Variational Dirac–Coulomb approach with explicitly correlated basis functions

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Motivation

- Theoretical description of high-precision spectroscopy (sub-ppb precision in energy)
- Relativistic and QED corrections are required for accurate description
- Pertubation theory
  - $1/Z$ expansion for high Z: relativistic zeroth order, electron-electron interaction as pertubation
  - Non-relativistic QED for low Z: non-relativistic as zero order, relativistic and QED effects as pertubation using power series of α and $Z\alpha$.
- Sucher's equal-time equation
  both relativistic and interparticle correlation of the zeroth order

Sucher's equal-time equation[f,h]

Bethe-Salpeter equation:

$$\Psi(x,x') = \int \mathrm{d}x_1^4 \mathrm{d}x_2^4 \mathrm{d}x_1'^4 \mathrm{d}x_2'^4 \cdot$$
$$\cdot G_0(x,x';x_2,x_2')(-\mathrm{i})\Sigma^*(x_2,x_2';x_1,x_1')\Psi(x_1,x_1')$$

$G_0(x,x';x_2,x_2')$ - Green function for free particles
$\Sigma^*(x_2,x_2';x_1,x_1')$ - Irreducible interaction potential

Sucher's equal-time wave function:

$$T = (t_1+t_2)/2, \quad \epsilon = t_1 - t_2 \quad \Psi(x,x') \overset{\int T}{\to} \psi(\epsilon, \boldsymbol{x}, \boldsymbol{x'})$$
$$\phi(\boldsymbol{x},\boldsymbol{x'}) = \int \mathrm{d}\epsilon\, \psi(\epsilon,\boldsymbol{x},\boldsymbol{x'})$$

Sucher's equal-time equation:

$$[H_{\mathrm{DC}}^{++} + H_\Delta(\epsilon)]\,\phi = E\phi$$

Floating Explicitly Correlated Gaussians (fECG)

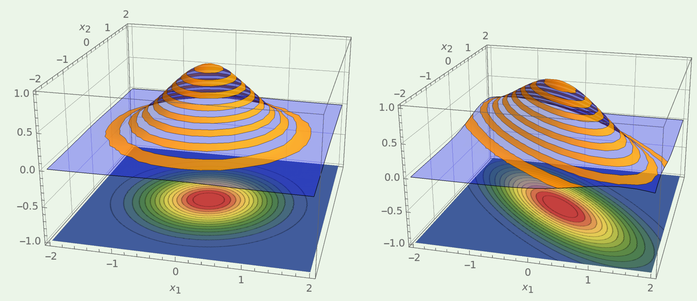
$$\Theta(\boldsymbol{r}) = \exp\left[-(\boldsymbol{r}-\boldsymbol{s})^T \boldsymbol{A} (\boldsymbol{r}-\boldsymbol{s})\right]$$

\+ Explicit correlation in the basis set level

\+ Analytical matrix elements

\+ nE_h precision for few-particles

— No cusp or singularity at short-range, too fast decay at long-range



Acknowledgement

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No-pair Dirac–Coulomb model for two particles

Hamiltonian:

$$H_{\mathrm{DC}}^{++} = \Lambda_{++}\left(h_1 \otimes I_2 + I_1 \otimes h_2 + V_{\mathrm{DC}}\right)\Lambda_{++}$$

$$h_i = \begin{pmatrix} U_i & c\boldsymbol{\sigma}_i\boldsymbol{p}_i \\ c\boldsymbol{\sigma}_i\boldsymbol{p}_i & U_i - m_i c^2 \end{pmatrix} \qquad V_{\mathrm{DC}} = 1/r_{12}$$

Eigenvalue equation:

$$H_{\mathrm{DC}}^{++}\,|\phi_{\mathrm{DC}}^{++}\rangle = E_{\mathrm{DC}}^{++}\,|\phi_{\mathrm{DC}}^{++}\rangle$$

Questions:

- How can we perform correct and efficient positive-energy projection?
- Are the obtained results physically meaningful?

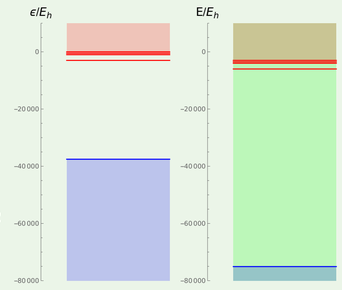
Positive-energy projection[a,b]

Distinction of e^- and e^+:
single-particle energies (ϵ_i)

For two particles:
$e^- - e^-$, $e^- - e^+$, $e^+ - e^+$

For determinants ϵ_i-s available
$E^0_{\mathrm{DC},ij} = \epsilon_i + \epsilon_j$

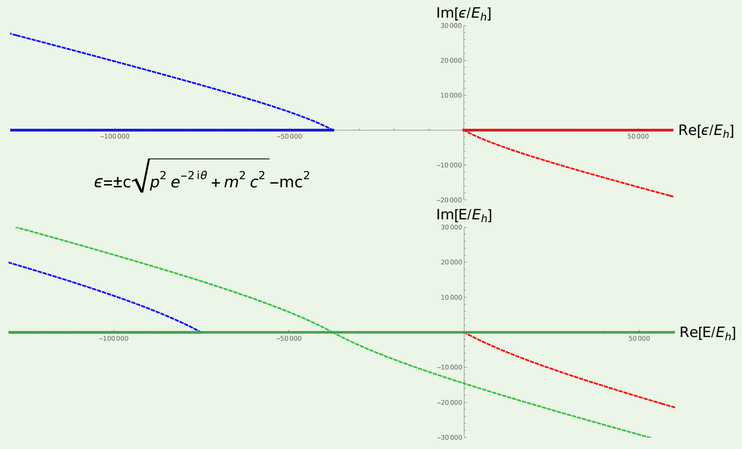
For ECGs (H_{noint}, $V_{\mathrm{DC}} = 0$)



\+ easy exact (ϵ_i) exact

— approximate inaccurate $\mathrm{Im}[E] \sim \theta$

- selection according to E^0_{DC} ✔
- determinant expansion ✗
- Complex Scaling, small θ ✔



He $(1\ ^1S_0)$	proj = CS
θ	$\mathrm{Re}(E_{\mathrm{DC}}^{++})[E_\mathrm{h}]$ $\quad$ $\mathrm{Im}(E_{\mathrm{DC}}^{++})[E_\mathrm{h}]$
0.000 000 1	−2.903 856 630 628 $\quad$ $1.47 \cdot 10^{-16}$
0.000 001	−2.903 856 630 628 $\quad$ $1.47 \cdot 10^{-15}$
0.000 01	−2.903 856 630 628 $\quad$ $1.47 \cdot 10^{-14}$
0.000 1	−2.903 856 630 628 $\quad$ $1.47 \cdot 10^{-13}$
0.001	−2.903 856 630 628 $\quad$ $1.46 \cdot 10^{-12}$
0.01	−2.903 856 630 656 $\quad$ $1.61 \cdot 10^{-11}$
0.1	−2.903 856 632 538 $\quad$ $1.29 \cdot 10^{-9}$
0.2	−2.903 856 632 442 $\quad$ $2.62 \cdot 10^{-9}$
0.5	−2.903 856 823 509 $\quad$ $-3.57 \cdot 10^{-7}$
proj = E^0_{DC}:	−2.903 856 630 628 $\quad$ 0

Perturbative expansion according to α

Fine-structure constant as a small parameter, $\alpha \approx 1/137$

$$E_{\mathrm{DC}}^{++} \approx E_{\mathrm{nonrel}} + \alpha^2 \epsilon_{\mathrm{DC}}^{\mathrm{FW}} + \alpha^3 \epsilon_{\mathrm{CC}}^{++} + \ldots$$

The second-order term form Foldy-Wouthuysen PT:

$$\epsilon_{\mathrm{DC}}^{\mathrm{FW}} = -\frac{1}{8}\sum_{i=1}^{2}\left\langle (\boldsymbol{\nabla}_i^2)^2 \right\rangle_{\mathrm{nr}} + \frac{\pi}{2}\sum_{i=1}^{2}\sum_{A=1}^{N_{\mathrm{nuc}}} Z_A \left\langle \delta(\boldsymbol{r}_{iA}) \right\rangle_{\mathrm{nr}} - \pi \left\langle \delta(\boldsymbol{r}_{12}) \right\rangle_{\mathrm{nr}}$$

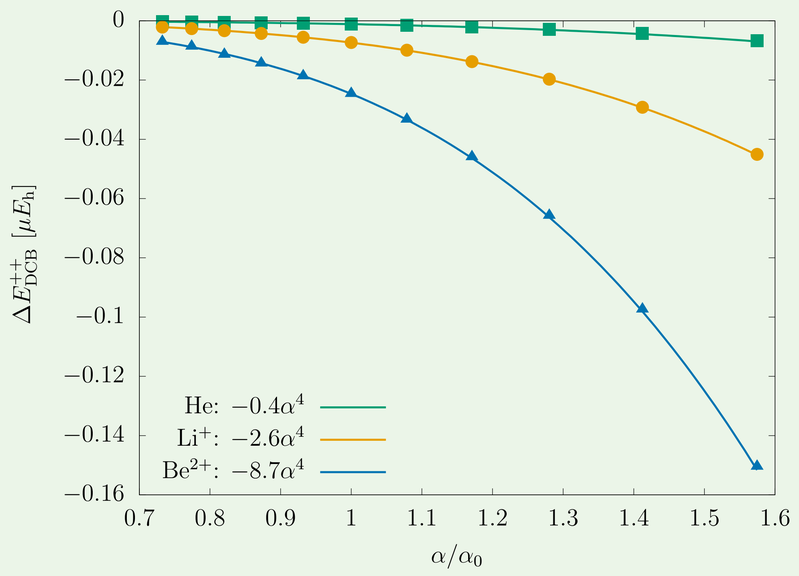
The third-order term from Sucher[g]:

$$\epsilon_{\mathrm{CC}}^{++} = -\left(\frac{\pi}{2} + \frac{5}{3}\right)\left\langle \delta(\boldsymbol{r}_{12}) \right\rangle_{\mathrm{nr}} \approx -3.24 \left\langle \delta(\boldsymbol{r}_{12}) \right\rangle_{\mathrm{nr}}$$

Contribution from triplet basis states[e]

- LS-coupling scheme
- $^1S^{\mathrm{e}}$ states of atoms: $J = 0$, $J_z = 0$, $p = +1$
  Coupled states: $^1S^{\mathrm{e}}$ and $^3P^{\mathrm{e}}$ (unnatural partity state)
- Non-relativistic optimization for each state. Then, the merged basis set is applied in the Dirac–Coulomb–Breit calculations to be able to compare with accurate reference values.
- 0.1 nE_h precision in the triplet corrections:
  $\Delta E_{\mathrm{DCB}}^{++} = E_{\mathrm{DCB,full}}^{++} - E_{\mathrm{DCB}}^{++}$

		He $(1\ ^1S_0^{\mathrm{e}})$			He $(2\ ^1S_0^{\mathrm{e}})$		
$[nE_\mathrm{h}]$	$N_P \setminus N_S$	400	500	700	400	500	700
$\Delta E_{\mathrm{DCB}}^{++}$	70	−0.7	−0.7	−0.7	−0.06	−0.06	−0.06
	100	−0.9	−0.9	−0.9	−0.08	−0.08	−0.08
	150	−0.9	−0.9	−1.0	−0.08	−0.08	−0.08
	200	−1.1	−1.1	−1.1	−0.09	−0.09	−0.09
	250	−1.1	−1.1	−1.1	−0.09	−0.09	−0.09
$\Delta E_{\mathrm{nrQED}}$		−1.113			−0.09582		

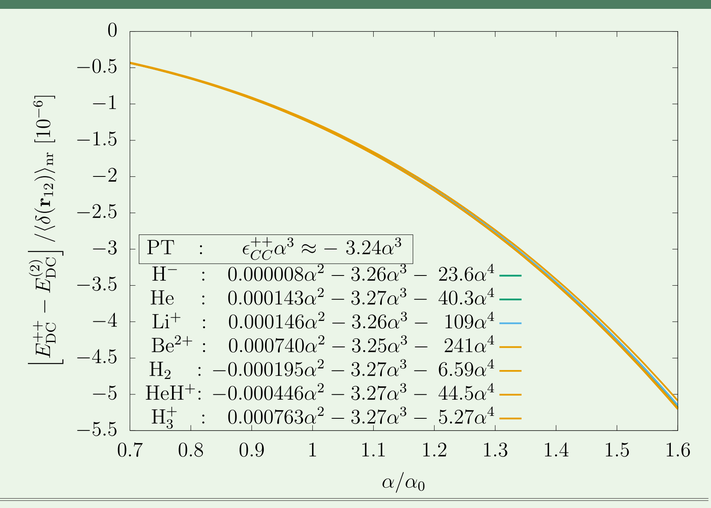


Conclusion and Outlook

- No-pair Dirac–Coulomb energy for two electrons is evaluated with high-precision using ECGs.
- The ppb relative precision of DC energies is reached for H^-, He $(1\ ^1S_0^{\mathrm{e}})$, He $(2\ ^1S_0^{\mathrm{e}})$, Li^+, Be^{2+},H_2, HeH^+, and H_3^+. The relation to the perturbation theory is found by scaling of α.
- Future plans: medium Z-region, pair corrections, higher-order radiative and retardation corrections.

Variational vs. perturbative energies using only singlet basis states[a,b]

$[E_\mathrm{h}]$	He $(1\ ^1S_0)$	He $(2\ ^1S_0)$	Li^+
E_{DC}^{++}	−2.903 856 631[a]	−2.146 084 791[a]	−7.280 698 899[a]
$E_{\mathrm{DC}}^{(2)}$	−2.903 856 486[i]	−2.146 084 769[i]	−7.280 698 064[i]
$E_{\mathrm{DC}}^{(3)}$	−2.903 856 620[i]	−2.146 084 780[i]	−7.280 698 735[i]
$\tilde{E}_{\mathrm{DC}}^{(4)}$	−2.903 856 630[j]	−2.146 084 791[j]	{n.a.}
$[E_\mathrm{h}]$	Be^{2+}	H_2	H_3^+
E_{DC}^{++}	−13.658 257 602[a]	−1.174 489 754[a]	−1.343 850 527[a]
$E_{\mathrm{DC}}^{(2)}$	−13.658 254 651[i]	−1.174 489 733[k]	−1.343 850 503[g]
$E_{\mathrm{DC}}^{(3)}$	−13.658 256 567[i]	−1.174 489 754[k]	−1.343 850 525[g]
$\tilde{E}_{\mathrm{DC}}^{(4)}$	{n.a.}	−1.174 489 754[d]	{n.a.}



$[E_\mathrm{h}/\alpha^2]$	H^-	He $(2S)$	He $(1S)$	Li^+	Be^{2+}	H_2	H_3^+	HeH^+
$\epsilon_{\mathrm{DC}}^{\mathrm{FW}}$	−0.107 279	−2.078 929	−2.481 823	−14.731 566	−50.477 690	−0.263 240	−0.279 367	−2.401 315
$O_{\alpha^2}[E_{\mathrm{DC}}^{++}]/\alpha^2$	−0.107 279	−2.079 251	−2.480 832	−14.734 771	−50.485 217	−0.263 250	−0.279 386	−2.401 752
$\epsilon_{\mathrm{DC,reg}}^{\mathrm{FW}}$	−0.107 283[i]	−2.079 256[j]	−2.480 848[i]	−14.734 859[i]	−50.485 330[i]	−0.263 255[k]	−0.279 399[g]	−2.401 709[a]