SUPERSTRUCTURE - AN ATOMIC STRUCTURE CODE

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Résumé — Nous présentons les propriétés atomiques calculables à l'aide du programme SUPERSTRUCTURE, principalement les energies des états liés en couplage LS et couplage intermédiaire ainsi que les données radiatives associées à ces états. Le code permet également d'évaluer les coefficients de couplage entre termes et les données radiatives incluant les effets de cascade. Nous présentons quelques résultats relatifs principalement à la série isoélectronique du Be, pour démontrer les capacités du programme et son domaine d'application. Les autres examples concernent les transitions dites interdites dans quelques ions de la série isoélectronique de N et de He.

Abstract — We summarize the properties of the atomic structure code SUPERSTRUCTURE, which yields bound state energies in LS coupling and intermediate coupling as well as associated radiative data. Other data that can be computed include term coupling coefficients and radiative data with allowance for cascading. Results are given, mainly for members of the Be isoelectronic sequence, to demonstrate the power and range of the code. Other examples deal with 'forbidden' transitions in N-like and He-like ions.

1   Introduction

The techniques underlying the computer programs SUPERSTRUCTURE, over the past 15 years among the widely used general purpose atomic structure codes, has been described in great detail by Eissner *et al.* (1974). The code evolved from a fully automatic non-relativistic structure program by Eissner and Nussbaumer (1969). At that time the advent of fast electronic computers made it tempting to apply the old Slater state approach (see Condon and Shortley 1951, in particular section 1[7]) in building up states for general N-electron atomic systems, with full allowance for configuration mixing. The second feature of the approach are radial functions that approximate the Coulomb interaction with the other $N-1$ electrons by a scaled Thomas-Fermi-Dirac-Amaldi potential (Gombás 1956); the scaling factors are variationally determined.

Jones (1970, 1971) extended the code to intermediate coupling using the low-Z Breit-Pauli hamiltonian. Term coupling coefficients derived from this extension were soon to be used for approximating electron-ion transitions between finestructure levels from collisional data obtained in LS coupling (Saraph 1972). A number of additional features were incorporated subsequently. Moreover the program was soon reformulated in pre-processable form, allowing for quick changes of array sizes as a function of primary parameters such as maximum number of configurations or number of closed shell or open shell electrons; similarly double precision or short word length statements and other facilities can be globally activated.

Part of the original design — and so very much in the spirit of Layzer's (1959) concept of a complex of configurations — is the loop structure: to compute data for any number of members of an isoelectronic sequence, which is specified by a set of N-electron configurations — spectroscopic plus merely correlational; in such a loop one may also want to vary the conditions for an element specified by the electric charge number Z, e.g. for different forms of the variational functional or a different number of variational parameters.

The paper is laid out as follows. Section 2 addresses the general approach, and two subsections deal with the non-relativistic case of LS coupling and with intermediate coupling in Breit-Pauli approximation, backed by results for Be-like ions. Electric and magnetic radiative transitions are the topic of section 3. In a short section 4 additional facilities are sketched, and section 5 summarizes future developments.

2 Atomic structure calculations

For an ion with N electrons a set of configurations

$$C = \prod_{nl} (nl)^{q_{nl}}, \tag{1}$$

where

$$\sum_i q_i = N, $$

defines a trial solution $\Psi(\ldots)$ to a suitable hamiltonian H — for electric charge number Z — in the form of a multiconfigurational sum

$$\Psi(\ldots|\boldsymbol{x}_1,\ldots\boldsymbol{x}_N) = \sum_k a_k \Phi_k(C_\kappa \ldots|\boldsymbol{x}_1,\ldots\boldsymbol{x}_N) \tag{2}$$

where $\boldsymbol{x}_i$ stands for position $\vec{r}_i$ and spin $\vec{\sigma}_i$ of an electron labelled i, while quantum numbers other than C_κ will relate to the eigenstates of a particular hamiltonian. The form (1) implies that the function Φ

$$\Phi(C\ldots|\boldsymbol{x}_1,\ldots\boldsymbol{x}_N) = \langle C_\kappa,\ldots|n_1 l_1 m_1 \mu_1,\ldots n_N l_N m_N \mu_N\rangle\langle n_1 l_1 m_1 \mu_1,\ldots n_N l_N m_N \mu_N|\mathcal{A}|\boldsymbol{x}_1,\ldots\boldsymbol{x}_N\rangle, \tag{3}$$

whith suitable vector coupling coefficients $\langle C_\kappa \ldots|n_1 l_1 m_1 \mu_1,\ldots n_N l_N m_N \mu_N\rangle$, is composed of N-fold products of one-electron wave functions

$$\langle nlm\mu|\boldsymbol{x}\rangle = \langle nl|r\rangle\langle lm|\hat{r}\rangle\langle s\mu|\vec{\sigma}\rangle : \tag{4}$$

$$\langle r|nl\rangle = P_{nl}(r), \quad \langle \hat{r}|lm\rangle = Y_{lm}(\vartheta,\varphi), \quad \text{and spin functions } \langle \vec{\sigma}|\tfrac{1}{2},\mu\rangle. \tag{5}$$

Antisymmetrization $\mathcal{A}$ in (3) yields 'Slater determinants'. Using Slater state techniques and basic angular momentum algebra we evaluate their algebraic left-hand sides, along with the coupling coefficients that reflect the angular symmetries of the respective hamiltonians. Wigner-Eckart reduced angular coefficients required for radiative transitions are also stored ahead of dealing with particular ions — which does not happen before specifying Z and solving the 'radial problem.'

Thus a set C_κ specifies a number of bound states within an iso-electronic sequence, usually the ground state and a fairly small number of lowest excited states. This implies truncation of an infinite series (2). As an example we take the Be isoelectronic sequence and consider selections among the configurations

$C_1 - C_3$	$C_1 - C_9$		$C_1 - C_6^*$	$C_1 - C_{15}^*$	
$C_1 = 2s^2$	$C_4 = 2s3s$	$C_7 = 2p3s$	$C_4^* = 2s\bar{3}d$	$C_4^* = 2s\bar{3}d$	$C_{10}^* = \bar{3}s^2$
$C_2 = 2s2p$	$C_5 = 2s3p$	$C_8 = 2p3p$	$C_5^* = 2p\bar{3}d$	$\vdots$	$\vdots$
$C_3 = 2p^2$	$C_6 = 2s3d$	$C_9 = 2p3d$	$C_6^* = \bar{3}d^2$	$C_9^* = 2p\bar{3}d$	$C_{15}^* = \bar{3}d^2$

for brevity omitting the common core shell $\bar{C} = 1s^2$, which is specified once and for all in input.

In the high-Z limit up a sequence a simple rule states which configurations to include along with one of interest. According to Layzer's (1959) scaling laws and his concept of a complex it suffices in this hypothetical non-relativistic limit to permute electrons within each shell characterized by the principal quantum number n; as the Coulomb interaction is parity-conserving only configurations associated with the same parity need be considered simultaneously. Such configurations are sometimes called 'quasi-degenerate', as the behaviour of orbitals nl approaches that of scaled hydrogenic orbitals when z increases, and hydrogenic orbitals nl associated with the same value n belong the the same energy eigenvalue (which scales as Z^2). The cases above account for both parities simultaneously. Thus the configurations $C_1 - C_3$ describe the full complex for one valence electron up in the M-shell. In a recent paper Eissner and Tully (1990–91) show what can happen to two-electron transition probabilities of the array $2p^2 - 3s3p$ when C_9 has been forgotten: one of the transitions changes by a factor of thirty!

At or near the neutral end inclusion of configurations beyond one complex becomes at least as important, and their number grows prohibitively large if high accuracy is required. As the code allows only

for trial functions of the form (4), which rules out explicit dependance upon the inter-electronic distance, only one way out is left: to simulate the missing portion of electron-electron correlation by configurations in part made up of artificial 'contracted' orbitals that strongly overlap with the ordinary or 'spectroscopic' orbitals of interest; we denote such orbitals by a bar above n (which equals the number of nodes in the usual way). This approach is reminiscent of properties of bound-state solutions in a potential not behaving as $1/r$, e.g. nuclear shell model orbitals. In addition to the set (1) SUPERSTRUCTURE allows to specify a parameter KCUT, which singles out C_κ with $\kappa \geq$ KCUT as mere correlation configurations; they will be denoted by a star. Terms SL not matched by any arising from the spectroscopic configurations are ignored. Configurations containing contracted orbitals should always be declared type C_κ^*.

2.1   ... in LS coupling

The time-independent Schrödinger equation

$$\left[\sum_{i=1}^{N}\left\{-\frac{\hbar^2}{2m_0}\Delta_i - \frac{Ze}{r_i} + \sum_{j>i}\frac{e}{r_{ij}}\right\}\right]\Psi = E\Psi \tag{6}$$

has solutions that are eigenvalues of total angular momentum L and spin S:

$$\Psi = \Psi(\gamma SLM_SM_L|\boldsymbol{x}_1,\ldots\boldsymbol{x}_N). \tag{7}$$

In an antisymmetrized configurational expansion (1–5) equations (6–7) yield the Hartree-Fock equations for coupled orbital functions $P_{nl}(r)$.

For computational work one extracts pure number equations, choosing the most natural or convenient unit for one quantity of each canonical pair — and phase invariance settles the case for the canonical conjugate! Using ALGOL notation for brevity we define the following dimensionless quantities instead of length, energy and angular momentum, parenthetically adding redefinitions that follow from phase space requirements:

$$r := \frac{r}{a_0} \qquad \text{where } a_0 = \frac{\hbar}{m_0c}/\alpha \qquad (= 0.529 \cdot 10^{-8}\,\text{cm}) \text{ is the Bohr radius}$$

(hence wave numbers $\frac{p}{\hbar}$ transform as $k := k \cdot a_0$)

$$E := \frac{E}{\text{Ry}} \qquad \text{where Ry} = \frac{\alpha^2}{2}m_0c^2 \qquad (= 13.59\,\text{eV}) \text{ is the hydrogenic ground state energy}$$

(hence $t := \frac{t}{\tau_0}$ where $\tau_0 = \frac{2a_0}{\alpha c} = 4.839 \cdot 10^{-17}\cdot\text{sec}$) \qquad (8)

$$d := \frac{d}{\hbar} \qquad \text{— since the uncertainty is } \Delta\varphi = 2\pi \text{ for closed orbitals}$$

and the symbols have the ususal meaning of rest mass, electric charge, and finestructure constant

$$\alpha = \frac{e^2}{\hbar c} \qquad (\approx 1/137.0360). \tag{9}$$

In tables though physical rather than reduced quantities will still be displayed for clarity.

Then the Hartree-Fock equations for coupled radial functions assume the form

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{l(l+1)}{r^2} + \frac{2Z}{r} + \epsilon_{nl}\right]P_{nl}(r) = 2\sum_{i,j}\left[V_{i,j}(r)P_{nl}(r) + \int_0^\infty \mathrm{d}r' W_{nl,j}(r,r')P_j(r')\right]$$
$$+ \sum_{n'}\Lambda_{nl,n'l}P_{n'l}(r); \tag{10}$$

the direct potential V is expanded in the usual way as spherical multipole potentials $y_\lambda(nl,n'l';r)$, in the exchange term $\int WP$ orbitals P_{nl} and P_j swap places, and the Lagrange sum with parameters $\Lambda_{n'l,nl}$ arises from orthogonality conditions imposed upon P_{nl} for algebraic convenience.

Table 1: Be-sequence: position of terms associated with the three lowest configurations $C_1 - C_3$ relative to the ground state. First entries: nonrelativistic calculation; second entries: in Breit-Pauli approximation. BESSS stands for the 15-configuration expansion by Berrington et al. (1987). For observed C III energies see Moore (1949). Appended rows show (i) ground state energy E_1 of the N-electron system — indicative of the variational effort, (ii) scaling factors obtained on optimizing $\mathcal{F}$ of (14) with $\mathcal{M}=6$, (iii) mean radii of the resulting orbitals — helpful for judging correlation due to overlap.

$\frac{(E_i-E_1)}{Ry}$		C III				Al X	Ca XVII	Fe XXIII	
i	C_κ SL	obs.	$C_1-C_{15}^*$	$C_1-C_6^*$	C_1-C_3	C_1-C_3	C_1-C_3	C_1-C_3	$C_1-C_6^*$
1	$2s^2$ ^1S	0.	0.	0.	0.	0.	0.	0.	0.
2	$2s2p$ ^3P		0.4763	0.4765	0.4860	1.4142	2.3268	3.1069	3.0985
		0.4777	0.4774	0.4778	0.4873	1.4573	2.5934	3.8949	3.8871
3	^1P		0.9515	0.9537	1.0325	2.8170	4.5572	6.0432	5.9583
		0.9327	0.9528	0.9550	1.0337	2.8606	4.8394	6.9396	6.8582
4	$2p^2$ ^3P		1.2585	1.2576	1.2673	3.6519	6.0000	8.0071	7.9978
		1.2528	1.2609	1.2605	1.2701	3.7434	6.5452	9.5257	9.5104
5	^1D		1.3414	1.3427	1.4176	4.1024	6.7471	9.0079	8.9466
		1.3293	1.3438	1.3455	1.4205	4.1960	7.3603	11.0130	10.9655
6	^1S		1.7017	1.7203	1.7794	5.0871	8.3420	11.1243	11.0630
		1.6633	1.7041	1.7230	1.7821	5.1750	8.9233	13.0138	12.9580
	$-E_1/$Ry		72.9594	72.9475	72.9459	383.5917	939.2550	1610.5416	1610.5443
			72.9892	72.9772	72.9756	384.4085	944.1530	1624.9528	1624.9577
	λ_s	see text		1.3113	1.3080	1.3166	1.3183	1.3189	1.3202
	λ_p	& BESSS		1.1489	1.1478	1.1559	1.1620	1.1650	1.1640
	ζ_d	(1987)		1.1040	—	—	—	—	1.8213
	$\langle \bar{3}d\lvert r\rvert \bar{3}d\rangle$		1.6283	1.6043	—	—	—	—	0.2510
	$\langle \bar{3}p\lvert r\rvert \bar{3}p\rangle$		1.3914	—	—	—	—	—	—
	$\langle \bar{3}s\lvert r\rvert \bar{3}s\rangle$		1.8895	—	—	—	—	—	—
	$\langle 2p\lvert r\rvert 2p\rangle$		1.2313	1.3554	1.3560	0.4625	0.2802	0.2096	0.2096
	$\langle 2s\lvert r\rvert 2s\rangle$		1.4550	1.3543	1.3552	0.5234	0.3248	0.2451	0.2451
	$\langle 1s\lvert r\rvert 1s\rangle$		0.2684	0.2695	0.2696	0.1196	.07676	.05873	.05873

SUPERSTRUCTURE uncouples (10), approximating the unipole terms by a statistical model potential and numerically computing normalized radial functions $P_{nl}(r)$ that are solutions to the eigenvalue equation

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{2\mathcal{Z}_{\text{eff}}(\lambda_l \cdot r; Z, N)}{r} + \epsilon_{nl}\right] P_{nl}(r) = 0, \tag{11}$$

with boundary conditions

$$\lim_{r\to 0} \sim r^{l+1}, \quad \lim_{r\to\infty} \sim r^{(z/\sqrt{-\epsilon_{nl}})} e^{-\sqrt{-\epsilon_{nl}} r}, \tag{12}$$

in a scaled statistical model (SM) potential $V^{\text{SM}}(r) = \dfrac{\mathcal{Z}_{\text{eff}}(\lambda_l \cdot r)}{r}$:

$$\lim_{r\to 0} \mathcal{Z}_{\text{eff}}(\lambda_l \cdot r) = Z, \quad \lim_{r\to\infty} \mathcal{Z}_{\text{eff}}(\lambda_l \cdot r) = z \equiv Z - (N-1) \quad \text{— the residual charge.} \tag{13}$$

The favourite choice among the functionals optimized on varying the scaling factors λ_l is of the form

$$\mathcal{F} = \sum_{i=1}^{\mathcal{M}} \eta_i E_i \tag{14}$$

where $i (= \gamma SL$, see (7)) denotes a term SL — we use the 'dominant' configuration and perhaps a degeneracy parameter for label γ. The sum runs over $\mathcal{M}$ eigenvalues of the matrix of expectation values $\langle i | H_{nr} | i' \rangle$,

$$\langle i | C\beta SL \rangle \langle C\beta S L M_S M_L | H_{nr} | C'\beta' S L M_S M_L \rangle \langle C'\beta' SL | i' \rangle = \delta_{ii'} E_i. \tag{15}$$

In most applications it is the $\mathcal{M}$ lowest lying terms one includes, preferably equally weighted, i.e. $\eta = 1.0$. Over the years two features have been added to the original design: (i) use of different potentials for orbitals with the same quantum number l (Nussbaumer and Storey 1978) — paying for more flexibility by some degree of asymmetry when orthogonalizing subsequent orbitals to those with preceding values of n, as such sets have to be mutually orthogonal for algebraic reasons; (ii) correlation orbitals computed in a scaled Coulomb potential $\mathcal{Z}_{eff}(\lambda_l \cdot r) = z^*$, usually and in all present applications marginally modified so as to meet cusp requirements in certain electron collision codes such as IMPACT (Crees et al. 1978):

$$\mathcal{Z}_{eff}^{PJS}(r) = Z[e^{-Zr/2} + \zeta_{nl}(1 - e^{-Zr/r})] \tag{16}$$

where ζ_{nl} is specified as $-(100 \cdot n + \lambda_{nl})$ in input, i.e. as a negative 'scaling factor' of value < -100; negative values > -100 are interpreted as effective charge $|\lambda| \cdot Z$ — an early facility in the code, as $\lambda_l = -1.0$ yields coefficients for expansions in powers of Z both for structure and for radiative transitions (for the latter see in particular the attempt by Smith and Wiese (1971) of a graphical compilation of f values versus $1/Z$ — and the last column in Table 3; see also Tully et al 1990).

Potential (13) can be a poor choice for contracted correlation orbitals, as (14) may poorly converge even for very large values of λ; by contrast scaled Coulomb potentials like (16) work very well and have therefore been choosen for all applications in this paper. The parameter ζ_l often converges to a value that implies an effective charge $> Z$, as can be seen in Table 1.

The main aim of Table 1 is the presentation of term energies for Be-like ions in fairly simple expansions. For C III 'target 2' of Berrington et al. 1987 has been reproduced with their parameters $\lambda_{1s} = 1.3707$, $\lambda_{2s} = 0.9889$, $\lambda_{2p} = 1.4355$, $\zeta_{3s} = 0.9828$, $\zeta_{3p} = 1.1793$ and $\zeta_{3d} = 1.0852$. For more extended calculations see Glass (1979a, b).

2.2   ... in intermediate coupling (IC)

Moreover the lower terms entries in Table 1, from averaging over finestructure levels of the Breit-Pauli calculation detailed in Table 2, demonstrate how relativistic effects take over as one moves up the sequence. Including effects of the Bohr magneton $\mu_B = \frac{e}{m}\frac{\hbar}{2c}$ along with all the other terms of relative order α^2 as a perturbation leads to wave functions in intermediate coupling,

$$\Psi = \Psi(\Gamma SLJM_J | \boldsymbol{x}_1, \ldots \boldsymbol{x}_N), \tag{17}$$

which are eigenvectors to the Breit-Pauli matrix $\langle k | H_{BP} | k' \rangle$ with eigenvalues E_k. We employ the low-Z Breit-Pauli approximation, which is valid as long as

$$\alpha^2 Z_{eff}^3 \ll 1, \tag{18}$$

One obtains the BP hamiltonian by adding a relativistic correction operator H_{rc} — with the usual abbreviations for c[ontact], d[arwin], m[ass], o[rbit] and s[pin], and a prime indicating 'other' — to the non-relativistic hamiltonian (6):

$$H_{BP} = H_{nr} + \sum_{i=1}^{N} \{f_i(m) + f_i(d) + f_i(so)\} + \frac{1}{2}\sum_{i \neq j}^{N} \{g_{ij}(so + so') + g_{ij}(ss') + g_{ij}(css') + g_{ij}(d) + g_{ij}(oo')\}. \tag{19}$$

While accounting for all the one-body terms,

$$\begin{aligned} f_i(m) &= -\frac{\alpha^2}{4}\nabla_i^4 \\ f_i(d) &= -\frac{Z\alpha^2}{4}\nabla_i^2(1/r_i) \\ f_i(so) &= \frac{Z\alpha^2}{r_i^3}\vec{l_i} \cdot \vec{s_i}, \end{aligned} \tag{20}$$

among the BP two-body operators only the finestructure (FS) terms are retained here:

$$g_{ij}(\text{so} + \text{so}') = -\alpha^2 \left\{ \left(\frac{\vec{r}_{ij}}{r_{ij}^3} \times \vec{p}_i \right) \cdot (\vec{s}_i + 2\vec{s}_j) + \left(\frac{\vec{r}_{ij}}{r_{ij}^3} \times \vec{p}_j \right) \cdot (\vec{s}_j + 2\vec{s}_i) \right\}$$

$$g_{ij}(\text{ss}') = 2\alpha^2 \left\{ \frac{\vec{s}_i \cdot \vec{s}_j}{r_{ij}^3} - 3 \frac{(\vec{s}_i \cdot \vec{r}_{ij})(\vec{s}_j \cdot \vec{r}_{ij})}{r_{ij}^5} \right\} \qquad (21)$$

where $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$. There is little point worrying about the omitted 2-body terms as long as one has not pushed ordinary configuration expansion (CI) — since interelectron correlation scales as $1/Z$ — sufficiently far for BP terms to matter.

Having written $\frac{1}{2} \sum_{j \neq i}$ rather than $\sum_{j>i}$ in the two-body sum — a difference of no great account as long as one deals with indistinguishable particles — smoothes the way towards the following verifying discussion. If one takes particle j for the 'fixed' nucleus then the mutual *spin–orbit* term $g_{ij}(\text{so})$ equals the one-body $f_i(\text{so})$ on changing electric charge sign and magnitude (while center-of-mass considerations take care of factors two). Since we assume the 'nucleus' j be at rest i experiences no *other orbit* and $g_{ij}(\text{so}')$ vanishes. So does the companion term $g_{ji}(\text{so}) = 0$, whereas spin–other-orbit term $g_{ji}(\text{so}')$ — on changing μ_B to protonic μ_p or in general to the magnetic moment of the nucleus — becomes the magnetic contribution to the hyperfine structure (HFS). However HFS effects have not been incorporated in SUPERSTRUCTURE.

The all-important scaling laws follow at a glance, on observing that the length r scales inversely with Z: consider the hydrogenic radial equation in $\rho = Zr$, i.e. after absorbing Z. Hence all the one-body BP terms scale as $\alpha^2 Z^4$ and — a feature familiar from H_{nr} — the two-body contributions one power less in Z. This has obvious repercussions on the scaling of the BP components in IC wavefunctions Ψ: expand perturbatively, observing in particular that the expectation value of $f(\text{so})$ vanishes for half-filled subshells nl, and equally take note that the energy denominator will scale as Z rather than Z^2 if there is no change in the principal quantum number for the dominant configurations.

SUPERSTRUCTURE follows Blume and Watson (1962) in absorbing the effects of the core $\bar{C}$ into the unscreened spin-orbit parameters $\zeta_{nl}^0 = \langle nl | (1/r)^3 | nl \rangle$ that arise from $f_i(\text{so})$ in (20); closed shells behave like an effective screening and yield reduced parameters ζ_{nl}'. Other savings can be made on specifying an input parameter KUTSS, which defaults to KCUT: for configurations C_κ with $\kappa \geq$ KUTSS the two-body terms (21) may often be ignored as unimportant.

Table 2: Be-sequence in intermediate coupling: level positions (in BP approximation). NBS data from Fuhr *et al.* (1981).

$(E_k - E_1)/Ry$			C III	Ne V	Al X	S XIII	Ca XVII	Fe XXIII		
k	C_κ	SLJ	$C_1 - C_{15}^*$	$C_1 - C_6^*$	$C_1 - C_6^*$	$C_1 - C_6^*$	$C_1 - C_6^*$	$C_1 - C_6^*$	$C_1 - C_{15}^*$	NBS
1	$2s^2$	$^1S_0$	0.	0.	0.	0.	0.	0.	0.	0.
2	$2s2p$	$^3P_0$	0.4769	1.4170	1.0168	1.8183	2.3577	3.1801	3.1723	
3		$^3P_1$	0.4771	1.0210	1.4320	1.8574	2.4593	3.4594	3.4594	3.4549
4		$^3P_2$	0.4776	1.0301	1.4651	1.9455	2.7065	4.2851	4.3217	
5		$^1P_1$	0.9528	1.9950	2.7767	3.5876	4.7560	6.8582	6.9002	6.8604
6	$2p^2$	$^3P_0$	1.2605	2.6558	3.7027	4.7843	6.2949	8.7219	8.7280	
7		$^3P_1$	1.2607	2.6558	3.7202	4.8344	6.4526	9.3540	9.3966	
8		$^3P_2$	1.2611	2.6637	3.7489	4.9974	6.6320	9.7619	9.8108	
9		$^1D_2$	1.3438	2.9246	4.1312	5.4053	7.3017	10.9655	11.0320	
10		$^1S_0$	1.7041	3.6507	5.1144	6.6414	8.8640	12.9580	13.0128	

3 Radiative transitions

For transition arrays arising from (1) SUPERSTRUCTURE computes Einstein coefficients and associated quantities for multipole transitions of low multipolarity, first of all for electric dipole (E1) radiation.

Electric quadrupole (E2) and magnetic dipole (M1) transitions come into their own only in intermediate coupling, even though electric multipole transitions formally exist already in LS coupling. Moreover it turns out that variants of the familiar electric dipole (E1) operator are also affected. As IC wavefunctions contain admixtures of order α^2 radiative operators *must* also be expanded up to BP order. We add them in M1 transitions but in the velocity formulation, where such terms also arise in the Coulomb gauge, the current code still omits them.

Table 3: Length (upper entries) and velocity (lower entries) gf-values in LS-coupling. The 'Coul.' column provides the slope when plotting gf versus $1/Z$.

transition	C III			$C_1 - C_3$		Fe XXIII		Coul.
$i - f$	$C_1 - C_{15}^*$	$C_1 - C_6^*$	$C_1 - C_3$	Al VIII	Ca XVII	$C_1 - C_3$	$C_1 - C_6^*$	$Z = 10$
$2s^2\,{}^1S - 2s2p\,{}^1P^\circ$	.761	.786	.787	.293	.178	.133	.133	0.3169
–	.794	.850	.646	.269	.168	.127	.160	0
$2s2p\,{}^3P^\circ -\;\;2p^2\,{}^3P$	2.511	2.556	2.785	1.021	.620	.464	.457	1.1013
–	2.702	2.752	2.040	.821	.510	.384	.522	0
${}^1P^\circ -\qquad\;{}^1D$	.550	.537	.763	.326	.205	.156	.151	0.3868
–	.555	.713	2.298	.794	.475	.353	.171	0
${}^1S$	.472	.443	.614	.224	.136	.102	.096	0.2409
–	.541	.429	.055	.026	.017	.013	.088	0

3.1 Electric dipole transitions

In the long wavelength low intensity approximation the probability for spontaneous emisssion by E1 radiation,

$$A_{i' \leftarrow i}^{\mathrm{E1}} = 2.6774 \cdot 10^9 \mathrm{sec}^{-1} \cdot \frac{(E_i - E_{i'})^3}{g_i} \cdot S^{\mathrm{E1}}(i, i'), \tag{22}$$

may be expressed in terms of the line strength

$$S_{\mathrm{L}}^{\mathrm{E}k}(i', i) = S(i, i') = \left| \langle i' \| R^{[k]} \| i \rangle \right|^2, \tag{23}$$

where the linestrength amplitude $\langle i' \| R^{[1]} \| i \rangle$ is Wigner-Eckart reduced from matrix element $\langle i' | R_\kappa | i \rangle$, R_κ being any spherical tensor component $\vec{e}_\kappa \cdot \vec{R}$ (with polarization 'direction' $\vec{e}_\kappa$) of

$$\vec{R} = \sum_{j=1}^{N} \vec{r}_j. \tag{24}$$

Subscript L indicates 'length'. On replacing

$$r \longrightarrow \frac{2}{E_i - E_{i'}} \left\{ \frac{\partial}{\partial r} + \frac{(l(l+1) - l'(l'+1))}{2r} \right\} \tag{25}$$

in the radial length integrals $\langle n'l' | r_j | nl \rangle$ that contribute to $\langle i' \| R \| i \rangle$ one obtains the velocity form $S_{\mathrm{V}}(i, i')$. Applying hypervirial relations once more leads to the acceleration form, and so forth.

We also consider oscillator strengths f^{abs} or f^{emi}; so as to avoid the need to distinguish between the absorption and emission oscillator strength one often prefers the symmetric (gf) value, by multiplying with the statistical weight g of the initial state:

$$(gf)_{i',i} = (gf)_{i,i'} = \frac{|E_i - E_{i'}|}{3} \cdot S(i, i'). \tag{26}$$

Turning to the operator problems we note that (20) is based on the commutator for a *non*relativistic hamiltonian (2) with spherical components r^κ: thus such an operator can give the same radiative results as the length operator only in LS coupling, and this only for *exact* wave functions (1); approximate wave functions yield differences depending upon the choice of gauge for the electromagnetic four-potential A.

Table 4: Length (L) and velocity (lower entries, V) gf-values in BP approximation. NBS values for carbon from Wiese *et al.*, for iron from Fuhr *et al.*

transition i − f		C III NBS	C III $C_1-C_{15}^*$	C III $C_1-C_6^*$	$C_1-C_6^*$ Ne V	$C_1-C_6^*$ Ca XVII	Fe XXIII $C_1-C_6^*$	Fe XXIII $C_1-C_{15}^*$	Fe XXIII NBS
$2s^2\,^1S_0$ −	$2s2p\,^3P_1^o$		1910.06	1908.23	892.55	370.53	263.42	263.42	263.76 Å
−	L	—	1.43(−7)	1.79(−7)	692(−6)	4.22(−4)	.0016	.0016	.0015
−	V		2.45(−7)	1.15(−6)	4.56(−5)	2.33(−3)	.0008	.0007	D
−	$^1P_1^o$	977.03	956.42	954.16	456.77	191.61	132.87	132.06	132.83 Å
−	L	.81	.762	.788	.407	.194	.159	.153	.155
−	V	D	.793	.848	.458	.194	.129	.104	B
$2s2p\,^3P_0^o$ −	$2p^2\,^3P_1$	.26	.279	.285	.152	.0754	.0641	.0628	.0643
−		D	.300	305	.165	.0688	.0458	.0373	B
$^3P_1^o$ −	$^3P_0$	.261	.279	.285	.151	.0710	.0560	.0542	.056
−		D	.300	.305	.166	.0734	.0538	.0303	B
−	$^3P_1$	.195	.209	.214	.114	.0549	.0448	.0438	.0547
−		D	.225	.229	.124	.0527	.0352	.0287	B
−	$^3P_2$	.33	.349	.356	.190	.0962	.0831	.0821	.085
−		D	.375	.381	.206	.0821	.0504	.0426	B
−	$^1D_2$	—	3.41(−6)	3.38(−6)	3.14(−5)	1.56(−3)	5.27(−3)	5.20(−3)	.0048
−			5.49(−6)	4.27(−6)	5.18(−5)	2.18(−3)	5.40(−3)	6.95(−3)	D
−	$^1S_0$	—	1.90(−7)	1.40(−7)	3.54(−6)	1.23(−4)	2.69(−4)	2.78(−4)	—
−			1.71(−7)	1.07(−7)	2.32(−6)	5.86(−5)	7.60(−5)	1.12(−4)	
$^3P_2^o$ −	$^3P_1$	.325	.349	.356	.188	.0862	.0657	.0064	.065
−		D	.375	.382	.208	.0941	.0699	.0057	B
−	$^3P_2$	1.0	1.05	1.067	.567	.253	.159	.154	.158
−		D	1.12	1.140	.622	.252	.145	.128	B
−	$^1D_2$	—	2.29(−5)	2.18(−5)	3.92(−4)	.0209	.0663	.0674	.068
−			2.12(−5)	1.86(−5)	3.18(−4)	.0151	.0406	.0466	C
$^1P_1^o$ −	$^3P_0$	—	2.67(−7)	2.23(−7)	8.16(−6)	3.64(−4)	8.27(−4)	7.96(−4)	8.4(−4)
−			1.66(−7)	1.99(−7)	1.57(−5)	8.85(−4)	2.69(−4)	1.30(−4)	E
−	$^3P_1$	—	5.24(−8)	5.20(−8)	2.00(−6)	1.24(−4)	4.76(−4)	4.93(−4)	4.5(−4)
−			7.04(−7)	6.58(−7)	1.44(−5)	6.62(−4)	2.08(−4)	1.83(−4)	E
−	$^3P_2$	—	6.79(−6)	6.31(−6)	1.23(−4)	8.04(−3)	.0271	.0271	.027
−			8.55(−6)	1.36(−5)	2.37(−4)	1.04(−2)	.0263	.0122	D
−	$^1D_2$	1.41	.551	.539	.388	.213	.165	.1621	.169
−		D(!)	.554	.710	.457	.186	.103	.0883	B
−	$^1S_0$	1247.37	1212.85	1186.65	550.38	221.83	149.39	149.08	[149] Å
−		.27	.472	.444	.264	.130	.103	.102	.109
−		D	.541	.429	.245	.112	.079	.092	B

3.2 Magnetic dipole transitions

In order to compute M1 transition probabilities

$$A_{fi}^{M1} = 3.5644 \cdot 10^4 \cdot \sec^{-1} \frac{(E_i - E_f)^3}{g_i} \cdot S^{M1}(i,f) \tag{27}$$

one constructs the reduced matrix element that makes up the line strength

$$S_{fi} = \left| \langle f \| Q/\mu_B \| i \rangle \right|^2 \tag{28}$$

in the usual manner from spherical tensor operator components $\vec{e}_\kappa \cdot \vec{Q}$ of

$$\vec{Q} = \sum_{j=1}^{N} \left\{ \vec{Q}_j^{I} + \sum_{j<i} \vec{Q}_{ij}^{II} \right\}. \tag{29}$$

Table 5: Transitions from the two levels of the first excited term to the ground state of N-like ions: $C_1 = 1s^2 2s^2 2p^3$, $C_2 = 1s^2 2p^5$, $C_3^* = 1s^2 2s 2p^3 \bar{3}d$, $C_4^* = 1s^2 2p^3 \bar{3}d^2$, $C_5^* = 1s^2 2s^2 2p \bar{3}d^2$; scaling factors λ_l and ζ_d at $\mathcal{M} = 4$. In addition to transition probabilities A observed and calculated finestructure splittings of the excited ^{2}D are given — rather sensitive as ordinary spin-orbit coupling vanishes! BP: with (30–31), TEC: all A's term energy corrected; for $r(\infty)$ see (32).

$1s^2 2s^2 2p^3$		N I	O II	Ne IV	Mg VI	S X	Fe XX
$^2D_{5/2} \to {}^4S_{3/2}$	obs.	5200Å	3729Å	2424Å	1847Å		
	calc.	4605Å	3458Å	2320Å	1749Å	1170Å	563.8Å
$A^{E2} \cdot$sec		1.2(-5)	5.3(-5)	5.1(-4)	2.8(-4)	3.5(-2)	3.5
$A^{M1} \cdot$sec		9.9(-7)	7.1(-6)	1.8(-5)	2.9(-3)	0.323	1196
	BP	1.7(-7)	1.6(-6)	7.3(-5)	1.7(-3)	0.274	1165
$^2D_{3/2} \to {}^4S_{3/2}$	$\Delta\lambda/$Å	-2.7	-2.7	-3.1	-1.0		
	calc.	-2.5	-2.8	-2.7	-0.8	+15.7	+150.2
$A^{E2} \cdot$sec		7.8(-6)	3.4(-5)	3.3(-4)	1.8(-3)	2.2(-2)	.77
$A^{M1} \cdot$sec		1.7(-5)	1.4(-4)	5.1(-3)	0.1126	14.92	15190
	BP	1.9(-5)	1.5(-4)	5.4(-3)	0.115	14.98	15120
		0.81	0.52	0.188	0.042	0.036	0.119
$r(\infty)$	BP	0.70	0.43	0.152	0.026	0.031	0.116
	TEC	0.56	0.36	0.119	0.055	0.030	0.115
λ_s		1.2249	1.2320	1.2430	1.2494	1.2559	1.2616
λ_p		1.1314	1.1332	1.1372	1.1403	1.1446	1.1503
ζ_d		0.8682	1.0088	1.2041	1.3379	1.5117	1.7229

Drake's (1971) one- and two-body parts can be written with Eissner and Zeippen (1981) as

$$\vec{Q}_j^{\mathrm{I}} = \mu_B \left(\quad (\vec{l}_j + 2\vec{s}_j)\left\{1 + \frac{\alpha^2}{2}\left[\left(\frac{\partial^2}{\partial r_j^2} - \frac{l(l+1)}{r_j^2}\right) - \frac{\mathcal{E}^2}{20}r_j^2\right]\right\} \right.$$
$$\left. + \frac{\alpha^2}{2}\left[\vec{p}_j \times (\vec{p}_j \times \vec{s}_j) + 2\vec{r}_j \times (\vec{r}_j \times \vec{s}_j)\left(\frac{\mathcal{E}^2}{20} - \frac{Z}{r_j^3}\right) + \frac{\mathcal{E}}{2}\vec{s}_j\right] \right) \quad (30)$$

$$\vec{Q}_{ij}^{\mathrm{II}} = \mu_B \alpha^2 \left(\frac{\vec{r}_{ij} \times [\vec{r}_{ij} \times (\vec{s}_i + \vec{s}_j)] + (\vec{r}_i \times \vec{r}_j)\vec{r}_{ij} \cdot (\vec{p}_i + \vec{p}_j)}{r_{ij}^3} - \frac{(\vec{r}_i \times \vec{p}_j) - (\vec{r}_j \times \vec{p}_i)}{r_{ij}} \right) \quad (31)$$

where $\mathcal{E}$ is essentially the photon energy.

In half-filled shells nl the one- and two-body BP terms in (29) compete in (28) to the *same* orders in α and Z with components due to the ordinary $(\vec{l} + 2\vec{s})$, which can lead to destructive interference in the transition amplitudes. This affects the calibration when using line intensity ratios $r(\mathcal{N}_{el})$ of such ions for electron density diagnostics. Table 5 shows for a number of nitrogen-like ions how radiative corrections of Breit-Pauli order change transition probabilities. For a long time the ratio

$$r(\infty) = \frac{3}{2} \frac{A^{E2}(^2D_{5/2}^\circ \to {}^4S_{3/2}^\circ) + A^{M1}(^2D_{5/2}^\circ \to {}^4S_{3/2}^\circ)}{A^{M1}(^2D_{3/2}^\circ \to {}^4S_{3/2}^\circ) + A^{E2}(^2D_{3/2}^\circ \to {}^4S_{3/2}^\circ)} \quad (32)$$

of the high electron density limit remained a mystery. At the time Eissner and Zeippen incorporated corrective terms of Breit-Pauli order into SUPERSTRUCTURE it was known form work by Zeippen *et al.* (1977) that such terms would be only part of necessary corrections: term energy corrections (TEC) must account for deficiencies in the truncated trial function expansion. This is also borne out in Table 5. The whole problem has been revisited several times, so by Zeippen (1982) and by Mendoza and Zeippen (1982). For O II there is now consistent agreement with the observed $r(\infty) \approx 0.35$.

A much older riddle and its solution by Drake (1971) provides an independent check on part of the Breit-Pauli correction. The first excited state of He-like ions decays exclusively via $\vec{Q}^{\mathrm{I}}$. For the transition $1s2s\,^3S_1 \to 1s^2\,^1S$ the matrix element of the 'ordinary' M1 operator of order α^0 vanishes, because this term

in (30) is purely angular and the state $|1s^2\,^1S\rangle$ — while orthogonal to $|1s2s\,^3S_1\rangle$ — is entirely isotropic. Two-body effects do not contribute either. Therefore (28) remains the sole cause for the $1s2s\,^3S_1$ decay in He-like ions; in fact they give rise to 14 distinct radial integrals. The transition therefore scales as Z^{10}: 6 powers coming from the energy factor and 4 from $\sim r^{-2}$ in (26) when squaring. Table 6 summarizes results in a number of approaches. While showing good results further down the table when only modestly complex configuration expansions involving pure SM orbitals are employed, it comes not unexpectedly that neutral helium requires a much greater effort. The label 'ID' in the trailing comment column marks a special approach, in which collision type bound orbitals 1s, 2s and 2p have been included in a 28-configuration expansion; these orbitals have been obtained in runs of the electron collision code IM-PACT (Crees *et al.* 1978): building up the He atom from He$^+$ orbitals, which provides 'frozen cores', and the IMPACT orbitals. For comparison Table 6 contains a second entry for neutral He: 28 configurations composed entirely of ordinary SM orbitals still give a poor result. For all ions correlation configurations had been included.

Table 6: M1 decay of He-like $1s2s\,^3S_1$ — the first excited level!
ex: extrapolated to the non-relativistic hydrogenic limit $A(2\,^3S_1) \to Z^{10} \times 1.7346 \cdot 10^6/\text{sec}$; Marrus and Mohr (1978) expand further, including the non-relativistic $\mathcal{O}(1/Z)$ due to configuration mixing as well as terms $\mathcal{O}(\alpha^2 Z^2)$ of Breit-Pauli order.

$1s2s\,^3S_1$ decay Z	observed τ/sec	Hata and Grant 1981 τ/sec	SSTRUCT τ/sec	$A^{M1}*\text{sec}$	Drake 1971 A^{M1}	
2 He	9.1±3(+3)	8.88(+3)	8.53(+3) 1.61(4)	1.172(-4) 6.208(-5)	1.272(-4)	ID SM
4 Be			2.47	4.141(-1)	5.618(-1)	SM
8 O			1.10(-3)	9.104(2)	1.044(3)	SM
14 Si			2.98(-6)	3.358(5)	3.563(5)	SM
16 S	7.06±.86(-7)	7.00(-7)	7.41(-7)	1.349(6)	1.408(6)	SM
18 Ar	2.02±.20(-7)	2.08(-7)	2.18(-7)	4.581(6)	4.709(6)	SM
22 Cr	2.58±.13(-8)	2.66(-8)	2.73(-8)	3.661(7)	3.656(7)	SM
23 V	1.69±.07(-8)	1.69(-8)	1.72(-8)	5.799(7)	5.751(7)	SM
26 Fe	4.8±.6(-9)	4.81(-9)	4.85(-8)	2.062(8)	2.002(8)	SM
36 Kr	1.70(-10)	1.71(-10)	1.65(-10)	6.049(9) 6.342(9)		SM ex

4   Other facilities

Orbital functions can be supplied numerically in a format as specified for the electron-ion collision code IMPACT (Crees *et al.* 1978) or as Slater type orbitals (STO's) on specifying the parameters as for the collision code RMATRIX (Berrington *et al.* 1978). Conversely radial output in IMPACT format can be generated as a card image file.

Of interest for excitation by electron impact are term coupling coefficients. They are always printed and optionally generated as an output file in a format processable by program JAJOM (Saraph 1972). A completely optional feature is the calculation of cascading data to electric dipole transitions.

5   Future additions

Publication of the entire code in Computer Physics Communications is overdue. One reason for the delay is the lack of provisions in the Standard version for inclusion of all radiative corrections of Breit-Pauli order — those existing are currently held on a module that can be linked into the standard version (such technical details need not be addressed here, as they may not be the last word). Most urgent is the

incorporation of correction terms of relative order α^2 in the velocity form of the electric dipole operator so as to make comparison of lenghth with velocity results in intermediate coupling for highly ionized species more meaningful than at present.

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