Atomic Structure Calculations: Fundamental Concepts

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Outline

Atomic Structure Calculations with the General Relativistic Atomic Structure Package (Grasp2K) based on the multiconfiguration method

- ▶ Fundamental concepts and examples (this lecture)
- ▶ Introduction to calculations with Grasp2K (tomorrow)
- ▶ Lab work with Grasp2K (tomorrow), documentation and extensive manual available
  http://webshare.mah.se/tsjoek/ictp/

Relativistic multiconfiguration methods

Relativistic multiconfiguration methods

- ▶ Conceptually easy
- ▶ Can be generally applied; complex shell structures
- ▶ Can be used to generate massive data sets
- ▶ Allows for systematic calculations giving uncertainty estimates

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General references

- ▶ C. Froese-Fischer, T. Brage, P. Jönsson
  Computational Atomic Structure: An MCHF Approach
  IoP 1997
- ▶ I. Grant
  Relativistic Quantum Theory of Atoms and Molecules: Theory and Computation
  Springer 2007
- ▶ The CompAS group
  A practical guide to Grasp2K, 2015

Code and material from Compas page

Electronic states in Be-like Fe in LSJ coupling

Goal of calculations

The goal of calculations is to give:

- ▶ energies for hundreds of levels (states)
- ▶ labels and composition of states (jj- or LSJ coupling)
- ▶ rates or gf-values for E1, M1, E2, M2, .. transitions
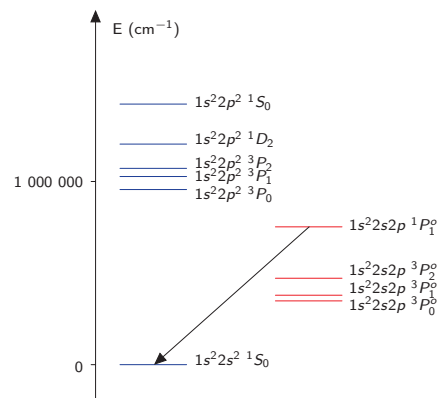- ▶ other quantities: g_J-factors, hfs, isotope shift

The goal is also to provide uncertainty estimates.

Reach spectroscopic accuracy, aid line identification in plasma

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Fundamentals

- ▶ A state of an N-electron atom is described by a wave function

  $$\Psi(\mathbf{r}_1, .., \mathbf{r}_N)$$

  $\mathbf{r}_i$ are the space co-ordinates
- ▶ The wave function is a solution to the wave equation

  $$\mathcal{H}\Psi(\mathbf{r}_1, .., \mathbf{r}_N) = E\Psi(\mathbf{r}_1, .., \mathbf{r}_N),$$

  $\mathcal{H}$ is the Hamiltonian operator and E the energy.
- ▶ From the wave functions properties can be computed

  $$P = \langle \Psi(\mathbf{r}_1, .., \mathbf{r}_N) |\mathcal{P}| \Psi(\mathbf{r}_1, .., \mathbf{r}_N) \rangle$$

Fundamentals

In relativistic calculations the *Dirac-Coulomb* Hamiltonian is used

$$\mathcal{H}_{DC} = \sum_{i=1}^{N} \left(c\, \boldsymbol{\alpha}_i \cdot \mathbf{p}_i + V_{nuc}(r_i) + \beta_i c^2 \right) + \sum_{i>j}^{N} \frac{1}{r_{ij}}$$

$\boldsymbol{\alpha}$ and β are 4×4 Dirac matrices, c is the speed of light

$\mathbf{p} \equiv -i\boldsymbol{\nabla}$ the electron momentum operator.

$V_{nuc}(r)$ potential from extended nuclear charge distribution

Fundamentals

Transverse photon (TP) effects should be added: magnetic interactions and retardation effects

$$\mathcal{H}_{TP} = -\sum_{j>i}^{N} \left[\frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j \, \cos(\omega_{ij} r_{ij}/c)}{r_{ij}} + \right.$$

$$\left. (\boldsymbol{\alpha}_i \cdot \boldsymbol{\nabla}_i)(\boldsymbol{\alpha}_j \cdot \boldsymbol{\nabla}_j) \frac{\cos(\omega_{ij} r_{ij}/c) - 1}{\omega_{ij}^2 r_{ij}/c^2} \right]$$

QED effects: self energy (SE), vacuum polarization (VP)

Total operator is called Dirac-Coulomb-Breit + QED

$$\mathcal{H}_{DCB+QED} = \mathcal{H}_{DC} + \mathcal{H}_{TP} + \mathcal{H}_{SE} + \mathcal{H}_{VP}$$

Symmetries

The wave functions $\Psi(\mathbf{r}_1, .., \mathbf{r}_N)$ have the following symmetries:

- antisymmetric (fermion system)
- parity: even or odd
- eigenfunction to angular momentum operators $\mathbf{J}^2, J_z$
- angular symmetry defined by JM quantum numbers (M normally suppressed)
- labels given by symmetry (parity, J) and order-number within symmetry

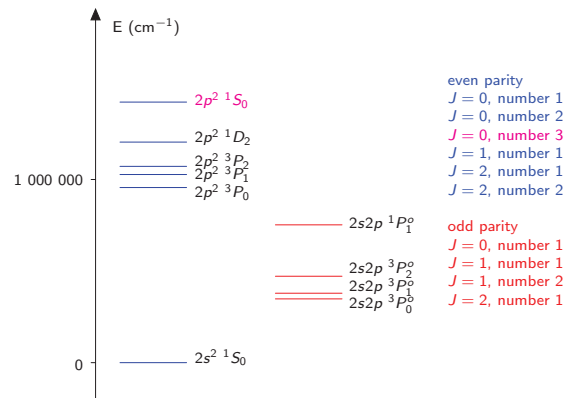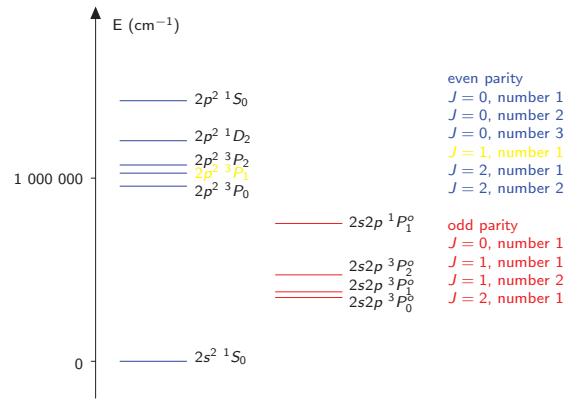## Symmetry and order-number in practice
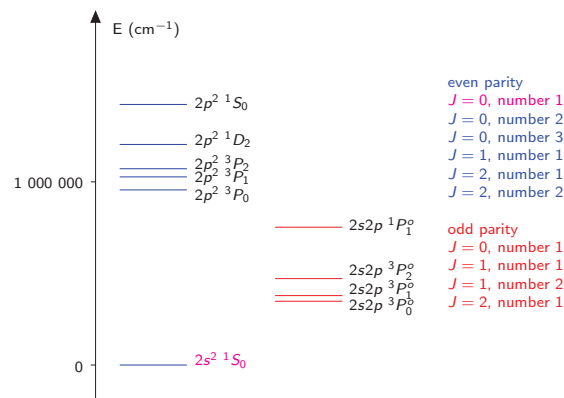
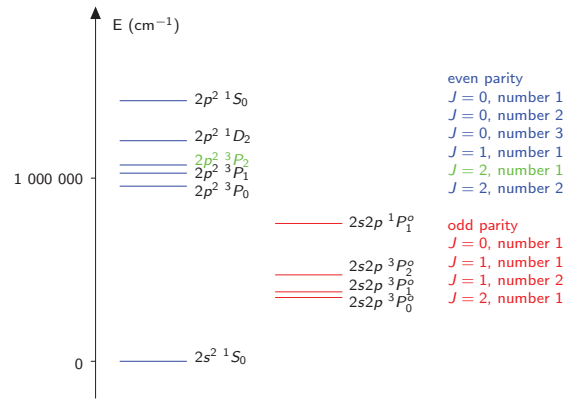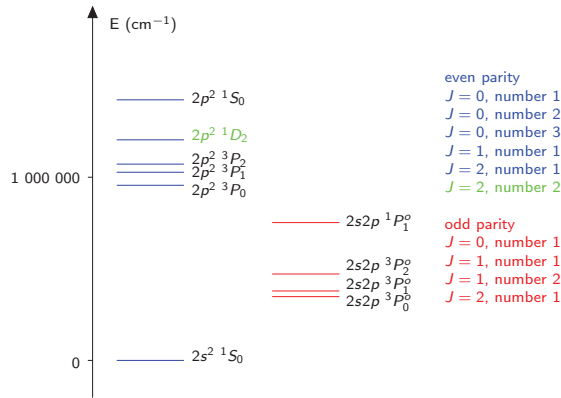## Specification with symmetry and order-number
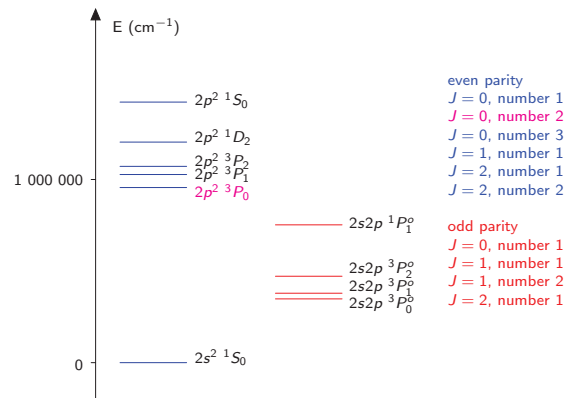
Specification with symmetry and order-number

Specification with symmetry and order-number

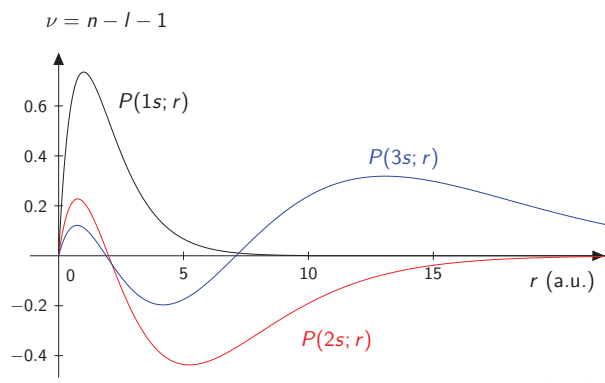## Specification with symmetry and order-number

Specification with symmetry and order-number

E (cm^{-1})

1 000 000

$2p^2\ {}^1S_0$
$2p^2\ {}^1D_2$
$2p^2\ {}^3P_2$
$2p^2\ {}^3P_1$
$2p^2\ {}^3P_0$

$2s2p\ {}^1P_1^o$

$2s2p\ {}^3P_2^o$
$2s2p\ {}^3P_1^o$
$2s2p\ {}^3P_0^o$

0    $2s^2\ {}^1S_0$

even parity
$J = 0$, number 1
$J = 0$, number 2
$J = 0$, number 3
$J = 1$, number 1
$J = 2$, number 1
$J = 2$, number 2

odd parity
$J = 0$, number 1
$J = 1$, number 1
$J = 1$, number 2
$J = 2$, number 1

One-electron systems: spin-orbitals

Wave functions (spin-orbitals)

$$\Psi(nlsjm; \mathbf{r}) = \frac{1}{r}\begin{pmatrix} P(nlj; r)\,\Omega_{lsjm}(\theta, \varphi) \\ i\,Q(nlj; r)\,\Omega_{\tilde{l}sjm}(\theta, \varphi) \end{pmatrix}$$

$P(r)$, $Q(r)$ radial functions represented on a grid r_i, $i = 1, 2, .., M$

$P(r)$, $Q(r)$ large and small component: $|P(r)| >> |Q(r)|$

$\Omega_{lsjm}(\theta, \varphi)$ spherical two-spinors

$$\Omega_{lsjm}(\theta, \varphi) = \sum_{m_l m_s} \langle lm_l \tfrac{1}{2} m_s | jm \rangle\, Y_{lm_l}(\theta, \varphi)\, \chi_{m_s}^{(1/2)}$$

Spectroscopic notation of spin-orbitals

Mapping between spectroscopic notation and quantum numbers lsj

$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$	$f_{5/2}$	$f_{7/2}$	$g_{7/2}$	$g_{9/2}$
s	p-	p	d-	d	f-	f	g-	g
l 0	1	1	2	2	3	3	4	4
j 1/2	1/2	3/2	3/2	5/2	5/2	7/2	7/2	9/2

Numerical solution of one-electron systems

- Apply variational principle on the energy functional

$$\mathcal{E}(\Psi) = \langle \Psi(nlsjm; \mathbf{r}) | \mathcal{H}_{DC} | \Psi(nlsjm; \mathbf{r}) \rangle$$

- Radial and angular parts separate
- Coupled equations for $P(nlj; r)$, $Q(nlj; r)$, solved on the grid.
- Infinite number of solutions for a given symmetry.
- Correct solution enforced by node counting.
- Solution is essentially exact

Node structure of orbitals

Number of nodes ν of $P(nlj; r)$ given by

$$\nu = n - l - 1$$

$P(1s; r)$

$P(3s; r)$

$P(2s; r)$

r (a.u.)

Many-electron systems: atomic state functions

- Electronic state given by an atomic state function $\Psi(\Gamma JM)$ which is expanded in configuration state functions $\Phi(\gamma_\alpha JM)$

$$\Psi(\Gamma JM) = \sum_{\alpha=1}^{NCSF} c_\alpha \Phi(\gamma_\alpha JM)$$

- The label Γ of the state is given by the label of the leading configuration state function (CSF)
- The label can be transformed to LSJ coupling

Many-electron systems: configuration state functions

Construction of CSFs:

- start from a configuration, i.e. distribution of nlj quantum numbers
- create product functions of spin-orbitals with the same distribution of nlj quantum numbers but different values of m
- antisymmetrize product functions
- couple (make linear combinations) to produce eigenfunctions of $\mathbf{J}^2$, J_z.

Example $1s^2 2s^2 2p^2$

Configuration $1s^2 2s^2 2p^2$: 6 CSFs (GRASP2K notation)

```
1s ( 2)  2s ( 2)  2p ( 2)
                    0
                   0+
1s ( 2)  2s ( 2)  2p-( 2)

                   0+
  *
1s ( 2)  2s ( 2)  2p-( 1)  2p ( 1)
              1/2        3/2
                              1+
  *
1s ( 2)  2s ( 2)  2p ( 2)
                    2
                   2+
1s ( 2)  2s ( 2)  2p-( 1)  2p ( 1)
              1/2        3/2
                              2+
```

Numerical solution of many-electron systems

Determination of atomic state functions

$$\Psi(\Gamma_j J_j M) = \sum_{\alpha=1}^{NCSF_j} c_\alpha^j \Phi(\gamma_\alpha^j J_j M), \quad j = 1, \ldots, Nstates$$

Denote the spin-orbitals needed for the construction of the CSFs by $P(a,r), Q(a,r), P(b,r), Q(b,r)$ etc

Numerical solution of many-electron systems

Multiconfiguration-Dirac-Hartree Fock (MCDHF)

- Apply variational principle on the energy functional $\mathcal{F}$
- Coupled equations for radial orbitals $P(a,r)$, $Q(a,r)$, $P(b,r)$, $Q(b,r)$ etc solved on the grid.
- Correct solution enforced by node counting for orbitals building dominating CSFs
- Energies for states and expansion coefficients for CSFs obtained by diagonalizing the Hamiltonian matrix for each symmetry
- Solve iteratively until radial orbitals and expansion coefficients are converged

Numerical solution of many-electron systems

Relativistic Configuration Interaction (RCI)

- Use the radial orbitals $P(a,r)$, $Q(a,r)$, $P(b,r)$, $Q(b,r)$ etc from the step above
- Add Breit and QED correction to the Dirac-Coulomb Hamiltonian and determine energies for states and expansion coefficients for the CSFs by diagonalizing the matrix for each symmetry
- RCI much faster than MCDHF, larger CSF expansions can be used

Numerical solution of many-electron systems

Set up the energy functional

$$\mathcal{F} = \sum_{j=1}^{Nstates} w_j \underbrace{\mathbf{c}^{jT} \mathbf{H}^j \mathbf{c}^j}_{E_j} + \text{orthogonality constraints}$$

$\mathbf{c}^{jT} = (c_1^j, c_2^j, \ldots, c_{NCSF}^j)$ and $\mathbf{H}^j$ the Hamiltonian matrix

$$H_{\alpha\beta}^j = \langle \Phi(\gamma_\alpha^j J_j M)|\mathcal{H}_{DC}|\Phi(\gamma_\beta^j J_j M)\rangle$$

Integration over angles give matrix elements angular coefficients times radial integrals

$$H_{\alpha\beta}^j = \sum_{ab} t_{ab}^{\alpha\beta j} I(a,b) + \sum_{abcd;k} v_{abcd;k}^{\alpha\beta j} R^k(ab,cd)$$

Algorithm

```
Starting estimates P(a,r), Q(a,r), P(b,r), Q(b,r) etc

Until converged
    compute angular coeff. and radial integrals
    diagonalize Hamilton matrices to get energies and
        expansion coefficients for CSFs
    solve differential equations for P(a,r), Q(a,r),
        P(b,r), Q(b,r) etc
```

Selection of CSFs

- Accuracy of wave function and computed results depends of the CSF expansion and the radial orbitals
- The CSFs should be systematically enlarged and convergence monitored
- Convergence pattern give uncertainty estimates
- CSF expansions can be targeted to improve wave functions in different regions of space
- For transition energies and transition rates it is important to improve the outer (valence) region

Selection of CSFs

Selection of CSFs guided by Z-dependent perturbation theory (applicable mainly on highly charged systems)

- Zero-order wave function; expansion over CSFs in the *complex*, accounts for most important effects
- The complex; CSFs that can be formed from orbitals with the same distribution of principal quantum numbers n.
- Instead of complex we use multireference (MR), same as complex but includes CSFs from additional important configurations
- Complex (MR) built from *spectroscopic orbitals*, orbitals with the same node structure as hydrogenic orbitals.

Example 1: $1s^2 2s^2 2p^2$ in Fe XXI

Primary data source		Query NIST Bibliographic Database for **Fe XXI** (new window)				
Sugar and Corliss 1985 ; Shirai et al. 2000			Literature on Fe XXI Energy Levels			
Configuration	**Term**	**J**	**Level (cm⁻¹)**	**Leading percentages**		**Reference**
$2s^2 2p^2$	^3P	0	0	90	7 $2s^2 2p^2$ ^1S	L7185
		1	73 851	99	1 $2p^4$ ^3P	
		2	117 354	75	24 $2s^2 2p^2$ ^1D	
$2s^2 2p^2$	^1D	2	244 561	75	24 $2s^2 2p^2$ ^3P	
$2s^2 2p^2$	^1S	0	371 980	87	9 $2s^2 2p^2$ ^3P	

Example 1: $2s^2 2p^2$ in Fe XXI

Wave functions and energies for all the states belonging to
$1s^2 2s^2 2p^2$. For simplicity we use a non-relativistic notation.

- The wave functions are expansions of CSFs in the complex
- Complex (or MR) consists of all CSFs that can be formed
  from spin-orbitals belonging to the configurations

  $$\{1s^2 2s^2 2p^2, \quad 1s^2 2p^4\}$$

- Number of CSFs in the complex:
  $J = 0, 4; \quad J = 1, 2; \quad J = 2, 4$

Example 1: $2s^2 2p^2$ in Fe XXI

```
-------------------------------------------------
 J  P     MCDHF       RCI        NIST
                E (cm^-1)
-------------------------------------------------
 0  +        0          0          0
 1  +     76 694     74 013     73 851
 2  +    123 846    118 176    117 354
 2  +    253 498    246 848    244 561
 0  +    373 489    369 200    371 980
-------------------------------------------------
```

Example 2: $2p^6 3s^2$, $2p^6 3s3p$, $2p^6 3p^2$ in Fe XV

Primary data source	Query NIST Bibliographic Database for **Fe XV** (new window)	
Sugar and Corliss 1985 : Shirai et al. 2000	Literature on Fe XV Energy Levels	

Configuration	Term	J	Level (cm⁻¹)	Leading percentages	Reference
$2p^6 3s^2$	^1S	0	0		L7185
$3s3p$	$^3P°$	0	233 842		
		1	239 660		
		2	253 820		
$3s3p$	$^1P°$	1	351 911		
$3p^2$	^3P	0	554 524		
		1	564 602		
		2	581 803		
$3p^2$	^1D	2	559 600		
$3p^2$	^1S	0	659 627		

Example 2: $2p^6 3s^2$, $2p^6 3s3p$, $2p^6 3p^2$ in Fe XV

Wave functions and energies for all states belonging to the even
configurations $2p^6 3s^2$, $2p^6 3p^2$.

- Wave functions are expansions of CSFs in the complex
- Complex (or MR) consists of all CSFs that can be formed
  from spin-orbitals belonging to the configurations

  $$\{2p^6 3s^2, \quad 2p^6 3p^2, \quad 2p^6 3d^2, \quad 2p^6 3s3d\}$$

- Number of CSFs in the complex:
  $J = 0, 5; \quad J = 1, 3; \quad J = 2, 7$

Example 2: $2p^6 3s^2$, $2p^6 3s3p$, $2p^6 3p^2$ in Fe XV

Wave functions and energies for all states belonging to the odd
configuration $2p^6 3s3p$.

- Wave functions are expansions of CSFs in the complex
- Complex (or MR) consists of all CSFs that can be formed
  from spin-orbitals belonging to the configurations

  $$\{2p^6 3s3p, \quad 2p^6 3p3d\}$$

- Number of CSFs in the complex:
  $J = 0, 2; \quad J = 1, 5; \quad J = 2, 5$

Example 2: $2p^6 3s^2$, $2p^6 3s3p$, $2p^6 3p^2$ in Fe XV

```
-------------------------------------------------
 J  P     MCDHF        RCI        NIST
                 E (cm^-1)
-------------------------------------------------
 0  +
 0  -    232 465     232 482    233 842
 1  -    238 507     238 340    239 660
 2  -    252 959     252 397    253 820
 1  -    356 753     356 318    351 911
 0  +    556 476     556 162    554 524
 2  +    560 273     559 445    559 600
 1  +    566 635     566 000    564 602
 2  +    583 986     582 795    581 803
 0  +    666 558     665 632    659 627
-------------------------------------------------
```

Improving the wave functions

Zero-order wave functions can be improved by:

- generating configurations by single (S) and double (D)
  substitutions of orbitals in the configurations in the complex
  (or the MR) with orbitals in an active orbital set
- adding the CSFs from the generated configurations to the
  CSFs in the complex
- systematically enlarging the active orbital set
- additional orbitals needed to build the correcting CSFs are
  called correlation orbitals. No restriction on node structure.

Different types of electron correlation

Often necessary to impose restrictions on the SD substitutions

- If SD substitutions are allowed only from the outer orbitals
  the CSF expansion accounts for *valence correlation*
- If SD substitutions are allowed from the outer orbitals and in
  addition at most S substitutions from the core, the CSF
  expansions account for *valence and core-valence correlation*
- For most systems only valence and core-valence correlation
  effects need to be considered

Example 1: $2s^2 2p^2$ in Fe XXI

Improve wave functions and energies by accounting for valence and core-valence correlation.

- ▶ Complex (or MR): all CSFs belonging to $\{1s^2 2s^2 2p^2, \quad 1s^2 2p^4\}$
- ▶ SD substitutions from the configurations in the complex to orbitals in an active set, at most S substitutions from the $1s^2$ core. CSFs from the generated configurations
- ▶ Increase active orbital set layer by layer: $\{1s, 2s, 2p\}$, $\{1s, 2s, 2p, 3s, 3p, 3d\}$, $\{1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f\}$ etc

Example 1: $2s^2 2p^2$ in Fe XXI

Configurations in the complex $\{1s^2 2s^2 2p^2, \quad 1s^2 2p^4\}$
Active orbital set $\{1s, 2s, 2p, 3s, 3p, 3d\}$

S-substitution

$\quad 1s^2 2s^2 2p3p$

Example 1: $2s^2 2p^2$ in Fe XXI

Configurations in the complex $\{1s^2 2s^2 2p^2, \quad 1s^2 2p^4\}$
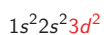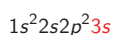Active orbital set $\{1s, 2s, 2p, 3s, 3p, 3d\}$

D-substitution

$\quad 1s^2 2s^2 3s^2$

Example 1: $2s^2 2p^2$ in Fe XXI

Configurations in the complex $\{1s^2 2s^2 2p^2, \quad 1s^2 2p^4\}$
Active orbital set $\{1s, 2s, 2p, 3s, 3p, 3d\}$

D-substitution

$\quad 1s^2 2s^2 3p^2$

Example 1: $2s^2 2p^2$ in Fe XXI

Configurations in the complex $\{1s^2 2s^2 2p^2, \quad 1s^2 2p^4\}$
Active orbital set $\{1s, 2s, 2p, 3s, 3p, 3d\}$

D-substitution

$\quad 1s^2 2s^2 3d^2$

Example 1: $2s^2 2p^2$ in Fe XXI

Configurations in the complex $\{1s^2 2s^2 2p^2, \quad 1s^2 2p^4\}$
Active orbital set $\{1s, 2s, 2p, 3s, 3p, 3d\}$

D-substitution

$\quad 1s^2 2s^2 3s3d$

Example 1: $2s^2 2p^2$ in Fe XXI

Configurations in the complex $\{1s^2 2s^2 2p^2, \quad 1s^2 2p^4\}$
Active orbital set $\{1s, 2s, 2p, 3s, 3p, 3d\}$
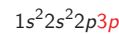
S-substitution (D-substitution from $1s^2 2p^4$)

$\quad 1s^2 2s 2p^2 3s$

Example 1: $2s^2 2p^2$ in Fe XXI

Configurations in the complex $\{1s^2 2s^2 2p^2, \quad 1s^2 2p^4\}$
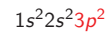Active orbital set $\{1s, 2s, 2p, 3s, 3p, 3d\}$

S-substitution (D-substitution from $1s^2 2p^4$)

$\quad 1s^2 2s 2p^2 3d$

Example 1: $2s^2 2p^2$ in Fe XXI

Configurations in the complex $\{1s^2 2s^2 2p^2, \quad 1s^2 2p^4\}$
Active orbital set $\{1s, 2s, 2p, 3s, 3p, 3d\}$

D-substitution

$\quad 1s^2 2s 2p \, 3s3p$

Example 1: $2s^2 2p^2$ in Fe XXI

Configurations in the complex $\{1s^2 2s^2 2p^2, \quad 1s^2 2p^4\}$
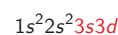Active orbital set $\{1s, 2s, 2p, 3s, 3p, 3d\}$

S-substitution from $1s^2$ core

$\quad 1s 2s^2 2p^2 \, 3s$

Example 1: $2s^2 2p^2$ in Fe XXI

Configurations in the complex $\{1s^2 2s^2 2p^2, \quad 1s^2 2p^4\}$
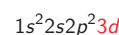Active orbital set $\{1s, 2s, 2p, 3s, 3p, 3d\}$
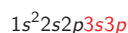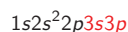
D-substitution, S substitution from $1s^2$ core and S substitution
from valence (account for core-valence correlation)

$\quad 1s 2s^2 2p \, 3s3p$

Example 1: $2s^2 2p^2$ in Fe XXI

Number of CSFs as a function of the active orbital set

Complex	10
$n = 3$	980
$n = 4$	4 723
$n = 5$	12 771

Example 1: $2s^2 2p^2$ in Fe XXI

```
---------------------------------------------------------
 J   P      MR       n = 3    n = 4    n = 5      NIST
                      E (cm^-1)
---------------------------------------------------------
 0   +        0        0        0        0          0
 1   +    74 013   73 476   73 686   73 775     73 851
 2   +   118 176  117 437  117 354  117 365    117 354
 2   +   246 848  245 690  244 938  244 779    244 561
 0   +   369 200  374 065  372 986  372 468    371 980
---------------------------------------------------------
```

Example 2: $2p^6 3s^2, \quad 2p^6 3s3p, \quad 2p^6 3p^2$ in Fe XV

Improve wave functions and energies by accounting for valence and
core-valence correlation. Separate calculations for even and odd
states.

- Complex (or MR): all CSFs belonging to
  $\{2s^2 2p^6 3s^2, \quad 2s^2 2p^6 3p^2, \quad 2s^2 2p^6 3d^2, \quad 2s^2 2p^6 3s3d\}$ and
  $\{2s^2 2p^6 3s3p, \quad 2s^2 2p^6 3p3d\}$
- SD substitutions from the configurations in the complex to
  orbitals in an active set, at most S substitutions from the
  $2s^2 2p^6$ core ($1s^2$ is always closed). CSFs from the generated
  configurations
- Increase the active orbital set layer by layer:
  $\{1s, 2s, 2p, 3s, 3p, 3d\}$, $\{1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f\}$
  etc

Example 2: $2p^6 3s^2, \quad 2p^6 3s3p, \quad 2p^6 3p^2$ in Fe XV

Number of CSFs as a function of the active orbital set

	even	odd
Complex	15	12
$n = 4$	3 806	3 740
$n = 5$	13 833	13 474
$n = 6$	33 152	32 135

Example 2: $2p^6 3s^2, \quad 2p^6 3s3p, \quad 2p^6 3p^2$ in Fe XV

```
-----------------------------------------------------------
 J   P      MR       n = 4    n = 5    n = 6      NIST
                      E (cm^-1)
-----------------------------------------------------------
 0   +
 0   -   232 482  233 503  233 590  233 691    233 842
 1   -   238 340  239 352  239 433  239 531    239 660
 2   -   252 397  253 504  253 578  253 680    253 820
 1   -   356 318  353 122  352 765  352 411    351 911
 0   +   556 162  554 574  554 464  554 479    554 524
 2   +   559 445  559 685  559 653  559 696    559 600
 1   +   566 000  564 539  564 449  564 490    564 602
 2   +   582 795  581 786  581 701  581 748    581 803
 0   +   665 632  662 392  661 461  660 793    659 627
-----------------------------------------------------------
```

Labeling of states

- Label of state is the same as the label for the dominating CSF.
- Labels in relativistic calculations given in jj-coupling
- Labels in jj-coupling unsuitable but can be transformed to labels in LSJ-coupling

Composition of $J = 0$ states in $2s^2 2p^2$ in Fe XXI

Primary data source		Query NIST Bibliographic Database for **Fe XXI** (new window)				
Sugar and Corliss 1985 ; Shirai et al. 2000.			Literature on Fe XXI Energy Levels			
Configuration	Term	J	Level (cm⁻¹)	Leading percentages		Reference
$2s^2 2p^2$	³P	0	0	90	7 $2s^2 2p^2$ ¹S	L7185
		1	73 851	99	1 $2p^4$ ³P	
		2	117 354	75	24 $2s^2 2p^2$ ¹D	
$2s^2 2p^2$	¹D	2	244 561	75	24 $2s^2 2p^2$ ³P	
$2s^2 2p^2$	¹S	0	371 988	87	9 $2s^2 2p^2$ ³P	

Example 1: $2s^2 2p^2$ in Fe XXI

Composition and label of $J = 0$ states

```
Pos   J   Parity      Energy Total      Comp. of ASF
 1    0     +          -940.389925444      99.204%
      0.89592391   1s(2).2s(2).2p(2)3P2_3P
      0.09221480   1s(2).2s(2).2p(2)1S0_1S
      0.00292347   1s(2).2p(4)1S0_1S

 2    0     +          -938.692836229      99.929%
      0.87003632   1s(2).2s(2).2p(2)1S0_1S
      0.09465318   1s(2).2s(2).2p(2)3P2_3P
      0.03413268   1s(2).2p(4)1S0_1S
```
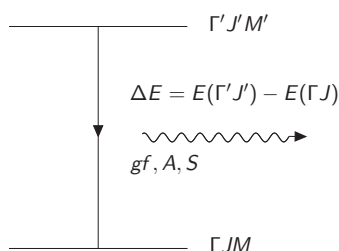
Computation of properties

From the wave functions properties can be computed

$$P = \langle \Psi(\Gamma J M) | \mathcal{P} | \Psi(\Gamma J M) \rangle$$

Inserting $\Psi(\Gamma J M) = \sum_{\alpha=1}^{NCSF} c_\alpha \Phi(\gamma_\alpha J M)$ and performing integration over angles gives

$$P = \sum_{\alpha,\beta,a,b} c_\alpha c_\beta t_{ab}^{\alpha\beta} I(a,b)$$

Dependent on the operator $\mathcal{P}$ properties may be important to outer- or inner part of the wave function

Computation of properties, Landé g_J factors

- The Landé g_J factor described by the operator

$$\sum_{j=1}^{N} -i \frac{\sqrt{2}}{2\alpha} r_j \left(\alpha_j \mathbf{C}^{(1)}(j) \right)^{(1)}$$

- g_J dependent on the outer part of the wave function
- Monitor the convergence of property as the active orbital set is increased

Example 1: $2s^2 2p^2$ in Fe XXI

```
------------------------------------
  J   P       n = 5            LSJ
                gJ
------------------------------------
  1   +     1.49752           1.5
  2   +     1.37712           1.5
  2   +     1.11603           1.0
------------------------------------
```

EM transition

$$\Gamma' J' M'$$

$$\Delta E = E(\Gamma' J') - E(\Gamma J)$$

$$gf, A, S$$

$$\Gamma J M$$

Computation of transition properties

- Transition properties, gf, A, S between two states $\Gamma' J' M'$ and $\Gamma J M$ written in terms of

$$\langle \Psi(\Gamma J M) | \mathcal{P} | \Psi(\Gamma' J' M') \rangle$$

- Transition operator depends on ΔE and the multipole, E1,M1,E2,M2 etc
- For EM transitions two gauges, length and velocity.
- Length gauge is the preferred one
- Consistency between gauges can be used as an uncertainty estimator

Computation of transition properties

- Change representation of left- and right hand side wave functions so that the orbitals of left side become biorthnormal to the ones at the right side
- Compute transition properties in the normal way (sum over expansion coefficients and integrals)
- Monitor the convergence of transition properties as the active orbital set is increased

Transitions $2p^63s^2\ ^1S - 2p^63s3p\ ^{1,3}P$ in Fe XV
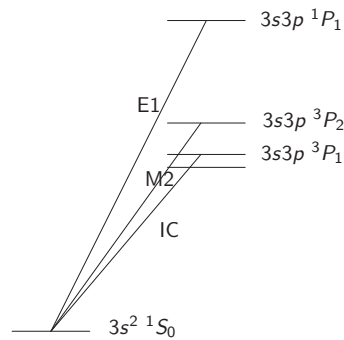
## Example 2: $2p^63s^2\ ^1S - 2p^63s3p\ ^{1,3}P$ in Fe XV

```
------------------------------------------------------------
          MR         n = 4       n = 5        n = 6
                        A (s-1)
------------------------------------------------------------
IC (L) 3.867+07     4.148+07    4.184+07     4.241+07
   (V) 3.934+07     4.349+07    4.385+07     4.478+07
E1 (L) 2.289+10     2.155+10    2.149+10     2.148+10
   (V) 2.332+10     2.169+10    2.165+10     2.169+10
M2     3.291+00     3.354+00    3.350+00     3.353+00
------------------------------------------------------------
```

Iso-electronic sequence

- Iso-electronic sequence, energies and properties as functions of Z
- Z parameter in

$$\mathcal{H}_{DC} = \sum_{i=1}^{N} \left(c\, \boldsymbol{\alpha}_i \cdot \mathbf{p}_i + V_{nuc}(r_i) + \beta_i c^2 \right) + \sum_{i>j}^{N} \frac{1}{r_{ij}}$$

  it follows that energies and properties should be smooth with respect to Z
- Based on hydrogenic approximations scaling laws can be worked pout

Iso-electronic sequences

Regularities along isoelectronic sequences

neutral	highly ionized
states arranged by nl	states arranged by n
correlation important	correlation relatively unimportant
relativistic effects small	relativistic and QED effects large
LSJ-coupling good	LSJ-coupling breaks down
IC transitions weak	IC transitions stronger
M1, E2, M2, E3 weak	M1, E2, M2, E3 more important

Iso-electronic sequence $2p^53s, 2p^53p, 2p^53d$

Iso-electronic sequence $2s^2\ ^1S - 2s2p\ ^{1,3}P$
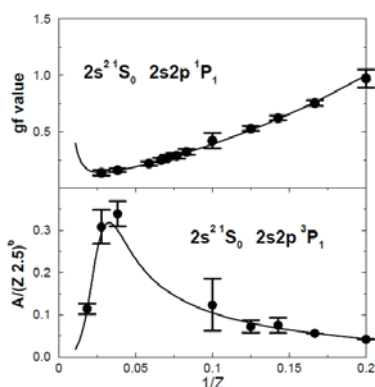
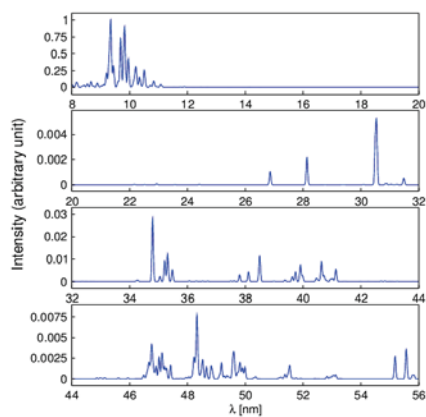Jönsson et al J. Phys B **31**, 3497 (1998).
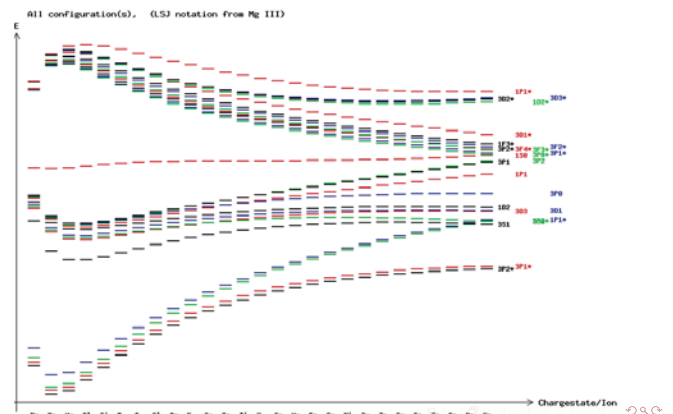
Spectrum calculations

- Spectrum calculations, simultaneous calculations of hundreds of states in different configurations
- Common calculation for the complex (or MR)
- Separate calculations for odd and even states
- Compute transitions between all states
- Apply model for population of states, generate synthetic spectra

Spectrum calculations

- Identify the configuration and states to be included (NIST tables, Chianti database etc)
- Generate all CSFs belonging to the above configurations
- Perform calculation for all states (even and odd) make sure that radial orbitals have correct number of nodes
- Perform separate MCDHF calculations for even and odd states, SD substitutions from configurations in the complex, generate CSFs from these configurations
- Final RCI calculations where the number of CSFs may be additionally increased to improve accuracy

Spectrum calculation for Na VII

Work in progress: Ekman, Jönsson, Träbert

- 67 lowest odd states belonging to
  $2s^2 2p$, $2p^3$, $2s^2 3p$, $2s2p3s$, $2s2p3d$, $2s^2 4p$, $2s^2 4f$, $2p^2 3p$, $2s2p4s$
- 66 lowest even states belonging to
  $2s2p^2$, $2s^2 3s$, $2s^2 3d$, $2s2p3p$, $2s^2 4s$, $2s^2 4d$, $2p^2 3s$, $2p^2 3d$.
- SD-substitutions to active orbital set up to $n = 10$
- 3 100 000 CSFs for each parity

Spectrum calculation for Na VII

- Good consistency with available energies, diff. < 0.02 %
- Some experimental energy levels are obviously wrong
- Some experimental energy levels have wrong labels
- Most experimental energy levels are missing

Example results

State	E_{RCI}	ΔE	E_{Koc}	ΔE	E_{exp}
$2s\,^2S\,2p\,^1P\,3s\,^2P^o_{1/2}$	1198244	-46	1198340	50	1198290
$2s\,^2S\,2p\,^1P\,3s\,^2P^o_{3/2}$	1198282	-8	1198372	82	1198290
$2s\,^2S\,2p\,^3P\,3d\,^2F^o_{5/2}$	1209815	-95	1210025	115	1209910
$2s\,^2S\,2p\,^3P\,3d\,^2F^o_{7/2}$	1211141	-99	1211326	86	1211240
$2s\,^2S\,2p\,^3P\,3d\,^2P^o_{3/2}$	1217038	-152	1217255	65	1217190
$2s\,^2S\,2p\,^3P\,3d\,^2P^o_{1/2}$	1217805	-145	1217961	11	1217950
$2s\,^2S\,2p\,^1P\,3p\,^2D_{3/2}$	1251929	259	1252070	400	1251670
$2s\,^2S\,2p\,^1P\,3p\,^2D_{5/2}$	1252084	74	1252215	205	1252010
$2s\,^2S\,2p\,^1P\,3p\,^2P_{1/2}$	1253401	51	1253544	194	1253350
$2s\,^2S\,2p\,^1P\,3p\,^2P_{3/2}$	1253800	20	1253937	157	1253780
$2s\,^2S\,2p\,^1P\,3p\,^2S_{1/2}$	1258410	-470	1259323	443	1258880
$2p^2(^1P)\,3P\,3s\,^4P_{1/2}$	1290926		1291009		
$2p^2(^1P)\,3P\,3s\,^4P_{3/2}$	1291676	1626	1291748	1698	1290050
$2s\,^2S\,2p\,^1P\,3d\,^2F^o_{7/2}$	1292639	309	1292916	586	1292330
$2s\,^2S\,2p\,^1P\,3d\,^2F^o_{5/2}$	1292643	313	1293153	823	1292330
$2p^2(^1P)\,3P\,3s\,^4S_{1/2}$	1292853	1273	1293190	1610	1291580
$2s\,^2S\,4s\,^2S_{1/2}$	1300068	5158			1294910
$2s\,^2S\,2p\,^1P\,3d\,^2D^o_{3/2}$	1303526	76	1303701	251	1303450?
$2s\,^2S\,2p\,^1P\,3d\,^2D^o_{5/2}$	1303727	117	1303885	275	1303610
$2s\,^2S\,2p\,^1P\,3d\,^2P^o_{1/2}$	1306511	41			1306470
$2s\,^2S\,2p\,^1P\,3d\,^2P^o_{3/2}$	1306704	234			1306470

Synthetic spectra

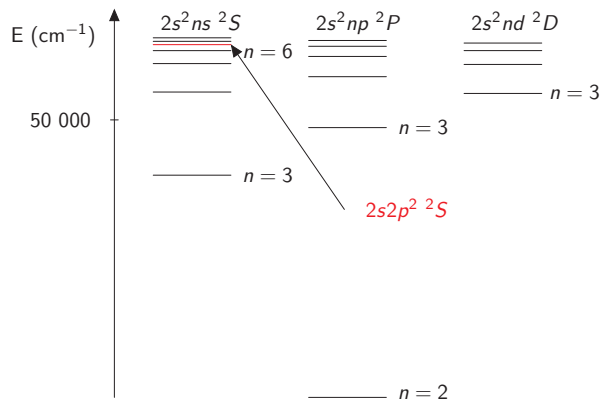## Challenges - complex shell structure

System with complex shell structure (many open shells)

- number of CSFs grows very rapidly with increasing active set
- only possible to account for valence correlation
- sometimes necessary to pick configurations one by one

Challenges - complex shell structure

Lowest even states belonging to $3s^2 3p^2$ in Si-like ions

- Configurations in complex
  $\{3s^2 3p^2,\ 3s^2 3d^2,\ 3s3p^2 3d,\ 3p^2 3d^2,\ 3p^4\}$
- n = 7, even : valence + core-valence 1 500 000 CSFs

Lowest odd states belonging to $3s3p^3$, $3s^2 3p3d$

- Configurations in complex
  $\{3s3p^3,\ 3s^2 3p3d,\ 3s3p3d^2,\ 3p^3 3d,\ 3p3d^3\}$
- n = 7, odd : valence + core-valence 4 600 000 CSFs

Perturbers and close degeneracies

- Rydberg series: quantum states where principal quantum number differs for one electron
- Perturber: quantum state with other charge distribution than the Rydberg states
- Perturber affects the properties of the Rydberg states

$2s2p^2$ perturber in $2s^2ns$ ^2S in B I

Experimental lifetimes in B I

State	Lifetime (ns)		Theory
	Experiment		
	This work	Others	This work
$2s^23s$ ^2S		4.0(2)[a]	3.97
$2s^24s$ ^2S		8.7(4)[a]	8.59
$2s^25s$ ^2S	11.0(6)		11.3
$2s^26s$ ^2S	7.7(4)		7.65
$2s2p^2$ ^2S	3.3(2)	3.6(3)[b]	3.65
$2s^27s$ ^2S	8.3(4)		8.01
$2s2p^2$ ^2D		23.1(2)[a]	26.4
$2s^23d$ ^2D		4.7(2)[a] 3.9(5)[b]	4.57
$2s^24d$ ^2D	10.3(5)	10.0(5)[a]	9.68
$2s^25d$ ^2D	17.5(8)		18.1
$2s^26d$ ^2D	31.5(2.0)		30.3

Lundberg et al PRA **63** 032505 (2001)

Future improvements

- ▶ Perturbative corrections to energies
- ▶ Use of PCFI: divide and conquer strategy that divides large calculations to a series of small ones. Allows close degeneracies to be handled more efficiently.
- ▶ Fine-tuning to deal with close degeneracies

Thank you for your attention