Accurate properties of lithium-like systems calculated using explicitly correlated functions

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- Hyperfine splitting of the ground state (Li, Be^+)
- Fine structure $^2\mathbf{P_J}$ (Li, Be^+)

Nonrelativistic QED (NRQED)

Energy levels are expanded in powers of the fine structure constant α

$$E(\alpha) = E^{(2)} + E^{(4)} + E^{(5)} + E^{(6)} + E^{(7)} + \cdots , \qquad E^{(n)} \sim m\,\alpha^n$$

- $E^{(n)}$ can be expanded in the mass ratio $\eta = -\frac{m}{M}$

$$E^{(n)}(\eta) = E^{(n,0)} + E^{(n,1)} + E^{(n,2)} \cdots , \qquad E^{(n,k)} \sim \eta^k$$

- Perturbative calculations of energy levels are based on the effective Hamiltonian
- All $E^{(n>2)}$ are calculated as mean values using the Schrödinger wave function Ψ

Solving the Schrödinger equation

- The Schrödinger-Coulomb equation

$$H_0\Psi = E_0\Psi, \qquad H_0 = \sum_a \frac{\vec{p}_a^{\,2}}{2\,m} - \frac{Z\,\alpha}{r_a} + \sum_{a>b} \frac{\alpha}{r_{ab}}$$

- Trial wave functions are represented in the variational set of functions $\{\psi_i\}_{1\ldots n}$

$$\Psi = \sum_i^N c_i\psi_i, \qquad \psi = \mathcal{A}[\phi\,\chi], \qquad \chi - \text{spin function}, \mathcal{A} - \text{antisymmetrizer}$$

- The general eigenvalue problem + optimization

$$\hat{H}\bar{c} = \lambda\hat{N}\bar{c}, \qquad \hat{H}_{pq} = \langle\psi_p|H|\psi_q\rangle \qquad \hat{N}_{pq} = \langle\psi_p|\psi_q\rangle$$

Explicitly correlated bases

- Hylleraas basis (1927)

$$\phi = r_{23}^{n_1}\, r_{31}^{n_2}\, r_{12}^{n_3}\, r_1^{n_4}\, r_2^{n_5}\, r_3^{n_6} \exp(-w_1\, r_1 - w_2\, r_2 - w_3\, r_3)$$

  - the most accurate nonrelativistic energies for three-electron atoms,
  - very complicated integrals (only two- and three-electron atoms)
  - difficulties in the second order calculations with Hylleraas functions

- Explicitly Correlated Gaussians (ECG) (Singer, Boys 1960)

$$\phi = \exp(-w_1\, r_1^2 - w_2\, r_2^2 - w_3\, r_3^2 - u_1\, r_{23}^2 - u_2\, r_{13}^2 - u_3\, r_{12}^2)$$

  - improper short- and long-range asymptotics - huge number of parameters
  - ECG integrals can be calculated for arbitrary number of electrons
  - compact expressions, fast algorithms
  - **very flexible in higher order calculations**

Matrix elements (Hylleraas, Slater case)

- Matrix elements of the Schrödinger Hamiltonian (and other operators)

$$\langle\psi|H_0|\psi'\rangle = \langle 2\,\phi(1,2,3) + 2\,\phi(2,1,3) - \phi(3,1,2) - \phi(2,3,1) - \phi(1,3,2) - \phi(3,2,1)|H_0\,|\phi'(1,2,3)\rangle/6$$

are expressed in terms of Hylleraas integrals

$$f(n_1,n_2,n_3,n_4,n_5,n_6) = \int \frac{d^3r_1}{4\,\pi} \int \frac{d^3r_2}{4\,\pi} \int \frac{d^3r_3}{4\,\pi}\, e^{-w_1\,r_1 - w_2\,r_2 - w_3\,r_3} \times r_{23}^{n_1-1} r_{31}^{n_2-1} r_{12}^{n_3-1} r_1^{n_4-1} r_2^{n_5-1} r_3^{n_6-1}$$

- Classes of Hylleraass integrals

  - nonrelativistic : n_i are non-negative integers
  - relativistic : single index $n_i = -1$
  - Leading QED (Araki-Sucher term): single index $n_i = -2$
  - higher orders : two indices $n_i = -1$, **no effective algorithms**

- Recurrence relations have been derived by the integration by parts methods Tkachov (1980), Chetyrkin, Tkachov (1981)

Calculations with ECG functions

- Analytical forms of the integrals required for matrix elements

$$f(n_1,\ldots,n_6) = \int \frac{d^3r_1}{\pi}\int \frac{d^3r_2}{\pi}\int \frac{d^3r_3}{\pi}\, r_1^{n_1} r_2^{n_2} r_3^{n_3} r_{12}^{n_4} r_{13}^{n_5} r_{23}^{n_6} \times \exp\Big[-\sum_a \alpha_a\, r_a^2 - \sum_{a<b} \beta_{ab}\, r_{ab}^2\Big]\,.$$

- Classes of integrals

  - nonrelativistic : n_i - all even (regular), $1/r$ (Coulomb)
  - relativistic : $1/r^2$, $1/(r_a\, r_b)$
  - QED (Araki-Sucher term): $\ln(r)$, $\ln(r)/r$
  - **higher order :** $1/(r_a^2\, r_b)$, $1/(r_a^2\, r_b)$, $1/(r_a\, r_b\, r_c)$.

Ground state energy

Basis	Size	Value	Uncertainty
		He	
Hylleraas	2358	-2.903 724 377 034 119 598 311(1)...	$\sim 10^{-22}$, Drake (2002)
Slater	5200,	-2.903 724 377 034 119 598 311 159 4(4)...	$\sim 10^{-26}$, Korobov (2002)
Hylleraas + log	24 099,	-2.903 724 377 034 ...	$< 10^{-40}$, Schwartz (2006), Nakatsuji (2007)
		Li	
ECG	10000	-7.478 060 323 8	$\sim 10^{-11}$, Adamowicz, Bubin et al. (2008)
Hylleraas	13 944	-7.478 060 323 910 1(3)	$\sim 10^{-14}$, Pachucki, Puchalski et al. (2009)
Hylleraas	34 020	-7.478 060 323 910 147(1)	$\sim 10^{-16}$, Wang, Yan, Drake (2012)
		Be^+	
Hylleraas	13 944	-14.324 763 176 790 43(22)	but we are ready $\sim 10^{-15}$, Pachucki, Puchalski
		we are ready	

Transition energy

Contribution	$^7\mathrm{Li}(3S_{1/2} - 2S_{1/2})$ MHz	Uncertainty
$\nu^{(2)}$	815 561 313.5(1)	numerical
$\nu^{(4)}$	62 628.0(7)	numerical
$\nu^{(5)}$	−5 632.2(6)	numerical
$\nu^{(6)}$	−175.**(17.)**	approximation
$\nu^{(7)}$	19.**(5.)**	approximation
$\nu^{\text{finite size}}$	−8.9(2)	charge radius
^{7}Li **PRA 78 (2008), 2011**	**815 618 170.(19.)**	
^{7}Li theor. Yan, Drake (2008)	815 618 166.(30.)	
^{7}Li exp. Nörtershäuser, *et al.* (GSI,2008)	815 618 181.57(18)	

Theoretical predictions are limited by the higher order QED $m\alpha^6$ and $m\alpha^7$

Calculations of QED $m\alpha^6$ is a challenging task, but it can be completed

Hyperfine splitting in the ground state

High-precision atomic spectroscopy makes possible an accurate determination of nuclear properties

- Hyperfine splitting energy including higher order corrections PRL. 111, 243001 (2013)

$$E_{\rm hfs} = \langle H^{(4)}_{\rm hfs}\rangle + \langle H^{(5)}_{\rm hfs}\rangle + \langle H^{(6)}_{\rm hfs}\rangle + 2\,\langle H^{(4)}\,\frac{1}{(E-H)'}\,H^{(4)}_{\rm hfs}\rangle + \langle H^{(6)}_{\rm rad}\rangle + \langle H^{(7)}_{\rm hfs}\rangle + \cdots .$$

$H^{(4)}$ is the Breit-Pauli Hamiltonian

- Leading order Hamiltonian $m\alpha^4$

$$H^{(4)}_{\rm hfs} = \varepsilon\left(\frac{g}{2}\,H^{A}_{\rm hfs} + H^{B}_{\rm hfs} + H^{C}_{\rm hfs}\right),$$

$$H^{A}_{\rm hfs} = \frac{4\,Z\,\alpha}{3\,m^3}\sum_a \vec{I}\cdot\vec{\sigma}_a\,\pi\,\delta^3(r_a)\,, \qquad H^{B}_{\rm hfs} = \frac{Z\,\alpha}{m^3}\sum_a \vec{I}\cdot\frac{\vec{r}_a\times\vec{p}_a}{r_a^3}\,, \qquad H^{C}_{\rm hfs} = -\frac{Z\,\alpha}{2\,m^3}\sum_a \frac{I^i\,\sigma_a^j}{r_a^3}\left(\delta^{ij} - 3\,\frac{r_a^i\,r_a^j}{r_a^2}\right),$$

$\vec{I}$ - spin, and μ - magnetic moment of the nucleus, $\varepsilon = \frac{m^2}{M}\,\frac{g_{\rm N}}{2}$, $g_{\rm N} = \frac{M}{Z\,m_{\rm p}}\,\frac{\mu}{\mu_{\rm N}}\,\frac{1}{I}$

- Hyperfine structure constant A

$$E_{\rm hfs} = \vec{I}\cdot\vec{J}\,A, \qquad A = \frac{1}{J\,(J+1)}\,\langle\vec{J}\cdot\vec{H}_{\rm hfs}\rangle, \qquad A = \varepsilon\left[\frac{g}{2}\,\alpha^4 A^{(4)} + \sum_{n=5}^{\infty}\alpha^n\,A^{(n)}\right]$$

Hyperfine splitting in the ground state

• Dirac-delta-like interaction with the coefficient obtained from the two-photon forward scattering amplitude. Friar, Payne, PRC 72, 014002 (2005)

$$H^{(5)}_{\rm hfs} = \frac{\pi\alpha^2}{2}\sum_a \delta^3(r_a)\int d^3r\, d^3r' \left\langle \left\{\rho(\vec{r}\,),\, \vec{\sigma}_a\cdot(\vec{r}-\vec{r}')\times\vec{j}(\vec{r}')\right\} |\vec{r}-\vec{r}'|\right\rangle = \varepsilon\, H^A_{\rm hfs}\,(-2\,Z\,\alpha\,m\,\tilde{r}_Z),$$

ρ and $\vec{j}$ are the nuclear charge and current density operators, respectively

$\tilde{r}_Z$ is the effective Zeemach radius .

This correction fundamentally limits an accuracy of theoretical predictions. We use an experimental hyperfine splitting value to obtain the nuclear structure contribution expressed in terms of an effective Zemach radius $\tilde{r}_Z$.

Hyperfine splitting in lithium ground state

$$
\begin{aligned}
A^{(6)} &= A^{(6)}_{AN} + A^{(6)}_{B} + A^{(6)}_{C} + A^{(6)}_{R}, \\
A^{(6)}_{AN} &= \frac{2}{J\,(J+1)} \left\langle \frac{4\,\pi\,Z}{3} \sum_a \vec{J}\cdot\vec{\sigma}_a\,\delta^3(r_a)\,\frac{1}{(E-H)'}\,H^A \right\rangle \\
&\quad + \frac{1}{J\,(J+1)} \left\langle \sum_a \vec{J}\cdot\vec{\sigma}_a \left[\frac{Z^2}{6}\,\frac{1}{r_a^4} - \frac{2\,Z}{3}\,p_a^2\,\pi\,\delta^3(r_a) + \sum_{b;b\neq a} \frac{Z}{6}\,\frac{\vec{r}_{ab}}{r_{ab}^3}\cdot\left(2\,\frac{\vec{r}_b}{r_b^3} - \frac{\vec{r}_a}{r_a^3}\right) \right] \right\rangle, \\
A^{(6)}_{B} &= \frac{2}{J\,(J+1)} \left\langle Z \sum_a \vec{J}\cdot\frac{\vec{r}_a\times\vec{p}_a}{r_a^3}\,\frac{1}{(E-H)'}\,H^B \right\rangle, \\
A^{(6)}_{C} &= \frac{2}{J\,(J+1)} \left\langle -\frac{Z}{2} \sum_a \frac{J^i\,\sigma_a^j}{r_a^3} \left(\delta^{ij} - 3\,\frac{r_a^i\,r_a^j}{r_a^2}\right) \frac{1}{(E-H)'}\,H^C \right\rangle,
\end{aligned}
$$

$\mathcal{A}^{(6)}_{AN}$ consists of two terms, which are separately divergent at small r_a. We obtained a finite expression by transforming operators in the second order matrix element by

$$
\begin{aligned}
H^A &\equiv H'^A + \frac{1}{4}\sum_a \left\{ \frac{Z}{r_a},\, E-H \right\}, \\
4\,\pi\,\delta^3(r_a) &\equiv 4\,\pi\,[\delta^3(r_a)]' - \left\{ \frac{2}{r_a},\, E-H \right\}.
\end{aligned}
$$

Hyperfine splitting in lithium ground state

- Calculations
  - In the leading order calculations $A^{(4)}$ we used the Hyllearaas basis
  - In $A^{(6)}$ the second order terms are calculated using ECG methods
  - $A_B^{(6)}$ and $A_C^{(6)}$ involve elements of P-even and D symmetry, respectively.
  - We reduce spin variables with the help of a computer algebra program.
  - In $A^{(6)}$ some of the first order terms are calculated using ECG methods e.g.

$$\sum_{b>c} p_b^2\, r_a^{-1}\, p_c^2, \quad \sum_{b\neq a} \frac{\vec{r}_{ab}}{r_{ab}^3}\cdot\frac{\vec{r}_b}{r_b^3}, \quad \sum_{b>c} p_b^i\, r_a^{-1}\,\left(\frac{\delta^{ij}}{r_{bc}}+\frac{r_{bc}^i\, r_{bc}^j}{r_{bc}^3}\right) p_c^j$$

  - $A^{(7)}$ is estimated from the hydrogenic formulas

Hyperfine splitting in the ground state

From the comparison to experimental values one can obtain information about the finite nuclear distribution ($\tilde{r}_Z$) PRL. 111, 243001 (2013)

	^{7}Li	^{6}Li
$\varepsilon\,\alpha^4\,g/2\,A^{(4)}$	401.654 08(21)	152.083 69(11)
$\varepsilon\,\alpha^5\,A^{(5)}_{\rm rec}$	−0.004 14	−0.001 80
$\varepsilon\,\alpha^6\,A^{(6)}$	0.260 08(2)	0.098 48(1)
$\varepsilon\,\alpha^7\,A^{(7)}$	−0.010 2(13)	−0.003 9(5)
$A_{\rm the}$ (point nucleus)	**401.899 8(13)(2)**	**152.176 5(5)(2)**
$A_{\rm exp}$ A. Beckmann, et al. (1974)	401.752 043 3(5)	152.136 839(2)
$(A_{\rm exp} - A_{\rm the})/A_{\rm exp}$	−368(3) ppm	−261(3) ppm
Ref. (nucl. calc.)	−369(23) ppm	−368(60) ppm
$\tilde{r}_Z$	**3.25(3) fm**	**2.30(3) fm**
r_E	2.390(30) fm	2.540(28) fm

- This model is an independent and very accurate (as accurate as the magnetic moment) method to approach nuclear magnetic moment distribution
- We observe that the Zemach radius for ^{6}Li is about 40% smaller than that of ^{7}Li.
- This calls for a deeper understanding of the Li nuclear structure, or signals the existence of some unknown spin-dependent short-range force between charged hadrons and the lepton.

Hyperfine splitting in the ground state

Contributions in MHz to the hyperfine splitting constant A in $^9Be^+$ PRA 89, 032510 (2014).

	$^9Be^+$
$\varepsilon\,\alpha^4\,g/2\,A^{(4)}$	$-624.600\,44$
$\varepsilon\,\alpha^5\,A^{(5)}_{\rm rec}$	$0.006\,85$
$\varepsilon\,\alpha^6\,A^{(6)}$	$-0.820\,96$
$\varepsilon\,\alpha^7\,A^{(7)}$	$0.021\,8(36)$
$A_{\rm the}$ **(point nucleus)**	$\mathbf{-625.392\,7(36)(16)}$
$A_{\rm exp}$ D. J. Wineland *et al.* (1983)	$-625.008\,837\,048(10)$
$(A_{\rm exp}-A_{\rm the})/A_{\rm exp}$	$-614(6)(3)$ ppm
Ref. (nucl. calc.)	$-514(16)$ ppm
$\tilde{r}_Z$	$\mathbf{4.07(5)(2)}$ fm
r_E	$2.519(12)$ fm

- This approach is an model independent and very accurate (as accurate as the magnetic moment) method to approach nuclear magnetic moment distribution. It can be applied to short-lived halo nuclei
- For other isotopes ^{7}Be and ^{11}Be Wada et al. PRL 101, 212502 (2008), PRL 112, 162502 (2014), although hyperfine splitting is known, the magnetic moment has not yet been directly measured.

Lithium fine structure $^2\mathbf{P_J}$ - $m\alpha^4$

- Fine splitting

$$\nu_{\rm fs} = \langle H_{\rm fs}\rangle_{3/2} - \langle H_{\rm fs}\rangle_{1/2}$$

- Leading order Hamiltonian

$$\begin{aligned} H^{(4)}_{\rm fs} \quad = \quad & \sum_a \frac{Z\,\alpha}{2\,r_a^3}\,\vec{s}_a\left[\frac{(g-1)}{m^2}\,\vec{r}_a\times\vec{p}_a - \frac{g}{m\,m_{\rm N}}\,\vec{r}_a\times\vec{p}_{\rm N}\right] \\ & + \sum_{a\neq b}\frac{\alpha}{2\,m^2\,r_{ab}^3}\,\vec{s}_a\left[g\,\vec{r}_{ab}\times\vec{p}_b - (g-1)\,\vec{r}_{ab}\times\vec{p}_a\right] \end{aligned}$$

- Hyperfine mixing - second order

$$\delta E(P_{1/2})_{m_1 m_2} = \sum_m \frac{\langle P_{1/2},m_1|H_{\rm hfs}|P_{3/2},m\rangle\,\langle P_{3/2},m|H_{\rm hfs}|P_{1/2},m_2\rangle}{E(P_{1/2})-E(P_{3/2})}$$

$$\delta E(P_{3/2})_{m_1 m_2} = \sum_m \frac{\langle P_{3/2},m_1|H_{\rm hfs}|P_{1/2},m\rangle\,\langle P_{1/2},m|H_{\rm hfs}|P_{3/2},m_2\rangle}{E(P_{3/2})-E(P_{1/2})}$$

Lithium fine structure $^2\mathbf{P_J}$ - $m\alpha^4$ (2009, Hylleraas method)

	^{6}Li (MHz)	^{7}Li (MHz)
$\nu_{\rm fs}^{(4)}$	$10\,053.707\,2(83)$	$10\,053.707\,2(83)$
finite mass	$-2.786\,8(6)$	$-2.389\,1(5)$
$\delta\nu_{\rm fs}$	$0.012\,17$	$0.159\,16$
Total ($\Delta^{6,7}\nu_{\rm fs}$)	$\mathbf{-0.544\,7(1)}$	$\mathbf{10\,051.477(8)}$
Wang *et al.* (2017) - theory	$\mathbf{-0.556(1)}$	
Brown *et al.et al.* (2013)	$-0.531(24)$	$10\,053.310(17)$
Sansonetti *et al.* (2011)		$10\,053.435(21)$
Das *et al.* (2007)	$-0.155(77)$	$10\,051.999(41)$
Noble *et al.* (2006)		$10\,053.119(58)$
Walls *et al.* (2003)		$10\,052.37(11)$
Orth *et al.* (1975)	$0.863(79)$	$10\,053.184(58)$
Brog *et al.* (1967)		$10\,053.24(22)$

$\Delta^{6,7}\nu_{\rm fs}$ the isotope shift with respect to ^{7}Li.

Corrections $O(\alpha^2)$ are needed to approach the accuracy of experiment

Fine structure of Be^+ (2015 experiments)

Theoretical predictions of $\Delta^{A,9}\nu_{\rm fs}$ for $^{7,10,11,12}Be^+$ with respect to $^{9}Be^+$ are confirmed experimentally Nörtershäuser PRL 115, 033002 (2015)

Isotope	$\nu_{\rm fs}$ (MHz)	$\Delta^{A,9}\nu_{\rm fs}$ (MHz)	
^{7}Be	197 058.4(14)	$4.9(2.1)$	$6.036(1)$
^{9}Be	197 063.2(16)	0.0	0.0
^{10}Be	197 065.3(9)	$-2.1(1.8)$	$-2.096(1)$
^{11}Be	197 067.1(17)	$-3.9(2.3)$	$-3.965(1)$
^{12}Be	197 068.7(9)	$-5.5(1.8)$	$-5.300(1)$

Lithium fine structure $^2\mathbf{P_J}$ - $m\alpha^6$

$$E^{(6)}_{\rm fs} = \langle\phi| H^{(4)}_{\rm fs} \frac{1}{(E_0 - H_0)'} H^{(4)} |\phi\rangle + \langle\phi| H^{(6)}_{\rm fs} |\phi\rangle,$$

- Douglas-Kroll correction (1974)

$$\begin{aligned} H^{(6)}_{\rm fs} \quad = \quad & \sum_a \Big\{ \frac{3}{16}\, p_a^2\, e\, \vec{\mathcal{E}}_a \times \vec{p}_a \cdot \vec{\sigma}_a + \frac{e}{4} \Big(2\, p_a^2\, \vec{p}_a \cdot \vec{\mathcal{A}}_a + p_a^2\, \vec{\sigma}_a \cdot \nabla_a \times \vec{\mathcal{A}}_a \Big) + \frac{e^2}{2}\, \vec{\sigma}_a \cdot \vec{\mathcal{E}}_a \times \vec{\mathcal{A}}_a \\ & + \frac{i\, e}{16} \Big[\vec{\mathcal{A}}_a \times \vec{p}_a \cdot \vec{\sigma}_a - \vec{\sigma}_a \cdot \vec{p}_a \times \vec{\mathcal{A}}_a \,, p_a^2 \Big] + \frac{e^2}{2}\, \vec{\mathcal{A}}_a^{\,2} \Big\} + \sum_{b \neq a} \Big\{ -\frac{i\, \pi\, \alpha}{8}\, \vec{\sigma}_a \cdot \vec{p}_a \times \delta^3(r_{ab})\, \vec{p}_a \\ & + \frac{\alpha}{4} \Big(-i \Big[\vec{\sigma}_a \times \frac{\vec{r}_{ab}}{r_{ab}}, \frac{p_a^2}{2} \Big]\, e\, \vec{\mathcal{E}}_b + \Big[\frac{p_b^2}{2}, \Big[\vec{\sigma}_a \times \frac{\vec{r}_{ab}}{r_{ab}}, \frac{p_a^2}{2} \Big] \Big]\, \vec{p}_b \Big) \Big\} \end{aligned}$$

The static electric field and the vector potential at the position of particle a

$$e\, \vec{\mathcal{E}}_a \equiv -\nabla_a V = -Z\, \alpha\, \frac{\vec{r}_a}{r_a^3} + \sum_{b \neq a} \alpha\, \frac{\vec{r}_{ab}}{r_{ab}^3}$$

$$e\, \mathcal{A}^i_a \equiv \sum_{b \neq a} \frac{\alpha}{2\, r_{ab}} \Big(\delta^{ij} + \frac{r^i_{ab}\, r^j_{ab}}{r^2_{ab}} \Big)\, p^j_b + \frac{\alpha}{2} \frac{(\vec{\sigma}_b \times \vec{r}_{ab})^i}{r^3_{ab}},$$

Lithium fine structure $^2\mathbf{P_J}$ - $m\alpha^7\ln(\alpha)$

- Pachucki, Yerokhin (2010) - complete $m\alpha^7$ in helium-like ions

- Only logarithmic part for lithium atom

$$E^{(7)}_{\rm fs,log} = \langle H^{(7)}_{\rm fs,log}\rangle + 2\left\langle H^{(4)}_B \frac{1}{(E_0-H_0)'} H^{(5)}_{\rm log}\right\rangle$$

where $H^{(4)}_B$ - spin-orbit part of the Breit-Pauli Hamiltonian

$$H^{(5)}_{\rm log} = \alpha^2 \ln[(Z\,\alpha)^{-2}]\left[\frac{4Z}{3}\sum_a \delta^3(r_a) - \frac{7}{3}\sum_{b<a}\delta^3(r_{ab})\right]$$

$$H^{(7)}_{\rm fs,log} = \alpha^2 \ln[(Z\,\alpha)^{-2}]\left[\frac{Z}{3}\sum_a i\,\vec{p}_a\times\delta^3(r_a)\,\vec{p}_a\cdot\vec{\sigma}_a - \frac{3}{4}\sum_{b\neq a} i\,\vec{p}_a\times\delta^3(r_{ab})\,\vec{p}_a\cdot\vec{\sigma}_a\right].$$

Calculations

- All $m\alpha^6$ and $m\alpha^7\log(\alpha)$ matrix elements are calculated with ECG functions
- Symmetries of intermediate states in the second order elements

$$\left\langle H^{(4)}_{\rm fs}\,\frac{1}{(E-H)'}\,H^{(4)}\right\rangle = \left\langle H^{(4)}_{\rm fs}\frac{1_{2,4}S_o + 1_{2,4}P + 1_{2,4}D_o + 1_4F}{(E-H)'}\,H^{(4)}\right\rangle$$

- Spin reduction of the second order matrix elements

$$\langle\Phi|\sum_{a<b}\sigma^i_a\sigma^j_b\,Q^{ij}_{ab}\,\frac{1_4F_o}{E-H}\sum_{c<d}\sigma^i_c\sigma^j_d\,Q^{ij}_{cd}|\Phi\rangle = \frac{\{0,3\}}{6}\left\langle\Psi^{kji}_A\frac{1_4F_o}{E-H}\Psi^{ijk}_A\right\rangle$$

$$\Psi^{ijk}_A = \mathcal{P}\Big[c^A_{123}\,(Q^{ij}_{13}-Q^{ij}_{23})\,\phi^k(r_1,r_2,r_3)\Big]$$

- Two dimensional representation of the permutation group S_3 for $S=1/2$. Spin operators mix directions.

Final results

Fine splitting in Li and Be^+. PRL 113, (2014), PRA 92, 012513 (2015)

	^{7}Li (MHz)	Ref.	$^9Be^+$ (MHz)	Ref.
$\nu_{\rm fs}^{(4,0)}$	10 053.707(8)		197 039.15(8)	
$\nu_{\rm fs}^{(4,1)}$	−2.389		−21.27	
$\nu_{\rm fs}^{(6,0)}$	**1.63(5)**		**45.4(4)**	
$\nu_{\rm fslog}^{(7,0)}$	0.15(7)		4.6(2.3)	
$\delta\nu_{\rm fs}$	0.159		0.03	
$\nu_{\rm fs}$(theo)	**10 053.25(9)**		**197 068.0(2.4)**	
$\nu_{\rm fs}$(exp)	10 053.310(17)	Brown *et al.* (2013)	197 063.48(52)	Nörtershäuser *et al.* (2015)
$\nu_{\rm fs}$(exp)	10 053.24(22)	Brog *et al.* (1967)		
$\nu_{\rm fs}$(exp)	10 053.184(58)	Orth *et al.* (1975)	197 150.(64)	Bollinger *et al.* (1985)
$\nu_{\rm fs}$(exp)	10 053.119(58)	Noble *et al.* (2006)		
$\nu_{\rm fs}$(exp)	10 053.435(21)	Sansonetti *et al.* (2011)		
$\nu_{\rm fs}$(exp)	10 051.999(41)	Das *et al.* (2007)		
$\nu_{\rm fs}$(exp)	10 052.37(11)	Walls *et al.* (2003)		

The uncertainty due to neglected terms is estimated to be 50% of $\nu_{\rm fslog}^{(7,0)}$

Summary

- This demonstrates the capability of NRQED theory and the numerical approach based on explicitly correlated functions in achieving high-precision predictions for energies and energy splittings in light, few-electron atoms.

- very inaccurate calculations of the fine structure based on the Dirac equation (RMBPT, MCDF)

- $m\alpha^6$ corrections to transition energies

- The g-factor of lithium-like ions