Recursive scheme of the perturbation theory for high-precision calculations in atoms and ions

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Outline

1. Motivation
2. Method
3. Results
   - Binding energies
   - Nuclear recoil effect
   - g factor
4. Outlook

Interelectronic interaction: Breit approximation

Dirac-Coulomb-Breit Hamiltonian

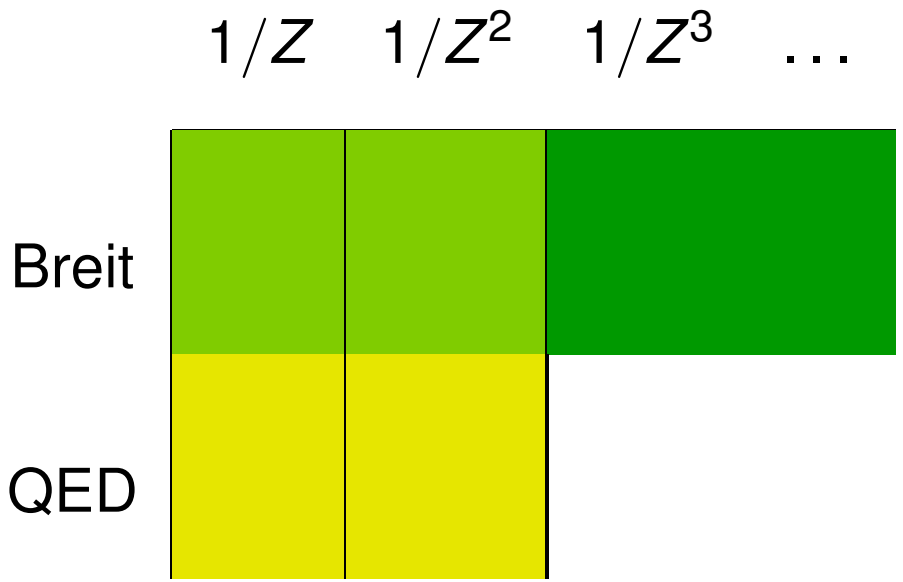
$$H = \Lambda_+ \left(\sum_j h(j) + \sum_{j<k} V_{\rm Breit}(j,k) \right) \Lambda_+$$

$$h = \boldsymbol{\alpha} \cdot \mathbf{p} + \beta m + V_{\rm nuc}(r)$$

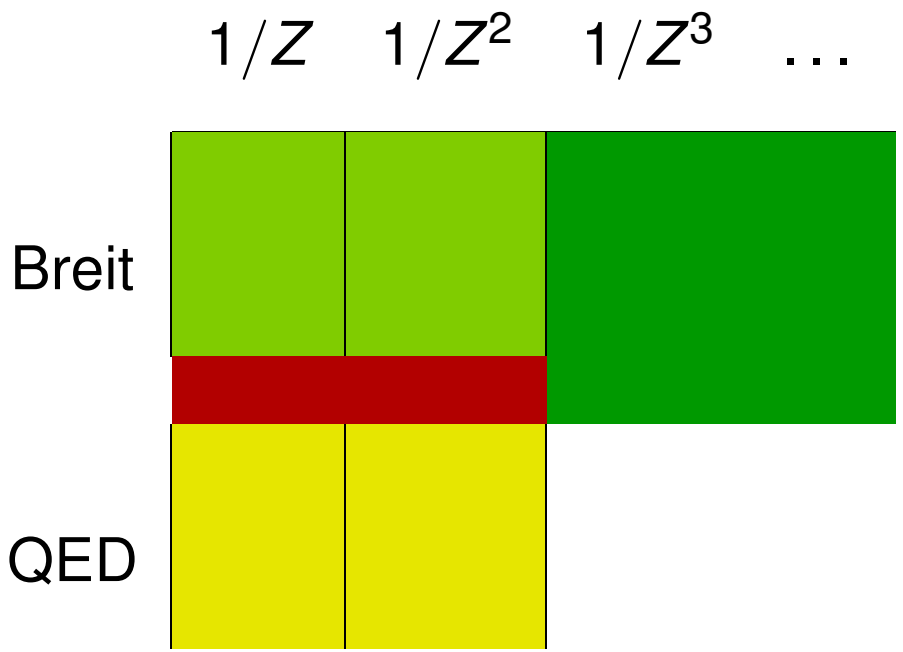
MBPT and various all-order methods based on:

- Dirac-Fock equation
- effective potentials
- configuration interaction
- coupled cluster
- CI-DFS
- MCDF
- RPP
- ...

Interelectronic interaction: QED+Breit



Interelectronic interaction: QED+Breit



Requirements to the new method

When the lowest orders are treated within QED and the remainder within the Breit approximation, there are special demands:

1. provide control over low orders of PT
2. take into account higher orders of PT
3. tame an exponential growth for higher orders

Concept of the new method

1. One-electron basis set: $|n\rangle = |n_r jlM\rangle$
   is constructed within the DKB-splines method
2. Many-electron basis set: $|N\rangle = |n_1, n_2, \ldots, n_s\rangle$
   consists of Slater determinants
3. Many-electron matrix elements
4. Recursive perturbation theory

DCB Hamiltonian with screening potential

Zeroth-order Hamiltonian

$$H_0 = \sum_j h(j)$$

$$h = \boldsymbol{\alpha} \cdot \mathbf{p} + \beta m + V_{\rm nuc}(r) + V_{\rm scr}(r)$$

Perturbation

$$H_1 = \sum_{j<k} V_{\rm Breit}(j,k) - \sum_j V_{\rm scr}(r_j)$$

$$V_{\rm Breit} = \alpha \left[\frac{1}{r_{12}} - \frac{\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2}{r_{12}} - \frac{1}{2} (\boldsymbol{\alpha}_1 \cdot \boldsymbol{\nabla}_1)(\boldsymbol{\alpha}_2 \cdot \boldsymbol{\nabla}_2) r_{12} \right]$$

Perturbation theory

Zeroth-order problem

$$H_0|A\rangle = E_A|A\rangle$$

Exact problem

$$(H_0 + H_1)|\tilde{A}\rangle = \tilde{E}_A|\tilde{A}\rangle$$

Perturbation expansion

$$\tilde{E}_A = \sum_{k=0}^{\infty} E_A^{(k)} \qquad E_A^{(0)} = E_A$$

$$|\tilde{A}\rangle = \sum_{k=0}^{\infty} |A^{(k)}\rangle \qquad |A^{(0)}\rangle = |A\rangle$$

Perturbation theory

For non-degenerate state $|A\rangle$ one finds

$$\Delta E^{(1)} = \langle A|H_1|A\rangle$$

$$\Delta E^{(2)} = \sum_N{}' \frac{\langle A|H_1|N\rangle\langle N|H_1|A\rangle}{E_A - E_N}$$

$$\Delta E^{(3)} = \sum_{M,N}{}' \frac{\langle A|H_1|M\rangle\langle M|H_1|N\rangle\langle N|H_1|A\rangle}{(E_A - E_M)(E_A - E_N)} - \langle A|H_1|A\rangle \sum_N{}' \frac{\langle A|H_1|N\rangle\langle N|H_1|A\rangle}{(E_A - E_N)^2}$$

$\Delta E^{(k)}$ comprises $(k-1)$-fold summation $\to \mathcal{N}^{k-1}$ terms

Perturbation theory: recursive scheme

$$\tilde{E}_A = \sum_{k=0}^{\infty} E_A^{(k)} \qquad |\tilde{A}\rangle = \sum_{k=0}^{\infty} |A^{(k)}\rangle = \sum_{k=0}^{\infty} \sum_{N} |N\rangle\langle N|A^{(k)}\rangle$$

$$E_A^{(k)} = \sum_{M} \langle A|H_1|M\rangle\langle M|A^{(k-1)}\rangle - \sum_{j=1}^{k-1} E_A^{(j)}\langle A|A^{(k-j)}\rangle$$

$$\langle N|A^{(k)}\rangle = \frac{1}{E_A - E_N}\left[\sum_{M} \langle N|H_1|M\rangle\langle M|A^{(k-1)}\rangle - \sum_{j=1}^{k-1} E_A^{(j)}\langle N|A^{(k-j)}\rangle\right]$$

$$\langle A|A^{(k)}\rangle = -\frac{1}{2}\sum_{j=1}^{k-1}\sum_{M} \langle A^{(j)}|M\rangle\langle M|A^{(k-j)}\rangle$$

Systems investigated to date

One-determinant states:

- He-like: $(1s)^2$
- Li-like: $(1s)^2 2s$, $(1s)^2 2p_J$
  - Total energy: $E[(1s)^2 2s]$, $E[(1s)^2 2p_j]$
  - Ionization energy: $E[(1s)^2 2s/2p_j] - E[(1s)^2]$
- Be-like: $(1s)^2(2s)^2$
- B-like: $(1s)^2(2s)^2 2p_J$
  - Total energy: $E[(1s)^2(2s)^2 2p_j]$
  - Ionization energy: $E[(1s)^2(2s)^2 2p_j] - E[(1s)^2(2s)^2]$
  - Fine structure: $E[(1s)^2(2s)^2 2p_{3/2}] - E[(1s)^2(2s)^2 2p_{1/2}]$

Lithium atom

- Coulomb potential
- CH: core-Hartree potential

$$V_{\rm scr}(r) = \int_0^\infty dr' \, \frac{\alpha}{\max(r, r')} \, \rho_{1s}(r')$$

$$\rho_{1s}(r) = 2\,(G_{1s}^2(r) + F_{1s}^2(r))$$

- CH_1: 1/2 of core-Hartree potential

$$\rho_{1s}(r) = (G_{1s}^2(r) + F_{1s}^2(r))$$

Glazov *et al.*, NIMB (2017)
MBPT: Yerokhin, Artemyev, Shabaev, PRA (2007)
all-order: Yan, Drake, PRL (1998)

Lithium atom: $(1s)^2 2s$ ionization energy [a.u.]

PT order	Coulomb	CH_1	CH
0	−1.125 169	−0.572 597	−0.183 10
1	1.193 706	0.435 989	−0.021 61
2	−0.250 663	−0.058 851	0.011 59
3	−0.008 396	−0.000 628	−0.009 40
4	−0.004 363	−0.001 662	0.008 40
5	−0.001 812	−0.000 280	−0.008 15
6	−0.000 741	−0.000 091	0.008 35
7	−0.000 328	−0.000 035	−0.008 91
8	−0.000 187	−0.000 012	0.009 79
9	−0.000 100	−0.000 004	−0.011 01
10	−0.000 029	−0.000 003	0.012 62
0–∞	−0.198 149	−0.198 176	?
all-order		−0.198 159 72	

Systems investigated to date

One-determinant states:

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  - Ionization energy: $E[(1s)^2 2s/2p_j] - E[(1s)^2]$
- Be-like: $(1s)^2(2s)^2$
- B-like: $(1s)^2(2s)^2 2p_J$
  - Total energy: $E[(1s)^2(2s)^2 2p_j]$
  - Ionization energy: $E[(1s)^2(2s)^2 2p_j] - E[(1s)^2(2s)^2]$
  - Fine structure: $E[(1s)^2(2s)^2 2p_{3/2}] - E[(1s)^2(2s)^2 2p_{1/2}]$

B-like argon: $(1s)^2(2s)^2 2p_j$ — ionization energies [eV]

	$2p_{1/2}$		$2p_{3/2}$	
PT order	LDF	PZ	LDF	PZ
3	0.3560	0.4209	0.4706	0.5294
4	−0.5623	−0.5219	−0.5970	−0.5535
5	0.1644	0.1284	0.1575	0.1222
6	0.0581	0.0583	0.0710	0.0689
7	−0.0608	−0.0474	−0.0669	−0.0520
...	...	...	...	...
12	0.0016	0.0011	0.0018	0.0013
13	−0.0005	−0.0001	−0.0006	−0.0002
14	−0.0003	−0.0002	−0.0002	−0.0002
15	0.0002	0.0001	0.0002	0.0001
3–∞	−0.0296	0.0471	0.0516	0.1249
CI-DFS	−0.0295	0.0470	0.0515	0.1246

B-like argon: $(1s)^2(2s)^2 2p_j$ — ionization energies [eV]

	$2p_{1/2}$		$2p_{3/2}$	
Term	LDF	PZ	LDF	PZ
$E^{(0)}_{\rm Dirac}$	−757.0075	−757.7629	−753.8815	−754.5449
$E^{(1)}_{\rm Breit}$	0.1972	1.5045	−0.0477	1.1541
$E^{(2)}_{\rm Breit}$	1.6916	1.0632	1.5335	0.9219
$E^{(\geqslant 3)}_{\rm Breit}$	−0.0295	0.0470	0.0515	0.1246
$E^{(1)}_{\rm QED}$	−0.0041	−0.0042	0.0018	0.0018
$E^{(2)}_{\rm QED}$	−0.0157	−0.0156	−0.0160	−0.0162
$E_{\rm rec}$	0.0040	0.0040	0.0039	0.0039
$E_{\rm total}$	−755.1639	−755.1640	−752.3545	−752.3546

Glazov *et al.*, NIMB (2017); Malyshev *et al.*, NIMB (2017)

Perturbation theory for matrix elements

$$\begin{aligned}\Delta E_A[W] &= \langle \tilde{A}|W|\tilde{A}\rangle \\ &= \sum_{k=0}^{\infty} \Delta E_A^{(k)}[W]\end{aligned}$$

$$\begin{aligned}\Delta E_A^{(k)}[W] &= \sum_{j=0}^{k} \langle A^{(j)}|W|A^{(k-j)}\rangle \\ &= \sum_{j=0}^{k} \sum_{M,N} \langle A^{(j)}|M\rangle\langle M|W|N\rangle\langle N|A^{(k-j)}\rangle\end{aligned}$$

Nuclear recoil effect

$$H_{\rm M} = H_{\rm NMS} + H_{\rm SMS} + H_{\rm RNMS} + H_{\rm RSMS}$$

$$H_{\rm NMS} = \frac{1}{2M} \sum_j \mathbf{p}_j^2$$

$$H_{\rm SMS} = \frac{1}{2M} \sum_{j\neq k} \mathbf{p}_j \cdot \mathbf{p}_k$$

$$H_{\rm RNMS} = -\frac{1}{2M} \sum_j \frac{\alpha Z}{r_j} \left[\boldsymbol{\alpha}_j + \frac{(\boldsymbol{\alpha}_j \cdot \mathbf{r}_j)\mathbf{r}_j}{r_j^2} \right] \cdot \mathbf{p}_j$$

$$H_{\rm RSMS} = -\frac{1}{2M} \sum_{j\neq k} \frac{\alpha Z}{r_j} \left[\boldsymbol{\alpha}_j + \frac{(\boldsymbol{\alpha}_j \cdot \mathbf{r}_j)\mathbf{r}_j}{r_j^2} \right] \cdot \mathbf{p}_k$$

Nuclear recoil effect: Li-like ions

Li-like ions

$2s$–$2p_J$ transitions: $E[(1s)^2 2p_J] - E[(1s)^2 2s]$

- CI-DFS: Kozhedub *et al.*, PRA **81**, 042513 (2010)
- $1/Z$ + CI-DFS: Zubova *et al.*, PRA **90**, 062512 (2014)

$$\Delta E[H_{\rm M}] = \frac{K}{M}$$

Li-like U: $(1s)^2 2p_{1/2}$–$(1s)^2 2s$

$Z = 92$ Coulomb potential [THz amu]

PT order	NMS	SMS	RNMS	RSMS
0	−3629.96	−4925.25	3930.05	3929.40
	−3629.93	−4925.25	3930.03	3929.40
1	−45.40	299.48	−28.38	−267.26
	−45.42	299.49	−28.37	−267.27
2	11.039	−6.879	−7.705	6.896
3	−0.327	0.112	0.255	−0.109
4	0.006	−0.002	−0.004	0.001
2–∞	10.72	−6.77	−7.46	6.79
	10.5	−6.7	−7.2	6.5
0–∞	−3664.64	−4632.54	3894.21	3668.93
	−3664.8	−4632.5	3894.4	3668.6

$1/Z$ + CI-DFS: Zubova *et al.*, PRA **90**, 062512 (2014)

Nuclear recoil effect: B-like ions

B-like ions

Fine structure: $E[(1s)^2(2s)^2 2p_{3/2}] - E[(1s)^2(2s)^2 2p_{1/2}]$

- CI-DFS: Zubova *et al.*, PRA **93**, 052502 (2016)

$$\Delta E[H_{\rm M}] = \frac{K}{M}$$

B-like ions: $2p_{3/2}$–$2p_{1/2}$ fine structure

$Z = 20$ [THz amu]

	NMS	SMS	RNMS	RSMS
KS	−1.8424	1.2661	1.4163	−1.9770
LDF	−1.8350	1.2593	1.4191	−1.9806
CI-DFS	−1.843	1.260	1.417	−1.978

$Z = 92$ [THz amu]

	NMS	SMS	RNMS	RSMS
CH	−2967.8	1967.9	2530.1	−2898.2
KS	−2967.8	1967.7	2529.4	−2896.8
CI-DFS	−2968.	1968.	2531.	−2899.

CI-DFS: Zubova *et al.*, PRA **93**, 052502 (2016)

g factor: positive-energy states

$$H_{\rm magn} = \mu_0 \mathcal{H} U \qquad \Delta E_A = g_A M_A \mu_0 \mathcal{H}$$

$$U = \sum_j \left[\boldsymbol{\alpha}_j \times \mathbf{r}_j\right]_z \qquad g_A[+] = \frac{1}{M_A}\langle \tilde{A}|U|\tilde{A}\rangle$$

$$\begin{aligned}\Delta g_A^{(k)}[+] &= \frac{1}{M_A}\sum_{j=0}^{k}\langle A^{(j)}|U|A^{(k-j)}\rangle \\ &= \frac{1}{M_A}\sum_{j=0}^{k}\sum_{M,N}\langle A^{(j)}|M\rangle\langle M|U|N\rangle\langle N|A^{(k-j)}\rangle\end{aligned}$$

g factor: negative-energy states

$$g_A[-] = \frac{2}{M_A} \sum_{p,n} \frac{\langle p|U|n\rangle}{\varepsilon_p - \varepsilon_n} \langle \hat{a}_n^+ \hat{a}_p \tilde{A}|H_1|\tilde{A}\rangle$$

$$\Delta g_A^{(k)}[-] = \frac{2}{M_A} \sum_{j=0}^{k-1} \sum_{M,N} \sum_{p,n} \frac{\langle p|U|n\rangle}{\varepsilon_p - \varepsilon_n} \times \langle A^{(j)}|M\rangle \langle \hat{a}_n^+ \hat{a}_p M|H_1|N\rangle \langle N|A^{(k-j-1)}\rangle$$

$$|p\rangle : \varepsilon_p > 0 \qquad |n\rangle : \varepsilon_n < 0$$

g factor of Li-like silicon

$$Z = 14$$

Dirac	1.998 254 751
QED $\sim \alpha$	0.002 324 044
QED $\sim \alpha^2$	−0.000 003 517 (1)
Nuclear recoil	0.000 000 039 (1)
Nuclear size	0.000 000 003
e-*e* interaction	0.000 314 809 (6)
Screened QED	−0.000 000 236 (5)
Total theory	2.000 889 892 (8)
Experiment	2.000 889 890 (2)

Wagner *et al.*, PRL **110**, 033003 (2013)
Volotka *et al.*, PRL **112**, 253004 (2014)

g factor of Li-like silicon

$$Z = 14$$

Coulomb potential

PT order	$\Delta g \times 10^9$
1	321 437.2
2	−6 826.0 (2)
3	108.0 (19)
4	−12.5 (8)
5	−2.1 (2)
total	314 704.6 (21)
3+	93.4 (21)
CI-DFS	85. (22)
CI	94.

Yerokhin *et al.*, arXiv:1705.04476

- the convergence of the PT expansion is good
- the uncertainty is determined by the 3rd-order term
- the uncertainty is 10 times smaller than with CI-DFS

g factor of Li-like silicon

$$Z = 14$$

Local Dirac-Fock potential

PT order	$\Delta g \times 10^9$
0	349 635.9
1	−33 960.4 (1)
2	−970.0 (2)
3	−1.1 (11)
4	−0.4 (3)
5	0.0 (2)
total	314 702.4 (12)
3+	−1.5 (12)
CI-DFS	−5.0 (60)

- the convergence of the PT expansion is even better
- the uncertainty is determined by the 3rd-order term
- the uncertainty is 5 times smaller than with CI-DFS
- the uncertainty is 2 times smaller than with Coulomb potential

g factor of Li-like silicon

$$Z = 14$$

Local Dirac-Fock potential

PT order	$\Delta g \times 10^9$	QED
0	349 635.9	
1	−33 960.4 (1)	+113.7
2	−970.0 (2)	−4.2
3	−1.1 (11)	±2.4
4	−0.4 (3)	
5	0.0 (2)	
total	314 702.4 (12)	314 813.5 (12)(24)

g factor of Li-like silicon

$$Z = 14$$

Dirac	1.998 254 751	
QED $\sim \alpha$	0.002 324 044	
QED $\sim \alpha^2$	−0.000 003 517 (1)	
Nuclear recoil	0.000 000 039 (1)	
Nuclear size	0.000 000 003	
e-*e* interaction	0.000 314 809 (6)	Volotka *et al.*, PRL (2014)
	0.000 314 809 (1)	Yerokhin et al., arXiv:1705.04476
	0.000 314 813 (3)	*this work*
Screened QED	−0.000 000 370 (7)	
Total theory	2.000 889 892 (8)	Volotka *et al.*, PRL (2014)
	2.000 889 892 (6)	Yerokhin *et al.*, arXiv:1705.04476
	2.000 889 896 (6)	*this work*
Experiment	2.000 889 890 (2)	Wagner *et al.*, PRL (2013)

g factor of Li-like calcium

$$Z = 20$$

Dirac	1.996 426 011	
QED $\sim \alpha$	0.002 325 555 (5)	
QED $\sim \alpha^2$	−0.000 003 520 (2)	
Nuclear recoil	0.000 000 062	
Nuclear size	0.000 000 014	
e-*e* interaction	0.000 454 290 (9)	Volotka *et al.*, PRL (2014)
	0.000 454 296 (4)	*this work*
Screened QED	−0.000 000 370 (7)	
Total theory	1.999 202 042 (13)	Volotka *et al.*, PRL (2014)
	1.999 202 048 (10)	*this work*
Experiment	1.999 202 041 (1)	Koehler *et al.*, NC (2016)

g factor of Li-like ions: conclusion

For low-Z Li-like ions:

- accuracy of $\Delta g_{\rm int}$ within the Breit approximation is improved by order of magnitude
- accuracy of $\Delta g_{\rm int}$ is now determined by the 3-photon QED contribution
- accuracy of g is now mostly determined by the screened QED contribution

Outlook

Further generalizations of the presented method

- (quasi-)degenerate states
- axially symmetric systems: DKB $\rightarrow$ ADKB
- $\langle \tilde{A}|W|\tilde{A}\rangle \rightarrow \sum_N \frac{\langle \tilde{A}|W_1|\tilde{N}\rangle\langle \tilde{N}|W_2|\tilde{A}\rangle}{\tilde{E}_A - \tilde{E}_N}$