Towards all-order self-energy computation for hydrogen molecular ions

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Motivation

Spin-averaged rovibrational transitions in hydrogen molecular ions

- Measurements have reached ppt level relative uncertainty
- Orders of magnitude improvement expected from single-ion experiments

Schiller, Bakalov, Korobov, Phys. Rev. Lett. 113, 023004 (2014).
Karr, J. Mol. Spectrosc. 300, 37 (2014).

- Currently the main limitation of the theory is higher-order ($m\alpha^{8+}$) contributions to one-loop self-energy
- E.g.: the $(N, \nu) = (3, 0) \rightarrow (3, 9)$ transition in HD^+

$$\begin{aligned} f_{\text{spin-avr,exp}} &= 415\,264\,925\,501.8(1.3)\ \text{kHz} \\ f_{\text{spin-avr,theo}} &= 415\,264\,925\,502.8(3.3)\ \text{kHz} \end{aligned}$$

Korobov, Karr, Phys. Rev. A 104, 032806 (2021).
Patra *et al.*, Science 369, 1238 (2020).
Alighanbari *et al.*, Nature 581, 152–158 (2020).

- Uncertainty from self-energy for this transition is 2.6 kHz
- All-order (in $Z\alpha$) evaluation of self-energy is desirable

Self-energy in light atoms

$$\Delta E_a^{\mathrm{SE}} = \frac{\alpha}{\pi}\frac{(Z\alpha)^4}{n^3}F(Z\alpha)mc^2$$

Light systems ($Z\alpha \ll 1$) NRQED

- $Z\alpha$ is a good expansion parameter, therefore

$$\begin{aligned} F(Z\alpha) = & A_{41}\ln(Z\alpha)^{-2} + A_{40} + (Z\alpha)A_{50} \\ & + (Z\alpha)^2\left[A_{62}\ln^2(Z\alpha)^{-2} + A_{61}\ln(Z\alpha)^{-2} + G_{\mathrm{SE}}\right] \end{aligned}$$

- Coefficients are expectation values of effective Hamiltonians
- For hydrogen atom G_{SE} was evaluated
  - partially from $Z\alpha$ expansion

Yerokhin, Pachucki, Patkóš, Ann. Phys. 531, 1800324 (2019).

  - from all-order computation of $F(Z\alpha)$

Jentschura, Mohr, Soff, Phys. Rev. Lett. 82, 53 (1999).
Yerokhin, Harman, Keitel, Phys. Rev. A 111, 012802 (2025).

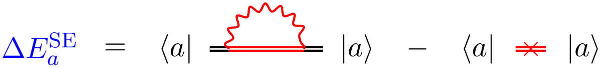
Self-energy of a bound electron

The renormalized bound-electron self-energy

$$\Delta E_a^{\mathrm{SE}} = 2\mathrm{i}\alpha \int_{\mathcal{C}_{\mathrm{F}}} \mathrm{d}z \int \mathrm{d}^3\boldsymbol{x}_1 \int \mathrm{d}^3\boldsymbol{x}_2 \, \underbrace{D(z, x_{12})}_{\substack{\text{photon}\\ \text{propagator}}} \psi_a^\dagger(\boldsymbol{x}_2)\alpha^\mu \underbrace{G\left(E_a - z, \boldsymbol{x}_2, \boldsymbol{x}_1\right)}_{\substack{\text{bound-electron}\\ \text{propagator}}} \alpha_\mu \psi_a(\boldsymbol{x}_1)$$

$$- \delta m \int \mathrm{d}^3\boldsymbol{x} \, \psi_a^\dagger(\boldsymbol{x})\beta\psi_a(\boldsymbol{x})$$

Finite difference of two infinite terms



$$\Delta E_a^{\mathrm{SE}} = \langle a| \quad |a\rangle - \langle a| \quad |a\rangle$$

For molecular ions

- Bound-electron propagator is not known analytically
- We have to rely on basis set expansion

Many-potential expansion

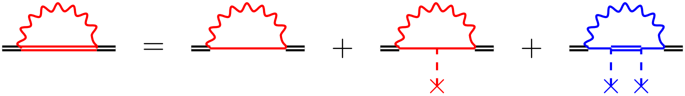
Canceling the infinities

$$H = H_{\mathrm{free}} + V$$

Expand bound-electron propagator

$$G(z) = \frac{1}{z-H} = \frac{1}{z-H_{\mathrm{free}}} + \frac{1}{z-H_{\mathrm{free}}} V \frac{1}{z-H_{\mathrm{free}}} + \frac{1}{z-H_{\mathrm{free}}} V \frac{1}{z-H} V \frac{1}{z-H_{\mathrm{free}}}$$

Inserting into the self-energy expression

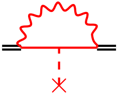


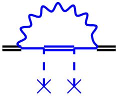
Snyderman, AP. 211, 43 (1991), Yerokhin, Shabaev, PRA. 60, 800 (1999)

Many-potential expansion

$\Delta E_a^{\mathrm{SE}} = \langle a|$  $|a\rangle - \langle a|$  $|a\rangle$

$= \langle a|$  $|a\rangle$ $\quad \langle a|\delta m - (Z_2^{-1} - 1)(\not{p} - m) + \Sigma_{\mathrm{R}}(p)|a\rangle$

$+ \langle a|$  $|a\rangle$ $\quad \langle a|(Z_2^{-1} - 1)(\not{p} - m) + \Gamma_{\mathrm{R}}^0(p,p')V(\boldsymbol{q})|a\rangle$

$+ \langle a|$  $|a\rangle$ $\quad + \Delta E_a^{\mathrm{mp}}$

$- \langle a|$  $|a\rangle$ $\quad \langle a|-\delta m|a\rangle$

$$= \langle a|\ \Sigma_{\mathrm{R}}(p)\ |a\rangle + \langle a|\ \Gamma_{\mathrm{R}}^0(p,p')V(|\boldsymbol{p} - \boldsymbol{p}'|)\ |a\rangle + \Delta E_a^{\mathrm{mp}}$$

Self-energy in a Gaussian basis set

Ferenc, Salman, Saue, PRA 111, L040802 (2025)

Gaussian basis set

- Widely used to describe molecular bound states
- Most integrals can be done analytically, e.g.: Fourier transform
- Does it work for self-energy?

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Ground state of hydrogen-like uranium (U^{91+}) in units of $F(Z\alpha)$

Term	Present work	Ref.[a]
zero-potential	−2.155 556	−2.155 55
one-potential	1.984 011	1.984 01
ΔE^{mp}	1.662 44(5)	1.662 45(2)
ΔE^{SE}	1.490 89(5)	1.490 91(2)

[a] Yerokhin, Shabaev, Phys. Rev. A. 60, 800 (1999)

Difficulties with low nuclear charge

Yerokhin, Harman, Keitel, Phys. Rev. A 111, 012802 (2025).

	$Z = 1$	$Z = 92$
	Feyn.	
Zero-potential	-168176.156251	-2.155556
One-potential	148579.466946	1.984011
$\lvert\kappa\rvert = 1$	19509.361426	1.632207
2	58.969181	0.012042
3	15.113947	0.008313
4	7.160396	0.003806
5	4.195914	0.001988
6	2.747051	0.001158
7	1.926565	0.000731
8	1.416615	0.000490
9	1.078199	0.000344
10	0.842481	0.000251
11	0.672055	0.000188
12	0.542109	0.000145
13	0.448352	0.000114

Difficulties with low nuclear charge

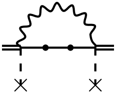
Large numerical cancellations

- Spurious terms appear in the zero- and one-potential terms in Feynman gauge, cancel after summation
- Solution: work in Coulomb gauge

Yerokhin, Harman, Keitel, PRA 111, 012802 (2025).

Slow convergence of partial-wave expansion

- Solution: Add and subtract approximate higher-order term of the many-potential expansion
- Must be calculable ***both*** in momentum- and coordinate-space
- Approximate two-potential term:



Sapirstein, Cheng, PRA 108, 042804 (2023).

Difficulties with low nuclear charge II.

Yerokhin, Harman, Keitel, PRA 111, 012802 (2025).

	$Z = 1$	$Z = 92$	$Z = 1$
	Feyn.		Coul.+Acc.
Zero-potential	-168176.156251	-2.155556	13.8494741
One-potential	148579.466946	1.984011	-2.8796816
Subtraction			-1.1277875
$\lvert\kappa\rvert = 1$	19509.361426	1.632207	0.4756257
2	58.969181	0.012042	-0.0047236
3	15.113947	0.008313	0.0019623
4	7.160396	0.003806	0.0007857
5	4.195914	0.001988	0.0003966
6	2.747051	0.001158	0.0002281
7	1.926565	0.000731	0.0001428
8	1.416615	0.000490	0.0000948
9	1.078199	0.000344	0.0000658
10	0.842481	0.000251	0.0000472
11	0.672055	0.000188	0.0000348
12	0.542109	0.000145	0.0000263
13	0.448352	0.000114	0.0000202

Two-center Dirac equation

The Hamiltonian

- Dirac equation

$$h_{\mathrm{D}}\psi_a(\boldsymbol{x}) = E_a\psi_a(\boldsymbol{x})$$

$$h_{\mathrm{D}} = (\beta - 1)mc^2 + c\boldsymbol{\alpha}\cdot\boldsymbol{p} + V = \begin{pmatrix} V & c\boldsymbol{\sigma}\cdot\boldsymbol{p} \\ c\boldsymbol{\sigma}\cdot\boldsymbol{p} & V - 2mc^2 \end{pmatrix}$$

- With a two-center potential

$$V(\boldsymbol{r}) = V_1(\boldsymbol{r}) + V_2(\boldsymbol{r}) = -\frac{Z_1}{|\boldsymbol{r} - \boldsymbol{R}_1|} - \frac{Z_2}{|\boldsymbol{r} - \boldsymbol{R}_2|}$$

- No reduction in spinor structure → four-component Hamiltonian
- Commutes with: j_z, and for $Z_1 = Z_2$ with P (parity operator)
- We can compute states with exact m_j quantum number and gerade/ungerade parity

Coordinate system

Cylindrical coordinates

- It is convenient to work in cylindrical coordinates

$$\begin{aligned} x &= r\cos\phi & r &= \sqrt{x^2+y^2} \\ y &= r\sin\phi & \phi &= \begin{cases} \arccos\left(\frac{x}{r}\right) & \text{if } y \geq 0 \\ -\arccos\left(\frac{x}{r}\right) & \text{if } y < 0 \end{cases} \\ z &= z & z &= z \end{aligned}$$

- Differential operators take the form

$$\Delta f = \frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial f}{\partial r} + \frac{1}{r^2}\frac{\partial^2 f}{\partial \phi^2} + \frac{\partial^2 f}{\partial z^2}$$

$$\boldsymbol{\sigma}\cdot\boldsymbol{p} = -\mathrm{i}\begin{pmatrix} \partial_z & \mathrm{e}^{-\mathrm{i}\phi}\left(-\frac{\mathrm{i}}{r}\partial_\phi + \partial_r\right) \\ \mathrm{e}^{\mathrm{i}\phi}\left(\frac{\mathrm{i}}{r}\partial_\phi + \partial_r\right) & -\partial_z \end{pmatrix}$$

Wave function

Wave function Ansatz

$$\psi_{m_j}(\boldsymbol{x}) = \begin{pmatrix} \mathrm{e}^{\mathrm{i}(m_j-1/2)\phi} f_1(r,z) \\ \mathrm{e}^{\mathrm{i}(m_j+1/2)\phi} f_2(r,z) \\ \mathrm{e}^{\mathrm{i}(m_j-1/2)\phi} f_3(r,z) \\ \mathrm{e}^{\mathrm{i}(m_j+1/2)\phi} f_4(r,z) \end{pmatrix}$$

- Eigenfunction of j_z with eigenvalue m_j
- $f_i(r,z)$ are expanded over Gaussian basis set

$$f_i(r,z) = \sum_{\mu=1}^{n_\mathrm{b}} c_\mu^{(i)} g_\mu^{(i)}(r,z)$$

$$g_\mu^{(i)}(r,z) = \mathcal{N}_\mu^{(i)} r^{|m_j \pm 1/2|} \left[\mathrm{e}^{-\zeta_{1\mu}\left(r^2+(z+R/2)^2\right)-\zeta_{2\mu}\left(r^2+(z-R/2)^2\right)} \pm (1 \leftrightarrow 2)\right]$$

- Symmetrized according to gerade/ungerade symmetry
- All Hamiltonian matrix elements can be calculated analytically

Convergence of the energy

$Z_1 = Z_2 = 1$, $R = 2.00$ a.u., values in atomic units

n_b	E_nr	E_rel
50	$-1.102\,634\,206\,491\,406\,987\,69$	$-1.102\,641\,573\,028\,653\,782\,04$
100	$-1.102\,634\,214\,488\,619\,779\,46$	$-1.102\,641\,581\,026\,249\,790\,40$
150	$-1.102\,634\,214\,494\,655\,356\,37$	$-1.102\,641\,581\,032\,362\,262\,94$
200	$-1.102\,634\,214\,494\,937\,030\,30$	$-1.102\,641\,581\,032\,568\,599\,22$
250	$-1.102\,634\,214\,494\,946\,422\,45$	$-1.102\,641\,581\,032\,577\,050\,46$
300	$-1.102\,634\,214\,494\,946\,456\,35$	$-1.102\,641\,581\,032\,577\,168\,96$
350	$-1.102\,634\,214\,494\,946\,461\,36$	$-1.102\,641\,581\,032\,577\,166\,48$
Ref.	$-1.102\,634\,214\,494\,946\,461\,508\,98$	$-1.102\,641\,581\,032\,577\,164\,118\,14$

Ref: Kullie, PRA 110, 052808 (2024).

- Basis set is optimized to minimize E_nr
- Convergence of the energy $\sim$ 18-19 digits
- Some other works:
  - Finite-element method ($\sim$20 digits): Kullie, PRA 110, 052808 (2024).
  - DPT ($\sim$20 digits): Nogueira, Korobov, Karr, PRA 105, L060801 (2022).
  - Exponential basis ($\sim$32 digits): Nogueira, Karr, PRA 107, 042817 (2023).

Zero-potential term

The momentum-space wave function

$$\psi(\boldsymbol{p}) = \begin{pmatrix} \mathrm{e}^{\mathrm{i}(m_j-1/2)\chi} f_1(p_\perp, p_z) \\ \mathrm{e}^{\mathrm{i}(m_j+1/2)\chi} f_2(p_\perp, p_z) \\ \mathrm{e}^{\mathrm{i}(m_j-1/2)\chi} f_3(p_\perp, p_z) \\ \mathrm{e}^{\mathrm{i}(m_j+1/2)\chi} f_4(p_\perp, p_z) \end{pmatrix} \qquad f_i(p_\perp, p_z) = \sum_{\mu=1}^{n_\mathrm{b}} c_\mu^{(i)} g_\mu^{(i)}(p_\perp, p_z)$$

$$g_\mu^{(i)}(p_\perp, p_z) = \mathcal{N}_\mu^{(i)} p_\perp^{|m_j \pm 1/2|} \left[\mathrm{e}^{-\frac{1}{4\zeta_{12,\mu}}\left(p^2 - 2\mathrm{i}Rp_z(\zeta_{1,\mu}-\zeta_{2,\mu})\right)} \pm (1 \leftrightarrow 2) \right]$$

Zero-potential term (in Coulomb gauge)

$$\begin{aligned} E_{\mathrm{R,C}}^{(0)} &= \int \mathrm{d}\boldsymbol{p}\, \bar{\psi}(\boldsymbol{p}) \Sigma_{\mathrm{R,C}}^{(0)}(\mathrm{p}) \psi(\boldsymbol{p}) \\ &= \frac{\alpha}{2} \int_0^\infty \mathrm{d}p_\perp\, p_\perp \int_{-\infty}^\infty \mathrm{d}p_z\, \Big[\left(\tilde{a}(\mathrm{p}) + \tilde{b}(\mathrm{p})\mathrm{p}^0 \right) \left(|f_1|^2 + |f_2|^2 \right) \\ &\quad + \frac{p^2}{mc} \tilde{c}(\mathrm{p}) \mathfrak{Re} \left(f_1^* f_3 + f_2^* f_4 \right) + \left(-\tilde{a}(\mathrm{p}) + \tilde{b}(\mathrm{p})\mathrm{p}^0 \right) \frac{p^2}{(2mc)^2} \left(|f_3|^2 + |f_4|^2 \right) \Big] \end{aligned}$$

Adkins, Phys. Rev. D 34, 2489 (1986).

Preliminary results for zero-potential term

Sanity check: hydrogen atom limit (in units of $F(Z\alpha)$)

$$E^{(0)}_{\mathrm{R,F}} = -168176.153\,752\,142(1) \qquad E^{(0)}_{\mathrm{R,C}} = 13.849\,474\,030(1)$$

$$E^{(0)}_{\mathrm{R,F}}(\mathrm{exact}) = -168176.153\,752\,140\,5 \qquad E^{(0)}_{\mathrm{R,C}}(\mathrm{exact}) = 13.849\,474\,031\,7$$

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Zero potential term for H_2^+ ($R = 2.00$ a.u., $F(Z\alpha)$ units)

n_{b}	$\Delta E^{(0)}_{\mathrm{R,C}}$	$\Delta E^{(0)}_{\mathrm{R,F}}$
50	20.541 435 280	−272 863.830 452 684
100	20.541 435 117	−272 863.830 442 730
150	20.541 435 135	−272 863.830 443 948
200	20.541 435 136	−272 863.830 444 041
250	20.541 435 136	−272 863.830 444 042

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One-potential term

- Same principle, but more complicated expressions

The many-potential term (work in progress)

Evaluation strategy

$$\Delta E_a^{\mathrm{SE}} = 2\alpha \int_{\mathcal{C}_\mathrm{F}} \mathrm{d}z \int \mathrm{d}\boldsymbol{x}_1 \int \mathrm{d}\boldsymbol{x}_2 D(z, \boldsymbol{x}_{12}) \psi_a^\dagger(\boldsymbol{x}_1) \alpha^\mu G(E_a - z, \boldsymbol{x}_1, \boldsymbol{x}_2) \alpha_\mu \psi_a(\boldsymbol{x}_2)$$

$$D_\mathrm{F}(\omega, \boldsymbol{x}_{12}) = -\,\mathrm{i} \int \frac{\mathrm{d}^3\boldsymbol{k}}{(2\pi)^3} \frac{\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}_{12}}}{\omega^2 - \boldsymbol{k}^2}$$

- Insert Dirac–Coulomb Green's function as sum over states, and integrate $\int_{\mathcal{C}_\mathrm{F}} \mathrm{d}z$ analytically

$$\Delta E_{a,\mathrm{F}}^{\mathrm{SE}} = -\frac{\alpha}{4\pi^2} \int \frac{\mathrm{d}^3\boldsymbol{k}}{k} \sum_n \frac{\langle \psi_a | \, \alpha^\mu \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}} \, | \psi_n \rangle \langle \psi_n | \, \alpha_\mu \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}} \, | \psi_a \rangle}{E_a - E_n - \mathrm{sgn}(E_n) k}$$

- Matrix elements can be computed analytically
(also in Coulomb gauge)

$$\langle \psi_a | \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}} | \psi_n \rangle \quad \to \quad \mathrm{e}^{\mathrm{i}(m_n - m_a)\chi} \langle g_{a,\mu} | \mathrm{e}^{\mathrm{i}k_z z} J_{|m_n - m_a|}(k_\perp r) | g_{n,\nu} \rangle_{\mathrm{rad}}$$

- Angular dependence (χ) of $\boldsymbol{k}$ drops out,
momentum integral reduces to a two-dimensional one

Summary & outlook

Takeaways

- Gaussians are efficient due to their analytical properties
- Basis set parameters can be variationally optimized
- Compact basis-set representation
- High-dimensional numerical integration can be (mostly) avoided
- Difficulties due to low Z can be mitigated

Current status

✓ High-precision Dirac–Coulomb energies and wave functions
✓ Zero-potential term
✓ One-potential term
✓ Convergence acceleration terms
Many-potential term

Thank you for your attention!