In memory of Prof. Ian Philip Grant

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Gediminas Gaigalas

Second-Order Rayleigh-Schrödinger Perturbation Theory for the GRASP2018 Package:

Three-particle Feynman Diagrams Contributions

Contents:

- RSMBPT research status up to 2025
- Relativistic second-order effective Hamiltonian in irreducible tensorial form for three-particle Feynman diagrams contributions to valence-valence correlations
- Relativistic second-order effective Hamiltonian in irreducible tensorial form for three-particle Feynman diagrams contributions to core-valence correlations
- Calculations
- Summary and conclusions

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Computational Atomic Structure Group

Vilnius University

Laima Kitovienė,
Gediminas Gaigalas,
Pavel Rynkun

Motivation for the approach

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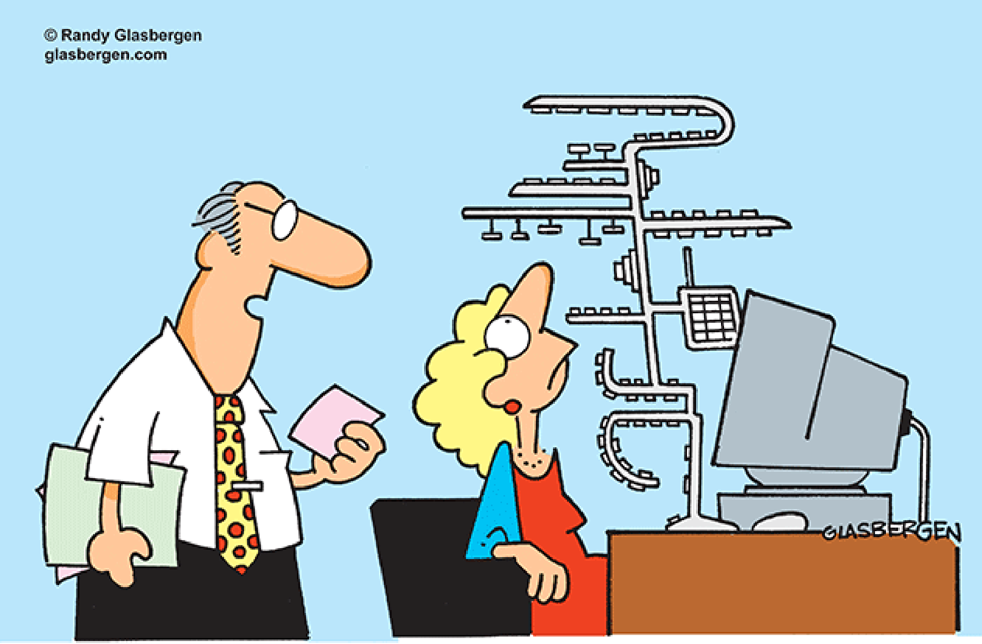
The same as in the talks:

- Ran Si “GRASP: Recent Code Developments and Applications”
- Shaofan Shi “GRASP: Basis Selection by Machine Learning”
- Sijie Wu "A partitioned correlation function interaction approach in GRASP"
- Per Jönsson “On the use of Natural Orbitals in GRASP Calculations”



“It’s an ergonomic keyboard. Once you learn how to use it, it will increase your speed by six percent!”

How to achieve higher data accuracy with GRASP, with fewer computing resources.

- Gediminas Gaigalas „Second-Order Rayleigh-Schrödinger Perturbation Theory for the GRASP2018 Package “

RSMBPT research st… up to 2025

The following correlations was not included in RSMBPT:

- **Valence correlations**

$$(n_m\ell_m)\, j_m^{w_m} \rightarrow (n_m\ell_m)\, j_m^{w_m-1}\, (n_r\ell_r)\, j_r$$

- **Core correlations**

$$(n_a\ell_a)\, j_a^{2j_a+1}\, (n_m\ell_m)\, j_m^{w_m} \rightarrow (n_a\ell_a)\, j_a^{2j_a}\, (n_m\ell_m)$$

- **Valence-valence correlations**

$$(n_a\ell_m)\, j_m^{w_m}\, (n_n\ell_n)\, j_n^{w_n} \rightarrow (n_m\ell_m)\, j_m^{w_m+1}\, (n_n\ell_n)\, j_n^{w_n-}$$

$$(n_a\ell_m)\, j_m^{w_m}\, (n_n\ell_n)\, j_n^{w_n}\, (n_p\ell_p)\, j_p^{w_p} \rightarrow (n_m\ell_m)\, j_m^{w_m+1}\, (n_n\ell_n)\, j$$

- **Core-valence correlations**

$$(n_a\ell_a)\, j_a^{2j_a+1}\, (n_m\ell_m)\, j_m^{w_m}\, (n_n\ell_n)\, j_n^{w_n} \rightarrow (n_a\ell_a)\, j_a^{2j_a}\, (n_m\ell_m)\, j$$

$$(n_a\ell_a)\, j_a^{2j_a+1}\, (n_m\ell_m)\, j_m^{w_m}\, (n_n\ell_n)\, j_n^{w_n}\, (n_p\ell_p)\, j_p^{w_p} \rightarrow (n_a\ell_a)\, j_a^{2j}$$

Relativistic second-order effective Hamiltonian in irreducible tensorial form for valence-valence correlations

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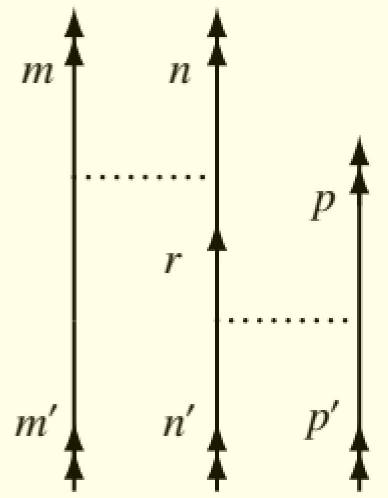

VV_3

A Feynman diagram that is independent of the potential at which the wave functions were obtained.

The third type of valence-valence correlations

$$(n_m\ell_m)\ j_m^{w_m}\ (n_n\ell_n)\ j_n^{w_n} \rightarrow (n_m\ell_m)\ j_m^{w_m+1}\ (n_n\ell_n)\ j_n^{w_n-2}\ (n_r\ell_r)\ j_r,$$

where all lines with the double arrow of diagram VV_3 is renamed in the following way: $m' = p \equiv m$ and $m = n = n' = p' \equiv n$.

RSMBPT research status up to 2025

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The following correlations was not included in RSMBPT:

- **Valence correlations**

$$(n_m\ell_m)\ j_m^{w_m} \to (n_m\ell_m)\ j_m^{w_m-1}\ (n_r\ell_r)\ j_r$$

- **Core correlations**

$$(n_a\ell_a)\ j_a^{2j_a+1}\ (n_m\ell_m)\ j_m^{w_m} \to (n_a\ell_a)\ j_a^{2j_a}\ (n_m\ell_m)\ j_m^{w_m+1}$$

- **Valence-valence correlations**

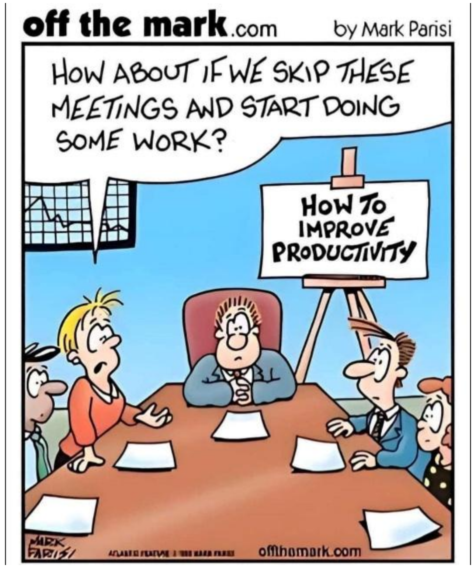
✓ $$(n_a\ell_m)\ j_m^{w_m}\ (n_n\ell_n)\ j_n^{w_n} \to (n_m\ell_m)\ j_m^{w_m+1}\ (n_n\ell_n)\ j_n^{w_n-2}\ (n_r\ell_r)\ j_r$$

✓ $$(n_a\ell_m)\ j_m^{w_m}\ (n_n\ell_n)\ j_n^{w_n}\ (n_p\ell_p)\ j_p^{w_p} \to (n_m\ell_m)\ j_m^{w_m+1}\ (n_n\ell_n)\ j_n^{w_n-1}\ (n_p\ell_p)\ j_p^{w_p-1}\ (n_r\ell_r)\ j_r$$

- **Core-valence correlations**

$$(n_a\ell_a)\ j_a^{2j_a+1}\ (n_m\ell_m)\ j_m^{w_m}\ (n_n\ell_n)\ j_n^{w_n} \to (n_a\ell_a)\ j_a^{2j_a}\ (n_m\ell_m)\ j_m^{w_m-1}\ (n_n\ell_n)\ j_n^{w_n+2}$$

$$(n_a\ell_a)\ j_a^{2j_a+1}\ (n_m\ell_m)\ j_m^{w_m}\ (n_n\ell_n)\ j_n^{w_n}\ (n_p\ell_p)\ j_p^{w_p} \to (n_a\ell_a)\ j_a^{2j_a}\ (n_m\ell_m)\ j_m^{w_m-1}\ (n_n\ell_n)\ j_n^{w_n+1}\ (n_p\ell_p)\ j_p^{w_p+1}$$



Relativistic second-order effective Hamiltonian in irreducible tensorial form for valence-valence correlations

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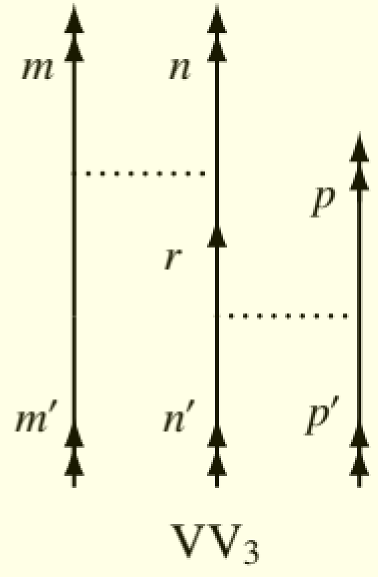

A Feynman diagram that is independent of the potential at which the wave functions were obtained.

The fourth type of valence-valence correlations

$$(n_m\ell_m)\, j_m^{w_m}\, (n_n\ell_n)\, j_n^{w_n}\, (n_p\ell_p)\, j_p^{w_p} \rightarrow (n_m\ell_m)\, j_m^{w_m+1}\, (n_n\ell_n)\, j_n^{w_n-1}\, (n_p\ell_p)\, j_p^{w_p-1}\, (n_r\ell_r)\, j_r.$$

where all lines with the double arrow of diagram VV_3 is renamed in the following way: $m = m' = n = n' = p' \equiv$???.

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Relativistic second-order effective Hamiltonian in irreducible tensorial form for valence-valence correlations

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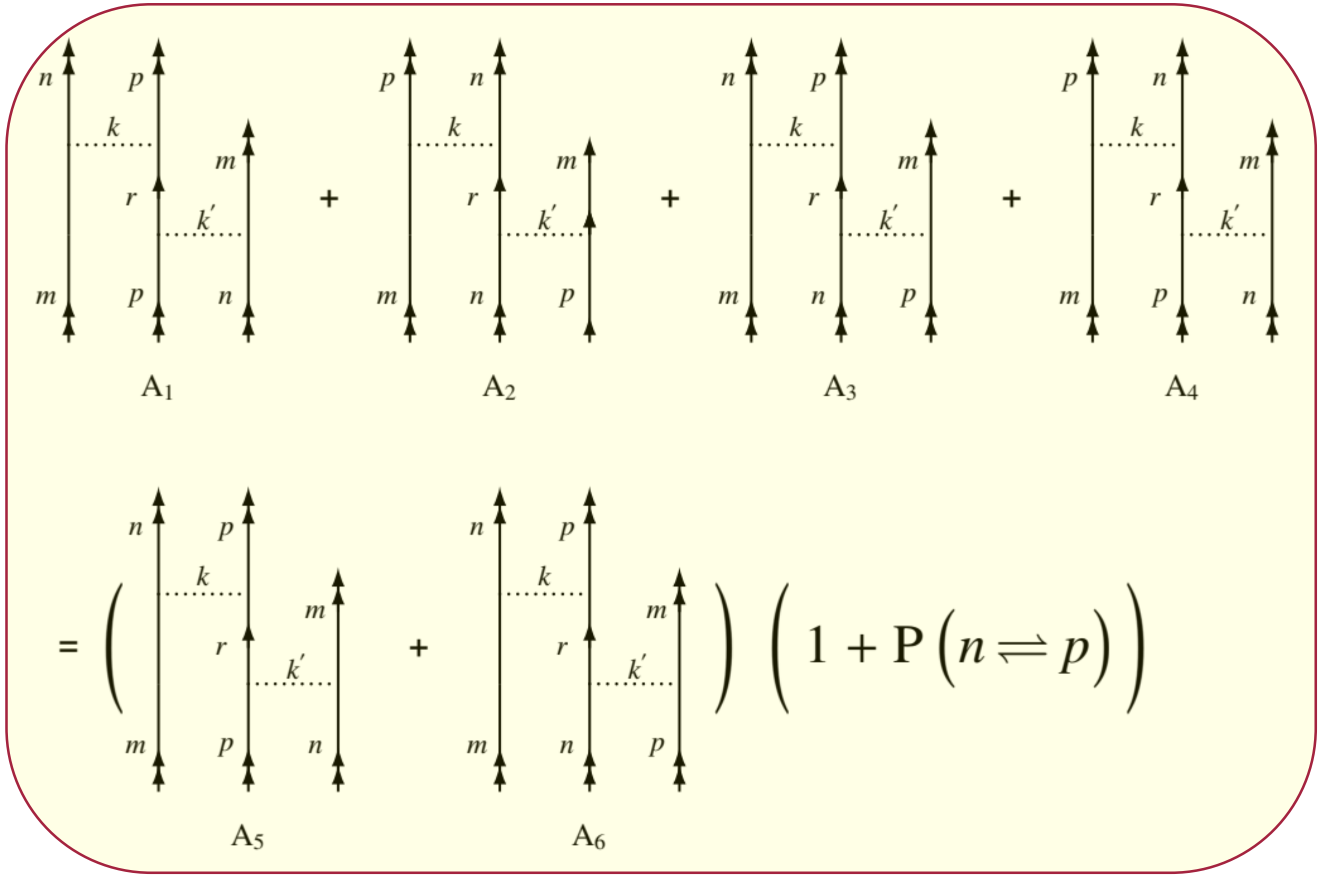

The VV Feynman diagrams of the second-order effective Hamiltonian, expressing the fourth type of valence-valence correlations

$$(n_m\ell_m)\, j_m^{w_m}\, (n_n\ell_n)\, j_n^{w_n}\, (n_p\ell_p)\, j_p^{w_p} \\ \rightarrow (n_m\ell_m)\, j_m^{w_m+1}\, (n_n\ell_n)\, j_n^{w_n-1}\, (n_p\ell_p)\, j_p^{w_p-1}\, (n_r\ell_r)\, j_r.$$

Relativistic second-order effective Hamiltonian in irreducible tensorial form for VV correlations

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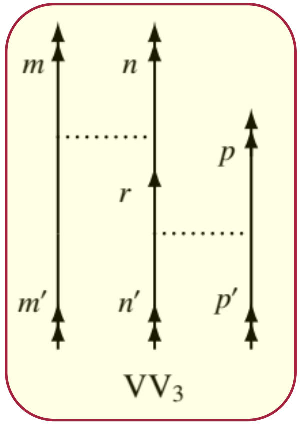
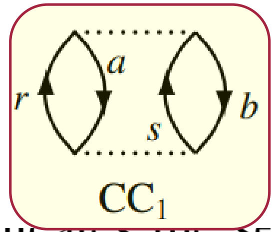
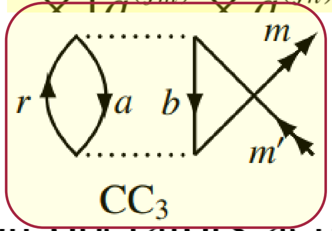


The spin-angular part of the third type of valence-valence correlations

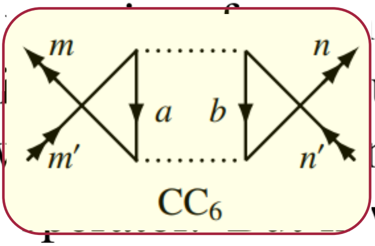
ov structure

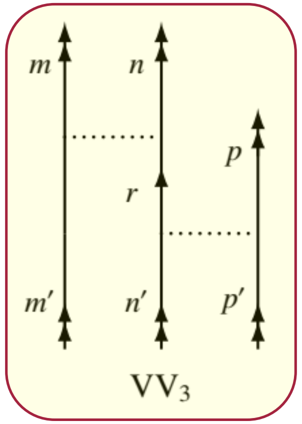


$a_3^{(j}$ … $\times [a^{(j_m)} \times \tilde{a}^{(j_n)}]^{(k')}]^{(0)}$, (1)



indicates the se … of the second quantization op-
he tensorial stru … d quantization
ond quantization operators acti … ubshells. This
e numbers 1 and 2 and a pair … mbers 5 and 6.
of the spin-angular part of this … we replace the





$a_3^{(j}$ … $[a_1^{(j_n)} \times \tilde{a}_6^{(j_n)}]^{(J_2)}]^{(J_1)}]^{(0)}$ (2)

ul … the spin-angular approach by Gaigalas (1996)
ic … r this type of correlations. **We also point out**
ri … n, including the quasispin symmetry, in the

Relativistic second-order effective Hamiltonian in irreducible tensorial form for VV correlations

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In this case, the diagram VV_3 has the following tensorial structure

$$\left[\left[[a_1^{(j_n)}\times\tilde{a}_2^{(j_m)}]^{(k)}\times[a_3^{(j_n)}\times\tilde{a}_4^{(j_n)}]^{(x)}\right]^{(k')}\times[a_5^{(j_m)}\times\tilde{a}_6^{(j_n)}]^{(k')}\right]^{(0)}, \tag{1}$$

The first tensorial product $[\tilde{a}_2^{(j_m)}\times a_5^{(j_m)}]^{(J_1)}$ is the one to which we want to bring the algebraic expression, i.e. (1), and the second one $\left[[a_3^{(j_n)}\times\tilde{a}_4^{(j_n)}]^{(x)}\times[a_1^{(j_n)}\times\tilde{a}_6^{(j_n)}]^{(J_2)}\right]^{(J_1)}$ consists of only two pairs of operators for the second quantization acting to the same subshell. These two sets of tensorial operators are obtained by applying the operator commutation rule to operators $a_1^{(j_n)}$ and $\tilde{a}_4^{(j_n)}$. This gives the following expression

$$\begin{aligned}&\left[\left[[a^{(j_n)}\times\tilde{a}^{(j_m)}]^{(k)}\times[a^{(j_n)}\times\tilde{a}^{(j_n)}]^{(x)}\right]^{(k')}\times[a^{(j_m)}\times\tilde{a}^{(j_n)}]^{(k')}\right]^{(0)}\\&=\sum_J B_1\left[[\tilde{a}^{(j_m)}\times a^{(j_m)}]^{(J)}\times[a^{(j_n)}\times\tilde{a}^{(j_n)}]^{(J)}\right]^{(0)}\\&+\sum_{J_1,J_2}B_2\left[[\tilde{a}^{(j_m)}\times a^{(j_m)}]^{(J_1)}\times\left[[a^{(j_n)}\times\tilde{a}^{(j_n)}]^{(x)}\times[a^{(j_n)}\times\tilde{a}^{(j_n)}]^{(J_2)}\right]^{(J_1)}\right]^{(0)}.\end{aligned} \tag{2}$$

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Relativistic second-order effective Hamiltonian in irreducible tensorial form for VV correlations

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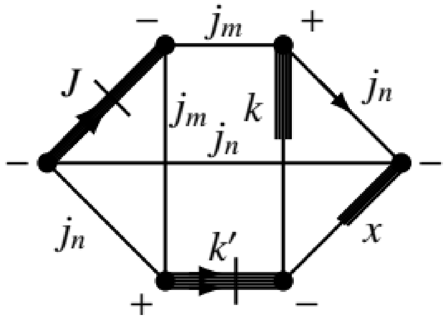
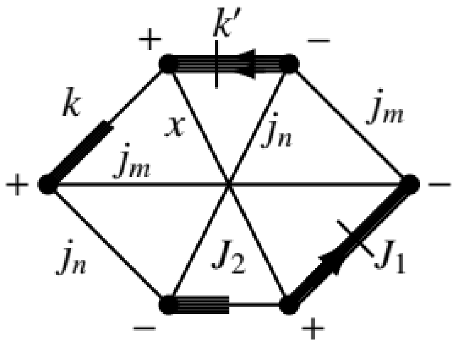


B_1



B_2

$$\left[\left[[a^{(j_n)}\times\tilde{a}^{(j_m)}]^{(k)}\times[a^{(j_n)}\times\tilde{a}^{(j_n)}]^{(x)}\right]^{(k')}\times[a^{(j_m)}\times\tilde{a}^{(j_n)}]^{(k')}\right]^{(0)}$$

$$=\sum_{J}B_1\left[[\tilde{a}^{(j_m)}\times a^{(j_m)}]^{(J)}\times[a^{(j_n)}\times\tilde{a}^{(j_n)}]^{(J)}\right]^{(0)}$$

$$+\sum_{J_1,J_2}B_2\left[[\tilde{a}^{(j_m)}\times a^{(j_m)}]^{(J_1)}\times\left[[a^{(j_n)}\times\tilde{a}^{(j_n)}]^{(x)}\times[a^{(j_n)}\times\tilde{a}^{(j_n)}]^{(J_2)}\right]^{(J_1)}\right]^{(0)}. \qquad (1)$$

The coefficients B_1 and B_2 in the expression (1) are the easiest to represent and their algebraic expressions are the easiest to obtain by using the generalized graphical method of the angular momentum theory.

Relativistic second-order effective Hamiltonian in irreducible tensorial form for VV correlations

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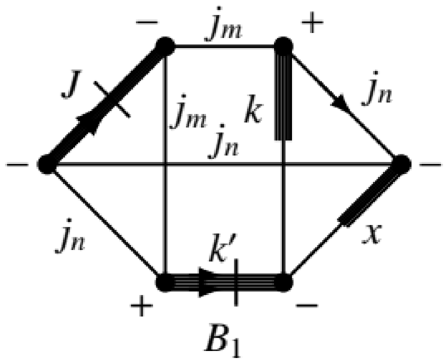

$$\propto \sum_{m_{j_m}, m_{j_{m'}}} \sum_{m_{j_n}, m_{j_{n'}}, m_{j_{n''}}} \sum_{m_k, m_{k'}, m_x} \sum_{m_J} (-1)^{\cdots} [\dots] \sqrt{[\dots]}$$

$$\begin{pmatrix} j_m & j_m & J \\ \pm m_{j_m} & \pm m_{j_{m'}} & \pm m_J \end{pmatrix} \begin{pmatrix} j_m & k & j_n \\ \pm m_{j_m} & \pm m_k & \pm m_{j_n} \end{pmatrix} \begin{pmatrix} j_n & j_n & x \\ \pm m_{j_n} & \pm m_{j_{n'}} & \pm m_x \end{pmatrix}$$

$$\begin{pmatrix} x & k & k' \\ \pm m_x & \pm m_k & \pm m_{k'} \end{pmatrix} \begin{pmatrix} k' & j_m & j_n \\ \pm m_{k'} & \pm m_{j_{m'}} & \pm m_{j_{n''}} \end{pmatrix} \begin{pmatrix} j_n & j_n & J \\ \pm m_{j_{n''}} & \pm m_{j_{n'}} & \pm m_{J_m} \end{pmatrix}$$

$$= (-1)^{j_m + j_n + k + x} \sqrt{[k, k', x]} \begin{Bmatrix} j_m & j_n & k \\ x & k' & j_n \end{Bmatrix} (-1)^J \sqrt{[J]} \begin{Bmatrix} j_m & j_m & J \\ j_n & j_n & k' \end{Bmatrix}$$

Implementation of Rayleigh-Schrödinger perturbation theory in irreducible tensorial form for VV in GRASP

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The admixed configurations from **VV correlations** can be added to usual energy of the term χJ of the configuration K and can be expressed as the energy $E_0(K)$, which does not depend on term, and the sum of product of Slater integrals and spin-angular coefficients, describing the interaction within open subshell and between them:

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$$
\begin{aligned}
E(K\chi J) \\
&= E_0(KJ) + \Delta\mathcal{E}_0(KJ) \\
&+ \sum_{n\ell j}\sum_{k>0} \widetilde{f}_k(\ell j^w,\ K\chi J)\left[\mathcal{F}^k(n\ell j,\ n\ell j) + \Delta\mathcal{F}^k(n\ell j,\ n\ell j)\right] \\
&+ \sum_{n\ell j}\sum_{n'\ell' j'>n\ell j}\left\{\sum_{k>0}\widetilde{f}_k\left(\ell j^w\ \ell' j'^{w'},\ K\chi J\right)\left[\mathcal{F}^k(n\ell j,\ n'\ell' j') + \Delta\mathcal{F}^k(n\ell j,\ n'\ell' j')\right]\right. \\
&+ \sum_k \widetilde{g}_k\left(\ell j^w\ \ell' j'^{w'},\ K\chi J\right)\mathcal{G}^k(n\ell j,\ n'\ell' j') \\
&\left.+ \sum_k \widetilde{v}_k\left(\ell j^w\ \ell' j'^{w'}, \ell j^{w-2}\ \ell' j'^{w'+2},\ K\chi J\ K'\chi' J\right)\mathcal{R}^k(n\ell jn\ell j,\ n'\ell' j'n'\ell' j')\right\} \\
&+ \sum_{\substack{n\ell j \\ n'\ell' j' \neq n\ell j}}\sum_{\substack{k>0 \\ k',x}}\left\langle\Psi\left\|\left[[\tilde{a}^{(j)}\times a^{(j)}]^{(k)}\times\left[[a^{(j')}\times\tilde{a}^{(j')}]^{(x)}\times[a^{(j')}\times\tilde{a}^{(j')}]^{(k')}\right]^{(k)}\right]^{(0)}\right\|\Psi\right\rangle \\
&\qquad\times\Delta\widetilde{\mathcal{R}}^{(k,k',x)}(n\ell j\ n'\ell' j'\ n'\ell' j') \\
&+ \sum_{\substack{n\ell j \\ n'\ell' j' \neq n\ell j \\ n''\ell'' j'' \neq n\ell j}}\sum_{\substack{k>0 \\ k',x}}\left\langle\Psi\left\|\left[\left[[\tilde{a}^{(j)}\times a^{(j)}]^{(k)}\times[a^{(j')}\times\tilde{a}^{(j')}]^{(x)}\right]^{(k')}\times[a^{(j'')}\times\tilde{a}^{(j'')}]^{(k')}\right]^{(0)}\right\|\Psi\right\rangle \\
&\qquad\times\Delta\widetilde{\mathcal{R}}^{(k,k',x)}(n\ell j\ n'\ell' j'\ n''\ell'' j''),
\end{aligned}
$$

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Implementation of Rayleigh-Schrödinger perturbation theory in irreducible tensorial form for VV in GRASP

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$\Delta\mathcal{E}_0$ corrections

$$\overbrace{(n_m\ell_m)\ j_m^{w_m}\ (n_n\ell_n)\ j_n^{w_n}}^{\text{valence subshells}} \rightarrow \overbrace{(n_m\ell_m)\ j_m^{w_m+1}\ (n_n\ell_n)\ j_n^{w_n-2}}^{\text{valence subshells}}\ \overbrace{(n_r\ell_r)\ j_r}^{\text{virtual subshell}}$$

$$-\frac{2([j_m]-w_m)w_n(w_n-1)}{[j_m,j_n]}\mathcal{A}'(0,\ nn,\ mr)$$

$$\overbrace{(n_m\ell_m)\ j_m^{w_m}\ (n_n\ell_n)\ j_n^{w_n}\ (n_p\ell_p)\ j_p^{w_p}}^{\text{valence subshells}} \rightarrow \overbrace{(n_m\ell_m)\ j_m^{w_m+1}\ (n_n\ell_n)\ j_n^{w_n-1}\ (n_p\ell_p)\ j_p^{w_p-1}}^{\text{valence subshells}}\ \overbrace{(n_r\ell_r)\ j_r}^{\text{virtual subshell}}$$

$$-(-1)^{j_m+j_n+j_p+j_r}\frac{([j_m]-w_m)w_nw_p}{[j_m,j_n,j_p]}\sum_k\left\{\frac{\mathcal{P}(kk,np,mr)}{[k]}+C(k,\ np,\ mr)\right\}\Big(1+\mathrm{P}(n\rightleftharpoons p)\Big)$$

Implementation of Rayleigh-Schrödinger perturbation theory in irreducible tensorial form for VV in GRASP

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$$\mathcal{A}'(x,\ ij,\ i'j') = \sum_{k,k'} \begin{Bmatrix} k & k' & x \\ j_i & j_i & j_{i'} \end{Bmatrix} \begin{Bmatrix} k & k' & x \\ j_j & j_j & j_{j'} \end{Bmatrix} \mathcal{P}(kk',\ ij,\ i'j'), \tag{1}$$

$$\mathcal{C}(x,\ ij,\ i'j') = \sum_{k} \begin{Bmatrix} x & j_i & j_{i'} \\ k & j_j & j_{j'} \end{Bmatrix} \mathcal{Q}(xk,\ ij,\ i'j').$$

Implementation of Rayleigh-Schrödinger perturbation theory in irreducible tensorial form for VV in GRASP

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$$\mathcal{P}(kk',\ ij,\ i'j') = \mathcal{R}^{k}(ij,\ i'j')\ \mathcal{R}^{k'}(i'j',\ ij)\ \mathcal{O}(K',K),$$

$$\mathcal{Q}(kk',\ ij,\ i'j') = \mathcal{R}^{k}(ij,\ i'j')\ \mathcal{R}^{k'}(i'j',\ ji)\ \mathcal{O}(K',K),$$

$$\mathcal{R}^{k}(ij,i'j') = \left\{\Big[1+\delta(i,j)\Big]\Big[1+\delta(i',j')\Big]\right\}^{-1/2} R^{k}\left(n_i j_i\, n_j j_j,\ n_{i'} j_{i'}\, n_{j'} j_{j'}\right)\left\langle \ell_i j_i \left\| C^{(k)} \right\| \ell_{i'} j_{i'}\right\rangle\left\langle \ell_j j_j \left\| C^{(k)} \right\| \ell_{j'} j_{j'}\right\rangle,$$

$$\mathcal{O}(K',K) = \frac{1}{\overline{E}(K') - \overline{E}(K)}.$$

Implementation of Rayleigh-Schrödinger perturbation theory in irreducible tensorial form for VV in GRASP

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$$\overbrace{(n_m\ell_m)\, j_m^{w_m}\;(n_n\ell_n)\, j_n^{w_n}}^{\text{valence subshells}} \rightarrow \overbrace{(n_m\ell_m)\, j_m^{w_m+1}\;(n_n\ell_n)\, j_n^{w_n-2}}^{\text{valence subshells}}\;\overbrace{(n_r\ell_r)\, j_r}^{\text{virtual subshell}}$$

Corrections	Slater integral	k values
$-4\,[k]\,\frac{([j_m]-w_m)}{[j_m]}\mathcal{A}'\,(k,\,nn,\,mr)$	$\Delta\mathcal{F}^k(n,n)$	$k>0$
$2\,[k]\sum_{k'}(-1)^{j_n+j_r+k'}\begin{Bmatrix} j_m & j_m & k \\ j_n & j_n & k' \end{Bmatrix} C\,(k',\,rm,\,nn)$	$\Delta\mathcal{F}^k(m,n)$	$k>0$
$2\,(-1)^{-j_m+j_n+x}\sqrt{[k,k',x]}\;\mathcal{G}\,(k\,k'\,x,\,nn,\,mr)$	$\Delta\widetilde{\mathcal{R}}^{(k,k',x)}\,(mnn)$	$k>0$

Table 1: Expressions for Slater integrals $\Delta\mathcal{F}^k(n,n)$, $\Delta\mathcal{F}^k(m,n)$, and $\Delta\widetilde{\mathcal{R}}^{(k,k',x)}\,(mnn)$ corrections corresponding to the third type of valence-valence correlations.

$$
\begin{aligned}
E(K\chi J) &\\
&= E_0(KJ) + \Delta\mathcal{E}_0(KJ) \\
&+ \sum_{n\ell j}\sum_{k>0} \widetilde{f}_k(\ell j^w,\ K\chi J)\left[\mathcal{F}^k(n\ell j,\ n\ell j) + \Delta\mathcal{F}^k(n\ell j,\ n\ell j)\right] \\
&+ \sum_{n\ell j}\sum_{n'\ell' j'>n\ell j}\left\{\sum_{k>0}\widetilde{f}_k\left(\ell j^w\ \ell' j'^{w'},\ K\chi J\right)\left[\mathcal{F}^k(n\ell j,\ n'\ell' j') + \Delta\mathcal{F}^k(n\ell j,\ n'\ell' j')\right]\right. \\
&+ \sum_k \widetilde{g}_k\left(\ell j^w\ \ell' j'^{w'},\ K\chi J\right)\mathcal{G}^k(n\ell j,\ n'\ell' j') \\
&\left.+ \sum_k \widetilde{v}_k\left(\ell j^w\ \ell' j'^{w'}, \ell j^{w-2}\ \ell' j'^{w'+2},\ K\chi J\ K'\chi' J\right)\mathcal{R}^k(n\ell j n\ell j,\ n'\ell' j' n'\ell' j')\right\} \\
&+ \sum_{\substack{n\ell j \\ n'\ell' j' \neq n\ell j}}\ \sum_{\substack{k>0 \\ k',x}}\left\langle\Psi\left\|\left[[\tilde{a}^{(j)}\times a^{(j)}]^{(k)}\times\left[[a^{(j')}\times\tilde{a}^{(j')}]^{(x)}\times[a^{(j')}\times\tilde{a}^{(j')}]^{(k')}\right]^{(k)}\right]^{(0)}\right\|\Psi\right\rangle \\
&\qquad\times \Delta\widetilde{\mathcal{R}}^{(k,k',x)}(n\ell j\ n'\ell' j'\ n'\ell' j') \\
&+ \sum_{\substack{n\ell j \\ n'\ell' j' \neq n\ell j \\ n''\ell'' j'' \neq n\ell j}}\ \sum_{\substack{k>0 \\ k',x}}\left\langle\Psi\left\|\left[\left[[\tilde{a}^{(j)}\times a^{(j)}]^{(k)}\times[a^{(j')}\times\tilde{a}^{(j')}]^{(x)}\right]^{(k')}\times[a^{(j'')}\times\tilde{a}^{(j'')}]^{(k')}\right]^{(0)}\right\|\Psi\right\rangle \\
&\qquad\times \Delta\widetilde{\mathcal{R}}^{(k,k',x)}(n\ell j\ n'\ell' j'\ n''\ell'' j''),
\end{aligned}
$$

Implementation of Rayleigh-Schrödinger perturbation theory in irreducible tensorial form for VV in GRASP

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$$\mathcal{G}(x_1\, x_2\, x,\; ij,\; i'j') = \sum_{k,k'} (-1)^{k'} \begin{Bmatrix} j_j & j_j & x \\ k & k' & j_{j'} \end{Bmatrix} \begin{Bmatrix} j_{i'} & j_i & k \\ x_1 & x_2 & x \\ j_{i'} & j_i & k' \end{Bmatrix} \mathcal{P}(kk',\; ij,\; i'j'),$$

6-j symbol

9-j symbol

RSMBPT research status up to 2025

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The following correlations was not included in RSMBPT:

- **Valence correlations**

$$(n_m\ell_m)\ j_m^{w_m} \to (n_m\ell_m)\ j_m^{w_m-1}\ (n_r\ell_r)\ j_r$$

- **Core correlations**

$$(n_a\ell_a)\ j_a^{2j_a+1}\ (n_m\ell_m)\ j_m^{w_m} \to (n_a\ell_a)\ j_a^{2j_a}\ (n_m\ell_m)\ j_m^{w_m+1}$$

- **Valence-valence correlations**

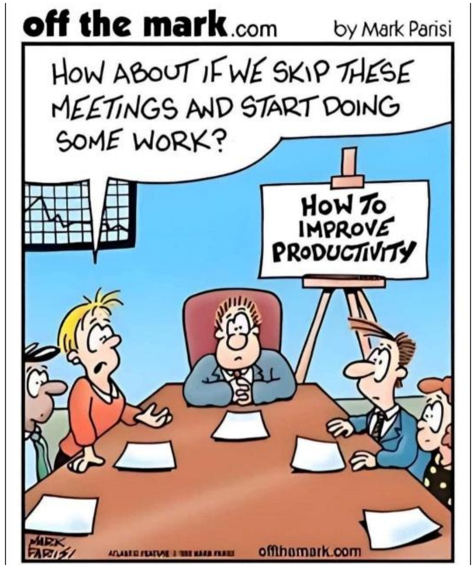
$$(n_a\ell_m)\ j_m^{w_m}\ (n_n\ell_n)\ j_n^{w_n} \to (n_m\ell_m)\ j_m^{w_m+1}\ (n_n\ell_n)\ j_n^{w_n-2}\ (n_r\ell_r)\ j_r$$

$$(n_a\ell_m)\ j_m^{w_m}\ (n_n\ell_n)\ j_n^{w_n}\ (n_p\ell_p)\ j_p^{w_p} \to (n_m\ell_m)\ j_m^{w_m+1}\ (n_n\ell_n)\ j_n^{w_n-1}\ (n_p\ell_p)\ j_p^{w_p-1}\ (n_r\ell_r)\ j_r$$

- **Core-valence correlations**

$$(n_a\ell_a)\ j_a^{2j_a+1}\ (n_m\ell_m)\ j_m^{w_m}\ (n_n\ell_n)\ j_n^{w_n} \to (n_a\ell_a)\ j_a^{2j_a}\ (n_m\ell_m)\ j_m^{w_m-1}\ (n_n\ell_n)\ j_n^{w_n+2}$$

$$(n_a\ell_a)\ j_a^{2j_a+1}\ (n_m\ell_m)\ j_m^{w_m}\ (n_n\ell_n)\ j_n^{w_n}\ (n_p\ell_p)\ j_p^{w_p} \to (n_a\ell_a)\ j_a^{2j_a}\ (n_m\ell_m)\ j_m^{w_m-1}\ (n_n\ell_n)\ j_n^{w_n+1}\ (n_p\ell_p)\ j_p^{w_p+1}$$



Relativistic second-order effective Hamiltonian in irreducible tensorial form for core-valence correlations

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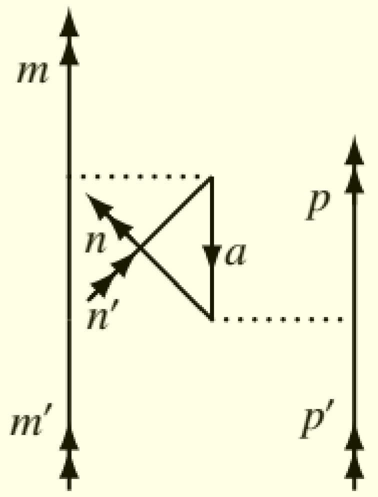


CV_7

A Feynman diagram that is independent of the potential at which the wave functions were obtained.

The third type of core-valence correlations

$$(n_a\ell_a)\, j_a^{2j_a+1}\,(n_m\ell_m)\, j_m^{w_m}\,(n_n\ell_n)\, j_n^{w_n} \rightarrow (n_a\ell_a)\, j_a^{2j_a}\,(n_m\ell_m)\, j_m^{w_m-1}\,(n_n\ell_n)\, j_n^{w_n+2}.$$

where all lines with the double arrow of diagram CV_7 is renamed in the following way: $p' \equiv m$ and $m' = n = n' = p \equiv n$.

RSMBPT research status up to 2025

Vilnius University

The following correlations was not included in RSMBPT:

- **Valence correlations**

$$(n_m\ell_m)\ j_m^{w_m} \rightarrow (n_m\ell_m)\ j_m^{w_m-1}\ (n_r\ell_r)\ j_r$$

- **Core correlations**

$$(n_a\ell_a)\ j_a^{2j_a+1}\ (n_m\ell_m)\ j_m^{w_m} \rightarrow (n_a\ell_a)\ j_a^{2j_a}\ (n_m\ell_m)\ j_m^{w_m+1}$$

- **Valence-valence correlations**

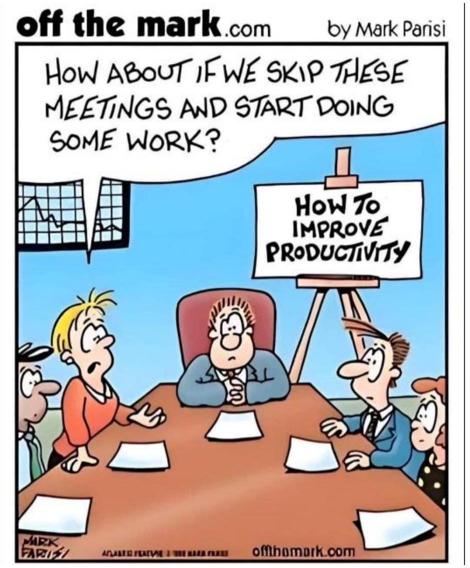
$$(n_a\ell_m)\ j_m^{w_m}\ (n_n\ell_n)\ j_n^{w_n} \rightarrow (n_m\ell_m)\ j_m^{w_m+1}\ (n_n\ell_n)\ j_n^{w_n-2}\ (n_r\ell_r)\ j_r$$

$$(n_a\ell_m)\ j_m^{w_m}\ (n_n\ell_n)\ j_n^{w_n}\ (n_p\ell_p)\ j_p^{w_p} \rightarrow (n_m\ell_m)\ j_m^{w_m+1}\ (n_n\ell_n)\ j_n^{w_n-1}\ (n_p\ell_p)\ j_p^{w_p-1}\ (n_r\ell_r)\ j_r$$

- **Core-valence correlations**

$$(n_a\ell_a)\ j_a^{2j_a+1}\ (n_m\ell_m)\ j_m^{w_m}\ (n_n\ell_n)\ j_n^{w_n} \rightarrow (n_a\ell_a)\ j_a^{2j_a}\ (n_m\ell_m)\ j_m^{w_m-1}\ (n_n\ell_n)\ j_n^{w_n+2}$$

$$(n_a\ell_a)\ j_a^{2j_a+1}\ (n_m\ell_m)\ j_m^{w_m}\ (n_n\ell_n)\ j_n^{w_n}\ (n_p\ell_p)\ j_p^{w_p} \rightarrow (n_a\ell_a)\ j_a^{2j_a}\ (n_m\ell_m)\ j_m^{w_m-1}\ (n_n\ell_n)\ j_n^{w_n+1}\ (n_p\ell_p)\ j_p^{w_p+1}$$



Relativistic second-order effective Hamiltonian in irreducible tensorial form for core-valence correlations

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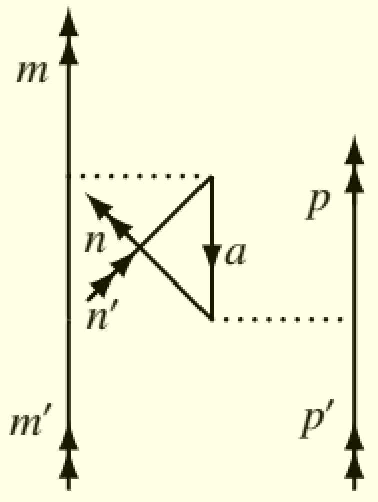

CV_7

A Feynman diagram that is independent of the potential at which the wave functions were obtained.

The fourth type of core-valence correlations

$$(n_a\ell_a)\, j_a^{2j_a+1}\, (n_m\ell_m)\, j_m^{w_m}\, (n_n\ell_n)\, j_n^{w_n}\, (n_p\ell_p)\, j_p^{w_p} \to (n_a\ell_a)\, j_a^{2j_a}\, (n_m\ell_m)\, j_m^{w_m-1}\, (n_n\ell_n)\, j_n^{w_n+1}\, (n_p\ell_p)\, j_p^{w_p+1}$$

where all lines with the double arrow of diagram VV_3 is renamed in the following way: $m = m' = n = n' = p' \equiv$???.

Relativistic second-order effective Hamiltonian in irreducible tensorial form for core-valence correlations

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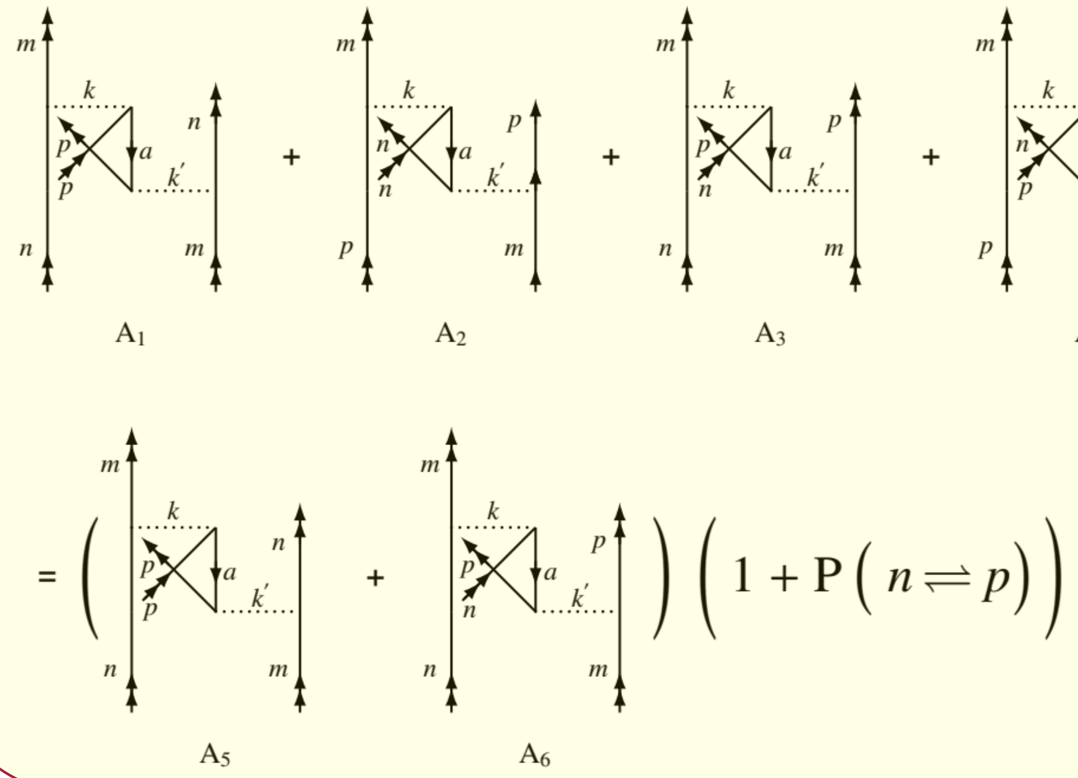

The CV Feynman diagrams of the second-order effective Hamiltonian, expressing the fourth type of core-valence correlations

$$(n_a\ell_a)\ j_a^{2j_a+1}\ (n_m\ell_m)\ j_m^{w_m}\ (n_n\ell_n)\ j_n^{w_n}\ (n_p\ell_p)\ j_p^{w_p}$$
$$\rightarrow (n_a\ell_a)\ j_a^{2j_a}\ (n_m\ell_m)\ j_m^{w_m-1}\ (n_n\ell_n)\ j_n^{w_n+1}\ (n_p\ell_p)\ j_p^{w_p+1}.$$

$$
\begin{aligned}
E(K\chi J) &= E_0(KJ) + \Delta\mathcal{E}_0(KJ) \\
&+ \sum_{n\ell j}\sum_{k>0} \widetilde{f}_k(\ell j^w,\ K\chi J)\left[\mathcal{F}^k(n\ell j,\ n\ell j) + \Delta\mathcal{F}^k(n\ell j,\ n\ell j)\right] \\
&+ \sum_{n\ell j}\sum_{n'\ell' j' > n\ell j} \left\{ \sum_{k>0} \widetilde{f}_k\left(\ell j^w\ \ell' j'^{w'},\ K\chi J\right)\left[\mathcal{F}^k(n\ell j,\ n'\ell' j') + \Delta\mathcal{F}^k(n\ell j,\ n'\ell' j')\right] \right. \\
&+ \sum_{k} \widetilde{g}_k\left(\ell j^w\ \ell' j'^{w'},\ K\chi J\right)\mathcal{G}^k(n\ell j,\ n'\ell' j') \\
&\left. + \sum_{k} \widetilde{v}_k\left(\ell j^w\ \ell' j'^{w'}, \ell j^{w-2}\ \ell' j'^{w'+2},\ K\chi J\ K'\chi' J\right)\mathcal{R}^k(n\ell j n\ell j,\ n'\ell' j' n'\ell' j') \right\} \\
&+ \sum_{\substack{n\ell j \\ n'\ell' j' \neq n\ell j}}\ \sum_{\substack{k>0 \\ k',x}} \left\langle \Psi \left\| \left[[\tilde{a}^{(j)} \times a^{(j)}]^{(k)} \times \left[[a^{(j')} \times \tilde{a}^{(j')}]^{(x)} \times [a^{(j')} \times \tilde{a}^{(j')}]^{(k')}\right]^{(k)}\right]^{(0)} \right\| \Psi \right\rangle \\
&\qquad \times \Delta\widetilde{\mathcal{R}}^{(k,k',x)}(n\ell j\ n'\ell' j'\ n'\ell' j') \\
&+ \sum_{\substack{n\ell j \\ n'\ell' j' \neq n\ell j \\ n''\ell'' j'' \neq n\ell j}}\ \sum_{\substack{k>0 \\ k',x}} \left\langle \Psi \left\| \left[\left[[\tilde{a}^{(j)} \times a^{(j)}]^{(k)} \times [a^{(j')} \times \tilde{a}^{(j')}]^{(x)}\right]^{(k')} \times [a^{(j'')} \times \tilde{a}^{(j'')}]^{(k')}\right]^{(0)} \right\| \Psi \right\rangle \\
&\qquad \times \Delta\widetilde{\mathcal{R}}^{(k,k',x)}(n\ell j\ n'\ell' j'\ n''\ell'' j''),
\end{aligned}
$$

Implementation of Rayleigh-Schrödinger perturbation theory in irreducible tensorial form for VV in GRASP

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Corrections	Slater integral	k values
$\overbrace{(n_m\ell_m)\, j_m^{w_m}\ (n_n\ell_n)\, j_n^{w_n}\ (n_p\ell_p)\, j_p^{w_p}}^{\text{valence subshells}} \rightarrow \overbrace{(n_m\ell_m)\, j_m^{w_m+1}\ (n_n\ell_n)\, j_n^{w_n-1}\ (n_p\ell_p)\, j_p^{w_p-1}}^{\text{valence subshells}}\ \overbrace{(n_r\ell_r)\, j_r}^{\text{virtual subshell}}$		
$(-1)^{jm+jn}\ [k]\ \sqrt{[k]}\ \frac{([jm]-w_m)}{\sqrt{[jm]}} \Big\{(-1)^{k+1}\ \mathcal{G}(0\,k\,k,\ np,\ mr) + \sum_{k_1,k_2,k_3} (-1)^{k_1+k} [k_3] \begin{Bmatrix} jn & jp & k_3 \\ k_1 & k_2 & jr \end{Bmatrix} Q\left(k_1 k_2, np, mr\right) \times C_{12j}\left(jm\, jn\, jp,\ k_1\, k_2\, k_3,\ 0\, k\, k\right)\Big\} \left(1 + \mathrm{P}\begin{pmatrix} n & \rightleftharpoons & p \\ k_1 & \rightleftharpoons & k_2 \end{pmatrix}\right)$	$\Delta\mathcal{F}^{k}(n, p)$	$k > 0$
$(-1)^{jm+jn}\ \sqrt{[k, k', x]} \Big\{(-1)^{x+1}\ \mathcal{G}\left(k\, k'\ x,\ np,\ mr\right) + \sum_{k_1,k_2,k_3} (-1)^{k+k'+k_1} [k_3] \begin{Bmatrix} jn & jp & k_3 \\ k_1 & k_2 & jr \end{Bmatrix} Q\left(k_1 k_2, np, mr\right) \times C_{12j}\left(jm\, jn\, jp,\ k_1\, k_2\, k_3,\ k\, k'\ x\right)\Big\} \left(1 + \mathrm{P}\begin{pmatrix} n & \rightleftharpoons & p \\ k_1 & \rightleftharpoons & k_2 \\ k' & \rightleftharpoons & x \end{pmatrix}\right)$	$\Delta\widetilde{\mathcal{R}}^{(k,k',x)}\ (mnp)$	$k > 0$

Table 1: Expressions for Slater integral $\Delta\mathcal{F}^{k}(n, p)$ and $\Delta\widetilde{\mathcal{R}}^{(k,k',x)}\ (mnp)$ corrections corresponding to the fourth type of valence-valence correlations.

Implementation of Rayleigh-Schrödinger perturbation theory in irreducible tensorial form for VV in GRASP

Vilnius University

$$C_{12j}(iji',\ k_1k_2k_3,\ J_1J_2J) = \sum_x [x] \left\{ \begin{array}{ccc} J_1 & j_j & x \\ j_j & J & J_2 \end{array} \right\} \left\{ \begin{array}{ccc} J & j_j & x \\ k_3 & j_{i'} & j_{i'} \end{array} \right\} \left\{ \begin{array}{ccc} j_{i'} & k_3 & x \\ k_1 & j_i & k_2 \end{array} \right\} \left\{ \begin{array}{ccc} j_i & k_1 & x \\ j_j & J_1 & j_i \end{array} \right\}.$$

12-j symbol

MCDHF and RCI calculations with MBPT

Calculations

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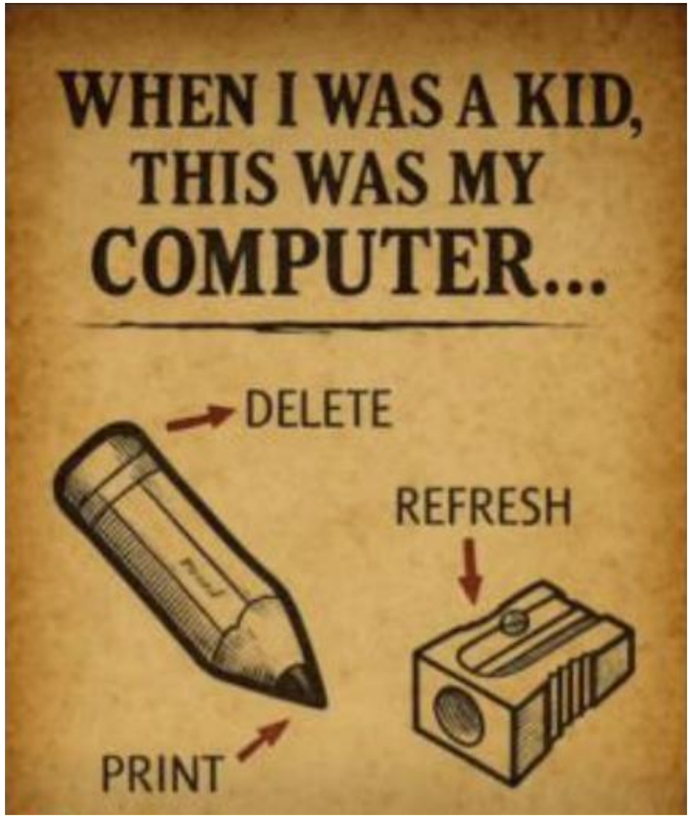
Calculations of core-valence, core and valence-valence (including these which are described by the three-particle Feynman diagram) correlations with a new approach

The energy structure calculations were performed for 105 lowest energy levels of the $4s^24p^2$, $4p^4$, $4s^24p\{4d, 4f, 5s, 5p, 5d, 6s, 6p\}$, $4s4p^3$, and $4s4p^2\{4d, 5s\}$ configurations of the **Se III** using the regular way and the RSMBPT method when CV, C, VV and VVT correlations were included.

The multireference (MR) set in the present calculations consists of the $4s^24p^2$, $4p^4$, $4s^24p\{4f, 5p, 6p\}$, $4s4p^2\{4d, 5s\}$ even and $4s^24p\{4d, 5s, 5d, 6s\}$, $4s4p^3$ odd configurations.



Calculations

Regular GRASP2018 calculations

Regular MCDHF computations including CV, C, and VV(T) correlations are marked as **CV+C+VV(T) MCDHF**.

In this computational scheme, single-double (SD) substitutions are allowed from the

4s, $4p_-$, 4p, $4d_-$, 4d, $4f_-$, 4f, 5s, $5p_-$, 5p, $5d_-$, 5d, 6s, $6p_-$, 6p valence orbitals of the MR set

and

S substitutions from the 3s, $3p_-$, 3p, $3d_-$ and 3d core orbitals to orbital set (OS)

OS_1={7s,$7p_-$,7p,$6d_-$,6d,$5f_-$,5f,$5g_-$,5g},

OS_2={8s,$8p_-$,8p,$7d_-$,7d,$6f_-$,6f,$6g_-$,6g}.

The 1s, 2s, $2p_-$, and 2p subshells are defined as inactive core subshells.

The radial wavefunctions of the new OS are estimated using the Thomas-Fermi potential, and further self-consistent field equations are solved. When a new OS is computed, the previous orbitals are frozen.

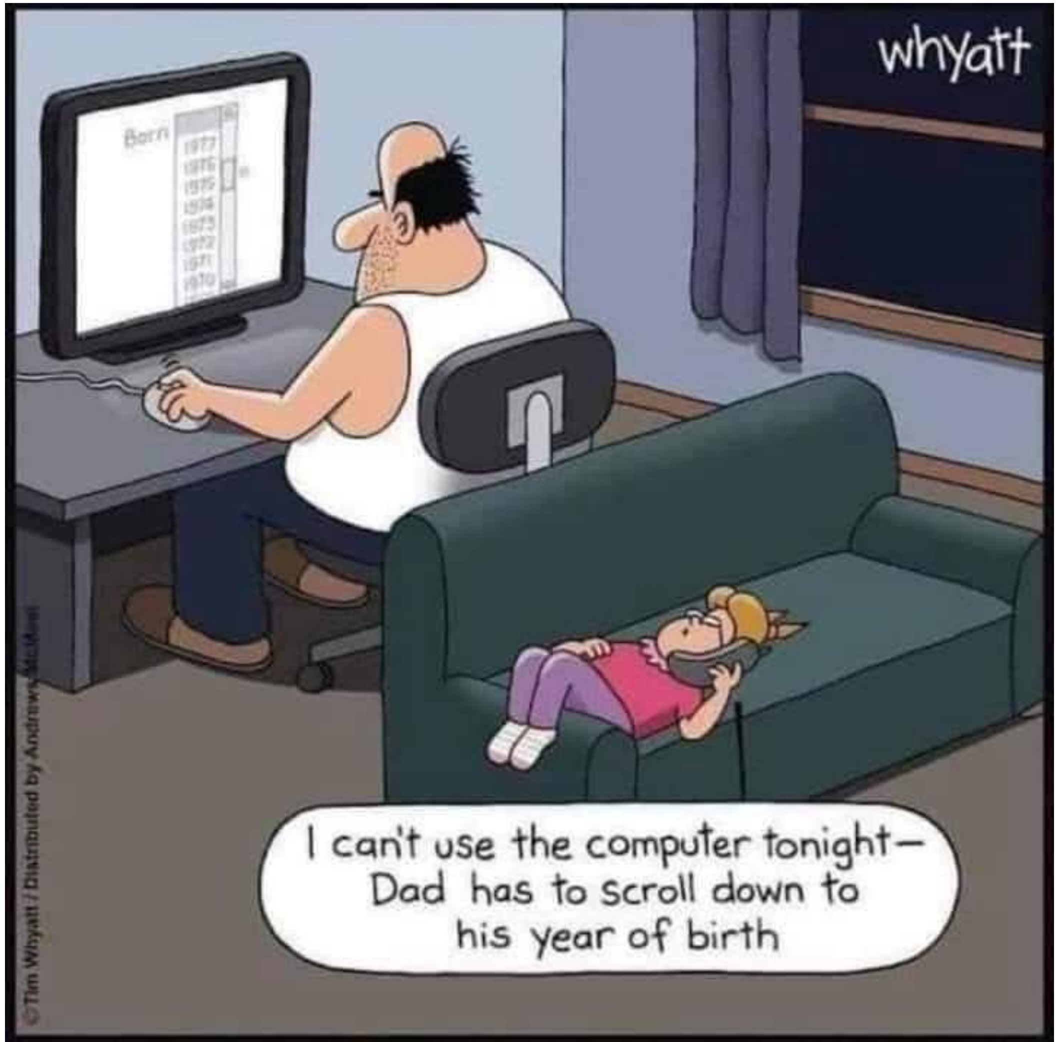
Based on the orbitals from the MCDHF calculations, further RCI calculations are performed. Regular RCI calculations are marked as **CV+C+VV(T) RCI**.

Calculations

Calculations using the RSMBPT method

The 1s, 2s, $2p_-$ and 2p subshells are defined as inactive core subshells in the calculations, the same as it is done in the regular GRASP2018 calculations. The 3s, $3p_-$, 3p, $3d_-$ and 3d subshells are defined as core subshells (that correspond to F set), 4s, $4p_-$, 4p, $4d_-$, 4d, $4f_-$, 4f, 5s, $5p_-$, 5p, $5d_-$, 5d, 6s, $6p_-$, 6p as valence subshells (that correspond to F' set), and subshells belonging to OS_1 and OS_2 as virtual ones (that correspond to G set). Such space distribution is consistent with regular GRASP2018 calculations described above.

The RSMBPT calculation procedure is analogous to that used in previous research. The contribution of each K' configuration for CSF for which energy needs to be calculated is computed according to Rayleigh-Schrödinger perturbation theory in an irreducible tensorial. K' configurations are sorted in descending order according to the impact of the correlations for each level. Further, K' configurations are selected by CV, C and VV(T) correlations impact with the specified fraction (expressed in the percentage: 95, 99, 99.5, 99.95 and 100%) of the total correlations contribution.



Calculations

Results from RCI computations including CV, C and VV(T) correlations according to the RSMBPT method are marked as **CV+C+VV(T) RCI (RSMBPT)**.

Results from MCDHF computations including CV, C and VV(T) correlations according to the RSMBPT method are marked as **CV+C+VV(T) MCDHF (RSMBPT)**.

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Calculations

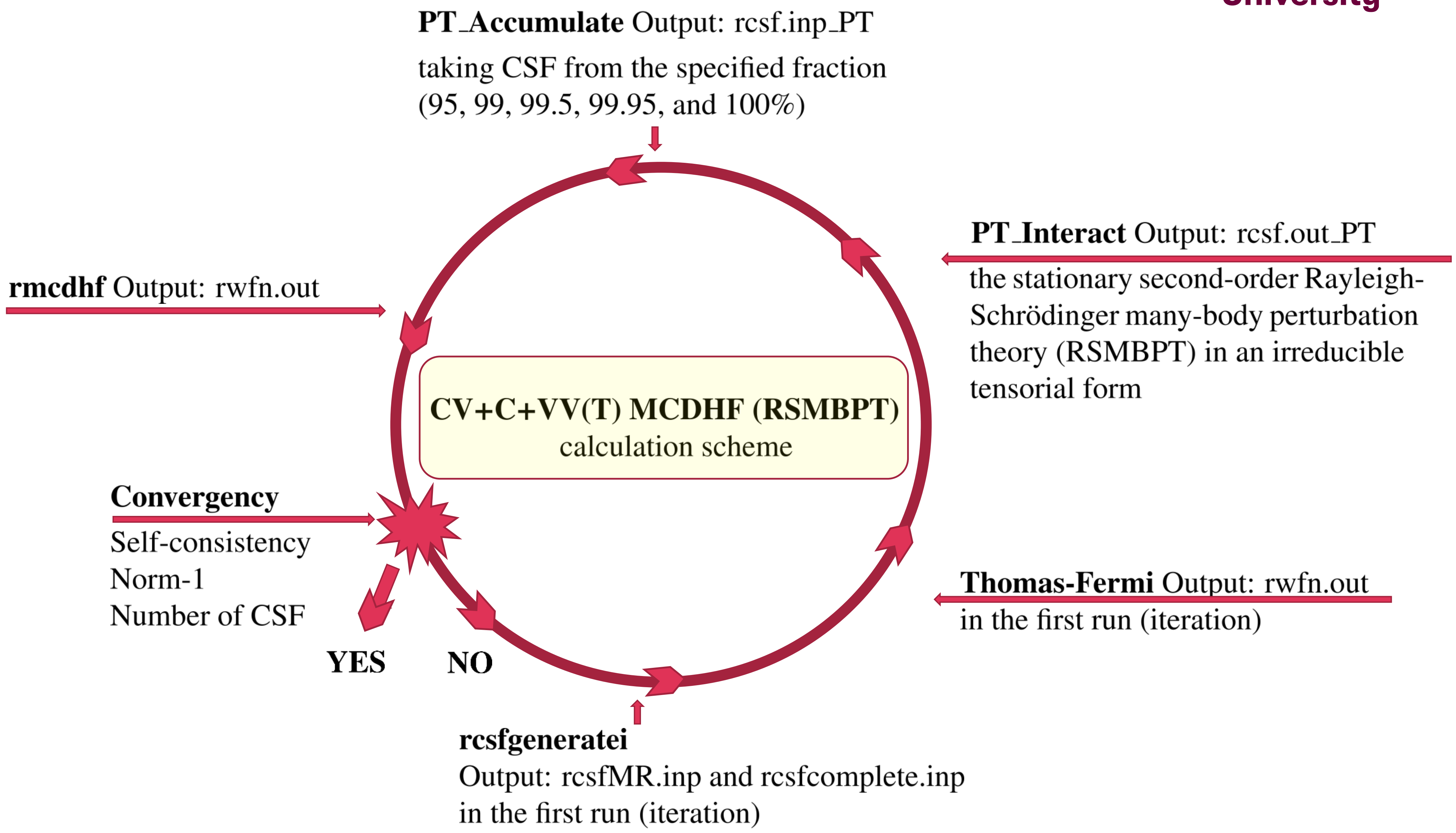

Table 1: Self-consistency and norm-1 parameters solving the MCDHF equations of the OS_1 for even parity states in cases 95%. Columns with 'x' var. means the number of variations with the constructed CSF basis. In. and Fin. means the initial and final results of solving the MCDHF equations for these parameters.

Subshell	1 var.		2 var.		3 var.		4 var.	
	In.	Fin.	In.	Fin.	In.	Fin.	In.	Fin.
				Self-consistency in case 95%				
7s	1.81E-02	2.64E-06	2.28E-04	4.33E-07	5.38E-06	3.79E-07	1.67E-06	8.78E-08
7p_	1.15E-02	3.14E-06	1.27E-03	3.15E-07	4.69E-05	3.75E-07	6.12E-06	1.63E-07
7p	1.90E-02	3.92E-06	1.00E-03	4.43E-07	6.31E-05	5.47E-07	4.24E-06	1.70E-07
6d_	3.98E-02	3.11E-06	8.25E-04	3.94E-07	3.24E-05	3.95E-07	1.54E-06	1.31E-07
6d	5.43E-02	3.86E-06	7.64E-04	4.15E-07	5.49E-05	4.54E-07	5.82E-06	1.40E-07
5f_	2.10E-02	1.02E-06	1.14E-03	9.71E-08	5.72E-05	1.34E-07	1.26E-05	1.02E-07
5f	2.66E-02	1.33E-06	1.03E-03	1.10E-07	8.63E-05	1.95E-07	1.26E-05	9.47E-08
5g_	8.45E-03	1.15E-07	4.24E-04	1.90E-08	5.72E-05	1.45E-07	7.87E-07	8.94E-09
5g	9.43E-03	1.24E-07	4.46E-04	1.33E-08	3.22E-05	4.11E-08	3.22E-08	1.28E-08
				Norm-1 in case 95%				
7s	3.78E-01	-3.58E-05	-2.72E-03	-5.36E-06	6.35E-05	-4.69E-06	1.76E-05	-1.12E-06
7p_	1.44E-01	-2.25E-05	-9.27E-03	-3.82E-06	-4.61E-04	-4.38E-06	-6.77E-05	-1.81E-06
7p	1.57E-01	-2.86E-05	-6.43E-03	-3.47E-06	-4.94E-04	-4.58E-06	-3.22E-05	-1.41E-06
6d_	1.35E-01	-1.60E-05	-4.55E-03	-2.47E-06	-7.01E-06	-2.25E-06	4.48E-06	-7.90E-07
6d	1.67E-01	-1.70E-05	-2.03E-03	-1.99E-06	-1.25E-05	-2.05E-06	3.47E-06	-6.43E-07
5f_	8.54E-02	-8.77E-06	-7.73E-03	-8.07E-07	-5.17E-04	-1.10E-06	-9.83E-05	-8.04E-07
5f	1.03E-01	-9.51E-06	-5.84E-03	-7.81E-07	-6.61E-04	-1.37E-06	-8.08E-05	-6.57E-07
5g_	4.80E-01	3.68E-06	-1.28E-02	6.16E-07	-2.00E-03	-5.38E-06	-2.47E-05	2.81E-07
5g	4.81E-01	3.45E-06	-1.20E-02	3.69E-07	-8.74E-04	-1.38E-06	-7.48E-07	3.76E-07

Calculations

Vilnius University

Table 1: Number of CSF in the MCDHF computations of OS_1 and OS_2 using regular way and the RSMBPT method.

Case	OS_1				OS_2			
	1 var.	2 var.	3 var.	4 var.	1 var.	2 var.	3 var.	4 var.
				Even				
95%	508364	569574	570467	571019	733794	1023336	1141939	1147646
99%	689625	785778	898767	897052	1194590	1746407	1806590	1847202
99.5%	772411	880322	980963	981664	1398101	1979519	2071879	2111506
99.95%	966043	1144631	1173196	1173442	1944852	2525688	2567785	2567315
100%	1287673	1303671	1303659	1303659				
Regular	1303709				2923523			
				Odd				
95%	197074	226517	245285	248960	280434	422802	439826	442597
99%	269522	322049	340528	340543	465186	685001	700179	700938
99.5%	303520	353355	371760	371834	550123	783504	799867	799302
99.95%	380829	444754	450637	450656	764152	973620	974618	974715
100%	500591	507233	507231	507231				
Regular	507234				1126622			

Table 1: Self-consistency and norm-1 parameters solving the MCDHF equations of the OS_1 for even parity states in cases 95%. Columns with 'x' var. means the number of variations with the constructed CSF basis. In. and Fin. means the initial and final results of solving the MCDHF equations for these parameters.

Subshell	1 var.		2 var.		3 var.		4 var.	
	In.	Fin.	In.	Fin.	In.	Fin.	In.	Fin.
Self-consistenc								
$5f_-$	2.10E-02	1.02E-06	1.14E-03	9.71E-				
Norm-1 in								
$5f_-$	8.54E-02	-8.77E-06	-7.73E-03	-8.07E-				
Self-consistenc								
$5f_-$	2.24E-02	2.02E-07	3.59E-04	1.62E-				
Norm-1 in								
$5f_-$	9.73E-02	-1.65E-06	-2.31E-03	-9.94E-				
Self-consistency								
$5f_-$	2.26E-02	2.02E-06	1.08E-04	1.12E-				
Norm-1 in								
$5f_-$	9.88E-02	-1.63E-05	-7.45E-04	-8.47E-				
Self-consistency								
$5f_-$	2.27E-02	7.84E-07	2.80E-04	8.41E-				
Norm-1 in c								
$5f_-$	9.95E-02	-6.06E-06	2.25E-03	-6.12E-				
Self-consistency								
$5f_-$	2.28E-02	1.29E-07	1.33E-06	3.12E-				
Norm-1 in								
$5f_-$	9.98E-02	-9.94E-07	-2.54E-06	-2.18E-				

Calculations

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University

CV+C+VV(T) MCDHF calculations and differences
' (**RSMBPT 95%**) and **CV+C+VV(T) MCDHF** ener-
/+C+VV(T) MCDHF)) for OS_1 even states of Se III are given
ded in the computations.

CV+C+VV(T) MCDHF (RSMBPT 95%))-(CV+C+VV(T) MCDHF)				
var.	2 var.	3 var.	4 var.	
719951	0.01069467	0.01063563	0.01062526	0.00044%
375750	0.00967381	0.00965265	0.00964992	
391853	0.00927581	0.00928841	0.00924708	
448714	0.00986784	0.00988351	0.00982101	
781291	0.01153240	0.01143447	**0.01143258**	0.00047%
389466	0.00995724	0.00988060	0.00989938	
349278	0.00947886	0.00940889	0.00941082	
373647	0.00941741	0.00938174	0.00937987	
044649	0.00589933	0.00588704	**0.00586482**	0.00024%
341043	0.00762622	0.00758052	0.00757921	
039475	0.00617209	0.00614063	0.00612786	
189693	0.00705631	0.00704251	0.00703630	
117159	0.00670039	0.00670372	0.00669024	
132566	0.00677823	0.00679079	0.00678568	
086952	0.00638539	0.00636967	0.00633954	
223365	0.00755601	0.00753338	0.00753415	0.00031%
039475	0.00589933	0.00588704	**0.00586482**	
781291	0.01153240	0.01143447	**0.01143258**	
274465	0.00850122	0.00847525	0.00847151	

Calculations

Vilnius University

Table 1: Min, max diff and rms of total energy in the MCDHF computations of OS_1 comparing regular way and the RSMBPT method.

	Even				Odd			
	1 var.	2 var.	3 var.	4 var.	1 var.	2 var.	3 var.	4 var.
OS_1								
Case 95%								
ΔE_{min} (in a.u.)	0.01039475	0.00589933	0.00588704	0.00586482	0.01078587	0.00619445	0.00410314	0.00378723
ΔE_{max} (in a.u.)	0.01781291	0.01153240	0.01143447	0.01143258	0.01615159	0.00844032	0.00543860	0.00506363
rms (in a.u.)	0.01274465	0.00850122	0.00847525	0.00847151	0.01345016	0.00724574	0.00455746	0.00430101
Case 99%								
ΔE_{min} (in a.u.)	0.00479198	0.00241481	0.00044516	0.00044752	0.00444358	0.00147206	0.00072496	0.00072521
ΔE_{max} (in a.u.)	0.01010324	0.00488030	0.00122598	0.00123373	0.00864969	0.00231023	0.00107323	0.00105647
rms (in a.u.)	0.00692783	0.00366682	0.00081360	0.00081380	0.00723871	0.00182232	0.00086627	0.00086609
Case 99.5%								
ΔE_{min} (in a.u.)	0.00403621	0.00124726	0.00022377	0.00022392	0.00322708	0.00075465	0.00036678	0.00035865
ΔE_{max} (in a.u.)	0.00892285	0.00265308	0.00078628	0.00078657	0.00729924	0.00126755	0.00055566	0.00054793
rms (in a.u.)	0.00591419	0.00182666	0.00046031	0.00045983	0.00602911	0.00094146	0.00044813	0.00044605
Case 99.95%								
ΔE_{min} (in a.u.)	0.00248536	0.00011430	0.00002831	0.00002734	0.00352790	0.00005336	0.00003057	0.00003065
ΔE_{max} (in a.u.)	0.00591823	0.00032153	0.00017859	0.00017856	0.00581758	0.00013347	0.00007381	0.00007382
rms (in a.u.)	0.00422965	0.00021375	0.00007648	0.00007318	0.00479534	0.00009420	0.00005156	0.00005162
Case 100%								
ΔE_{min} (in a.u.)	0.00003567	0.00000000	0.00000000	0.00000000	0.00003871	0.00000000	0.00000000	0.00000000
ΔE_{max} (in a.u.)	0.00008260	0.00000078	0.00000078	0.00000078	0.00007884	0.00000001	0.00000003	0.00000003
rms (in a.u.)	0.00006240	0.00000015	0.00000015	0.00000015	0.00006174	0.00000001	0.00000001	0.00000001

Calculations

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Table 1: Min, max diff and rms of total energy in the MCDHF computations of OS_2 comparing regular way and the RSMBPT method.

	Even				Odd			
	1 var.	2 var.	3 var.	4 var.	1 var.	2 var.	3 var.	4 var.
				OS_2				
				Case 95%				
ΔE_{min} (in a.u.)	0.01514835	0.00565667	0.00465128	0.00476963	0.01905315	0.00664994	0.00635027	0.00628709
ΔE_{max} (in a.u.)	0.02611409	0.01186351	0.00944572	0.00948070	0.02458143	0.00895267	0.00824978	0.00825399
rms (in a.u.)	0.01959744	0.00889209	0.00680218	0.00676645	0.02082576	0.00747281	0.00703090	0.00698012
				Case 99%				
ΔE_{min} (in a.u.)	0.00879110	0.00085163	0.00081118	0.00076419	0.01077293	0.00157237	0.00150440	0.00150264
ΔE_{max} (in a.u.)	0.01554800	0.00279595	0.00235952	0.00232113	0.01502497	0.00238582	0.00228452	0.00228469
rms (in a.u.)	0.01167577	0.00205255	0.00177316	0.00168195	0.01235068	0.00183188	0.00177058	0.00177014
				Case 99.5%				
ΔE_{min} (in a.u.)	0.00770291	0.00034064	0.00041791	0.00041622	0.00862058	0.00093582	0.00081631	0.00081282
ΔE_{max} (in a.u.)	0.01361750	0.00188676	0.00154804	0.00153272	0.01279172	0.00150648	0.00140862	0.00140949
rms (in a.u.)	0.00996782	0.00133000	0.00107452	0.00101776	0.01058859	0.00111489	0.00104843	0.00104674
				Case 99.95%				
ΔE_{min} (in a.u.)	0.00388888	0.00005463	0.00007514	0.00007001	0.00450417	0.00014034	0.00012899	0.00012840
ΔE_{max} (in a.u.)	0.00911764	0.00047941	0.00040230	0.00040681	0.00806687	0.00040195	0.00038392	0.00038297
rms (in a.u.)	0.00571790	0.00033027	0.00026441	0.00026029	0.00624877	0.00024094	0.00026036	0.00026023

Calculations

Table 1: The smallest (ΔE_{min} in a.u.), the largest (ΔE_{max} in a.u.) differences and rms of total energies from the RCI computations of OS_1 and OS_2 comparing results from regular way and using the RSMBPT method.

	Even		Odd	
	First procedure	Second procedure	First procedure	Second procedure
		OS_2		
		Radial wavefunctions from case 95%		
ΔE_{min} (in a.u.)	0.00005090	0.00478032	0.00004574	0.00630025
ΔE_{max} (in a.u.)	0.00197267	0.00952692	0.00094435	0.00826736
rms (in a.u.)	0.00098455	0.00678775	0.00043676	0.00698827
		Radial wavefunctions from case 99%		
ΔE_{min} (in a.u.)	0.00000458	0.00074870	0.00000710	0.00151110
ΔE_{max} (in a.u.)	0.00023362	0.00232700	0.00029347	0.00229393
rms (in a.u.)	0.00014306	0.00167533	0.00009579	0.00177984
		Radial wavefunctions from case 99.5%		
ΔE_{min} (in a.u.)	0.00000024	0.00041214	0.00000244	0.00081798
ΔE_{max} (in a.u.)	0.00008720	0.00154291	0.00014983	0.00141603
rms (in a.u.)	0.00004940	0.00102058	0.00004814	0.00105443
		Radial wavefunctions from case 99.95%		
ΔE_{min} (in a.u.)	0.00000018	0.00007105	0.00000004	0.00012925
ΔE_{max} (in a.u.)	0.00002741	0.00041042	0.00001590	0.00038453
rms (in a.u.)	0.00000952	0.00026222	0.00000824	0.00026121

In the first procedure using the RSMBPT method, the radial wavefunctions were taken from the **CV+C+VV MCDHF (RSMBPT)** calculations and the CSFs basis was taken from the regular GRASP2018 calculations.

In the second procedure, the radial wavefunctions were taken from the **CV+C+VV MCDHF (RSMBPT)** calculations and the CSF basis was constructed using the RSMBPT method with the same specified fraction as in the MCDHF.

Calculations

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Table 1: Energy levels (in cm^{-1}) from **CV+C+VV RCI** calculations and differences (in cm^{-1}) between **CV+C+VV RCI (RSMBPT)** and **CV+C+VV RCI** energies ($\Delta E_{\textbf{(CV+C+VV RCI (RSMBPT))-(CV+C+VV RCI)}}$) for OS_2 even states of Se III are given when CV, C and VV correlations are included in the computations.

No	Pos	J	**CV+C+VV RCI**	$\Delta E_{\textbf{(CV+C+VV RCI (RSMBPT))-(CV+C+VV RCI)}}$			
				First procedure		Second procedure	
				95%	99.95%	95%	99.95%
1	1	0	0.00	0.00	0.00	0.00	0.00
2	1	1	1682.62	3.75	-0.32	-330.09	-21.68
3	1	2	3889.34	6.04	-0.88	-411.08	-24.74
4	2	2	13797.80	23.17	1.86	-312.40	-20.79
5	2	0	29482.86	82.02	2.96	152.76	-4.49
6	2	1	151160.29	-98.23	-3.90	-257.70	27.52
7	3	1	153592.00	-99.55	-2.97	-330.38	25.41
8	3	2	153914.82	-102.93	-3.31	-325.03	25.14
9	3	0	155152.31	-89.78	-1.29	-193.47	34.01
10	4	1	156676.51	-91.53	-2.96	-341.68	26.93
11	1	3	157184.53	-103.16	-4.01	-140.65	35.61
12	4	2	158137.34	-89.27	-3.00	-322.07	27.12
13	5	1	159722.61	-95.52	-3.69	-354.90	26.77
14	5	2	161643.32	-86.43	-2.54	-314.04	26.27
15	4	0	167467.38	-75.92	-3.37	-122.41	27.77
16	2	3	191065.56	-528.12	-0.05	-485.28	43.60
N_{CSFs}				2923523	2923523	1148711	2567016
rms (in cm^{-1})				276.96	2.32	509.08	25.92

Summary and conclusions

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Summary and conclu

Are all types of correlations included in the RSMBPT?
The following correlations are not included in RSMBPT:

- **Valence correlations**

$$(n_m\ell_m)\, j_m^{w_m} \rightarrow (n_m\ell_m)\, j_m^{w_m-1}\, (n_r\ell_r)\, j_r$$

- **Core correlations**

$$(n_a\ell_a)\, j_a^{2j_a+1}\, (n_m\ell_m)\, j_m^{w_m} \rightarrow (n_a\ell_a)\, j_a^{2j_a}\, (n_m\ell_m)\, j_m^{w_m}$$

Summary and conclusions

This is the first time that CSF bases constructed using the RSMBPT method have been used to solve the self-consistent field equations. Previously, this method was only applied to RCI computations.

Thus, this work demonstrates a third way of the application of the RSMBPT method in atomic calculations (other two ways of it application are presented in a series of previous papers by G. Gaigalas, P. Rynkun and L. Kitovienė).

Summary and conclusions

The radial wavefunctions obtained using the RSMBPT method can be used in the RCI computations in several procedures:

i) these can be used with the extended CSF basis;

ii) these can be used with CSF basis constructed using the RSMBPT method with the specified fraction as in the MCDHF.

Results of both RCI computations are in good agreement with the results of the regular RCI computations.

Summary and conclusions

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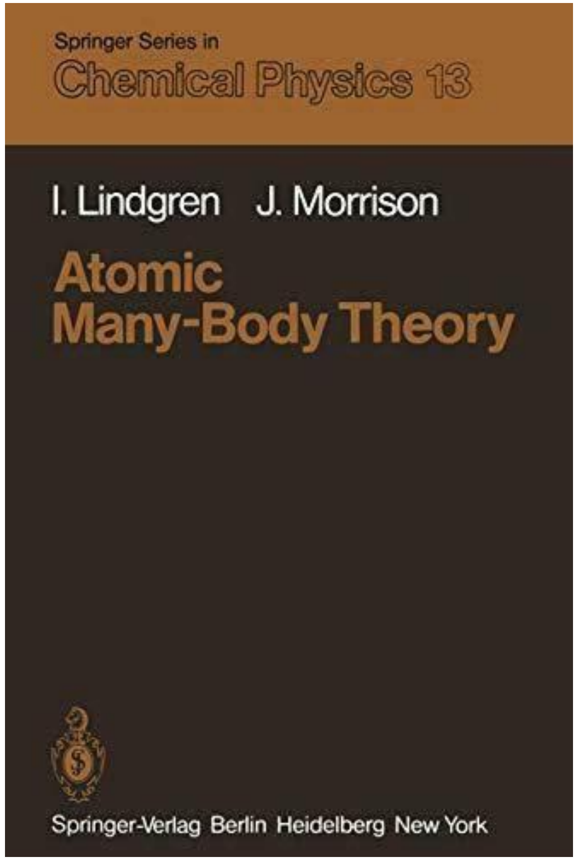
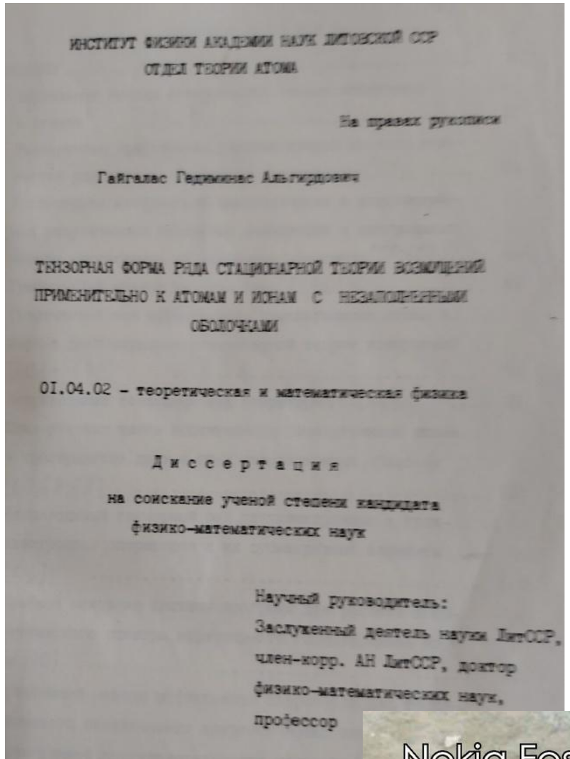



ИНСТИТУТ ФИЗИКИ АКАДЕМИИ НАУК ЛИТОВСКОЙ ССР
ОТДЕЛ ТЕОРИИ АТОМА

На правах рукописи

Гайгалас Гедиминас Альгирдович

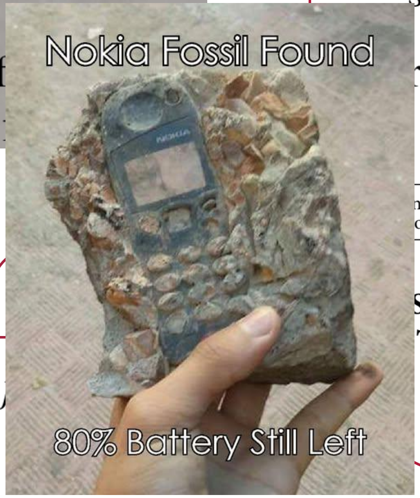
ТЕНЗОРНАЯ ФОРМА РЯДА СТАЦИОНАРНОЙ ТЕОРИИ ВОЗМУЩЕНИЙ ПРИМЕНИТЕЛЬНО К АТОМАМ И ИОНАМ С НЕЗАПОЛНЕННЫМИ ОБОЛОЧКАМИ

01.04.02 – теоретическая и математическая физика

Диссертация
на соискание ученой степени кандидата
физико-математических наук

Научный руководитель:
Заслуженный деятель науки ЛитССР,
член-корр. АН ЛитССР, доктор
физико-математических наук,
профессор

A general form of ... many-body perturbation theory was developed ...



The spin-angular part was developed, i.e. all expresions are in irreducible tensorial form (in *LS*-coupling).

The spin-angular and radial parts were developed (in ... for computer packages such as GRASP.

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SECOND-ORDER RAYLEIGH–SCHRÖDINGER PERTURBATION THEORY FOR THE GRASP2018 PACKAGE: CORE–VALENCE CORRELATIONS*

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SECOND-ORDER RAYLEIGH–SCHRÖDINGER PERTURBATION THEORY FOR THE GRASP2018 PACKAGE: VALENCE–VALENCE CORRELATIONS

G. Gaigalas, P. Rynkun, and L. Kitovienė

In memory

of Prof. Ian Philip Grant

Vilnius University