Calculation of weak lines

ABSTRACT

We describe the situations which give rise to small oscillator strengths, particularly those which are unusually small as a result of some form of cancellation. We discuss through specific examples the type of calculation which is needed to give accurate results.

INTRODUCTION

The importance of weak absorption lines in the determination of stellar and interstellar abundances has been described by Keenan et al. (1989) in these proceedings. We discuss in this article the theoretical situations which give rise to weak lines and the calculation of the corresponding small oscillator strengths (or alternatively transition probabilities).

The most obvious division which separates transition probabilities into "large" and "small" is between "allowed" (i.e. electric dipole or E1) transitions and "forbidden" (i.e. electric quadrupole (E2) or higher multipole (E λ) and magnetic multipole (M λ)) transitions. The formula for transition probabilities of $E\lambda$ or $M(\lambda-1)$ transitions contains the factor $\alpha^{2\lambda+1}$ where α ($\simeq 1/137$) is the fine structure constant. The presence of this factor implies that for "forbidden" transitions, the transition probabilities are normally several orders of magnitude smaller than for "allowed" transitions. A discussion of "forbidden" transitions is given by Zeippen(1989) in these proceedings, so we shall not consider them in this article. Instead, we shall investigate situations in which oscillator strengths of "allowed" transitions are small that is, smaller than the norm for "allowed" transitions.

METHOD OF CALCULATION

In principle, the oscillator strength of a transition can be expressed in an infinite number of different but (for exact calculations) equivalent forms. In practice, at most two forms are calculated:

length :
$$f_l = \frac{2\Delta E}{3q} |\langle \Psi_1 | \mathbf{r} | \Psi_2 \rangle|^2$$
 (1)

velocity :
$$f_v = \frac{2}{3g\Delta E} |\langle \Psi_1 | \nabla | \Psi_2 \rangle|^2$$
 (2)

where ΔE is the transition energy (in atomic units), Ψ_1 and Ψ_2 are the initial and final state wave functions and g is the multiplicity of the state with lower energy (either (2L+1)(2S+1) in LS coupling or (2J+1) in intermediate coupling). Of course, neither Ψ_1 nor Ψ_2 is known exactly, so in general the two forms f_l and f_v give different values. The extent of the agreement gives *some* measure of the accuracy of the results, even though complete agreement between them does not in itself guarantee their correctness. Some convergence of that agreement as the wave functions are improved is also necessary.

For atomic systems with more than one electron, the wave functions cannot be determined exactly. In practice, they are usually expanded in infinite series of basis functions. For systems with several electrons, the most common expansion method is known as configuration interaction (CI) of which MCHF (Multi-Configurational Hartree-Fock) and SOC (Superposition Of Configurations) are specific, important classes. In this method, we expand

$$\Psi_1 = \sum_i a_i \phi_i \tag{3}$$

$$\Psi_2 = \sum_i b_j \psi_j \tag{4}$$

so that, for example,

$$f_l = \frac{2\Delta E}{3g} |\sum_i \sum_j a_i b_j < \phi_i |\mathbf{r}| \psi_j > |^2$$
 (5)

Each of $\{\phi_i\}$, $\{\psi_j\}$ is a configuration state function. For many transitions for which $f_l \geq 0.1$, $a_1 \gg a_i (i=2,3,\ldots)$ and $b_1 \gg b_j (j=2,3,\ldots)$ where ϕ_1 and ψ_1 refer to the Hartree-Fock (HF) configurations of the two states (i.e. those associated with the normal labelling of the states). In such cases, the expansions (3) and (4) can be truncated after a fairly small number of terms and still result in quite accurate values for f_l (and similarly for f_v). In the next section, we shall consider situations where f_l is, for a number of different reasons, much smaller than 0.1. In these cases, the expansions (3) and (4) have to be much longer and the configurations chosen much more carefully in order to achieve a level of accuracy which gets even the first significant figure in f_l correct.

CAUSES OF SMALL OSCILLATOR STRENGTHS

We first discuss how abnormally small oscillator strengths occur.

Cancellation in the transition integral

The dipole matrix element $<\phi_i|\mathbf{r}|\psi_j>$ in (5) contains the radial integral

$$\int_0^\infty r P_{n_i l_i}(r) P_{n_j l_j}(r) dr \tag{6}$$

as a factor. In certain cases, this integral is approximately zero because the positive and negative parts of the integrand almost cancel. If also the coefficients of ϕ_i and ψ_j are close to unity in the expansions (3) and (4) respectively, so that all others are small, then the entire oscillator strength will be small.

Two specific instances of this situation are the 2s ²S - 3p ²P° transition in Li (Weiss 1963) and the 3s ²S - 4p ²P° transition in Mg II (Hibbert et al. 1983). The states of these alkali-like ions are well represented by the HF approximation so that the expansions (3) and (4) are each dominated by a single term. For both ions, the radial integral is close to zero. Although that means that the oscillator strength will be close to zero, it also means that the contributions from other terms in (3) and (4), while being small in absolute terms, are of comparable magnitude to the HF contribution. We shall discuss the Mg II transition in some detail later.

Cancellation due to CI

In the examples of the previous section, all the states are nearly 100% pure; in many other cases, the states are at least 90% pure (i.e. one coefficient in (3), say a_1 , dominates the rest, with $a_1^2 \geq 0.9$). But in some states, there is strong CI mixing so that although one coefficient is larger in magnitude than the rest, there are two and sometimes more which are fairly large, say with $a_1^2 \geq 0.2$. We have investigated astrophysically important transitions involving such states for a number of singly ionised species of second row elements. For example, in the case of the $3s^23p^2$ 3P - $3s3p^3$ 3P ° transition in P II (Hibbert 1986), the ground state 3P is over 90% pure, but the 3P ° state has an expansion (4) of the form

$$\Psi(^{3}P^{o}) = 0.81 \; \psi_{1}(3s3p^{3}) + 0.50 \; \psi_{2}(3s^{2}3p3d) + \dots$$

so that $b_1^2 = 0.66$, $b_2^2 = 0.25$ and the remaining terms are each fairly small.

This is a widely occurring situation. Other instances include the 2s²2p ²P° - 2s2p² ²D transition in C II (Weiss 1967) where there is strong mixing between 2s2p² ²D and 2s²3d ²D; also the 3s3p ¹P° - 3p² ¹D transitions in Mg-like ions (Froese Fischer and Godefroid 1982, Tayal and Hibbert 1984, Baluja and Hibbert 1985); the 3s²3p ³ ⁴S° - 3s3p⁴ ⁴P in S II (Ojha and Hibbert 1989); the 3s²3p ²P°

- 3s3p² ²D transition in Si II (Dufton *et al.* 1983); the 3s²3p⁵ ²P° - 3s3p⁶ ²S transition in Ar II (Hibbert and Hansen 1987). In all these transitions of the form 3s²3pⁿ - 3s3pⁿ⁺¹, the upper state exhibits strong CI mixing of the form

$$b_1\psi_1(3s3p^{n+1}) + b_2\psi_2(3s^23p^{n-1}3d) \tag{7}$$

with $b_1,b_2 \gg b_i$, $(i \ge 3)$, (Bauche et al. 1987). Moreover, as Bauche et al. discuss, the CI mixing (7) leads to small oscillator strengths because

$$b_1 < \phi_1 | \mathbf{r} | \psi_1 > + b_2 < \phi_1 | \mathbf{r} | \psi_2 > \simeq 0$$
 (8)

Neither of the two matrix elements in (8) is small, but the combination (8) is. The two contributions almost cancel each other out.

When this cancellation due to CI occurs, the contributions from the remaining configurations play proportionally a more significant rôle than they would in the absence of such cancellation. We shall discuss specific cases later.

Intercombination lines

The situations described above assumed LS coupling of angular momentum. The selection rules for transitions in LS coupling require $\Delta S=0$ and $\Delta L=0$ or 1 with $L=0 \rightarrow L'=0$ excluded. In that approximation, E1 transitions of the form $^1S-^3P^o$ are forbidden; i.e. their oscillator strengths are identically zero. If the fine structure of the $^3P^o$ state is taken into account, then although the oscillator strength of the $^1S_0-^3P_0^o$, $^3P_2^o$ E1 transitions remain zero, that of the $^1S_0-^3P_0^o$ transition becomes non-zero. Even in the approximation of one configuration per LS symmetry, we can write

$$\Psi_1(^1S_0) = a_1\phi_1(^1S_0) + a_2\phi_2(^3P_0) \tag{9}$$

$$\Psi_2(^3P_1^o) = b_1\psi_1(^3P_1^o) + b_2\psi_2(^1P_1^o) \tag{10}$$

so that

$$<\Psi_1|\mathbf{r}|\Psi_2> = a_1b_2 < \phi_1|\mathbf{r}|\psi_2> + a_2b_1 < \phi_2|\mathbf{r}|\psi_1>$$
(11)

Although a_2 and b_2 are generally small, they are non-zero so that the oscillator strength is non-zero, but normally small. We shall discuss important special cases in the next section.

EXAMPLES OF SMALL OSCILLATOR STRENGTHS

In this section, we discuss the calculation of a number of oscillator strengths in which we have used the general CI code CIV3 (Hibbert 1975, Glass and Hibbert 1978), which is of SOC type.

A. Hibbert 103

$$3s^2S - 4p^2P^o$$
 in Ma II

An extensive CI calculation of the oscillator strength of this transition was undertaken by Hibbert *et al.* (1983). Results were presented at different levels of approximation which we display in Table 1.

Table 1. Oscillator strengths of the 3s ²S - 4p ²P° transition in Mg II.

| | Hibbert e | t al. (1983) | Other calculations | |
|-----|-----------|----------------|--------------------|----------------|
| | fı | f _v | fı | f _v |
| A : | 0.00028 | 0.00033 | 0.00033ª | |
| B: | 0.00123 | 0.00101 | 0.00097^{b} | 0.00095 |
| C: | 0.00038 | 0.00037 | | |

Notes - a: Biémont (1975); b: Froese Fischer (1976)

The single configuration (HF) approximation gives oscillator strengths (calculation A) in close agreement with the work of Biémont (1975): the values are small, and length and velocity forms agree quite closely. The introduction of configurations describing the polarisation of the core - particularly 2p⁵3d4p ²S and 2p⁵3d3s ²P^o - increase the oscillator strength by a factor of three or four (calculation B). Again the values of Hibbert et al. are in general agreement with an MCHF calculation of Froese Fischer (1976) which similarly includes the effect of core polarisation. Again the length and velocity values agree satisfactorily. This shows that agreement between length and velocity forms is not in itself a guarantee of accuracy.

It is interesting to consider how such a substantial change arises. If we consider the expression

$$F_{ij} = \left(\frac{2\Delta E}{3a}\right)^{\frac{1}{2}} a_i b_j < \phi_i |\mathbf{r}| \psi_j > \tag{12}$$

then (5) becomes

$$f_l = \left(\sum_i \sum_j F_{ij}\right)^2 \tag{13}$$

In the velocity form, the equivalent F_{ij} associated with the two core polarising configurations given above are -0.052 and 0.060. Their combined effect is itself only 0.008, but because the interaction F_{11} between the HF configurations is only 0.018, the proportionate effect is substantial. Other F_{ij} also contribute to the considerable increase in f_i .

Hibbert et al. went further than this, and added other configurations, the most significant of which were 2p⁶ns ²S and 2p⁶np ²P^o, especially 2p⁶4s ²S (calculation C). The effect was to reduce once again the oscillator strength to around 0.0004. It is particularly interesting

that the inclusion of $2p^64s$ 2S should be so striking. In the approximation which includes only $2p^6ns$ 2S configurations in the ground state wave function, its coefficient a_i would be zero, (Brillouin's theorem): the Hamiltonian matrix element between 3s 2S and ns 2S is zero. These matrix elements remain zero as more configurations are added, but the expansion coefficients a_i change to albeit small non-zero values and the F_{ij} associated with the 4s 2S and 4p $^2P^o$ configurations has the value -0.017.

For this transition, all these values of F_{ij} are small. For an oscillator strength in the range 0.1 to 1.0, such as for the 3s 2 S - 3p 2 P° transition, the non-HF contributions F_{ij} have only a small influence on the value obtained. In many calculations, the corresponding configurations could probably be omitted. But because the oscillator strength is so small in this case, it is crucial that they are included, and an extensive CI calculation be undertaken, if accurate results are to be achieved.

The implications for interstellar magnesium abundances using these accurate results are discussed by Murray et al. (1984).

$$3s^23p^2$$
 $^3P - 3s3p^3$ $^3P^o$ in P II

We remarked earlier that the $^3P^\circ$ state is dominated not just by the $3s3p^3$ configuration but by a linear combination of $3s3p^3$ and $3s^23p3d$, as in (7). It is important to realise that the variationally optimum 3d function for this linear combination is not the same as that for the $3s^23p3d$ $^3P^\circ$ state. In fact, the $3s3p^3$ configuration interacts strongly with the $3s^23pnd$ Rydberg series: the wave function for each member contains a substantial contribution of $3s3p^3$, (though decreasing with n). Alternatively, if spectroscopic radial functions $P_{nd}(r)$ are used in the configurations in the expansion of the $3s3p^3$ state:

$$\Psi(3s3p^3) = b_1\psi_1(3s3p^3) + \sum_n b_n\psi_n(3s^23pnd) \qquad (14)$$

then the summation will need to contain many terms. Even then it will not be complete: it should also include the continuum (Hansen 1977). This problem can be overcome by replacing (14) by

$$\Psi(3s3p^3) = b_1\psi_1(3s3p^3) + b_2\psi_2(3s^23p\overline{3d}) \tag{15}$$

in which the radial function $P_{\overline{3d}}(r)$ is optimised on the lowest energy eigenvalue of the Hamiltonian matrix $\langle \phi_i | \mathbf{H} | \phi_j \rangle$, using the variational principle directly as in the SOC method (e.g. Hibbert 1975) or via MCHF equations (e.g. Froese Fischer 1978).

Hibbert (1986) discussed a set of calculations of the oscillator strength for this transition, with different levels of approximation. In all cases the oscillator strength is small. It is sufficient to look at the simplest of his calcula-

Table 2. Oscillator strengths of the 3s²3p² ³P - 3s3p³

3P° transition in P II.

| | fı | f_v | $\Delta E(3s3p^3 - 3s^23p3d)$ |
|------|---------|--------|-------------------------------|
| A | 0.0255 | 0.0304 | 0.1407 |
| В | 0.0192 | 0.0227 | 0.1282 |
| C | 0.0110 | 0.0113 | 0.1227 |
| Expt | 0.017 ± | 0.005ª | 0.1227 |
| | | | / |

Notes - a : Livingstone et al. (1975); energies in atomic units.

tions to see how the smallness arises. In terms of (12) and (15), $F_{11} = 0.440$, $F_{12} = -0.280$. The sum is 0.160. Hence by (13) an oscillator strength which would be 0.194 without the CI in (15) has been reduced to 0.026, a change of almost an order of magnitude (see calculation A of Table 2). The addition of further configurations reduced the oscillator strength still more (calculation B).

Although we noted above that P differs considerably from the 3d radial function appropriate to the 3s23p3d ³Po state, it transpires that it is important that at least the 3s23p3d 3Po state is as accurately represented as is 3s3p3 3Po, if the 3s23p2 3P - 3s3p3 3Po oscillator strength is to be calculated accurately. The two states interact strongly, over and above (15), and the extent of their mixing influences the coefficients b; for each state and thence the oscillator strength. A crucial measure of how accurately the mixing has been calculated is the energy splitting $\Delta E(3s3p^3 - 3s^23p3d)$. It can be seen from Table 2 that in this regard calculation B represents a substantial improvement over calculation A, but the splitting is still not small enough (so the mixing is not strong enough). Calculation B is an extensive CI calculation, and a final refinement can be made by making small adjustments to the diagonal Hamiltonian matrix elements, so that the eigenvalue separation correponds to the associated experimental energy separation. A justification for this process has been given by Brage and Hibbert (1989). It is necessarily approximate, but this fine tuning generally leads to results which are more accurate than the ab initio results from which they are derived. We give the resulting values as calculation C in Table 2. They are in good agreement with the best and most recent experimental values obtained using beam-foil spectroscopy. The results of calculation C were used by Dufton et al. (1986) to determine the abundance of phosphorus in the interstellar medium.

Again, as in our first example, an extensive CI calculation is necessary to obtain results which are at all accurate. It is worth pointing out that results based on CI expansions such as (14), where "spectroscopic orbitals" or "real state orbitals" are used, may indeed exhibit cancellation effects, but they will normally not be reliable because they do not treat the interaction with the continuum. Indeed, a finite CI treatment necessitates a proper variational treatment of the form of (15). Semi-empirical methods for handling such cases will not normally be adequate.

$$3s^2 {}^1S_0 - 3s3p {}^3P_1$$
 in Si III

This transition was discussed by Ojha et al. (1988) following a similar calculation for Al II by Hibbert and Keenan (1987). This intercombination line has a nonzero oscillator strength because of the fine-structure mixing of 3s3p $^{3}P_{1}^{\circ}$ and $^{1}P_{1}^{\circ}$, and to a lesser extent $^{3}E_{1}^{\circ}$, $^{2}E_{2}^{\circ}$ and $^{3}E_{2}^{\circ}$. To get that mixing right, it is necessary to obtain wave functions for all these states which give accurately the energy separations.

We compare in Table 3 the value of the associated emission transition probability calculated by Ojha et al. with that from experiment and those obtained by other theorists. All three calculations lie within a few per cent of the experimental value. Each involves extensive CI though the details of the calculations are different. Nussbaumer (1986) used the SUPERSTRUCTURE code (Eissner et al. 1974) which is of SOC type with the radial functions obtained using a scaled-Thomas-Fermi potential. Laughlin and Victor (1979) used a model potential approach which incorporates core polarisation (see Laughlin 1989 - these proceedings - for further discussion of this method). Ojha et al. (1988) used CIV3, together with the fine-tuning which we discussed above.

Table 3. Transition probabilities of the 3s² ¹S₀ - 3s3p ³P₁ transition in Si III:

Comparison of results.

| Source | Nature of Work | A-value (s-1) |
|--------|--|-------------------------|
| a | CI with model potential | 1.78 × 10 ⁴ |
| Ъ | Large-scale CI | 1.8×10^4 |
| c | Large-scale CI with core polarisation | 1.672 × 10 ⁴ |
| ď | Lifetime measurement using ion-trap | 1.67×10^4 |

Notes - a : Laughlin and Victor (1979); b : Nussbaumer (1986); c : Ojha et al. (1988); d : Kwong et al. (1983).

It is this fine-tuning which leads to such good agreement with experiment. We display in Table 4 a series of calculations using CIV3, both in *ab initio* form ("uncorrected") and with the fine-tuning added ("corrected"). The three calculations consisted of:

- A: valence-shell correlation only
- B: A + core polarisation treated by model potentials (similar to the scheme of Laughlin and Victor)

A. Hibbert 105

C: A + extra configurations to allow for the explicit polarisation of the core

Table 4. Transition probabilities of the 3s² ¹S₀ - 3s3p

³P₁^o transition in Si III:

Convergence of calculations. (Ojha *et al.* 1988)

| Calculation | Uncorrected | Corrected | |
|----------------|------------------------|------------------------|--|
| A ^a | 1.368 ×10 ⁴ | 1.642 ×10 ⁴ | |
| В | 1.799 ×104 | 1.683 ×104 | |
| C | 1.649 ×104 | 1.672 ×104 | |

Note - a : see text.

The "uncorrected" transition probabilities vary quite substantially. This is mainly because the $^3P_1^{\circ}$ - $^1P_1^{\circ}$ energy splitting is over-estimated by 5% in calculation A, underestimated by 3% in calculation B, whereas in calculation C it is correct to within 0.2%. On the other hand, the "corrected" results, obtained by adjusting diagonal matrix elements so that the eigenvalue differences agree with the experimental energy differences, are much more consistent. This demonstrates that this process of fine-tuning an already good calculation can lead to rather accurate transition probabilities, especially for intercombination lines.

CONCLUSIONS

We have described in this article a variety of situations which give rise to small oscillator strengths. Their common feature is that, for a reliable value to be obtained theoretically, a careful and extensive calculation is necessary, and preferably one which gives special attention to those particular transitions. Values of small oscillator strengths which arise from simpler calculations, or from calculations which consider simultaneously a wide range of transitions, must be treated with caution, because it is unlikely that the values so obtained will have converged with respect to the addition of further configurations.

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A. Hibbert 107