrl) as *unperturbed* system.
Main messages

1. If one tries to construct a quasi-relativistic theory at operator level, one encounters unsurmountable difficulties.

2. In the presence of a Coulomb potential the transformation cannot be performed in closed form.

3. A formal expansion in powers of $c^{-1}$ is possible, but it converges only for bound states. It does not lead to a full quasi-relativistic Hamiltonian.

4. The expansion in powers of the coupling strength in the sense of the Douglas-Kroll transformation leads to highly singular operators, and is extremely tedious.

5. The so-called regular approximation (RA) does not lead to a full quasi-relativistic Hamiltonian.
6. Even if an exact quasi-relativistic Hamiltonian could be constructed, it would be rather useless for a matrix representation in a regular basis.

7. Everything becomes easy, if one does not care for a transformation at matrix level, but rather for a transformation of the matrix representation of the Dirac operator. Why is this the right way?

8. At matrix level an exact quasi-relativistic theory can be constructed simply by a fast iteration scheme or even non-iteratively.

9. The rather good performance of the now obsolete Douglas-Kroll-Hess (DKH) transformation is due to the fact that at the very beginning it was formulated implicitly as a matrix theory.

10. It is essential the a relativistic bispinor can to any desired accuracy be expanded in a kinetically balanced basis.
FIRST PART

THEORY IN TERMS OF OPERATORS AND WAVE FUNCTIONS
The key relation and the non-hermitian quasirelativistic Hamiltonian

Dirac equation (8) in component form:

\[ 0 = (V - E_k)\varphi_k + c\vec{\sigma} \cdot \vec{p}\chi_k \]  
\[ 0 = c\vec{\sigma} \cdot \vec{p}\varphi_k + (V - 2mc^2 - E_k)\chi_k \]  

Mapping of all \( \varphi_k \) to the corresponding \( \chi_k \) symbolized by the operator \( X \).

\[ \chi_k = X\varphi_k \]  
\[ 0 = (V - E_k + c\vec{\sigma} \cdot \vec{p}X)\varphi_k \]  
\[ 0 = \{c\vec{\sigma} \cdot \vec{p} + (V - 2mc^2 - E_k)X\}\varphi_k \]

Two conditions for \( X, E_k, \varphi_k \). Linear combination (20) - \( X \) (19)

\[ 0 = \{c\vec{\sigma} \cdot \vec{p} + (V - 2mc^2)X - XV - cX\vec{\sigma} \cdot \vec{p}X\}\varphi_k \]  

21
This implies the operator equation

\[ 0 = c\vec{\sigma} \cdot \vec{p} + [V, X] - 2mc^2X - cX\vec{\sigma} \cdot \vec{p}X \]  

(22)

Defining the \textit{non-hermitian} quasi-relativistic Hamiltonian

\[ L = c\vec{\sigma} \cdot \vec{p}X + V \]  

(23)

we get the \textit{quasi-relativistic eigenvalue equation}

\[ L\phi_k = E_k\phi_k \]  

(24)

Eq. (22) is quadratic in \( X \) and has hence \textit{two independent solutions}.

If \( X \) is solution of (22), then \( Y = -(X^\dagger)^{-1} \) is a solution of (22) as well.
Hermitian quasi-relativistic Hamiltonians

Let us consider the following transformation of the Dirac operator

\[
\Omega \dagger (D - mc^2) \Omega = \begin{pmatrix}
\tilde{L} & 0 \\
0 & \tilde{L}_p - 2mc^2
\end{pmatrix}; \quad \Omega = \begin{pmatrix}
1 & -X^\dagger \\
X & 1
\end{pmatrix} \tag{25}
\]

This transformation is not unitary, since

\[
\Omega \dagger \Omega = \begin{pmatrix}
1 + X^\dagger X & 0 \\
0 & 1 + XX^\dagger
\end{pmatrix} \tag{26}
\]

For arbitrary \( X \) the diagonal blocks of the transformed operator \( \text{[25]} \) are, \( \tilde{L} \) and \( \tilde{L}_p - 2mc^2 \) for electrons and positrons respectively (the subscript \( p \) symbolizes positrons) with:

\[
\tilde{L} = V + c\vec{\sigma} \cdot \vec{p}X + cX^\dagger \vec{\sigma} \cdot \vec{p} + X^\dagger (V - 2mc^2)X \tag{27}
\]
The following three expressions are equivalent to $\tilde{L}$, provided that (22) is satisfied

$$L' = (1 + X^\dagger X)L$$  \hspace{2cm} (28)

$$L'^\dagger = L^\dagger(1 + X^\dagger X)$$  \hspace{2cm} (29)

$$\bar{L} = \frac{1}{2}\{(1 + X^\dagger X)L + L^\dagger(1 + X^\dagger X)\}$$  \hspace{2cm} (30)

Hermitian eigenvalue problems with non-unit metric:

$$\tilde{L}\varphi = E\tilde{S}\varphi = E(1 + X^\dagger X)\varphi$$  \hspace{2cm} (31)

equivalent to the nonhermitian one. Both sets of equations have the upper component $\varphi$ of the Dirac bispinor $\varphi$ as solutions.
Hermitian eigenvalue problems with *unit metric*

\[ \phi = (1 + X^\dagger X)^{1/2} \varphi \]  
\[ L^+ \phi = E \phi \] 
\[ L^+ = \frac{1}{2} \left\{ (1 + X^\dagger X)^{1/2} L (1 + X^\dagger X)^{-1/2} + (1 + X^\dagger X)^{-1/2} L^+ (1 + X^\dagger X)^{1/2} \right\} \]

They have the same *eigenvalues* as before. All quasirelativistic operators are expressible through \( X \).

**FW transformation**

\[ W = \begin{pmatrix} 1 & -X^\dagger \\ X & 1 \end{pmatrix} \begin{pmatrix} (1 + X^\dagger X)^{-1/2} & 0 \\ 0 & (1 + XX^\dagger)^{-1/2} \end{pmatrix} \]  
\[ \]
The free electron

For the very special case of a free particle, a closed solution is possible.

\[
D^{(0)} = \beta mc^2 + c\vec{\alpha} \vec{p}; \quad X^{(0)} = \frac{c}{2} \left( \sqrt{1 + \frac{2T}{mc^2}} - 1 \right) T^{-1} \vec{\sigma} \cdot \vec{p} \tag{36}
\]

\[
W^{(0)} = \left( \frac{1 - y}{1 + y} \right)^{1/4}; \quad y = \frac{\beta \vec{\alpha} \vec{p}}{mc}; \quad L^{(0)} = \beta \sqrt{m^2 c^4 + c^2 \vec{p}^2} \tag{37}
\]

The eigenstates of \( D^{(0)} \) are also eigenstates of \( \vec{p} \), use \( \vec{p} \) to label these. The nrl for a free particle is obviously

\[
X^{(0)} = \frac{1}{2mc} \vec{\sigma} \cdot \vec{p} + O(c^{-3}); \quad L^{(0)} = \beta (mc^2 + T) + O(c^{-2}); \quad W^{(0)} = 1 - \frac{1}{2} y + O(c^{-2}); \tag{38}
\]

A convergent expansion in powers of \( c^{-2} \) is, however, only possible for states with \(|p| < mc\), i.e. not for ultra-relativistic states.
Expansion in powers of $c^{-1}$

Formally one can expand the operator $X$ in powers of $c^{-1}$.

\[
 cX = \sum_{k=0}^{\infty} c^{-2k} X_{2k} \quad (39)
\]

\[
 X_0 = \frac{1}{2m} \vec{\sigma} \vec{p} \quad (40)
\]

\[
 X_2 = \frac{1}{2m} [V, X_0] - X_0^3 = \frac{1}{2m} (V X_0 - X_0 H_0) \quad (41)
\]

\[
 X_4 = \frac{1}{2m} [V, X_2] - X_0^2 X_2 - X_2 X_0^2 = \frac{1}{2m} \{(V - T) X_2 - X_2 H_0\} \quad (42)
\]

\[
 X_6 = \frac{1}{2m} [V, X_4] - X_2 X_0 X_2 - X_4 X_0^2 - X_0^2 X_4 \quad (43)
\]

Convergence only, if applied to bound states. Leads to DPT, QD-DPT, but not to a full quasi-relativistic theory. Do not start from FW transformation!
Properties of the exact quasi-relativistic Hamiltonian

For the Coulomb potential of a point nucleus no closed expressions for the quasi-relativistic Hamiltonian is known.

However, we know some exact properties of the quasi-relativistic Hamiltonian.

Very far from a Coulomb singularity, where the term \([X, V]\) is negligible in (12), \(X\) behaves as for a free particle, i.e. is dominated by the term \(X_0\).

This guarantees an exponential decay of the wave function far from all nuclei, as in the non-relativistic regime.
Close to a nucleus $mc^2$ and $E_k$ are negligible, such that

$$X = -cV^{-1} \vec{\sigma} \cdot \vec{p} = \frac{c}{Z} r \vec{\sigma} \cdot \vec{p}$$  \hspace{1cm} (44)$$

$X$ behaves radially as $\sim r \frac{\partial}{\partial r}$. If the spherically symmetric part of $\varphi$ goes as $r^\nu$, the $(p_1^2)$-part of $\chi$ goes as $-\frac{c}{Z} r^\nu$. Near a nucleus $L$ goes in the spherical average as

$$-\frac{c^2}{Z} \left( r \frac{\partial^2}{\partial r^2} + 3 \frac{\partial}{\partial r} \right) - \frac{Z}{r}$$  \hspace{1cm} (45)$$

For $\varphi \sim r^\nu$, $L \varphi = E \varphi$ can be satisfied near a nucleus, only if

$$\nu^2 + 2\nu + Z^2/c^2 = 0; \quad \nu = \sqrt{1 - Z^2/c^2} - 1$$  \hspace{1cm} (46)$$

Not surprising, since $\varphi$ is identical with the upper component of the Dirac spinor, which behaves like this. The FW $\phi$ is more seriously singular.
One of the reasons to care for a quasi-relativistic theory has been to have the ground for a genuine variational approach. This is guaranteed if $\chi$ and $\varphi$ satisfy the key relation.

However, this is only possible, if both $\chi$ and $\varphi$ have the correct weak singularities at the position of a nucleus. We want to expand $\varphi$ in a regular basis. This is incompatible with satisfying the key relation.

The quasi-relativistic Hamiltonian derived at operator level is not the right choice if one wants to expand $\varphi$ in a regular basis. So, even if we knew this Hamiltonian, this would not help us.

Do not care for a pointwise convergent expansion. Convergence in a Hilbert space norm is all that is needed. Satisfy the key relation only in the norm!
The Douglas-Kroll transformation

The names Douglas-Kroll (DK) and Douglas-Kroll-Hess (DKH) transformation are being used synonymously. We propose to use the name DK for a transformation at operator level, and to reserve DKH for a transformation at matrix level, as used by Hess and others.

DK and Hess wanted to avoid the singularities of the FW transformation by using an alternative expansion parameter, namely the coupling strength. In this approach the potential $V$ is formally multiplied with a perturbation parameter $\lambda$ and the limit $\lambda \to 0$ corresponds to a relativistic free particle.

Actually the expansion in powers of $\lambda$ does not lead to less singular operators as that in powers of $c^{-1}$. What saved Hess was that he did not perform the DK transformation at operator level, but rather introduced early a basis representation, such the DKH transformation has always been a transformation at matrix level.
The DK transformation is a FW transformation (13) with the special feature that the transformation operator \( W \) is split into two factors, one of which is the known one \( W^{(0)} \) (37) of the free-particle FW transformation

\[
W = W^{(0)}W'; \quad L_{FW} = (W')^\dagger W^{(0)}^\dagger DW^{(0)}W' = (W')^\dagger L_{DK} W' \tag{47}
\]

\[
L_{DK} = W^{(0)}^\dagger DW^{(0)} = \beta \sqrt{m^2 c^4 + c^2 p^2} + \left( \frac{1 + y}{1 - y} \right)^{1/4} V \left( \frac{1 - y}{1 + y} \right)^{1/4} \tag{48}
\]

Leading order \( L_{DK} \) not block diagonal, but take the upper diagonal block as an approximate quasi-relativistic Hamiltonian,

\[
\frac{1}{4} (1 + \beta) L_{DK} (1 + \beta) \tag{49}
\]

If this is not good enough, one can try to construct \( W' \) by successive approximations, and arrive so at higher order DK schemes, which corresponds essentially to an expansion of \( W \) in powers of \( V \).

Even the leading order has never been performed at operator level.
The transformation which leads to $L_{DK}$ can only be performed in momentum space, hence $L_{DK}$ and its eigenfunctions are only defined in momentum space. The same holds for the resolvent of this operator, which is needed when one wants to construct higher order approximations by means of perturbation theory.

$L_{DK}$ has some similarities with two other Hamiltonians for electrons only (with two-component spinor solutions):

(a) the Hamiltonian with relativistic kinematics

$$L_{RK} = \sqrt{m^2 c^4 + c^2 p^2} + V \quad (50)$$
(b) the free-particle-no-pair projected Hamiltonian

\[
L_{FPP} = P^+_F P^+_D P^+_F
\]

\[
P^+_F = \frac{1}{2} W^{(0)} (1 + \beta) W^{(0)\dagger} = \frac{1}{2} \left( \frac{1 - y}{1 + y} \right)^{1/4} (1 + \beta) \left( \frac{1 + y}{1 - y} \right)^{1/4}
\]

\[
= \frac{1}{2} \left[ 1 + \beta \left( \frac{1 + y}{1 - y} \right)^{1/2} \right] = \frac{1}{2} \left[ 1 + \beta \frac{(1 + y)}{(1 - y^2)^{1/2}} \right]
\]

\[
L_{FPP} = \frac{1}{4} W^{(0)} (1 + \beta) L_D K (1 + \beta) W^{(0)\dagger}
\]

The free-particle no-pair projected Dirac operator (53) is nothing but the DK Hamiltonian (49) transformed back to a 4-component spinor framework by means of an inverse free-particle FW transformation. The two Hamiltonians (49) and (53) have the same eigenvalues, and their eigenfunctions are trivially related to each other.
All three Hamiltonians have rather unpleasant mathematical properties.

The eigenstates are (at variance with those of the Dirac operator) not analytic in $c^{-2}$. If one tries to expand $L_{FPP}$ in $c^{-1}$, automatically a term in $c^{-3}$ and one in $c^{-4}\ln c$ arise.

The eigenfunctions of these Hamiltonians are much more singular at the position of a nucleus than are the upper components $\varphi_k$ of the Dirac bispinors.

They go as $r^{\nu}$ with a $\nu < 0$, but with $\nu = O(Z/c)$ rather than $\nu = O(Z^2/c^2)$ as for the $\varphi_k$. For $L_{FPP}$, and hence also $L_{DK}$, one has $\nu = -\frac{Z}{c\pi}$.

The limits $r \to 0$ and $c^{-1} \to 0$ do not commute.

These properties make it much more problematic than for $\varphi_k$ to expand the eigenstates of $L_{DK}$ in a regular basis. Anyway, this has not yet been done.
The 'regular approximation' 

Elimination of the small component, ESC: Solve (17) for $\chi$ and insert this into (16):

$$\chi = c(V - 2mc^2 - E)^{-1}\vec{\sigma}\vec{p}\psi; \quad E\psi = L(E)\psi$$ \hspace{1cm} (54)

Eigenvalue equation for an energy-dependent quasirelativistic Hamiltonian $L(E)$. Alternative way to DPT: Expand the operator inverse in $L(E)$ in powers of $c^{-2}$.

This expansion converges if $|E - V| = |E + Z/r| < 2mc^2$, i.e. not for small $r$ close to a nucleus. Rearrange to:

$$L(E) = V + \frac{1}{2m}\vec{\sigma}\vec{p}\frac{2mc^2}{2mc^2 - V} \left\{1 + \frac{E}{2mc^2 - V}\right\}^{-1}\vec{\sigma}\vec{p}$$

$$= \quad V + \frac{1}{2m}\vec{\sigma}\vec{p}\frac{2mc^2}{2mc^2 - V} \left\{1 - \frac{E}{2mc^2 - V} + \left(\frac{E}{2mc^2 - V}\right)^2 + \ldots\right\}\vec{\sigma}\vec{p}$$ \hspace{1cm} (55)
This argument is actually not fully convincing, because for an operator \textit{local} properties are not relevant. What matters is whether the application of an operator on a function in its domain leads to a convergent expansion. This is the case for the expansion of the operator $L(E)$ applied to $\varphi$ if this is the upper component of a Dirac bispinor for a \textit{bound state}.

A new \textit{formal expansion operator}, without any direct physical meaning. The leading approximation of (55), referred to as ZORA (zeroth-order regular approximation) is

$$L_{\text{ZORA}} = V + \vec{\sigma}\vec{p}(2m - Vc^{-2})^{-1}\vec{\sigma}\vec{p}$$

(56)

The ZORA Hamiltonian is $E$-independent, while higher order approximations involve $E$-dependent operators.

The eigenstates of the ZORA Hamiltonian are good approximations to \textit{bound} exact states, because $L_{\text{ZORA}}$ differs from the exact ESC Hamiltonian only in the neglect of $E$ with respect to $mc^2 - V$. 
ZORA has been formulated at operator level. Generalization beyond leading order difficult. (Matrix form recently by Filatov and Cremer)

The RA does not open a way towards the construction of a quasi-relativistic Hamiltonian at operator level. Convergence only for bound states, like for DPT.

A minor drawback of ZORA is that it is not gauge-independent, i.e. a change of the zero in the energy scale does effect the result.

Conclusions of part I: There is no satisfactory way towards a quasirelativistic operator, neither with, nor without an expansion operator. If we had such an operator, we could not expand it in a regular basis.
SECOND PART

THEORY IN A

MATRIX REPRESENTATION
Matrix representation a priori vs. posteriori

To construct the matrix representation of a quasirelativistic Hamiltonian in a basis one has two choices:

(a) to transform first the *Dirac operator* to a quasirelativistic operator, and to construct then the matrix representation of the latter – or

(b) to *expand first the Dirac operator in a basis*, and then transform the matrix representation of the Dirac operator to a *quasirelativistic matrix*.

We have seen that the way (a) is generally not feasible, and that even if it were, it would not be recommended, since it requires a basis which is able to describe the *weakly singular* behavior of the wave function at the *position of a nucleus* correctly.

20 years ago nobody would have guessed that (b) is the right way.
Around 1980 the *variational collapse* (VC) was a big concern. If one chooses the basis for a matrix representation inappropriately, one finds physically meaningless eigenvalues in the *forbidden region* between the electronic ground state and the onset of the negative-energy continuum. This survives even in the nrl.

**Cause:** In a brute-force basis expansion one does not impose the key relation \( \chi = X\varphi \) between \( \varphi \) and \( \chi \) for an electronic state. The kinetic energy does not 'tame' the potential energy, the energy is not bounded from below.

**It was hoped** that by a transformation to a quasirelativistic theory the problem of the variational collapse would automatically be eliminated. (see the beginning of this lecture).

In 1984 I proposed the 'back-forth free-particle Foldy-Wouthuysen transformation to avoid the VC. It worked, but the kinetic balance (KB) took over. Both schemes try to impose the key relation approximatively.
The choice of a basis for the expansion of the Dirac operator is the only approximation that we introduce. The subsequent transformation to a quasirelativistic Hamiltonian matrix can be done numerically to any desired precision. In particular we do not introduce any ad hoc completeness insertions.

Among the quasirelativistic methods in current use, the Douglas-Kroll-Hess (DKH) method [13, 14] has always been implemented as a matrix transformation, including its modification by Barysz et al.[15].

*Direct perturbation theory* has been formulated and applied in two versions, one (DPT) at operator level [16] for exactly solvable problems, and one (S-DPT, stationary direct perturbation theory) at matrix level [17] for numerical solutions.

The *regular approximation* (RA) [18] has been formulated and implemented as an operator transformation with subsequent basis expansion, only recently a variant of RA at matrix level has been studied [19]. The *normalized elimination of the small component* (NESC) [9] has from the very beginning been a matrix theory.
Matrix representation of the Dirac operator in a kinetically balanced basis

Expand the upper and lower components $\varphi$ and $\chi$ of the bispinor $\psi$ in a kinetically balanced basis, constructed from the regular basis $\{g_\mu\}$ for the upper component.

$$\varphi = \sum_\mu a_\mu g_\mu$$  \hspace{1cm} (57)

$$\chi = \sum_\mu b_\mu f_\mu = \sum_\mu b_\mu \vec{\sigma} \vec{p} g_\mu$$  \hspace{1cm} (58)

The kinetically balanced (KB) basis has originally been proposed as a kind of compromise. The idea behind it had been that one wanted to satisfy the key relation between $\varphi$ and $\chi$ to a good degree of approximation, but in a way that is independent of the potential, because one wanted a general recipe, valid for all possible potentials.
It has been believed for a long time that results for the energy obtained with a KB basis are only correct to the leading relativistic order, and that errors of $O(\alpha^4)$ are to be expected.

We now know (W.K. JCP published online) that a KB basis is complete for the expansion of relativistic wave functions in the same sense as an ordinary Gaussian basis is complete in the non-relativistic regime, even with a similar rate of convergence. This is so, although there is no pointwise convergence, and although the key relation cannot be satisfied pointwise in such a basis (only in the mean).

If we expand a bispinor in a KB basis, we are on the safe side, independently of whether we take the matrix representation of the original Dirac operator, or the transformation of this matrix to quasi-relativistic form.

It is somewhat unexpected that the KB basis also describes positronic (negative-energy) states. To get a quasi-relativistic Hamiltonian one must satisfy a key relation at matrix level.
Transformation of the matrix representation of the Dirac operator

We start from the representation of the Dirac operator in a finite regular kinetically balanced basis and we want to apply a transformation to it such that the result is a quasi-relativistic Hamiltonian, again in a basis representation. The eigenstates of the new quasi-relativistic Hamiltonian will be the same as those of the matrix representation of the Dirac Hamiltonian. Unlike the FW transformation operator the transformation matrix can be constructed exactly, and it is not necessary to consider a specific expansion parameter. In the matrix theory a matrix $X$ will play a similar role as the operator $X$ at operator level.

Expand $\varphi$ and $\chi$ in a kinetically balanced basis, constructed from the $m$-dimensional regular basis $\{g_\mu\}$ for the upper component. We express the relation between $\chi$ and $\varphi$ as [7]

$$\chi_k = \tilde{X} \varphi_k$$

(59)

with $\tilde{X}$ the same for all states expandable in the given basis.
This \( \tilde{X} \) cannot be identical with the \( X \) that satisfies the key relation at operator level, because the exact \( \chi \) and \( \varphi \) cannot be expanded in a regular basis, but \( \tilde{X} \) can be regarded as an approximation to \( X \). We shall only need the matrix representation \( X \) (64) rather than \( \tilde{X} \) itself.

\[
\varphi = \sum_{\mu} a_{\mu} g_{\mu} \tag{60}
\]

\[
\chi = \sum_{\mu} b_{\mu} f_{\mu} = \sum_{\mu} b_{\mu} \vec{\sigma} \vec{p} g_{\mu} = \tilde{X} \varphi = \sum_{\mu} a_{\mu} \tilde{X} g_{\mu} \tag{61}
\]

The scalar product from the left with \( g_\nu \) or \( \vec{\sigma} \vec{p} g_\nu \) is:

\[
\langle g_\nu | \varphi \rangle = \sum_{\mu} a_{\mu} \langle g_\nu | g_\mu \rangle \tag{62}
\]

\[
\langle g_\nu | \vec{\sigma} \vec{p} | \chi \rangle = \sum_{\mu} b_{\mu} 2m \langle g_\nu | T | g_\mu \rangle = \langle g_\nu | \vec{\sigma} \vec{p} \tilde{X} | \varphi \rangle
\]

\[
= \sum_{\mu} a_{\mu} \langle g_\nu | \vec{\sigma} \vec{p} \tilde{X} | g_\mu \rangle \tag{63}
\]
We define the matrices $S$, $V$, $T$, $X$, and $U$ through their matrix elements

\[
S_{\nu\mu} = \langle g_\nu | g_\mu \rangle; \quad V_{\nu\mu} = \langle g_\nu | V | g_\mu \rangle; \quad T_{\nu\mu} = \langle g_\nu | T | g_\mu \rangle
\]

\[
X_{\nu\mu} = \langle g_\nu | \vec{\sigma} \vec{p} \tilde{X} | g_\mu \rangle; \quad U_{\nu\mu} = \langle g_\nu | \vec{\sigma} \vec{p} V \tilde{\sigma} \tilde{p} | g_\mu \rangle
\]  

(64)

and represent $\varphi$ as well as $\chi$ by the vectors $\vec{a}$ and $\vec{b}$ of their coefficients $a_\mu$ and $b_\mu$. We can then write (63) as

\[
T \vec{b} = \frac{1}{2m} X \vec{a}; \quad \vec{b} = \frac{1}{2m} T^{-1} X \vec{a}
\]  

(65)

which relates the expansion coefficients of $\chi$ and $\varphi$. 

47
Expectation value of the Dirac operator for an electronic eigenstate:

\[
< D - mc^2 > = \frac{\langle \psi | D - mc^2 | \psi \rangle}{\langle \psi | \psi \rangle} \\
= \frac{\langle \varphi | V | \varphi \rangle + 2c \text{Re} \langle \chi | \bar{\sigma} \bar{p} | \varphi \rangle - 2mc^2 \langle \chi | \chi \rangle + \langle \chi | V | \chi \rangle}{\langle \varphi | \varphi \rangle + \langle \chi | \chi \rangle} \\
= \frac{\bar{a}^\dagger V \bar{a} + 2mc \bar{a}^\dagger \bar{T} \bar{b} + 2mc \bar{b}^\dagger \bar{T} \bar{a} + \bar{b}^\dagger U \bar{b} - 4m^2 c^2 \bar{b}^\dagger \bar{T} \bar{b}}{\bar{a}^\dagger S \bar{a} + 2m \bar{b}^\dagger \bar{T} \bar{b}}
\]  

(66)

Conditions for stationarity with respect to variations of \( \bar{a} \) and \( \bar{b} \):

\[
0 = V \bar{a} + 2mc \bar{T} \bar{b} - ES \bar{a} \\
0 = 2mc \bar{T} \bar{a} + U \bar{b} - 4m^2 c^2 \bar{T} \bar{b} - 2mE \bar{T} \bar{b}
\]  

(67)  

(68)

These are the equations that we try to satisfy in a matrix representation of the Dirac equation.
Alternatively an eigenvalue equation with double dimension, and non-unit metric

\[
\begin{pmatrix}
V & 2mcT \\
2mcT & U - 4m^2c^2T
\end{pmatrix}
\begin{pmatrix}
\vec{a} \\
\vec{b}
\end{pmatrix}
= E
\begin{pmatrix}
S & 0 \\
0 & 2mT
\end{pmatrix}
\begin{pmatrix}
\vec{a} \\
\vec{b}
\end{pmatrix}
\] (69)

which is recognized as the modified Dirac equation of Dyall [21], that was first proposed by one of the present authors [3].
The key relation at matrix level

Eliminate $\vec{b}$ from (67, 68) via (65).

\[
0 = \mathbf{V}\vec{a}_k + c\mathbf{X}\vec{a}_k - E_k\mathbf{S}\vec{a}_k \quad (70)
\]

\[
0 = 2mc\mathbf{T}\vec{a}_k + \frac{1}{2m}\mathbf{UT}^{-1}\mathbf{X}\vec{a}_k - 2mc^2\mathbf{X}\vec{a}_k - E_k\mathbf{X}\vec{a}_k \quad (71)
\]

Two equations for the determination of $\mathbf{X}$, $\vec{a}_k$, and $E_k$.

Premultiply (70) by $-\mathbf{XS}^{-1}$ and add this to (71).

\[
0 = (-\mathbf{XS}^{-1}\mathbf{V} - c\mathbf{XS}^{-1}\mathbf{X} + 2mc\mathbf{T} + \frac{1}{2m}\mathbf{UT}^{-1}\mathbf{X} - 2mc^2\mathbf{X})\vec{a}_k \quad (72)
\]

An equation independent of $E_k$, that must hold for all $\vec{a}_k$, i.e. that implies

\[
\mathbf{X} = c^{-1}\mathbf{T} + \frac{1}{4mc^2c^2}\mathbf{UT}^{-1}\mathbf{X} - \frac{1}{2mc^2}\mathbf{XS}^{-1}\mathbf{V} - \frac{1}{2mc}\mathbf{XS}^{-1}\mathbf{X} \quad (73)
\]
Having constructed $X$ from (73), we have to build the quasi-relativistic Hamiltonian, from which we get the $E_k$ and $\vec{a}_k$.

Define the non-hermitian quasirelativistic Hamiltonian matrix

$$L = V + cX$$

such that $\vec{a}_k$ satisfies the eigenvalue equation

$$L\vec{a}_k = E_kS\vec{a}_k$$

While $S$, $T$ and $U$ are constants, $X$ and $L$ change from iteration to iteration. Spin-orbit effects are entirely in the factor $U$. So the dimension of $U$ is twice that of $S$ and $T$, and of the iteration start for $X$ and $L$.

A spinfree theory is obtained if we replace $U$ by its spinfree counterpart. The nonrelativistic limit (nrl) is obviously:

$$X_{nr} = c^{-1}T; \quad L_{nr} = V + T = H_0$$
Hermitian quasirelativistic Hamiltonians

We can get the $\varphi$ or the $\vec{a}$ from the non-hermitian eigenvalue problem (75) or alternatively from a hermitian one (80) with non-unit metric. From $\vec{a}$ we get $\vec{b}$, which represents $\chi$, via (65).

Right eigenvectors $\vec{a}_k$ and $\vec{a}_l$ to different eigenvalues are not orthogonal. From the orthonormality of the full Dirac bispinors we get

$$\delta_{\mu\nu} = \vec{a}_\mu^\dagger \tilde{S} \vec{a}_\nu; \quad \tilde{S} = S + \frac{1}{2m} X^\dagger T^{-1} X \quad (77)$$

To formulate the hermitian eigenvalue problem, we start from the energy expectation value (66), and use (65) in order to eliminate $\vec{b}$ in favor of $X$.

$$E = \frac{\vec{a}^\dagger \tilde{L} \vec{a}}{\vec{a}^\dagger \tilde{S} \vec{a}} \quad (78)$$

$$\tilde{L} = V + cX + cX^\dagger + \frac{1}{4m^2} X^\dagger T^{-1} UT^{-1} X - c^2 X^\dagger T^{-1} X \quad (79)$$
This is the expectation value of a hermitian operator, but with a non-unit metric. If we make this stationary with respect to variation of $\vec{a}$, we get the condition

$$\tilde{L}\vec{a} = E\tilde{S}\vec{a} \quad (80)$$

This hermitian eigenvalue problem is much more complicated than, but equivalent to the non-hermitian one (75). The eigenvector $\vec{a}$ still represents the upper-component spinor $\varphi$.

Three more reformulations of $\tilde{L}$ are possible, that are equivalent to (79), provided that $X$ satisfies the matrix key relation. These are

$$L' = \tilde{S}S^{-1}L \quad (81)$$
$$L'^\dagger = LS^{-1}\tilde{S} \quad (82)$$
$$\tilde{L} = \frac{1}{2}(L' + L'^\dagger) \quad (83)$$

It is trivial that (75) implies $L'\vec{a} = \tilde{S}\vec{a}$ and vice versa.
Proof of the equivalence of $L'$ and $\tilde{L}$:

\[
L' = (S + \frac{1}{2m}X^\dagger T^{-1}X)S^{-1}L = L + \frac{1}{2m}X^\dagger T^{-1}(XS^{-1}L)
\]

\[
= L + \frac{1}{2m}X^\dagger T^{-1}(2mcT - 2mc^2X + \frac{1}{2m}UT^{-1}X)
\]

\[
= V + cX + cX^\dagger - c^2X^\dagger T^{-1}X + \frac{1}{4m^2}X^\dagger T^{-1}UT^{-1}X = \tilde{L}(84)
\]

This is obviously hermitian, and agrees with (79), but only so if $X$ satisfies the matrix key relation. If this not the case, the symmetrized form (83) is preferable to (81).

The most robust expression is obviously (79), since it is valid even if $X$ is not exact. The energy will always converge faster if it is evaluated in terms of $\tilde{L}$ rather than $L'$ or $\bar{L}$. 
The equivalence of \( \mathbf{L}' \) or \( \tilde{\mathbf{L}} \), under the stationarity condition, implies the following interesting identity, first explicitly formulated by Filatov, starting from an earlier paper by Dyall

\[
\mathbf{S}^{-1}\mathbf{L} = \tilde{\mathbf{S}}^{-1}\tilde{\mathbf{L}} 
\]
Matrix counterpart of the FW spinor (15), represented by the vector

\[ \vec{d} = S^{-\frac{1}{2}} \tilde{S}^{\frac{1}{2}} \tilde{a} \]  

(86)

\[ \langle \phi_k | \phi_l \rangle = \vec{d}_k^\dagger S \vec{d}_l = \tilde{a}_k^\dagger \tilde{S} \tilde{a}_l = \delta_{kl} \]  

(87)

\[ \mathbf{L}^+ \vec{d} = \frac{1}{2} \left\{ S^{\frac{1}{2}} \tilde{S}^{\frac{1}{2}} S^{-1} \mathbf{L} \tilde{S}^{-\frac{1}{2}} S^{\frac{1}{2}} + h.c. \right\} \vec{d} = E S \vec{d} \]  

(88)

Matrix analog of the FW transformation, restricted to the electronic part. If (85) holds, the following expression

\[ \tilde{\mathbf{L}}^+ = S^{\frac{1}{2}} \tilde{S}^{-\frac{1}{2}} \tilde{\mathbf{L}} \tilde{S}^{-\frac{1}{2}} S^{\frac{1}{2}} \]  

(89)

is equivalent to \( \mathbf{L}^+ \). This \( \tilde{\mathbf{L}}^+ \) is related to \( \mathbf{L}^+ \) in the same way as \( \tilde{\mathbf{L}} \) is related to \( \bar{\mathbf{L}} \).
Construction of the matrix $X$.

Solve (73) for $X$, the matrix counterpart of the key-relation (12). A quadratic equation for the unknown matrix $X$. The solution is entirely a problem of numerical mathematics. Physical pictures or expansion parameters are rather irrelevant.

We can construct $X$ either as solution of the quadratic matrix equation (73) or of the coupled system of pseudo-linear equations.
Simple linear iteration

Formally simplest iterative solution by means of the algorithm

\[
X^{(n+1)} = c^{-1}T + \frac{1}{4m^2c^2}UT^{-1}X^{(n)} - \frac{1}{2mc^2}X^{(n)}S^{-1}L^{(n)} \quad (90)
\]

\[
L^{(n)} = V + cX^{(n)} \quad (91)
\]

Inspired by direct perturbation theory (DPT). Start iteration the nrl. Poor convergence. Some improvement by the use of (85) and the NR update.

One should like to have all terms linear in \(X\) on the l.h.s. It is simple to shift two of the three terms linear in \(X\) to the l.h.s. Two possibilities, but none of them really helps. One of them is in the spirit of the regular approximation (RA) \([18]\), and the start iteration is the \textit{zeroth-order regular approximation} (ZORA) in the matrix representation. For a variant the start iteration is the \textit{infinite-order regular approximation} (IORA).
Refined linear iteration

The key relation can be solved for \( X \) in a single step, in a basis, in which either \( L \) or \( U \) is diagonal. An iteration is necessary, nevertheless, because we have to repeat the same procedure with an updated \( L \). Choose a basis \( \vec{a}_k \) in which \( L \) is diagonal, in the sense

\[
L^{(n)}\vec{a}_\mu^{(n)} = E_\mu^{(n)} \vec{S}\vec{a}_\mu^{(n)}
\]  

(92)

We then try to solve

\[
\left(1 - \frac{1}{4m^2c^2} UT^{-1} + \frac{1}{2mc^2} E_\mu^{(n)}\right)\vec{X}^{(n+1)}\vec{a}_\mu^{(n)} = c^{-1} \vec{T}\vec{a}_\mu^{(n)}
\]  

(93)

This is related to the elimination of the small component (at matrix level).
Construct the vectors

\[ \vec{k}_{\mu}^{(n)} = \left\{ c - \frac{1}{4m^2c}UT^{-1} + \frac{1}{2mc}E_{\mu}^{(n)} \right\}^{-1}T\vec{a}_{\mu}^{(n)} \]  \hspace{1cm} (94)

from the \( E_{\mu}^{(n)} \) and \( \vec{a}_{\mu}^{(n)} \) of the previous iteration and then obtain \( X^{(n+1)} \) from the set of equations

\[ X^{(n+1)}\vec{a}_{\mu}^{(n)} = \vec{k}_{\mu}^{(n)} \]  \hspace{1cm} (95)

combined to the matrix equation

\[ \mathbf{K}^{(n+1)} = X^{(n+1)}\mathbf{A}^{(n)}; \quad X^{(n+1)} = \mathbf{K}^{(n)}\left\{ \mathbf{A}^{(n)} \right\}^{-1} \]  \hspace{1cm} (96)

with the vectors \( \vec{k}_{\mu}^{(n)} \) combined to a matrix \( \mathbf{K}^{(n)} \) and the vectors \( \vec{a}_{\mu}^{(n)} \) combined to a matrix \( \mathbf{A}^{(n)} \). From \( X^{(n+1)} \) we get \( L^{(n+1)} \), and from this the \( E_{p}^{(n+1)} \) and \( \vec{a}_{\mu}^{(n+1)} \)
In a basis, in which \( \mathbf{U} \) is diagonal, we proceed in the following way. We choose a basis \( h_\mu \), such that

\[
\mathbf{U} \vec{h}_\mu = U_\mu \mathbf{T} \vec{h}_\mu \tag{97}
\]

which implies (since \( \mathbf{U} \) is hermitian)

\[
\vec{h}_\mu^\dagger \mathbf{U} = U_\mu \vec{h}_\mu^\dagger \mathbf{T} \tag{98}
\]

We then get

\[
\vec{h}_\mu^\dagger \mathbf{X}^{(n+1)} \left( 1 - \frac{1}{4m^2c^2} U_\mu + \frac{1}{2mc^2} \mathbf{S}^{-1} \mathbf{L}^{(n)} \right) = c^{-1} \vec{h}_\mu^\dagger \mathbf{T} \tag{99}
\]

or the hermitian conjugate

\[
(c - \frac{1}{4m^2c} U_\mu + \frac{1}{2mc} \mathbf{L}^{(n)} \mathbf{S}^{-1}) \mathbf{X}^{(n+1)} \vec{h}_\mu = \mathbf{T} \vec{h}_\mu \tag{100}
\]
The corresponding iterative scheme is somewhat simpler than that based on \((92)\), since the vectors \(\vec{h}_\mu\) and the eigenvalues \(U_\mu\) do not change during the iterations, so only \(X\) and \(L\) have to be updated. We construct

\[
\vec{g}^{(n+1)}_\mu = X^{\dagger(n+1)} \vec{h}_\mu = \left( c - \frac{1}{4m^2c} U_\mu + \frac{1}{2mc} L^{(n)} S^{-1})^{-1} T \vec{h}_\mu \right)^{(101)}
\]

Combining the \(\vec{g}^{(n+1)}_\mu\) and the \(\vec{h}_\mu\) to matrices \(G^{(n+1)}\) and \(H\) respectively, we get

\[
X^{\dagger(n+1)} = G^{(n+1)} H^{-1}
\]

from which we obtain \(X^{(n+1)}\) as the hermitian conjugate.
Use the relation (85) in order to eliminate $L$ and $S$ in favor of $\tilde{L}$ and $\tilde{\tilde{L}}$. 

\[ \tilde{L}^{(n)} \tilde{a}_{\mu}^{(n)} = E_{\mu}^{(n)} \tilde{S} \tilde{a}_{\mu}^{(n)} \]  

(103)

\[ \tilde{h}_{\mu}^\dagger X^{(n+1)} (1 - \frac{1}{4m^2c^2} U_{\mu} + \frac{1}{2mc^2} \tilde{S}^{-1} \tilde{L}^{(n)}) = c^{-1} \tilde{h}_{\mu}^\dagger T \]  

(104)

\[ (c - \frac{1}{4m^2c} U_{\mu} + \frac{1}{2mc} \tilde{L}^{(n)} \tilde{S}^{-1}) X^{(n+1)} \tilde{h}_{\mu} = T \tilde{h}_{\mu} \]  

(105)
Iterative solution of the quadratic equation for $X$

Consider the quadratic equation (73) and solve this directly for $X$. Iterative scheme inspired by the DKH approximation. Multiply $V$ (and consequently $U$) formally by the expansion parameter $\lambda$

\[
\begin{align*}
X &+ (2mc)^{-1}XS^{-1}X = c^{-1}T \\
&- \lambda\{(2mc^2)^{-1}XS^{-1}V - (4m^2c^2)^{-1}UT^{-1}X\}
\end{align*}
\]  

(106)

The zeroth-order equation in $\lambda$ for $X$ becomes then

\[
X^{(0)} + (2mc)^{-1}X^{(0)}S^{-1}X^{(0)} = c^{-1}T
\]

(107)
Since \( \mathbf{X}^{(0)} \) and \( \mathbf{X}^{(0)} \mathbf{S}^{-1} \mathbf{X}^{(0)} \) have the same eigenvectors \( \vec{d}_k \), these must also be eigenvectors of \( \mathbf{T} \).

\[
\mathbf{T} \vec{d}_k = t_k \mathbf{S} \vec{d}_k
\]

\[
\mathbf{X}^{(0)} \vec{d}_k = x_k \mathbf{S} \vec{d}_k
\]

\[
\mathbf{X}^{(0)} \mathbf{S}^{-1} \mathbf{X}^{(0)} \vec{d}_k = x_k \mathbf{X}^{(0)} \vec{d}_k = (x_k)^2 \mathbf{S} \vec{d}_k
\]

\[
x_k = -mc + \sqrt{m^2 c^2 + 2mt_k}
\]

So we can construct \( \mathbf{X}^{(0)} \) from the eigenstates of \( \mathbf{T} \). In the next iterations one replaces \( \mathbf{T} \) by

\[
\mathbf{T}' = \mathbf{T} - (2mc)^{-1} \mathbf{X} \mathbf{S}^{-1} \mathbf{V} + (4m^2 c)^{-1} \mathbf{U} \mathbf{T}^{-1} \mathbf{X}
\]

and proceeds as before, being aware that \( \mathbf{T}' \) is non-hermitian and has complex eigenvalues.
Iteration with quadratic convergence

The eqn. (73) that we want to solve, is of the general type:

\[ F(X) = f(X) - X = 0 \]  \hspace{1cm} (113)

We start from a guess \( X^{(n)} \) for \( X \) and write

\[ X^{(n+1)} = X^{(n)} + \Delta \]  \hspace{1cm} (114)

Then \( \Delta \) must satisfy the linear matrix equation

\[ F(X^{(n)}) + \left( \frac{1}{4m^2c^2} \mathbf{U} \mathbf{T}^{-1} - \frac{1}{2mc} X^{(n)} S^{-1} \right) \Delta - \Delta \frac{1}{2mc^2} S^{-1} L^{(n)} - \Delta = 0 \]  \hspace{1cm} (115)

Let this act on the eigenvectors \( \tilde{a}_\mu^{(n)} \) of \( L^{(n)} \) with metric \( S \) and eigenvalues \( E_\mu^{(n)} \)

\[ 0 = F(X^{(n)}) \tilde{a}_\mu^{(n)} + \left[ \left( \frac{1}{4m^2c^2} \mathbf{U} \mathbf{T}^{-1} - \frac{1}{2mc} X^{(n)} S^{-1} - \frac{1}{2mc^2} E_\mu^{(n)} \right) - 1 \right] \Delta \tilde{a}_\mu^{(n)} \]  \hspace{1cm} (116)
From this we get the vectors

$$\vec{d}_\mu = \Delta \vec{a}_\mu$$  \hspace{1cm} (117)

This scheme is of *regula-falsi* type and converges quadratically – if it converges. One must hence take care of having a reasonable starting iteration. This Newton-Raphson (NR) update can be combined with any of the iteration schemes just discussed.
Non-iterative construction of $X$

One construct $X$ and $L$ \textit{without any iteration}, by solving the double-dimension eigenvalue problem (69) and combining the relations (65) for all states $\vec{a}_k, \vec{b}_k$ to the matrix equation

$$B = \frac{1}{2m} T^{-1} X A; \quad X = 2m T B A^{-1}$$

(118)

The eigenvalue problem (69) has twice as many eigenstates as its quasirelativistic counterpart, and one must discard the eigenstates corresponding to positrons.

This non-iterative scheme has probably been first studied by Dyall [9].
Numerical results

In table I the number of iterations sufficient to obtain convergence in the sense of a rather severe criterion are collected.

In the first 2 columns the results for the simple linear iteration schemes are collected. These schemes only converge for small $Z$ and small basis sets. The replacement of $S^{-1}L$ by $\tilde{S}^{-1}\tilde{L}$ as well as the Newton-Raphson update lead to some improvement.

The improved linear iteration schemes are definitely better, especially in the variants in which $S^{-1}L$ is replaced by $\tilde{S}^{-1}\tilde{L}$. In these variants, combined with the NR update, convergence in 3 or 4 iterations has been achieved in all studied cases.

A very robust scheme appears to be that inspired by the DKH transformation, in which a set of quadratic equations is solved at every iteration [7]. This scheme converges in nearly all cases (one exception), even without a NR update, but with this update convergence never requires more than 4 iterations.
Table 1: Number of iterations necessary to converge the ten lowest electronic energies for atomic one-electron ions with charge $Z$ to ten significant digits. (Newton-Raphson update in parentheses).

<table>
<thead>
<tr>
<th>$Z$</th>
<th>basis</th>
<th>based on eqn. number</th>
<th>(90)</th>
<th>(85)</th>
<th>(92)</th>
<th>(103)</th>
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<td>(3)</td>
<td>(3)</td>
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<td>(10)</td>
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<td>(10)</td>
<td>(3)</td>
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The Douglas-Kroll-Hess (DKH) method

In the Douglas-Kroll-Hess (DKH) method one searches for a unitary matrix $W$ that transforms the matrix representation $D$ of the Dirac operator in such a way that in a first step the matrix representation $D_0$ of the Dirac operator for a free particle is transformed to block diagonal form. This is achieved by the matrix representation $W_0$ of the free-particle Foldy-Wouthysen transformation, which is easily performed. It requires only the diagonalization (108) of the matrix $T$ and the solution of a quadratic equation for each eigenvalue.

Transforming $D$ by $W_0$, an off-diagonal block remains, that can be removed by a sequence of further transformations, corresponding to an expansion in powers of the 'coupling strength' (essentially the external potential $V$).

The main difference between the DKH scheme and one variant of our method is that we formulate the theory in terms of the matrix $X$, which satisfies much simpler equations than $W$, and that we do not care to construct $W$ from $X$, before the iteration scheme has converged.
So our scheme is significantly simpler and more efficient than that of DKH, and there is no increase of complexity with the increase of order. In table II and fig. 1 the performance of our iterative scheme, in the variant inspired by DKH, is compared with that of the genuine DKH expansion. For the electronic ground state of Hg$^{79+}$ in a 50s basis the DKH method leads at 14th order to a result with 7 figures accuracy. Our method, without NR update leads to the same accuracy after 6 iterations, while with NR update we obtain 9-figure accuracy after only 3 iterations and 8-figure accuracy after 2 iterations.
Figure 1: The ground state energy of Hg$^{79+}$ from the iteratively constructed quasi-relativistic Hamiltonian, and for different orders of the DKH transformation.
Table 2: The electronic ground state of Hg$^{79+}$ obtained with 50 Gaussian $s$ functions$^a$, in the DKH-like iteration scheme based on eqns. (104, 107), in comparison with various orders of the Douglas-Kroll-Hess (DKH) transformation. NRU: Newton-Raphson update.

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<th>Iteration</th>
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<th>with NRU</th>
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<th>DKH$^c$</th>
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<td>-3532.19267</td>
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</table>


$^b$Oscillation starts from the 15th iteration due to numerical instability.


$^d$75 Gaussian $s$ functions were used therein.

$^e$Four-component Dirac energy value with the same basis set from Ref. $a$.

$^f$Analytic Dirac energy value.
The method of Barysz, Sadlej, and Snijders (BSS)

The method of Barysz, Sadlej, and Snijders (BSS) [15], in its more recent formulation also known as 'infinite-order two-component' (IOTC) method, is closely related to DKH. Like in DKH the first step is the transformation of $D$ with the free-particle Foldy-Wouthysen transformation $W_0$ at matrix level. The remaining transformation $W'$, such that $W = W_0 S^{-1} W'$ is, however, not formulated as a sequence of unitary transformations, but as a single transformation, expressed in terms of a matrix $R$, from which $W'$ is constructed in an iterative way, like in our scheme the full transformation $W$ is constructed from $X$. So the BSS method is somewhere in between DKH and our scheme. Like the DKH method it appears to converge in all cases of interest, though the convergence is often rather slow. A NR update should also be possible within the BSS scheme, but has not yet been tried. An advantage with respect to high-order DKH is that (like in our scheme) there is no increased complexity with increasing order. However, as already mentioned, the way via the free-particle Foldy-Wouthysen transformation, common to DKH and BSS, is only one of several options in our approach.
Spin-orbit couplings in Hg in Hartree

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<tr>
<th>shell</th>
<th>DKS</th>
<th>SESC</th>
<th>Δ</th>
<th>ZORA</th>
<th>Δ</th>
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<td>15.836</td>
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</tr>
<tr>
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<td>0.154</td>
<td>-0.001</td>
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Spectroscopic constants of E117$_2$

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<th>$\omega_e$ [cm$^{-1}$]</th>
<th>$D_e$ [eV]</th>
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<td>$\Delta$ ZORA</td>
<td>0.00250</td>
<td>0.3110</td>
<td>0.01886</td>
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Conclusions

The problem to construct a quasi-relativistic Hamiltonian, that is equivalent (for electronic states) to the original Dirac Hamiltonian, is solved. This construction is possible in an iterative way, starting from the matrix representation of the Dirac operator in a kinetically balanced basis, but cannot be achieved at operator level.

The transformation from the matrix representation of the Dirac operator to a quasi-relativistic Hamiltonian matrix involves a matrix $X$. There are three efficient strategies for the construction of $X$: (1) The iterative solution of a quadratic matrix equation for $X$ and passing by the transformation of the free-particle Dirac Operator to quasirelativistic form. (‘DKH-like’).

However, no obligation to pass via the quasi-relativistic Hamiltonian for free-particles.
(2) and (3) are based on the iterative solution of a coupled set of two pseudolinear matrix equations in terms of $X$ and the quasi-relativistic Hamiltonian $L$, with two ingredients. (a) The pseudolinear equation for $X$ is solved non-iteratively, iterations are only necessary, because there are two coupled matrix equations, and $L$ has to be updated. (b) The iteration is formulated in terms of the hermitean quasirelativistic Hamiltonian $\tilde{L}$ rather than the nonhermitean one, which appears originally.

With a Newton-Raphson update all three schemes converge (for all eigenstates) within 3 or 4 iterations, even for large $Z$ and ‘difficult’ basis sets (involving very steep basis functions).

The non-iterative construction via diagonalization of the matrix representation of the Dirac operator is hardly more demanding than the iterative schemes favored here.

The way via the transformation of the matrix representation of the Dirac operator works because the KB basis is complete for the expansion of the Dirac bispinor. The eigenvalues of the Dirac matrix converge to their exact counterparts.
Completeness of a KB basis

It is shown that the exact relativistic wave function of the ground state of H-like ions can be expanded in a kinetically balanced even-tempered Gaussian basis. Starting point is the existence of a Gaussian integral transformation for the exact relativistic ground state wave function of H-like ions $\psi = (\varphi, \chi)$ with

\[
\begin{align*}
\varphi &= R_g(r) \eta_m^{\kappa_{-1}}; \quad R_g(r) = N_g r^\nu e^{-Zr}; \quad N_g = 2^{\nu+1} Z^{\nu+\frac{3}{2}} \sqrt{2 + \nu} / \sqrt{\Gamma(3 + 2\nu)} \\
\chi &= i R_f(r) \eta_m^{\kappa_1}; \quad R_f(r) = N_f r^\nu e^{-Zr}; \quad N_f = -2^{\nu+1} Z^{\nu+\frac{3}{2}} \sqrt{-\nu} / \sqrt{\Gamma(3 + 2\nu)}
\end{align*}
\]

where $\eta_m^{\kappa}$ is a normalized function of angular and spin variables for the quantum numbers $\kappa$ and $m = m_j$, and $\nu = -1 + \sqrt{1 - Z^2/c^2}$
The integral transformation for the radial wave function $R_g(r)$ of the large (upper) component is

$$R_g(r) = \int_0^\infty f_g(s, Z) \exp(-sr^2)dr$$

$$f_g(s, Z) = Z^{\nu + \frac{5}{2}} 2^{\nu + 1} s^{-\nu - 1} \left[ \Gamma(2\nu + 3) \right]^{-\frac{1}{2}} \sqrt{2 + \nu}$$

$$\times \left\{ Z^{-1} \left[ \Gamma\left(-\frac{\nu}{2}\right) \right]^{-1} M\left(1 + \frac{\nu}{2}, \frac{1}{2}, -\frac{Z^2}{4s}\right) \right.$$

$$\left. - s^{-\frac{1}{2}} \left[ \Gamma\left(-\frac{\nu + 1}{2}\right) \right]^{-1} M\left(\frac{3 + \nu}{2}, \frac{3}{2}, -\frac{Z^2}{4s}\right) \right\}$$

with $M(a, b, x)$, also known as $\,_1F_1(a, b, x)$, Kummer's confluent hypergeometric function. A similar relation holds for the lower (small) component.
This resembles the familiar, and much simpler, non-relativistic counterpart.

\[ \phi_n(\vec{r}) \phi = R_{nr}(r)Y_0^0(\theta, \phi); \quad R_{nr}(r) = 2Z^\frac{3}{2}e^{-Zr} \]

\[ R_n(r) = \int_0^\infty f_n(s, Z) \exp(-sr^2)ds \]

\[ f_n(s, Z) = Z^\frac{5}{2}s^{-\frac{3}{2}} \exp(-\frac{Z^2}{4s}) \]

By means of a variable transformation one can change the integration domain to \((-\infty, +\infty)\). Truncation of the integration limits to finite values and discretization of the integral leads to an approximate expansion of \(R_g(r)\) in a Gaussian basis. The error of the overlap integral between exact and approximate wave functions depends as \(\sim n^{3+\nu} \exp[-\pi \sqrt{\frac{3}{2} + \nu} n]\), with \(\nu = -1 + \sqrt{1 - Z^2/c^2}\), on the size \(n\) of the basis, both for the large and the small component. Even the error of the energy has essentially the same dependence on \(n\) and decays only slightly slower than its nonrelativistic counterpart, which goes as \(\sim n^3 \exp[-\pi \sqrt{\frac{3n}{2}}]\).
Appendix A. Solution of linear and quadratic matrix equations.

For the sake of simplicity we assume in this appendix that all relevant matrices are normal, i.e. can be diagonalized by means of a unitary transformation. If this is not the case, some modifications are necessary, e.g. independent left and right eigenvectors must be considered, or one must only choose approaches that do not involve a diagonalization of matrices.

We want to solve

\[ 0 = \mathbf{F}(\mathbf{X}) = \mathbf{f}(\mathbf{X}) - \mathbf{X} = \mathbf{A} + \mathbf{B}\mathbf{X} + \mathbf{X}\mathbf{C} - \mathbf{X} \quad (119) \]

this is trivial if \( \mathbf{B} = 0 \) or \( \mathbf{C} = 0 \). Then

\[ \mathbf{X} = (1 - \mathbf{B})^{-1}\mathbf{A}; \quad \text{for} \; \mathbf{C} = 0 \; \quad (120) \]

\[ \mathbf{X} = \mathbf{A}(1 - \mathbf{C})^{-1}; \quad \text{for} \; \mathbf{B} = 0 \; \quad (121) \]
Also the case $C = -B$ or

$$0 = \mathbf{F}(\mathbf{X}) = \mathbf{A} + [\mathbf{B}, \mathbf{X}] - \mathbf{X} \quad (122)$$

is rather simple. In the basis, in which $\mathbf{B}$ is diagonal, we get

$$X_{\mu,\mu} = A_{\mu,\mu} \quad (123)$$
$$X_{\mu,\nu} = A_{\mu,\nu} + (B_{\mu,\mu} - B_{\nu,\nu})X_{\mu,\nu}; \; \mu \neq \nu \quad (124)$$

In the case where $B \neq 0; \; C \neq 0$ we can either choose the basis in which $\mathbf{B}$ is diagonal, or that in which $\mathbf{C}$ is diagonal. Let us make the second choice and assume that

$$\mathbf{C} \vec{c}_\mu = \gamma_\mu \vec{c}_\mu \quad (125)$$

Let us define

$$\vec{b}_\mu = \mathbf{X} \vec{c}_\mu \quad (126)$$

and consider

$$0 = \mathbf{F}(\mathbf{X}) \vec{c}_\mu = (\mathbf{A} + [\mathbf{B} + \gamma_\mu - 1] \mathbf{X}) \vec{c}_\mu \quad (127)$$
$$0 = [\mathbf{B} + \gamma_\mu - 1]^{-1} \mathbf{A} \vec{c}_\mu + \vec{b}_\mu \quad (128)$$
So for each $\mu$ we can construct $\vec{b}_\mu$. Combining the $\vec{c}_\mu$ and $\vec{b}_\mu$ to matrices $c$ and $b$ respectively, we can combine (126) for all $\mu$ to a matrix equation

$$b = Xc; \ X = bc^{-1}$$

which allows us to obtain $X$, in a somewhat indirect, but non-iterative way. It may sometimes be simpler to construct $X$ iteratively by the procedure

$$X^{(n+1)} = f(X^{(n)})$$

this requires that $B$ and $C$ are sufficiently small. The convergence is then linear, i.e. it goes like a geometrical series.

For a quadratic matrix equation a non-iterative solution is usually not possible, but a Newton-Raphson (or rather *regula falsi*) type approach is recommended.

We want to solve

$$0 = F(X) = f(X) - X = A + BX + XC + XDX - X$$

(131)
with now a different meaning of $F(X)$ and $f(X)$. In a naive iteration scheme we construct

$$X^{(n+1)} = f(X^{(n)}) \quad (132)$$

In a Newton-Raphson (NR) type approach we start from $F^{(n)} = F(X^{(n)})$ and we want to solve

$$0 = F(X^{(n+1)}) = F(X^{(n)} + \Delta) = F^{(n)} + G(\Delta, X^{(n)}) \quad (133)$$

$$G(\Delta, X) = (B + XD)\Delta + \Delta(C + DX) - \Delta \quad (134)$$

for $\Delta$. In $G$ we ignore terms quadratic and of higher order in $\Delta$, and get so a linear system of equations for $\Delta$, to be solved as indicated above.

In the case, in which we are interested, we have

$$F(X) = c^{-1}T + \frac{1}{4m^2c^2}UT^{-1}X - \frac{1}{2mc^2}XS^{-1}V - \frac{1}{2mc}XS^{-1}X - X \quad (135)$$

$$G(\Delta, X) = \left(\frac{1}{4m^2c^2}UT^{-1} - \frac{1}{2mc}XS^{-1}\right)\Delta$$
\[- \Delta \left( \frac{1}{2mc^2} S^{-1} V + \frac{1}{2mc} S^{-1} X \right) - \Delta \]

\[= \left( \frac{1}{4m^2c^2} U T^{-1} - \frac{1}{2mc} X S^{-1} \right) \Delta - \Delta \frac{1}{2mc^2} S^{-1} L - \Delta \]  \\

(136)

We let this act on the eigenvectors $\vec{a}_\mu$ of $L$ with metric $S$ and eigenvalues $E_\mu$

\[0 = F_n \vec{a}_\mu + \left( \frac{1}{4m^2c^2} U T^{-1} - \frac{1}{2mc} X S^{-1} + \frac{1}{2mc^2} E_\mu - 1 \right) \Delta \vec{a}_\mu \]  \\

(137)

From this we get the vectors

\[\vec{d}_\mu = \Delta \vec{a}_\mu \]  \\

(138)

and from the $\vec{a}_\mu$ and $\vec{d}_\mu$ finally $\Delta$, that we use to update $X$. 
References


