All-Order Methods in Relativistic Atomic Structure Theory

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Abstract

The single-double (SD) method, in which single and double excitations of the Hartree-Fock wave function are summed to all-orders in perturbation theory, is described.

– $\mathrm{N_D}$ Atomic Physics – 07/99

Outline

- Quick Review of Relativistic MBPT.
- Single-Double Equations.
- Reduction to 3-rd Order – Triples?
- Energies & Fine-Structure Intervals.
- Dipole Matrix Elements & Polarizabilities.
- Hyperfine Constants.
- PNC Amplitudes. under construction

Dirac Hamiltonian

One-electron atoms:

$$h_0 = c\,\boldsymbol{\alpha}\cdot\boldsymbol{p} + \beta mc^2 + U(r) + V_{\rm nuc}\,.$$

$$h_0\phi_i = \epsilon_i\phi_i$$

The spectrum of h_0 consists of electron bound states ($0 < \epsilon_i \le mc^2$), electron scattering states ($\epsilon_i > mc^2$) and positron states ($\epsilon_i < -mc^2$).

Many-electron atoms:

The *no-pair* Hamiltonian

is a many-electron generalization obtained from the field-theoretic Hamiltonian of QED by performing a contact transformation to eliminate the electron - photon interaction to order e^2.

The *no-pair* Hamiltonian[1] can be written

$$H = H_0 + V$$

$$H_0 = \sum_i \epsilon_i \, a_i^\dagger a_i$$

$$V = \frac{1}{2} \sum_{ijkl} v_{ijkl} \, a_i^\dagger a_j^\dagger a_l a_k - \sum_{ij} U_{ij} \, a_i^\dagger a_j \, ,$$

where,

1. the sums are restricted to electron states only,

2. v_{ijkl} is a two-particle matrix element of the sum of the Coulomb and Breit interactions,

3. U_{ij} compensates for including $U(r)$ in h_0.

[1] Brown, G.E. & Ravenhall, D.G. 1951 *Proc. R. Soc. London,* Ser. A **208**, 552-559.

MBPT (One Valence Electron)

Choose $U = V_{\rm DHF}$ then $\Psi^{(0)} = \Psi_{\rm DHF}$

$$\Psi = \Psi^{(0)} + \Psi^{(1)} + \ldots$$
$$E = E^{(0)} + E^{(1)} + \ldots$$

$$E_v^{(0)} = \epsilon_v$$
$$E_v^{(2)} = -\sum_{bmn} \frac{v_{mnvb}\tilde{v}_{vbmn}}{\epsilon_{mn} - \epsilon_{vb}} + \sum_{abn} \frac{v_{vnab}\tilde{v}_{abvn}}{\epsilon_{vn} - \epsilon_{ab}}$$
$$E_v^{(3)} = \sum_{bmnrs} \frac{\tilde{v}_{vbmn}v_{mnrs}v_{rsvb}}{(\epsilon_{vb} - \epsilon_{mn})(\epsilon_{vb} - \epsilon_{rs})}$$
$$+ \quad \cdots \quad \text{(11 more lines)}$$

($\epsilon_{ij} = \epsilon_i + \epsilon_j$, above)

The sums over virtual states $m, n, \ldots$ above are restricted to positive-energy states only.

Examples from MBPT

Table 1: MBPT energies (cm^{-1})

	K $(4s)$		Cs $(6s)$	
k	$E^{(k)}$	$\Delta^{(k)}$	$E^{(k)}$	$\Delta^{(k)}$
0	32370	2640	27954	3453
2	35104	-94	31865	-458
3	34655	355	30529	878
$Expt.$	35010		31407	

- Perturbation theory oscillates back and forth without signs of convergence.

- It is necessary to go beyond 3rd-order MBPT.

Single-Double Equations

$$\Psi_v = \Psi_{\rm DHF} + \delta\Psi$$

$$\delta\Psi = \left\{ \sum_{am} \rho_{ma}\, a_m^\dagger a_a + \frac{1}{2}\sum_{abmn} \rho_{mnab}\, a_m^\dagger a_n^\dagger a_b a_a \right.$$

$$\left. + \sum_{m\neq v} \rho_{mv}\, a_m^\dagger a_v + \sum_{bmn} \rho_{mnvb}\, a_m^\dagger a_n^\dagger a_b a_v \right\} \Psi_{\rm HF}$$

$$E_C = E_C^{\rm HF} + \delta E_C$$

$$E_v = E_v^{\rm HF} + \delta E_v$$

Later, we will discuss triples

Core Excitation Equations

$$(\epsilon_a - \epsilon_m)\rho_{ma} = \sum_{bn} \tilde{v}_{mban}\rho_{nb}$$

$$+ \sum_{bnr} v_{mbnr}\tilde{\rho}_{nrab} - \sum_{bcn} v_{bcan}\tilde{\rho}_{mnbc}$$

$$(\epsilon_a + \epsilon_b - \epsilon_m - \epsilon_n)\rho_{mnab} = v_{mnab}$$

$$+ \sum_{cd} v_{cdab}\rho_{mncd} + \sum_{rs} v_{mnrs}\rho_{rsab}$$

$$+ \Big[\sum_{r} v_{mnrb}\rho_{ra} - \sum_{c} v_{cnab}\rho_{mc} + \sum_{rc} \tilde{v}_{cnrb}\tilde{\rho}_{mrac}\Big]$$

$$+ \left[\ a \leftrightarrow b \quad m \leftrightarrow n\ \right]$$

$$\delta E_C = \frac{1}{2}\sum_{abmn} v_{abmn}\tilde{\rho}_{mnab}$$

$\approx$ 15,000,000 ρ_{mnab} coefficients for Cs ($\ell = 6$).

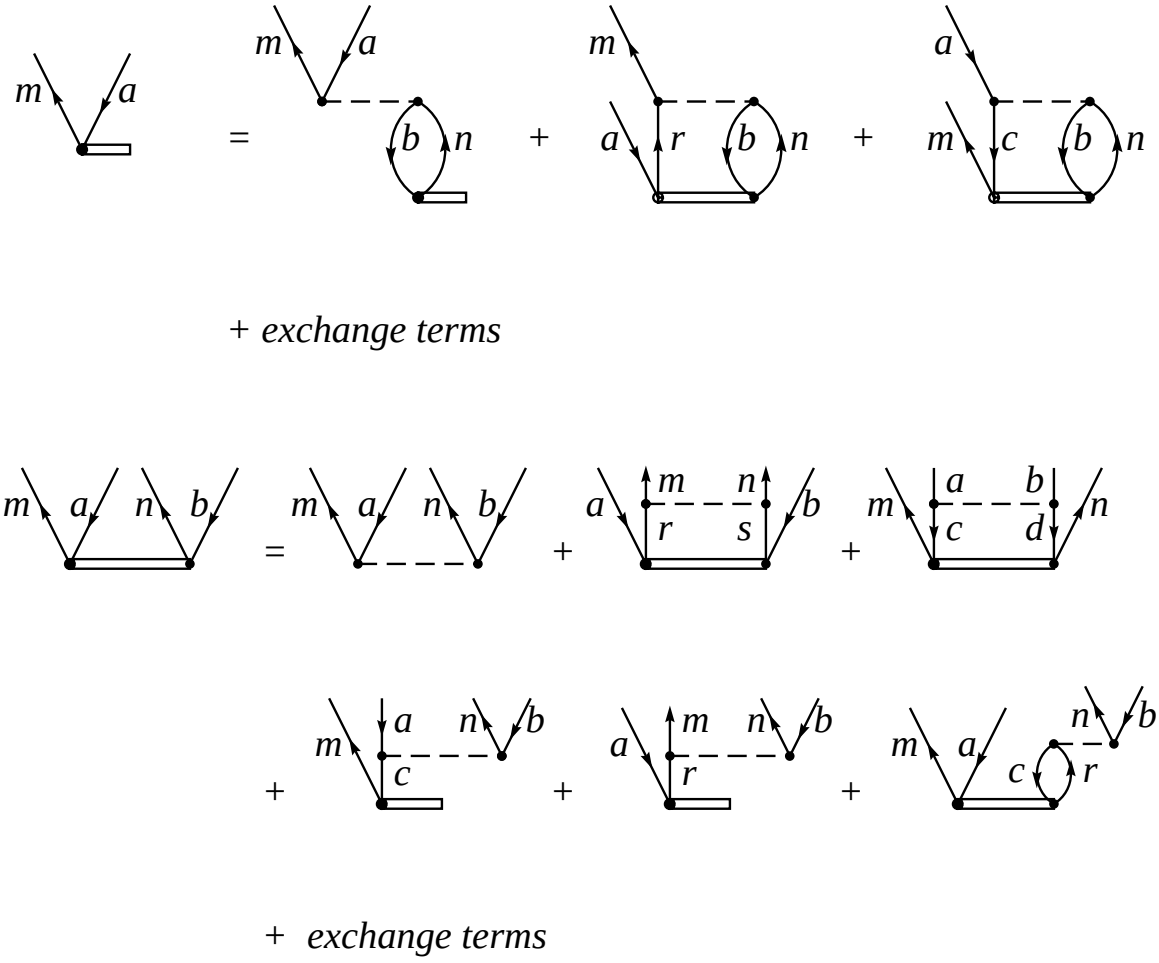

Figure 1: Brueckner-Goldstone Diagrams for the core SD equations.

Valence Equations

$$(\epsilon_v - \epsilon_m + \delta E_v)\rho_{mv} = \sum_{bn} \tilde{v}_{mbvn}\rho_{nb}$$
$$+ \sum_{bnr} v_{mbnr}\tilde{\rho}_{nrvb} - \sum_{bcn} v_{bcvn}\tilde{\rho}_{mnbc}$$

$$(\epsilon_v + \epsilon_b - \epsilon_m - \epsilon_n + \delta E_v)\rho_{mnvb} = v_{mnvb}$$
$$+ \sum_{cd} v_{cdvb}\rho_{mncd} + \sum_{rs} v_{mnrs}\rho_{rsvb}$$
$$+ \Big[\sum_{r} v_{mnrb}\rho_{rv} - \sum_{c} v_{cnvb}\rho_{mc} + \sum_{rc} \tilde{v}_{cnrb}\tilde{\rho}_{mrvc}\Big]$$
$$+ \left[\ v \leftrightarrow b \quad m \leftrightarrow n\ \right]$$

$$\delta E_v = \sum_{ma} \tilde{v}_{vavm}\rho_{ma} + \sum_{mab} v_{abvm}\tilde{\rho}_{mvab}$$
$$+ \sum_{mna} v_{vbmn}\tilde{\rho}_{mnvb}$$

$\approx$ 1,000,000 ρ_{mnvb} coefficients for each state (Cs)

Expansion of Core Energy

Second-Order

$$\begin{aligned} \rho^{(1)}_{mnab} &= \frac{v_{mnab}}{\epsilon_a + \epsilon_b - \epsilon_m - \epsilon_n} \\ \rho^{(1)}_{ma} &= 0 \end{aligned}$$

From these, it follows

$$\delta E^{(2)}_C = \frac{1}{2} \sum_{mnab} \frac{v_{abmn} \tilde{v}_{mnab}}{\epsilon_a + \epsilon_b - \epsilon_m - \epsilon_n}$$

- δE_C agrees with MBPT through second-order.

Third-Order

$$\rho^{(2)}_{mnab} = \frac{1}{\epsilon_{ab} - \epsilon_{mn}} \left\{ \sum_{cd} \frac{v_{cdab} v_{mncd}}{\epsilon_{cd} - \epsilon_{mn}} + \sum_{rs} \frac{v_{mnrs} v_{rsab}}{\epsilon_{ab} - \epsilon_{rs}} + \left[\sum_{rc} \frac{\tilde{v}_{cnrb} \tilde{v}_{mrac}}{\epsilon_{ac} - \epsilon_{mr}} + \left(\begin{array}{c} a \leftrightarrow b \\ m \leftrightarrow n \end{array} \right) \right] \right\}$$

We find

$$\delta E^{(3)}_c = \frac{1}{2} \sum_{mnabcd} \frac{\tilde{v}_{abmn} v_{cdab} v_{mncd}}{(\epsilon_{ab} - \epsilon_{mn})(\epsilon_{cd} - \epsilon_{mn})} + \frac{1}{2} \sum_{abmnrs} \frac{\tilde{v}_{abmn} v_{mnrs} v_{rsab}}{(\epsilon_{ab} - \epsilon_{mn})(\epsilon_{ab} - \epsilon_{rs})} + \sum_{abcmnr} \frac{\tilde{v}_{abmn} \tilde{v}_{cmbr} \tilde{v}_{nrac}}{(\epsilon_{ab} - \epsilon_{mn})(\epsilon_{ac} - \epsilon_{nr})}$$

- δE_C agrees with MBPT through third-order.

Expansion of Valence Energy

Second-order

$$\begin{aligned} \rho^{(1)}_{mnvb} &= \frac{v_{mnvb}}{\epsilon_v + \epsilon_b - \epsilon_m - \epsilon_n} \\ \rho^{(1)}_{mv} &= 0 \end{aligned}$$

From these it follows

$$\delta E^{(2)}_v = \sum_{mab} \frac{v_{abvm}\tilde{v}_{mvab}}{\epsilon_{ab} - \epsilon_{mv}} + \sum_{mna} \frac{v_{vbmn}\tilde{v}_{mnvb}}{\epsilon_{vb} - \epsilon_{mn}}$$

- δE_v agrees with MBPT through second order.

$$\delta E_v^{(3)} =$$

$$\sum_{mabcd} \frac{\tilde{v}_{abvm} v_{cdab} v_{mvcd}}{(\epsilon_{ab} - \epsilon_{vm})(\epsilon_{cd} - \epsilon_{mv})} + \sum_{mabrs} \frac{\tilde{v}_{abvm} v_{mvrs} v_{rsab}}{(\epsilon_{ab} - \epsilon_{vm})(\epsilon_{ab} - \epsilon_{rs})}$$

$$+ \sum_{mabcr} \frac{\tilde{v}_{abvm} \tilde{v}_{cvrb} \tilde{v}_{mrac}}{(\epsilon_{ab} - \epsilon_{vm})(\epsilon_{ac} - \epsilon_{mr})} + \sum_{mabcr} \frac{\tilde{v}_{abvm} \tilde{v}_{cmra} \tilde{v}_{vrbc}}{(\epsilon_{ab} - \epsilon_{vm})(\epsilon_{bc} - \epsilon_{vr})}$$

$$+ \sum_{mabnr} \frac{\tilde{v}_{vavm} v_{mbnr} \tilde{v}_{nrab}}{(\epsilon_{a} - \epsilon_{m})(\epsilon_{ab} - \epsilon_{nr})} - \sum_{mabcn} \frac{\tilde{v}_{vavm} v_{bcan} \tilde{v}_{mnbc}}{(\epsilon_{a} - \epsilon_{m})(\epsilon_{bc} - \epsilon_{mn})}$$

$$+ \sum_{mnbcd} \frac{\tilde{v}_{vbmn} v_{cdvb} v_{mncd}}{(\epsilon_{vb} - \epsilon_{mn})(\epsilon_{cd} - \epsilon_{mn})} + \sum_{mnbrs} \frac{\tilde{v}_{vbmn} v_{mnrs} v_{rsvb}}{(\epsilon_{vb} - \epsilon_{mn})(\epsilon_{vb} - \epsilon_{rs})}$$

$$+ \sum_{mnbrc} \frac{\tilde{v}_{vbmn} \tilde{v}_{cnrb} \tilde{v}_{mrvc}}{(\epsilon_{vb} - \epsilon_{mn})(\epsilon_{vc} - \epsilon_{mr})} + \sum_{mnbrc} \frac{\tilde{v}_{vbmn} \tilde{v}_{cmrv} \tilde{v}_{nrbc}}{(\epsilon_{vb} - \epsilon_{mn})(\epsilon_{bc} - \epsilon_{nr})}$$

- $\delta E_v^{(3)}$ disagrees with $E_v^{(3)}$ from MBPT!!

Add triple excitations to wave function

$$\frac{1}{6}\sum_{abmnr}\rho_{mnrvab}a_m^\dagger a_n^\dagger a_r^\dagger a_v a_b a_a\,\Psi_{\rm HF}$$

$$E_{v\,\rm extra}=\frac{1}{2}\sum_{mnab}\tilde{v}_{abmn}\rho_{mnvvab}$$

$$E^{(3)}_{v\,\rm extra}=$$

$$\sum_{mnabc}\frac{\tilde{v}_{abmn}\tilde{v}_{cmav}\tilde{v}_{nvbc}}{(\epsilon_{ab}-\epsilon_{mn})\,(\epsilon_{bc}-\epsilon_{nv})}+\sum_{mnabs}\frac{\tilde{v}_{abmn}\tilde{v}_{nvas}\tilde{v}_{msvb}}{(\epsilon_{ab}-\epsilon_{mn})\,(\epsilon_{vb}-\epsilon_{ms})}$$

$$+\sum_{mnabc}\frac{v_{abmn}\tilde{v}_{cvbv}\tilde{v}_{mnca}}{(\epsilon_{ab}-\epsilon_{mn})\,(\epsilon_{ca}-\epsilon_{mn})}+\sum_{mnabs}\frac{v_{abmn}\tilde{v}_{mvsv}\tilde{v}_{nsba}}{(\epsilon_{ab}-\epsilon_{mn})\,(\epsilon_{ab}-\epsilon_{ns})}$$

$$+\sum_{mnabs}\frac{v_{abmn}\tilde{v}_{mnvs}v_{vsba}}{(\epsilon_{ab}-\epsilon_{mn})\,(\epsilon_{ab}-\epsilon_{vs})}+\sum_{mnabc}\frac{v_{abmn}\tilde{v}_{cvba}v_{mnvc}}{(\epsilon_{ab}-\epsilon_{mn})\,(\epsilon_{vc}-\epsilon_{mn})}$$

$$+\sum_{mnabc}\frac{v_{abmn}\tilde{v}_{cmab}\tilde{v}_{vnvc}}{(\epsilon_{ab}-\epsilon_{mn})\,(\epsilon_c-\epsilon_n)}+\sum_{mnabs}\frac{v_{abmn}\tilde{v}_{mnas}\tilde{v}_{vsvb}}{(\epsilon_{ab}-\epsilon_{mn})\,(\epsilon_b-\epsilon_s)}$$

- $\delta E_v^{(3)}+E^{(3)}_{v\,\rm extra}$ gives the entire third-order valence correlation energy

$$E_v^{(3)} = \delta E_v^{(3)} + E_{v\ \mathrm{extra}}^{(3)}$$

Table 2: Na $3s$ and $3p$ states (a.u.)

Term	$3s_{1/2}$	$3p_{1/2}$	$3p_{3/2}$
$\delta E_v^{(3)}$	-3.446[-4]	-1.454[-4]	-1.449[-4]
$E_{v\ \mathrm{extra}}^{(3)}$	-0.418[-4]	-0.070[-4]	-0.072[-4]
$E_v^{(3)}$	-3.865[-4]	-1.525[-4]	-1.521[-4]

Correlation Energy

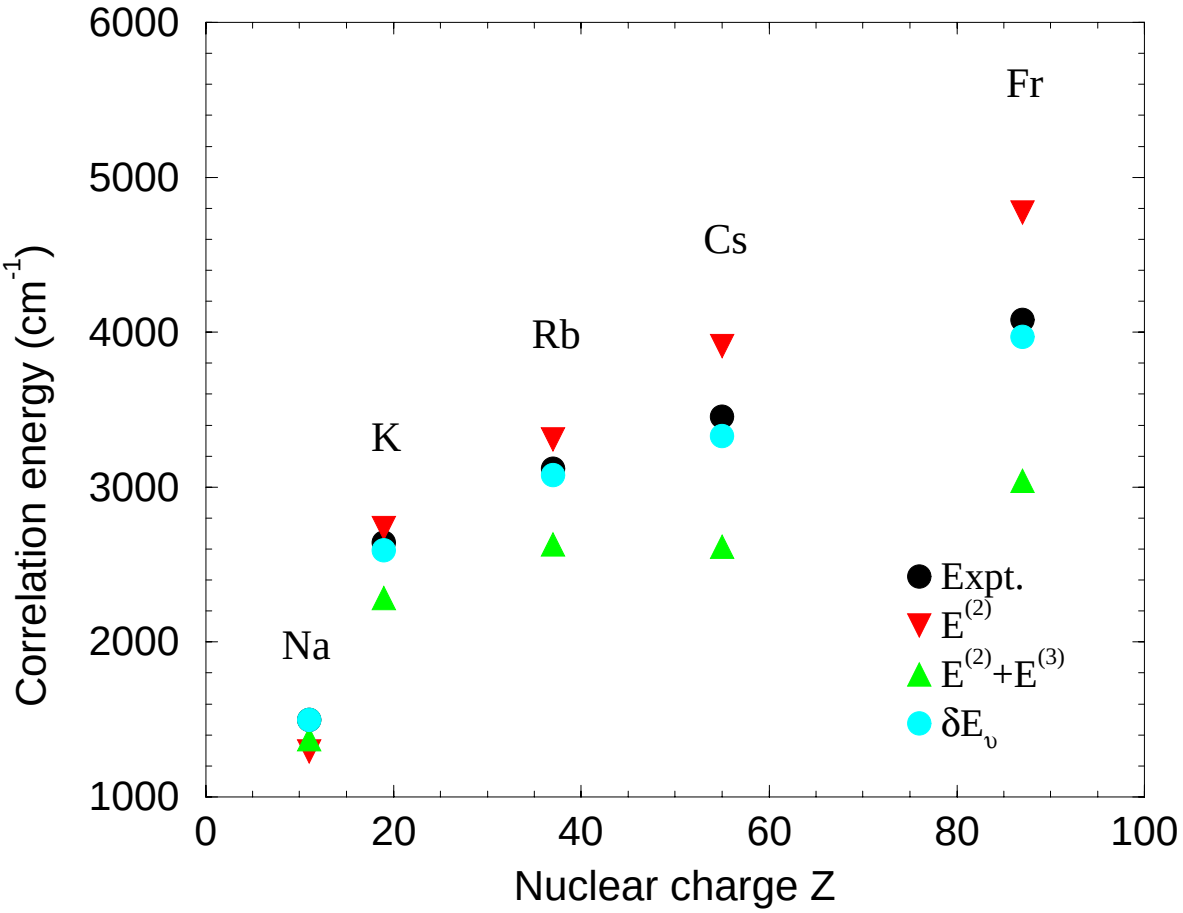

Figure 2: Energy comparisons for alkali-metal atoms.

Higher-order terms

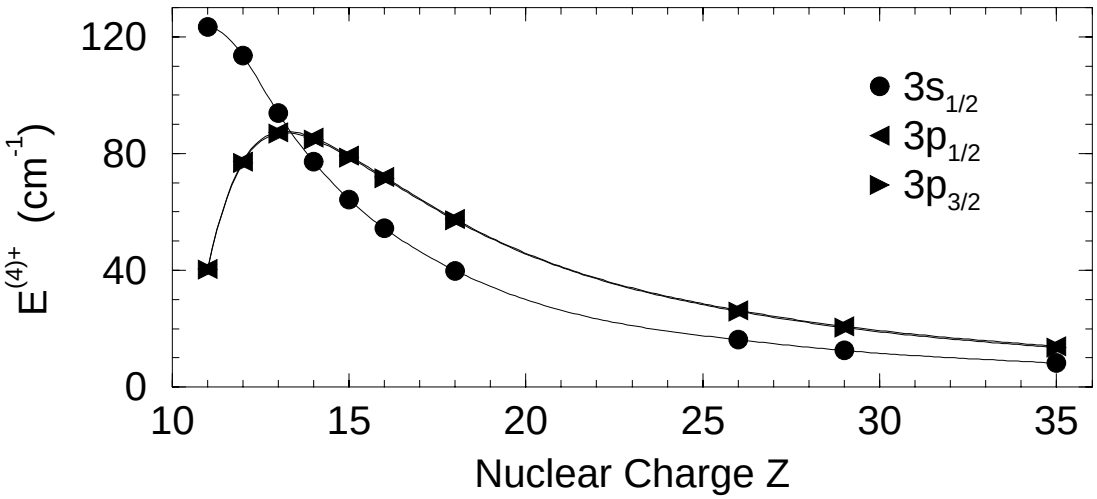

Figure 3: Contributions beyond 3rd-order for Na-like ions.

- $E^{(4)+} < 1\%$ of correlation energy for $Z > 20$

All-order energies

Table 3: Summary for sodium $3s$ and $3p$ states (cm^{-1})

Term	$3s$	$3p_{1/2}$	$3p_{3/2}$
DHF	-39951.6	-24030.4	-24014.1
δE	-1488.8(4)	-463.9	-461.6
$E^{(3)}_{\mathrm{extra}}$	-9.2	-1.5	-1.6
Breit	1.2	1.4	0.1
RM+MP	1.0	0.5	0.5
Theory	-41447.3(4)	-24493.9	-24476.7
Expt.	-41449.4	-24493.3	-24476.1

Results for Heavy Atoms

Table 4: Energies for cesium and francium cm^{-1}

Cs	$6s$	$7s$	$8s$	$9s$
Theory	31262	12801	7060	4479
Expt.	31407	12871	7089	4496
Cs	$6p_{1/2}$	$7p_{1/2}$	$8p_{1/2}$	$9p_{1/2}$
Theory	20204	9621	5687	3760
Expt.	20228	9641	5698	3769
Fr	$7s$	$8s$	$9s$	$10s$
Theory	32735	13051	7148	4522
Expt.	32849	13106	7168	4538
Fr	$7p_{1/2}$	$8p_{1/2}$	$9p_{1/2}$	$10p_{1/2}$
Theory	20583	9712	5724	3782
Expt.	20612	9736	*5738*	*3795*

Fine Structure Intervals

Table 5: Fine-structure for Na-like ions (cm^{-1})

Z	$3p_{3/2} - 3p_{1/2}$	
	Theory	NIST
11	17.15	17.20
12	91.33	91.57
13	233.13	233.67
14	459.93	461.10
15	793.96	795.38
16	1260.53	1264.10

Table 6: Fine-structure in alkali-metal atoms (cm^{-1}).

		This work	Expt.
K	$4p_{3/2} - 4p_{1/2}$	57.3	57.7
	$5p_{3/2} - 5p_{1/2}$	18.5	18.8
	$6p_{3/2} - 6p_{1/2}$	8.5	8.4
	$7p_{3/2} - 7p_{1/2}$	4.4	4.5
Rb	$5p_{3/2} - 5p_{1/2}$	236.5	237.6
	$6p_{3/2} - 6p_{1/2}$	76.5	77.5
	$7p_{3/2} - 7p_{1/2}$	34.8	35.1
	$8p_{3/2} - 8p_{1/2}$	18.6	18.9
Cs	$6p_{3/2} - 6p_{1/2}$	552.2	554.1
	$7p_{3/2} - 7p_{1/2}$	178.6	181.0
	$8p_{3/2} - 8p_{1/2}$	81.4	82.6
	$9p_{3/2} - 9p_{1/2}$	43.9	44.7
Fr	$7p_{3/2} - 7p_{1/2}$	1676	1687
	$8p_{3/2} - 8p_{1/2}$	536	545
	$9p_{3/2} - 9p_{1/2}$	244	*250*
	$10p_{3/2} - 10p_{1/2}$	132	*136*

Transitions

$$\langle w|\left[\sum_{ij} z_{ij}\, a_i^\dagger a_j\right]|v\rangle = \frac{z_{wv} + \sum_{i=a}^{t} Z_{wv}^{(i)}}{N_w N_v}$$

where

$$\begin{aligned}
Z_{wv}^{(a)} &= \sum_{am} z_{am}\tilde{\rho}_{wmva} + \text{c.c.} \quad \text{(RPA)} \\
Z_{wv}^{(b)} &= -\sum_{a} z_{av}\rho_{wa} + \text{c.c.} \\
Z_{wv}^{(c)} &= \sum_{m} z_{wm}\rho_{mv} + \text{c.c.} \qquad \text{(BO)} \\
&\cdots \quad \text{(15 similar terms)} \\
Z_{wv}^{(s)} &= -\sum_{abmn} \rho^*_{nmwa} z_{bv}\tilde{\rho}_{mnab} + \text{c.c.} \\
Z_{wv}^{(t)} &= -\sum_{abmn} \rho^*_{mnba} z_{mv}\tilde{\rho}_{nwab} + \text{c.c.}
\end{aligned}$$

Matrix elements are complete through 3rd order!

Dipole Transitions

Table 7: Matrix Elements for heavy alkali metals (a.u.)

	K	Rb	Cs	Fr
$p_{1/2}$–s	$n=4$	$n=5$	$n=6$	$n=7$
SD	4.098	4.221	4.478	4.256
Expt.	4.102(5)	4.231(3)	4.489(7)	4.277(8)
$p_{3/2}$–s	$n=4$	$n=5$	$n=6$	$n=7$
SD	5.794	5.956	6.298	5.851
Expt.	5.800(8)	5.977(4)	6.324(7)	5.898(15)

Polarizabilities

For a valence s state:

$$\begin{aligned}
\alpha_v &= \frac{1}{3}\sum_m \left(\frac{|\langle v||z||mp_{1/2}\rangle|^2}{E_{mp_{1/2}} - E_v} + \frac{|\langle v||z||mp_{3/2}\rangle|^2}{E_{mp_{3/2}} - E_v} \right) \\
\alpha_c &= \frac{2}{3}\sum_{ma} \frac{|\langle a||z||m\rangle|^2}{E_m - E_a} \\
\alpha_{vc} &= \frac{1}{3}\sum_a \frac{|\langle a||z||v\rangle|^2}{E_a - E_v}
\end{aligned}$$

Table 8: Static polarizabilities (a.u.) of alkali-metal atoms.

	Na	K	Rb	Cs	Fr
$\alpha_v^{\rm main}$	162.06	284.70	308.43	383.8	294.0
$\alpha_v^{\rm tail}$	0.08	0.07	0.14	0.2	1.4
α_c	0.95	5.46	9.08	15.8	20.4
α_{vc}	-0.02	-0.13	-0.26	-0.5	-0.9
α^{SD}	163.07	290.10	317.39	399.3	314.9
Recom.	162.6(3)	290.2(8)	318.6(6)	399.9(1.9)	317.8(2.4)
Expt.	162.7(8)	293.6(6.1)	319.9(6.1)	403.6(8.1)	

Hyperfine Interaction

Table 9: ^{23}Na hyperfine constants A (MHz)

	$3s_{1/2}$	$3p_{1/2}$	$3p_{3/2}$
DHF	623.5	63.39	12.59
SD	888.1	94.99	18.84
SD (Liu)	884.5	92.4	19.3
CI	882.2	94.04	18.80
CCSD	883.8	93.02	18.318
MBPT	860.9	91.40	19.80
Expt.	885.81	94.44(13)	18.534(12)

^{23}Na quadrupole hyperfine constant B (MHZ):

$(B/Q)_{\rm SD} = 26.85$ (MHz/barn)

$B_{\rm expt} = 2.724(30)$MHz $\Longrightarrow Q = 101.4(11)$ mb

Muonic atom experiments give $Q = 100.6(20)$ mb.

Summary

The SD theory gives:

- Removal energies: 1–100 cm^{-1}
- Fine-structure intervals: 0.5%
- Transition Amplitudes: 0.3 – 1%
- Polarizabilities: 0.1 – 1%
- Hyperfine constants: 0.1 – 1%
- PNC in cesium and francium: ???