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Successes and Difficulties in Calculating Atomic Oscillator Strengths and Transition Rates

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Abstract: There is an on-going need for accurate oscillator strengths to be used in astrophysical applications, particularly in plasma diagnostics and in the modelling of stellar atmospheres and the interstellar medium. There are several databases in regular use which contain some of the required data, although often insufficiently complete, and sometimes not sufficiently accurate. In addition, several atomic structure packages are available through the literature, or from their individual authors, which would allow further calculations to be undertaken. Laboratory measurements provide an important check on the accuracy of calculated data, and the combined efforts of theorists and experimentalists have succeeded in providing data of an accuracy sufficient for some astrophysical applications. However, the insufficiency or inadequacy of atomic data is a continuing problem. We discuss in the context of appropriate examples some of the principal steps which researchers have taken to calculate accurate oscillator strengths, including both *ab initio* results and also various extrapolation processes which attempt to improve such results. We also present some examples of the main causes of difficulty in such calculations, particularly for complex (many-electron) ions, and indicate ways in which the difficulties might be overcome.

Keywords: E1 transitions; configuration interaction calculations; transition rates; remaining challenges to accuracy

1. Introduction

For more than half a century, calculations of atomic oscillator strengths and transition rates have been undertaken with a level of accuracy and a range of atomic systems studied that have increased with increasing computer power. Should it not, by now, be a straightforward matter to calculate the atomic data needed for any astrophysical application? Indeed, should there not be electronic banks of data stored for most atomic systems, and of an adequate accuracy, which can be accessed easily by astrophysical modellers?

Of course, some databanks do exist and are widely used. However, they are by no means complete, and some of the data have been found not necessarily to be of sufficient accuracy. Additionally, the improvement of computer power has happened alongside the improvement of resolution of observational data, particularly from space-based observations. This has resulted in both increased accuracy of observational data, and the observation of transitions which were previously too weak to discern. However, even so, could not the additional data now required be calculated in a manner which would be quite straightforward by today's standards?

That opens the question of how accurate the atomic data needs to be, and how "straightforward" a calculation would be needed to achieve results whose level of accuracy can be determined, or at least estimated. The purpose of this paper is to explore these issues, to demonstrate something of the progress which has been made and to draw attention to the difficulties which remain in undertaking such work. We do not intend to be comprehensive, although an overview of the extensive sets of calculations

which have been undertaken or of the achievements which have been reached. Instead, we use some specific examples to illustrate how success has come about and to point to challenges which remain, indeed which increase as the range and complexity of atomic systems needed to be studied grows. As a background, a useful summary of the relationship between oscillator strengths, transition rates and a number of other transition parameters was provided by Hilborn (1982) [1].

2. Methods

Various methods have been used to calculate wave functions for evaluating oscillator strengths, ranging from very simple models (particularly in the early calculations) to sophisticated methods which seek to capture most of the electron correlation and which can, in principle, be extended towards exact wave functions, although in reality exactness cannot be achieved except for one-electron systems. In this section, rather than discuss all the main methods of calculation, we focus on what type of calculation would be needed to achieve oscillator strengths of a desired accuracy. We illustrate the key features through a small number of examples.

2.1. The Inadequacy of Very Simple Calculations

For many-electron systems, one of the simplest and earliest approaches is the use of the Hartree–Fock (HF) approximation for determining wave functions. These wave functions are represented by a single-configuration approximation. For most calculations, two forms of the oscillator strengths are determined—length (f_l) and velocity (f_v). These would be equal for exact wave functions, but in most cases the two forms give differing results.

Table 1 shows those values for the $1s^2 2s^2 \ ^1S-1s^2 2s 2p \ ^1P^o$ transition in several members of the Be-isoelectronic sequence. Even in this few-electron case, the length and velocity forms give values differing by more than a factor of two. Burke et al. (1972) [2] showed that, when a small number of correlation configurations was added to the HF configuration, while still retaining the $1s^2$ core in each of them, much better agreement (within about 5%) for the two forms could be achieved, as well as improved agreement between the calculated and experimental transition energies. The most significant correlation configurations in achieving better agreement between length and velocity forms are $1s^2 2p^2 \ ^1S$ and $1s^2 2p 3d \ ^1P^o$.

Table 1. Be sequence: Oscillator strengths of $2s^2 \ ^1S-2s 2p \ ^1P^o$ transition.

		C III	N IV	O V
Single configuration [2]	f_l	1.0746	0.8569	0.7055
	f_v	0.5627	0.3713	0.3039
	ΔE (a.u.)	0.4494	0.5607	0.6756
Valence Correlation [2]	f_l	0.7930	0.6293	0.5250
	f_v	0.8047	0.5954	0.4922
	ΔE (a.u.)	0.4773	0.6055	0.7334
Valence + Core Correlation CIV3 [3–5]	f_l	0.759	0.609	0.511
	f_v	0.757	0.610	0.510
	ΔE (a.u.)		0.5972	0.7253
Valence + Core Correlation MCHF [4]	f_l		0.6085	
	f_v		0.6086	
	ΔE (a.u.)		0.5960	
Valence + Core Correlation MCDF [6]	f_l	0.757	0.610	0.508
	f_v	0.753	0.608	0.507
	ΔE (a.u.)	0.4681	0.5974	0.7264
Experiment [7]	ΔE (a.u.)	0.4664	0.5955	0.7235

ΔE are the transition energies, in LS coupling, with averaging over the fine structure levels for experimental energies.

We also display in Table 1 some later calculations of Fleming et al. [3–5]. They used the Breit–Pauli versions of the the general configuration interaction code CIV3 [8] and the MCHF (Multi-Configurational Hartree–Fock) code [9] and found that, with a larger number of correlation configurations, and in both the valence and core shells, the length and velocity forms show excellent agreement. Additionally, in an independent calculation using the alternative, MultiConfigurational Dirac–Fock/Dirac–Hartree–Fock (MCDF/MCDHF) method, Ynnerman and Froese Fischer (1995) [6] obtained very similar results to those of Fleming et al. [5]. Table 1 also shows that these larger calculations have calculated energies in good agreement with experiment.

There are certain conclusions we can draw from this set of results. Firstly, in general, single configurations do not give good agreement between length and velocity forms. Consequently, at least one of them (usually both) must be incorrect. However, even though exact agreement between the two forms is achieved in a local potential approximation, the common value is not necessarily correct. It is sometimes possible to achieve good length and velocity agreement even in the HF approximation (a non-local potential method), but again the common value can be incorrect. For example, Weiss (1967, 1969) [10,11] found that for the transition $2s^2 2p^2 \text{P}^o - 2s 2p^2 \text{D}$ in C II, the HF (length, velocity) values were (0.263, 0.262) while the configuration interaction values were (0.121, 0.124): the closeness of the length and velocity forms in the HF approximation gave no assurance of correctness. Secondly, a sequence of calculations providing systematic improvement in the wave functions gives more confidence in the sense of convergence of the results. Thirdly, comparison with other methods of determining the oscillator strengths can lead to a greater consensus of what should be the correct results.

2.2. Towards More Accurate Wave Functions

The accuracy of oscillator strengths is largely dependent on the quality of the wave functions used in their calculation. The HF method, being variational in character, ensures that in going beyond that approximation, the energy corrections are of second order, but errors in the calculation of other atomic properties are of first order. Hence, the HF calculations of oscillator strengths tend to be rather inaccurate; more sophisticated wave functions are needed for more accurate oscillator strengths.

The method of configuration interaction (CI) provides a systematic means of improving on HF results. In LSJ coupling, the wave functions take the form

$$\Psi(J) = \sum_{i=1}^M a_i \Phi_i(L_i S_i J) \quad (1)$$

where Φ_i are configuration state functions (CSFs). If we form the Hamiltonian matrix with typical elements $H_{ij} = \langle \Phi_i | H | \Phi_j \rangle$, then the variationally optimal values of the CI mixing coefficients a_i are the components of the eigenvector of this matrix, corresponding to an eigenvalue E_i which represents the energy of a state or level. We can then systematically increase the size M of the expansion, and consider the convergence of energies and wave functions with respect to M . Of course, M should be infinite, but that is not practicable, so the CI expansion, Equation (1), has to be truncated.

Such a process allows us to undertake extrapolation to improve the results. This can be done in a number of ways. For example, HFR, the relativistic HF/CI method (Cowan 1981) [12] allows for a scaling of Slater integrals (Cowan and Griffin 1976) [13], typically by multiplicative factors of around 0.80–0.85, and this has proven very successful in achieving good agreement between calculated and experimental energy differences. In our own work, we have often used a process which we have termed “fine-tuning”. In this, small changes are made to the ab initio diagonal elements of the Hamiltonian matrix in order to bring the calculated and experimental energy levels into good agreement (Hibbert (1996) [14].

2.3. Indicators of Accuracy

Any extension of the CI expansion will lead to a monotonic lowering of the calculated energy eigenvalues. However, there is no such guaranteed monotonic lowering of the transition energy (an energy *difference*) involved in an oscillator strength. Nor can a monotonic improvement in the multipole integral be achieved. Hence, it is necessary to establish certain indicators for the accuracy of oscillator strengths, to serve as useful guides to users of calculated oscillator strengths, and to offer a means of estimating the level of accuracy of the final results. Such indicators have been discussed in some detail by Hibbert (1996) [14], and include :

1. Calculated energy separations
2. Length/velocity comparison
3. Convergence of results
4. Extrapolation processes
5. Comparison with other work

Indicator 1 is clearly important in relation to transition energies, but it is also important for energy separations between interacting states/levels if the CI mixing coefficients a_i are to be determined accurately. Indicator 2 relates to the two main forms of the oscillator strength calculation; exact wave functions would achieve agreement between them, so that disagreement between them suggests further improvements could be sought; however, agreement between them is no guarantee of accuracy, as discussed in Section 2.1. Indicator 3 allows us to examine the changes in the oscillator strengths as the CI expansions are extended, thereby setting up a sequence of results which can be used in an extrapolation process, as discussed above, leading to Indicator 4. Indicator 5 is particularly important, with the “other work” preferably including calculations using different methods, experimental determinations and, if possible, oscillator strengths derived from astrophysical observations.

In Table 1, we demonstrate all but Indicator 4: no fine-tuning has been undertaken. As correlation effects are systematically added, improvements in energy separations and the length/velocity agreement occur, as required by Indicators 1–3, while through results obtained from an alternative method, Indicator 5 provides some confidence in the accuracy of the results.

The transitions shown in Table 1 are between two isolated states (in the sense that they do not interact significantly with other states). In Table 2, we present some transitions which require us to consider states whose interaction is the prime cause of non-zero oscillator strengths. These intercombination transitions are critically dependent on the accuracy of the mixing between the upper $2s2p^3\ ^5S_2^o$ level and the $2s2p^3\ ^3P_2^o, ^3D_2^o$ levels, as well as $2s^22p3s\ ^3P_2^o$ and $2s^22p3d\ ^3P_2^o, D_2^o$ levels, all of which allow a contribution to the dipole operator for transitions to the ground state levels.

Table 2. $2s^22p^2\ ^3P_{1,2}-2s2p^3\ ^5S_2^o$ in N II [15].

Method	Orbitals	A-Values—Transition Rates (s^{-1})			Lifetime (in ms)
		$^5S_2-^3P_1$	$^5S_2-^3P_2$	Ratio of A-Values	
ab initio	$n \leq 4$	43.8	106.5	2.432	6.65
	$n \leq 5$	46.9	114.8	2.448	6.18
	$n \leq 6$	49.2	120.1	2.441	5.91
fine-tuned	$n \leq 4$	52.6	127.9	2.432	5.54
	$n \leq 5$	51.4	125.6	2.444	5.65
	$n \leq 6$	50.9	124.1	2.438	5.71
“Converged”			2.44	5.75	
Experiment			2.24 ± 0.06 [16] 2.45 ± 0.07 [18]	5.88 ± 0.03 [17]	

Our calculations [15] were undertaken using the CIV3 code [8,19]. We found that the mixing between the odd-parity levels changes as more CSFs are added to the wave functions. In Table 2, the effects of a systematic improvement in the wave functions is displayed, starting with the inclusion of possible CSFs with nl orbitals up to $n = 4$, and then with up to $n = 5$ and finally $n = 6$. We also applied our fine-tuning process, principally to improve the mixing between the odd parity levels. It is interesting to observe that while the increase in the number of CSFs uniformly increases the transition rates, the fine-tuned transition rates reduce, and each set seems to be converging to a common value. Not all comparisons between *ab initio* and “extrapolated” results lead to such a degree of convergence, but our experience has found that the fine-tuning process does tend to over-estimate transition rates, but that the fine-tuned results are much more stable to systematic increase in the CI expansions, and this gives us increased confidence in the “fine-tuned” results. We also show in Table 2 our estimates of the convergence of both sets of results. Comparison with experiment can be obtained by using the transition rates to compute the theoretical lifetime of the upper level and also the ratio of the A-values of the two transitions contributing to the lifetime. Table 2 shows that there is good agreement with experiment for both parameters. Thus, Indicators 1 and 3–5 have been used to determine a level of confidence in the calculated results. We were not able to use Indicator 2. Only the length form of the transition rate is shown. Drake (1976) [20] showed that the normal dipole length operator is correct to order α^2 , α being the fine-structure constant, whereas the corresponding velocity operator would require additional relativistic corrections to achieve the same level of accuracy. Typically, these are not included in Breit–Pauli calculations. Instead, the length/velocity agreement for allowed E1 transitions is normally checked before the Breit–Pauli operators are added to the Hamiltonian.

3. Resolution of Differences between Sets of Data

In the previous section, we discuss the processes and characteristics needed to achieve a good level of accuracy, at least when only a few levels were involved in the calculation. Below, we consider the more complicated situation when many, often strongly interacting, levels need to be studied simultaneously. However, first, we show how systematic calculations can help resolve differences between conflicting sets of data, whether theoretical or experimental.

As an example, we consider the $3p^4 4p-3p^4 4d$ transitions in Ar II. The NIST tabulations [7] quote transition rates (A-values) from two experimental sources, both from around 50 years ago—Bennett et al. [21], and Rudko and Tang [22]. The problem is that the A-values given by these two experiments differ considerably. The data from Bennett et al. [21] are quoted in the NIST tabulations, where possible, but for other transitions, only the data of Rudko and Tang [22] is available.

Recently, new experiments have been undertaken by Belmonte et al. (2014) [23], building on the earlier work of Aparicio et al. [24]. These new results compare well with Bennett et al. [21], but differ considerably from Rudko and Tang [22]. Until recently, there were no theoretical results with which to compare. These were provided by Hibbert (2017) [25], using the CI method together with the fine-tuning process to improve the accuracy of the oscillator strength calculations. Some comparisons between calculation and experiment are shown in Table 3, for a representative sample of the transitions. Our work [25], while not being completely definitive in that length and velocity values differed typically by up to 10–15%, confirmed the results of Belmonte et al. (2014) [23] and provided an independent verification of the 10–15% level of accuracy claimed by their most recent experiments [23].

Table 3. A-values (10^8 s^{-1}) for 4p–4d transitions in Ar II.

Transition		Hibbert [25]		Reference [23]	Reference [21]	Reference [22]
4p	4d	A_l	A_v			
$4P_{5/2}^o$	$4F_{3/2}$	0.074	0.066	0.086		0.236
$4P_{1/2}^o$	$4F_{3/2}$	0.105	0.094	0.13	0.155	0.348
$4P_{5/2}^o$	$4F_{7/2}$	0.0031	0.0026	0.002		
$4P_{5/2}^o$	$4P_{5/2}$	0.625	0.551	0.49	0.52	1.00
$4P_{3/2}^o$	$4P_{5/2}$	0.524	0.455	0.43	0.49	0.817
$4P_{5/2}^o$	$4P_{3/2}$	0.469	0.421	0.36	0.37	0.627
$4P_{3/2}^o$	$4P_{1/2}$	1.18	1.05	1.07	1.1	1.99
$4P_{1/2}^o$	$4P_{3/2}$	0.763	0.678	0.60	0.63	1.00
$4P_{1/2}^o$	$4P_{1/2}$	0.459	0.405	0.41	0.42	0.733
$4D_{3/2}^o$	$4D_{1/2}$	0.258	0.235	0.19	0.269	0.267
$4D_{5/2}^o$	$4D_{7/2}$	0.051	0.046	0.049	0.048	0.047

4. Remaining Challenges in the Calculation of Oscillator Strengths

In the earlier sections, we have provided a few examples in which, by systematic inclusion of CSFs, sometimes in conjunction with the fine-tuning process, it has been possible to reach levels of accuracy in the calculated oscillator strengths which are sufficient for the needs of those who use this data in their modelling of, for example, stellar atmospheres or the determination of elemental abundances in stars or the interstellar medium. However, these examples required just a small number of levels to be calculated simultaneously, even though in some cases they interact strongly. While it is true that the Ar II work did require a larger number of levels to be considered, many of them were spectroscopically fairly pure: they did not exhibit strong interactions. However, difficulties arise when a much larger number of strongly interacting levels have to be included in the same calculation, either because they do interact strongly, or because they are quite high-lying in energy and all levels with lower energy also need to be included in the calculation. Ions with open d-shells are particularly challenging, and we consider now some calculations which have proven and continue to prove difficult for theorists in their attempts to provide oscillator strengths of sufficient accuracy, and with an accuracy which can be substantiated.

4.1. The 2507.552, 2509.097 Å Lines in Fe II

These two lines are prominent in the spectrum of η Carinae (Verner et al. 2002) [26]. Notionally, they correspond to the transitions [7]

λ	Transition
2507.552 Å	$c \ 4F_{7/2-x} \ 6F_{9/2}^o$
2509.097 Å	$c \ 4F_{7/2-w} \ 4G_{9/2}^o$

One would expect the former, being an intercombination line, to have a small oscillator strength, while the latter, being an allowed line, would be expected to have a comparatively large oscillator strength. On this assumption, Verner et al. (2002) [26] found they could not properly model this part of the spectrum, but could do so if the oscillator strengths were chosen to be equal.

The oscillator strengths of the two transitions have been calculated by a number of researchers, as shown in Table 4.

Table 4. Oscillator strengths of the 2507, 2509 Å lines in Fe II.

Source	2507.552	2509.097	Sum
Kurucz [27]	0.001	0.297	0.298
Raassen and Uylings [28]	0.233	0.045	0.278
Corr�eg�e and Hibbert [29]	0.138	0.136	0.274

The results of Kurucz (2010) [27] fit the expected pattern of allowed and intercombination lines. Those of Raassen and Uylings (1998) [28] do not; indeed, their values reverse the expected size order. Our own calculations (Corr eg e and Hibbert) (2005) [29] were completed, though not published, before we became aware of the proposal of Verner et al. [26] to abandon the data already published at that time and adopt equal oscillator strengths for the two transitions in their modelling. We sought to understand how it was that our calculated oscillator strengths were indeed of comparable size, contrary to expectations but in accord with the needs of Verner et al. [26]. We notice that the total oscillator strength from these two transitions is quite similar in all three sets of results. This suggests that we are seeing a different distribution of the total oscillator strength in each of the three calculations. We found that the A-values were entirely dependent on the proportion of 4G symmetry in the upper states. The two transitions have a common lower level, so that the upper level of 2507Å is $90,067.4 \text{ cm}^{-1}$, while the upper level of 2509Å is $90,042.8 \text{ cm}^{-1}$.

In Table 5, we show the main percentage compositions given by Corr eg e and Hibbert (2005) [29] and those of Raassen and Uylings [28]. During our studies of these transitions, it became apparent that while the upper levels did exhibit strong configuration mixing, a third main component, corresponding to the $3d^65p \ ^4F^o$ configuration, also interacted strongly. It also became apparent that it was the size of the component of $4p \ ^4G^o$ in the wave function of each of the three levels that determined the size of the oscillator strengths of the transitions. It can be seen in Table 5 that our fine-tuning process, following on from an already extensive ab initio calculation, resulted in the two upper levels of these lines having almost equal components of the $^4G^o$ configuration, resulting in our two calculated oscillator strengths being almost equal.

Table 5. Comparison of mixings in $J = 9/2$ level in Fe II.

Level (cm^{-1})	Percentages		
	$4p \ ^4G^o$	$5p \ ^6F^o$	$5p \ ^4F^o$
Corr�eg�e and Hibbert [29]			
90,042.8	43	29	13
90,067.4	41	27	16
90,386.5		25	65
Raassen and Uylings [28]			
90,040.5	13	36	41
90,072.7	76	9	8
90,407.2		48	47
Corr�eg�e and Hibbert [29], fine-tuned to Raassen & Uylings [28]			
90,040.5	15	18	63
90,072.7	78	4	11
90,407.2		74	21

Our fine-tuning process allowed us also to fine-tune to the energy levels given by Raassen and Uylings. In doing so, we found fairly good quantitative agreement with the percentage compositions which Raassen and Uylings obtained, as displayed in Table 5.

On reflection, we were perhaps rather fortunate in arriving at results which, unbeknown to us at the time, fitted the requirements of Verner et al. [26]. We would wish to highlight that, for most of

the transitions which both Kurucz and Raassen and Uylings studied, their results are of good quality and can be used with confidence. In this instance though, the upper levels were so close in energy that small modifications to the fine-tuning corrections led to very different mixings and therefore oscillator strengths. In all three sets of results, a large-scale calculation had been undertaken, with the wave functions of many levels having to be determined simultaneously. That always leaves open the possibility that for a small proportion of the wave functions, when CI mixing is particularly strong, the mixing coefficients can be wrong. Oscillator strengths determined using heavily mixed wave functions need to be treated with caution. In particular, extrapolation such as our fine-tuning process, needs to be undertaken very carefully, moving from the ab initio calculation in small steps.

4.2. Correlation in Open 3d Subshells

The capture of the effect of electron correlation in wave functions is generally a slowly-converging process. This is particularly true in the case of open 3d subshells, as found in iron group elements, and therefore of considerable importance when the wave functions are used in the calculation of oscillator strengths of transitions of astrophysical importance. The key configurations are of the form $3d^n ml$, $3d^{n+1}$, $3d^{n-1} m'l'$. Challenges in calculations arise because both the radial dependence of the 3d orbitals and also the level of correlation in the 3d subshell are state-dependent.

The state-dependency of electron correlation implies that even for a large-scale calculation, there is some level of inaccuracy in the calculated energy levels, and therefore in the determination of oscillator strengths in an ab initio calculation. The scale of such calculations is so extensive that undertaking a systematic enlargement of the CI expansions becomes a prohibitive exercise, and so alternative extrapolation procedures, such as fine-tuning or the scaling of Slater integrals [12], is then a better approach, even though (as we have seen) much care has to be exercised in using these extrapolation processes, as they can lead to erroneous results.

Difficulties are also encountered by the state-dependence of the radial functions. For example, in their studies of E1 Fe II transitions, Corrége and Hibbert (2005) [29], as well as Deb and Hibbert (2014) [30] found it better to choose a 3d function optimised on the energy of the ground $3d^6 4s^6 D$ state, whereas Deb and Hibbert (2010a,b,2011) [31–33], in studying forbidden transitions involving $3d^7$ levels, found that much better results could be obtained by optimising the 3d function on the $3d^7^4 F$ state. This is possible when a calculation is limited to certain types of transition, or even to a very small number of transitions. On the other hand, if a comprehensive study of both allowed and forbidden transitions is to be undertaken, the use of orthogonal orbitals (and therefore a single choice of 3d function for all transitions) requires the introduction of many CSFs to compensate for the non-optimal choice of radial functions for some of the levels. Ideally, non-orthogonal orbitals would allow different 3d functions to be used for different occupancies of the 3d subshell arising within the same calculation, and this could profitably be pursued to reduce the overall number of CSFs required.

4.3. Open d-Subshells with Differing Seniority

Open 3d-subshells with between three and seven electrons can have more than one level with the same LSJ combination, but differing by their seniority. For example, for the $^4F_{3,5}$ levels in Fe II, $3d^6 4s$ have two distinct levels, which are usually written either as [7] $3d^6(^3F_1)4s$ and $3d^6(^3F_2)4s$, or as $3d^6(^3_2F)4s$ and $3d^6(^3_4F)4s$, respectively. In the latter notation, the subscripts denote the seniority of the 3d-subshell. Even in a large-scale calculation, it is difficult to achieve a calculated energy difference between these two $^4F_{3,5}$ levels which agrees with experiment.

If we include just these two configurations, the Hamiltonian matrix is of the form

$$\mathcal{H} = \begin{pmatrix} a & c \\ c & b \end{pmatrix} \quad (2)$$

The eigenvalues and eigenvectors depend solely on the magnitudes of $|a - b|$ and c . We find that for these ${}^4F_{3,5}$ levels in Fe II, in atomic units, $|a - b| = 0.0915$, $c = 0.0643$, so that the eigenvectors are respectively

$$\begin{pmatrix} 0.8887 \\ 0.4585 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} -0.4585 \\ 0.8878 \end{pmatrix}$$

with the eigenvalue difference 0.1579, compared with the experimental value of 0.1248. With fine-tuning, the smallest eigenvalue difference achievable is $2|c| = 0.1286$, so that this simple model cannot achieve agreement with experiment.

However, when we use the radial functions listed by Deb and Hibbert (2014) [30] in a large-scale CI calculation, and then apply our fine-tuning process, we can at least obtain agreement with experiment. Specifically, we find that the eigenvector corresponding to the lower of the two eigenvalues and dominated by these CSFs in an ab initio calculation has the following components for the two principal configurations

$$\begin{pmatrix} -0.4789 \\ 0.8446 \end{pmatrix}$$

with the two eigenvalues differing by 0.1335. The fine-tuning process results in the lower eigenvalue having mixing coefficients with

$$\begin{pmatrix} -0.5303 \\ 0.7998 \end{pmatrix}$$

for the two principal CSFs, and the two eigenvalues then differ by 0.1248, in agreement with experiment. Fine-tuning results in similar agreement with experiment for some other mixings between levels differing only in the seniority of the 3d subshell.

However, it is not so in every case. Another situation where there is strong mixing between levels differing only in the seniority of the 3d subshell occurs in the case of $3d^6({}^3P_1)4s\ {}^4P_{1,5}$ and $3d^6({}^3P_2)4s\ {}^4P_{1,5}$ of Fe II. In the terminology used above, we found that, in atomic units, $|a - b| = 0.0037$ and $c = 0.0785$, so that in an ab initio calculation with just these two CSFs, the eigenvectors are

$$\begin{pmatrix} 0.7852 \\ 0.6192 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} -0.6192 \\ 0.7852 \end{pmatrix}$$

with the eigenvalue difference 0.1616, compared with the experimental value of 0.1262. With fine-tuning, the smallest eigenvalue difference achievable is $2|c| = 0.1570$. The large-scale CI calculation, using the same orbitals as previously, gives the eigenvector components of these two CSFs for the lower of the two eigenvalues as

$$\begin{pmatrix} -0.6218 \\ 0.7128 \end{pmatrix}$$

with the two lowest eigenvalues differing by 0.1393. Fine-tuning did not really help, since, even with equal components of the two principal configurations, we found an eigenvalue difference of 0.1332.

Thus, even though the same orbitals and CSFs were able to provide results in good agreement with experiment for some transitions [29], it would seem that, as yet, insufficient electron correlation has been captured in these calculations to give us confidence in the results. We have considered the inclusion of another range of orbitals for each of $l = 0, 1, 2, 3$, but this would lead to a large number of additional CSFs. Instead, we noticed the absence of a 5g orbital: a $3d \rightarrow 5g$ substitution could be a significant correlation effect, though normally small for many wave functions. Accordingly, we added

CSFs of the form $3d^54s5g$ and $3d^44s5g^2$ to our earlier calculations. This resulted in the components of the lower eigenvalue changing to

$$\begin{pmatrix} -0.6014 \\ 0.7535 \end{pmatrix}$$

with the two lowest eigenvalues differing by 0.1329. This ab initio energy difference is then marginally better than the best possible fine-tuned difference without the 5g orbital. However, the introduction of 5g does not entirely solve the difficulty, because we find that the smallest fine-tuned energy difference is 0.1297 a.u., still higher than the experimental value of 0.1262. Clearly, further correlation CSFs would need to be introduced to bring these closer together.

There are of course other methods of extrapolating ab initio results. One such method is customarily employed when using the Cowan code [12]. Specifically, several radial integrals may be scaled by appropriate factors, notably the two-electron Slater integrals which are scaled customarily by factors of 0.80 to 0.85. However, both $a - b$ and c involve only the Slater integrals $F^2(3d,3d)$ and $F^4(3d,3d)$. If a common scaling parameter is used, the mixing coefficients are unchanged by this scaling. This process could indeed result in agreement with energy separations between levels differing only in the seniority of the 3d subshell, which our fine-tuning could not completely achieve. However, we saw above that, when additional correlation CSFs are used instead, the mixing coefficients do change. Hence, although the energy separations are in agreement with experiment, the mixing coefficients may still contain inaccuracies.

5. Concluding Remarks

What are we to make of this? We, along with quite a number of other researchers, have been very successful in obtaining accurate oscillator strengths of many transitions of astrophysical significance. Where possible—that is, where the calculations do not become prohibitively large—systematic ab initio calculations are the most reliable, and accuracy which is sufficient for astrophysical modelling has been achieved in a large number of cases. However, for a number of reasons, this is not always possible. One reason is the size of the calculation, although this becomes more possible as computer power increases. Another, more significant, reason is the absence of some experimental energy levels in the literature. The spectrum of Fe II is a case in point. The work of Nave and Johansson [34] made great strides in extending the number of known levels, compared with previous listings. However, many gaps remain. Even some of the levels of $3d^64s$ or of levels arising from other low-lying configurations are missing. Certainly, fine-tuning is an important though not exact tool in improving the accuracy of ab initio calculations. However, without experimental energy levels, it cannot be undertaken reliably (although one can make intelligent guesses as to the size of the corrections needed).

There is also a temptation for theorists to undertake large-scale calculations of many transitions simultaneously, for that is the need of users. However, it must be stressed that, while it may be possible to provide some sort of overall assessment of the level of accuracy of the results, the same degree of accuracy cannot be guaranteed for every transition in the ensuing (usually large) set of oscillator strengths, even if it might be valid for many of them.

The best way for making progress is for providers (both theorists and experimentalists) and users of atomic data to work together, so that, if users find published results which appear not to fit, in their analysis of observational data, with the use of other atomic data, then this can be drawn to the attention of the providers of data, who can then try to focus on the offending transitions and try to improve the accuracy of their data.

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