Computational Issues in Relativistic MBPT Calculations of Atomic Structures

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Abstract

Calculation of 3rd-order transition matrix elements for alkali-metal atoms illustrates some of the computational issues faced in relativistic MBPT calculations.

3rd-Order - Why bother?

- 1st-order (DHF) matrix elements:
  - Gauge-dependent (L≠V)
  - Differ from precise measurements by 1 – 20%
- 2nd-order:
  - Account for core shielding of dipole operator
  - Are gauge independent when extended to RPA
  - Differ from precise measurements by 0.5 – 10%
- 3rd-order:
  - Account for polarization and structural radiation
  - Are gauge independent with 'dressed' amplitudes
  - Differ from precise measurements by 0.1 – 1%

Point of Departure

One-electron atoms:

$$h_0 = c\,\boldsymbol{\alpha}\cdot\boldsymbol{p} + \beta mc^2 + V_{\rm HF}(r) + V_{\rm nuc}\,.$$

$$h_0\phi_i = \epsilon_i\phi_i$$

Many-electron atoms (no-pair Hamiltonian):[1]

$$H = \sum_i \epsilon_i\, a_i^\dagger a_i + \frac{1}{2}\sum_{ijkl} v_{ijkl}\, a_i^\dagger a_j^\dagger a_l a_k\,,$$

The two-particle matrix element of the Coulomb + Breit interaction v_{ijkl} are the 'building blocks' of the theory.

[1] Brown, G.E. & Ravenhall, D.G. 1951 *Proc. R. Soc. London,* Ser. A **208**, 552-559.

Computational Bottleneck

$$v_{ijkl} \propto \int_0^\infty P_i(r) P_k(r)\, v_L(j,l,r)\, dr \ ,$$

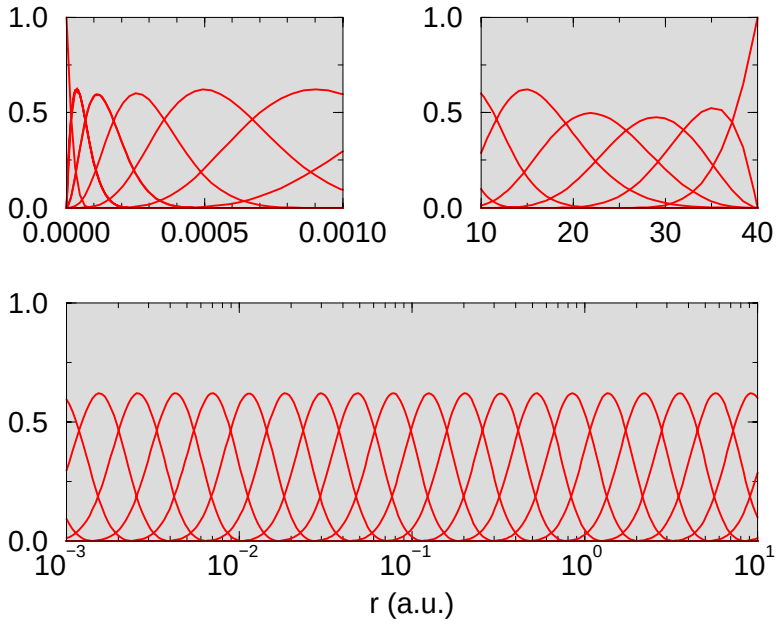
where

$$v_L(j,l,r) = \frac{1}{r^{L+1}} \int_0^r s^L\, P_j(s) P_l(s)\, ds + r^L \int_r^\infty \frac{1}{s^{L+1}}\, P_j(s) P_l(s)\, ds$$

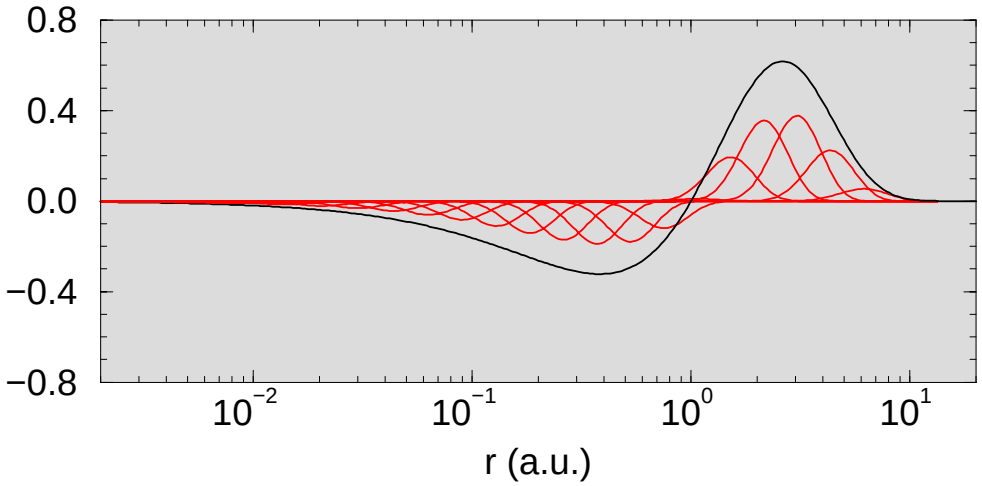
Evaluating the Hartree screening potentials $v_L(j,l,r)$ is intrinsically slow. Moreover, such calculations are not amenable to parallelization.

Our solution: Avoid repeated evaluation; evaluate and store as many v_{ijkl} as needed.

B-spline Basis Functions

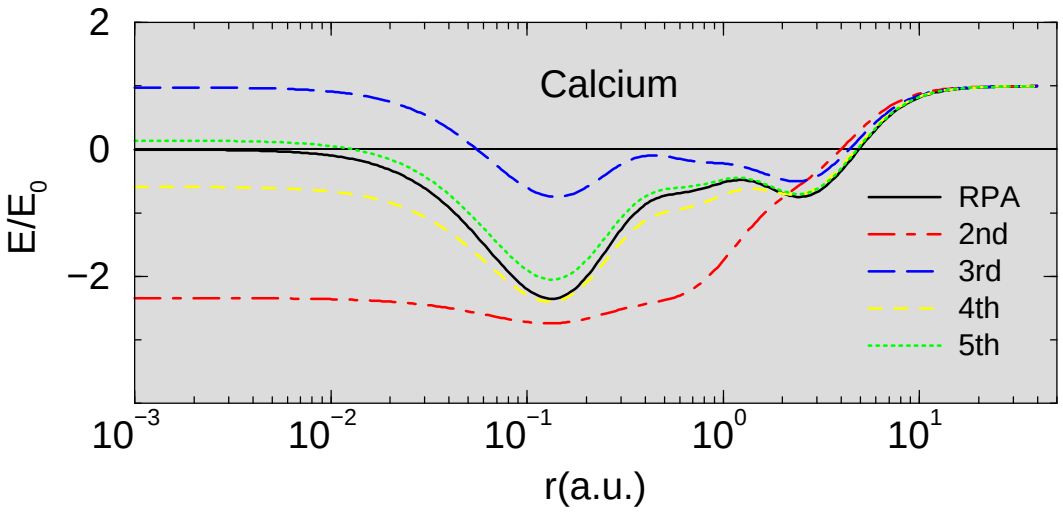


Basis sets consist of ~ 40 functions for each angular momentum obtained as combinations of B-splines.



2nd-Order - Core Shielding

$$T^{(2)}_{wv} = t_{wv} + \sum_{bm} \frac{t_{bm}\ \tilde{v}_{wmvb}}{\epsilon_b - \epsilon_m - \omega} + \sum_{bm} \frac{\tilde{v}_{wbvm}\ t_{mb}}{\epsilon_b - \epsilon_m + \omega}$$



If $t_{an} \to T^{\rm RPA}_{an}$ then $T^{(2)}_{wv}$ becomes gauge-independent!

$$T^{\rm RPA}_{an} = t_{an} + \sum_{bm} \frac{T^{\rm RPA}_{bm}\ \tilde{v}_{amnb}}{\epsilon_b - \epsilon_m - \omega} + \sum_{bm} \frac{\tilde{v}_{abnm}\ T^{\rm RPA}_{mb}}{\epsilon_b - \epsilon_m + \omega}$$

$$T^{\rm RPA}_{na} = t_{na} + \sum_{bm} \frac{T^{\rm RPA}_{bm}\ \tilde{v}_{nmab}}{\epsilon_b - \epsilon_m - \omega} + \sum_{bm} \frac{\tilde{v}_{nbam}\ T^{\rm RPA}_{mb}}{\epsilon_b - \epsilon_m + \omega}$$

Iterative Solution to RPA Equations

$5s_{1/2} - 5p_{1/2}$ dipole matrix element in Rb

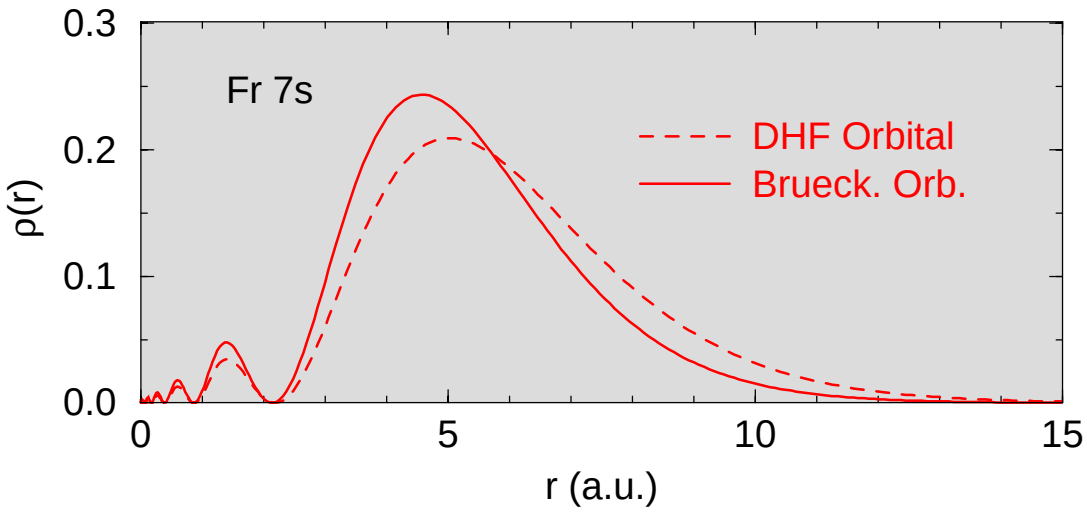
Order	Length	Velocity
DHF	-4.818890	-4.640076
2	0.223661	0.027782
3	-0.028020	-0.008318
4	0.020880	0.011510
5	-0.005981	0.000276
6	0.003121	0.002287
7	-0.001101	0.000105
8	0.000509	0.000394
9	-0.000194	0.000015
10	0.000085	0.000065
11	-0.000034	0.000001
12	0.000014	0.000011
13	-0.000006	0.000000
14	0.000002	0.000002
15	-0.000001	0.000000
RPA	-4.605946	-4.605946

3rd-Order – Core Polarization

$$T^{(3)} = T^{(3)}_{\rm CorePol.} + T^{(3)}_{\rm St.Rad.} + T^{(3)}_{\rm Norm}$$

(48 Brueckner-Goldstone diagrams)

Note: The 16 $T^{(3)}_{\rm RPA}$ diagrams already included in the iterated 2nd order amplitude are excluded here.



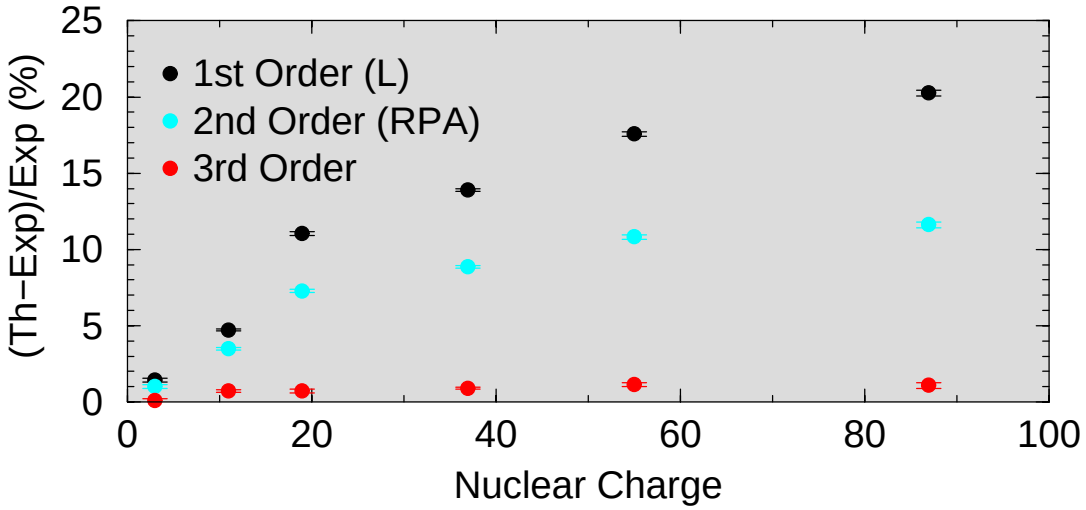
'Derivative' Terms

$$T^{(3)}(\omega) \to T^{(3)}(\omega_0) + \left.\frac{dT^{(1)}(\omega)}{d\omega}\right|_{\omega_0} \delta\omega^{(2)}$$

Theorem 1. *If bare amplitudes are replaced by RPA amplitudes and the derivative term is added, then* $T^{(3)}$ *becomes gauge independent!*

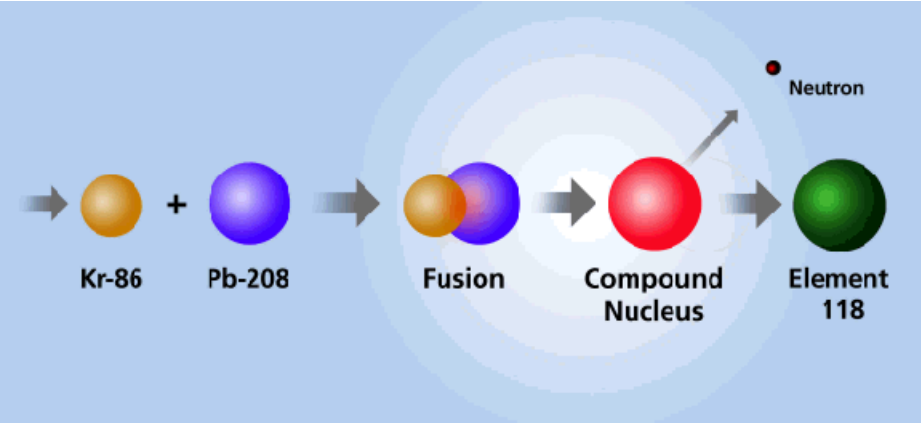
	Single			Double	
Term	L	V	Term	L	V
br1	-0.0503	0.0715	br2	0.5036	-0.5665
br3	0.0051	-0.0583	br4	-0.0190	0.0572
top1	-0.0003	0.0130	top2	0.0201	-0.5058
top3	0.0000	-0.0084	top4	-0.0233	0.5747
bot1	0.0003	0.0024	bot2	0.0220	0.5429
bot3	0.0001	0.0044	bot4	-0.0257	-0.6160
cen1	-0.0001	-0.0020	cen2	0.0003	-0.0004
cen3	0.0001	-0.0022	cen4	-0.0184	-0.0439
Sum	-0.0452	0.0203	Sum	0.4597	-0.5579
Deriv	0.0655	0.0000	Deriv	-1.0176	0.0000
Total	0.0203	0.0203	Total	-0.5580	-0.5579

Dipole Matrix Elements



Term	L	V	L	V
Rb	$5s_{1/2} - 5p_{1/2}$		$5s_{1/2} - 5p_{3/2}$	
1st	4.8189	4.6401	6.8017	6.5399
2nd	4.6059	4.6059	6.5052	6.5052
3rd	4.2685	4.2684	6.0249	6.0248
Cs	$6s_{1/2} - 6p_{1/2}$		$6s_{1/2} - 6p_{3/2}$	
1st	5.2777	5.0371	7.4265	7.0662
2nd	4.9747	4.9747	7.0137	7.0137
3rd	4.5402	4.5400	6.3892	6.3891
Fr	$7s_{1/2} - 7p_{1/2}$		$7s_{1/2} - 7p_{3/2}$	
1st	5.1438	4.8402	7.0903	6.6424
2nd	4.7741	4.7741	6.6268	6.6268
3rd	4.3236	4.3234	5.9450	5.9448

Eka-Francium



V. Ninov *et al.* Phys. Rev. Letts. **83**, 1104 (1999).

Element 118 is a noble gas; the (as yet) undiscovered element 119 is an alkali-metal atom (eka-francium). What are its $8s - 8p$ dipole matrix elements?

Problem: The RPA perturbation does not converge for element 119. Solution: Solve exactly as a system ($\approx 6400 \times 6400$ for 40 splines) of linear equations.

	$8s - 8p_{1/2}$		$8s - 8p_{3/2}$	
Order	L	V	L	V
1st	4.531	4.011	5.528	4.996
2nd	3.988	3.988	4.993	4.993
3rd	3.635	3.635	4.449	4.449

Conclusions

- (Dirac) Hartree-Fock calculations of transition amplitudes are fast, inaccurate, and ambiguous (gauge dependent).
- Second-order RPA calculations are gauge independent. They partially account for differences with precision measurements. Perturbation theory fails for the heaviest systems.
  Time: ~ 30 min, Size: ~ 400 Mb
- Third-order MBPT calculations using dressed amplitudes are gauge independent and agree with precision measurements to $\sim 1\%$.
  Time: ~ 30 min, Size: ~ 1600 Mb

Computational Challenge

Apply gauge-independent 3rd-order MBPT to atoms and ions with 2, 3, or more valence electrons!

- Data in demand for plasma physics studies
- Theory developed for one-electron systems
- Gauge-independent second-order theory for 2 and 3 electron atoms already developed (Safronova, $et\ al.$)