NRC "Kurchatov Institute" – PNPI, Gatchina
Quantum Chemistry Laboratory

Intermediate Hamiltonian Fock space coupled cluster theory for incomplete main model spaces and its practical applications using the EXP-T program package

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http://www.qchem.pnpi.spb.ru/expt

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Contents

Intermediate Hamiltonian for incomplete model spaces: theory in brief

Theory: main points

- conventional form of the Fock space coupled cluster (FS CC) method:
  a lot of important advantages for atomic / molecular excited state modelling -
  - ✓info on many states simultaneously
  - ✓exact size consistency
  - ✓rather low cost
  - ✓controllable accuracy
  - ✓maintains good symmetry

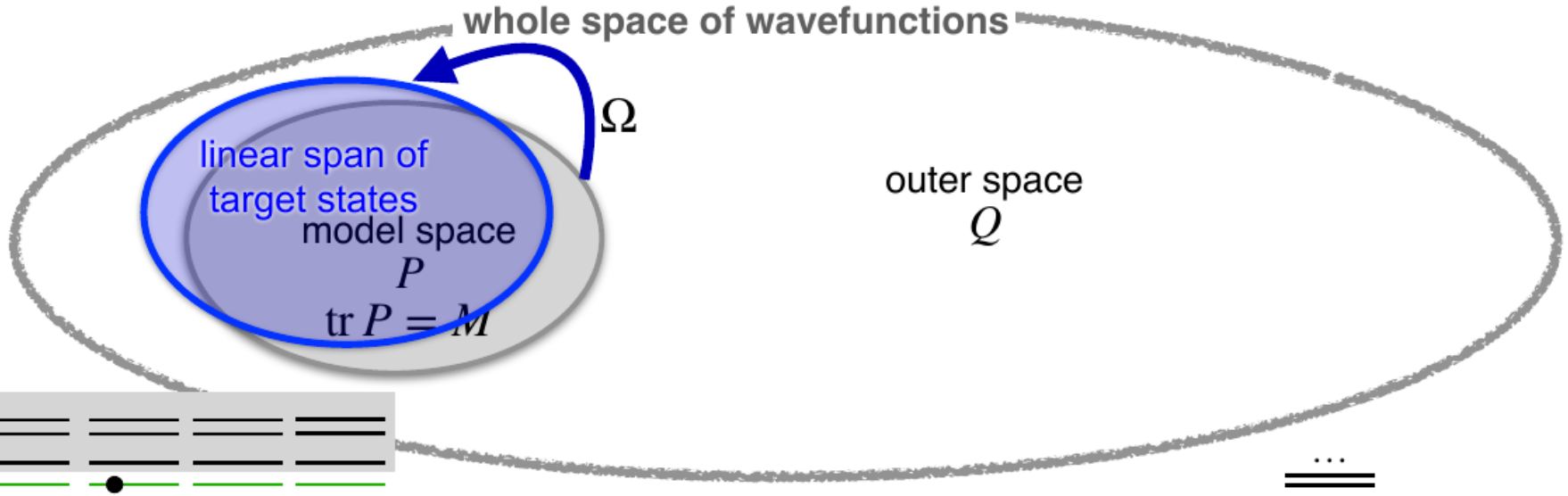
  - works fine **when it works** (rather rare situation, especially for molecules and for approximations beyond singles+doubles 😡)

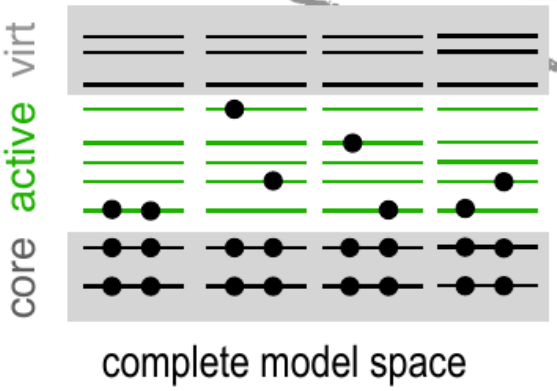
- a recent intermediate-Hamiltonian FS CC reformulation with incomplete main model spaces is implemented within the *exp-t* program complex and **for now** seems quite practical and rather universal.

- to be presented / discussed:
  - origins of the intruder-state problem for FS CC
  - intermediate-Hamiltonian FSCC:
    - general concepts
    - specific features of the present formulation
    - price to be paid for the stability and performance
    - means to estimate the reliability; limitations
  - a few applications

Effective-Hamiltonian Fock-space CC

target H eigenstates: $H\psi_\mu = E_\mu \psi_\mu, \quad \mu = 1,\ldots,M$

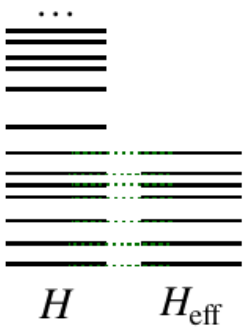




effective Hamiltonian

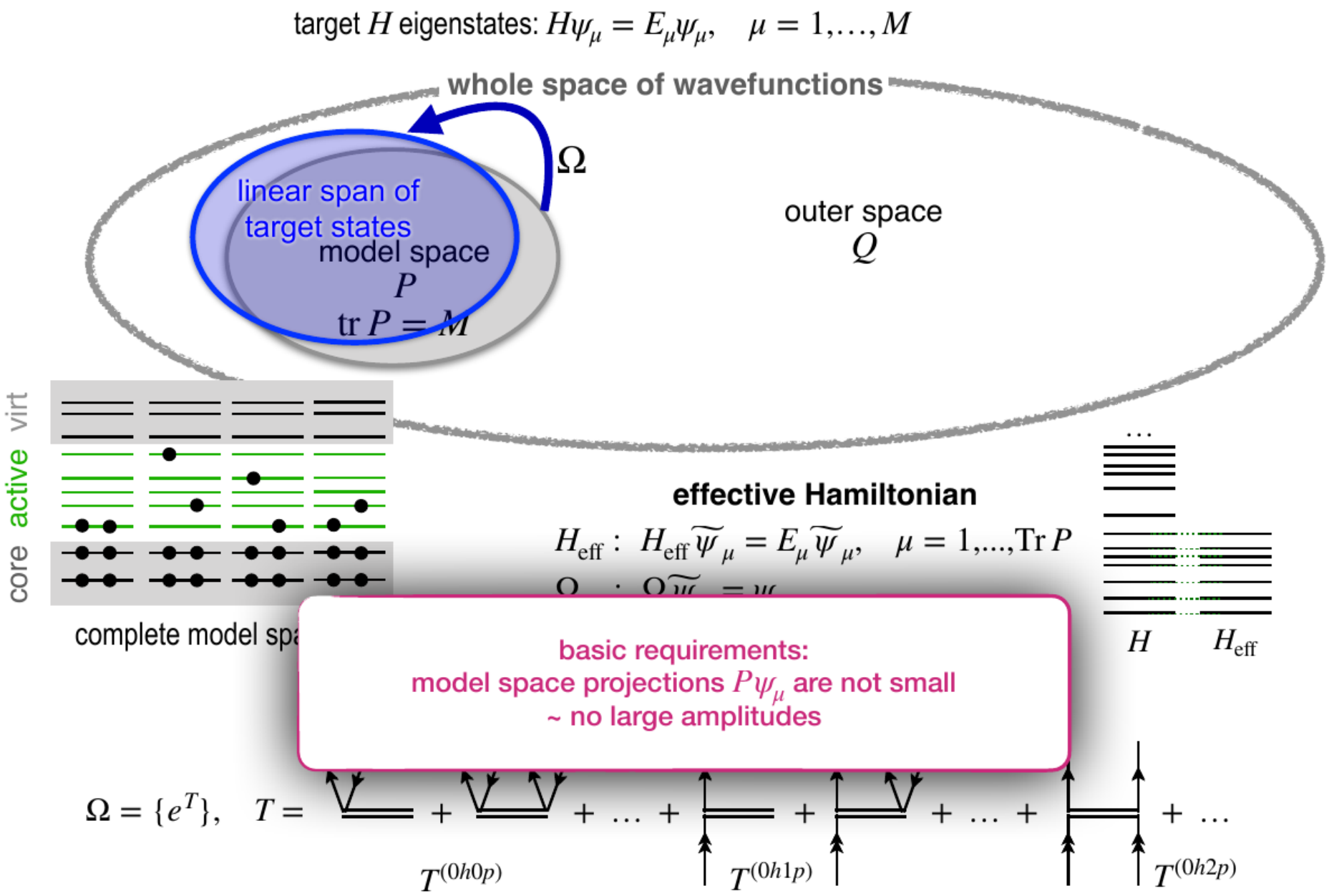
$$H_{\text{eff}}: \; H_{\text{eff}}\widetilde{\psi}_\mu = E_\mu \widetilde{\psi}_\mu, \quad \mu = 1,\ldots,\mathrm{Tr}\,P$$
$$\Omega \; : \; \Omega\widetilde{\psi}_\mu = \psi_\mu$$

$$(H\Omega - \Omega P H_{\text{eff}})P = 0$$



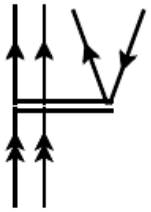
$$\Omega = \{e^T\}, \quad T = T^{(0h0p)} + \ldots + T^{(0h1p)} + \ldots + T^{(0h2p)} + \ldots$$

Effective-Hamiltonian Fock-space CC



Intruder state problem

amplitude of the excitation $K \rightarrow L$ $(A_L^\dagger A_K)$



L list of creation operators

K list of destruction operators

amplitude equations

$$t_K^L = \frac{1}{D_K^L}\left(\overline{V\Omega} - \overline{\Omega V}_{\text{eff}}\right)_K^L$$

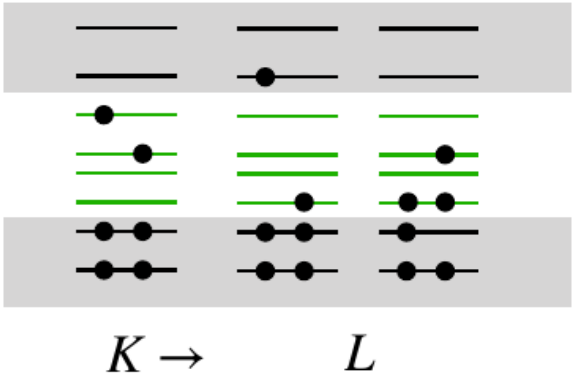
$V = H - H_0$
$V_{\text{eff}} = H_{\text{eff}} - H_0$
H_0: mean-field $1e$ Hamiltonian

$K \rightarrow L$ excitation amplitude

$K \rightarrow L$ energy denominator

$$\sum_i^{\text{in}} \varepsilon_i - \sum_j^{\text{out}} \varepsilon_j$$

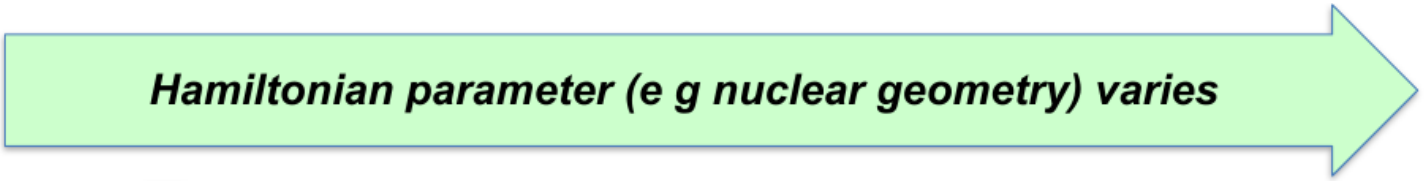
nightmarish structure made of amplitudes & integrals

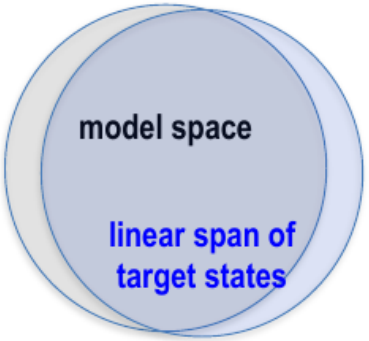


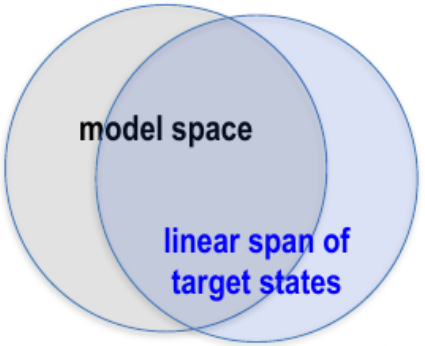
small $D_K^L \rightarrow$ no convergence of iterative scheme

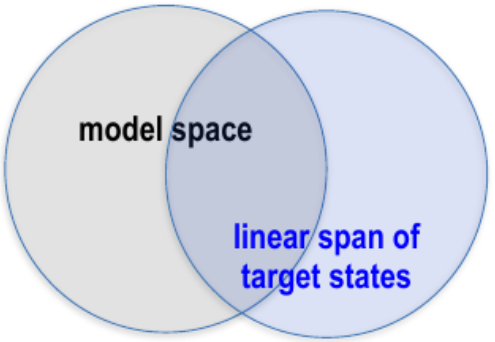
- ✓ nobody is obliged to use Jacobi iterative scheme.
- ✓ solutions can always be obtained by (more expensive) techniques
- ✓ but are these solutions really good?

Intruder state problem









properly chosen model space: large projections of all target states

↓

stable solutions

smooth variation of the model space when the geometry varies

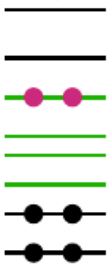
model space projections of some target states become small:

↓

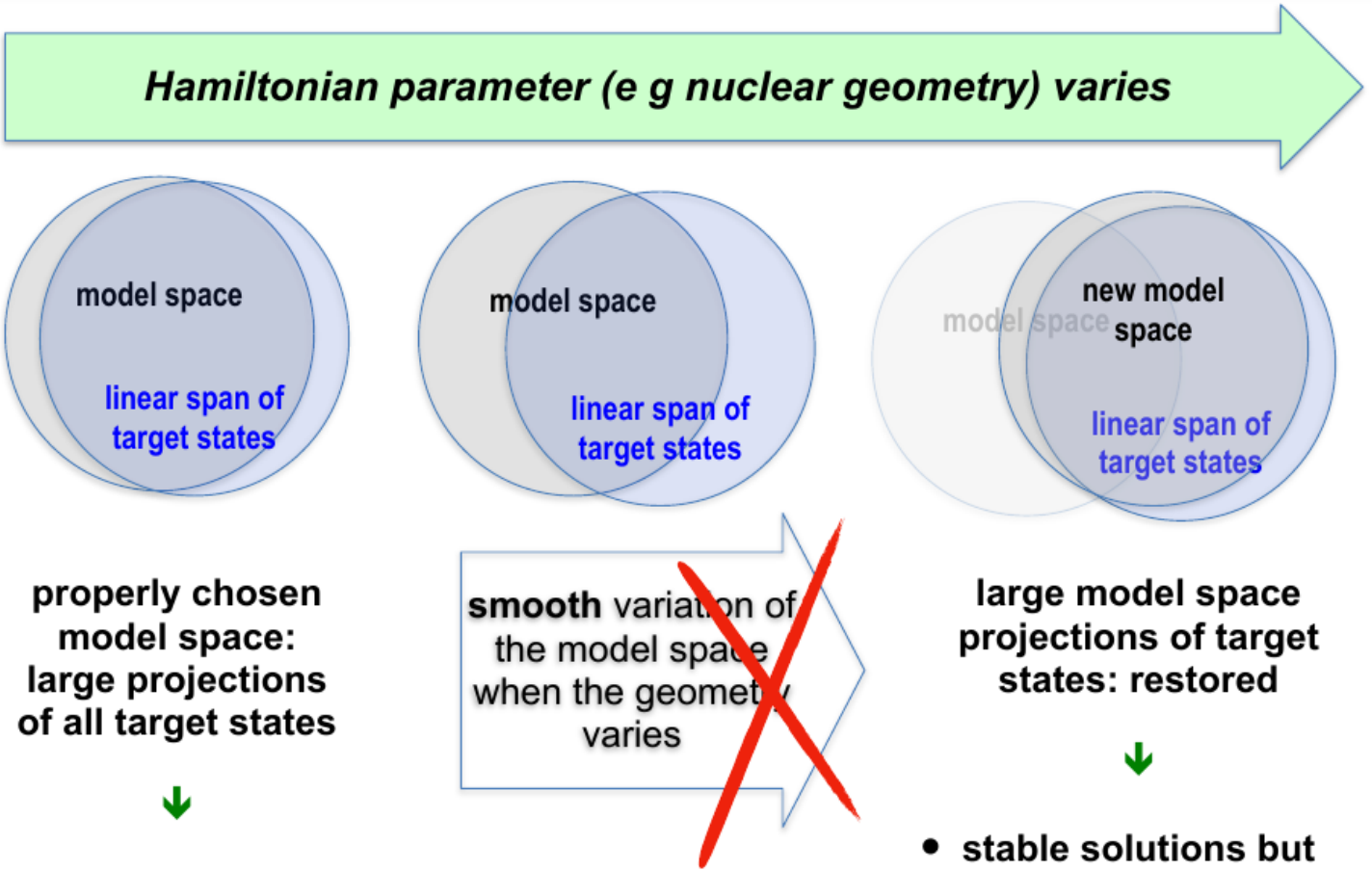
- **numerical instabilities**
- **large cluster amplitudes = failure of finite-rank appoximations**

☹

large complete model spaces:
highly excited dets correspond
to states embedded into continuum

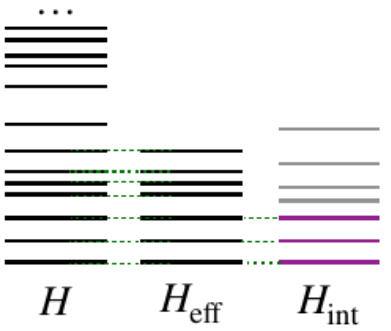


Intruder state problem

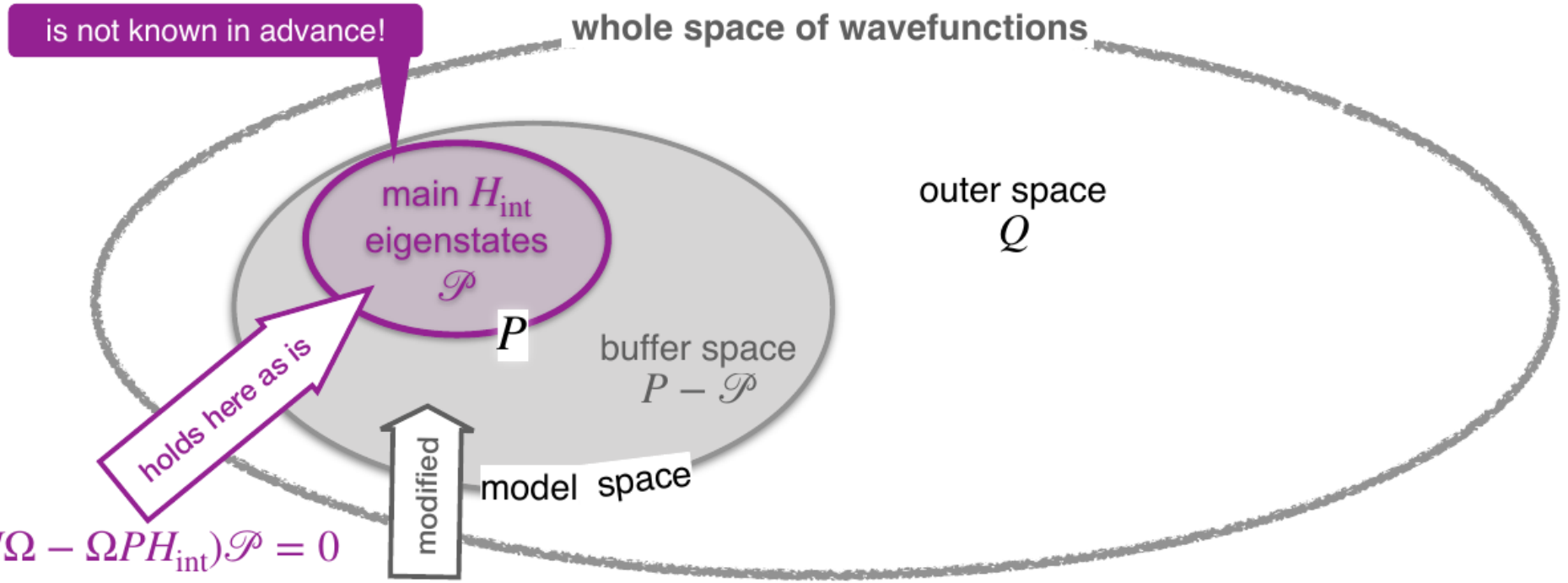


Intermediate Hamiltonians: relaxed requirements

$$\left.\begin{array}{ll} H_{\text{int}}: & H_{\text{int}}\widetilde{\psi}_\mu = E_\mu \widetilde{\psi}_\mu \\ \Omega & : \Omega\widetilde{\psi}_\mu = \psi_\mu \end{array}\right\} \mu = 1,\ldots,M, \quad M < \operatorname{Tr} P$$



[*Malrieu et al 1985*]



$$(H\Omega - \Omega P H_{\text{int}})\mathscr{P} = 0$$

$$(H\Omega - \Omega P H_{\text{int}} + W)(P - \mathscr{P}) = 0$$

+−arbitrary

$$(H\Omega - \Omega P H_{\text{int}} + W)P = 0, \quad W\mathscr{P} = 0$$

[*Zaitsevskii Heully 1992, Mukhopadhyay et al 1992*]

Intermediate Hamiltonians: practical approach

- pre-defined *Main Model Space, MMS* (P_M) and *intermediate space* (P_I)

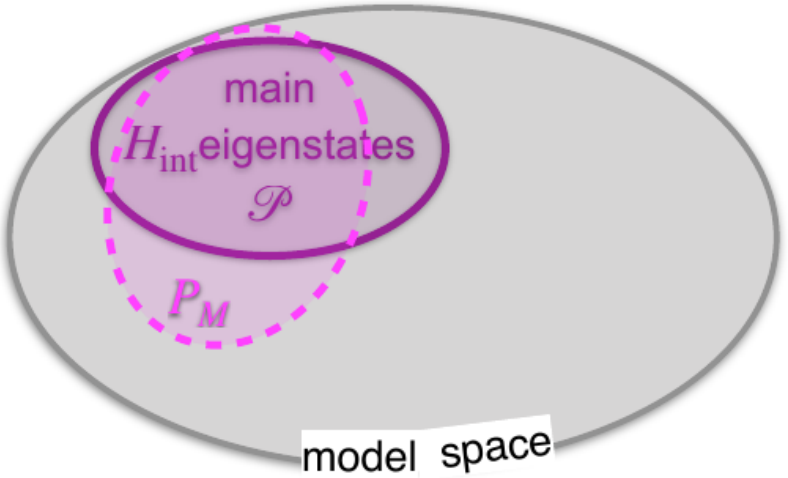
linear spans of dets

$$P_M + P_I = P$$

(*Malrieu et al 1985*)

- main model space should (approximately) include all main H_{int} eigenvectors -

$$P_M \mathscr{P} \approx \mathscr{P}, \quad P_I \mathscr{P} \approx 0$$



!!! to this end, MMS size should normally be *larger* than the number of target states

$$\text{tr}\, P_M > \text{tr}\, \mathscr{P}$$

(i.e. differs essentially from the main model space à la Malrieu)

- replace the requirement $W\mathscr{P} = 0 \Longrightarrow WP_M = 0$
- adapt the form of W to that of other terms of Bloch equation

Intermediate-Hamiltonian Fock space CC

1. no problem appears in low sectors
   e.g. for the target sector $(0h2p)$
   $(0h0p)$ and $(0h1p)$ equations are solves, $T^{(0h0p)}$ and $T^{(0h1p)}$ are known

$$(H\Omega - \Omega P H_{\mathrm{int}} + W)P = 0$$

$$WP_M = 0$$

Intermediate-Hamiltonian Fock space CC

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   $(0h0p)$ and $(0h1p)$ equations are solves, $T^{(0h0p)}$ and $T^{(0h1p)}$ are known

$$(H\Omega - \Omega P H_{\rm int} + W^{(0h2p)})P^{(0h2p)} = 0$$

$$W^{(0h2p)} P_M^{(0h2p)} = 0$$

correspondence within this sector

each term $t_K^L A_L^\dagger A_K$ of $T^{(0h2p)}$ $\Longrightarrow$ one model det $A_K^\dagger |vac\rangle$

Intermediate-Hamiltonian Fock space CC

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   $(0h0p)$ and $(0h1p)$ equations are solves, $T^{(0h0p)}$ and $T^{(0h1p)}$ are known

$$(H\Omega - \Omega P H_{\rm int} + W^{(0h2p)})P^{(0h2p)} = 0$$

$$W^{(0h2p)}P_M^{(0h2p)} = 0$$

$$W^{(0h2p)} = \left(\sum_{\substack{K:\ A_K|vac\rangle \notin MMS \\ L}} A_L^\dagger t_K^L S_K^L A_K \right)$$

Wick theorem

cancellation of disconnected terms

$$t_K^L = \frac{1}{D_K^L}\left(\overline{V\Omega} - \overline{\Omega V_{\rm int}}\right)_K^L, \qquad \text{if } A_K^\dagger|vac\rangle \in MMS$$

$$t_K^L = \frac{1}{(D_K^L + S_K^L)}\left(\overline{V\Omega} - \overline{\Omega V_{\rm int}}\right)_K^L \quad \text{otherwise}$$

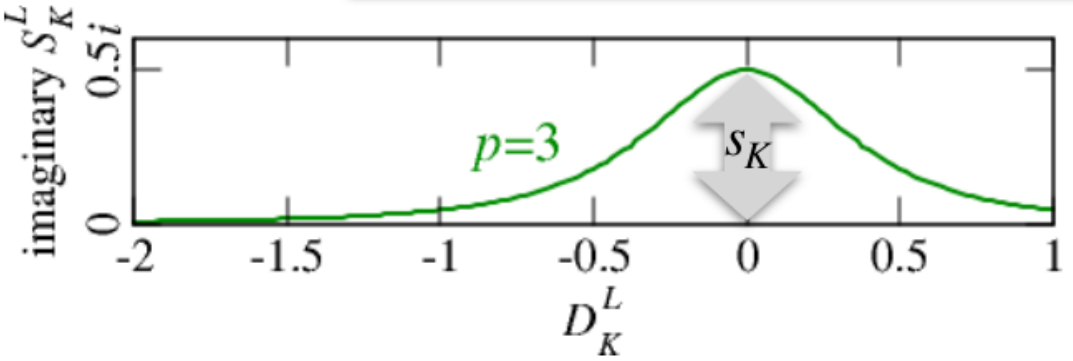
formally connected

(= would be connected if $W^{(0h2p)}$ was connected)

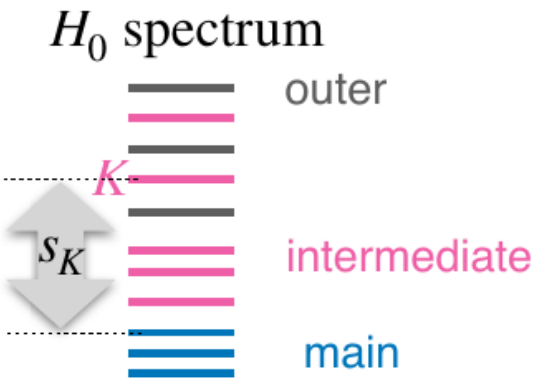
Choice of the shift parameters

goal:

- suppress ill-defined denominators
- affect minimally well-defined denominators
- treat the excitations from MMS and intermediate dets with close energies ≈ on equal footing
- reduce the deviation of H_{int} from H_{eff} $\Longrightarrow$ small deviations from size consistency



$$S_K^L = i s_K \left(\frac{|s_K|}{|D_K^L + i s_K|} \right)^p$$



"real simulation": $\dfrac{1}{D_K^L + S_K^L} \Longrightarrow \mathrm{Re}\left(\dfrac{1}{D_K^L + S_K^L} \right)$

Intermediate Hamiltonians: practical approach

✓ the use of **incomplete** main model spaces is essential

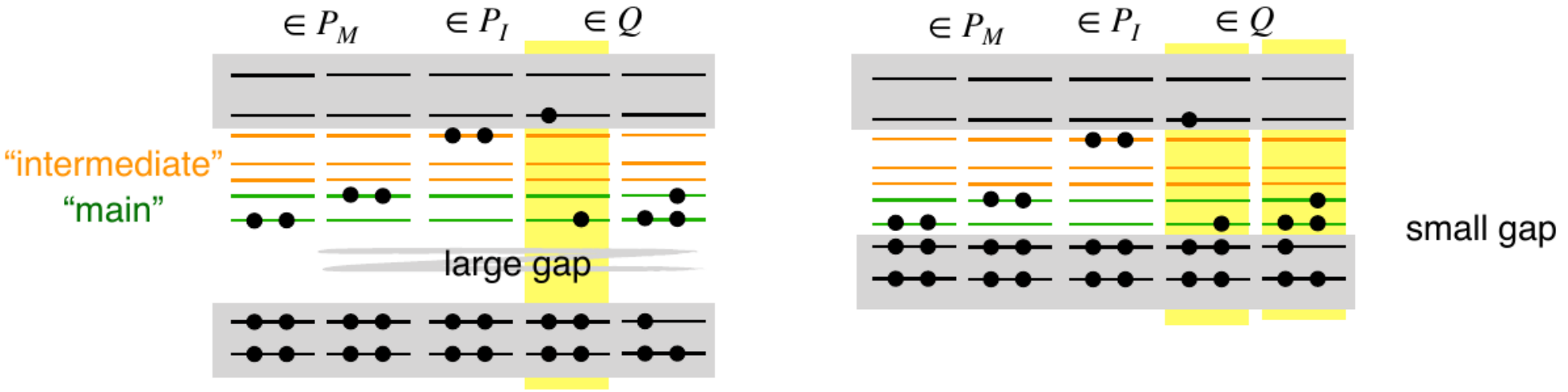
complete MMS (*Landau et al 2001, 2004, Eliav et al 2005*)

active spinors

"main" "intermediate"

main model dets: *all* with only "main" spinors involved

sector $(0h2p)$



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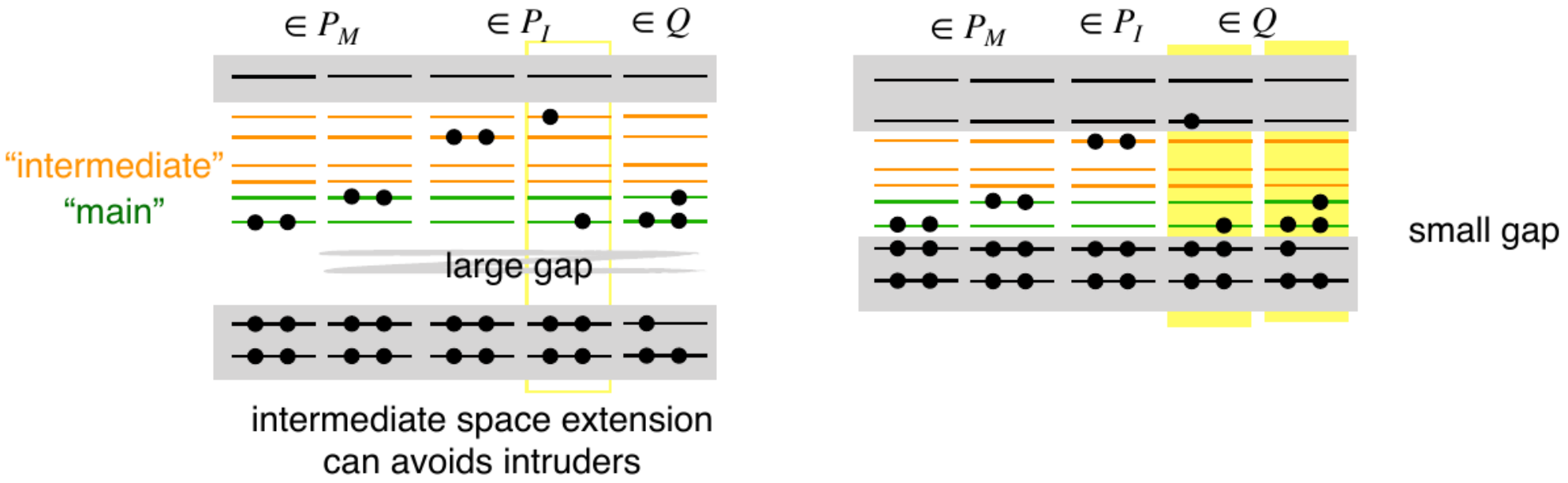

intermediate space extension
can avoids intruders

Intermediate Hamiltonians: practical approach

✓ the use of incomplete main model spaces is essential

complete MMS (*Landau et al 2001, 2004, Eliav et al 2005*)

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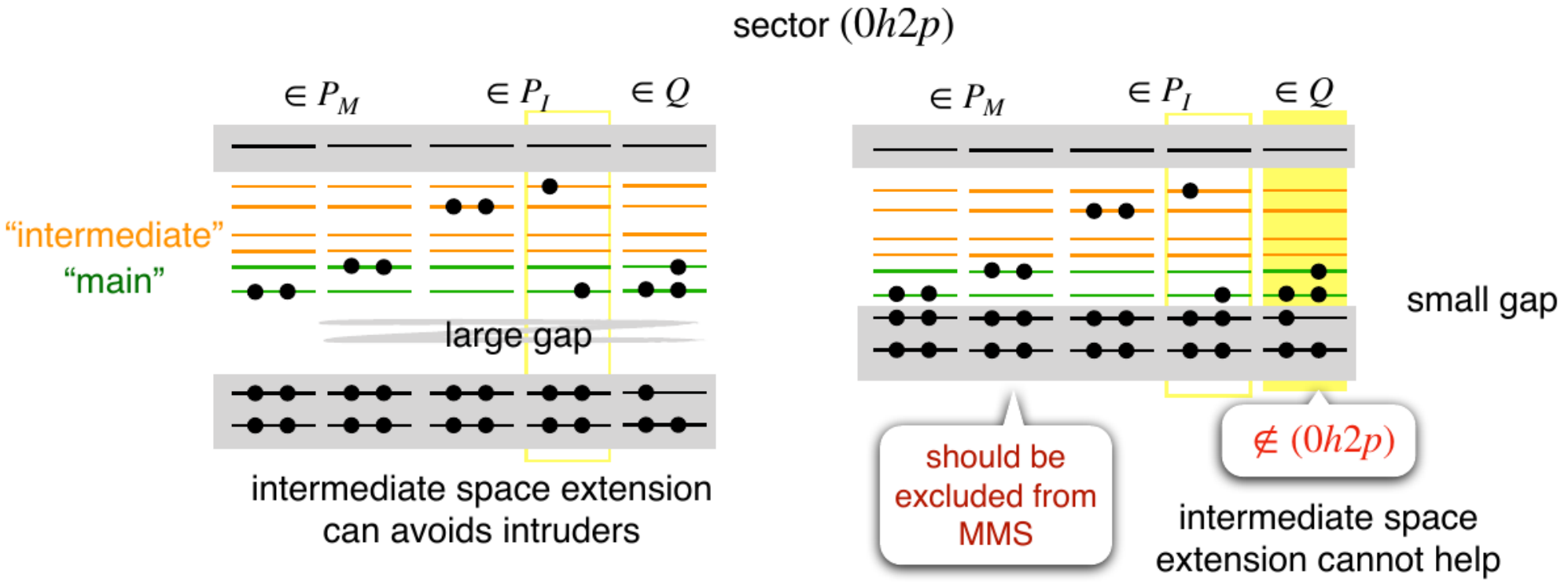


Intermediate-Hamiltonian Fock space CC

2. to solve low-sector problems, shifts are necessary
   e.g. for the target sector $(0h2p)$
   in the $(0h1p)$ sector $W^{(0h1p)}$ had to be introduced

$$(H\Omega - \Omega P H_{\rm int} + W^{(0h2p)})P^{(0h2p)} = 0$$

$$W^{(0h2p)} P_M^{(0h2p)} = 0$$

$$W^{(0h2p)} = \left(\sum_{\substack{K:\ A_K|vac\rangle \notin MMS \\ L}} A_L^\dagger t_K^L S_K^L A_K \right)$$

Wick theorem

no simple cancellation of disconnected terms

$$t_K^L = \frac{1}{D_K^L} \left(\bar{V}\Omega - \Omega \bar{V}_{\rm int} \right)_K^L, \qquad \text{if } A_K|vac\rangle \in MMS$$

$$t_K^L = \frac{1}{(D_K^L + S_K^L)} \left(\bar{V}\Omega - \Omega \bar{V}_{\rm int} \right)_K^L \quad \text{otherwise}$$

if we forget about W-dependent terms in lower sectors

effect of this approximation on the target states can be reduced if

$$W^{(0h1p)} P_M^{(0h2p)} = 0$$

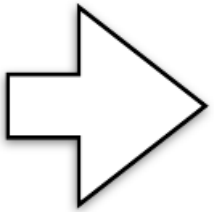
Intermediate-Hamiltonian Fock space CC: reliability

general considerations (for atoms)

or / and

preliminary approximate FS CC calculations with dynamic denominator shifts

(*Zaitsevskii et al 2017*)



main model space

was the choice of MS (P) and MMS (P_M) reasonable?

one has to check *a posteriori* whether

✓ amplitudes in all sectors are moderate

✓ MMS projections of target $H_{\rm int}$ eigenvectors are large (i.e. $P_M\mathscr{P} \approx \mathscr{P}$)

if NOT, then possibly

- total model space should be extended

and/or

- MMS size should be modified

or

- one has to wait for the development of good mixed-sector FS CC

Generalized relativistic pseudopotentials (GRPPs)

Generalized (Gatchina) effective core potentials (GRPPs)

$$\hat{U} = U_{LJ}(r)$$
$$+ \sum_{lj} \left[U_{lj}(r) - U_{LJ}(r)\right] P_{lj}$$

ordinary semilocal RPP
(in DIRAC, etc)

$$+ \sum_{n_c} \sum_{lj} \left\{\tilde{P}_{n_c lj} \left[U_{n_c lj}(r) - U_{lj}(r)\right] + \left[U_{n_c lj}(r) - U_{lj}(r)\right] \tilde{P}_{n_c lj}\right\}$$
$$+ \sum_{n_c n_c'} \sum_{lj} P_{n_c lj} \left[\frac{U_{n_c lj}(r) + U_{n_c' lj}(r)}{2} - U_{lj}(r)\right] P_{n_c' lj}$$

non-local part,
GRPP-specific,
potential from
outercore shells

$P_l = \sum_m |lm\rangle \langle lm|$

$P_{lj} = \sum_m |ljm\rangle \langle ljm|$

$\tilde{P}_{n_c lj} = \sum_m |n_c ljm\rangle \langle n_c ljm|$

$\rightarrow$ projectors onto outercore pseudospinors

$\rightarrow$ depend on r

A. V. Titov, N. S. Mosyagin. Generalized relativistic effective core potential: Theoretical grounds. Int. J. Quantum Chem. 71(5), 359 (1999)

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$$+ \sum_{n_c n_c'} \sum_{lj} P_{n_c lj} \left[\frac{U_{n_c lj}(r) + U_{n_c' lj}(r)}{2} - U_{lj}(r) \right] P_{n_c' lj}$$

non-local part,
GRPP-specific,
potential from
outercore shells

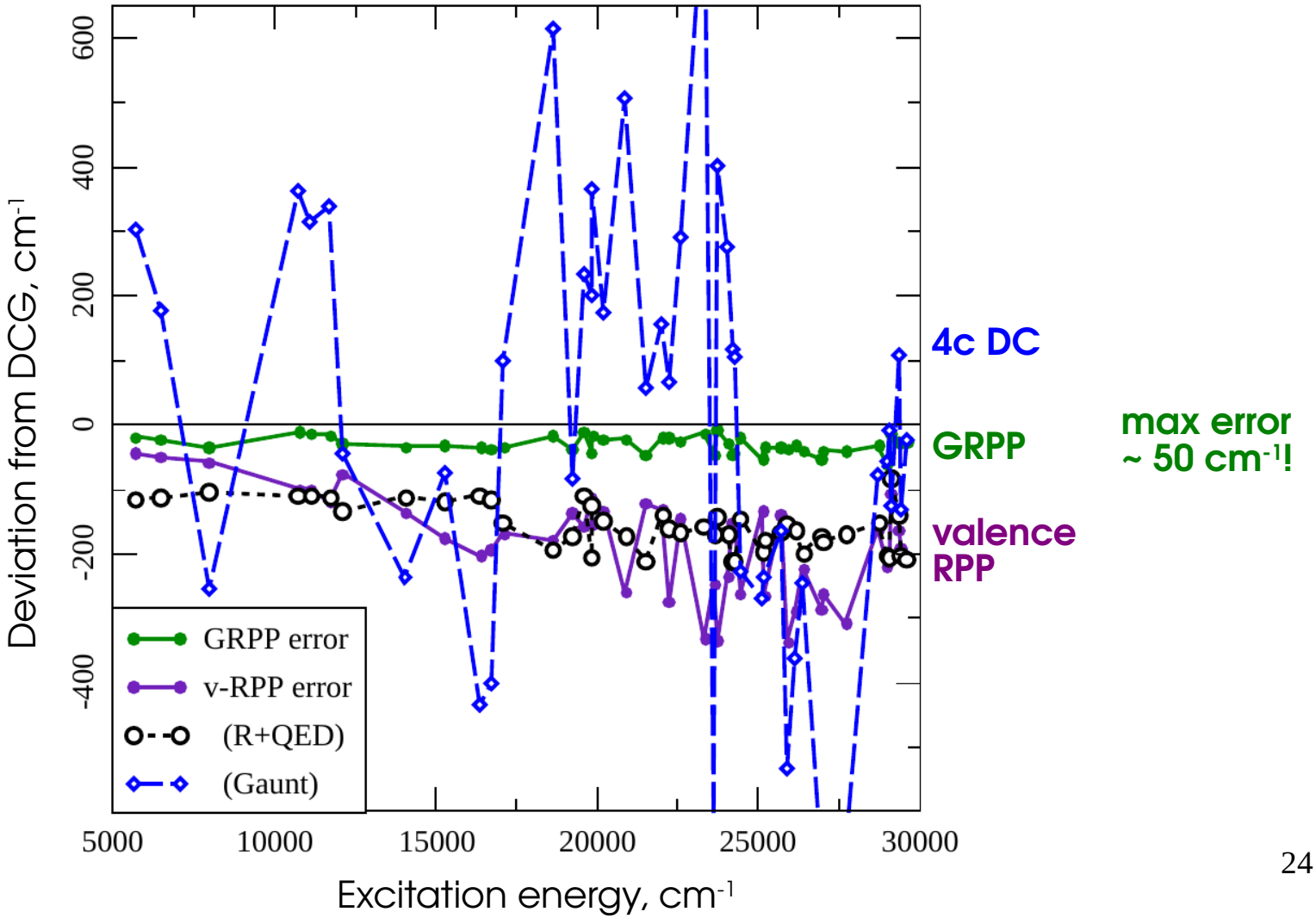
- GRPP: finite nucleus + Breit + QED (MLSO)
- integrals of the GRPP operator over Gaussian basis functions: **the LIBGRPP library**
- LIBGRPP is written **from scratch in C99**
- algorithm: McMurchie-Davidson + numerical radial integrals (to avoid instabilities)
- **interfaced to DIRAC-19**

A. V. Titov, N. S. Mosyagin. Generalized relativistic effective core potential: Theoretical grounds. Int. J. Quantum Chem. 71(5), 359 (1999)

Generalized (Gatchina) effective core potentials (GRPPs)

GRPP vs four-component Hamiltonian (x2c-mmf DCG)

ThO molecule electronic states, FS-RCCSD, 28e in core



Practical calculations

U^{4+} ion: U^{6+} vacuum state (sector 0h2p)

U^{6+} (0h0p) → U^{5+} (0h1p) → U^{4+} (0h2p)

Symmetry	Type	Expt.[c]	
$^3H_4$	$5f^2$	...	(Rn) $5f^2$
$^3F_2$	$5f^2$	4 161	
$^3H_5$	$5f^2$	6 137	
$^3F_3$	$5f^2$	8 983	
$^3F_4$	$5f^2$	9 434	
$^3H_6$	$5f^2$	11 514	
$^1D_2$	$5f^2$	16 465	
$^1G_4$	$5f^2$	16 656	
$^3P_0$	$5f^2$	17 128	
$^3P_1$	$5f^2$	19 819	
$^1I_6$	$5f^2$	22 276	
$^3P_2$	$5f^2$	24 652	
$^1S_0$	$5f^2$	43 614	
$^3H_4$	$5f6d$	59 183	(Rn) $5f6d$
$^3F_2$	$5f6d$	59 640	
$^3G_3$	$5f6d$	63 053	
$^1G_4$	$5f6d$	65 538	
$^3F_3$	$5f6d$	67 033	
$^3H_5$	$5f6d$	67 606	
$^3F_2$	$5f7s$	94 070	(Rn) $5f7s$
$^3F_3$	$5f7s$	94 614	
$^3F_4$	$5f7s$	101 612	
$^1F_3$	$5f7s$	102 407	
$^3G_3$	$5f7p$	139 141	(Rn) $5f7p$
$^3F_2$	$5f7p$	140 642	
$^3G_4$	$5f7p$	146 926	
$^3D_3$	$5f7p$	147 170	
$^3F_3$	$5f7p$	156 493	

IP ~ 380000 см$^{-1}$

I. Infante, E. Eliav, M. J. Vilkas, Y. Ishikawa, U. Kaldor et al. A Fock space coupled cluster study on the electronic structure of the UO2, UO2+, U4+, and U5+ species Citation: J. Chem. Phys. 127, 124308 (2007). doi: **10.1063/1.2770699**

U^{4+} ion: U^{6+} vacuum state (sector 0h2p)

U^{6+} (0h0p) → **U^{5+}** (0h1p) → **U^{4+}** (0h2p)

gerade:

1	3/2g−	1	−	−7.012416439361
2	1/2g+	1	−	−7.012416439331
3	5/2g+	1	−	−6.697036598529
4	1/2g+	1	−	−6.697036598472
5	3/2g−	1	−	−6.697036598414
6	1/2g+	1	−	−4.599685009259
7	3/2g−	0	a	−1.841512871380
8	1/2g+	0	a	−1.841512871373
9	5/2g+	0	a	−1.803353411254
10	3/2g−	0	a	−1.803353411248
11	1/2g+	0	a	−1.803353411232
12	1/2g+	0	a	−1.626284030638
13	3/2g−	0	−	−0.986759047259
14	1/2g+	0	−	−0.986759047259
15	3/2g−	0	−	−0.971802701076
16	1/2g+	0	−	−0.971802701069
17	5/2g+	0	−	−0.971802701058
18	1/2g+	0	−	−0.936639827231

ungerade:

227	1/2u+	1	−	−12.868769808958
228	3/2u−	1	−	−10.821751459723
229	1/2u+	1	−	−10.821751459692
230	1/2u+	1	−	−3.714590546867
231	1/2u+	1	−	−3.267732481589
232	3/2u−	1	−	−3.267732481516
233	3/2u−	0	a	−2.200043341541
234	5/2u+	0	a	−2.200043341279
235	1/2u+	0	a	−2.200043341254
236	3/2u−	0	a	−2.169092108641
237	7/2u−	0	a	−2.169092108630
238	5/2u+	0	a	−2.169092108623
239	1/2u+	0	a	−2.169092108615
240	1/2u+	0	a	−1.396385390875
241	3/2u−	0	a	−1.298983344136
242	1/2u+	0	a	−1.298983344100
243	3/2u−	0	−	−1.003310867069
244	1/2u+	0	−	−1.003310867035
245	5/2u+	0	−	−1.003310867027

U^{4+} ion: U^{6+} vacuum state (sector 0h2p)

U^{6+} (0h0p) → U^{5+} (0h1p) → U^{4+} (0h2p)

gerade:

1	3/2g−	1	−	−7.012416439361
2	1/2g+	1	−	−7.012416439331
3	5/2g+	1	−	−6.697036598529
4	1/2g+	1	−	−6.697036598472
5	3/2g−	1	−	−6.697036598414
6	1/2g+	1	−	−4.599685009259
7	3/2g−	0	a	−1.841512871380
8	1/2g+	0	a	−[illegible]73
9	5/2g+	0	a	−[illegible]54
10	3/2g−	0	a	−[illegible]48
11	1/2g+	0	a	−[illegible]32
12	1/2g+	0	a	−[illegible]38
13	3/2g−	0	−	−[illegible]59
14	1/2g+	0	−	−0.986759047259
15	3/2g−	0	−	−0.971802701076
16	1/2g+	0	−	−0.971802701069
17	5/2g+	0	−	−0.971802701058
18	1/2g+	0	−	−0.936639827231

6d: max 1

7s: max 1

ungerade:

227	1/2u+	1	−	−12.868769808958
228	3/2u−	1	−	−10.821751459723
229	1/2u+	1	−	−10.821751459692
230	1/2u+	1	−	−3.714590546867
231	1/2u+	1	−	−3.267732481589
232	3/2u−	1	−	−3.267732481516
233	3/2u−	0	a	−2.200043341541
234	5/2u+	0	a	−2.200043341279
235	1/2u+	0	a	−2[illegible]4
236	3/2u−	0	a	−2[illegible]1
237	7/2u−	0	a	−2[illegible]0
238	5/2u+	0	a	−2.169092108623
239	1/2u+	0	a	−2.169092108615
240	1/2u+	0	a	−1[illegible]5
241	3/2u−	0	a	−1[illegible]6
242	1/2u+	0	a	−1[illegible]0
243	3/2u−	0	−	−1.003310867069
244	1/2u+	0	−	−1.003310867035
245	5/2u+	0	−	−1.003310867027

5f: max 2

7p: max 1

Target states: **$5f^2$, 5f6d, 5f7s, 7f7p**

Main determinants:

5f 5f 5f 6d 5f 7s 5f 7p

Intermediate determinants:

6d 6d 7s 6d 7s 7p 7p 7p

U^{4+} ion: U^{6+} vacuum state (sector 0h2p)

U^{6+} (0h0p) → U^{5+} (0h1p) → U^{4+} (0h2p)

gerade:

1	3/2g−	1	−	−7.012416439361
2	1/2g+	1	−	−7.012416439331
3	5/2g+	1	−	−6.697036598529
4	1/2g+	1	−	−6.697036598472
5	3/2g−	1	−	−6.697036598414
6	1/2g+	1	−	−4.599685009259
7	3/2g−	0	a	−1.841512871380
8	1/2g+	0	a	−[illegible]73
9	5/2g+	0	a	−[illegible]54
10	3/2g−	0	a	−[illegible]48
11	1/2g+	0	a	−[illegible]32
12	1/2g+	0	a	−[illegible]38
13	3/2g−	0	−	−[illegible]59
14	1/2g+	0	−	−0.986759047259
15	3/2g−	0	−	−0.971802701076
16	1/2g+	0	−	
17	5/2g+	0	−	
18	1/2g+	0	−	

6d: max 1

7s: max 1

ungerade:

227	1/2u+	1	−	−12.868769808958
228	3/2u−	1	−	−10.821751459723
229	1/2u+	1	−	−10.821751459692
230	1/2u+	1	−	−3.714590546867
231	1/2u+	1	−	−3.267732481589
232	3/2u−	1	−	−3.267732481516
233	3/2u−	0	a	−2.200043341541
234	5/2u+	0	a	−2.200043341279
235	1/2u+	0	a	−2[illegible]4
236	3/2u−	0	a	−2[illegible]1
237	7/2u−	0	a	−2[illegible]0
238	5/2u+	0	a	−2.169092108623
239	1/2u+	0	a	−2.169092108615
240	1/2u+	0	a	−1[illegible]5
241	3/2u−	0	a	−1[illegible]6
			a	−1[illegible]0
			−	−1.003310867069
			−	−1.003310867035
			−	−1.003310867027

5f: max 2

7p: max 1

```
ih_imms
  sectors 0h2p
  subspace energy -2.4 -2.0   # 5f
  subspace energy -2.0 -1.7   # 6d
  subspace energy -1.7 -1.5   # 7s
  subspace energy -1.5 -1.2   # 7p
  main_occ 2 0 0 0      # 5f^2
  main_occ 1 1 0 0      # 5f6d
  main_occ 1 0 1 0      # 5f7s
  main_occ 1 0 0 1      # 5f7p
end
```

Target states: **$5f^2$, 5f6d, 5**

U^{4+} ion: U^{6+} vacuum state (sector 0h2p)

U^{6+} (0h0p) → U^{5+} (0h1p) → U^{4+} (0h2p)

EXP-T input file (ccsd.inp):

```
sector 0h2p
nactp 32        # 7s, 7p, 6d, 5f

maxiter 500
memory 2000 gb
conv 1e-7
disk_usage 0
nthreads 8
diis 200
flush 1 iter

ih_imms
  sectors 0h2p
  subspace energy -2.4 -2.0   # 5f
  subspace energy -2.0 -1.7   # 6d
  subspace energy -1.7 -1.5   # 7s
  subspace energy -1.5 -1.2   # 7p
  main_occ 2 0 0 0      # 5f^2
  main_occ 1 1 0 0      # 5f6d
  main_occ 1 0 1 0      # 5f7s
  main_occ 1 0 0 1      # 5f7p
end
```

Step 1: DIRAC

SCF + integral transformation

```
pam --inp=TRA.inp --mol=U
--get="MRCONEE MDCINT MDPROP"
```

Step 2: EXP-T

FS-CC calculation

```
expt.x ccsd.inp > ccsd.out
```

More on EXP-T and keywords in manual:

http://www.qchem.pnpi.spb.ru/data/oleynichenko/expt/manual_en.pdf

U^{4+} ion: U^{6+} vacuum state (sector 0h2p)

Level	Re(eigenvalue)	...	Rel eigv, eV	Rel eigv, cm-1	% **main**	deg	symmetry	
@ 1	-4.0586509093	...	0.0000000000	0.000000	**100.0**	9	0g 1g+ 1g-	...
@ 2	-4.0396641270	...	0.5166566665	4167.117044	**100.0**	5	0g 1g+ 1g-	...
@ 3	-4.0309457670	...	0.7538953285	6080.575896	**100.0**	11	0g 1g+ 1g-	...
@ 4	-4.0179157501	...	1.1084601500	8940.334042	**100.0**	7	0g 1g+ 1g-	...
@ 5	-4.0157979548	...	1.1660882949	9405.136378	**100.0**	9	0g 1g+ 1g-	...
@ 6	-4.0065654216	...	1.4173183231	11431.443208	**100.0**	13	0g 1g+ 1g-	...
@ 7	-3.9831812977	...	2.0536327498	16563.665175	**100.0**	9	0g 1g+ 1g-	...
@ 8	-3.9830732736	...	2.0565722367	16587.373735	**100.0**	5	0g 1g+ 1g-	...
@ 9	-3.9780887240	...	2.1922087410	17681.355921	**100.0**	1	0g	...
. . .		...						...
@ 55	-3.3115090934	...	20.3307645322	163978.674614	**97.9**	3	0g 1g+ 1g-	...
@ 56	-3.3062734516	...	20.4732336029	165127.765164	**100.0**	5	0g 3g+ 3g-	...
@ 57	-3.3062734405	...	20.4732339067	165127.767614	**100.0**	4	1g+ 1g- 2g+	...
@ 58	-3.3051727456	...	20.5031853398	165369.342214	**100.0**	9	0g 1g+ 1g-	...
@ 59	-3.3051727282	...	20.5031858121	165369.346023	**100.0**	2	5g+ 5g-	...
@ 60	-3.2996057361	...	20.6546713866	166591.159580	**94.6**	5	0g 1g+ 1g-	...
@ 61	-3.2545082327	...	21.8818369692	176488.917505	**5.5**	3	0g 1g+ 1g-	...
@ 62	-3.2492481945	...	22.0249698993	177643.362442	**96.1**	1	0g	...
@ 63	-3.2458086736	...	22.1185640310	178398.250023	**5.7**	5	0g 1g+ 1g-	...
@ 64	-3.2154570679	...	22.9444732988	185059.657511	**3.2**	7	0g 1g+ 1g-	...
@ 65	-3.1819629629	...	23.8558943257	192410.763849	**9.0**	5	0g 1g+ 1g-	...

main states

intermediate states

Ra atom

- GRPP (60 core e, Fermi nucleus, Breit, QED)
- sector $(0h2p)$ - closed-shell Ra^{2+} + $2e$
- MS (P): CAS $2e$ / (6d7sp) or
  $2e$ / (5f6d7spd8sp)
- 6s6p spinors of Tl^{2+}
- Main MS (P_M): $7s^2$, $7s6d_{3/2,5/2}$, $7s7p_{1/2,3/2}$
- limitation: basis up to i functions

excitation energies from $7s^2\ ^1S_0$, cm^{-1}

	exptl	calc-exptl				
		FS CCSD	$+\Delta_T$	FS CCSD	$+\Delta_T$	effect $l>6$
		MS (6d7sp)		MS (5f6d7spd8sp)		
$7s7p\ ^3P_0^o$	13 078	102	unacceptably large $T_2^{(0h2p)}$ amplitudes in FS CCSDT	9	51	
$7s6d\ ^3D_1$	13 716	-203		10	-110	↑
$7s6d\ ^3D_2$	13 994	-185		14	-109	↑
$7s7p\ ^3P_1^o$	13 999	110		12	45	
$7s6d\ ^3D_3$	14 707	-126		43	-75	↑
$7s7p\ ^3P_2^o$	16 689	194		36	44	
$7s6d\ ^1D_2$	17 081	55		99	-17	↑
$7s7p\ ^1P_1^o$	20 715	324		66	9	

Tl^+ ion

- GRPP (28 core e, Fermi nucleus, Breit, QED)
- sector $(0h2p)$ - closed-shell Tl^{2+} + $2e$
- MS (P): CAS $2e$ / 6s6p spinors of Tl^{2+}
- Main MS (P_M): $6s^2$, $6s6p_{1/2}$, $6s6p_{3/2}$
- limitation: basis up to i functions

excitation energies, cm^{-1}			
$6s^2\,{}^1S_0 \rightarrow$	exptl	calc-exptl	
		FS CCSD	$+\Delta_T$
$6s6p\,{}^3P_0$	49451	−394	−128
$6s6p\,{}^3P_1$	52394	-312	-38
$6s6p\,{}^3P_2$	61727	-181	8
$6s6p\,{}^1P_1$	75663	272	173

https://arxiv.org/abs/2208.12296

At this point

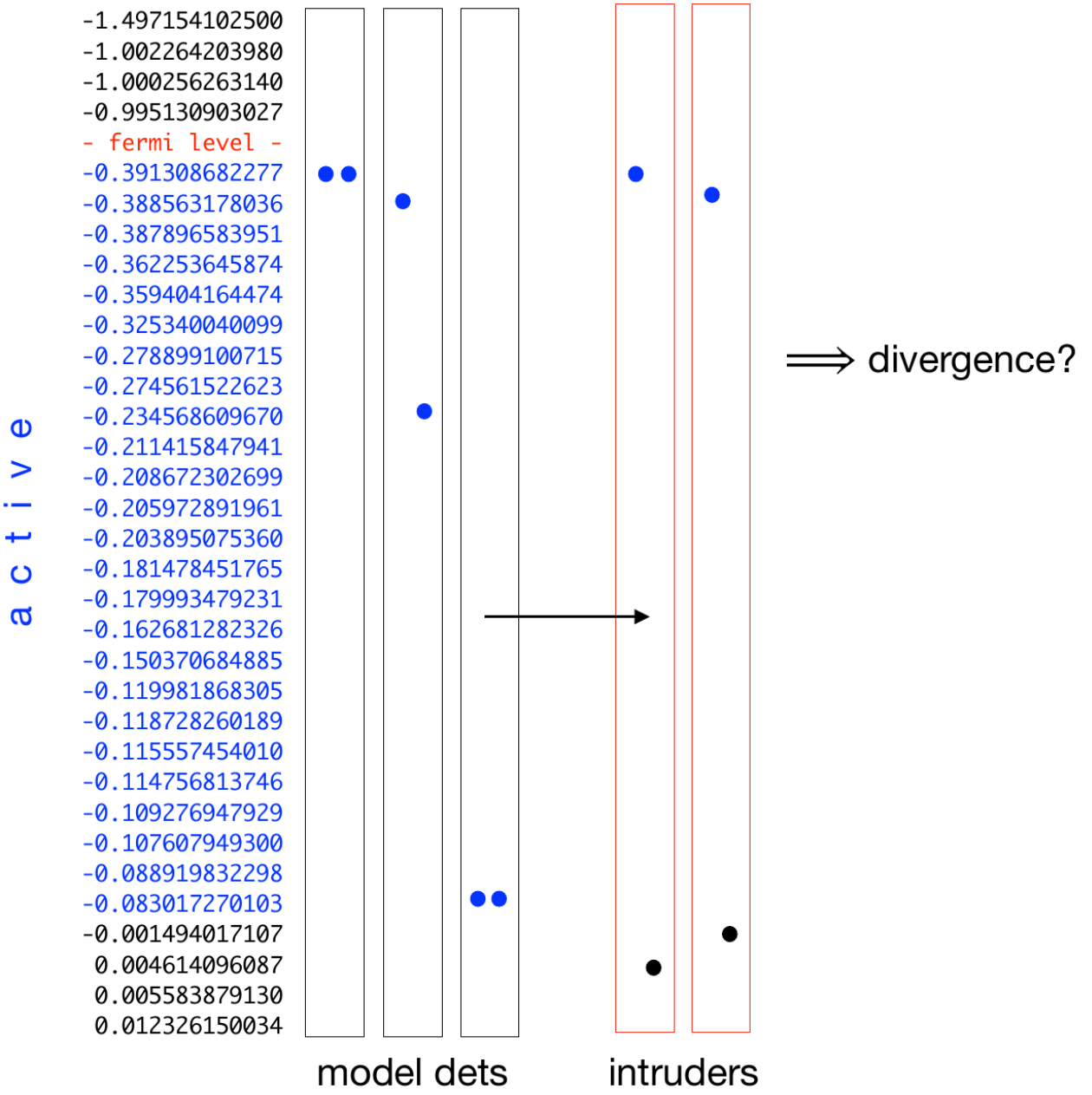
- Declaration of main model space seems to be physically clear
- Which states are desired? (for experiment, etc)
- **We should know something about target electronic states**

- Atoms: we have data from NIST
- Molecules: previous publications or **preliminary rough FS-CC calculation**

  simple dynamic shift instead of IH ?
- A construction of a model space can be an "iterative" process

LaF: LaF^{++} vacuum state

```
sector 0h2p
nactp 50
```



all active spinors are localized on La

⇓

no chance to describe charge-transfer states

LaF: LaF^{++} vacuum state

dynamic imaginary denominator shifts

```
sector 0h2p
nactp 50

shifttype realimag
shift 0h1p 3 -0.15 -0.30
shift 0h2p 3 -0.30
```

shift
-0.15(≈1/2 active zone width) × i
for **bad** single excitation denominators

shift
-0.3(≈active zone width) × i
for **bad** double excitation denominators

attenuation of shifts for
good denominators
0 - uniform shift
...
3 - rapid decrease of shifts for good denominators
...
∞ - no shifts of non-zero denominators

LaF vertical spectrum (FS RCCSD), cm^{-1}

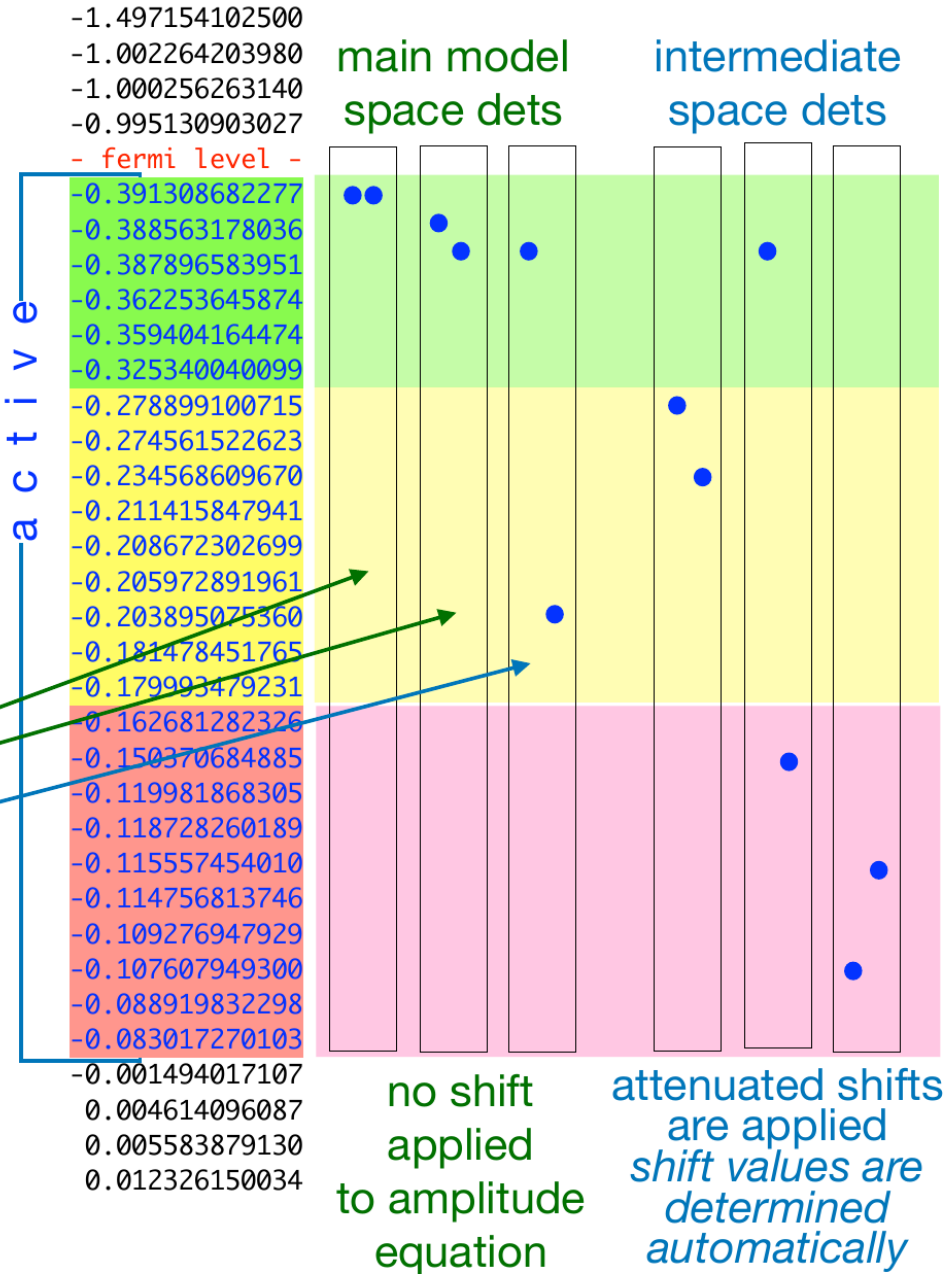
	$(0h2p)$
Ω	dynamic shift
0	0
1	1 666
2	2 032
3	2 521
2	5 866
0	7 379
0	7 420
1	7 724
2	8 223
1	9 580
0	11 105
1	11 394
2	12 096
0	12 837
3	12 892
0	12 897
1	12 909
4	13 474
4	14 080
1	14 136
0	14 224
0	14 230
2	14 346

LaF: LaF^{++} vacuum state

intermediate Hamiltonians
incomplete main model spaces

```
sector 0h2p
nactp 50
ih_imms
 sectors 0h2p
 shift_type realimag
 npower 3
 subspace energy -0.42 -0.30
 subspace energy -0.30 -0.17


 main_occ 2 0
 main_occ 1 1
end
```



Main determinants:

Intermediate determinants:

LaF vertical spectrum (FS RCCSD), cm^{-1}

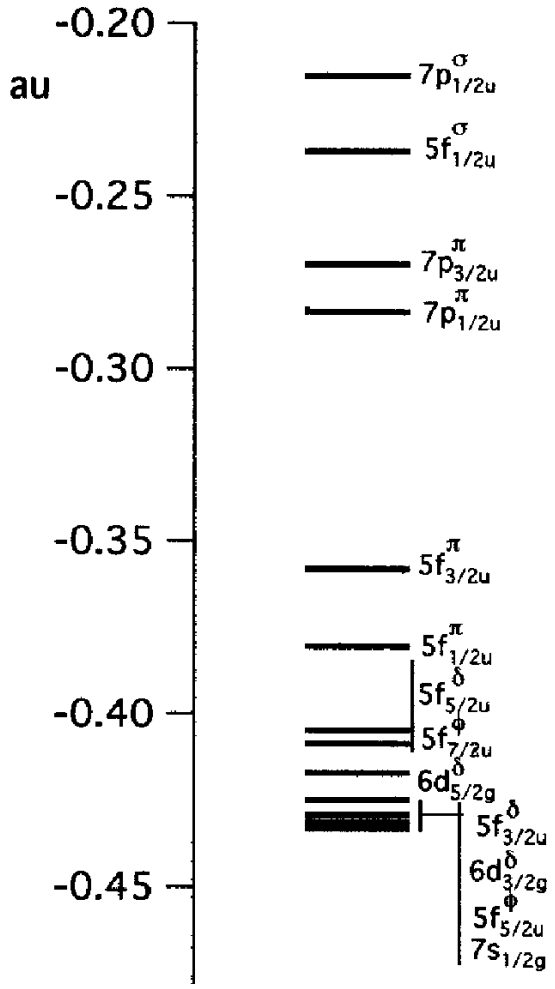
Ω	$(0h2p)$ dynamic shift	$(0h2p)$ IH IMMS	% in MMS
0	0	0	99.3
1	1 666	1 656	98.7
2	2 032	2 022	98.5
3	2 521	2 511	98.4
2	5 866	5 865	97.7
0	7 379	7 375	98.8
0	7 420	7 417	98.8
1	7 724	7 720	98.7
2	8 223	8 219	98.6
1	9 580	9 583	98.0
0	11 105	11 078	98.3
1	11 394	11 364	98.8
2	12 096	12 083	98.0
0	12 837	12 821	96.5
3	12 892	12 878	97.9
0	12 897	12 906	98.4
1	12 909	12 919	98.4
4	13 474	13 450	97.2
4	14 080	14 051	96.7
1	14 136	14 122	97.4
0	14 224	14 211	97.5
0	14 230	14 215	97.5
2	14 346	14 329	97.6

✓IH IMMS:
model vectors
are almost entirely
within the main model space

✓dynamic shift
work flawlessly

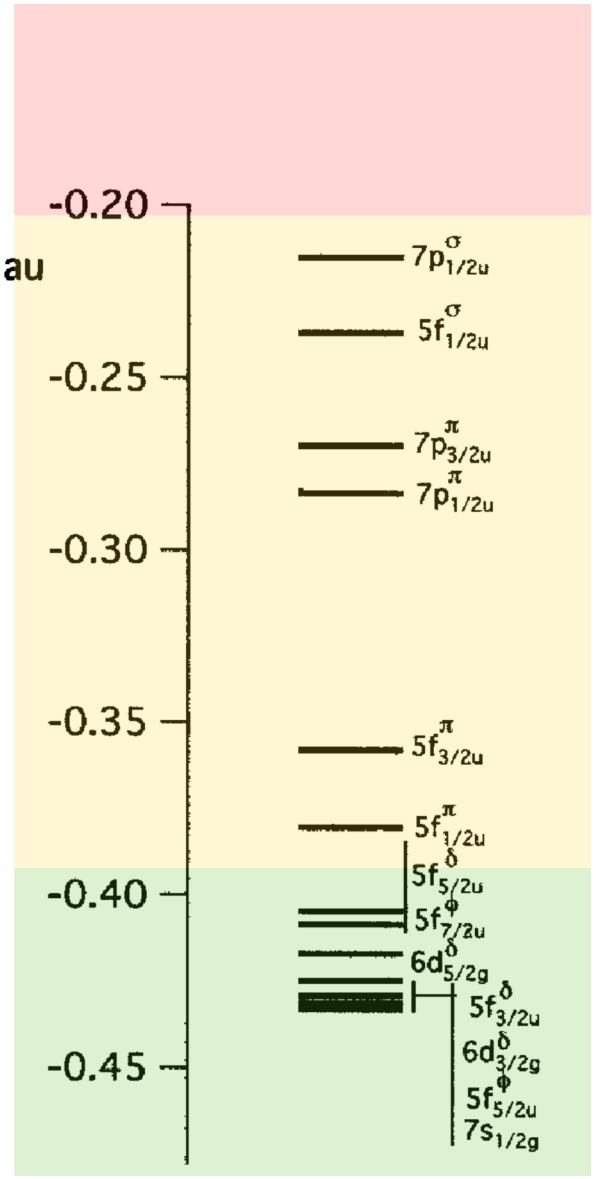
(but only when moderate
shift parameters
are sufficient)

UO_2: UO_2^{++} vacuum state



I. Infante, E. Eliav, M. J. Vilkas, Y. Ishikawa, U. Kaldor et al. A Fock space coupled cluster study on the electronic structure of the UO2, UO2+, U4+, and U5+ species Citation: J. Chem. Phys. 127, 124308 (2007). doi: **10.1063/1.2770699**

UO_2: UO_2^{++} vacuum state



n = 0

n = 0,1

n = 1, 2

```
ih_imms
  sectors 0h2p
  subspace energy -0.5 -0.4
  subspace energy -0.4 -0.2
  main_occ 2 0 0
  main_occ 1 1 0
end
```

Main determinants:

Intermediate determinants:

I. Infante, E. Eliav, M. J. Vilkas, Y. Ishikawa, U. Kaldor et al. A Fock space coupled cluster study on the electronic structure of the UO2, UO2+, U4+, and U5+ species Citation: J. Chem. Phys. 127, 124308 (2007). doi: **10.1063/1.2770699**

UO_2: UO_2^{++} vacuum state

	Level	Re(eigenvalue)	...	Rel eigv, eV	Rel eigv, cm-1	% **main**	deg	symmetry
@	1	-0.7935817645	...	0.0000000000	0.000000	**99.8**	2	2u+ 2u-
@	2	-0.7918703290	...	0.0465705333	375.616683	**99.8**	2	3u+ 3u-
@	3	-0.7839364467	...	0.2624624692	2116.902577	**99.8**	2	1u+ 1u-
@	4	-0.7822710847	...	0.3077792766	2482.407278	**99.7**	2	2u+ 2u-
@	5	-0.7662449872	...	0.7438716052	5999.729115	**99.8**	2	4u+ 4u-
@	6	-0.7652923132	...	0.7697951849	6208.816886	**98.3**	2	4u+ 4u-
@	7	-0.7645564697	...	0.7898185072	6370.315872	**99.8**	2	3u+ 3u-
@	8	-0.7619746163	...	0.8600743186	6936.967206	**99.7**	2	3u+ 3u-
@	9	-0.7607512624	...	0.8933634719	7205.462335	**99.7**	2	2u+ 2u-
.	. .		...					
@	114	-0.6161629900	-...	4.8278108008	38938.920135	**84.0**	2	2g+ 2g-
@	115	-0.6149980723	...	4.8595098256	39194.590012	**83.5**	2	2g+ 2g-
@	116	-0.6149815886	-...	4.8599583699	39198.207766	**96.5**	1	0u
@	117	-0.6146890109	...	4.8679198134	39262.421139	**99.4**	2	4u+ 4u-
@	118	-0.6144714356	...	4.8738403400	39310.173406	**95.1**	1	0g
@	119	-0.6141258027	...	4.8832454916	39386.031070	**72.1**	2	2g+ 2g-
@	120	-0.6140329431	-...	4.8857723285	39406.411384	**94.6**	1	0u
@	121	-0.6137103032	...	4.8945518089	39477.222669	**0.4**	2	4u+ 4u-
@	122	-0.6134537458	...	4.9015330908	39533.530504	**71.8**	2	4g+ 4g-
@	123	-0.6132838846	...	4.9061552479	39570.810716	**33.1**	2	1u+ 1u-
@	124	-0.6132493686	...	4.9070944765	39578.386105	**99.2**	2	3u+ 3u-
@	125	-0.6111057507	-...	4.9654252932	40048.855870	**6.2**	1	0u
@	126	-0.6106633742	...	4.9774629698	40145.946279	**8.3**	1	0u

```
Max T{0h0p}_1 amplitude (t{00}_ia) [ 382 -> 389 ] = 0.11717695
Max T{0h0p}_2 amplitude (t{00}_ijab) [ 573 382 -> 580 389 ] = 0.03702607
Max T{0h1p}_1 amplitude (t{01}_ia) [ 587 -> 597 ] = 0.11116927
Max T{0h1p}_2 amplitude (t{01}_ijab) [ 385 382 -> 389 385 ] = 0.06538470
Max T{0h2p}_2 amplitude (t{02}_ijab) [ 195 19 -> 195 25 ] = 0.20661232
```

ThO molecule

- sector $(0h2p)$ - closed-shell ThO^{2+} + $2e$
- MS: CAS $2e$ / 48 lowest-energy virtual spinors of ThO^{2+} (dim **1128**)
- Main MS: CAS $2e$ / 12 spinors ("7s+6d Th") + all dets with H_0-energies in the same range (dim **234**)

max amplitudes

	$T^{(0h0p)}$	$T^{(0h1p)}$	$T^{(0h2p)}$
S	0.038	0.148	
D	0.027	0.046	0.175

Ω	T, cm^{-1}	% in MMS
0	0	98.0
1	5659	98.2
2	6455	98.0
3	7932	98.1
0	10732	98.1
0	11097	97.9
1	11700	97.8
2	12086	95.2
2	14021	97.3
1	15223	97.2
0	16341	98.1
1	16692	97.6
0	17061	97.0
2	18600	97.6
0	19206	95.7
0	19598	98.0
1	19775	95.6
0	19836	97.4
1	20175	96.9
3	20855	97.6

References

- A. Zaitsevskii, N. S. Mosyagin, A. V. Stolyarov, E. Eliav

  Approximate relativistic coupled-cluster calculations on heavy alkali-metal diatomics: Application to the spin-orbit-coupled $A^1\Sigma^+$ and $b^3\Pi$ states of RbCs and Cs_2
  Phys. Rev. A, 96(2), 022516 (2017)

- A. Zaitsevskii, N. S. Mosyagin, A. V. Oleynichenko, E. Eliav

  Generalized relativistic small-core pseudopotentials accounting for quantum electrodynamic effects: construction and pilot applications
  arXiv:2208.12296 (physics.atom-ph)

- http://qchem.pnpi.spb.ru/recp
- http://qchem.pnpi.spb.ru/expt
- https://github.com/aoleynichenko/EXP-T