the use of non-relativistic symmetries in relativistic electronic structure calculations

relativistic wavefunctions symmetry:

- ray irreps of symmetry group $\mathcal{G}$ or
- vector irreps of double group $\overline{\mathcal{G}}$

nonrelativistic limit: spin-free H
$\Longrightarrow$ *higher symmetry* $\mathcal{G} \times SU(2)$

"two-component" method
one-electron basis: spinorbital=orbital×spin
many-electron basis: Slater determinants

	non-relativistic	*relativistic*
dets with diff S_z	no interaction	interact
dets with diff $\mathcal{G}$ symmetry	no interaction	interact
full symmetry adaptation ($\longrightarrow$ CSF)	:(all) $\mathcal{G}$ irrep spin values	:only bosonic or only fermionic $\overline{\mathcal{G}}$ irreps
complex arithmetics	normally avoidable	unavoidable at least for some $\overline{\mathcal{G}}$

$\Longrightarrow$ goal: to combine the use of non-relativistic symmetries at computational bottleneck with

- applicability to excited states
- correct elecronic structure description for wide ranges of geometries including avoided crossing regions
- correct description of interferences (correlations) / (non-scalar relativistic effects), e.g.
  - correlation contraction $\rightarrow$ + SO splitting
  - spatial contraction / expansion of SO-stabilized / destabilized component $\rightarrow$ different correlation effects etc
- applicability to heavy/hyperheavy element compounds
  typical SO splittings $\geq$ typical SO-free term separations

step #0: separation of the scalar part of relativistic Hamiltonian

$$H = \underset{\substack{\mathcal{G}\times SO(2)\\ symmetry}}{h} + \underset{\substack{\overline{\mathcal{G}}\\ symmetry}}{W}$$

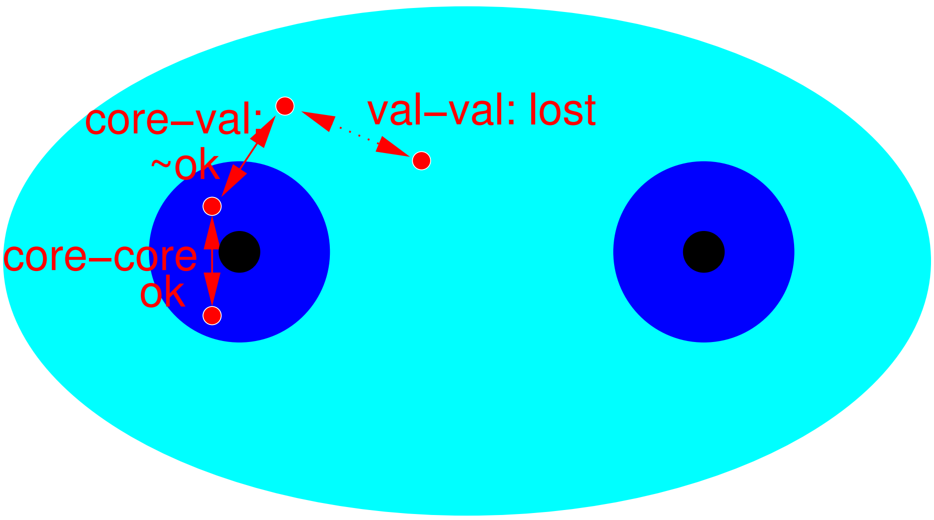
well defined for numerous types of H
(e.g. for Dirac–Coulomb or Dirac–Breit Hamiltonians)

suitable model: relativistic effective core potentials

$$H = \sum_{i}^{val\ \ el} (-\Delta_i/2 + U(i)) + \sum_{i>j}^{val\ \ el} \frac{1}{r_{ij}}$$

$$U = \sum_{\gamma}^{atoms} \sum_{l_\gamma j_\gamma} u_\gamma^{l_\gamma, j_\gamma}$$

- $u_\gamma \longleftarrow$ four-component (fully relativistic) atomic calculations
- implicitly incorporates the bulk of effects appearing as *two-particle SO interactions* in all-electron two-component theories



- more stable numerically than all-electron two-component theories

separation

$$U(i) = \underset{\substack{spin- \\ averaged}}{U^{Sc}(i)} + \underset{\substack{spin- \\ dependent}}{U^{SO}(i)}$$

$$H = \underset{\substack{scalar \\ relativistic}}{h} + \underset{\substack{spin- \\ orbit}}{W}$$

$$\underset{\substack{symmetry \\ 1\ \&\ 2-el}}{\mathcal{G} \times SO(2)} \qquad \underset{\substack{symmetry \\ 1-el}}{\overline{\mathcal{G}}}$$

General approach to the analysis:

model space $\mathcal{L}_P$ projected by P $(Q = 1 - P)$

$$h = h_0 + v \quad (h_0 P = P h_0), \qquad H = h_0 + v + W$$

$\Longrightarrow$ double perturbation theory for effective Hamiltonian acting upon $\mathcal{L}_P$

$$\begin{aligned}
H_{eff} &= P h_0 P + PvP + PWP && 0{+}1^{st}\ ord\ (PHP) \\
&+ PvG\,[v] && 2^{nd}\ ord \\
&+ PvG\,[W] + PWG\,[v] && -\text{''}- \\
&+ PWG\,[W] && -\text{''}- \\
&+ PvG\,[vG\,[v]] - PvG\,[G\,[v]\,v] && 3^{rd}\ ord \\
&+ PvG\,[vG\,[W]] - PvG\,[G\,[v]\,W] && -\text{''}- \\
&+ \ldots
\end{aligned}$$

$G\,[X] = G\,[QXP]$ — unperturbed resolvent

interaction of spin-scalar states

(*Ch. Teichteil; A.Alekseyev ...*)

$$h\psi_m = E_m\psi_m$$

$\mathcal{L}_P$ spanned by few lowest (quasi)degenerate solutions: $P = \sum_m |\psi_m\rangle\langle\psi_m|$

Lowest order H_{eff}

$$H_{eff} = PHP = \sum_m |\psi_m\rangle E_m \langle\psi_m| + PWP$$

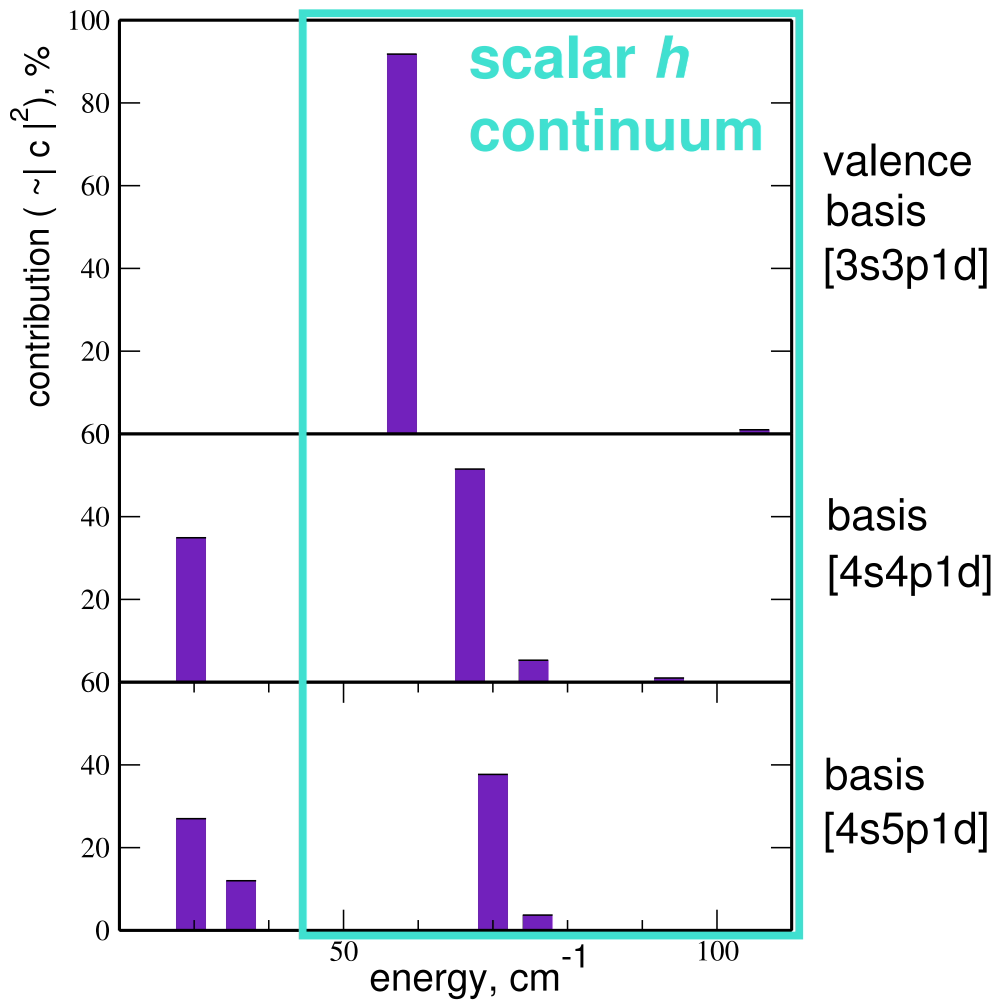
nearly all calculations are performed in NR symmetry

$$PvQ = 0, \quad G[v] = 0$$

$$\begin{array}{lll} H_{eff} & = & Ph_0P + PvP + PWP \quad 0+1^{st}\, ord\, (PHP) \\ & + & \sout{PvG[v]} \qquad 2^{nd}\, ord \\ & + & \sout{PvG[W] + PWG[v]} \qquad -''- \\ & + & PWG[W] \qquad -''- \\ & + & \ldots \end{array}$$

$\Longrightarrow$ no 2^{nd} order terms proportional to v^2 or vW
$\Longrightarrow$ easily extendable to 2-body non-scalar Hamiltonians
$\Longrightarrow$ works perfectly for rather weak SO interactions

Strong SO case: extend the $\{\psi_m\}$ set ???
Tl atom, $\Delta E(^2P_{3/2} - ^2P_{1/2})$, $\mathcal{L}_P = span\{(1)^3P\}$
ca. 800 cm^{-1} of 7800 cm^{-1} lost

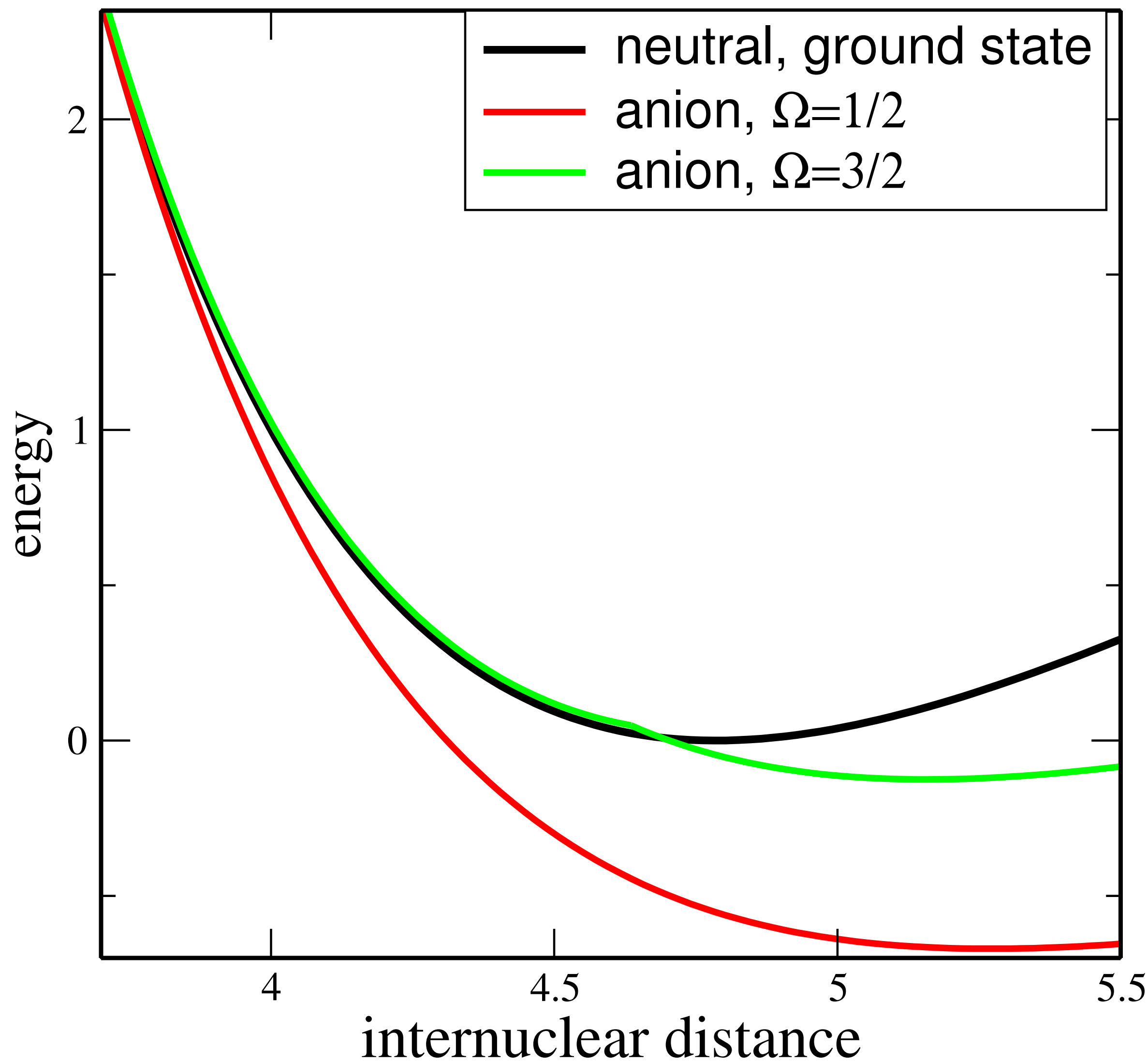


Contributions of higher scalar problem eigensolutions to full CI ground state function of Tl

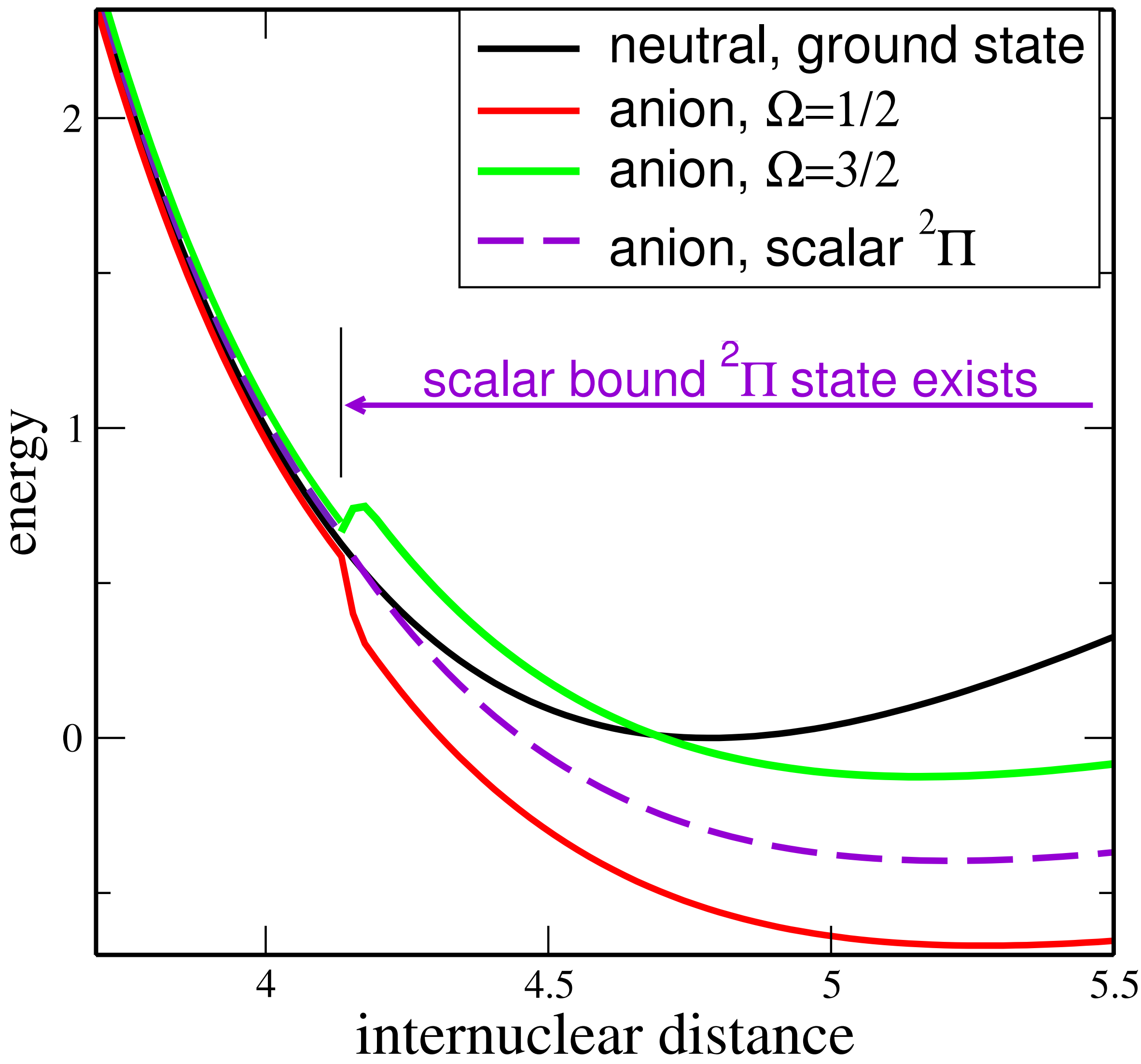
$\Longrightarrow$ "scalar eigenstates" of primary importance are embedded into the continuum
$\Longrightarrow$ flexible basis set $\longrightarrow$ we shall never reach these states

electron attachment to a closed-shell-like polar diatomic

anionic states (SO-split components of $^2\Pi$) exist at large R,
neutral system + scattered electron at small R



interacting spin-scalar states approximation



(-) spurious "bound 3/2 state" above threshold

(-) splitting disappears when the scalar state becomes scattered

(-) incorret location of lowest state crossing

making use of the one-body nature of W

model space: reference configurations (determinants) + single excitations

basic approximation:

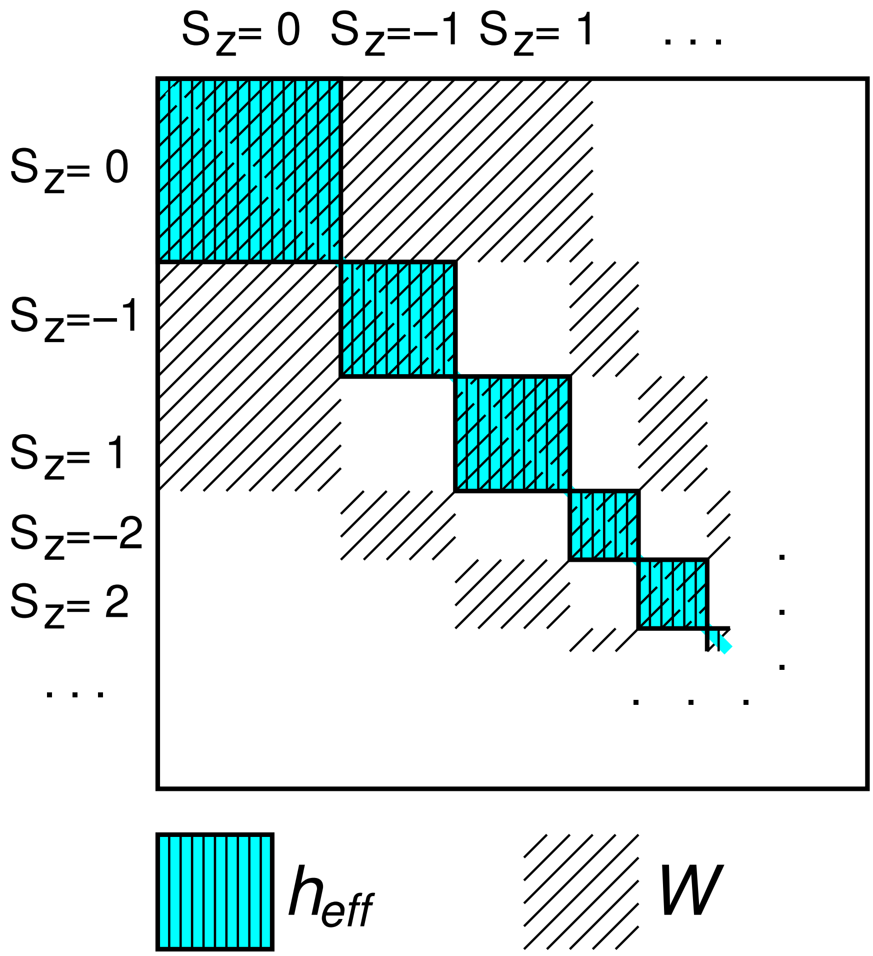
$$H \Longrightarrow h + PWP$$

$$\begin{aligned} H_{eff} &= Ph_0P + PvP + PWP && 0+1^{st}\ ord\ (PHP) \\ &+ PvG\,[v] && 2^{nd}\ ord \\ &+ \cancel{PvG\,[W] + PWG\,[v]} && -''- \\ &+ \cancel{PWG\,[W]} && -''- \\ &+ PvG\,[vG\,[v]] - PvG\,[G\,[v]\,v] && 3^{rd}\ ord \\ &+ \cancel{PvG\,[vG\,[W]]} - \boxed{PvG\,[G\,[v]\,W]} && -''- \\ &+ \ldots \end{aligned}$$

$$H_{eff} = h_{eff} + PWP - PvG\,[G\,[v]\,W] + \ldots$$

(3^{rd} and higher orders)

Structure of the $H_{eff} = h_{eff} + PWP$ matrix in the basis of Slater determinants



- h_{eff} is evaluated within the non-relativistic symmetry; each block consists of subblock if $\mathcal{G}$ is non-trivial

- only h_{eff} block with $S_z = 0$ should be computed, the remainder can be obtained by the action of $\widehat{S}$

diagonalization *after* incorporating correlations and SO

$\longrightarrow$ correlation/SO interferences o.k.

problem:

wide spread of h_{eff} spectrum $\Longrightarrow$ few hopes to construst a good true (state-universal) h_{eff} because of *intruder states*

solution (?): state-selective (intermediate) h_{eff}

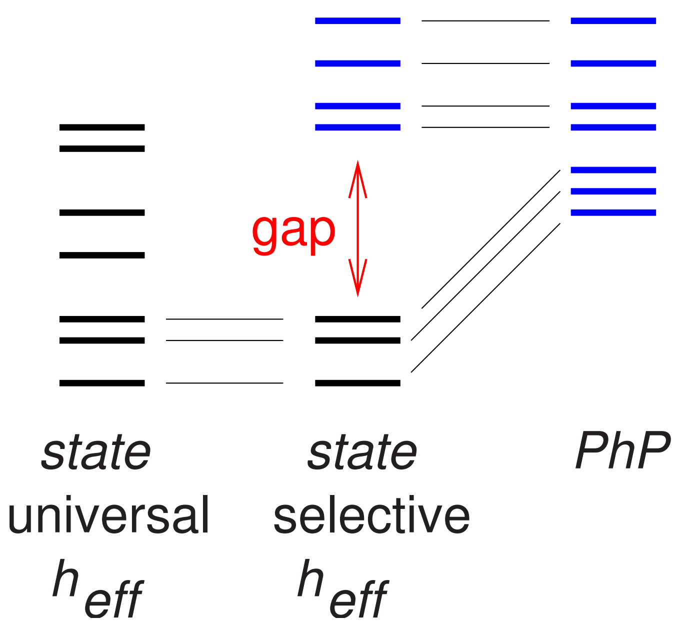
but the PT argumentation above is based on the state-universality ...

good but suspicious idea: "partial dressing"

naive version (ch.teichteil *et al.*, **epciso-2000**)

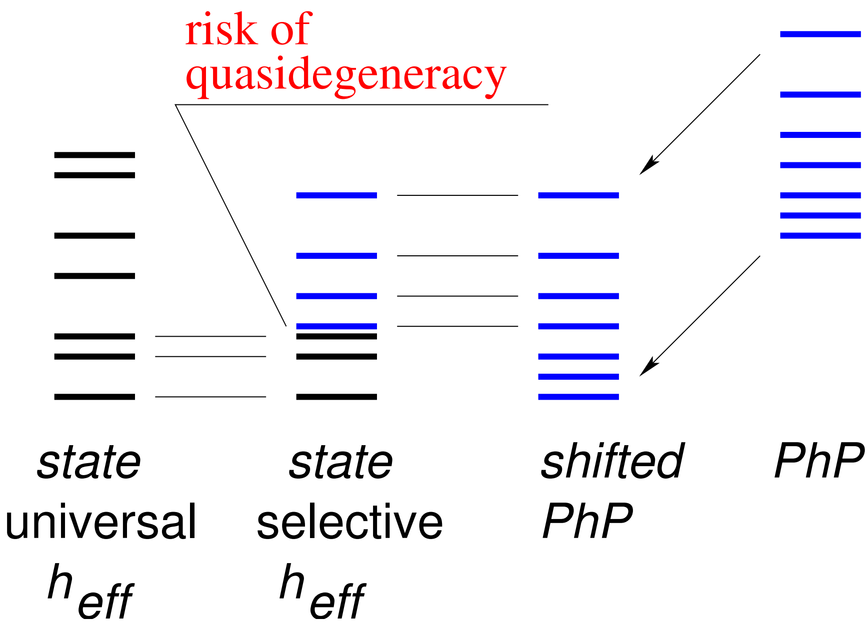
$$PhP\phi_m = e_m\phi_m \qquad h\psi_m = E_m\psi_m$$

$$h_{eff} \approx PhP + \sum_m^{few\ lowest} |\phi_m\rangle(E_m - e_m)\langle\phi_m|$$



$H_{eff} = h_{eff} + PWP$: the gap almost switches off "main" — "intermediate" SO interactions improved version (f.rakowitz, l.seijo *et al.*, **sfss**)

$$h_{eff} \approx PhP + (E_{gr} - e_{gr})P + \sum_{m}^{few\ lowest} |\phi_m\rangle(E_m - E_{gr} - e_m + e_{gr})\langle\phi_m|$$



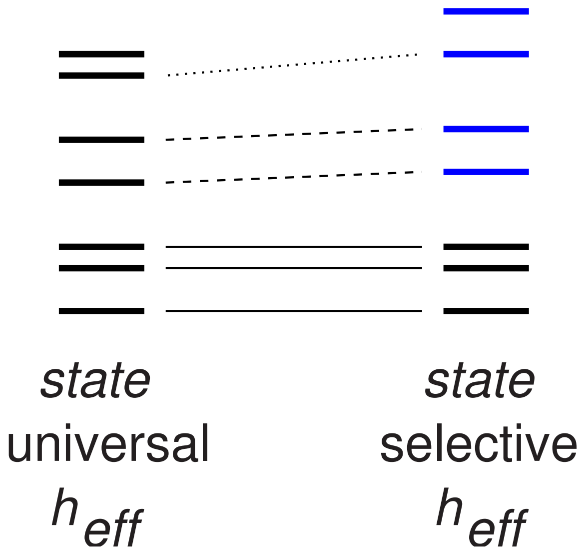
dangerous gap replaced by the risk of dangerous quasidegeneracies

in both cases only eigenvalues are o.k.
eigenvectors are those of PhP

- ≈ok for atoms
- excited states of molecules: can ruin because of "main" — "intermediate" avoided crossing ...

$\Longrightarrow$ adaptation to the case of strong correlation interference: $\phi_m \to \psi_m$ (?)

solution (!): “dressed” state-selective h_{eff}
resembling state-universal h_{eff}



at least low-lying ”intermediate” levels quite close to “exact” ones

example: Feshbach-Löwdin Hamiltonian

$$h_{eff} = PhP + Ph(Q(E-H)Q)^{-1}HP$$

(+) E-dependence is moderate
$\longrightarrow$ PT argumentation holds
$\longrightarrow$ quasi-equal-footing treatment of the states quasidegenerate with the 'main'

(−) one "main" level. multistate generalization is not easy to treat (zaitsevskii dement'ev 1990)

(−) well suited only for Brillouin–Wigner PT construction

alternative solutions

- state-selective "dressed" h_{eff} by model-space shifts (zaitsevskii heully 1992)$\longrightarrow$ Rayleigh – Schrödinger expansions
- state-selective "dressed" h_{eff} by Rayleigh – Schrödinger – like multipartitioning PT (zaitsevskii malrieu 1997) $\longrightarrow$ Rayleigh–Schródinger expansions, accurate second-order results

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