Helium atom and Helium-like ions - where we are today

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Physics is experimental science

Isaac Newton

Basics in physics:

★ Experimental results must be reproducible (old)

★ Results of computations must be reproducible (new)

. . . the more accurate the calculations became, the more the concepts tended to vanish into thin air

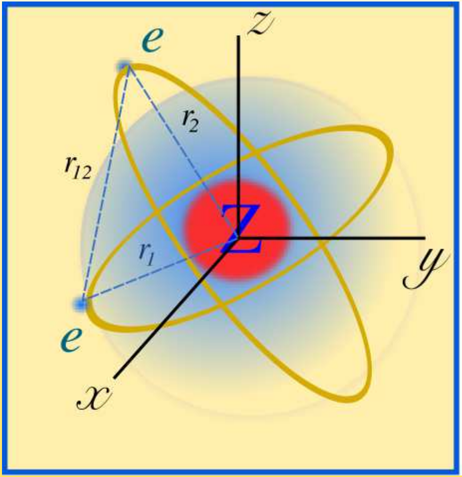
R.S. Mulliken (1965, Nobel Prize (1966))

in *Molecular Scientists and Molecular Science: Some Reminiscences*

J. Chem. Phys. **43** S2 (1965)

Helium two-electron sequence $(Z; e, e)$:

$H^{-}(Z = 1)$, He $(Z = 2)$, $Li^{+}(Z = 3)$ etc



Non-relativistic Hamiltonian for 3 Coulomb charges

$$\mathcal{H} \;=\; -\frac{1}{2\,M_Z}\Delta_Z \;-\frac{1}{2\,m_e}\Delta_1 \;-\; \frac{1}{2\,m_e}\Delta_2 \;-\; \frac{Z}{r_1} \;-\; \frac{Z}{r_2} \;+\; \frac{1}{r_{12}}$$

Static approximation: $M_Z = \infty$

$(M_{(Z=2)} \sim 8000 m_e)$

The Schrödinger equation

$$\mathcal{H}\Psi \;=\; E\Psi$$

Helium Atom - non-relativistic ground state energy
(about 150 calculations in 1929 - 2020)

$$E =$$

$$-2.903\,\mathbf{7}24\,3\mathit{77}\,03\mathbf{4}\,\mathbf{1}19\,598\,311\,159\,245\,194\,404\,\mathbf{4}46\,696\,9\mathit{05}\,\mathit{37}$$

41 s.d. – Schwartz, *Int. J Mod. Phys.* **E** (2006) (UC Berkeley)
45 s.d. – the most accurate energy for the 3-body Schrödinger equation, Nakashima-Nakatsuji, *J Chem Phys* (2007) (Tokyo)

13 s.d. – confirmed in $1/Z$-expansion and by Lagrange Mesh – in two different methods (H.O.P.+J.C.L.V.+A.T. 2016) (Mexico)

35 (24) s.d. – confirmed by Aznabaev, Bekhaev, Korobov (2000-2), *Phys Rev A* (2018) (Dubna, Kazakhstan-Russia),

22,000 terms, 100 digit arithmetic, $\sim 10^5$ parameters!

Nakashima-Nakatsuji data (2007-8), $Z = 1, 2, \ldots, 10$:

[1, −0.527751016544 377196590814566747511*38304502*]

[2, −2.903724377034 119598311159245194404446696905 37]

[3, −7.279913412669 305964919459221006611682572 35]

[4, −13.655566238423 586702081730194612159391360 60]

[5, −22.030971580242 781541655702043566870379775 99]

[6, −32.406246601898 530310557357969530254566016 97]

[7, −44.781445148772 704645185760848954056776028 12]

[8, −59.156595122757 925558549892445559527700907 85]

[9, −75.531712363959 491104878015579533576560909 77]

[10, −93.906806515037 549421469184180000241066651 70]

Three Questions:

(I) What about expectation values?

$\sim$ Six studies **ONLY** in $\sim$ 90 years!! Still **OPEN problem**, there are controversies ...

What about $< \delta(r_1) >$? – it defines probability of catalysis, e.g. $\alpha + e \to \ldots$.

(II) How to store energies and ABK parameters $\sim 10^5$ with 100 s.d. each if they would be known?

Can these calculations be repeated - when no variational parameters known?

(III) Do exist function(s) which generates these numbers?

Helium Atom (ground state energy)

$\sim$ 150 calculations in NRQED!

First calculation: E Hylleraas (1929, p.114)

$$E = -\mathbf{2.903}\,2$$

Last (and concluding but final) calculations:

Nakashima - Nakatsuji (2007-8) - Korobov (2018) - 35-44 s.d.

(it was checked and confirmed in Lagrange mesh method up to 13 s.d.)

$$E = -2.903\,724\,377\,0\ldots \text{(infinite mass)}$$

$$E = -2.903\,304\,557\,7\ldots \text{(finite mass)}$$

$$\Delta E_{mass} = 0.000\,420\ldots$$

$$\Delta E_{QED+rel} = -0.000\,112\ldots \;(Yerokhin - Pachucki, 2010)$$

Mg^{10+}(magnesium) - ($Z = 12$)-two-electron Ion (ground state energy)

First accurate calculation (*in bold*):

Thakkar-Smith (1977)

Last (and final(?)) calculation:

Turbiner-Lopez V-Olivares P (2016-18)
in $1/Z$*-expansion*

(it was checked, confirmed and extended in Lagrange mesh method up to 13 d.d.)

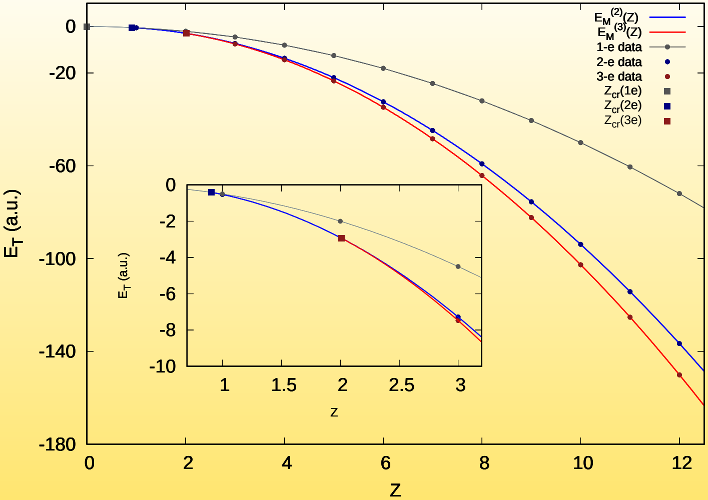
$$E = -\mathbf{136.656\,94}8\,312\,647\ldots \text{(infinite mass)}$$

(T-S $->$ bold)

$$E = -136.653\,788\,023\,4\ldots \text{(finite mass)}$$

$$\Delta E_{mass} = 0.003\,2\ldots$$

$$\Delta E_{QED+rel} = -0.250\ldots \; (Yerokhin - Pachucki, 2010)$$



Ground state energy *vs* Z for 1-, 2-, 3-electron atoms in NRQED in static approximation. Critical charges marked by filled squares.

How to describe/interpolate these curves?

Ettore Majorana
(August 5, 1906 - March 25, 1938)

In fact, E Majorana asked (in his unpublished notes, circa 1930):

Can we interpolate the energy behavior at small and large Z

using simple function but with high accuracy?

Majorana was the first who proposed to consider the charge Z as continuous parameter.

Let us try to answer!

• At small Z (near threshold, the Schwinger theory: *how the level enter to continuum*) :

there exists $Z_B > 0$ for which the energy is given by the Puiseux expansion at $Z = Z_B$

$$E(Z) \; = \; E_B + p_1\,(Z - Z_B) + q_3\,(Z - Z_B)^{3/2} + p_2\,(Z - Z_B)^2$$

$$+q_5\,(Z - Z_B)^{5/2} + p_3\,(Z - Z_B)^3 + q_7\,(Z - Z_B)^{7/2} + p_4\,(Z - Z_B)^4 + \ldots$$

where $E_B = E(Z_B)$

• *Critical charge Z_B is a value of Z which separates the domains "existence ($Z > Z_B$)/non-existence ($Z < Z_B$)" of solutions in the Hilbert space*

$$Z_B^{(2e)} \; = \; 0.904854$$

• F Stillinger and D Stillinger (qualitative, He, 1966, 1974)

• Y Cizek et al, A Turbiner at al (quantitative, He,Li 2010-1, 2016, 2019)

$p_{1,2,3,4}$ and $q_{3,5,7}$ are calculated (2019)

• **Critical charge Z_B separates the domains "existence ($Z > Z_B$)/non-existence ($Z < Z_B$)" of solutions of the Schrödinger equation in Hilbert space**

$\Rightarrow$ algebraic branch point in $E(Z)$ may exist at $Z = Z_B$

• **Critical charge Z_{cr} is a value of Z for which the ionization energy $I(Z = Z_{cr}) = 0$**

$\Rightarrow$ essential singularity **at most** in $E(Z)$ may exist,

$$Z_B \neq Z_{cr}$$

$$Z_{cr}^{(2e)} = 0.911028224077$$

He: Drake et al, PRL (2014) and Olivares Pilon - Turbiner, PLA (2015)

- At large Z – celebrated $1/Z$-expansion:

$$E(Z) \;=\; -B_0 Z^2 + B_1 Z + B_2 + O\left(\frac{1}{Z}\right)$$

$$B_0^{(2e)} \;=\; 1 \;,\; B_1^{(2e)} \;=\; \frac{5}{8} \;,\; B_2^{(2e)} \;=\; -0.15766642946915$$

(short dramatic story: it must be convergent series *(the Kato Theorem)*, asymptotics of coeffs is not analytically established yet as well as positions and type of singularities)

About $1/Z$: Make a rescaling $r \to \frac{r}{Z}$ of $\mathcal{H} \to \frac{\hat{\mathcal{H}}}{Z^2}$

$$\hat{\mathcal{H}} = -\frac{1}{2}(\Delta_1 + \Delta_2) - \frac{1}{r_1} - \frac{1}{r_2} + \left(\frac{1}{Z}\right)\frac{1}{r_{12}}$$

$$\hat{E} \to \frac{E}{Z^2}$$

- Develop perturbation theory in $1/Z$

$$\hat{E} = \sum_{n=0}^{\infty} e_n \frac{1}{Z^n}$$

- This is the famous convergent $1/Z$-**expansion**

$$e_0 = -1 \,, \; e_1 = \frac{5}{8}$$

At $Z \to \infty$

- Exact solution, two non-interactive Hydrogen atoms:

$$E_0 = -Z^2$$

$1/Z$-expansion is perturbation theory from two Hydrogen atoms!

- Correlation energy

$$E_c = E + Z^2$$

$e_0 =$	-1
$e_1 =$	$+5/8$
$e_2 =$	−0.157 666 429 469 1**50 94**
$e_3 =$	+0.008 699 031 52**7 989 8**
$e_4 =$	−0.000 888 707 284 **667 8**
$e_5 =$	−0.001 036 371 84**7 099 2**
$e_6 =$	−0.000 612 940 52**1 924 4**
$e_7 =$	−0.000 372 175 57**4 257 0**
$e_8 =$	−0.000 242 877 97**6 020 2**
$e_9 =$	−0.000 165 661 05**2 028 2**
$e_{10} =$	−0.000 116 179 20**3 700 1**
$e_{20} =$	−0.000 007 686 16**3 321 308**
$e_{30} =$	−0.000 001 011 388 **064 240**
$e_{40} =$	−0.000 000 177 41**8 138**
$e_{50} =$	−0.000 000 036 533 **598**

Table: First e_n found by C Schwartz (Berkeley, 2013, unpublished) with $\sim$ 3000 terms at 60-70-digit arithmetics, modified (in bold) in comparison with ones found in Baker et al, 1990 (30-digits, 476 terms)

New Idea: **INTERPOLATION**

- Introduce New Variable

$$\lambda^2 = Z - Z_B$$

Now both expansions, at small and large λ, do not contain fractional degrees, they are Taylor and Laurent expansions!

- Let us match two expansions constructing Two Point Pade approximation

$$E_{N,4}(\lambda(Z)) = \frac{P_{N+4}(\lambda)}{Q_N(\lambda)} \equiv \text{gPade}(N+4/N)_{n_0,n_\infty}(\lambda)$$

n_0 coeffs reproduced exactly in $\lambda = 0$ - Puiseux expansion

n_∞ coeffs reproduced exactly in $\lambda = \infty$ - Laurent expansion

Results

(I) In NRQED let us choose $N = 5$ for ground state energy:

$$\mathrm{gPade}(9/5)(\lambda)_{3,4} \; = \frac{E_B + a_1\lambda + a_2\lambda^2 + a_3\lambda^3 + a_4\lambda^4 + a_5\lambda^5 + a_6\lambda^6 + a_7\lambda^7 + a_8\lambda^8 + a_9\lambda^9}{1 + b_1\lambda + b_2\lambda^2 + b_3\lambda^3 + b_4\lambda^4 + b_5\lambda^5}$$

$\rightarrow$ (3+4) exact coeffs plus **eight** free parameters
hence, **eight** points are needed to be used in interpolation only

• **gPade$(9/5)(\lambda)_{3,4}$ reproduces 12-13 s.d. for all physics domain of $Z \leq 50$ (for two-electron case, He-like)** and $Z \leq 20$ (for three electron case, Li-like)

• Larger $N > 5$ should lead to even higher accuracies
The problem is solved, but why such a high accuracy is reached in so complicated problem? - open question!

[1, −**0.527751016544** 37719659081456674751*1138304502*]

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[3, −**7.279913412669** 305964919459221006611682572 35]

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[9, −**75.531712363959** 491104878015579533576560909 77]

[10, −**93.906806515037** 549421469184180000241066651 70]

(II) Let us choose $N = 0$

- **Forth degree polynomial**

$$\text{gPade}(4/0)(\lambda)_{2,1} \;=\; E_B \;-\; a_2\lambda^2 \;-\; a_3\lambda^3 - B_0\lambda^4$$

$$a_2 \;=\; (0)\ 1.18489\ (3.48521)\ ,\ a_3 \;=\; (0)\ 0.000027\ (0.002469)$$

- reproduces 3-4 s.d. ($\sim 99.9\%$) in the whole physics domain of $Z < 50$ for 1-, 2-, 3-electron atoms (ions).

Hence, it describes non-relativistic QED ground state energy in its domain of applicability!

(III) Majorana formula: $N = 0, a_2 = 0$

$$E_M^{(2)}(Z) \ = \ -e_2 Z^2 + e_1 Z + e_0 \ , \quad e_2 = 1$$

(E Majorana, circa 1930, from unpublished notes for He-like ions)

If

$$e_{1,\mathrm{fit}} \ = \ 0.624583 \qquad , \qquad e_{0,\mathrm{fit}} = -0.153282$$

for He-like sequence, or

$$E_M^{(3)}(Z) \ = \ -e_2 Z^2 + e_1 Z + e_0 \ , \quad e_2 = 9/8$$

$$e_{1,\mathrm{fit}} \ = \ 1.023260 \qquad , \qquad e_{0,\mathrm{fit}} = -0.416432$$

for Li-like sequence,

• **It reproduces 3-4 s.d. ($\sim 99.9\%$) in the whole physics domain of $Z < 50$ for 1-, 2-, 3-electron atoms-ions.**

$\rightarrow$ What is physics reason behind or is it a pure phenomenology ?

[1, −0.527 751016544 377196590814566747*51138304502*]

[2, −2.903 724377034 119598311159245194404446690537]

[3, −7.279 913412669 305964919459221006611682572335]

[4, −13.655 566238423 586702081730194612159391360 60]

[5, −22.030 971580242 781541655702043566870379775 99]

[6, −32.406 246601898 530310557357969530254566016 97]

[7, −44.781 445148772 704645185760848954056776028 12]

[8, −59.156 595122757 925558549892445559527700907 85]

[9, −75.531 712363959 491104878015579533576560909 77]

[10, −93.906 806515037 549421469184180000241066651 70]

Relativistic + QED corrections to energy *vs* Z

First 3 significant digits (figures):

$$D_{rQED}^{I,\mathrm{He-like}} = (-7.174+11.046\,Z-7.976\,Z^2+3.749\,Z^3-1.324\,Z^4)\times 10^{-5}$$

$\rightarrow$ for He-like ions for $Z \in [1, 50]$

$$D_{rQED}^{\mathrm{Li-like}} = (-37.22+26.33\,Z-5.925\,Z^2+0.8735\,Z^3-0.1629\,Z^4)\times 10^{-4}$$

$\rightarrow$ for Li-like ions for $Z = 3$ and $Z \in [10, 20]$

(no reliable calculations for $Z \in [4, 9]$)

Two questions

(I) Will Majorana formula work for excited states of Helium sequence?

For some states - Yes! (lowest spin-triplet state)

(II) Will Majorana formula work for k-electron ions?

For $k = 3$ - Yes!

What about wave function for NRQED ground state in its domain of applicability?

$$\Psi_0 \;=\; \frac{1}{2}(1+P_{12})\left[(1-ar_1+br_{12})\,e^{-\alpha Z r_1-\beta Z r_2}\right]\,e^{\gamma \hat{r}_{12}}$$

where P_{12} permutation and

$$\hat{r}_{12} \;=\; r_{12}\,\frac{1\;+\;Ar_{12}}{1\;+\;Br_{12}}$$

(J.C. del Valle, D.J. Nader, J.C. Lopez Vieyra, A.V.T.)

It solves the problem: for any $Z \in [1, 20]$, **4-5 s.d.** in energy are exact and for 6 expectation values **2-3 s.d.** are exact; all 7 parameters are smooth, easy fitted functions of Z

- continuation

Relative deviation from exact function

$$\left|\frac{\Psi_0 - \Psi_{exact}}{\Psi_{exact}}\right| \leq 10^{-3} \text{ for } \forall r$$

One can introduce the effective potential of NRQED

$$V_{eff} = \frac{\Delta\Psi_0}{\Psi_0}$$

it reproduces the Coulomb singularities and tends to constant(s) at large r, deviates from original potential at $r \sim 1 \rightarrow$, pert theory in deviation $(V - V_{eff})$ is convergent!

How to go beyond domain of applicability of NRQED?

using perturbation theory

- "quantum corrections" wrt deviation $(V - V_{eff})$ (or variationally, standard way)

- relativistic, in powers v/c

- QED, in powers of α