Quantum 3-body Coulomb problem: a numerical challenge (?)

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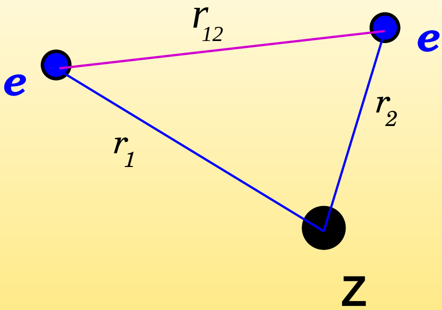

r_{12}
e
e
r_2
r_1
Z

Reduced 3-body problem:

$$(Ze, M) \text{ and two identical } (-e, m)$$

$$V = -\frac{mM}{r_1} - \frac{mM}{r_2} - \frac{m^2}{r_{12}}$$

Kepler problem

$$V = -\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}$$

Coulomb problem

Two Particular Cases:

One-center case $M = \infty$

(Helium-like atom)

Two-center case $m = \infty$

(H_2^+-like molecular ion)

The Hamiltonian

$$\mathcal{H} \;=\; -\frac{1}{2M}\Delta \;-\; \frac{1}{2m}(\Delta_1 + \Delta_2) \;-\; \frac{Z}{r_1} \;-\; \frac{Z}{r_2} \;+\; \frac{1}{r_{12}}$$

with $r \in \mathbf{R}^6 \oplus \mathbf{R}^3 \quad \rightarrow$ *Centre-of-Mass can be separated out*

The Schrödinger equation

$$\mathcal{H}\Psi(x) \;=\; E\Psi(x) \quad , \quad \Psi(x) \in L^2(\mathbf{R}^6)$$

not always has solutions.

• **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_{cr} - **The ionization energy is zero, the system can decay at $Z < Z_{cr}$**

$$(Zp, e, e) \Rightarrow (Zp, e) \;+\; e$$

Are these Z_B and Z_{cr} related?

EXAMPLE: the Hydrogen atom ($M = \infty$)

$$\mathcal{H} \; = \; -\frac{1}{2}\Delta \; - \; \frac{Z}{r}$$

Ground state energy

$$E_0 \; = \; -\frac{Z^2}{2}$$

is entire function in Z (no singularities), but

$$Z_{cr} = 0$$

(potential is equal to zero)
No analytic continuation of E_0 to negative Z !

$$\Psi_0 \; = \; e^{-Zr} \; , \; Z > 0$$

Rigorous mathematical results:

- Energy $E(Z)/Z^2$ is analytic around $Z = \infty$ (T. Kato, 1951)
  it is given by convergent Taylor expansion - what is radius of convergence?

- At $Z = 2$ there are infinitely-many bound states but at $Z = 1$ - finitely-many (D. Yafaev, 1972)
  there must be Z^* where the transition happened - *infinitely-many bound states disappear* - how it happened?

- Ground state $\Psi(x; Z = Z_{cr})$ is normalizable (B. Simon, 1977)

Methods used to solve:

- Variational (linear and recently, nonlinear)
- Non-uniform lattice - Lagrange mesh (D Baye , H Olivares)

Physics: integer $Z = 1, 2, 3, \ldots$

- Energies (…Nakashima-Nakatsuji, 2007)
- Z_{cr} (…Drake et al, 2014, H Olivares & AT 2014)
- Transition amplitudes (D Baye, … , H Olivares 2014)

The two-electron ion sequence (helium isoelectronic sequence) $(M = \infty)$

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

at $Z > 2 \quad \Rightarrow \quad$ 2e-ion (infinitely-many bound states)
at $Z = 2 \quad \Rightarrow \quad$ Helium atom (infinitely-many bound states)
at $Z = 1 \quad \Rightarrow \quad$ Negative Hydrogen ion (single bound state)

Critical charge

$$Z_{cr} \ \sim \ 0.91 \ \ldots$$

the ionization energy is zero, the system can decay at $Z < Z_{cr}$

$$(Zp, e, e) \Rightarrow (Zp, e) \ + \ e$$

Does it imply no solution of Schrödinger Eq in L^2 at $Z < Z_{cr}$ unlike at $Z \geq Z_{cr}$ or what ?

- (Can it be a level embedded to continuum?)

QUESTIONS:

How to find Z_{cr}, where $I(Z = Z_{cr}) = 0$, and Z_B?

Is there any singularity in Z-plane of ground state energy associated with Z_{cr}, and Z_B?

Make a rescaling $r \to \frac{r}{Z}$ of $\frac{\mathcal{H}}{Z^2}$

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

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

- Develop perturbation theory in $\lambda = 1/Z$

$$\hat{E} = \sum_{n=0}^{\infty} e_n \, \lambda^n$$

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

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

- All other coefficients SEEM **non**-rational numbers.

• As early as 1930 E. Hylleraas found next 3 coefficients (somehow wrong!)

$$e_2 \;=\; -0.15744\,(67)\;,\; e_3 \;=\; 0.00876\,(0)\;,\; e_4 \;=\; -0.00274\,(089)$$

• At 1990 J.D.Baker, D.E.Freund, R.N.Hill, J.D.Morgan III, Jr calculated 401 coefficients **overpassing** all $\sim$ 150 previous calculations!

The famous paper: about 200 citations, no single attempt to verify, improve or challenge for 20 years!

Keypoint: Quadruple precision! ($\sim$30 figures), *476-term function*

They extracted the *Asymptotic* behavior from $e_{25} \div e_{401}$:

$$e_n \;=\; Z_{cr}^n n^{\beta} e^{-\alpha n^{\frac{1}{2}}} \left(1 \;+\; \frac{c_{1/2}}{n^{1/2}} \;+\; \frac{c_1}{n} \;+\; \frac{c_{3/2}}{n^{3/2}} \;+\; \frac{c_2}{n^2} + \ldots\right.$$

with $\alpha = 0.272$ and $\beta = -1.94$; $e_{200} \sim 10^{-16}$ and $e_{400} \sim 10^{-25}$

Quite unique convergent expansion in physics! (Kato Theorem)

• What is radius of convergence?

$$R = 1/Z_{cr}$$

• Where is the singularity? - At real Z-axis

(W. Reinhardt conjecture)

• What is a nature of singularity? - might be smth horribly complicated...

(algebraic branch point with exp=7/6 plus essential singularity at $Z_{cr} = Z_B = 0.911028$)

(Baker et al, '90)

1st challenge (2010):

J Zamastil, J Cizek et al , Phys Rev A 81 (2010) - some long-established conclusions are wrong(!):

$$Z_{cr} = 0.9021\ldots$$

it differs in 2nd digit from established!

Statement: the 1990's calculation is wrong!

• *asymptotics* e_n at $n \to \infty$ extracted from $e_{13} \div e_{19}$ differs from *Baker et al*,'s one: $\alpha = 0$ and $\beta = -5/2$. **Inconsistency!**

• *Energy*

$$E(\lambda) = (\lambda - 1/Z_{cr})^{\frac{1}{2}} f_1(\lambda - 1/Z_{cr}) + f_2(\lambda - 1/Z_{cr})$$

$f_{1,2}$ are regular at $\lambda = 1/Z_{cr}$ and $f_1(0) = 0$ (the so called Darboux function)

• *Singularity*

Branch point of the 2nd order with exponent 3/2 (!) - contrary to '90 result

but in agreement with F.H.Stillinger, 1966, 1974

However, F.H.Stillinger said more:

radius of convergence

$$R > 1/Z_{cr}$$

It may imply the existence of the level embedded to continuum at $Z < Z_{cr}$!

2nd challenge (2011):

• N Guevara and AT (Phys Rev A 84, 2011) :

Let us calculate the singularity at $Z = Z_B$ directly (*assuming the Reinhardt conjecture holds:* $I(Z_B) = 0$) making approximation by

$$E_{total} = -\frac{Z_B^2}{2} - 1.142552(Z - Z_B) - 0.174110(Z - Z_B)^{3/2}$$

$$- 0.770010(Z - Z_B)^2 - 0.139923(Z - Z_B)^{5/2}$$

$$+ 0.022469(Z - Z_B)^3 + 0.008730(Z - Z_B)^{7/2} \dots$$

at $Z > Z_B = 0.91085$ (Puiseux expansion) ,
7 s.d. reproduced at 12 points in E at $Z \in [0.95, 1.35]$

• We did **not** confirm the result by 2010 for Z_{cr} being in close agreement with '90 result $Z_{cr} = 0.911029$

• But we confirm (?) that

Branch point of the 2nd order with exponent 3/2!

• We did **not** confirm the asymptotics by Baker et al, '90 (and large-order coeffs, even in the 1st digits)

A complete mess!

How Baker et al, '90 calculated Z_{cr} ?

Two options:

either
Making approximation of e_n,

or,

by Solving equation $I(Z_{cr}) = 0$

That paper gives NO definite answer ...

Suspicion: **quadruple precision failure** *or* **error accumulation**

Let us check it →

The First Observation: we do not confirm the statement from Baker et al (p.1254):

The sum of the e_n's for n running from 0 to 401 is

$$-0.527\,751\,016\,544\,\mathbf{266}$$

which at the time we did our calculations was the most accurate estimate of the energy for the ground state of H^-.

Our result

$$-0.527\,751\,016\,544\,\mathbf{160}$$

differs in the last three decimal digits,
(i) ifort q-precision real*16 (quadruple precision),
(ii) Maple Digits=30 in Maple 13
(iii) C Schwartz (Berkeley) multiple precision arithmetic package (but MATEMATICA)

The Second Observation:

$$\text{for } E(Z=1) \ = \sum^{401} e_n$$

neither Baker et al,

$$-0.527\,751\,016\,544\,\mathbf{266}$$

nor, our accurate sum of Baker's coeffs

$$-0.527\,751\,016\,544\,\mathbf{160}$$

coincide to Nakashima-Nakatsuji (2007) exact(!) result

$$-0.527\,751\,016\,544\,\mathbf{377}\ , \ \ldots$$

- Similar story for $Z = 2$!

Conclusion:

certainly, e_n beyond 12 decimal digits were calculated **unreliably/wrongly**!

$e_0 =$	-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 perturbation coefficients e_n found by C Schwartz (2013) with $\sim$ 3000 terms at 60-70-digit arithmetics, modified (in bold) in comparison with ones found in Baker:1990 (30-digits, 476 terms)

Z	E (a.u.) from PT	E (a.u.)
1	-0.527 751 016 544 37**1**	-0.527 751 016 544 377
2	-2.903 724 377 034 119	-2.903 724 377 034 119
3	-7.279 913 412 669 305	-7.279 913 412 669 305
4	-13.655 566 238 423 586	-13.655 566 238 423 586
5	-22.030 971 580 242 781	-22.030 971 580 242 781
6	-32.406 246 601 898 530	-32.406 246 601 898 530
7	-44.781 445 148 772 704	-44.781 445 148 772 704
8	-59.156 595 122 757 925	-59.156 595 122 757 925
9	-75.531 712 363 959 491	-75.531 712 363 959 491
10	-93.906 806 515 037 549	-93.906 806 515 037 549
11	-114.281 883 776 072 721	-114.281 879 ($*$)
12	-136.656 948 312 646 929	-136.656 944 ($*$)

Table: Left column: $E(Z)$ - perturbative energies (partial sums)
Right column: Nakashima-Nakatsuji (Tokyo, 2007) ,
C. Schwartz (Berkeley, 2006) at $(Z = 2)$
($*$) Thakkar-Smyth (Ontario, 1977)

Conclusion: *No non-analytic terms in energy* $\sim e^{-Z}$
(Kato's Theorem confirmed!)

Epilogue (about $1/Z$-expansion): what to do?

We have to come back to 1990, repeat the calculations of the higher orders e_n, extract asymptotic behavior, find radius of convergence R and, possibly, singularity,
(situation with e_n for 2^1S state is unsatisfactory as well)

Or,

• *Is there a way to calculate asymptotics analytically?*
(like for anharmonic oscillators in QM (*a la* Bender-Wu), or in QFT for Gellmann-Low functions (*a la* Lipatov etc) and in stat mechanics for free energy)

• Or, to solve the spectral problem at threshold

$$\left(-\frac{1}{2}(\Delta_1+\Delta_2) - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{2}\right)\Psi \;=\; \frac{1}{Z}\,\frac{1}{r_{12}}\Psi \quad , \quad \Psi(x) \in L^2(\mathbf{R}^6)$$

and find $\frac{1}{Z_{cr}}$ ... how to do it?

• Variationally (triple set with non-linear parameters, 2276 terms), $E_{var} = E(Z)$ (*PRL*, Drake et al (April, 2014)):

$$Z_{cr} = 0.91102\mathbf{822407725573}$$

• Lagrange mesh (non-uniform lattice) (*PLA*, Olivares-Pilon and AT, Jan 2015):

12 decimals are confirmed

• Pseudospectral method (*PRA*, Grabovski and Burke, March 2015):

11 decimals are confirmed

However, Drake et al (April, 2014) predict the bound state even for $Z < Z_{cr}$ contrary to intuitive statement
$(< r_1 >\sim 1 a.u.\ ,\ < r_2 >\sim 5 a.u.)$.
Hence, **the level embedded to continuum!!**

Is it an artifact of variational study by Drake et al?

- At $Z = 0.91$ the ground state energy (September 2014):

Olivares-Pilon and AT,	-0.41379921124	a.u.	(Lagrange mesh)
Drake et al,	-0.413799211244	a.u.	(variational)

$$R > \frac{1}{Z_{cr}}$$

in agreement with Stillinger !

We are back to the question by E. Hylleraas:

How to find $R(= \frac{1}{Z_B})$?

F.H. Stillinger (1966):

Take Hylleraas-Eckart-Chandrasekhar trial function

$$\Psi_{HEC}(r_1, r_2) = \Psi_0(r_1, r_2) + \Psi_0(r_2, r_1)\,,\ \Psi_0(r_1, r_2) = e^{-\alpha_1 r_1 - \alpha_2 r_2}\,,\ \alpha_1 \neq \alpha_2$$

- There exist both $Z_{cr} (= 0.9538)$ and $Z_B (= 0.9276)$
- There exist two different expansions for variational energy:

$$E(Z) = -\frac{Z_{cr}^2}{2} + a_1(Z - Z_{cr}) + a_2(Z - Z_{cr})^2 + a_3(Z - Z_{cr})^3 + \dots$$

which is the Taylor expansion, and

$$E(Z) = b_0 + b_1(Z - Z_B) + c_1(Z - Z_B)^{\frac{3}{2}} + b_2(Z - Z_B)^2 + c_2(Z - Z_B)^{\frac{5}{2}} + \dots$$

which is the Puiseux expansion

Four different choices for trial function Ψ_0 lead to the same expansions!

$$\Psi = \Psi_{HEC}(r_1, r_2)(1 + cr_{12})e^{-\beta r_{12}}$$

(B Carballo, talk on June 2014)

The more accurate

$$Z_{cr} = 0.9195 \quad \text{and} \quad Z_B = 0.8684$$

parameters vs Z behave like in catastrophe theory (swallow tail)!

Exact energies are reproduced with 1-2-3 decimal digits for $Z \in [0.91 - 2.]$ (!)

Accurate Calculations:

Z	E (a.u.)	Lagrange mesh
1.00	-0.527 751 016 544 377[a]	-0.527 751 016 544 38
0.95	-0.462 124 684 390 [b]	-0.462 124 699 683 8
0.94	–	-0.449 669 043 929 7
0.93	–	-0.437 451 308 772 3
0.92	–	-0.425 485 281 676
0.912	–	-0.416 111 395 53
Z_{cr}^{EBMD}	-0.414 986 212 532 679 [c]	-0.414 986 212 53
0.91	-0.413799211244 [c]	-0.41379921124

Lagrange mesh for Ground state energy E for a two-electron system vs Z compared with
Nakashima-Nakatsuji: 2007 [a],
Guevara-AT: 2011 (Korobov basis) [b],
Drake et al.: 2014 [c]

I. *Approximation (ground state):*

$$E_B(Z) = -0.407924347 - 1.12347455\,(Z-Z_B) - 0.19778459\,(Z-Z_B)^{\frac{3}{2}}$$

$$-0.7528418\,(Z-Z_B)^2 - 0.1082589\,(Z-Z_B)^{\frac{5}{2}} - 0.014135\,(Z-Z_B)^3$$

$$+0.00854\,(Z-Z_B)^{\frac{7}{2}} + 0.00483\,(Z-Z_B)^4 - 0.000056\,(Z-Z_B)^{\frac{9}{2}}$$

$$Z_B(1^1S) = 0.90485374$$

close to 0.9023 by Zamastil et al, 2010

Reproduces 8-7-6 decimals for $Z \in [0.91\ ,\ 2.0]$,

$$E_{approx}(Z=2) = -2.903724\ ,\ E_{exact}(Z=2) = -2.903724$$

II. *Approximation (ground state):*

$$E_c(\lambda) \;=\; -\frac{1}{2} - 0.2451882222\,(\lambda{-}\lambda_{cr}) - 0.7833241391\,(\lambda{-}\lambda_{cr})^2 + \ldots$$

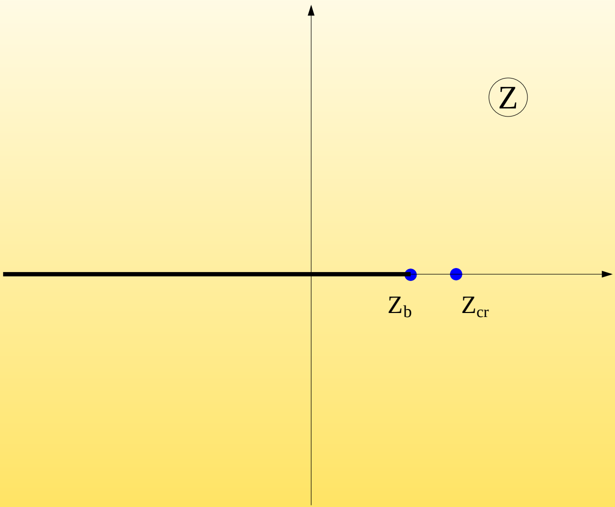
where $\lambda = 1/Z$ at $Z \in [0.905\ ,\ 0.91\ ,\ Z_{cr}^{EBMD}\ ,\ 0.912]$ in 11-12 decimals.

Comparing with coeff in front of linear term by Drake et al. (April, 2014) using virial theorem

$$b_1 = -0.2451890639$$

No singularity ...

Ground state ^1S energy:



• *Analytic continuation around singularity (ground state → excited state):*

$$E_B(Z) = -0.407924347 - 1.12347455\,(Z-Z_B) + 0.19778459\,(Z-Z_B)^{\frac{3}{2}}$$

$$-0.7528418\,(Z-Z_B)^2 + 0.1082589\,(Z-Z_B)^{\frac{5}{2}} - 0.014135\,(Z-Z_B)^3$$

$$-0.00854\,(Z-Z_B)^{\frac{7}{2}} + 0.00483\,(Z-Z_B)^4 + 0.000056\,(Z-Z_B)^{\frac{9}{2}}$$

$$Z_B(^1S) = 0.90485374 \qquad Z_{cr}^{excited} = 0.912003$$

Excited state:

$$E_B(Z=1) \;=\; -0.515541 \; a.u.$$

$Z = 1.0$, $E = -0.527445881114$, Fit H- 2nd branch $= -0.5153038$

$$E_B(Z=2) \;=\; -2.201 \; a.u.$$

What state can it be?

Likely, spin-singlet

$$(1s2s)\; 2^1S$$

$E_{exact}(Z=2) \;=\; -2.175229$ a.u. (Drake et al)

(almost) Conclusion:

• based on analytic continuation of energy around $Z_B(1^1S)$ we predict the existence of the excited state of negative hydrogen ion H^- of the same symmetry as the ground state at

$$E_{excited}(Z=1) \;=\; -0.515541 \; a.u.$$

Transition energy:

$$\Delta E = 0.01221 \; a.u.$$

But ... what about its wavefunction? – No single method leads (so far) to normalizable eigenfunction of an excited state at $Z=1$!

Can it be $(1s2s)\,2^1S$ *??* – **No!** - but what?

• Expanding $\hat{E} \;=\; \frac{E_B}{Z^2}$ in powers of λ we coincide with Baker et al coeffs in two significant decimals for $e_{10,20,50,100}$!! (consistency check)

$(1s2s)\, 2^1S$ state

Z	E (a.u.)	Lagrange mesh
2.	-2.145 974 046 054	-2.145 974 046 054 4
1.01	-0.510 092 281 314	-0.510 092 281 314
1.005	-0.505 023 856 993	-0.505 023 856 99
1.002	-0.502 003 917	-0.502 000
1.001	-0.501 000 988	-0.501 001

$(1s2s)\, 2^1S$ state energy E for (Z, e, e) in two different methods:
Karr-Hilico (left column, $\sim 10^6$ configurations in d.p.)
Lagrange mesh (right column,$\sim$ 90x90x20 in d.p.)

Error accumulations?

For $(1s2s)\,2^1 S$

Approximation:

$$E_B(Z) \;=\; -0.492672 - 0.976927\,(Z-Z_B) - 0.126843\,(Z-Z_B)^{\frac{3}{2}}$$

$$-0.431150\,(Z-Z_B)^2 + 0.117963\,(Z-Z_B)^{\frac{5}{2}} - 0.172930\,(Z-Z_B)^3$$

$$-0.073129\,(Z-Z_B)^{\frac{7}{2}} - 0.007198\,(Z-Z_B)^4 + 0.033670\,(Z-Z_B)^{\frac{9}{2}}$$

Reproduces 7-6 decimals for $Z \in [1.01\ ,\ 2.0]$,

$$E_B(Z=2) = -2.145974\ ,\ E_{exact}(Z=2) = -2.145974$$

$$Z_B((1s2s)\,2^1 S) \;=\; 0.992606$$

Hence, $(1s2s)\,2^1S$ excited state is **NOT** 2^1S state at

$$Z_B(1^1S) \; < \; Z \; < \; Z_B(2^1S)$$

or, in concrete, at

$$0.904854 \; < \; Z \; < \; 0.992606$$

What this excited state is? (if exists) $\Leftrightarrow$ A meaning of analytic continuation in Z
Open question: to localize the level crossing $1S - 2S$ (Landau-Zener singularities)
- it may shed light on the situation
(no single attempt known)

Finite masses $< - - - >$ full geometry

Three Coulomb Charges:

$$\bullet\,(Z, M) \quad + \quad \bullet\,(z, m) \quad + \quad \bullet\,(z, m)$$

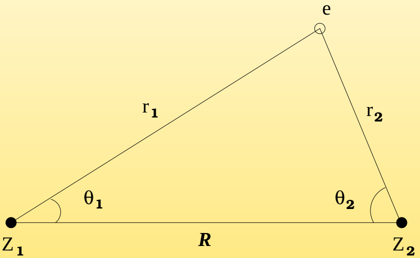
(I) Helium-like $(H^-, He, Li^+ \ldots, one - center)$: $z = 1$ and $M \to \infty$

(II) H$_2^+$-like $(H_2^+, D_2^+, T_2^+ \ldots, two - center)$: $Z = 1$ and $m \to \infty$

(III) Positronium-like $(Ps^{\pm}, Mu^{\pm}, Pr^{\pm} \ldots)$: $z = 1$ and $M \ = \ m$

$$\left(z_1, z_2, e\right)$$

Two fixed charged (fixed) centers at distance R and one electron



$z_1 = z_2 = 1 \quad \Rightarrow \quad$ *Molecular Hydrogen ion* H_2^+ (stable)

$z_1 = z_2 = 2 \quad \Rightarrow \quad$ Molecular Helium ion He_2^{3+}
(it does not exist, no bound states)

$$\mathcal{H}(R) \;=\; -\frac{1}{2}\Delta^{(3)} \;-\; \frac{z_1}{r_1} \;-\; \frac{z_2}{r_2} \;+\; \frac{z_1 z_2}{R}$$

- Variables are separated in prolate spheroidal (elliptic) coordinates

$$\xi = \frac{r_1 + r_2}{R}\ ,\ \eta = \frac{r_1 - r_2}{R}\ ,\ \varphi$$

(the perimetric coordinates in Hylleraas notation ($\varphi \to r_{12} = R$) !)

- It has the property of **complete integrability**

$$I_1 = L_\varphi\ ,\ I_2 = L_1 L_2 + 2R(z_1 \cos\theta_1 + z_2 \cos\theta_2)$$

♦ Classical case: $\to$ Euler (implicitly), Erikson-Hill (1949, explicitly)

♦ Quantum case: $L_1 L_2 \;\to\; \frac{1}{2}\{\mathcal{L}_1 \mathcal{L}_2\}_+$

Erikson-Hill (1949)

Lowest (ground state) eigenfunctions: one of positive and one of negative parity, $1s\sigma_g$ $(0,0,0,+)$ and $2p\sigma_u$ $(0,0,0,-)$

$$\Psi^{(\pm)}_{0,0,0} \; = \; \frac{1}{(\gamma+\xi)^{1-\frac{R}{p}}} \; e^{-\xi\,\frac{\alpha+p\xi}{\gamma+\xi}}$$

$$\frac{1}{(1+b_2\eta^2+b_3\eta^4)^{1/4}} \; \left[\begin{array}{c} \cosh \\ \sinh \end{array} \; \left(\eta\frac{a_1+pa_2\eta^2+pb_3\eta^4}{1+b_2\eta^2+b_3\eta^4}\right)\right]$$

Six free parameters α, γ and $a_{1,2}, b_{2,3}$ plus "parameter" $p=\sqrt{-E'R^2/4}$.

Energy $E(R)$ for $R \in [1,50] \rightarrow$ 10 - 11 decimals : variationally and in Lagrange mesh

(Olivares-Pilon and AT, 2011)

For $z_1 = z_2 = z$ (H Medel and A.T., 2011)

- The Critical point

$$z_B \approx 1.439$$

♦ the ground state potential curve $E = E(R; z = z_B)$ has no minimum but saddle point at $R_{eq} = 2.985$ a.u.

(maximum disappears, it implies coincidence of the minimum and maximum, it happens at a finite distance)

♦ $0 \leq z \leq z_B$ the system is bound,
(the 2nd critical point is at $z_{cr} = 0$, the potential is zero)

♦ for $z \geq z_B$ the system is unbound

- The Critical point

$$z_{cr} \approx 1.237$$

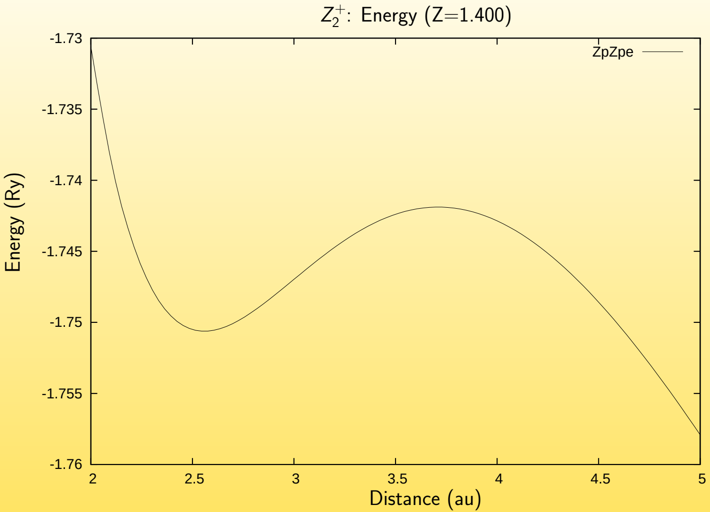
⧫ Stability:

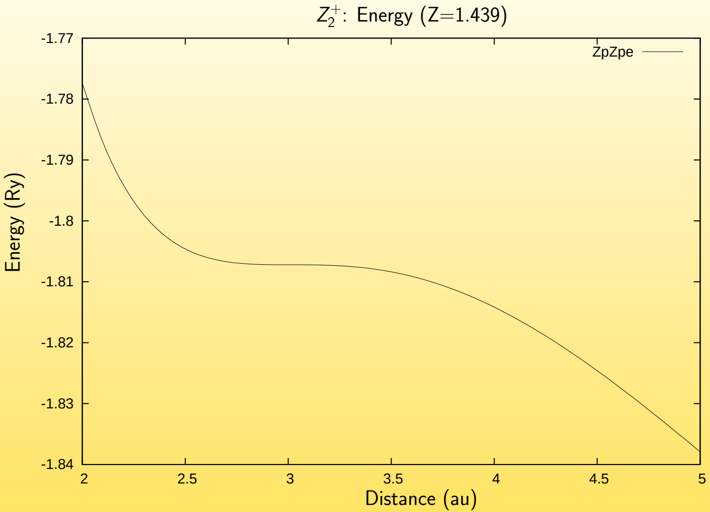
◇ if $z \in (1.237, 1.439)$ the system $(\mathrm{z}, \mathrm{z}, e)$ is metastable

$$(\mathrm{z}, \mathrm{z}, e) \to (\mathrm{z}, e) + \mathrm{z}$$

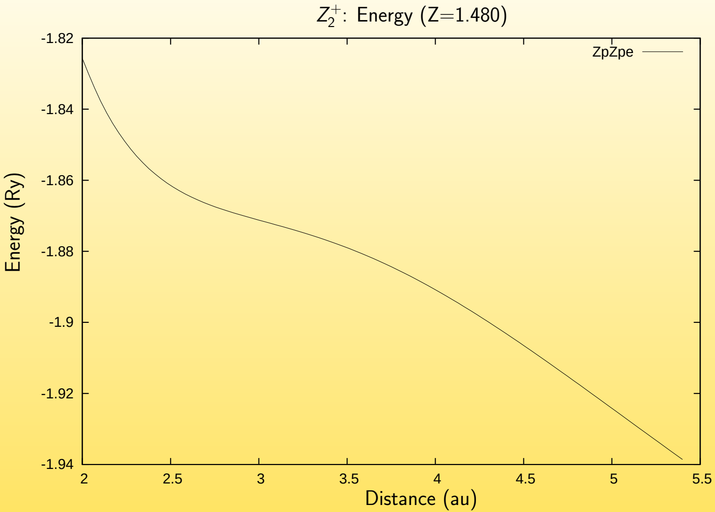
$$\Rightarrow E_{(\mathrm{z},\mathrm{z},e)}(R = R_{eq}(z)) > E_{(\mathrm{z},e)}$$

◇ if $z < 1.237$ it is stable


Z_2^+: Energy (Z=1.400)
ZpZpe
Energy (Ry)
-1.73
-1.735
-1.74
-1.745
-1.75
-1.755
-1.76
2
2.5
3
3.5
4
4.5
5
Distance (au)



Z_2^+: Energy (Z=1.439)
ZpZpe
Energy (Ry)
-1.77
-1.78
-1.79
-1.8
-1.81
-1.82
-1.83
-1.84
2
2.5
3
3.5
4
4.5
5
Distance (au)


Z_2^+: Energy (Z=1.480)
ZpZpe
Energy (Ry)
-1.82
-1.84
-1.86
-1.88
-1.9
-1.92
-1.94
2
2.5
3
3.5
4
4.5
5
5.5
Distance (au)

♦ Behavior (fit) at $z = z_B = 1.439$:

$$E(z; R = R_{eq}(z)) \; = \; -1.8072 + 1.5538\,(z_B - z) - 0.5719\,(z_B - z)^{3/2} +$$

$$+0.1129\;(z_B - z)^2 + 0.7777\;(z_B - z)^{5/2} - 0.4086\;(z_B - z)^3 + \ldots$$

$$\text{at } z \to z_B^-$$

Branch point of the 2nd order(!) with exponent 3/2

♦ No indication to singularity at $z = z_{cr} = 1.237$

$$E(z; R = R_{eq}(z)) \; = \; 1.5292 + 1.341(1.237 - z) + 0.08(1.237 - z)^2 \ldots$$

Two fundamental plots are built:

- Behavior $Z_{cr} = Z_{cr}(\mu \equiv \frac{m}{M})$

$$Z_{cr}(0) = 0.91103\ ,\ Z_{cr}(1) = 0.92180\ ,\ Z_{cr}(\mu_t) = 0.81182$$

$$Z_{cr}(\infty) = 0.80862$$

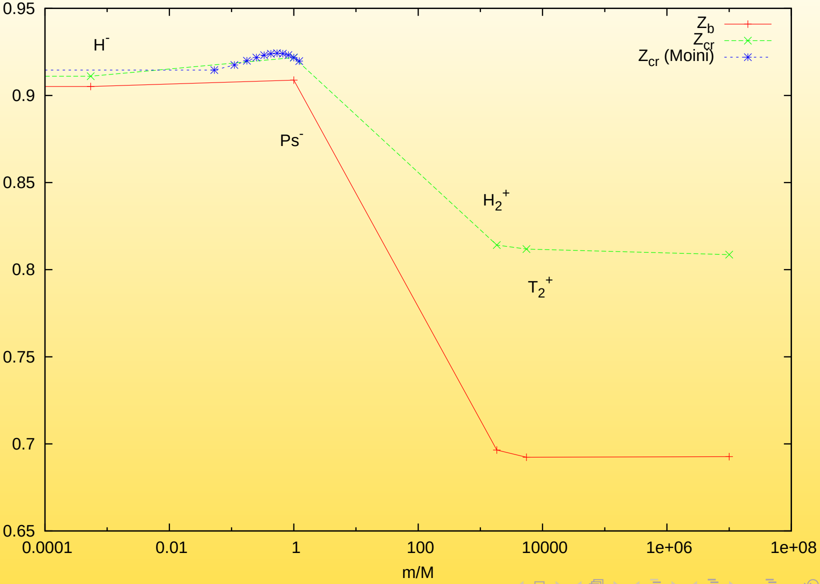
at $\mu \in [0, 1]$ (Moini & Drake, 2014), $\mu_t = 5496.92158$ (triton). It is seen no singularity at $Z = Z_{cr}$ for fixed $\frac{m}{M}$. Can it be confirmed?

- Behavior $Z_B = Z_B(\mu)$

$$Z_B(0) = 0.90485\ ,\ Z_B(1) = 0.90886\ ,\ Z_B(\mu_t) = 0.69235$$

$$Z_B(\infty) = 0.69267$$

Singularity in $Z = Z_B$ at fixed μ of square-root type with exponent 3/2 (!)



0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.0001
0.01
1
100
10000
1e+06
1e+08
m/M
H^-
Ps^-
H_2^+
T_2^+
Z_b
Z_{cr}
Z_{cr} (Moini)

It was studied the critical charge Z_B for n centers and k electron problems (nZ, ke):

- one-center case
  $(Z, 2e)$, $(Z, 3e)$
- two-center case
  $(2Z, e)$, $(2Z, 2e)$
- three-center case
  $(3Z, e)$, $(3Z, 2e)$
- and many center, one-electron case
  $(4Z, e)$, $(5Z, e)$, $(6Z, e)$

Everywhere square-root branch point with exponent $3/2$ occurred as well as no singularity at Z_{cr} associated with dissociation.

> **Conjecture:** *for any many-body Coulomb system (nZ, ke) the critical charge Z_B exists and is associated with square-root branch point with exponent 3/2*

(it is a property of Coulomb system)

Conclusions

- We are unable to interpolate energies $E(Z)$ better than 6-7s.d. – Why? All our qualitative conclusions are valid with 6-7.s.d. - what is beyond?
- We solved the Schrodinger eq. wrongly at $Z < Z_{cr}$; there must be $\mathrm{Im} E(Z) \neq 0$ – the system can decay
- (Wild) Guess: $E(Z) = A(Z) + B(Z)$ such that

  $$|\frac{B(Z)}{A(Z)}| \lesssim 10^{-(6\div 7)}$$

  where $A(Z)$ is our interpolation(s). It is like in a separation of variables.

  What do we know about $B(Z)$?

J-P Karr (Paris, 2015) calculated (in complex rotation method) imaginary part of $E(Z)$ at $Z < Z_{cr}$:

$$B(Z) \approx i\ a|Z - Z_{cr}|^{1/2}\ e^{-\frac{b}{|Z-Z_{cr}|}}\ ,\ b > 0$$

the interpolation. It signals to essential singularity at $Z = Z_{cr}$:
(i) At $Z > Z_{cr}$ it gives a contribution to 8-7-6 decimal digits in energy in $Z \in [Z_{cr}, 1]$
(ii) In $1/Z$-expansion in gives a contribution to 3s.d. at coeffs e_{10-100}.
Can the guess be justified? – It is NOT a numerical question.