

Precise Relativistic many-body calculations for alkali-metal atoms

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Abstract

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

Why this project?

1. Relativistic effects in atoms can be large.
2. Correlation effects in alkali-metals can be large.
3. Precise *ab-initio* theory is needed in PNC studies.

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. (Safronova thesis project)

Dirac Hamiltonian

One-electron atoms:

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

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

The spectrum of h_0 consists of electron bound states ($0 < \epsilon_i \leq mc^2$), 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* Hamiltonian¹ 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 .

¹BROWN, G.E. & RAVENHALL, D.G. 1951 *Proc. R. Soc. London, Ser. A* **208**, 552-559.

MBPT (One Valence Electron)

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

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

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

$$E_v^{(0)} = \epsilon_v$$

$$E_v^{(2)} = - \sum_{bmn} \frac{v_{mnb} \tilde{v}_{vbmn}}{\epsilon_{mn} - \epsilon_{vb}} + \sum_{abn} \frac{v_{nab} \tilde{v}_{abvn}}{\epsilon_{vn} - \epsilon_{ab}}$$

$$E_v^{(3)} = \sum_{bmnrs} \frac{\tilde{v}_{vbmn} v_{mnr} v_{rsb}}{(\epsilon_{vb} - \epsilon_{mn})(\epsilon_{vb} - \epsilon_{rs})}$$

+ ... (11 more lines)

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

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

Examples from MBPT

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

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

- Perturbation theory oscillates back and forth without signs of convergence.
- It is necessary to go beyond 3rd-order MBPT to obtain energies accurate to $\sim 1\%$.

Single-Double Equations

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

$$\delta\Psi = \left\{ \begin{aligned} &\sum_{am} \rho_{ma} a_m^\dagger a_a + \frac{1}{2} \sum_{abmn} \rho_{mnab} a_m^\dagger a_n^\dagger a_b a_a \\ &+ \sum_{m \neq v} \rho_{mv} a_m^\dagger a_v + \sum_{bmn} \rho_{mnbv} a_m^\dagger a_n^\dagger a_b a_v \end{aligned} \right\} \Psi_{\text{DHF}}$$

$$E_C = E_C^{\text{DHF}} + \delta E_C$$

$$E_v = E_v^{\text{DHF}} + \delta E_v$$

Later, we will discuss triples

Core Excitation Equations

$$\begin{aligned}
 (\epsilon_a - \epsilon_m)\rho_{ma} &= \sum_{bn} \tilde{v}_{mban}\rho_{nb} \\
 &+ \sum_{bnr} v_{mbnr}\tilde{\rho}_{nrab} - \sum_{bcn} v_{bcan}\tilde{\rho}_{mncb}
 \end{aligned}$$

$$\begin{aligned}
 (\epsilon_a + \epsilon_b - \epsilon_m - \epsilon_n)\rho_{mnab} &= v_{mnab} \\
 &+ \sum_{cd} v_{cdab}\rho_{mncd} + \sum_{rs} v_{mnr s}\rho_{rsab} \\
 &+ \left[\sum_r v_{mnr b}\rho_{ra} - \sum_c v_{cnab}\rho_{mc} + \sum_{rc} \tilde{v}_{cnrb}\tilde{\rho}_{mrac} \right] \\
 &+ [a \leftrightarrow b \quad m \leftrightarrow n]
 \end{aligned}$$

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

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

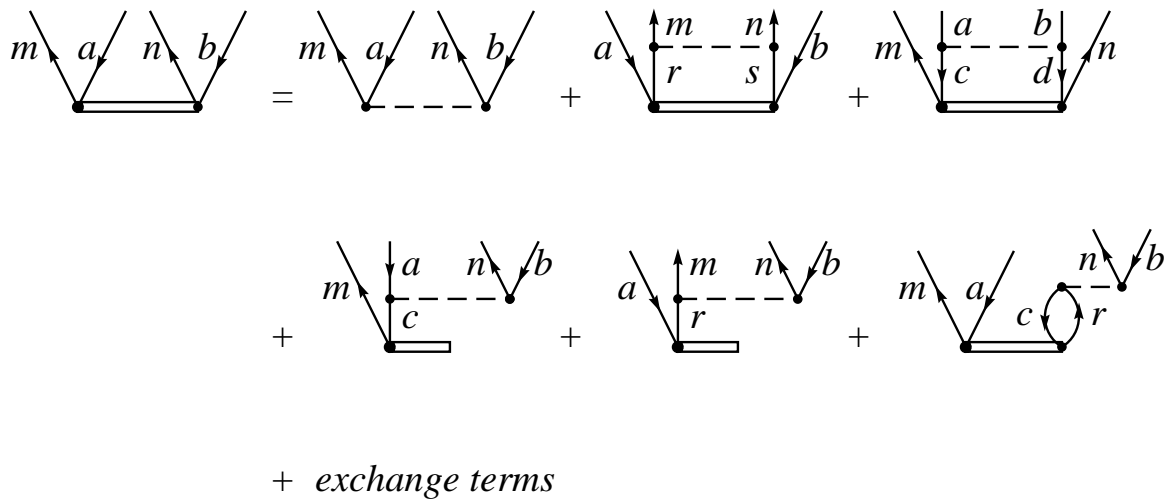
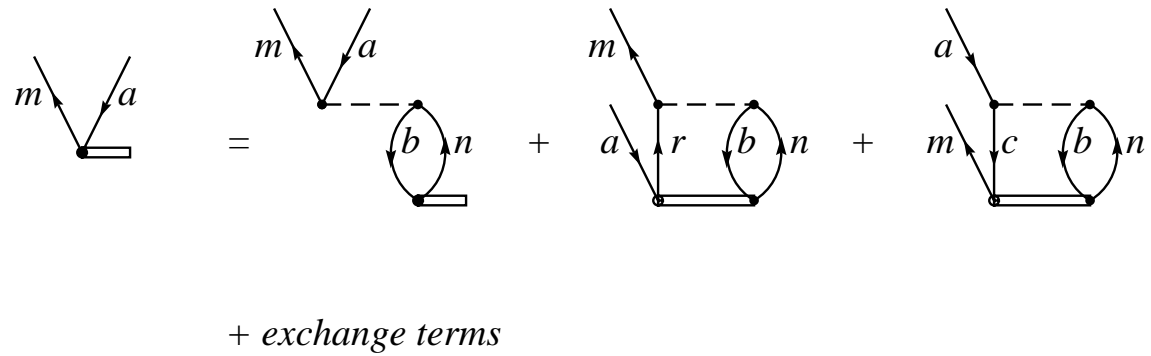


Figure 1: Brueckner-Goldstone Diagrams for the core SD equations.

Valence Equations

$$\begin{aligned}
 (\epsilon_v - \epsilon_m + \delta E_v) \rho_{mv} &= \sum_{bn} \tilde{v}_{mbvn} \rho_{nb} \\
 &+ \sum_{bnr} v_{mbnr} \tilde{\rho}_{nrub} - \sum_{bcn} v_{bcvn} \tilde{\rho}_{mnb}
 \end{aligned}$$

$$\begin{aligned}
 (\epsilon_v + \epsilon_b - \epsilon_m - \epsilon_n + \delta E_v) \rho_{mnvb} &= v_{mnvb} \\
 &+ \sum_{cd} v_{cdvb} \rho_{mncd} + \sum_{rs} v_{mnrsv} \rho_{rsvb} \\
 &+ \left[\sum_r v_{mnrsv} \rho_{rv} - \sum_c v_{cnvb} \rho_{mc} + \sum_{rc} \tilde{v}_{cnrb} \tilde{\rho}_{mrv} \right] \\
 &+ [v \leftrightarrow b \quad m \leftrightarrow n]
 \end{aligned}$$

$$\begin{aligned}
 \delta E_v &= \sum_{ma} \tilde{v}_{vavm} \rho_{ma} + \sum_{mab} v_{abvm} \tilde{\rho}_{mvab} \\
 &+ \sum_{mna} v_{vbmna} \tilde{\rho}_{mnvb}
 \end{aligned}$$

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

Expansion of Core Energy

Second-Order

$$\rho_{mnab}^{(1)} = \frac{v_{mnab}}{\epsilon_a + \epsilon_b - \epsilon_m - \epsilon_n}$$

$$\rho_{ma}^{(1)} = 0$$

From these, it follows

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

- δE_C agrees with MBPT through second-order.

Third-Order

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

We find

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

- δE_C agrees with MBPT through third-order.

Expansion of Valence Energy

Second-order

$$\rho_{mnbv}^{(1)} = \frac{v_{mnbv}}{\epsilon_v + \epsilon_b - \epsilon_m - \epsilon_n}$$

$$\rho_{mv}^{(1)} = 0$$

From these it follows

$$\delta E_v^{(2)} = \sum_{mab} \frac{v_{abvm} \tilde{v}_{mvab}}{\epsilon_{ab} - \epsilon_{mv}} + \sum_{mna} \frac{v_{vbm n} \tilde{v}_{mnbv}}{\epsilon_{vb} - \epsilon_{mn}}$$

- δE_v agrees with MBPT through second order.

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

$$\begin{aligned} & \sum_{mabcd} \frac{\tilde{v}_{abvm} v_{cdab} v_{mvcd}}{(\epsilon_{ab} - \epsilon_{vm})(\epsilon_{cd} - \epsilon_{mv})} + \sum_{mabrs} \frac{\tilde{v}_{abvm} v_{mvrs} v_{rsab}}{(\epsilon_{ab} - \epsilon_{vm})(\epsilon_{ab} - \epsilon_{rs})} \\ & + \sum_{mabcr} \frac{\tilde{v}_{abvm} \tilde{v}_{cvrb} \tilde{v}_{mrac}}{(\epsilon_{ab} - \epsilon_{vm})(\epsilon_{ac} - \epsilon_{mr})} + \sum_{mabcr} \frac{\tilde{v}_{abvm} \tilde{v}_{cmra} \tilde{v}_{vrbc}}{(\epsilon_{ab} - \epsilon_{vm})(\epsilon_{bc} - \epsilon_{vr})} \\ & + \sum_{mabnr} \frac{\tilde{v}_{vavm} v_{mbnr} \tilde{v}_{nrab}}{(\epsilon_a - \epsilon_m)(\epsilon_{ab} - \epsilon_{nr})} - \sum_{mabcn} \frac{\tilde{v}_{vavm} v_{bcan} \tilde{v}_{mnbc}}{(\epsilon_a - \epsilon_m)(\epsilon_{bc} - \epsilon_{mn})} \\ & + \sum_{mnbcd} \frac{\tilde{v}_{vbm n} v_{cdvb} v_{mncd}}{(\epsilon_{vb} - \epsilon_{mn})(\epsilon_{cd} - \epsilon_{mn})} + \sum_{mnbrs} \frac{\tilde{v}_{vbm n} v_{mnr s} v_{rsvb}}{(\epsilon_{vb} - \epsilon_{mn})(\epsilon_{vb} - \epsilon_{rs})} \\ & + \sum_{mnbrc} \frac{\tilde{v}_{vbm n} \tilde{v}_{cnrb} \tilde{v}_{mrvc}}{(\epsilon_{vb} - \epsilon_{mn})(\epsilon_{vc} - \epsilon_{mr})} + \sum_{mnbrc} \frac{\tilde{v}_{vbm n} \tilde{v}_{cmrv} \tilde{v}_{nrbc}}{(\epsilon_{vb} - \epsilon_{mn})(\epsilon_{bc} - \epsilon_{nr})} \end{aligned}$$

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

Add triple excitations to wave function

$$\frac{1}{6} \sum_{abmnr} \rho_{mnr} v_{ab} a_m^\dagger a_n^\dagger a_r^\dagger a_v a_b a_a \Psi_{\text{HF}}$$

$$E_{v \text{ extra}} = \frac{1}{2} \sum_{mnab} \tilde{v}_{abmn} \rho_{mnr} v_{ab}$$

$$E_{v \text{ extra}}^{(3)} =$$

$$\begin{aligned} & \sum_{mnabc} \frac{\tilde{v}_{abmn} \tilde{v}_{cmav} \tilde{v}_{nvbc}}{(\epsilon_{ab} - \epsilon_{mn})(\epsilon_{bc} - \epsilon_{nv})} + \sum_{mnabs} \frac{\tilde{v}_{abmn} \tilde{v}_{nvas} \tilde{v}_{msvb}}{(\epsilon_{ab} - \epsilon_{mn})(\epsilon_{vb} - \epsilon_{ms})} \\ & + \sum_{mnabc} \frac{v_{abmn} \tilde{v}_{cvbv} \tilde{v}_{mnca}}{(\epsilon_{ab} - \epsilon_{mn})(\epsilon_{ca} - \epsilon_{mn})} + \sum_{mnabs} \frac{v_{abmn} \tilde{v}_{mvsv} \tilde{v}_{nsba}}{(\epsilon_{ab} - \epsilon_{mn})(\epsilon_{ab} - \epsilon_{ns})} \\ & + \sum_{mnabs} \frac{v_{abmn} \tilde{v}_{mnvs} v_{vsba}}{(\epsilon_{ab} - \epsilon_{mn})(\epsilon_{ab} - \epsilon_{vs})} + \sum_{mnabc} \frac{v_{abmn} \tilde{v}_{cvba} v_{mnvc}}{(\epsilon_{ab} - \epsilon_{mn})(\epsilon_{vc} - \epsilon_{mn})} \\ & + \sum_{mnabc} \frac{v_{abmn} \tilde{v}_{cmab} \tilde{v}_{vnvc}}{(\epsilon_{ab} - \epsilon_{mn})(\epsilon_c - \epsilon_n)} + \sum_{mnabs} \frac{v_{abmn} \tilde{v}_{mnas} \tilde{v}_{vsvb}}{(\epsilon_{ab} - \epsilon_{mn})(\epsilon_b - \epsilon_s)} \end{aligned}$$

- $\delta E_v^{(3)} + E_{v \text{ extra}}^{(3)}$ gives the **entire** third-order valence correlation energy

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

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]
$E_{v \text{ extra}}^{(3)}$	-0.418[-4]	-0.070[-4]	-0.072[-4]
$E_v^{(3)}$	-3.865[-4]	-1.525[-4]	-1.521[-4]

Correlation Energy

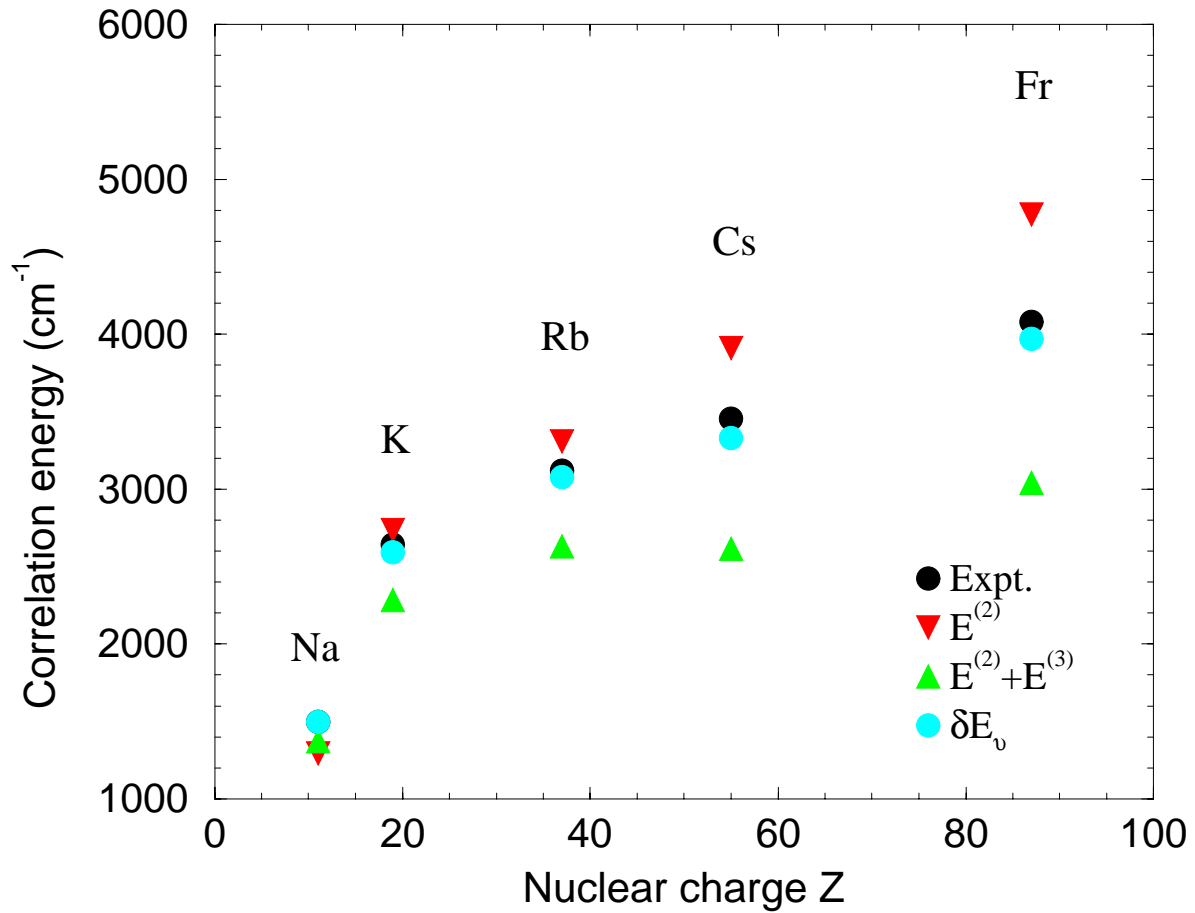


Figure 2: Energy comparisons for alkali-metal atoms.

Higher-order terms

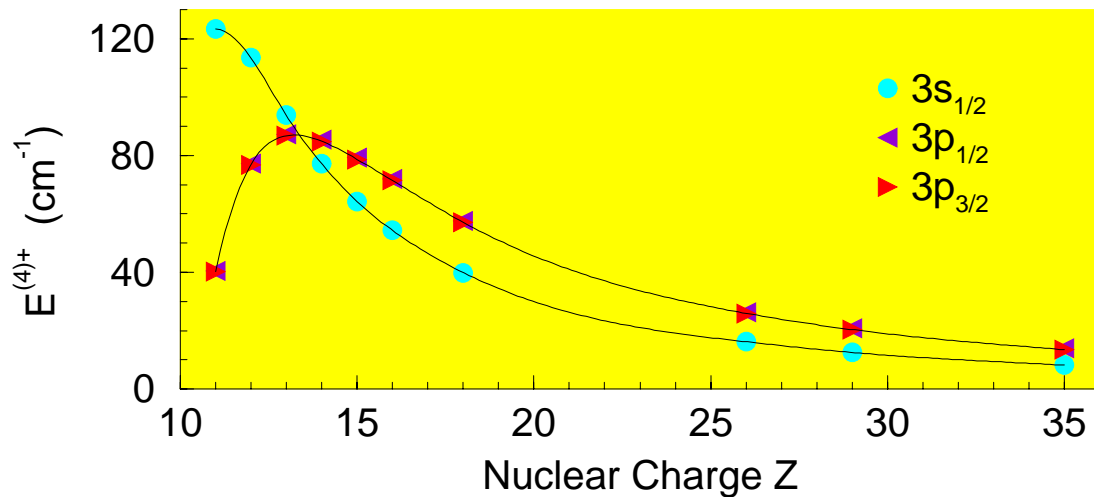


Figure 3: Contributions beyond 3rd-order for Na-like ions.

- $E^{(4)+} < 1\%$ 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
$E_{\text{extra}}^{(3)}$	-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	<i>5738</i>	<i>3795</i>

Fine Structure Intervals

Table 5: Fine-structure (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	<i>250</i>
	$10p_{3/2} - 10p_{1/2}$	132	<i>136</i>

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

$$Z_{wv}^{(a)} = \sum_{am} z_{am} \tilde{\rho}_{wmva} + \text{c.c.} \quad (\text{RPA})$$

$$Z_{wv}^{(b)} = - \sum_a z_{av} \rho_{wa} + \text{c.c.}$$

$$Z_{wv}^{(c)} = \sum_m z_{wm} \rho_{mv} + \text{c.c.} \quad (\text{BO})$$

... (15 similar terms)

$$Z_{wv}^{(s)} = - \sum_{abmn} \rho_{nmwa}^* z_{bv} \tilde{\rho}_{mnab} + \text{c.c.}$$

$$Z_{wv}^{(t)} = - \sum_{abmn} \rho_{mnba}^* z_{mv} \tilde{\rho}_{nwab} + \text{c.c.}$$

Matrix elements are complete through 3rd order!

Dipole Transitions

Table 6: 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:

$$\alpha_v = \frac{1}{3} \sum_m \left(\frac{|\langle v || z || mp_{1/2} \rangle|^2}{E_{mp_{1/2}} - E_v} + \frac{|\langle v || z || mp_{3/2} \rangle|^2}{E_{mp_{3/2}} - E_v} \right)$$

$$\alpha_c = \frac{2}{3} \sum_{ma} \frac{|\langle a || z || m \rangle|^2}{E_m - E_a}$$

$$\alpha_{vc} = \frac{1}{3} \sum_a \frac{|\langle a || z || v \rangle|^2}{E_a - E_v}$$

Table 7: Static polarizabilities (a.u.) of alkali-metal atoms.

	Na	K	Rb	Cs	Fr
α_v^{main}	162.06	284.70	308.43	383.8	294.0
α_v^{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(0.3)	290.2(0.8)	318.6(0.6)	399.9(1.9)	317.8(2.4)
Expt.	162.7(0.8)	293.6(6.1)	319.9(6.1)	403.6(8.1)	

Hyperfine Interaction

Table 8: ^{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):

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

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

Muonic atom experiments give $Q = 100.6(20) \text{ mb}$.

Summary

The SD theory gives:

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