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LETTER TO THE EDITOR

Accurate calculation of transition probabilities using orthogonal operators

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Abstract. The accuracy of transition probabilities calculated from orthogonal operators is increased by including valence correlations in the transition matrix. In this way, the interaction with infinitely many configurations can be included perturbatively without the need to deal with huge matrices. The effectiveness of the method is exemplified by a comparison of the transition array $5d^9 \rightarrow 5d^8 6p$ in Hg IV, Tl V, Pb VI and Bi VII calculated with the strongly interacting $5d^8 6s$ taken into account both explicitly and using the above perturbative procedure.

The availability of accurate wavelengths and transition probabilities is indispensable in the analysis of astrophysical spectra that are presently observed by satellites such as the Hubble Space Telescope. Large-scale *ab initio* calculations are carried out with the configuration interaction version 3 code (CIV3, Hibbert 1975), with Cowan's RCN/RCG suite (Cowan 1981) and within the opacity project (Seaton 1987) using the *R*-matrix method in close coupling. Extensive compilations are published and updated regularly (Martin *et al* 1988, Fuhr *et al* 1988). Databases containing growing amounts of atomic data are present and readily accessible (Kurucz 1993, Wiese and Deters 1993). Conferences in the field are organized frequently, e.g. the Workshop on Laboratory and Astronomical High Resolution Spectra (1994), Brussels, Belgium or the 5th International Colloquium on Atomic Spectra and Oscillator Strengths for Astrophysical and Laboratory Plasmas (1995), Meudon, France.

As in many branches of atomic physics, the challenge of the calculation lies in finding an efficient way to include correlations and, secondary, relativity. The power of a particular approach varies considerably with the type of system at hand. Roughly, we may distinguish two cases:

(i) The element is 'light' ($Z < 20$) or contains less than three electrons outside closed shells. This results in energy spectra with a few, relatively well separated levels. Most of the above-mentioned calculations apply to this case. Here, correlation determines the eigenvector composition of the levels to a considerable degree. As electrostatic effects dominate the description of the system, the mixing is limited to terms with the same *SL*-value. Nevertheless, massive configuration interaction (CI) calculations are necessary to include the right amount of correlation.

(ii) The energy structure is 'complex', i.e. there are several d- or f-electrons outside closed shells. The configurations contain quite a number of levels of the same *J*-value in a relatively small energy interval. Here, the eigenvector composition of the levels is mainly determined by the (non-diagonal) magnetic interactions and the spacing between the levels.

In the present work, we will focus on the second case. To calculate energy spacings in complex systems as accurately as possible, an effectively complete set of orthogonal operators has been introduced (Hansen *et al* 1988a, b, van het Hof *et al* 1991). Explicit configuration interaction can be included in this approach by full diagonalization of a more-configuration space (Uylings *et al* 1993). The calculation of transition probabilities now proceeds in three steps:

(i) Calculation of the eigenvectors (expanded in pure $|SLJ\rangle$ coupled states) of both the even and the odd system.

(ii) *Ab initio* calculation of the transition integrals from fully relativistic Dirac-Hartree-Fock (MCDHF) wavefunctions (Parpia and Grant 1991).

(iii) Calculation of the final transition matrix by transforming the pure SLJ transition matrix, including the above transition integral(s), by means of the fitted eigenvectors.

Due to the large amount of possibly unknown levels, the fitting procedure is inherently restricted to a limited number of strongly interacting configurations. Energy effects from configurations outside the model space can be fitted with 'effective' operators based on perturbation theory. Still, the eigenvectors will be truncated to the components of the model space only. The resulting transition probabilities, very sensitive to correlation, therefore remain somewhat defective. It is the aim of the present work to include correlation with the large number of configurations outside the reference space with second-order perturbation theory. Let $|\Psi\rangle$ and $\langle\Psi'|$ refer to the full odd and even states of the system, to be approximated by the model states $|\alpha\rangle$ and $\langle\alpha'|$, respectively,

$$\langle\Psi'|r|\Psi\rangle = \langle\alpha'|r|\alpha\rangle + \sum_{\beta} \frac{\langle\alpha'|r|\beta\rangle \langle\beta|V|\alpha\rangle}{E_{\alpha} - E_{\beta}} + \sum_{\gamma} \frac{\langle\alpha'|V|\gamma\rangle \langle\gamma|r|\alpha\rangle}{E_{\alpha'} - E_{\gamma}}. \quad (1)$$

The summation in the above runs over all states $\beta(\gamma)$ with the same parity as $\alpha(\alpha')$ that are not included in the model space. To illustrate that even the effects of a strong configuration interaction like $5d^N \leftrightarrow 5d^{N-1}6s$ are reasonably well described by (1), we considered a pilot case where $\langle\alpha'| = \langle 5d^9|$, $|\alpha\rangle = |5d^86p\rangle$ with $|\gamma\rangle = |5d^86s\rangle$ as the only excited state. We calculated the following three cases:

$$\langle\Psi'|r|\Psi\rangle \approx \langle 5d^9|r|5d^86p\rangle \quad (2a)$$

$$\langle\Psi'|r|\Psi\rangle \approx \langle 5d^9 + 5d^86s|r|5d^86p\rangle \quad (2b)$$

$$\langle\Psi'|r|\Psi\rangle \approx \langle 5d^9|r|5d^86p\rangle + \frac{\langle 5d^9|V|5d^86s\rangle \langle 5d^86s|r|5d^86p\rangle}{E_{5d} - E_{6s}}. \quad (2c)$$

The radial factors entering equations (2a)–(2c) are calculated from MCDHF (Parpia and Grant 1991) which was adapted by us for this purpose; they are given in table 1 with the usual definitions:

$$T_L(5d, 6p) = \int_0^{\infty} P_{5d} r P_{6p} dr \quad (3a)$$

$$T_V(5d, 6p) = \frac{1}{\varepsilon_{6p} - \varepsilon_{5d}} \int_0^{\infty} P_{5d} \left(\frac{d}{dr} - \frac{2(2+1) - 1(1+1)}{2r} \right) P_{6p} dr \quad (3b)$$

$$C(5d, 6s, 6p) = \frac{R^2(5d, 5d; 5d, 6s) \int_0^{\infty} P_{6s} r P_{6p} dr}{\varepsilon_{6s} - \varepsilon_{5d}}. \quad (3c)$$

The respective approaches are:

- (a) single configuration ($5d^86s$ neglected),
- (b) full diagonalization ($5d^86s$ included in model space),
- (c) perturbation ($5d^86s$ outside model space).

Table 1. Radial factors of equations (2a)–(2c) in au, as defined in (3a)–(3c). The transition integrals are both in length (T_L) and velocity (T_V) form.

	$T_L(5d, 6p)$	$T_V(5d, 6p)$	$T_L(6s, 6p)$	$T_V(6s, 6p)$	$C(5d, 6s, 6p)$
Hg IV	0.919	0.840	–2.325	–2.231	–0.698
Tl V	0.829	0.761	–2.147	–2.064	–0.447
Pb VI	0.756	0.697	–2.003	–1.926	–0.315
Bi VII	0.696	0.645	–1.882	–1.811	–0.236

Table 2. Calculated gA -values (in s^{-1}) of the $5d^9 \rightarrow 5d^86p$ transitions from Hg IV to Bi VII. The states are labelled by J -value and additionally, in the second column, numbered in increasing order of energy. The columns headed a, b and c correspond to (2a)–(2c); here, the notation $x(y)$ means $x \times 10^y$.

$5d^9 \rightarrow 5d^86p$	λ (Å)	a	b	c
Hg IV				
$3/2 \rightarrow 5/2(1)$	809.21	8.29(5)	8.83(7)	5.13(7)
$3/2 \rightarrow 5/2(3)$	722.33	7.10(5)	9.20(7)	5.60(7)
$5/2 \rightarrow 3/2(1)$	720.92	4.91(6)	1.21(8)	1.10(8)
$3/2 \rightarrow 3/2(4)$	669.41	7.29(7)	9.33(4)	5.07(6)
$5/2 \rightarrow 7/2(9)$	529.46	6.48(8)	7.78(7)	1.31(7)
Tl V				
$3/2 \rightarrow 5/2(1)$	599.52	3.40(6)	1.04(8)	7.06(7)
$3/2 \rightarrow 5/2(3)$	540.36	3.20(6)	2.67(7)	1.51(7)
$5/2 \rightarrow 3/2(1)$	540.95	1.06(7)	1.42(8)	1.32(8)
$3/2 \rightarrow 3/2(4)$	504.99	1.67(8)	1.57(7)	3.29(7)
$5/2 \rightarrow 7/2(9)$	404.81	8.01(8)	1.39(8)	5.79(7)
Pb VI				
$3/2 \rightarrow 5/2(1)$	470.40	9.27(6)	1.32(8)	9.78(7)
$3/2 \rightarrow 5/2(3)$	426.65	1.01(7)	9.02(6)	4.35(6)
$5/2 \rightarrow 3/2(1)$	427.69	2.51(7)	1.89(8)	1.78(8)
$3/2 \rightarrow 3/2(4)$	400.01	2.74(8)	4.70(7)	7.33(7)
$5/2 \rightarrow 7/2(9)$	323.52	9.88(8)	2.22(8)	1.27(8)
Bi VII				
$3/2 \rightarrow 5/2(1)$	383.66	1.51(7)	1.56(8)	1.20(8)
$3/2 \rightarrow 5/2(3)$	349.44	1.51(7)	3.55(6)	1.36(6)
$5/2 \rightarrow 3/2(1)$	350.49	6.27(7)	2.82(8)	2.69(8)
$3/2 \rightarrow 3/2(4)$	327.81	4.37(8)	1.12(8)	1.51(8)
$5/2 \rightarrow 7/2(9)$	266.75	1.03(9)	2.41(8)	1.49(8)

To compare the power of the perturbational and the full diagonalization approach we selected five ‘worst case’ transitions, for which the gA -values of methods (2a) and (2b) differ by at least a factor of ten. Results are given in table 2 and illustrated for two cases in figures 1 and 2. Here perturbation theory seems to be a good approximation to the diagonalization approach, even though the interaction strength in this case would highly favour the latter over the former method. Therefore, the correction terms on the RHS of (1), i.e. the summations over the states β and γ , are included into our programs. Contrary to the example shown in (3c), where only one correlating configuration was involved, the radial factors normally cover complete series (discrete and continuum) of single electron orbitals for each excitation to a channel with a particular angular momentum. In this way, valence correlation corrections can be added routinely if needed. The channels are constructed from B-splines (Hansen *et al* 1993, Froese Fischer and Brage 1994) and summed over;

Figure 1. Examples of gA -values (in s^{-1}) of $5d^9 \rightarrow 5d^8 6p$ transitions from Hg IV to Bi VII, labelled as in table 2: (a) $5/2 \rightarrow 3/2(1)$, (b) $5/2 \rightarrow 7/2(9)$. (—) single configuration and (---) full diagonalization and (· · ·) perturbation.

use of B-splines is considered more accurate than summing and integrating over explicit Hartree-Fock orbitals.

Two refinements, next to (1), have also been implemented and tested:

Core polarization is included into the transition integral by means of the replacement:

$$r \rightarrow r \left(1 - \frac{\alpha_d}{r^3} W_3 \left(\frac{r}{r_\alpha} \right) \right) \quad (4)$$

where the cut-off function W_3 was introduced by Laughlin (1992).

Purely relativistic transitions based on spin-dependent transition integrals are added to the transition program.

However, these corrections turned out to be relatively unimportant in the case presently considered, so their discussion is postponed. In summary, application of perturbative corrections in addition to diagonalizing the most relevant configurations seems a promising way towards calculating accurate transition probabilities with orthogonal operators. More complete calculations and comparison with experiment are on their way.

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