GEMINALS IN DIRAC-COULOMB HAMILTONIAN EIGENVALUE PROBLEM

Grzegorz Pestka, Mirosław Bylicki, Jacek Karwowski

Instytut Fizyki, Uniwersytet Mikołaja Kopernika, Toruń

Third International meeting:

MATHEMATICAL METHODS FOR AB INITIO QUANTUM CHEMISTRY

Laboratoire J. A. Dieudonneé
CNRS et Université de Nice-Sophia-Antipolis
19-20 October 2007

CONTENTS

DIRAC, LÉVY-LEBLOND AND SCHRÖDINGER EQUATIONS

Dirac equation:

$$\begin{bmatrix} (\mathsf{V}-E)\mathsf{I}_2, & c(\boldsymbol{\sigma}\cdot\mathbf{p}) \\ c(\boldsymbol{\sigma}\cdot\mathbf{p}), & (\mathsf{V}-E-2mc^2)\mathsf{I}_2 \end{bmatrix} \begin{bmatrix} \Psi^{\mathrm{l}} \\ \Psi^{\mathrm{s}} \end{bmatrix} = 0,$$

Ψ^{l}, Ψ^{s} - two-component spinors;
$\boldsymbol{\sigma}$ – 2×2 Pauli matrices;
I_2 – 2×2 unit matrix

The non-relativistic limit ($c \to \infty$) – Lévy-Leblond equation:

$$\begin{bmatrix} (\mathsf{V}-E)\mathsf{I}_2, & (\boldsymbol{\sigma}\cdot\mathbf{p}) \\ (\boldsymbol{\sigma}\cdot\mathbf{p}), & -2m\mathsf{I}_2 \end{bmatrix} \begin{bmatrix} \Psi^{\mathrm{l}} \\ c\Psi^{\mathrm{s}} \end{bmatrix} = 0.$$

DIRAC, LÉVY-LEBLOND AND SCHRÖDINGER EQUATIONS

The second pair of LL equations:

$$c\Psi^{\mathrm{s}} = \frac{1}{2m}(\boldsymbol{\sigma} \cdot \mathbf{p})\, \Psi^{\mathrm{l}}.$$

Elimination of Ψ^{s} from the first pair gives:

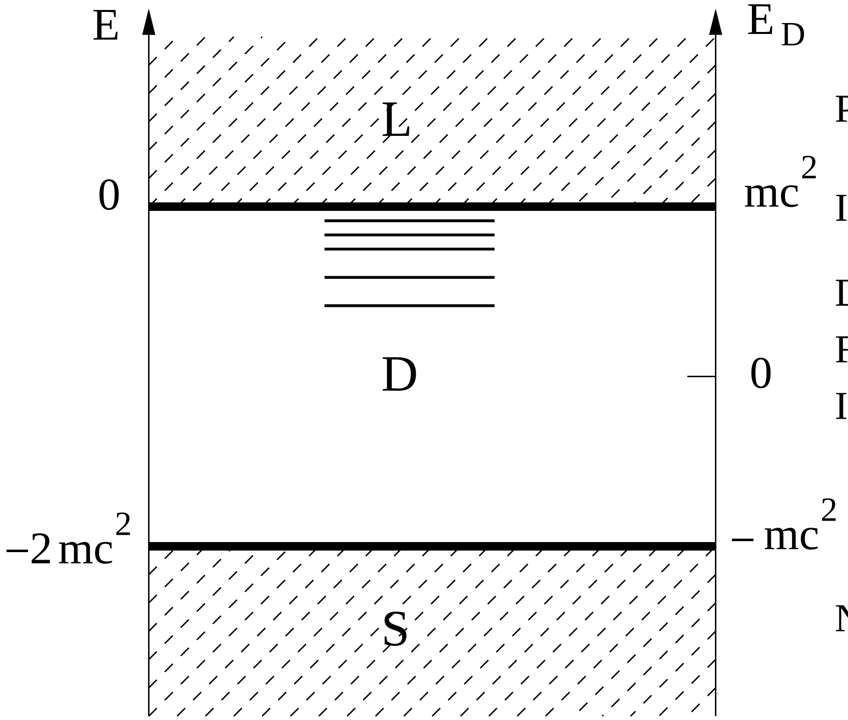
$$\left[\frac{(\boldsymbol{\sigma} \cdot \mathbf{p})^2}{2m} + (\mathsf{V} - E)\mathsf{I}_2\right] \Psi^{\mathrm{l}} = 0,$$

Since $(\boldsymbol{\sigma} \cdot \mathbf{p}) = \mathsf{p}^2\, \mathsf{I}_2$, we get two identical Schrödinger equations.

Their solution ψ correspond to two spinorbitals with spins α and β:

$$\Psi^{\mathrm{l}}_{\alpha} = \psi \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad \text{and} \quad \Psi^{\mathrm{l}}_{\beta} = \psi \begin{bmatrix} 0 \\ 1 \end{bmatrix}.$$

SPECTRUM OF ONE-ELECTRON DIRAC HAMILTONIAN



POSITIVE−ENERGY CONTINUUM

IONIZATION THRESHOLD

DISCRETE BOUND−STATE ENERGIES,

FORBIDDEN ENERGY GAP

IN THE CASE OF A FREE ELECTRON

NEGATIVE−ENERGY CONTINUUM

ENERGY FUNCTIONAL

Rayleigh quotient: $$K[\Phi] = \frac{\langle\Phi|\mathsf{H}|\Phi\rangle}{\langle\Phi|\Phi\rangle}, \quad \Phi = \begin{bmatrix} c_a\Phi^{\mathrm{l}} \\ c_b\Phi^{\mathrm{s}} \end{bmatrix}$$

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

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

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

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

ENERGY FUNCTIONAL

LL energy functional: $K[\Phi]_L = T + \frac{\langle \Phi^{\rm l} | \mathsf{V} | \Phi^{\rm l} \rangle}{\langle \Phi^{\rm l} | \Phi^{\rm l} \rangle}$

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

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

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

Kinetic balance condition $\Rightarrow$ $\left\{ \begin{array}{l} \text{variational LL and Schrödinger} \\ \text{eigenvalue problems are equivalent.} \end{array} \right.$

ALGEBRAIC REPRESENTATION: MODEL SPACE

Basis set expansion of the components of the trial function

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

leads to the algebraic approximation to the Dirac equation.

The kinetic balance condition implies

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

where $\mathcal{H}\{\Phi\}$ – space in which Φ is expanded.

This condition is necessary for the correct behaviour of the variational procedure applied to the Dirac equation.

ALGEBRAIC REPRESENTATION

Dirac equation: variation of $K[\Phi]$ leads to an algebraic $2N \times 2N$ eigenvalue problem:

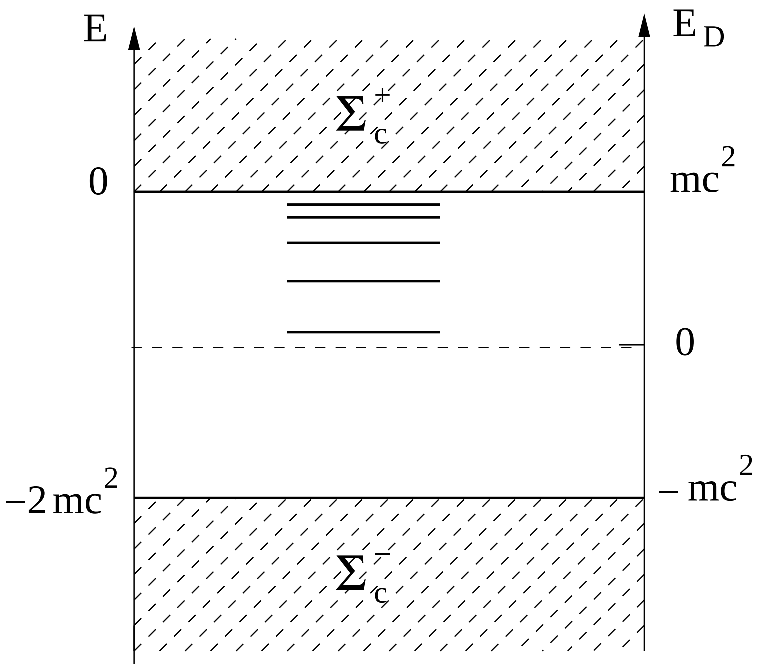
$$\begin{pmatrix} \boldsymbol{H}_{\mathrm{LL}} - E\boldsymbol{S}_{\mathrm{LL}} & c\,\boldsymbol{H}_{\mathrm{LS}} \\ c\,\boldsymbol{H}_{\mathrm{SL}} & \boldsymbol{H}_{\mathrm{SS}} - E\boldsymbol{S}_{\mathrm{SS}} \end{pmatrix} \begin{pmatrix} \boldsymbol{C}^{\mathrm{L}} \\ \boldsymbol{C}^{\mathrm{S}} \end{pmatrix}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

Lévy-Leblond equation: $N \times N$ matrix eigenvalue equation:

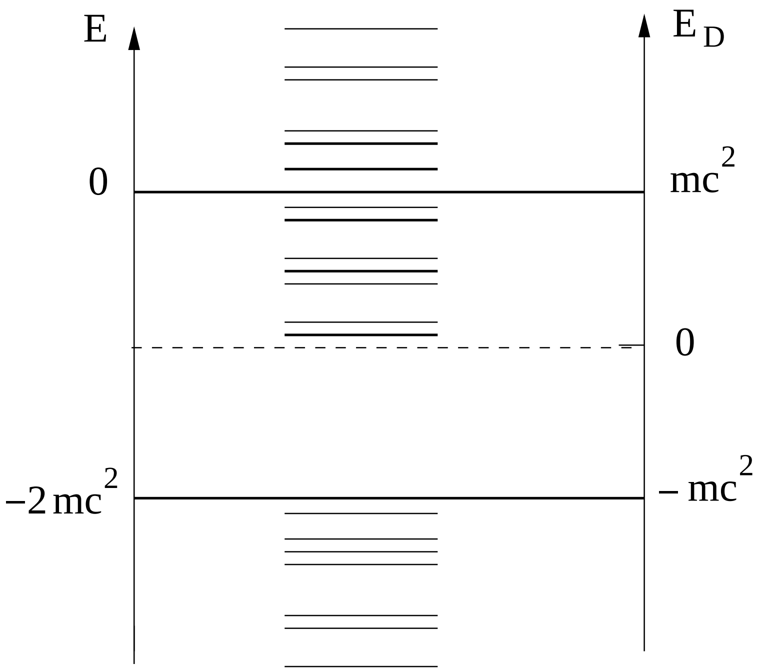
$$(\boldsymbol{H} - E\boldsymbol{S}_{\mathrm{LL}})\,\boldsymbol{C}^{\mathrm{L}} = 0,$$

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

ALGEBRAIC REPRESENTATION: SPECTRUM



EXACT SPECTRUM



ALGEBRAIC REPRESENTATION

EXAMPLE: HYDROGEN-LIKE ATOM

Symmetry-adapted basis functions:

$$\Phi^{\rm l} = \frac{\phi^{\rm l}(r)}{r} A^{\rm l}(\Omega), \qquad \Phi^{\rm s} = \frac{\phi^{\rm s}(r)}{r} A^{\rm s}(\Omega)$$

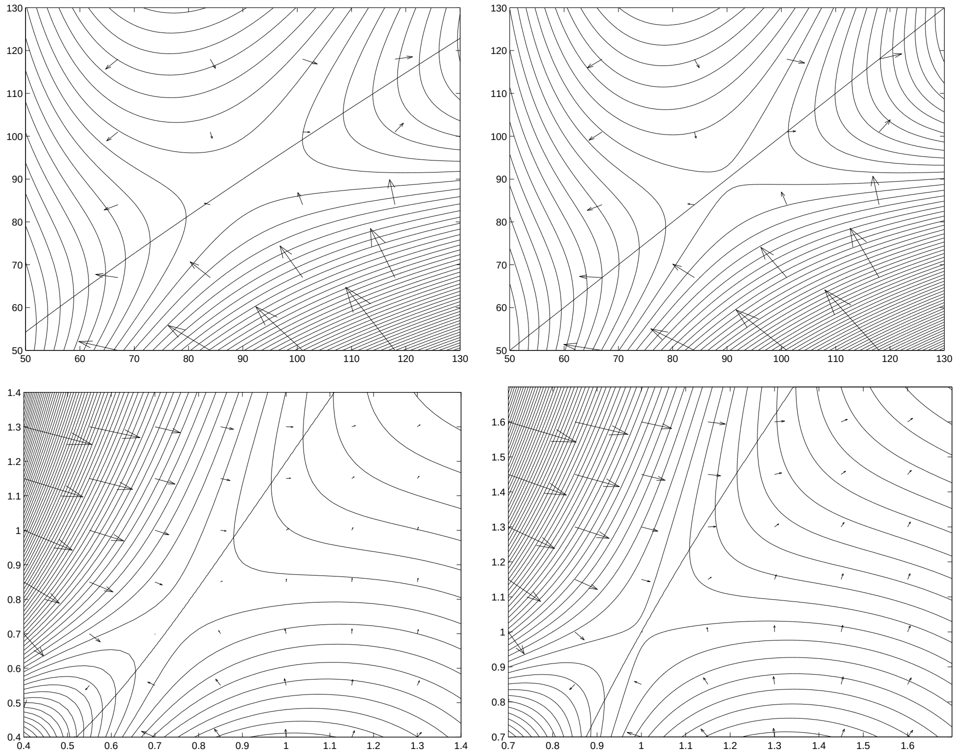
$A(\Omega)$ – exact spin-angular functions

$$\phi^{\rm l} = \sum_{k=1}^{N} C_k^{\rm L}\, r^{l_k} {\rm e}^{\alpha_k}, \qquad \phi^{\rm s} = \sum_{k=1}^{N} C_k^{\rm S}\, r^{s_k} {\rm e}^{\beta_k}$$

STRUCTURE OF THE SADDLE POINT

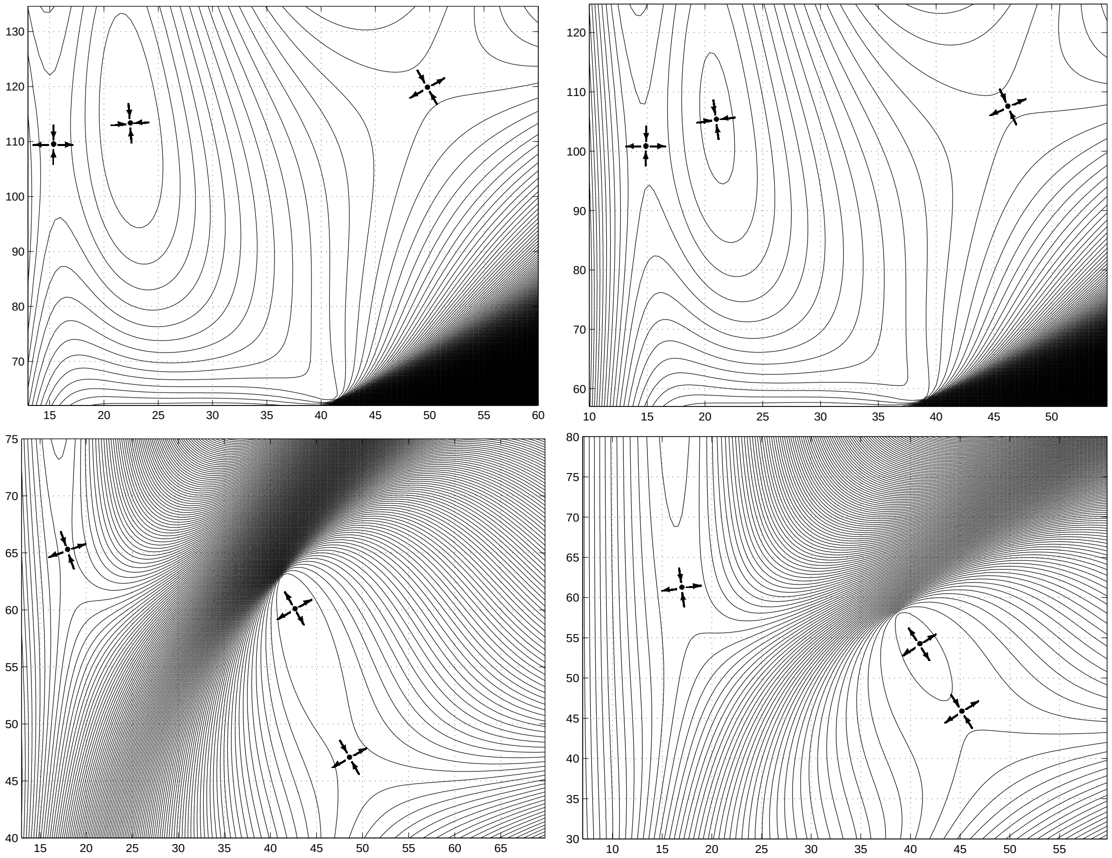
Ground state of $Z = 90$ H-like atom, $N = 1$, Dirac (left), LL (right)

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



M. Stanke *et al*, in ’Quantum systems in chemistry and physics’, Kluwer 2001

$P_{1/2}$ states of $Z = 90$ H-like atom, $N = 2$, Dirac (left), LL (right)
$E = E(\alpha_1, \beta_1)|_{l_1 = s_1 = \mathrm{exact}}$ first (up) and second (down) eigenvalue.



Extrema in $P_{1/2}$ energy surfaces of $Z = 90$ H-like atom (boldface).

Exact energies: $E_{1s_{1/2}} = -4618$, $E_{2P_{1/2}} = -1192$, $E_{3p_{1/2}} = -512$.

${}_N E_m$ – the m-th eigenvalue in N-element basis set.

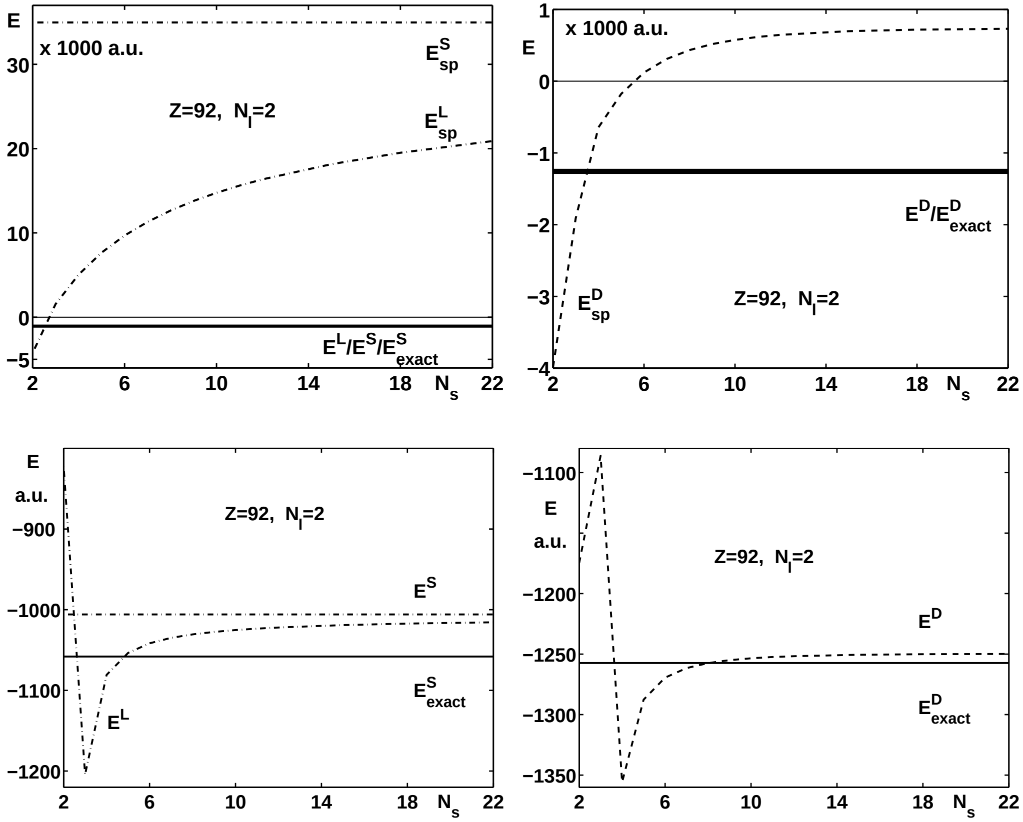
Subscripts: s-saddle, n-minimum, x-maximum.

α	β	${}_1E_1$	${}_2E_1$	${}_2E_2$	${}_3E_1$	${}_3E_2$
22	112	$-\mathbf{1125}_s$	$-\mathbf{1125}_x$	-438	-1148	-587
50	120	-922	$-\mathbf{1220}_s$	2296	$-\mathbf{1220}_s$	-387
15	109	-1057	$-\mathbf{1149}_s$	-527	-1102	-547
18	65	-1149	-1206	$-\mathbf{500}_s$	-1172	$-\mathbf{500}_s$
42	61	-2604	-1599	$-\mathbf{1198}_n$	$-\mathbf{1198}_x$	-732
48	48	-3804	-4430	$-\mathbf{1192}_s$	-4585	$-\mathbf{1192}_n$

The exact $2p_{1/2}$ state ($\alpha = \beta = 48$) appears as the **second** root.

The lowest, **spurious** root is close to the energy of $1s_{1/2}$.

Spurious roots correspond to incorrectly represented states of the positive continuum – they enter the continuum for sufficiently large N_{s}.



[*G. Pestka*, Phys. Scripta **68** (2003) 254-258]

BOUNDS TO EIGENVALUES: MINIMAX PRINCIPLE

- Relativistic variational principle: A recipe for reaching the stationary point in the energy hypersurface in the space of variational parameters:

$$\boldsymbol{E} = \min_{\{\mathrm{l}\}} \left[\max_{\{\mathrm{s}\}} \frac{\langle \boldsymbol{\Psi} | \mathbf{H} | \boldsymbol{\Psi} \rangle}{\langle \boldsymbol{\Psi} | \boldsymbol{\Psi} \rangle} \right].$$

- Hylleraas-Undheim-McDonald bound conditions are fulfilled if

$$\bigcup_{\nu=1}^{N_{\mathrm{l}}} \left[\left(\tilde{E}_\nu + 2mc^2 - \mathsf{V} \right)^{-1} (\boldsymbol{\sigma} \cdot \mathbf{p})\ \mathcal{H}^{\mathrm{l}} \right] \subset \mathcal{H}^{\mathrm{s}},$$

V - a non-positive-defined external potential.

- Coulomb-like potentials - approximated by asymptotic balance condition

$$\left[(\boldsymbol{\sigma} \cdot \mathbf{p})\ \mathcal{H}^{\mathrm{l}} \right] \cup \left[r\, (\boldsymbol{\sigma} \cdot \mathbf{p})\ \mathcal{H}^{\mathrm{l}} \right] \subset \mathcal{H}^{\mathrm{s}}.$$

BOUNDS TO EIGENVALUES

- The first correct formulation of the minimax principle:
  J. Wood, I. P. Grant and S. Wilson, J. Phys. B **18**, 3027 (1985)
- Structuring into a universal principle:
  J. D. Talman, Phys. Rev. Letters **57**, 1091 (1986)
  S. N. Datta and G. Deviah, Pramana, **30**, 387 (1988)
- A critical review:
  W. Kutzelnigg, Chem. Phys. **225**, 203 (1997)
- Correct large – small-component space relations ⇒ correct results:
  J. Dolbeault, M. J. Esteban, E. Séré and M. Vanbreugel, Phys. Rev. Letters **85**, 4020 (2000)
- Bounds to the algebraic eigenvalues; asymptotic balance condition:
  G. Pestka, Phys. Scri. 69 (2004) 203-207.

TWO-ELECTRON DIRAC-COULOMB EQUATION

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

Dirac-Coulomb Hamiltonian:

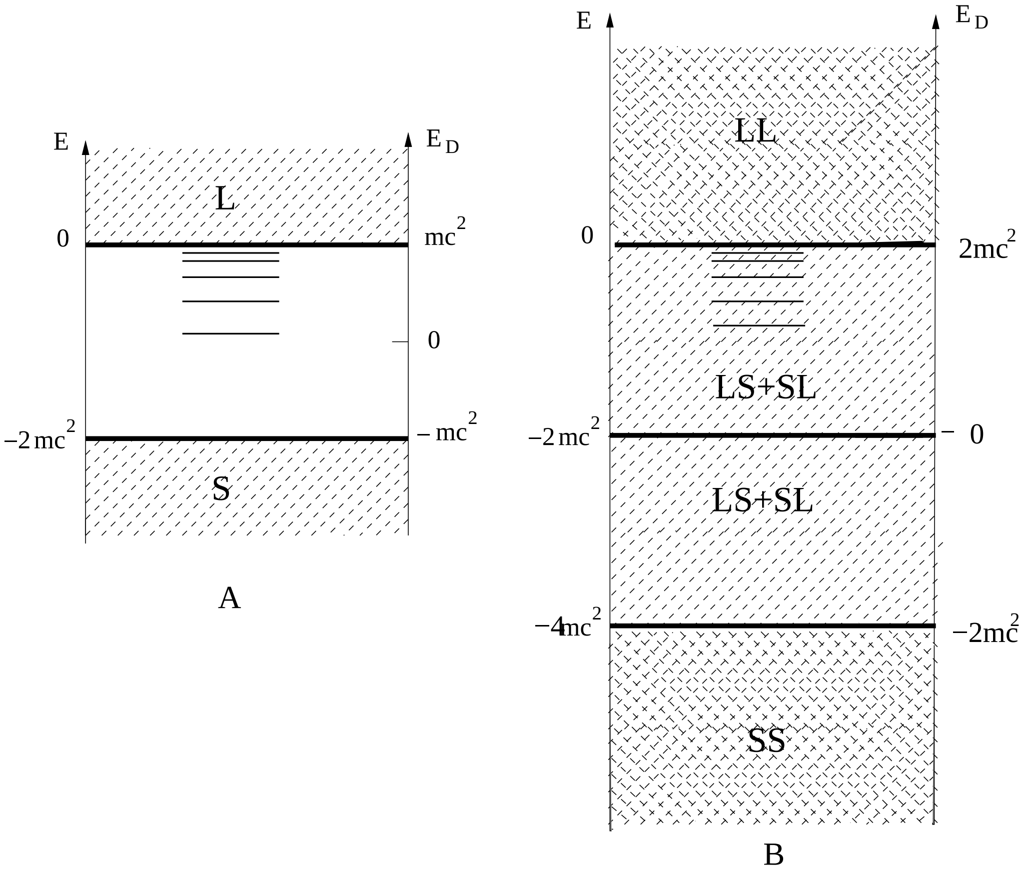
$$H_{\mathrm{DC}}(1,2) = \mathcal{H}_{\mathrm{D}}(1) + \mathcal{H}_{\mathrm{D}}(2) + \frac{1}{r_{12}}$$

A strange hybrid composed of a relativistic one-electron part and a non relativistic two-electron term. Its eigenvalue problem has been a subject of controversy for more than half a century, since Brown and Ravenhall noticed in 1951 that the eigenvalues corresponding to the bound-state solutions are embedded in a continuum spreading from $-\infty$ to $+\infty$ and that the discrete and the continuum spectra are coupled by the electron-electron interaction. This effect is known as the Brown-Ravenhall disease and the continuum is referred to as the Brown-Ravenhall continuum.

Note: It is nothing special if discrete and continous spectra overlap.
The trouble starts when the corresponding states cannot be decoupled.

SPECTRUM OF DIRAC-COULOMB EQUATION

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



Two-electron discrete and continuous (LS+SL) spectra overlap.

ARTIFACTS OF DIRAC-COULOMB EQUATION

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

CONTROVERSY ABOUT DIRAC-COULOMB EQUATION

- J. Sucher, PRL 1985: *Configuration-space Hamiltonians obtained from quantum field theory invariably involve positive-energy projection operators surrounding the interparticle potentials ().*
- P. Indelicato, PRA 1995: *The necessity of using projection operators to avoid mixing of positive and negative energy eigenstates () is discussed. () The convergence problems observed at high* Z *() are due to the absence of such projection operators in previous calculations.*
- W. R. Johnson *et al.*, a review, 2004: *()* E_{Dirac} *may look perfectly normal () when negative-energy basis functions are also included. Nevertheless, it is very difficult, if not impossible, to identify and correct the intrinsic errors in* E_{Dirac} *and the use of many-electron Dirac Hamiltonian without the projection operators should be avoided ().*

CONTROVERSY ABOUT DIRAC-COULOMB EQUATION

- I. P. Grant, Il Cioco REHE conference, 1995: *Maintaining integrity of Dirac states simplifies calculations and stays closer to physics. Suggested solutions as projection operators and two-component methods, are not needed.*

- I. P. Grant & H. M. Quiney, IJQCh 2000: *It is commonly believed that variational methods cannot be used with Dirac-Coulomb operators (). Sucher warns that one should try to eliminate negative energy states by surrounding every operator by projection operators. () Projection operators used in this way play no part in our formulation.*

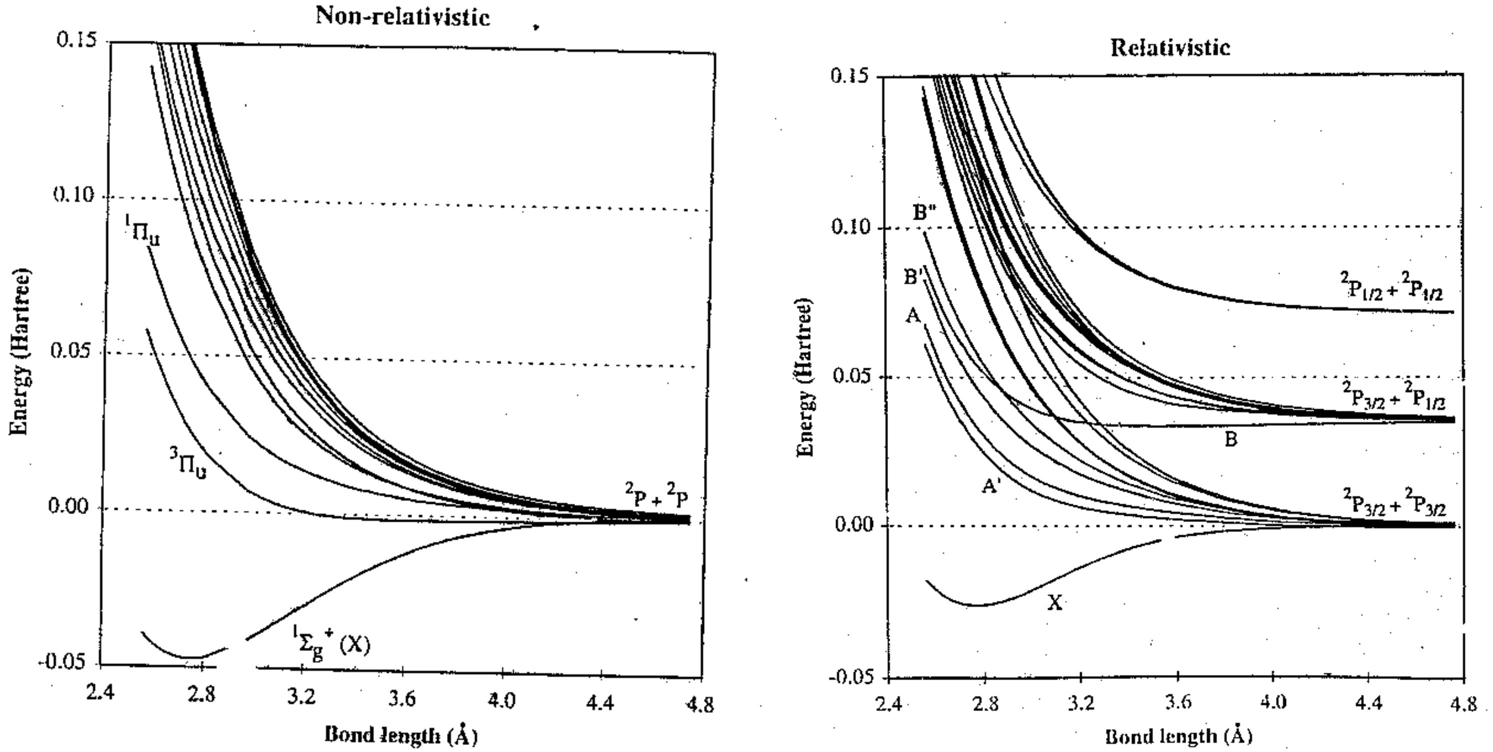
- I. P. Grant & H. M. Quiney, PRA 2000: *() The partition between positive- and negative-energy states depends on the choice of potential, eposing the major flaw in proposals to eliminate the influence of negative-energy states with projection operators.*

AN EMPIRICAL OBSERVATION:

The most successful and commonly used relativistic models of atoms and molecules have been derived from variational methods applied to a non-projected Dirac-Coulomb equation

Note: Some researchers claim that the projection operators are present implicitly in these models. However, to my knowledge, nobody either extracted these implicit projectors from the models or defined their form.

EXAMPLE: POTENTIAL ENERGY CURVES



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

EXAMPLE: X-RAY SPECTRA

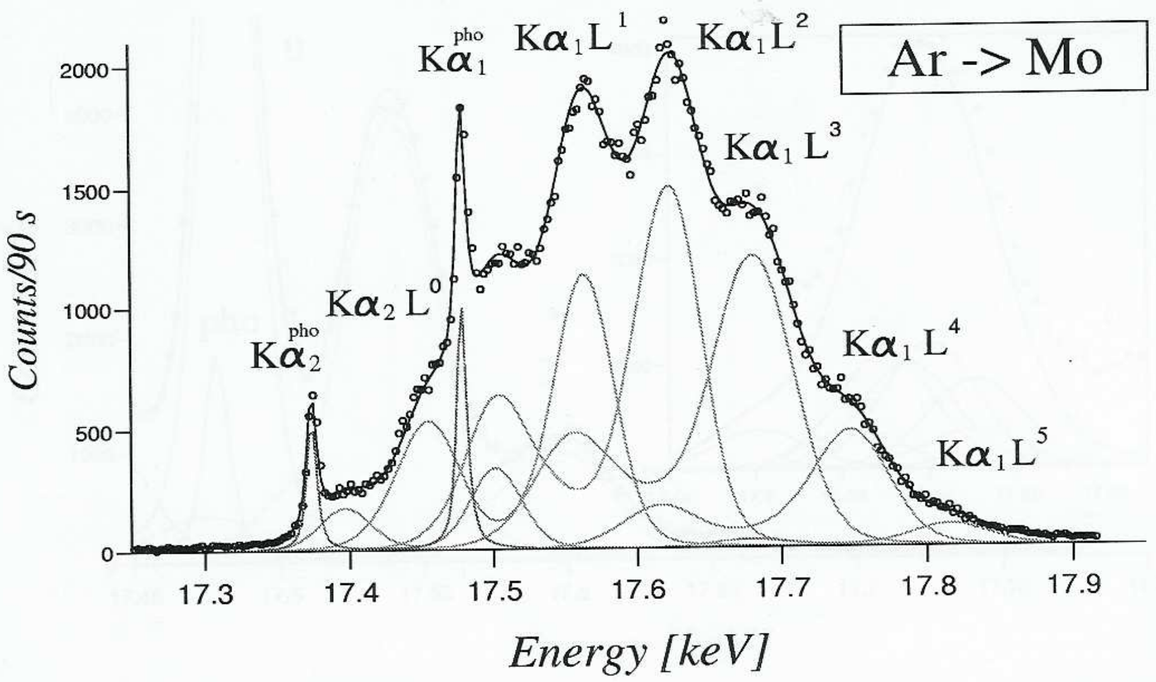


Figure 1: High-resolution crystal spectrometer spectrum of molybdenum $K\alpha$ x-rays. The metallic target was bombarded by Argon ions, accelerated by the cyclotron to an energy of 280 MeV. The dots correspond to the experimental points and the curve to the fit. The figure shows the $K\alpha L$ satellite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

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

CI, HYLLERAAS-CI AND MCDF

CI: $\Psi^{(\mathrm{t})}_{\mathrm{CI}} = \sum_{i\in B_t} C_i \Phi_i^{(\mathrm{t})}\left(\{\phi\}\right),$ fixed orbitals $\{\phi_p\}_{p=1}^K,$

Hy-CI: $\Psi_{\mathrm{HyCI}} = \sum_t r_{12}^t \sum_{i\in B_t} C_{ti}\Phi_i^t\left(\{\phi\}\right)$ fixed orbitals $\{\phi_p\}_{p=1}^K,$

MCDF: $\Psi_{\mathrm{MCDF}} = \sum_i C_i \Phi_i\left(\{\phi\}\right)$ orbitals optimized.

where $\phi_p = \sum_j c_{jp}\chi_j$. Coefficients C_i or C_{ti} are always optimized. Coefficients c_{jp} are optimized in MCDF but predetermined and fixed in CI and in Hy-CI.

Non-relativistic correlation energy: $E^{\mathrm{corr}}_{\mathrm{nr}} = E_{\mathrm{Schr}} - E_{\mathrm{HF}},$

Relativistic correlation energy: $E^{\mathrm{corr}}_{\mathrm{rel}} = E_{\mathrm{DC}} - E_{\mathrm{DF}},$

Relativity-correlation cross corrections: $E_{\mathrm{x}} = E^{\mathrm{corr}}_{\mathrm{rel}} - E^{\mathrm{corr}}_{\mathrm{nr}}.$

ALGEBRAIC APPROXIMATION

In many-electron case the DC Hamiltonian eigenvalue problem is replaced by an eigenvalue problem of its matrix representative in a properly constructed **model space**. In a two-electron case it is convenient to split the model space to three subspaces:

- LL – In the one-electron picture both electrons occupy the positive-energy space (PES). In the non-relativistic limit it is the model space of the Lévy-Leblond equation.
- $\mathrm{LS} + \mathrm{SL}$ – In the one-electron picture one electron occupies PES and the other one the negative energy space. This subspace describes the *Brown-Ravenhall continuum* spreading from $-\infty$ to $+\infty$.
- SS – Both electrons occupy the negative-energy space. This subspace corresponds to the negative continuum of the DC Hamiltonian, spreading from $-4mc^2$ to $-\infty$.

ALGEBRAIC APPROXIMATION

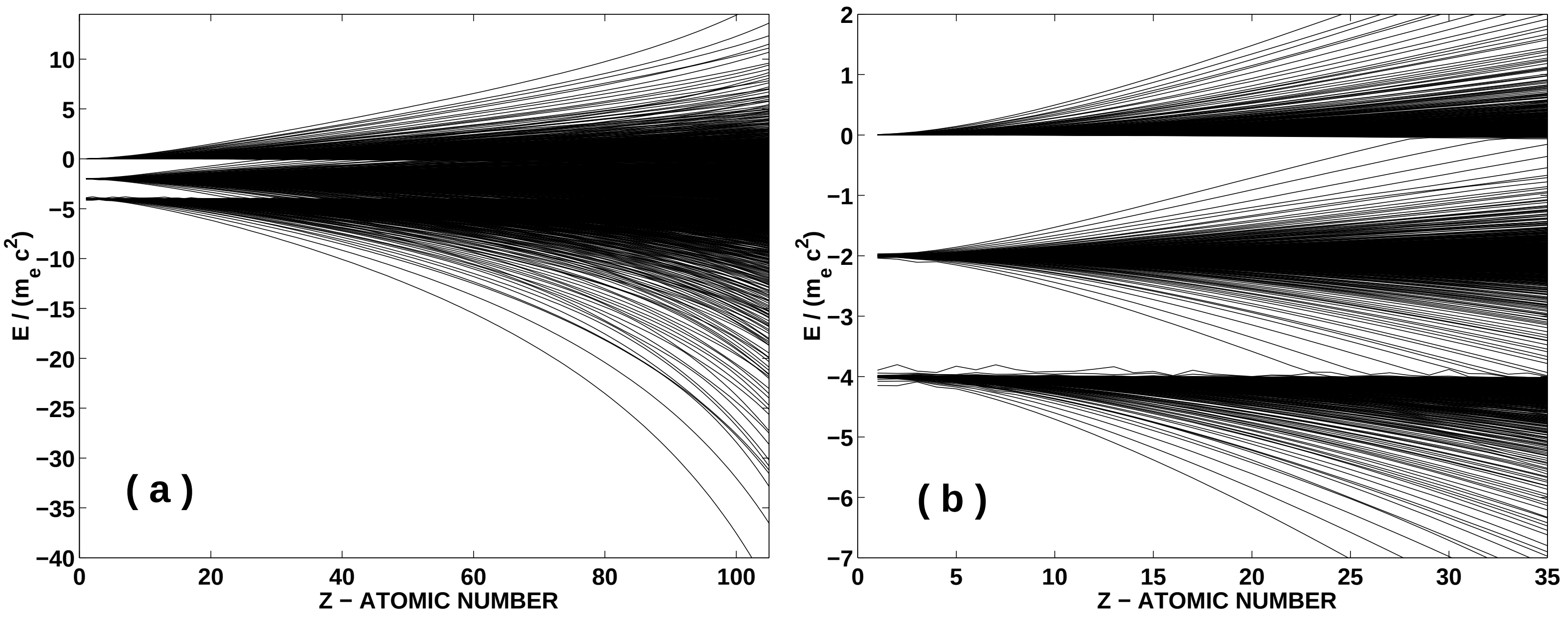
Each of these subspaces is spanned by a separate basis set of the primitive functions. The basis sets have to be related by two-electron generalizations of the kinetic balance condition.

The two-electron wavefunctions are obtained as a result of the diagonalization of the Hamiltonian matrix. Each wavefunction contains contributions from all subspaces of the model space.

The eigenvalues of the Hamiltonian matrix form a finite and discrete set. Some of them represent either the bound or the autoinizing states, but the majority correspond to the three continua of the DC Hamiltonian.

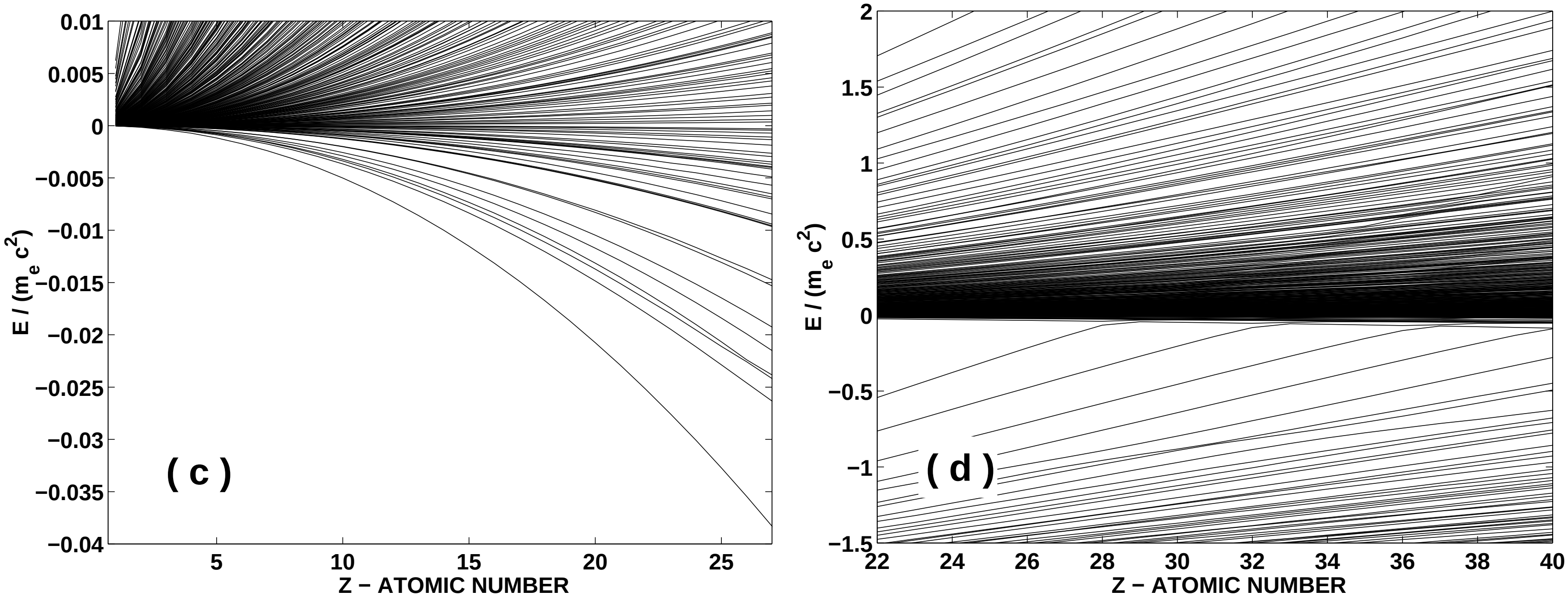
ALGEBRAIC APPROXIMATION

Eigenvalues of the Dirac Hamiltonian matrix for helium like atoms. The bundles of lines correspond to LL, LS + SL and SS subspaces of 1131-dimensional Hy-CI model space. The number of the eigenvalues in each bundle is equal to the dimension of the corresponding subspace of the model space.



ALGEBRAIC APPROXIMATION

Enlargement of the area corresponding to the discrete spectrum. The lowest line in (c) and the low edge of the black area in (d) correspond to the ground state. Crossings between LS + SL and the discrete eigenvalues in (d) are the numerical manifestations of the Brown-Ravenhall disease. They are responsible for the numerical instabilities in variational calculations.



ELECTRON-ELECTRON INTERACTION

$$h_2(1,2) = \frac{1}{r_{12}}$$

The electron correlation cusp [Kato 1957, Kutzelnigg 1989]:

$$\Psi(\vec{r}_1, \vec{r}_2) \sim a\, r_{12}^{q} + b\, r_{12}^{q+1}, \quad \text{if} \;\; r_{12} \to 0$$

a, b - state-dependent constants

$$q = \sqrt{1 - \alpha^2/4} - 1 = \begin{cases} 0 & \text{nonrelativistic theory} \\ -1.3 * 10^{-5} & \text{relativistic theory} \end{cases}$$

Due to a poor representation of the cusp by expansions in the orbital space, a fast convergence of CI expansions may only be obtained if r_{12}-dependent terms are present in the trial function.

TWO-ELECTRON DIRAC-COULOMB EQUATION

Hamiltonian:

$$\mathbf{H}(\mathbf{1},\mathbf{2}) =$$

$$\begin{pmatrix} V(1,2) & c\,(\boldsymbol{\sigma}_2 \cdot \boldsymbol{p}_2) & c\,(\boldsymbol{\sigma}_1 \cdot \boldsymbol{p}_1) & \mathbf{0} \\ c\,(\boldsymbol{\sigma}_2 \cdot \boldsymbol{p}_2) & V(1,2) - 2mc^2 & \mathbf{0} & c\,(\boldsymbol{\sigma}_1 \cdot \boldsymbol{p}_1) \\ c\,(\boldsymbol{\sigma}_1 \cdot \boldsymbol{p}_1) & \mathbf{0} & V(1,2) - 2mc^2 & c\,(\boldsymbol{\sigma}_2 \cdot \boldsymbol{p}_2) \\ \mathbf{0} & c\,(\boldsymbol{\sigma}_1 \cdot \boldsymbol{p}_1) & c\,(\boldsymbol{\sigma}_2 \cdot \boldsymbol{p}_2) & V(1,2) - 4mc^2 \end{pmatrix}$$

$$V(1,2) = -\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

TWO-ELECTRON DIRAC-COULOMB EQUATION

Wavefunction:

$$\Psi(\mathbf{1},\mathbf{2}) = \begin{pmatrix} \psi^{\mathrm{ll}}(\boldsymbol{x}_1,\boldsymbol{x}_2) \\ \psi^{\mathrm{ls}}(\boldsymbol{x}_1,\boldsymbol{x}_2) \\ \psi^{\mathrm{sl}}(\boldsymbol{x}_1,\boldsymbol{x}_2) \\ \psi^{\mathrm{ss}}(\boldsymbol{x}_1,\boldsymbol{x}_2) \end{pmatrix},$$

The antisymmetry condition $\Psi(\mathbf{1},\mathbf{2}) = -\Psi(\mathbf{2},\mathbf{1})$ implies:

$$\psi^{\mathrm{ll}}(\mathbf{1},\mathbf{2}) = -\psi^{\mathrm{ll}}(\mathbf{2},\mathbf{1})$$

$$\psi^{\mathrm{ls}}(\mathbf{1},\mathbf{2}) = -\psi^{\mathrm{sl}}(\mathbf{2},\mathbf{1})$$

$$\psi^{\mathrm{ss}}(\mathbf{1},\mathbf{2}) = -\psi^{\mathrm{ss}}(\mathbf{2},\mathbf{1})$$

TWO-ELECTRON LÉVY-LEBLOND EQUATION

$$\begin{aligned}
(\boldsymbol{\sigma}_2 \cdot \boldsymbol{p}_2)\psi_\nu^{\mathrm{ls}} + (\boldsymbol{\sigma}_1 \cdot \boldsymbol{p}_1)\psi_\nu^{\mathrm{sl}} &= (E_\nu^0 - V)\psi_\nu^{\mathrm{ll}}, \\
(\boldsymbol{\sigma}_2 \cdot \boldsymbol{p}_2)\psi_\nu^{\mathrm{ll}} &= 2\mathfrak{m}\psi_\nu^{\mathrm{ls}}, \\
(\boldsymbol{\sigma}_1 \cdot \boldsymbol{p}_1)\psi_\nu^{\mathrm{ll}} &= 2\mathfrak{m}\psi_\nu^{\mathrm{sl}},
\end{aligned}$$

If

$$\begin{pmatrix} (\boldsymbol{\sigma}_2 \cdot \boldsymbol{p}_2) \\ (\boldsymbol{\sigma}_1 \cdot \boldsymbol{p}_1) \end{pmatrix} \mathcal{H}^{\mathrm{ll}} \subset \mathcal{H}^{ls} \oplus \mathcal{H}^{sl},$$

then LL equation transforms to two-electron Schrödinger equation.

TWO-ELECTRON KINETIC BALANCE CONDITIONS

$$\left[\begin{pmatrix} (\boldsymbol{\sigma}_2 \cdot \boldsymbol{p}_2) \\ (\boldsymbol{\sigma}_1 \cdot \boldsymbol{p}_1) \end{pmatrix} \mathcal{H}^{\mathrm{ll}} \cup \begin{pmatrix} (\boldsymbol{\sigma}_1 \cdot \boldsymbol{p}_1) \\ (\boldsymbol{\sigma}_2 \cdot \boldsymbol{p}_2) \end{pmatrix} \mathcal{H}^{\mathrm{ss}}\right] \subset \mathcal{H}^{ls} \oplus \mathcal{H}^{sl},$$

$$\left[(\boldsymbol{\sigma}_1 \cdot \boldsymbol{p}_1)\,,\,(\boldsymbol{\sigma}_2 \cdot \boldsymbol{p}_2)\right]\left[\mathcal{H}^{ls} \oplus \mathcal{H}^{sl}\right] \subset \mathcal{H}^{\mathrm{ss}}.$$

The conditions generate new correlation factors:

$$\left[(\boldsymbol{\sigma}_1 \cdot \boldsymbol{p}_1) f_n^{[r]}(r_{12})\right] \quad \text{in} \;\; \Phi^{\mathrm{ls}}$$

$$\left[(\boldsymbol{\sigma}_1 \cdot \boldsymbol{p}_1)(\boldsymbol{\sigma}_2 \cdot \boldsymbol{p}_2) f_n^{[r]}(r_{12})\right] \quad \text{in} \;\; \Phi^{\mathrm{ss}},$$

TWO-ELECTRON BASIS FUNCTIONS IN $\mathcal{H}^{\mathrm{ab}}$

Radial functions, $(\Gamma = \{n_1, n_2, \gamma_1, \gamma_2, \beta_1, \beta_2\})$:

$$\Phi^{[r],JM\Pi}_{n,\Gamma;\Lambda}(\boldsymbol{x}_1, \boldsymbol{x}_2) = f^{[r]}_n(r_{12}) r_1^{\gamma_1+n_1} r_2^{\gamma_2+n_2}\, e^{-(\beta_1 r_1+\beta_2 r_2)} \Omega^{JM\Pi}_{\Lambda}(\hat{\boldsymbol{r}}_1, \hat{\boldsymbol{r}}_2),$$

Angular spinors, $(\hat{\boldsymbol{r}} = \boldsymbol{r}/r)$:

$$\Omega^{JM\Pi}_{\Lambda}(\hat{\boldsymbol{r}}_1, \hat{\boldsymbol{r}}_2) = \sum_{m_1,m_2} \begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M \end{pmatrix} \phi_{\lambda_1\lambda_2}(\hat{\boldsymbol{r}}_1, \hat{\boldsymbol{r}}_2)$$

$\lambda_j \equiv \{j_j, m_j, \pi_j\}$, J, M, Π - angular momentum and parity q.n.

$$\phi_{\lambda_1\lambda_2}(\hat{\boldsymbol{r}}_1, \hat{\boldsymbol{r}}_2) = \varphi_{j_1 m_1 \pi_1}(\hat{\boldsymbol{r}}_1) \otimes \varphi_{j_2 m_2 \pi_2}(\hat{\boldsymbol{r}}_2),$$

$\varphi_{jm\pi}(\hat{\boldsymbol{r}})$ - spin and angular part of the one-electron Pauli spinor.

MATRIX ELEMENTS

Matrix elements may be expressed in terms of the primitive two-electron integrals: $\langle B|f(r_{12})\hat{\tau}|K\rangle$, where

$$\hat{\tau} = \mathbf{1},\ (\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2)\,,\ (\boldsymbol{\sigma}_a \cdot \hat{\boldsymbol{r}}_a)\,,\ (\boldsymbol{\sigma}_a \cdot \hat{\boldsymbol{r}}_b)\,,\ [(\boldsymbol{\sigma}_1 \cdot \hat{\boldsymbol{r}}_1)\,(\boldsymbol{\sigma}_2 \cdot \hat{\boldsymbol{r}}_2)]$$

$$f(r_{12}) = \begin{cases} r_{12}^s, & s > -1 \in \boldsymbol{R}, \\ r_{12}^n, & n = -1, 0, 1, 2, \ldots, \\ \ln(r_{12}). & \end{cases}$$

Algorithms:

G. Pestka, J. Phys. A: Math. Gen. **31**, 6243 (1998)

G. Pestka and J. Karwowski,

Two-electron one-center integrals in relativistic Hy-CI method

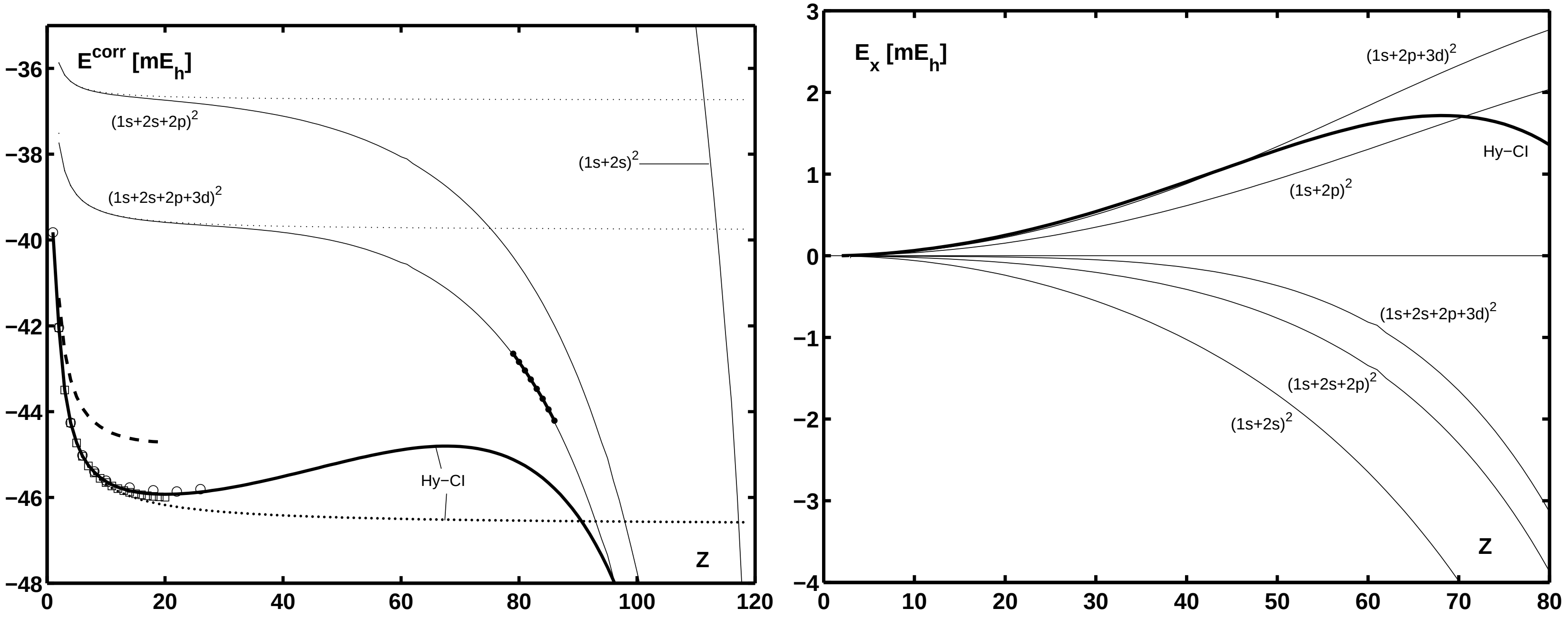
in *“Integrals over Slater orbitals”*, Ed. T. Ozdogan and M. B. Ruiz, 2008.

Pattern of convergence of He-like atom MCDF correlation energies and relativity-correlation cross-term corrections to the Hy-CI values.

Broken line: MCDF up to $(5g)^2$.

Squares: extrapolation to the complete expansion.

Circles: all configurations with $n < 7 +$ extrapolation.



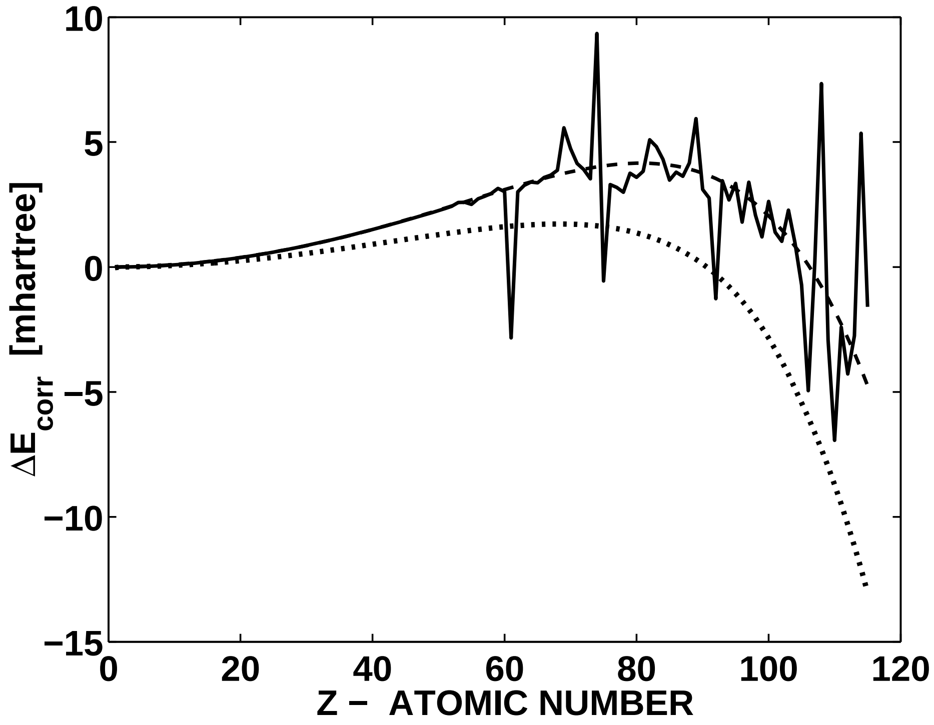
[*G. Pestka, H. Tatewaki, J. Karwowski*, Phys. Rev. A **70**, 024501 (2004)]

RELATIVISTIC AND CORRELATION CORRECTIONS

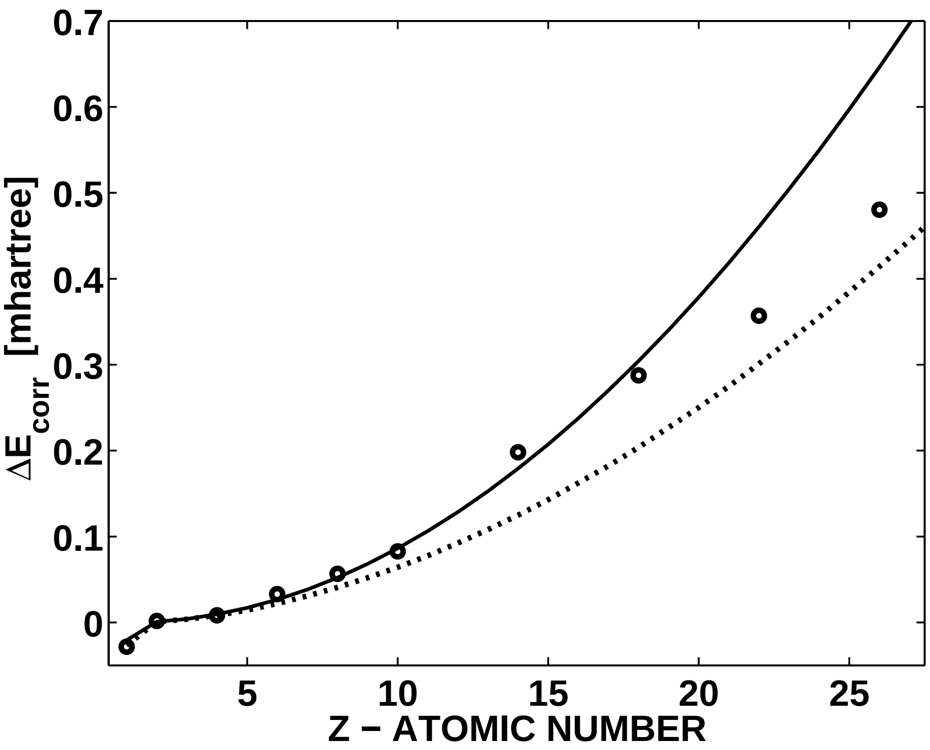
Ground state energies of helium-like atoms (in milihartree):

Z	E_{HF}	$E_{DF} - E_{HF}$	E_{nr}^{corr}	E_x	$\Delta E_{\rm BR}$
2	-2861.67999	-0.13331	-42.0444	0.0035	0.0001
20	-387611.057	-2055.707	-46.177	0.351	0.164
40	-1575111.03	-34794.26	-46.42	1.36	1.57
60	-3562611.02	-188364.94	-46.50	2.70	4.70
80	-6350111.01	-656335.85	-46.55	3.16	10.54
100	-9937611.00	-1859249.0	-46.6	0.0	21.6
118	-13850361.0	-4494444.1	-46.6	-18.4	36.4

$\Delta E_{\rm BR}$ - difference between non-projected and PES-projected energies, i.e. the energy shift due to the interaction with the Brown-Ravenhall continuum (all-order contribution to the non-relativistic part of Coulomb interaction).



Hy-CI relativity-correlation cross-term energies in He isoelectronic series. Dotted line: 502 functions. Solid line: 1131 functions. The degeneracies of the ground-state energy with the BR continuum eigenvalues result in the instabilities.



Enlargement of the small-Z part of the previous plot. Circles: extrapolated MCDHF results of Parpia & Grant, J. Phys. B **23** (1990) 211.

Conclusion: High accuracy implies very large Hy-CI basis.

COMPLEX SCALING

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

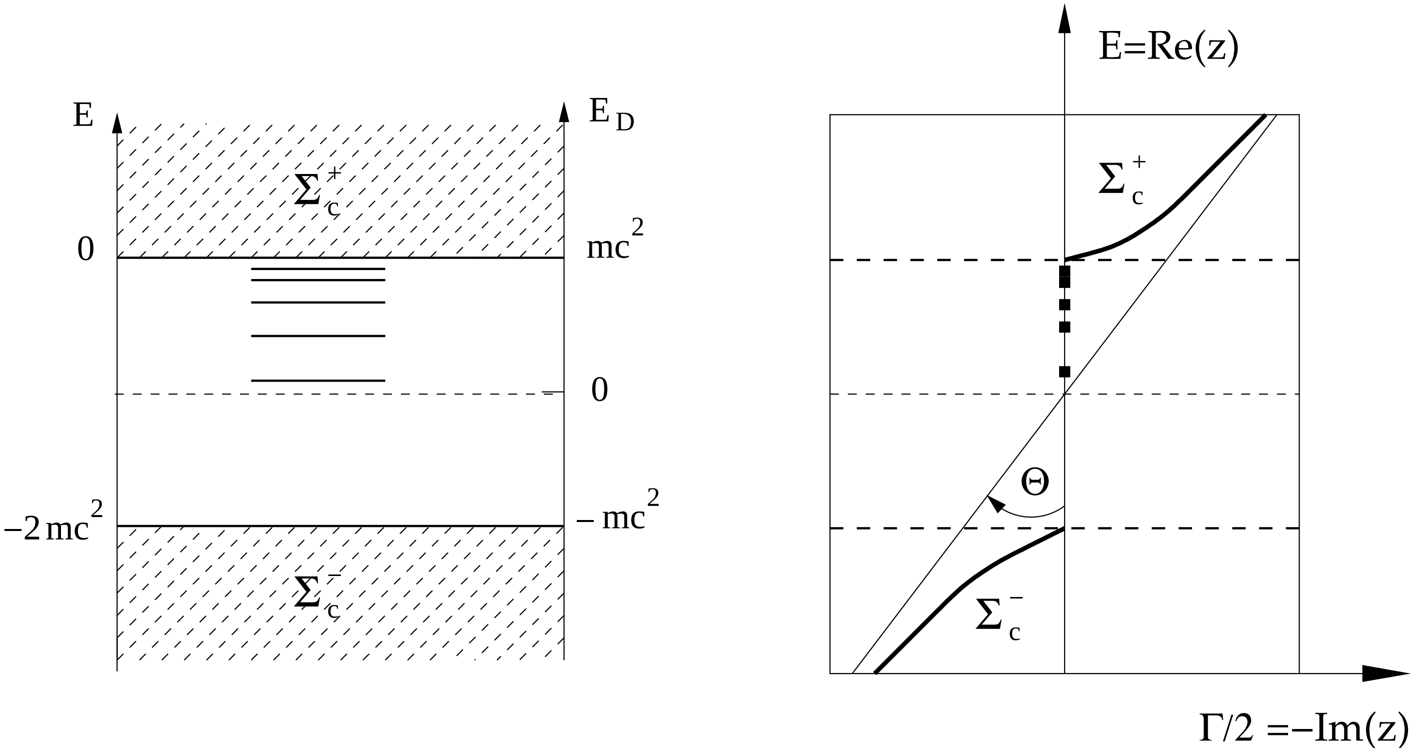
Basic theorem: *Bound state energies of a Hamiltonian do not change under the complex rotation of coordinates,*

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

whereas the continua move to the complex plane.

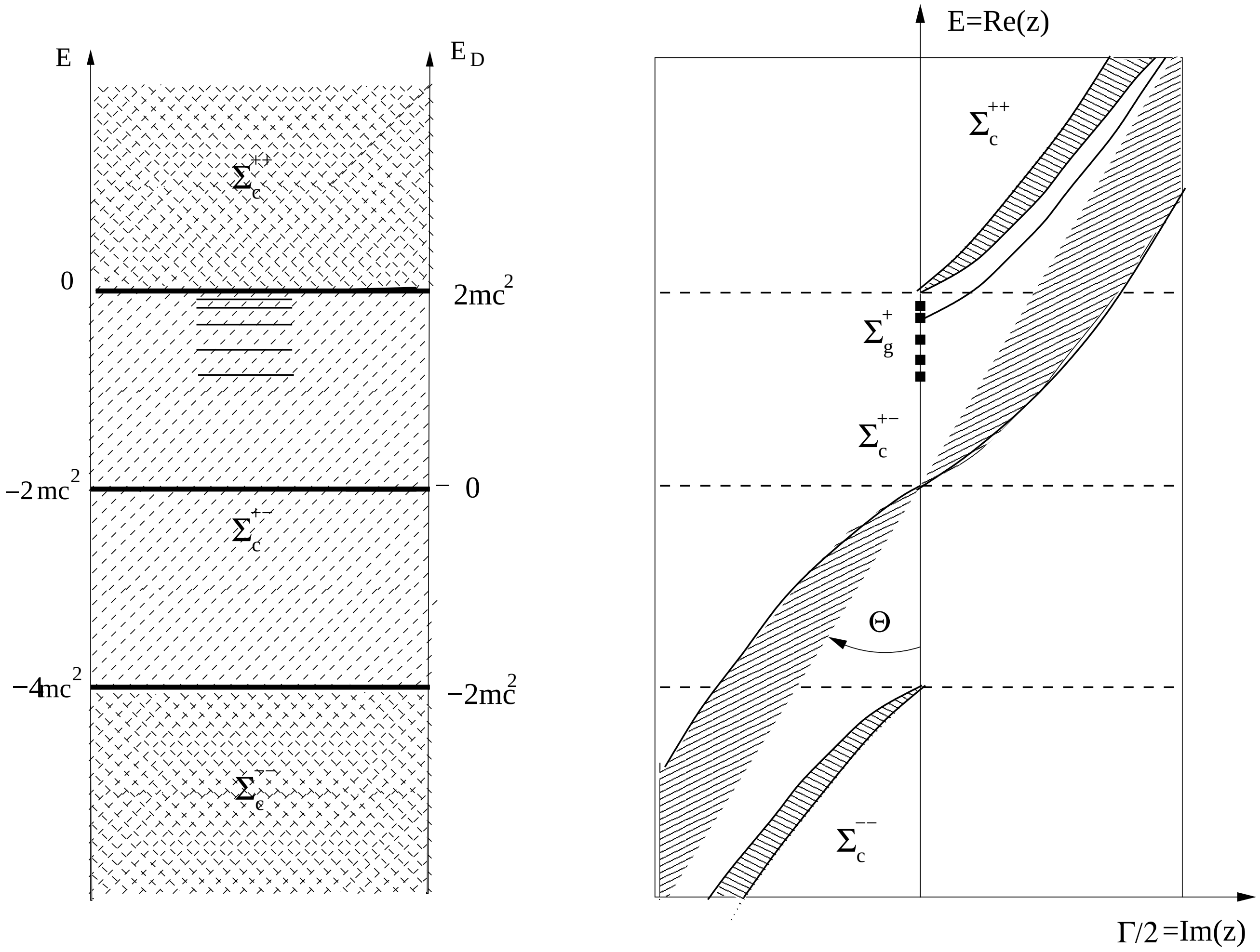
From the formal point of view discrete eigenvalues of a many-electron DC Hamiltonian are resonances. It is surprising that CCR method has not been used to study the properties of DC equation until very recently:
G. Pestka, M. Bylicki, J. Karwowski, *Complex-coordinate rotation in the relativistic Hylleraas-CI*, J Phys B, **39**, 2979 (2006); **40**, 2249 (2007).

EFFECT OF COMPLEX COORDINATE ROTATION



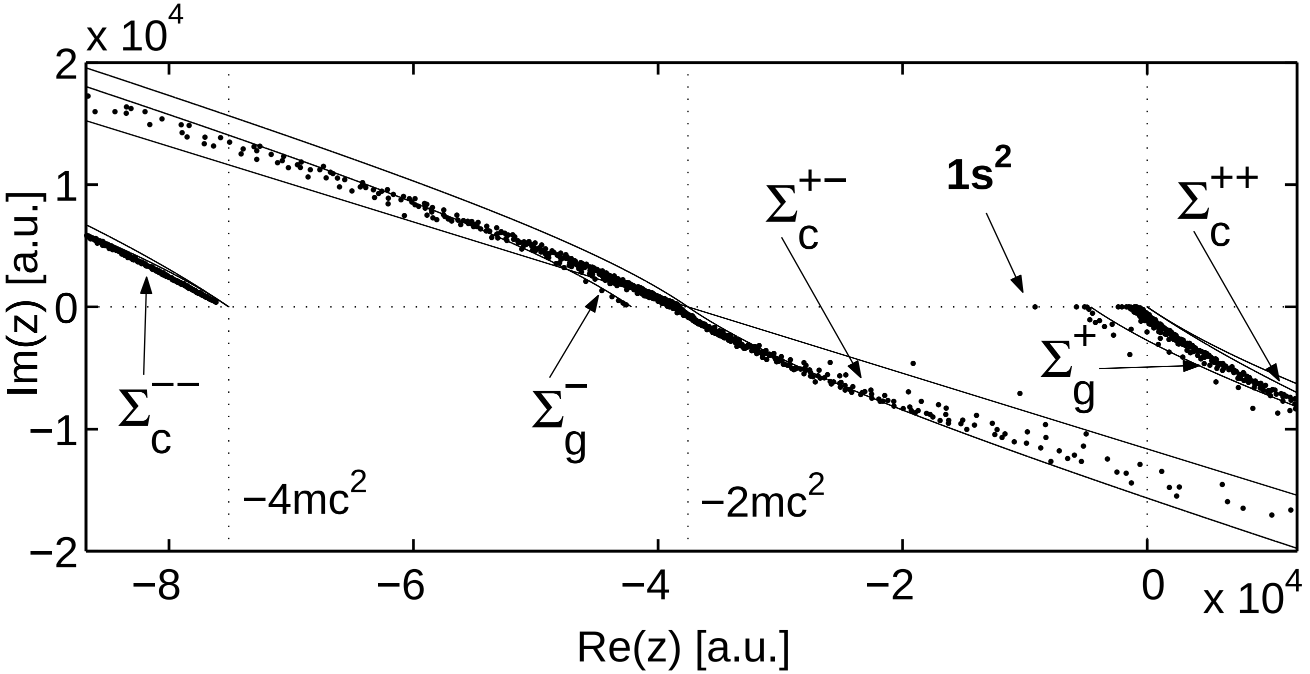
Standard (left) and CCR (right) spectrum of a one-electron Dirac Hamiltonian. Solid lines represent the positive, Σ_c^+, and the negative, Σ_c^-, continua. The points in the real axis represent bound-state energies.

SPECTRUM OF A TWO-ELECTRON DC HAMILTONIAN



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

Hy-CI-CCR SPECTRUM OF Z=90 HELIUM-LIKE ATOM

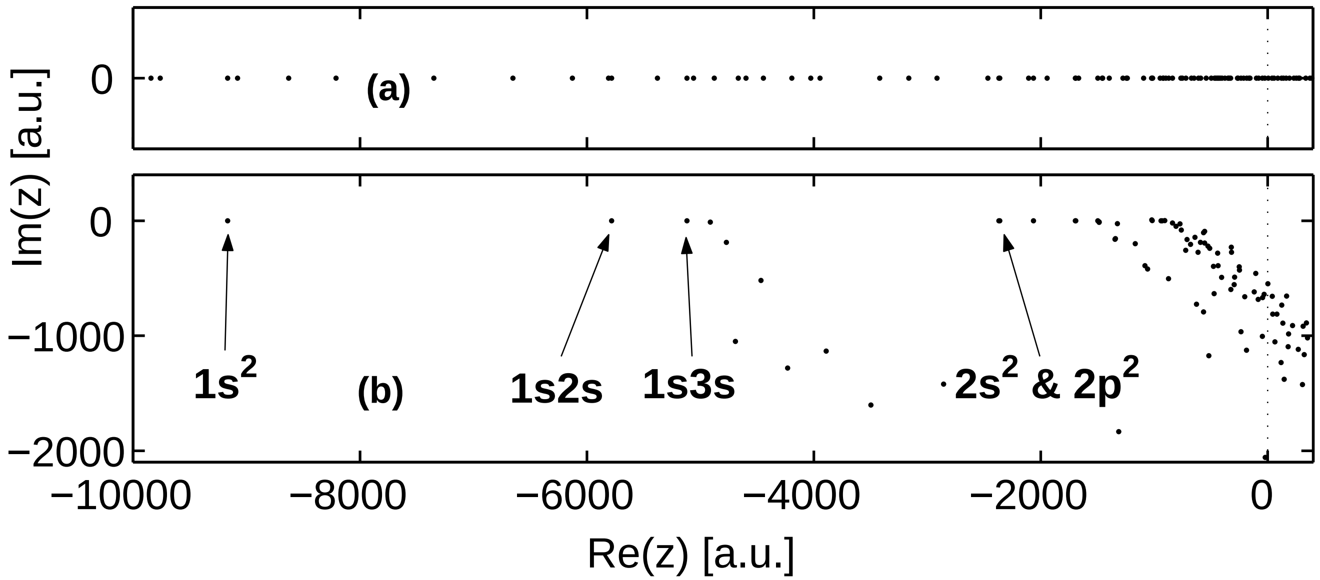


Basis of 1826 explicitly correlated functions; $\Theta = 0.3$.

Dots – the computed eigenvalues.

Lines – areas covered by the non-interacting-particle continua.

SPECTRUM OF Z=90 HELIUM-LIKE ATOM



Enlargement of the bound- and the resonance-state-energy region.

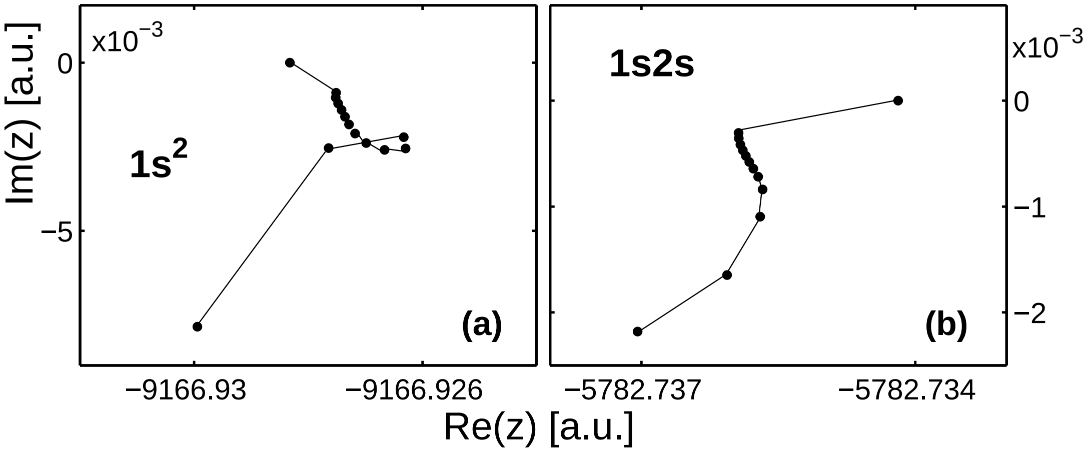
Upper part: No complex rotation.

The discrete state energies are mixed with the continuum ones.

Lower part: The rotated spectrum $(\theta = 0.3)$.

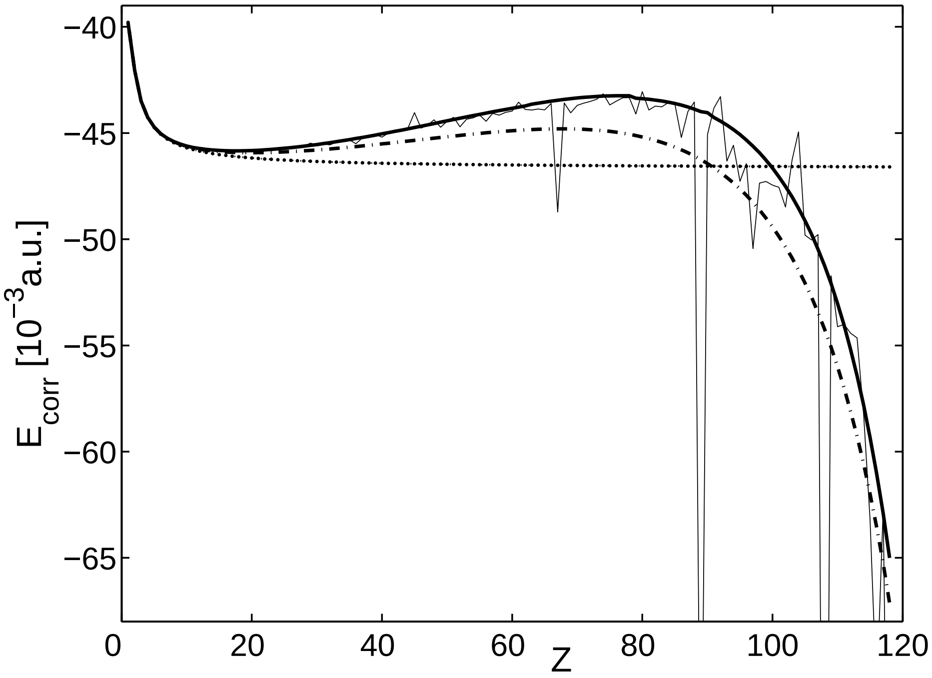
The continuum eigenvalues are moved to the complex plane.

BOUND-STATE θ-TRAJECTORIES FOR $Z = 90$.



The consecutive dots in the trajectories correspond to equidistant values of θ. The value of $\mathrm{Re}(z)$ at the part of the trajectory with the weakest θ-dependence corresponds to the energy of the state.

Hy-CI CORRELATION ENERGIES OF HELIUM-LIKE ATOMS

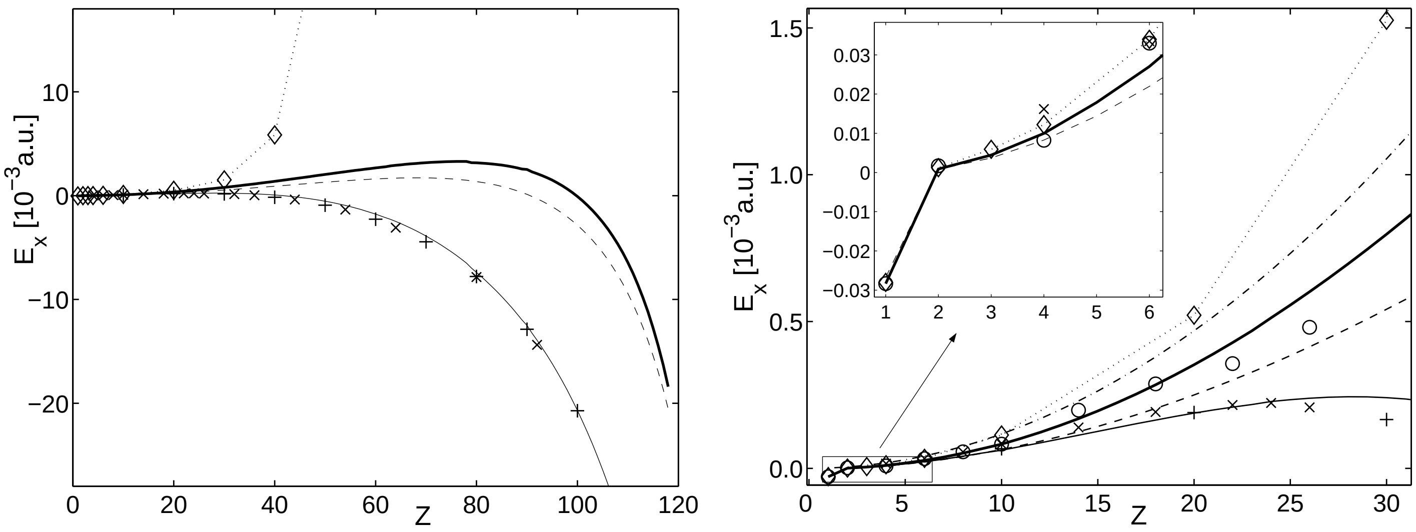


(Dash-dotted)/(thin solid) lines: Hy-CI results in 502/1826-function bases.

Thick solid line: Hy-CI-CCR results in 1826-function basis

Dotted line: Non-relativistic correlation energy.

RELATIVITY-CORRELATION CROSS-TERM ENERGIES



Thick solid (broken) line – Hy-CI-CCR in 1826 (502) function basis.

Thin solid line – Hy-CI-CCR energy shifted by $\Delta E_{\mathrm{BR}} = (Z\alpha)^3/(6\pi)$

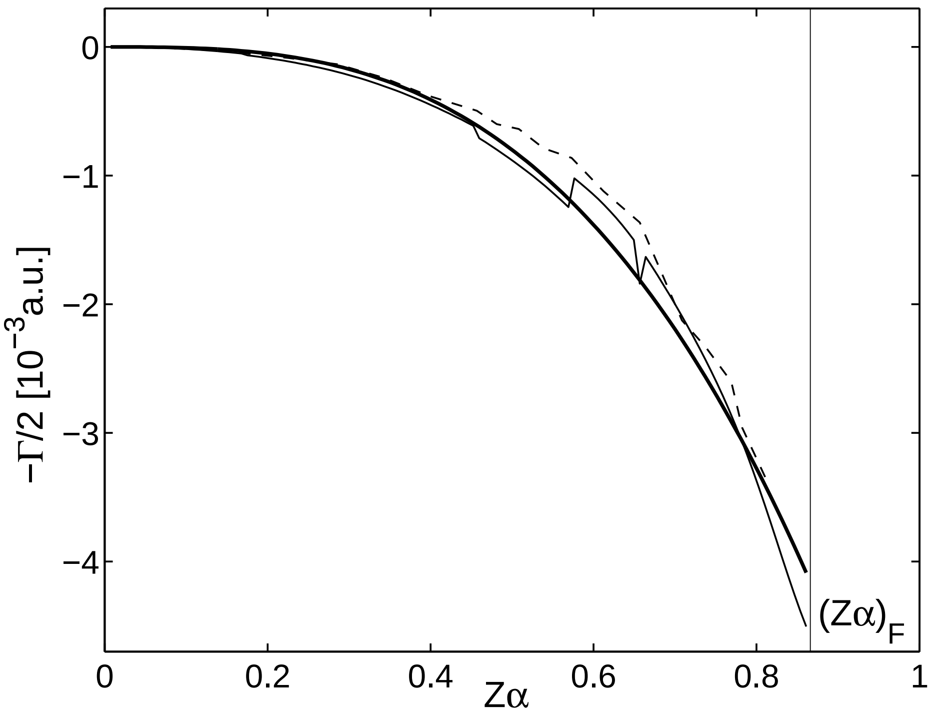
Dash-dot line – estimates based on MCDF and Z-expansion

+ / × – CI/MBPT PES-projected energies [Johnson *et al.* 1994]

○ – MCDF [Parpia & Grant 1990]

◇ – DPT [Ottschowski & Kutzelnigg 1997]

THE IMAGINARY PARTS OF Hy-CI EIGENVALUES

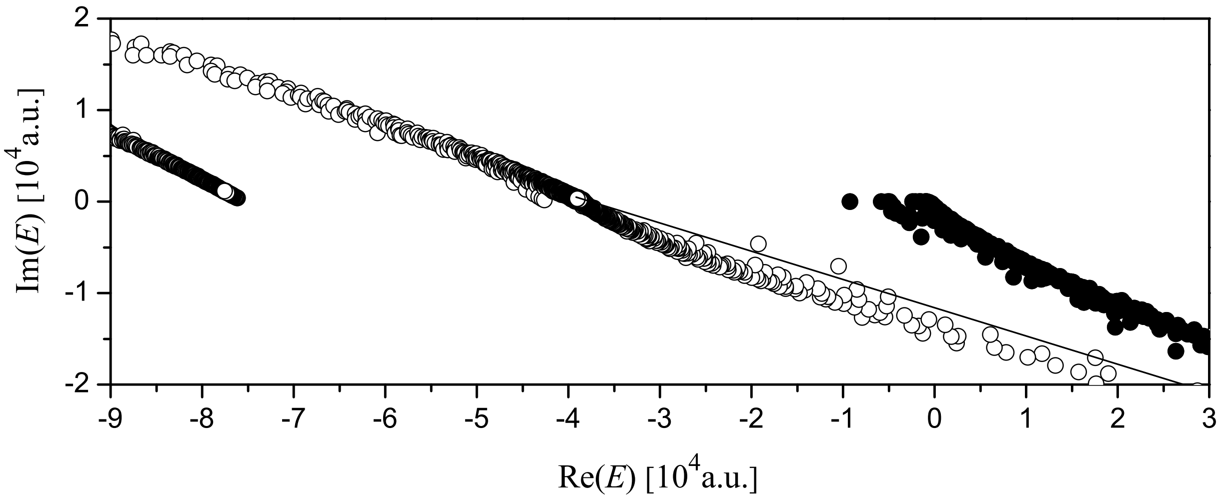


$\mathrm{Im}(E) = -\Gamma/2$ as a functions of α (broken line) and Z (thin solid line).

Thick solid line – a fit: $-6.4\,(Z\alpha)^3 \cdot 10^{-3}$ a.u.

Vertical line: $(Z\alpha)_{\mathrm{F}} = \sqrt{3}/2$ – the applicability limit of the method.

POSITIVE-ENERGY-SPACE-PROJECTED Hy-CI

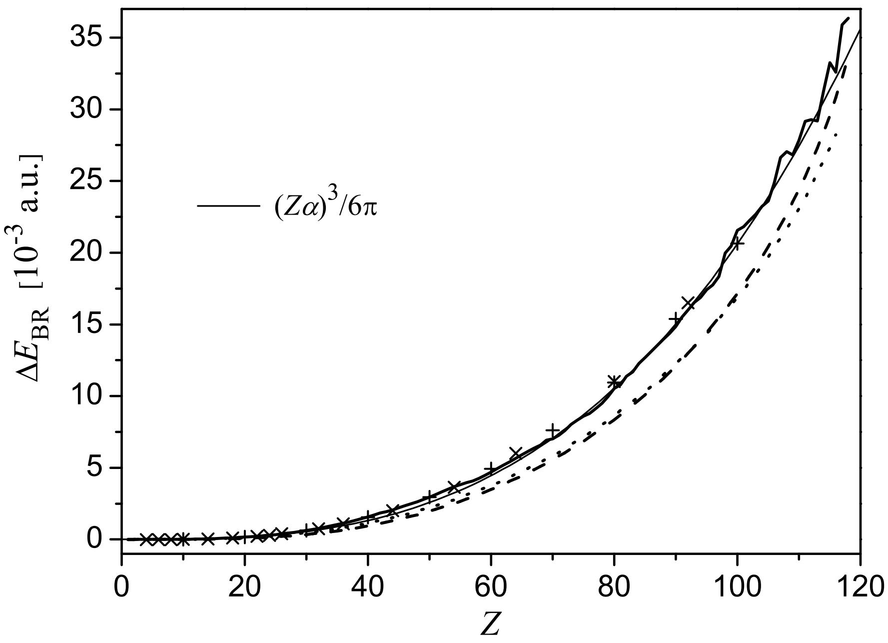


The CCR spectrum of $Z = 90$ He-like atom with electron-electron interaction neglected, in a 1826-function Hy-CI basis.

Full circles – positive energy space (PES) eigenvalues.

Solid line – theoretical border between PES eigenvalues and the BR continuum. In a complete basis set all eigenvalues with imaginary parts not larger than 0 and to the right of the border line correspond to PES.

SHIFT DUE TO THE BR CONTINUUM



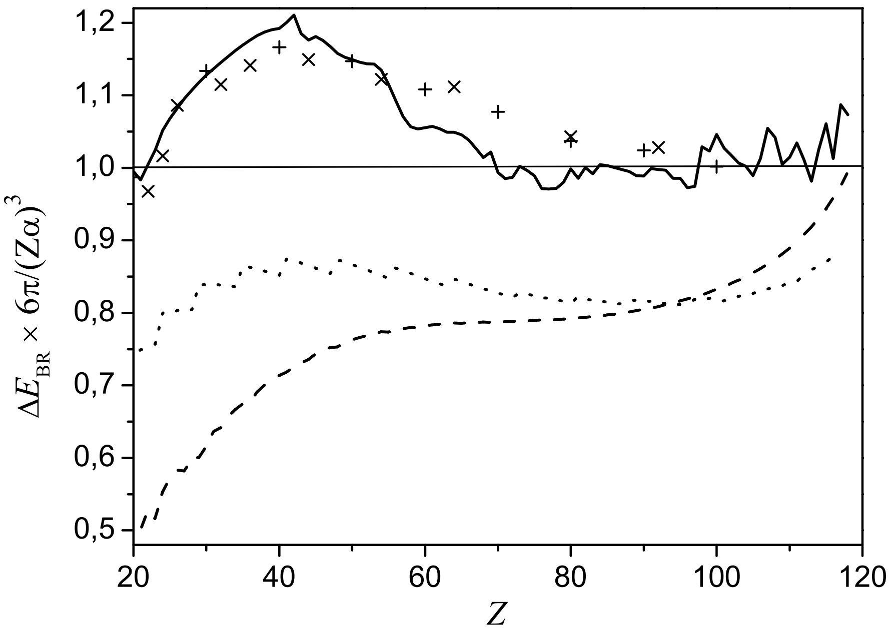
Differences between non-projected and PES-projected energies:

Solid line – Hy-CI-CCR in 1826-function basis.

Dotted line – CI in large Gaussian basis set [Watanabe *et. al* 2007].

Broken line – Hy-CI-CCR in 502-function basis.

+ / × – difference between non-projected 1826-function Hy-CI and PES projected CI/MBPT [Johnson, Sapirstein *et al.* 1994].



The ratio of the calculated energy shift (difference between non-projected and PES-projected energies) to the first-order perturbation value $(Z\alpha)^3/6\pi$.

Solid line	–	Hy-CI in 1826-function basis.
Dotted line	–	CI in large Gaussian basis set [Watanabe *et. al* 2007].
Broken line	–	Hy-CI in 502-function basis.
+ / ×	–	difference between non-projected 1826-function Hy-CI and PES projected CI/MBPT [Johnson, Sapirstein *et al.* 1994].

FINAL REMARKS

- If the quality of the basis set is sufficiently high relative to its dimension and to the value of Z, so that there is a sufficintly large energy gap between the ground state energy and the eigenvalues representing the BR continuum, then neither PES projection nor CCR are necessary.
- For very high accuracy results and, particularly, for large values of Z, when the disturbing influence of the BR states becomes noticeable, CCR offers an adequate way of removing this influence and, simultaneously, retaining the completeness of the model space.
- The PES projected (no-pair) and the non-projected approaches converge to different limits. The difference is of the order $(Z\alpha)^3$. Thus, it is beyond the limits of validity of the DC model. The corresponding term can either be included or neglected while introducing QED corrections.

The truncation of the Hy-CI model space corresponding to a PES projection is feasible but it is not necessary and has some disadvantages:

- The absence of the negative energy states in PES-projected methods has to be corrected if we are interested in other than energy quantities.
- The PES projection is not unique even if the original space is complete. Therefore the results are gauge- and basis-set-dependent.
- Maintaining integrity of Dirac states simplifies calculations and stays closer to physics (I. P. Grant, 1995).

There are also some advantages of the PES projection:

- The eigenvalue problem is bounded from below and for the same quality of the energy a smaller model space is necessary.
- Combining PES projection with CCR may simplify computations: We need a diagonalization of $\boldsymbol{H}$ for one Θ in PES-projected and for many Θs in non-projected methods.

FINAL REMARKS

- A vast majority of relativistic results for atoms containing more than two electrons and, probably, for all molecules have been obtained at the level of accuracy which is managable by the basis set selection using non-projected approaches.
- In Dirac-Fock calculations we have an effective one-electron problem and the correct relations between the components of the spinors combined with the bound-state boundary conditions are always sufficient.
- In multi-configuration calculations a PES projection may allow for higher accuracy limit [P. Indelicato, PRA, **51** (1995) 1132].
- An implementaion of CCR-based approaches to QED calculations for high-Z atoms seems to be a most attractive challenge.