Most diverse, successful, and fascinating theory ever developed, and some of my experiences with MBPT

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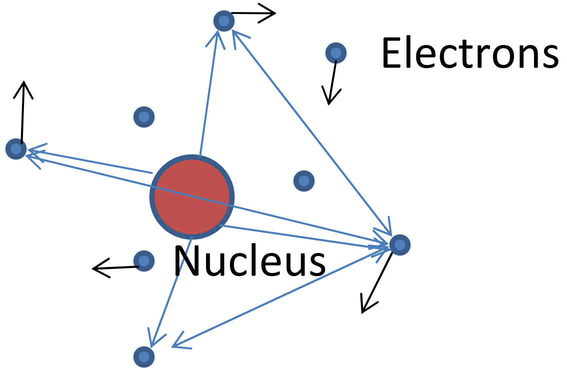
Definition of the theory

- One-electron Potential
- Basis
- Perturbation theory
- Many-body diagrams/formulas
- Relativity
- Angular reduction
- Numerical computation

Complexity of many-electron atom

Many-electron atoms and ions are extremely complex systems: 100-body system with pair interactions between all electrons. Even classically, with strong electric Interaction, it is a hard problem to solve, but with quantum effects "quantum computer" has to be used?



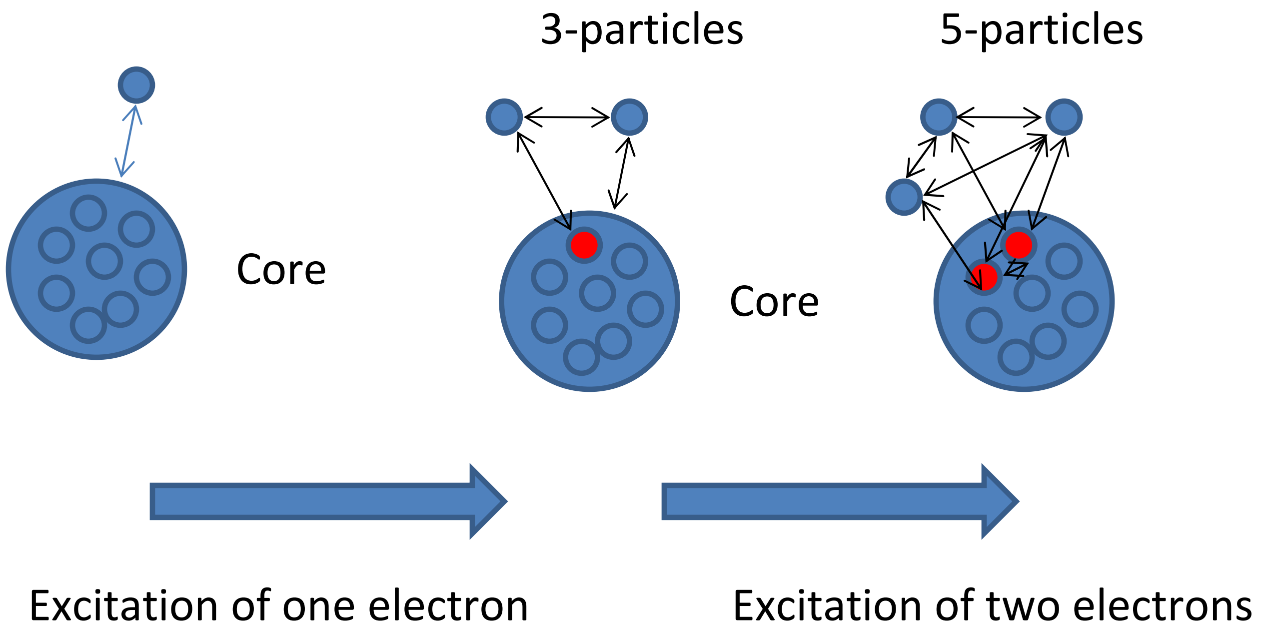
Shrodinger equation for N electrons to solve with finite difference method would need 3*N dimensions, and if we use 10 grid point per dimension we End up with 10^{3N} grid points, for N=100 we obtain a number with 300 zeros.

$$H = \sum_i -\frac{\nabla_i^2}{2} - \frac{Z}{r_i} + u(r_i) + \sum_{i>j} \frac{1}{r_{ij}}$$

Hartree-Fock theory

Fascinating? Successful?

However, if assume that electrons move in some effective potential to which they contribute self-consistently, then the problem becomes very simple for our modern computers. And great miracle is that this model can explain properties of many atoms. Here is the first glimpse on success of the theory: periodic table is explained. However, HF theory is not very accurate, how can we improve it?



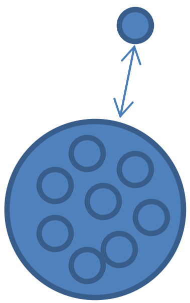
Theory becomes progressively more accurate and complicated

Perturbation theory

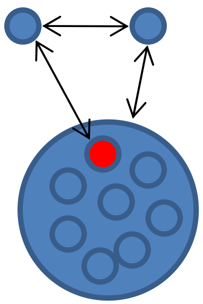
It is hard to solve many-body problem exactly, but fortunately the atomic states in many cases have only small admixture of multi-particle excitations

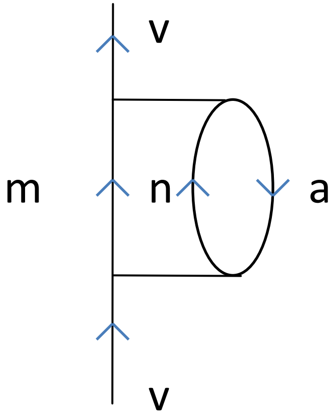
$H=H_0+V$

3-particles



+ small number of these





$$\varepsilon_v^{(2)} = \varepsilon_v - \sum_i \frac{g(vamn)\tilde{g}(mnva)}{\varepsilon_v + \varepsilon_a - \varepsilon_m - \varepsilon_n}$$

Theory works the better, the higher Z of an ion, 1/Z expansion

For neutral atoms, expansion does not converge in general

Relativity

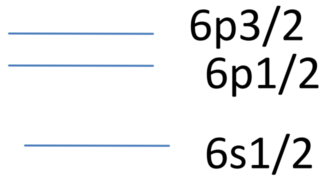
Diverse? Fascinating? Successful?

Do electron move fast? Yes, in heavy atoms and ions some electrons might move close to the speed of light.

Obviously, Dirac equation should be used …

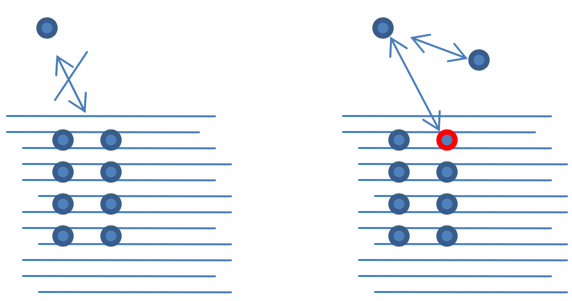
Energies of p1/2 and p3/2 are quite different!

Cs atom



It is easy to solve one Dirac one-particle equation, but how about many-body system?

One has to use QED to understand this, and to avoid a big trouble, we project out negative-energy states, but they contribute!



If we do so, length and velocity forms will be different!

Dirac sea needs to be filled up
And electron normally do not feel it

Include NES in second-order for helium, and magically L and V are the same

Third-order NES

In helium, we find that in triplet-triplet magnetic dipole transitions, the contributions from negative energy states are very large, comparable to that of positive-energy ones

We derived a selection rule, that if total spin does not change, then NES effects are large

Negative-energy contributions to transition amplitudes in helium-like ions, A. Derevianko, I. Savukov, W.R. Johnson, and D.R. Plante, Phys. Rev. A**58**, 4453-61 (1998)

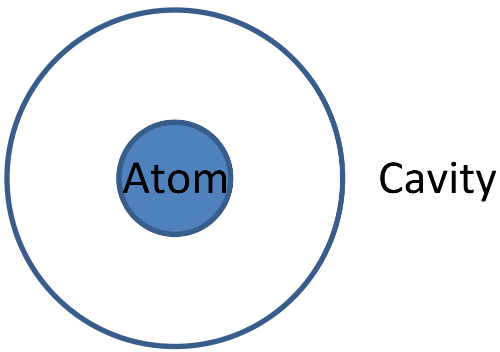
And we went beyond rather simple 2nd-order RMPBT with NES

Third-order negative-energy contributions to transition amplitudes in heliumlike ions, I.M. Savukov, L.N. Labzowsky, and W.R. Johnson, Phys. Rev. A 72, 012504 (2005).

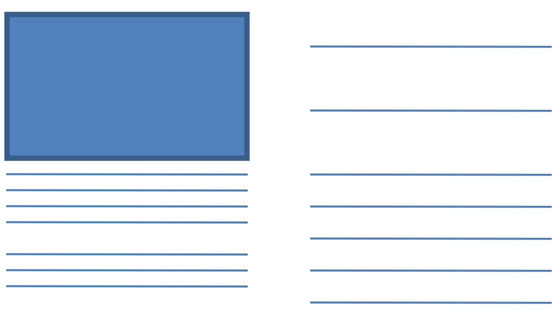
One interesting observation is that if we formally apply RMBPT, the results are different from QED, so we have to use QED

Basis

In perturbation theory we have summation over excited states, infinite number of them!



Cavity is large enough that atom does not change its
Lowest energy states under consideration, but the number
Of intermediate states becomes finite
(how about 40 vs Infinity, who wins?)



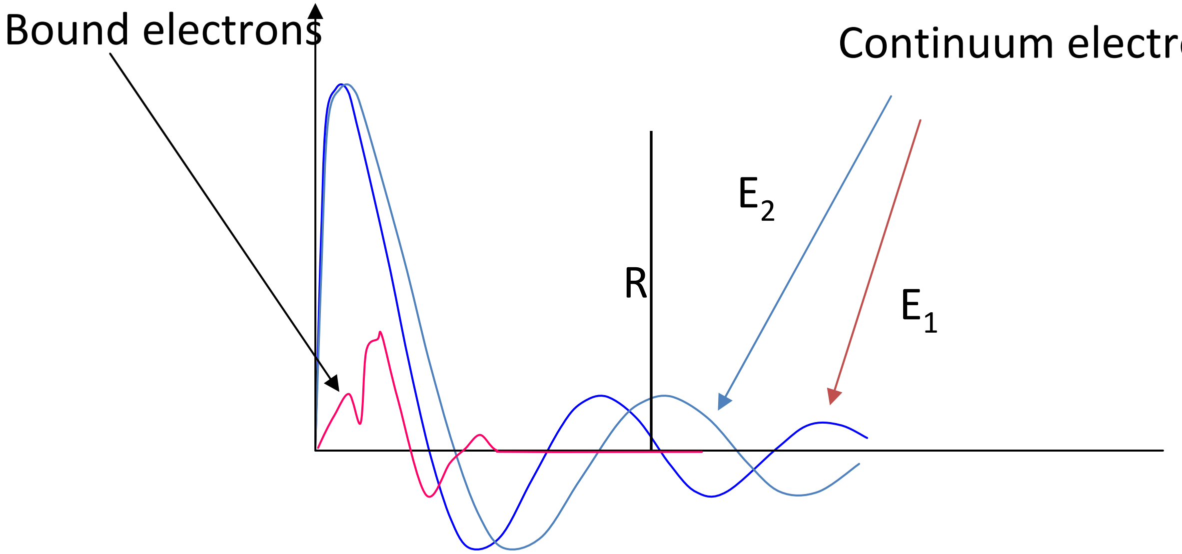
Real miracle is that the perturbation expression gives the same results with or without cavity as long in both case complete summation is performed

What happened to continuum ?

Are quasi-continuum states real?

Quasi – resembling, seeming, virtual, does not sound as real

However, radial functions of quasi and real continuum states are identical if the energies are the same. Cavity of course shifts and splits atomic states, but after its action, the wavefunctions will be the same inside cavity.



Mathematics makes it clear

If we perform partial wave expansion

$$\Psi(r) = \sum_{lm} Y_l^m(\theta, \phi) \frac{P_l(r)}{r}$$

we will obtain second-order linear differential equation

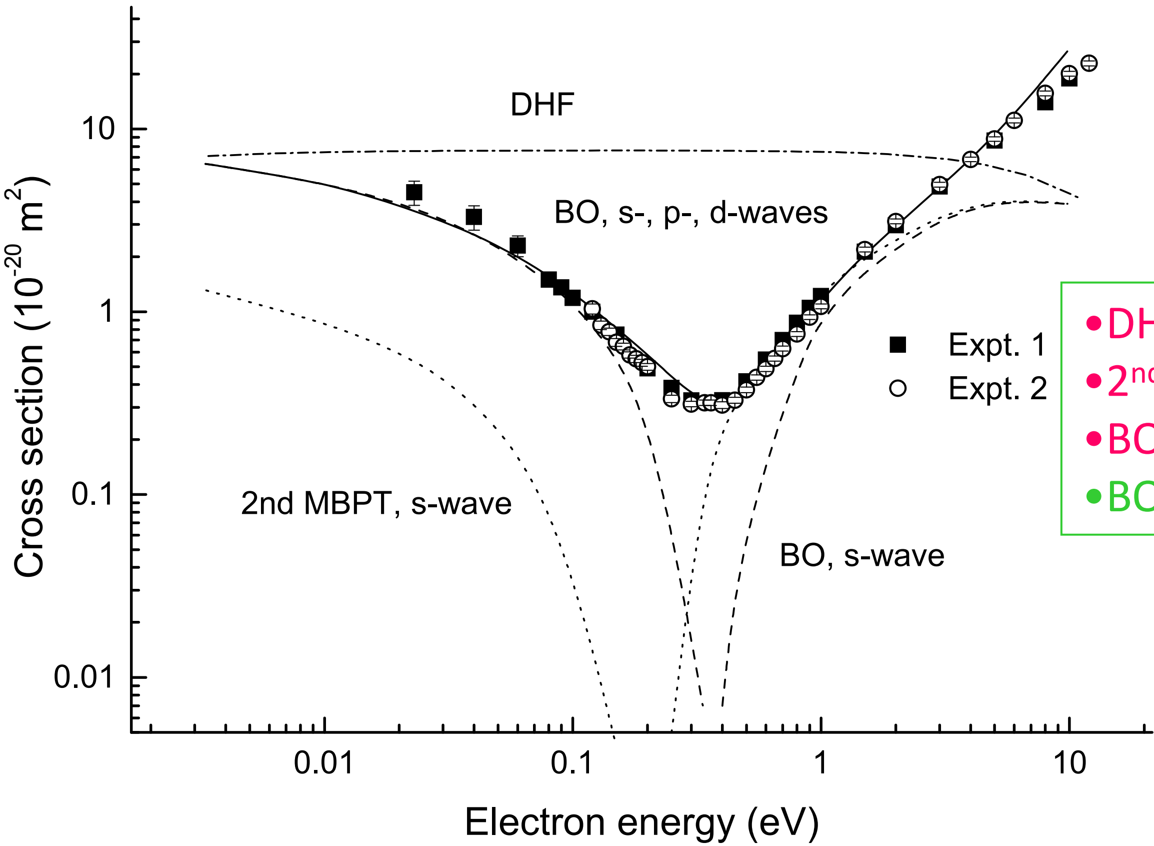
$$\frac{d^2 P_l(r)}{dr^2} + [k^2 - U(r) - \frac{l(l+1)}{r^2}] P_l(r) = 0$$

Solution is real (not complex)
The same boundary conditions at the origin
Energy is fixed
or the external boundary condition is set

Diverse? Fascinating? Successful?

Just to prove the point

Argon elastic cross-section



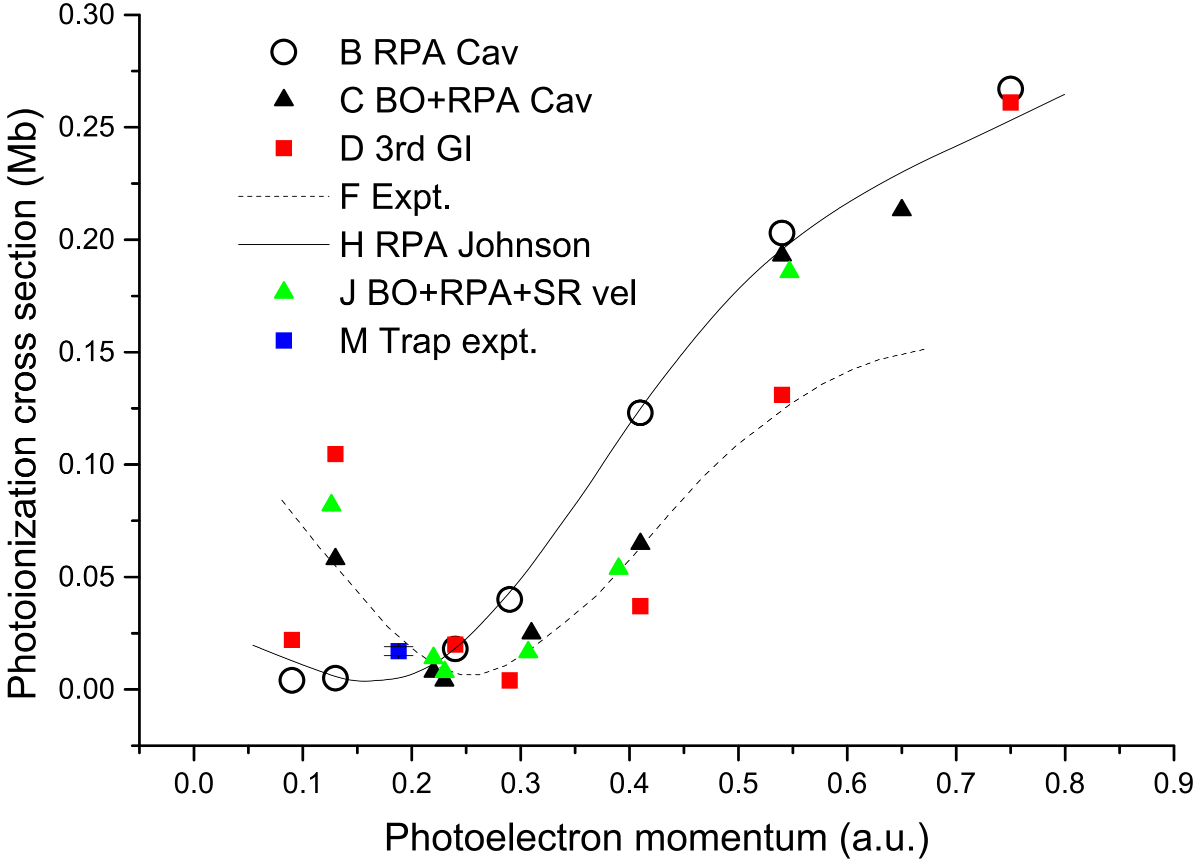
- DHF completely wrong
- 2nd MBPT, still wrong
- BO, s-wave, still wrong
- BO s,p,d waves- right!

Expt.1: Gus'kov *et al.,* Zh. Tekh. Fiz. **48**, 277 (1978)

Expt.2: Buckman & Lohmann, J. Phys. B **19**, 2547 (1986)

I. M. Savukov, Phys. Rev. Lett. 96, 073202 (2006).

For skeptics

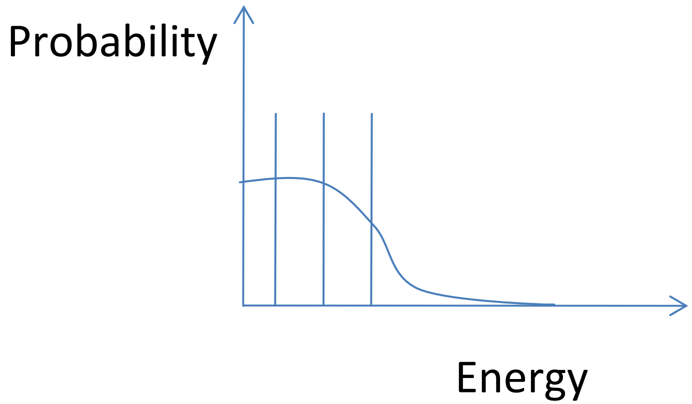


Quasicontinuum relativistic many-body perturbation theory photoionization cross sections of Na, K, Rb, and Cs, I. M. Savukov**,** [Phys. Rev. A. 76, 032710 (2007).]()

Power of quasi-continuum, coming soon: Average atom

Average atom model can be based on quasi (really?) continuum states

Featured with:
Exact exchange interaction – no local approximation
Summation over quasi-continuum states including L=50
No Thomas-Fermi approximation
Relativistic effect
Fermi-Dirac distribution over discrete states, no integrals



Instead of “whole-some or healthy” distribution of electrons in states, one or nothing, we allow fractional distribution, and solve HF equation. Using cavity basis, you can also solve HF equation but everything is done inside the cavity

Miracle? Fascinating? Successful?

Form Invariance

Local potential case – this you might expect

$$T^{(3)} = \Xi + \Delta + \Gamma + N + S + D$$

Breakdown of third-order on FI terms

$$\Xi_1 = \delta\omega^{(1)} \left\{ \sum_{an} \frac{t_{an} \tilde{g}_{wnva}}{(\varepsilon_n - \varepsilon_a + \omega_0)^2} - \sum_{an} \frac{\tilde{g}_{wnvn} t_{na}}{(\varepsilon_n - \varepsilon_a - \omega_0)^2} \right\}$$

$$\Xi_2 = \frac{dT^2_{RPA}}{d\omega} \delta\omega^{(1)} = -\delta\omega^{(1)} \left\{ \sum_{an} \frac{dt_{an}}{d\omega} \frac{\tilde{g}_{wnva}}{\varepsilon_n - \varepsilon_a + \omega_0} + \sum_{an} \frac{\tilde{g}_{wavn}}{\varepsilon_n - \varepsilon_a - \omega_0} \frac{dt_{na}}{d\omega} \right\}$$

Example of the simplest FI term

$$\mathrm{T}^{(3)} = T^{(3)}(\omega_0) + \frac{dT^{(2)}}{d\omega} \delta\omega^{(1)} + \frac{dT^{(1)}}{d\omega} \delta\omega^{(2)} + \frac{1}{2} \frac{d^2 T^{(1)}}{d\omega^2} (\delta\omega^{(1)})^2$$

Derivative contribution

$3s_{1/2}$-$3p_{3/2}$ transition amplitude of Na

Term	Length	Velocity
Ξ	0.004042	0.004042
Δ	0.023752	0.023750
Γ	-0.001448	-0.001448
S	0.001710	0.001710
D	0.019280	0.019276

Equality of length-form and velocity-form transition amplitudes in relativistic many-body perturbation theory, I. M. Savukov and W. R. Johnson, Phys. Rev. A**62**, 052506, 1-10 (2000).

Miracle? Fascinating? Successful?

Form invariance in non-local DHF potential?

First order matrix elements are not form invariant, only if full RPA is done, then second order MBPT in HF potential becomes form invariant

$$T^{(3)} = N + S + D$$

Only 3 terms remain

$$\mathrm{T}_{deriv}^{(3)} = \frac{dT^{(1)}}{d\omega}\delta\omega^{(2)}$$

One derivative term remains

In all other expressions, “dressed” full RPA matrix elements should be used

The tricks are: first, FI subsets exist in HF basis
Second, full RPA matrix elements replace first order ones
Some magic happens and we get complete equality of velocity and form

Form-independent third-order transition amplitudes for atoms with one valence electron, I. M. Savukov and W. R. Johnson, Phys. Rev. A **62**, 052512, 1-7 (2000).

Seriously

- Our complicated codes have been verified and mistakes were found
- Numerical accuracy and basis completeness provide 6-digit form invariance
- Beautiful analytical proof
- Two-valence atoms can be done form invariant

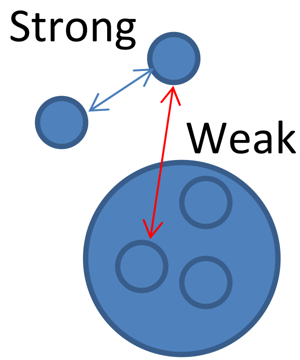
B II	4.99[-4]	15%
C III	9.94[-4]	6%
N IV	1.64[-3]	5%
O V	2.43[-3]	0.1%

Allowed transitions have 0.2%

FI and accuracy
Which one is better?

Relativistic configuration-interaction perturbation-theory calculations of forbidden and allowed transitions for light berylliumlike ions, I. M. Savukov, Phys. Rev. A**70**, 042502 (2004).

Divalent atoms/ions – CI+MBPT



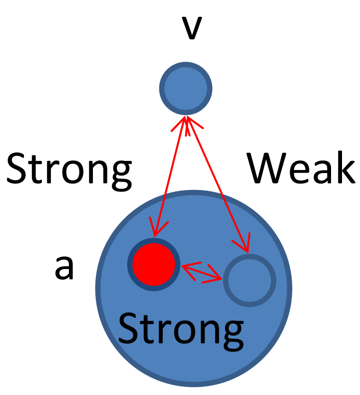
Strong interaction between valence electrons can not Be treated perturbatively, has to be solved with an all-order method such as CI

Weaker interaction of valence electrons with the core is still important, and MBPT can be used

CI is computationally more expensive than MBPT for the same number of electrons, and combination of CI and MBPT is ideal optimized method

Combined CI+MBPT calculations of energy levels and transition amplitudes in Be, Mg, Ca, and Sr, I. M. Savukov and W. R. Johnson, Phys. Rev. A 65, 042503 (2002) .

Close-shell atoms



Valence-hole strong, CI should be used
Valence-core weak, MBPT should be used
Hole-core, strong, MBPT does not work well, but we need to use it.

One trick is to start with SD theory for hole-core
Then the dominant contribution can be included by modification of the denominator

Mixed configuration-interaction and many-body perturbation-theory calculations of energies and oscillator strengths of J=1 odd states of neon, I. M. Savukov, W. R. Johnson, and H. G. Berry, [Phys. Rev. A66, 052501 (2002)]

Summary

- RMBPT is a lot of fun
- Diverse, fascinating, successful theory
- I am deeply grateful to Walter Johnson for help and giving me the opportunity to learn and apply RMBPT
- Many discoveries would be impossible otherwise