

On the use of AUTOSTRUCTURE for (near- and) neutral heavy species.

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1 Introduction

This document describes features in AUTOSTRUCTURE (AS) that require use of the current development version (29.x) which can be found at: <http://amdpp.phys.strath.ac.uk/autos/autos-29/> and requires the usual userid and password to access it — ask me if you have forgotten them. The discussion below assumes a working knowledge of AS and familiarity with the contents of the current WRITEUP file.

1.1 Motivation

Spectral absorption and emission in near- and neutral heavy species (I–IV) dominate the opacity of kilonovae (Tanaka *et al* 2020) and black-hole/neutron star mergers (Kasen *et al* 2013). Sputtering of heavy metals from the surfaces of magnetic fusion plasma devices can be monitored by spectral modelling (Ref).

1.2 What do we mean by heavy species?

Typically, the elements beyond Zn and on through the lanthanides and actinides, although some of the features we describe may also be of use for the transition metals.

1.3 Background

AS evolved from SS which was developed with astrophysical applications in mind: elements up to Zn and primarily ions thereof. Its default operation and the usual optimization strategy do not work well for heavy species. For example, take any open-shell heavy neutral and input the lowest 3 or 4 configurations as detailed by NIST¹ and run AS in its default mode — Thomas-Fermi potential with unit scaling parameters. The result is usually poor configuration ordering and often the incorrect ground one.

2 Strategy

The executive summary of the approach to be described in detail below is:

- (0) Use kappa-averaged relativistic radial functions!
- (1) Use a unique Slater-Type-Orbital (STO) model potential.
- (2) Apply the usual unique set of scaling parameters to the STO sub-shell potentials.
- (3) Use a unique set of occupation numbers for the STO sub-shells — those of the ground configuration of the next higher charge-state, for example.
- (4) Base optimization around (arithmetic or statistical) mean configuration energies, i.e. include none or all terms of a configuration in the energy functional.
- (5) Form the energy functional from the arithmetic mean of these (arithmetic or statistical) mean configuration energies.
- (6) Given (4) and (5), determine the optimal optimization method in configuration-average coupling. If necessary, refine is LS. IC should never be needed here.

¹The one plus of heavy species is that there is much information on the low-lying energy levels of the lowest-lying configurations. We can make use of this.

2.1 Discussion

A Slater-Type-Orbital (STO) is a nodeless hydrogenic radial function which has the correct asymptotic form at large radii (Slater, 1930):

$$P_i(\rho_i) = A_i \rho_i^{n_i} \exp(-\rho_i/2) \quad (1)$$

where

$$\rho_i = \frac{2z_i \lambda_i r}{n_i} \quad (2)$$

and z_i is the effective charge seen by an electron of sub-shell i with principal quantum number n_i (and orbital angular momentum l_i). It is taken to be (Burgess *et al* 1989)

$$z_i = Z - \frac{1}{2}(q_i - 1) - \sum_{j < i} q_j \quad (3)$$

where q_j are the occupation numbers of sub-shell j and Z is the nuclear charge. The normalization factor (A_i) is given by

$$A_i^2 = \frac{2z_i \lambda_i}{n_i (2n_i)!} \quad (4)$$

We note that while an STO has an explicit dependence on the principal quantum number, it also has an implicit dependence on the orbital angular momentum via the effective charge z_i , which in turn depends on the standard/user order of the sub-shells via $\sum_{j < i}$ in equ. (3). This should be born in mind by time one reaches the actinides and the closed $5s, 5p, 4f, 6s, 6p$ or $4f, 5s, 5p, 6s, 6p$. The one-electron binding energies should be the guide. Of course, the role of the scaling parameters can mitigate against different choices.

The adjustable scaling parameters (λ_i) introduced by Burgess (Burgess *et al*, 1989) optimize the effective charge which, in turn, scales the radial coordinate and contracts/expands the radial function. So, although we will determine a unique potential, it is optimized at different mean radii ($\langle r \rangle_i^{\text{STO}} = n_i(2n_i + 1)/(2z_i \lambda_i)$) and can hope to represent multiple final radial functions with corresponding mean radii.

Each electron produces a static potential which can be evaluated analytically using STOs. Summing over all sub-shells, the potential (V_i) seen by an electron in sub-shell i is (Burgess *et al*, 1989)

$$V_i(r) = \frac{1}{r} \left\{ Z - \sum_j (q_j - \delta_{ij}) \left[1 - \frac{e^{-\rho_j}}{2n_j} \sum_{m=0}^{2n_j-1} \frac{(2n_j - m)}{m!} \rho_j^m \right] \right\} \quad (5)$$

We note that the sum over j is over *all* occupied sub-shells ($j < i$, $j = i$, $j > i$). This is our Slater-Type-Orbital model potential.

The static (i.e. direct) potential can be supplemented by a local exchange term due to Lindgren & Rosèn (1971, 1972) or Cowan (1981) — see the WRITEUP.

2.1.1 Forming the model potential: (1)–(3)

(1) Configuration ordering within our heavy species is very sensitive to small changes in the potential scaling parameters. Our single constraint of minimizing an energy functional does not sufficiently constrain multiple variational parameters which lead to different potentials. In the work of Kasen *et al* (2013) we found it necessary to constrain as many optimized (Thomas–Fermi) potentials as possible to be the same with as few as possible different valence ones. Experience has shown that a unique potential is conducive to good configuration energy ordering. The structureless Thomas–Fermi potential is somewhat limited then, there being a single variational parameter.²

(2) The original Burgess STO potential (Slater 1930, Burgess *et al* 1983) assigned scaling parameters to each nl -subshell. It is only the default STO potential implementation in AS that applies a single scaling

²We note that Bautista (2008) has attempted to introduce two additional parameters for each Thomas–Fermi potential.

parameter to all sub-shells so that a different scaling parameter/potential can be used/generated for each orbital, analogous to the Thomas-Fermi potential usage. In fact, the Burgess approach was also coded-for originally in AS but has rarely, if ever, been used since then (indeed, it had recently fallen into disuse.) The SMINIM logical switch BALAN controls which form is used. BALAN=.TRUE. applies the original Burgess formulation while .FALSE. is the default.

Aside: the use of a unique local model potential leads to orthogonal radial functions on solving the Schrödinger and Dirac equations. However, it does *not* in the case of the non-linear kappa-averaged equation. Cowan has shown that the use of non-orthogonal orbitals is no bar to the accurate description of heavy species. In AS one can test switching-on the overlaps taken to be unity by default or can Schmidt orthogonalize the orbitals (during optimization). Such tests indicate that the connection between a unique potential and orthogonality appears to be a red herring in this instance.

(3) The default AS operation in constructing STO potentials is to use a different set of sub-shell occupation numbers for each orbital's potential — this is independent of BALAN. The default choice is to average-over the occupation numbers of each (non-correlation) configuration which contains the orbital. Alternatively, the user can specify which configuration to use for the occupation numbers — it must contain the orbital whose potential is being constructed. Both of these options solve the self-screening problem but they are not consistent with the first commandment **(1)**.

The SMINIM variable NOCC tells AS to read a single set of NOCC user-supplied *valence* occupation numbers, i.e. $\text{NOCC} \leq \text{MXVORB}$. The corresponding closed-shell occupation numbers are already known of course. Closed and valence refer to the user set-up using (KCOR1,) KCOR2 and MXVORB, not the physical case. If we have an N-electron atom then we require the sum of all occupation numbers (core plus valence) to be equal to N-1. This gives the (unique) potential the correct asymptotic form (at large distances). AS checks for a valid sum of occupation numbers but both N-1 and N are 'allowed'. In the latter case the appropriate self-screening is omitted for each orbital potential being formed. This would violate the first commandment but otherwise it is a perfectly valid option and so AS cannot save you from yourself, so take care!

2.1.2 Optimization: (4)–(6)

There are three SMINIM variables which the user will be familiar with: INCLUD, NLAM, NVAR.

INCLUD \neq 0 tells AS which energies to include in the energy functional to be minimized.

NLAM $>$ 0 tells AS to read NLAM initial values for the scaling parameters.

NVAR $>$ 0 tells AS to read which NVAR parameters are to be varied.

There are two more SMINIM variables, which the user maybe less/not familiar with: NFIX, IWGHT.

NFIX works with NLAM and NVAR to constrain (some) scaling parameters during optimization.

IWGHT tells AS how to form the energy functional from the INCLUD energies.

NFIX: If one wants to use the same value for two scaling parameters, e.g. 2s and 3s, then one simply sets them to the same value, when INCLUD=0. On optimizing, we only have one independent variational parameter, the 3s say, but we want the 2s to be fixed to whatever is the current 3s value during optimization. NFIX $>$ 0 tells AS to read NFIX values which map or fix one scaling parameter to another. The default (NFIX= 0) is of course 1-to-1, 2-to-2, 3-to-3... Like NLAM which reads scaling parameters associated with orbitals 1, 2, 3,... NLAM with no gaps, i.e. the position tells AS which orbital the scaling parameter is to be assigned-to, NFIX would read the default assignment as simply 1 2 3... NFIX. But if we want to fix the 2s to the 3s then we would need to read 1 4 3 4, assuming standard/user ordering 1s, 2s, 2p, 3s. So, the 1s and 2p must be listed even though they are the default values since the input depends on position. The 2s in position 2 is fixed to scaling parameter 4, which is the 3s.)Actually, there is no need for the final 4 for the 3s, since it is its default value, which in turn means that the default 3 is unnecessary.) All values $>$ NFIX are taken to be their default ones. Of course, we expect '4' to be listed as one of the NVAR values, but it does not have to be — in such an instance the 2s would simply be assigned the initial 3s scaling parameter. One can fix as many scaling parameters as one likes to a single other, e.g. NFIX=6 with 6 6 6 6 6 6 means that 1s, 2s, 2p, 3s, 3p, 3d all use the 3d scaling parameter. This is frequently done for closed-shells. For safety, any NFIX values are ignored if INCLUD= 0 — if you want two or more scaling parameters to be the same then set them so. NFIX was used extensively in the calculations by Kasen *et al* (2013).

IWGHT tells AS how to weight the INCLUD energies to be added to the energy functional. The AS default (IWGHT=1) is to weight them equally, i.e. the energy functional is the arithmetic mean of the energies included. (The SS default is to weight them statistically. This can be recovered via IWGHT=2.) Thus, the AS default gives roughly equal weight to a ¹S as a ³D energy, the choice is yours. These weights are always written as part of the energy ordered-listing in the olg output. While we use the word ‘term’, implying LS-coupling, the IWGHT/INCLUD discussion is equally applicable to IC usage since optimization is based around fine-structure weighted terms. For CA usage just replace ‘term’ by ‘configuration’ where it is meaningful to do so.

(4) Heavy species configurations can have $\sim 10^4$ terms, e.g. open f-subshell. Rather than think about which term energies to optimize on, it is more useful to think about configurations as a whole. Thus, we choose to include *all* terms of a configuration in the energy functional, or none at all. (An alternative manageable strategy might be to include the lowest term of any configuration. The usual optimization strategy and options apply then.)

(5) If we include all terms of configuration then the default (IWGHT=1) leads the contributions to the energy functional being proportional to the number of terms in a configuration, which can vary by two orders of magnitude. (IWGHT=2 leads to proportionality by the statistical weight of the configuration.) We choose to weight ‘equally’ each configuration’s contribution to the energy functional. We do so via IWGHT=-1, which forms the arithmetic mean of the arithmetic mean configuration energies. (IWGHT=-2 again forms the arithmetic mean, but of the statistically weighted mean configuration energies — there is little difference for complex configurations, and we use IWGHT=-1.) An additional useful feature of IWGHT < 0 is that it causes AS to treat all INCLUD indexing as algebraic configuration numbers, not terms³. We now just need to decide which configurations to include in the energy functional.

(6) Given (4) and (5), we should not be too surprised that configuration-average coupling gives us a very good representation of what is determined by optimization in LS-coupling (or IC). Indeed, arguably good enough for government work. CA is very fast. You can include all configurations that you think you want/need but only those INCLUDED affect the optimization (there being no mixing of course.) For safety, do set IWGHT=-1 so that the first INCLUD algebraic configuration energies are included in the energy functional. Start by INCLUDING just the ground configuration. While the resulting CA energies are a good representation of the LS/IC mean configuration energies, we can’t compare them with observed since the NIST listings are incomplete in most instances. However, we can compare the CA energies with the NIST positions of the ground term/level for each configuration. And, of course, we can do the same in LS (or IC) using these CA scaling parameters, albeit (much) more slowly in many cases.

An important effect to study in CA is the relative position of configurations of the form nd^q (or nf^q) compared to nd^{q-1} (or nf^{q-1}) plus-electron, for $q \gtrsim 3$. One should include a similar weighting of such configurations, using explicit weights via INCLUD < 0 if necessary.

If you want to see the effect of optimizing in LS, e.g mixing, be careful. If MXCONF > |INCLUD| optimization can drive the mixing in unphysical directions.

It should be noted here that configuration is not a good quantum number in LS-coupling and some terms maybe ‘mis-labelled’ or even a 50-50 mix. Given the large number of terms in these configurations, a few such examples are not a problem. Relevant here as well is the important observation by Cowan (1981) regarding properties of the rare earths: *“Although the various configurations overlap greatly and configuration interactions are by no means negligible, strong configuration mixings tend to be limited to a comparatively few isolated pairs of levels.”*

Given this observation, we should not be too worried about small misalignments of configurations. We can likely ignore them from an opacity perspective while for applications where obtaining the correct ground level is important, for example, we can simply slide whole configurations up-and-down relative to each other while maintaining the term/level splittings within each configuration. We do this

³Recall, the default IWGHT with INCLUD > 0 includes the *lowest* INCLUD energies. This can cause the contributions to the energy functional to change mid-optimization as term energies, say, change their energy order. This would be even less helpful for complex configurations when IWGHT < 0, hence INCLUD > 0 uses the algebraic configuration order then, for all coupling schemes, including configuration-average. In this sense, INCLUD > 0 with IWGHT < 0 behaves very much like the SMINIM KCUT. However, INCLUD < 0 has no such simple analogue.

by reference of our calculated lowest-level of the lowest few configurations to the ‘observed’. There is the extensive NIST database and where we note in particular the compilation of Martin *et al* (1978) on the Lanthanides (I–IV). Brewer (1971a, b) has also estimated the positions of the lowest term/level of the lowest few configurations for all Lanthanides and Actinides (I–IV) by combining thermodynamic data with spectroscopic data. Clearly, in all such comparisons it is necessary that the AS configuration label for these levels is the same as that used by NIST etc. however they may have obtained them. You should satisfy yourself that all those used are consistent.

We align our calculated lowest level for the lowest few configurations with the ‘observed’ by flagging the read (via &SMINIM ISHFTIC=-1) of a SHFTIC file which contains the algebraic configuration index and the energy (relative to the ground) to which its lowest calculated level is to be moved to, all other levels in the configuration are shifted by the same amount. The first line of the file flags the number of label/energy pairs to be read (along with the energy units). The difference in operation compared to the historic one described in the AS WRITEUP file is flagged by the number of pairs being negative.

The SHFTIC file for W I is:

```
-5 1.
1 0.0
2 0.027
3 0.177
4 0.243
5 0.396
```

and it is applicable to any W I calculation which lists the first 5 configurations as

```
A.S. W (Z=74) I
&SALGEB RUN=' ' RAD='NO' CUP='ICR' MXCONF=5 MXVORB=4 KCOR1=1 KCOR2=-12
ICFG=0 BTIME=.FALSE. MSTART=0 &END
1 0 2 0 2 1 3 0 3 1 3 2 4 0 4 1 4 2 5 0 5 1 4 3
5 2 6 0 6 1 7 0
4 2 0 0 0
5 1 0 0 0
4 1 1 0 0
5 0 1 0 0
4 1 0 1 0
```

It does not matter whether the calculated ground level belongs to algebraic configuration 1, or not. Nor does it matter if the calculated ground configuration matches the observed. If not then simply set to zero the SHFTIC energy of (the lowest level of) the algebraic configuration which corresponds to the observed ground one. And set the SHFTIC energy of what was the calculated ground configuration to that of the observed lowest level of said configuration, relative to the ‘observed’ ground level.

These level shifts are made after diagonalization of the Breit–Pauli Hamiltonian $H(IC)$ and so the positioning is exact. As noted in the WRITEUP, these level shifts can be combined with term energy corrections (TECs) via ISHFTLS=-1 and a corresponding SHFTLS file. TECs introduce off-diagonal corrections to $H(IC)$. Since we are moving configurations as whole relative to each other, the main effect of using TECs is due to mixing between configurations. As such, there is likely little to be gained by using them but they might tell us something about the sensitivity to configuration mixing. This has yet to be explored. Note, there is likely no need to construct an independent SHFTLS file with the lowest ‘observed’ term energies.

2.1.3 RESTART and other tips

(0) Set &SALGEB BTIME=.TRUE. This will write timing information to UNIT=IW so that you can view the progression of the calculation and identify the most time consuming part of it. The default is IW=0, output to the screen, which is instantaneous. IW=6 writes to olg but likely gets stuck in the output buffer as it is not flushed. Nothing else is allowed, on health and safety grounds.

(1) Unless your structure is for use in electron-impact excitation (which means it is ‘small’) you should generate a RESTART file (&SALGEB MSTART=1) as soon as you have decided upon a configuration set. Generate the maximal one needed for your problem, e.g. CUP='ICR' RAD='YES'. You can always read it back-in (MSTART=5) with CUP='LSR' and/or RAD='NO'. (CUP='CAR' ignores any MSTART.) Note that while you cannot change the order of your original input configurations⁴

⁴Actually, any user input configurations are read and then ignored when MSTART> 1.

when reading back the RESTART file, you can select an arbitrary set of configurations for inclusion in the energy functional during optimization by use of INCLUD< 0 (and IWGHT< 0, of course). See the fifth commandment.

A final word of warning: if you have AS executables compiled with both SP=4 and SP=8 default integer precisions (as is quite possible for complex systems) a RESTART file written by one executable type cannot be read one of the other type. Well, it can, it is just that the run will fail opaquely, e.g. an ALLOCATION failure.

(2) If you run-out of memory⁵ to store the vector-coupling coefficients (dimension MAXDC) then set &SALGEB KUTDSK=-1 and they are stored on disk and only a small memory buffer is used to I/O them. The file can get very large. It has STATUS='SCRATCH' and so should clean-up after itself (unless the run aborts). Make sure your TMPDIR environment variable is pointing to the correct location as you want the fastest I/O on your system. KUTDSK=-1 can also be used if you don't want to recompile AS with a default of INTEGER*8 (SP=8), as is required if MAXDC > 2³¹ - 1.

(3) Similarly, if you run-out of memory (dimension MAXJU) to store the e-vectors (for the calculation of radiative data) then set &SMINIM KUTDSK=-1 and they are again stored on disk with one (scratch) file per algebraic symmetry.

(4) Do set &SMINIM PRINT='UNFORM'!!! To aid you, the CAVES/TERMS/LEVELS are now still written then.

(5) Use the serial BLAS/LAPACK version of AS (asdeck29_lap.f95) and ensure that you have access to a manufacturer supplied performance BLAS/LAPACK library, not one you have compiled yourself since that one will be no faster than the original non-LAPACK code. The Intel MKL for ifort or gfortran is highly recommended. Ensure multi-threading is 'switched-on' via the OMP_NUM_THREADS environment variable: 8- to 12-cores likely saturates.

(6) If the calculation is still taking too long then you can go back and set &SALGEB KUTLS=-1. This will require a new RESTART file. KUTLS=-1 restricts LS-mixing to be within a configuration. (On the upside, configuration is a good quantum number then!) Matrix diagonalization and rate formation using the resultant shorter eigenvectors can be speeded-up significantly, unless one configuration completely dominates the problem.

2.1.4

We close this section by noting that the Strategy outlined in **Sec. 2 (1)–(6)** appears to be similar to that used by HULLAC (Bar-Shalom *et al* 2001).

3 References

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⁵This is usually indicated by an '...ALLOCATION FAILS FOR XXX' error message from AS.