R-matrix electron-impact excitation cross sections in intermediate coupling: an MQDT transformation approach

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Abstract. A widely used alternative to a full Breit–Pauli R-matrix calculation of electron-impact excitation is the transformation of S- or K-matrices, calculated in pure LS coupling, to intermediate coupling. Here we present a transformation method, based on multi-channel quantum defect theory (MQDT), that eliminates the problems associated with standard transformation methods and leads to accurate level-to-level electron-impact excitation cross sections. Instead of transforming the physical S- or K-matrices, we employ MQDT to generate unphysical K-matrices in pure LS coupling; we then treat all channels as open and transform these matrices to intermediate coupling. Finally, we generate the physical K-matrices from the intermediate-coupled unphysical K-matrices. To illustrate the accuracy of this method, we compare cross sections for several transitions in Fe^{14+} determined using: (i) the standard transformation method in which the LS-coupled physical S-matrices are transformed to intermediate coupling; (ii) an MQDT transformation method, used by others, in which the unphysical LS-coupled K-matrices are transformed to pure jK coupling; (iii) our intermediate coupling frame transformation (ICFT) method and (iv) a full Breit–Pauli R-matrix calculation. It is shown that our ICFT method eliminates the problems associated with the other two transformation methods and leads to cross sections that agree very well with those determined from a full Breit–Pauli R-matrix calculation. Furthermore, the ICFT method can be applied to complex atomic systems which are intractable to a full Breit–Pauli calculation.

1. Introduction

There is significant current interest in inelastic collisions of electrons with complex atoms and ions. This is due primarily to the need for accurate atomic data for the modelling of laboratory and astrophysical plasmas. For example, collisional–radiative modelling of such species requires, among other data, electron-impact excitation rates between individual levels. However, the theoretical calculation of accurate excitation cross sections and rates in complex open-shell atoms and ions presents a formidable problem for atomic physics. Such calculations must simultaneously include the effects of configuration interaction and intermediate coupling on the bound-state levels as well as the coupling of these levels due to the presence of the scattered electron.

The R-matrix close-coupling approximation is an efficient method for performing accurate calculations of electron-impact excitation. In particular, the Breit–Pauli R-matrix codes (see Berrington *et al* 1995) make it possible to perform calculations of electron-impact excitation in intermediate coupling. However, for complex species, the number of

spectroscopic and pseudo-states that need to be included in the configuration-interaction expansion of the N-electron target and the number of closely spaced levels that must be included in the close-coupling expansion make such calculations difficult indeed. First, the size of the $(N+1)$-electron Hamiltonian matrix that must be diagonalized in the inner region can become very large; furthermore, one must solve the coupled equations in the asymptotic outer region at a large number of energies in order to resolve the many narrow resonances associated with the closely spaced levels.

Clearly alternative methods are needed in order to permit the determination of accurate level-to-level electron-impact excitation cross sections for atomic species that are sufficiently complex that a full Breit–Pauli R-matrix calculation would be impractical. In the next section, we consider methods based on the transformation of S- or K-matrices, calculated in pure LS coupling, and we introduce our intermediate-coupling frame transformation (ICFT) method that employs multi-channel quantum defect theory (MQDT) and has the capability of producing accurate excitation cross sections between individual levels. In section 3, we present the results of a set of model calculations of electron-impact excitation in Fe^{14+} in order to compare the ICFT method with various other transformation methods and full Breit–Pauli R-matrix calculations. Finally, in section 4 we summarize our findings and suggest future directions.

2. Transformation methods

An alternative to full Breit–Pauli R-matrix close-coupling calculations, that has been employed for a number of years, is to perform an R-matrix calculation in LS coupling and then transform the resulting (physical) S- or K-matrices to intermediate coupling. For example, we can transform the LS-coupled K-matrix to jK coupling using the equation

$$K(\gamma_i L_i S_i J_i \ell_i K_i J; \gamma_f L_f S_f J_f \ell_f K_f J) = (-1)^{(2J+1-\ell_i-\ell_f-J_i-J_f)}\sqrt{(2J_i+1)(2K_i+1)}$$
$$\times\sqrt{(2J_f+1)(2K_f+1)}\sum_{LS}(2L+1)(2S+1)$$
$$\times\begin{Bmatrix} L & S & J \\ \frac{1}{2} & K_i & S_i \end{Bmatrix}\begin{Bmatrix} L_i & \ell_i & L \\ K_i & S_i & J_i \end{Bmatrix}$$
$$\times K(\gamma_i L_i \ell_i L S_i S; \gamma_f L_f \ell_f L S_f S)\begin{Bmatrix} L & S & J \\ \frac{1}{2} & K_f & S_f \end{Bmatrix}\begin{Bmatrix} L_f & \ell_f & L \\ K_f & S_f & J_f \end{Bmatrix}. \quad (1)$$

For light atoms and ions in low stages of ionization, this algebraic transformation alone provides a means for calculating level-to-level excitation cross sections to a good approximation.

However, when the spin–orbit mixing of the levels is important, intermediate coupling is required. For such cases, one can use term-coupling coefficients (Jones 1975) to transform the K-matrices in jK coupling to full intermediate coupling:

$$K(\beta_i J_i \ell_i K_i J; \beta_f J_f \ell_f K_f J) = \sum_{\substack{\gamma_i L_i S_i \\ \gamma_f L_f S_f}} Y_{J_i}(\beta_i, \gamma_i L_i S_i) K(\gamma_i L_i S_i J_i \ell_i K_i J; \gamma_f L_f S_f J_f \ell_f K_f J)$$
$$\times Y_{J_f}(\beta_f, \gamma_f L_f S_f) \quad (2)$$

where $Y_{J_i}(\beta_i, \gamma_i L_i S_i)$ represents the term-coupling coefficients for the initial level $\beta_i J_i$. The term-coupling coefficients (TCCs) are calculated by first performing a configuration-interaction calculation in pure LS coupling to determine the eigenvectors of the LS terms as linear combinations of LS-coupling configuration-state functions (see Froese Fischer 1977).

The mass–velocity and Darwin relativistic corrections are included within the LS-coupling calculation. One then performs a Breit–Pauli structure calculation to allow the LS terms to mix through the spin–orbit interaction and expresses the eigenvectors for the levels as linear combinations of the eigenvectors of the multi-configuration terms; the coefficients in this final expansion are the TCCs.

The transformation procedure using equations (1) and (2) works well when all levels are open. However, significant problems arise in the resonance region, where there are both open and closed channels. In this region, some of the terms included in the term-coupling expansion for a given level will be open, while others will be closed. In order to handle this situation, the standard procedure has been to include only those components of the TCCs that correspond to open terms, and then to renormalize the TCCs. Furthermore, the splitting of the terms into the individual levels presents problems in the resonance region. Some of the channels that are closed for a given term may become open for levels with higher energies and some of the channels that are open for a given term may become closed for levels with lower energies. To avoid this problem, the energies of all levels of a given term are often set equal to the term energy. These are reasonable approximations as long as the spin–orbit interaction is not very large. However, in heavy atomic systems or highly ionized species, the mixing of terms can be very strong and the energy splitting between the levels can become significant; this approximation will then lead to serious problems.

The program JAJOM, written by Saraph (1972, 1978) and modified over the years, can be used to carry out the standard transformation procedure described above. The version of this program that we have employed carries out an algebraic transformation of the S-matrix to jK coupling and then uses the TCCs to determine the level-to-level cross sections in intermediate coupling. Because of the problems discussed above when there are both open and closed channels, the energies employed for all levels of a given term are set equal to the term energy, and the TCCs include only open terms and are then renormalized. This can lead to poor threshold energies; incorrect resonance structures, since the Rydberg series of resonances converge on terms rather than on levels and to rather strange shapes in the cross sections, as the terms included in the TCCs open up. Thus, it is now generally accepted that such transformation procedures are not valid for species in which the effects of intermediate coupling are important; instead, it is assumed that full Breit–Pauli calculations must be performed in such cases (see, for example, Zhang and Pradhan 1995).

Multi-channel quantum defect theory (MQDT) has been employed extensively in conjunction with the eigenchannel R-matrix method to analyse complex resonance structures in photoionization (see the review by Aymar *et al* 1996). However, its use in conjunction with the Wigner–Eisenbud R-matrix approach employed by the Belfast suite of codes has been primarily restricted to high-lying Rydberg states. Recently, however, Badnell *et al* (1998) made extensive modifications to the unpublished asymptotic codes STGF and STGBF (Seaton 1981, 1985, 1986, Berrington *et al* 1987) to incorporate MQDT as an option. This has made it possible to analyse the detailed resonance structures found in electron-impact excitation and photoionization while only solving the coupled equations in the asymptotic region at a relatively small number of energies. In this paper, we restrict ourselves to the study of electron-impact excitation.

In the MQDT mode, the unphysical K-matrices ($\mathcal{K}$) or the unphysical S-matrices ($\mathcal{S}$) are calculated on a rather coarse energy mesh (normally a few hundred points); these matrices, which have a slow variation with energy, are then easily interpolated onto a much finer energy mesh. Finally, one can then generate the physical K-matrix (K) or the physical

S-matrix (S) on the fine energy mesh from the equations:

$$K = \mathcal{K}_{oo} - \mathcal{K}_{oc} \left[\mathcal{K}_{cc} + \tan(\pi \nu) \right]^{-1} \mathcal{K}_{co} \tag{3}$$

and

$$S = \mathcal{S}_{oo} - \mathcal{S}_{oc} \left[\mathcal{S}_{cc} - \exp(-2\pi i \nu) \right]^{-1} \mathcal{S}_{co} \tag{4}$$

where the matrices are partitioned by the open (o) and closed (c) channels; ν denotes the effective quantum numbers; and $\tan(\pi\nu)$ and $\exp(-2\pi i\nu)$ are diagonal matrices. Deeply closed channels can give rise to some numerical problems, but they are not intractable. In fact, we find that STGF in the MQDT mode is able to produce a complex resonance structure in excellent agreement with that generated by the program in the standard (non-MQDT) mode, including allowance for the perturbative treatment of the outer-region coupling potentials.

The development of an MQDT version of STGF also provides an additional advantage. It should now be possible to develop an LS coupling to intermediate coupling transformation program that would eliminate the problems associated with the methods used in programs such as JAJOM, by working with the unphysical K-matrices instead of the physical ones. We note that the eigenchannel R-matrix method has been employed in conjunction with MQDT to carry out what is referred to in the review by Aymar *et al* (1996) as a 'spin–orbit frame transformation' for the calculation of level-to-level photoionization cross sections. In this paper we will refer to this transformation method as a geometrical frame transformation (GFT).

In these calculations, LS-coupled unphysical S-matrices, and the associated unphysical dipole matrices, are transformed to a pure coupling scheme such as jK or jj coupling. Then, equation (4) for the transformed S-matrices, and the corresponding equation for the transformed dipole matrices, are applied to generate the physical S-matrices and the physical dipole matrices. However, the effective quantum numbers ν appearing in these equations are determined from the experimental level energies. This procedure has been applied with great success to neutral species where the effects of intermediate coupling are relatively small.

Based on their experience with photoionization calculations for neutrals, Aymar *et al* (1996) argue that, because of the use of *experimental* level energies in the determination of the physical S-matrices and the physical dipole matrices, this method will normally work well for cases in which the bound-state level structure is adequately described by a Breit–Pauli calculation. On the other hand, Robicheaux and Greene (1993) have found that for the photoionization of neutral halogens, one must include the effects of spin–orbit mixing and transform the unphysical S-matrices and the dipole matrices to intermediate coupling. As we will demonstrate, the effects of the spin–orbit mixing of the terms are significant in the determination of electron-impact excitation cross sections for the cases considered in the present work and, in general, should be important to the determination of electron-impact excitation cross sections in a large number of ionic species.

We have now developed a program based on what we refer to as the intermediate-coupling frame transformation (ICFT) method. It reads the LS-coupled unphysical K-matrices generated by STGF, transforms them to jK coupling using equation (1), and finally transforms them to full intermediate coupling using equation (2). The physical K-matrices are then calculated by applying equation (3), with the effective quantum numbers determined from the theoretical or experimental level energies. Since all channels are treated as open when using the TCCs to transform from jK coupling to intermediate coupling, this method eliminates the problems associated with the transformation of the physical S- or

K-matrices. We will show in the next section that the ICFT method can be applied with great accuracy to cases where the effects of intermediate coupling are sufficiently large so that the GFT method described by Aymar *et al* (1996) is no longer valid.

3. Model calculations of electron-impact excitation in Fe^{14+}

We have performed a series of model calculations on Fe^{14+} to compare cross sections determined from four different methods: (i) the transformation of the physical LS-coupled S-matrices to intermediate coupling, using the program JAJOM; (ii) our version of the GFT, in which the unphysical LS-coupled K-matrices are transformed to pure jK coupling; (iii) our intermediate-coupling frame transformation and (iv) the full Breit–Pauli R-matrix approximation.

We chose the case of Fe^{14+} for these calculations because we have found that reasonably good results can be obtained in LS coupling with the inclusion of only eight terms in the close-coupling expansion. These eight terms lead to only 14 levels and make it possible to carry out a full Breit–Pauli R-matrix calculation for this system in a relatively short amount of time. Secondly, the size of the resonant contributions to the excitation cross sections in this ion have been shown to be very sensitive to the exact positions of the $(N + 1)$-electron resonance states (see Griffin *et al* 1994, Badnell *et al* 1994), and it should serve as an excellent test of the accuracy of these various methods. Finally, this ion has sufficient spin–orbit mixing of the terms so as to provide an adequate test of the transformation methods. However, it should be noted that we refer to these as model calculations since a definitive calculation for this ion would include many more terms in the configuration-interaction expansion of the target; however, this would only require more computational time and would add nothing to our comparison of the methods.

The 14 levels included in the intermediate coupling calculations of electron-impact excitation in Fe^{14+} are given in table 1, along with their calculated energies and TCCs.

Table 1. Energies and term-coupling coefficients employed in the calculations on Fe^{14+}.

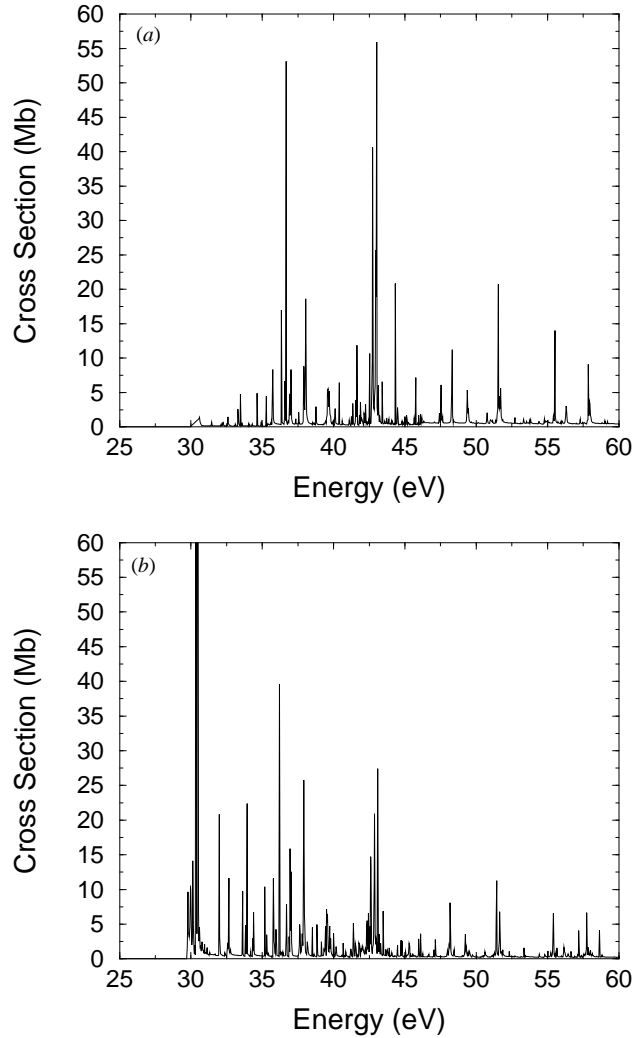| Index	Level	Energy (eV)	Term-coupling coefficients
1	$3s^2\ ^1S_0$	0.0	$0.999\,9863\ 3s^2\ ^1S - 0.005\,2238\ 3p^2\ ^3P - 0.000\,1362\ 3p^2\ ^1S$
2	$3s3p\ ^3P_0$	29.0	$1.000\,0000\ 3s3p\ ^3P$
3	$3s3p\ ^3P_1$	29.7	$0.997\,7314\ 3s3p\ ^3P + 0.067\,3206\ 3s3p\ ^1P$
4	$3s3p\ ^3P_2$	31.4	$1.000\,0000\ 3s3p\ ^3P$
5	$3s3p\ ^1P_1$	46.3	$0.997\,7314\ 3s3p\ ^1P - 0.067\,3206\ 3s3p\ ^3P$
6	$3p^2\ ^3P_0$	69.1	$0.989\,5234\ 3p^2\ ^3P + 0.144\,2790\ 3p^2\ ^1S + 0.005\,1888\ 3s^2\ ^1S$
7	$3p^2\ ^1D_2$	69.3	$-0.929\,3230\ 3p^2\ ^1D + 0.369\,1659\ 3p^2\ ^3P + 0.005\,3076\ 3s3d\ ^3D$ $-0.006\,8663\ 3s3d\ ^1D$
8	$3p^2\ ^3P_1$	70.2	$1.000\,0000\ 3p^2\ ^3P$
9	$3p^2\ ^3P_2$	72.1	$-0.929\,1352\ 3p^2\ ^3P - 0.369\,2182\ 3p^2\ ^1D + 0.019\,4293\ 3s3d\ ^1D$ $+0.002\,9002\ 3s3d\ ^3D$
10	$3p^2\ ^1S_0$	84.4	$-0.989\,5370\ 3p^2\ ^1S + 0.144\,2777\ 3p^2\ ^3P + 0.000\,6189\ 3s^2\ ^1S$
11	$3s3d\ ^3D_1$	84.4	$1.000\,0000\ 3s3d\ ^3D$
12	$3s3d\ ^3D_2$	84.6	$0.999\,8788\ 3s3d\ ^3D + 0.014\,3233\ 3s3d\ ^1D + 0.006\,0142\ 3p^2\ ^1D$ $+0.001\,0307\ 3p^2\ ^3P$
13	$3s3d\ ^3D_3$	84.8	$1.000\,0000\ 3s3d\ ^3D$
14	$3s3d\ ^1D_2$	96.6	$0.999\,6850\ 3s3d\ ^1D - 0.014\,3459\ 3s3d\ ^3D + 0.020\,5790\ 3p^2\ ^1D$ $+0.000\,7067\ 3p^2\ ^3P$

Figure 1. *R*-matrix electron-impact excitation cross section for the transition $3s^2 \; ^1S_0 \rightarrow 3s3p \; ^3P_1$ in Fe^{14+}: (*a*) from a transformation of the physical *S*-matrices in *LS* coupling to intermediate coupling using JAJOM; (*b*) from a geometrical frame transformation (GFT), as defined by Aymar *et al* (1996); (*c*) from our intermediate-coupling frame transformation (ICFT); (*d*) from a full Breit–Pauli calculation.

We will focus on the transitions from the $3s^2 \; ^1S_0$ ground level to the $3s3p \; ^3P_1$ and $3s3p$ $^1P_1$ excited levels, and from the $3s3p \; ^3P_2$ metastable level to the $3s3p \; ^1P_1$ and the $3p^2 \; ^1D_2$ excited levels. These particular transitions illustrate the level of agreement one gets between the various methods considered here for cases when the spin–orbit mixing is relatively small and when it is more pronounced.

In our Breit–Pauli structure calculation, the spin–orbit interaction between configurations, as well as within configurations, is included; this is the reason that there is mixing between terms from different configurations of the same parity in table 1. We also note
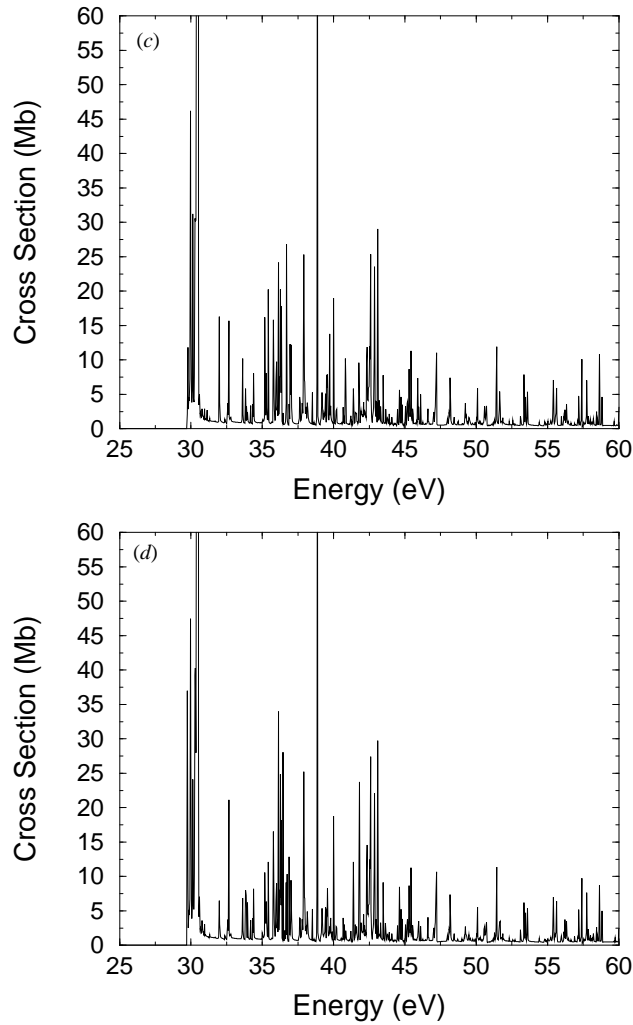
Figure 1. Continued.

from table 1 that the 3s3p ^{3}P and 3s3p ^{1}P term mixing in the 3s3p ^{3}P$_1$ and 3s3p ^{1}P$_1$ levels is relatively small. On the other hand, the 3p^2 ^{3}P and 3p^2 ^{1}D term mixing in the 3p^2 ^{3}P$_2$ and 3p^2 ^{1}D$_2$ levels is much more pronounced. As we shall see, these differences show up in the cross sections calculated using the various transformation methods.

In figure 1, we show the cross sections for the transition from the 3s^2 ^{1}S$_0$ level to the 3s3p ^{3}P$_1$ level calculated in the four different ways described above. We see that this spin-changing transition is completely dominated by resonances. It is this 3s^2 ^{1}S to 3s3p ^{3}P transition that previous studies, performed in *LS* coupling (Griffin *et al* 1994, Badnell *et al* 1994), have shown to be particularly sensitive to the exact position of the strongly interacting resonances. We note that the resonance structure from the JAJOM calculation is quite different from that obtained using either the GFT or the ICFT method; however, the resonance structures from the latter two calculations are quite similar, although there are
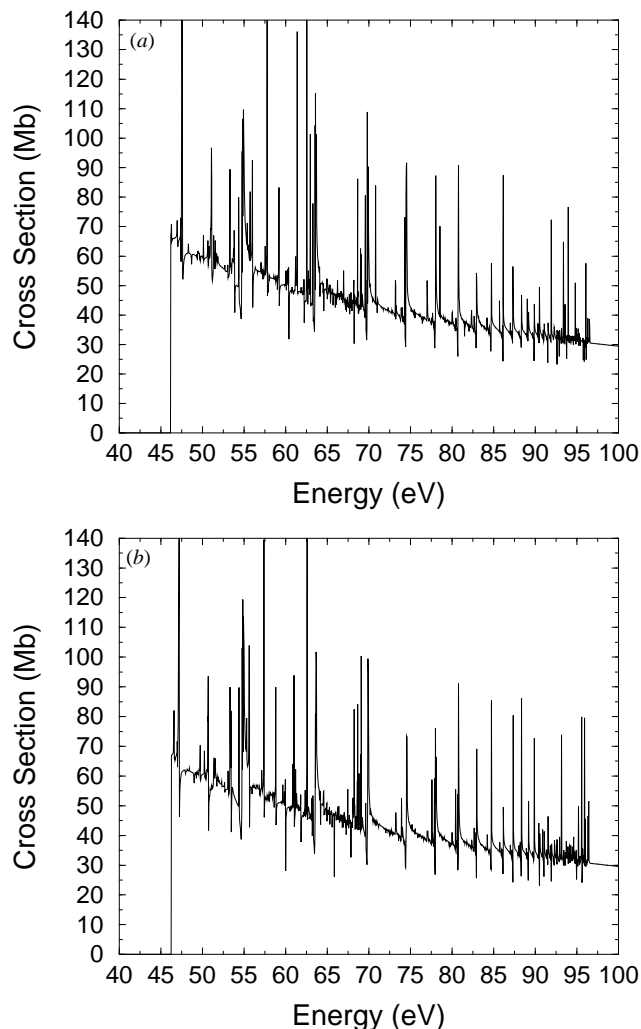
Figure 2. *R*-matrix electron-impact excitation cross section for the transition $3s^2 \ ^1S_0 \rightarrow 3s3p \ ^1P_1$ in Fe^{14+}: (*a*) from a transformation of the physical *S*-matrices in *LS* coupling to intermediate coupling using JAJOM; (*b*) from a geometrical frame transformation (GFT), as defined by Aymar *et al* (1996); (*c*) from our intermediate-coupling frame transformation (ICFT); (*d*) from a full Breit–Pauli calculation.

some differences in the details. We have found this to be true when the spin–orbit mixing between *LS*-coupled terms is relatively small, but the resonance structure is sensitive to the resonance positions, and therefore, the threshold energies.

Since JAJOM uses the term energies, rather than the energies of the individual levels, this has a pronounced effect on the resulting resonances. However, this structure is dominated by resonant states attached to the $3s3p \ ^1P$, $3s3d \ ^3D$ and $3s3d \ ^1D$ levels, for which the spin–orbit mixing is small (see table 1); thus, the transformation from jK coupling to intermediate coupling included in the ICFT method, but not the GFT method, has little effect on the resonances. However, it should be noted that, although the differences in
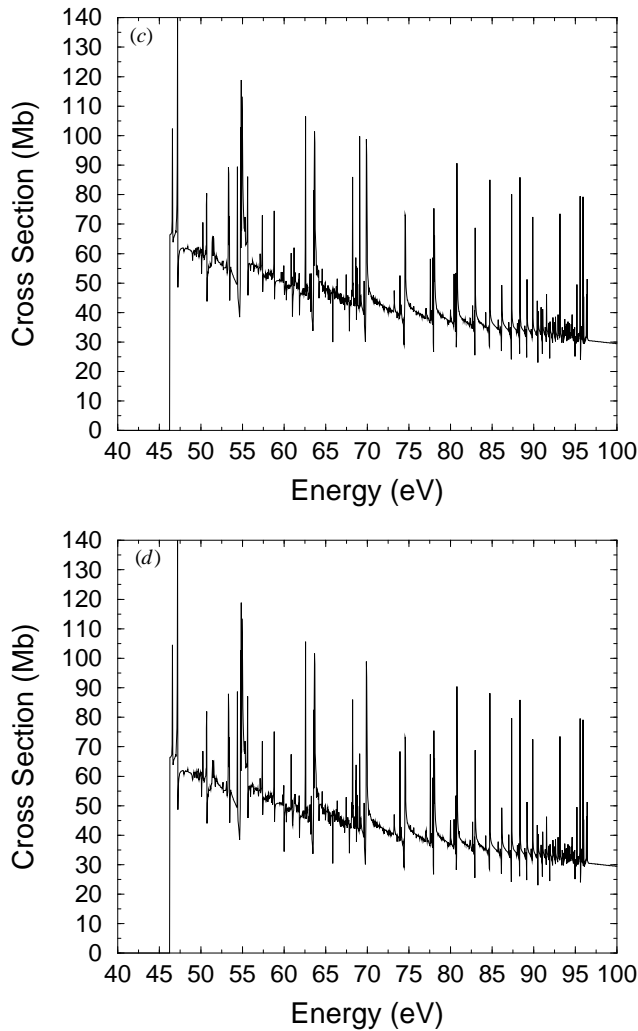
Figure 2. Continued.

the background cross sections from the ICFT and GFT methods are too small to be seen readily on the scale of figure 1, the small admixture of the 3s3p ^{1}P term included in the 3s3p ^{3}P$_1$ level (see table 1) is enough to make the background cross section from the ICFT calculation about twice that obtained from the GFT calculation. Finally, we see that the ICFT method leads to results that agree very well with those obtained from the full Breit–Pauli *R*-matrix calculation. This is true of the background cross section as well as the resonance structure.

In figure 2, we show the cross sections from our four calculations for the spin-allowed transition from the 3s^2 ^{1}S$_0$ level to the 3s3p ^{1}P$_1$ level. Here the agreement between the results of the JAJOM calculation and the other three is very good. Furthermore, the extremely good agreement between the results of the GFT calculation and those shown in figures 2(*c*) and (*d*) demonstrates how well this method works when the effect of spin–orbit mixing is relatively small.
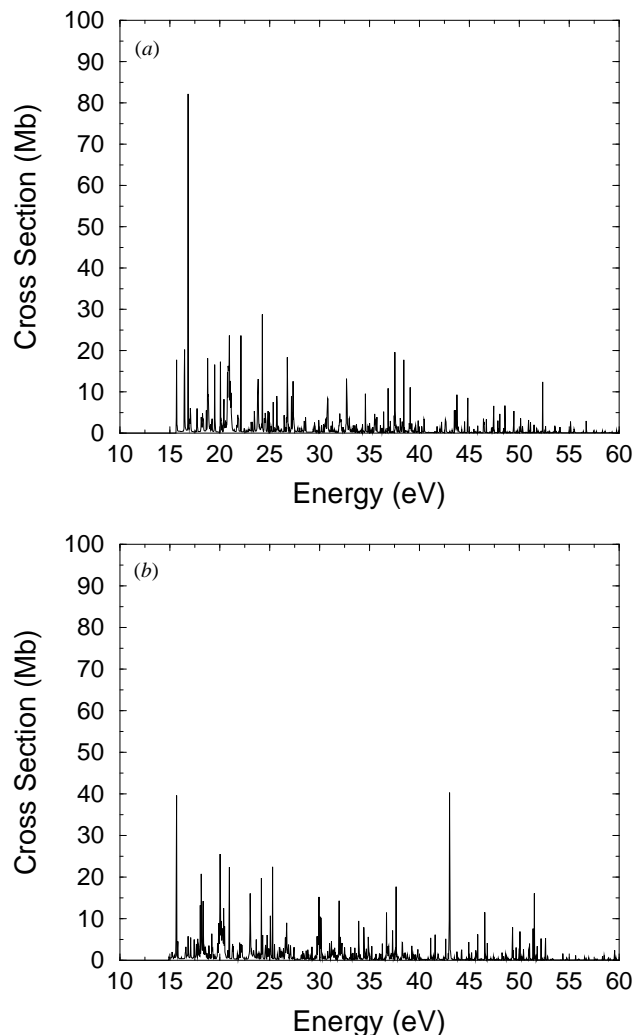
Figure 3. *R*-matrix electron-impact excitation cross section for the transition 3s3p ^{3}P$_2$ → 3s3p ^{1}P$_1$ in Fe^{14+}: (*a*) from a transformation of the physical *S*-matrices in *LS* coupling to intermediate coupling using JAJOM; (*b*) from a geometrical frame transformation (GFT), as defined by Aymar *et al* (1996); (*c*) from our intermediate-coupling frame transformation (ICFT); (*d*) from a full Breit–Pauli calculation.

In figure 3, we present our calculated cross sections for the transition from the 3s3p ^{3}P$_2$ metastable level to the 3s3p ^{1}P$_1$ level. Here again this spin-changing transition is dominated by resonances. Furthermore, the strongest contributions are from resonances attached to levels of the 3p^2 configuration, some of which are mixed significantly by the spin–orbit interaction (see table 1). We note that the resonant cross sections determined using JAJOM and the GFT method are much weaker than those determined from the ICFT or the Breit–Pauli *R*-matrix calculations. Furthermore, the results of the ICFT and the Breit–Pauli *R*-matrix calculations are in excellent agreement, demonstrating the accuracy of the ICFT method when the effects of spin–orbit mixing are significant.
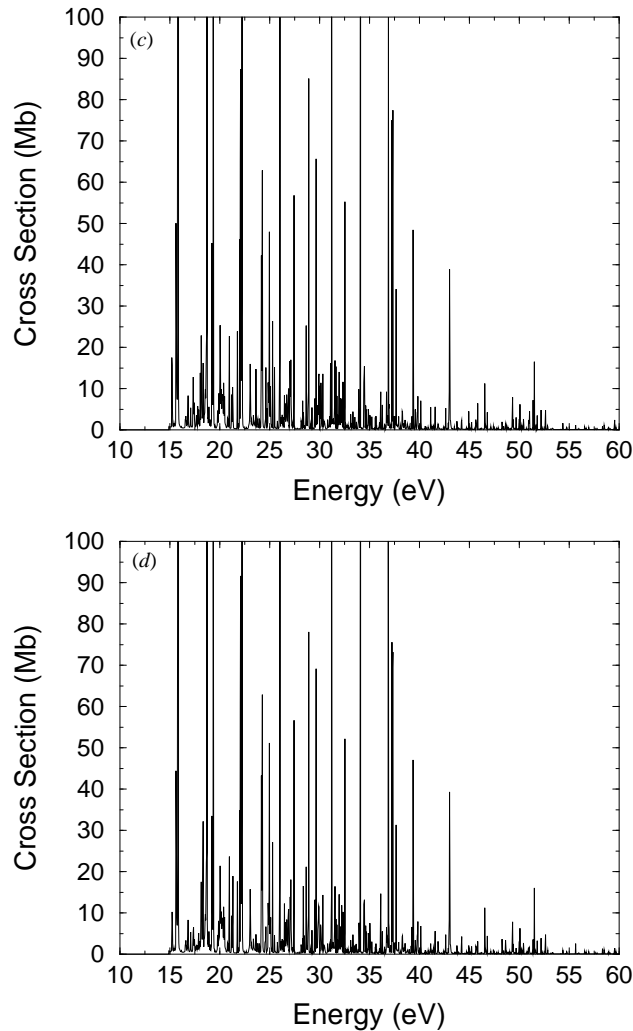
Figure 3. Continued.

The primary problem with the JAJOM calculation for this transition is that it only includes components of the TCCs corresponding to terms that are open. For example, the mixing between the ^{1}D and ^{3}P term is significant for the $3p^2$ ^{1}D$_2$ level. However, until the electron energy reaches a point where the $3p^2$ ^{3}P term is open, this mixing will not be included in the JAJOM calculation and the strength of the resonances attached to this level will be greatly diminished. There is no use of TCCs with the GFT method and this shows up in the greatly reduced resonant contribution presented in (*b*).

In figure 4, we make comparisons for the transition from the 3s3p ^{3}P$_2$ metastable level to the $3p^2$ ^{1}D$_2$ level. We see that the cross section from the JAJOM calculation undergoes a sudden increase at just over 40 eV, where the $3p^2$ ^{3}P term opens up. At lower energies, JAJOM does not include the mixing of the $3p^2$ ^{3}P term in the TCCs for the $3p^2$ ^{1}D$_2$ level and the cross section is quite small. However, above that energy this mixing is included,
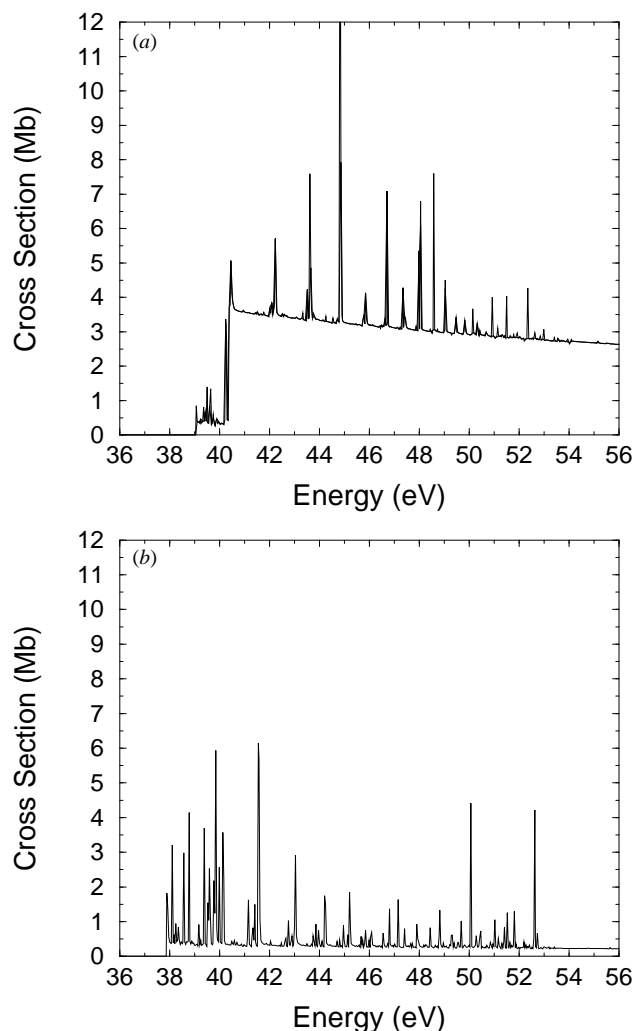
Figure 4. *R*-matrix electron-impact excitation cross section for the transition $3s3p\ ^3P_2 \rightarrow 3p^2\ ^1D_2$ in Fe^{14+}: (*a*) from a transformation of the physical *S*-matrices in *LS* coupling to intermediate coupling using JAJOM; (*b*) from a geometrical frame transformation (GFT), as defined by Aymar *et al* (1996); (*c*) from our intermediate-coupling frame transformation (ICFT); (*d*) from a full Breit–Pauli calculation.

and the background excitation cross section is very close to that obtained from the full Breit–Pauli *R*-matrix calculation shown in (*d*). On the other hand, the result from the GFT method has a very small background cross section throughout, and although the positions of the resonances are very similar to those obtained from the full Breit–Pauli *R*-matrix calculation, they are much weaker. It is clear that without the inclusion of the spin–orbit mixing in this calculation, the cross section is greatly underestimated. Finally, the results from the ICFT calculation are extremely close to those obtained from the full Breit–Pauli *R*-matrix calculation.
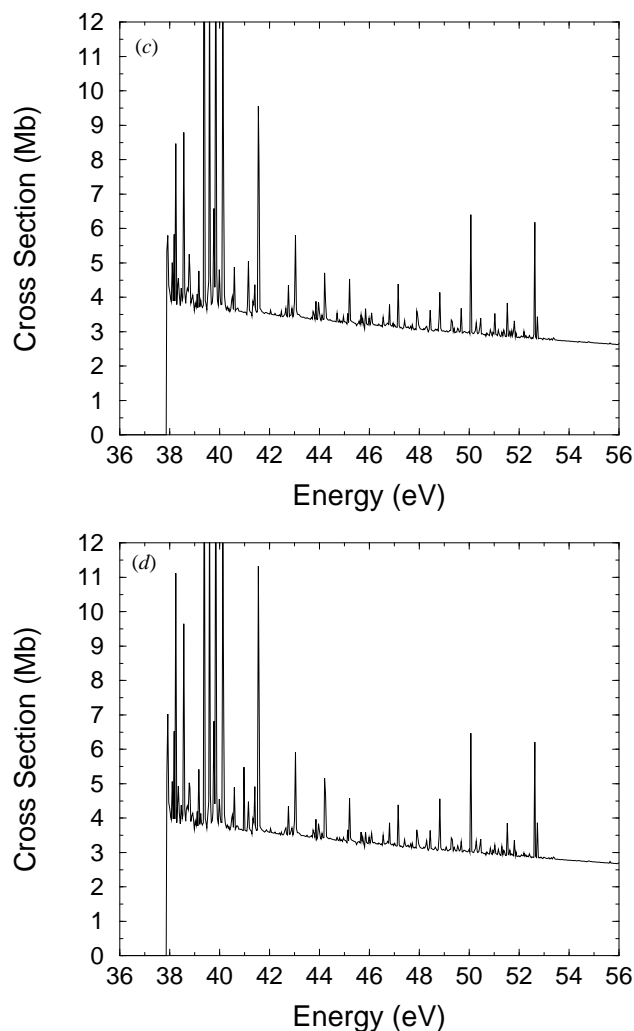
Figure 4. Continued.

The comparisons of cross sections given above were necessary in order to provide a detailed test of the various methods considered in this paper. However, for modelling purposes, we are primarily interested in rate coefficients, rather than cross sections. For that reason, we present rate coefficients in table 2, calculated from the cross sections presented in each of the four figures. The temperature for each of the transitions was chosen to be approximately equal to the threshold energy. Like the cross sections, these rate coefficients are presented for comparison only. Our LS-coupling R-matrix calculations were carried out with partial waves up to only $L = 12$, which provides complete K-matrices in intermediate coupling up to $J = \frac{21}{2}$. Thus, accurate rate coefficients would not only require a larger configuration-interaction expansion of the target states, but also the inclusion of higher partial waves.

The differences between the rate coefficients calculated from the various methods are about what we might expect on the basis of our detailed comparisons of the cross sections.

Table 2. Rate coefficients for selected transitions in Fe^{14+} in units of 10^{-10} cm^3 s^{-1}, calculated using the four methods discussed in the text.

Transition	T (eV)	JAJOM	GFT	ICFT	Breit–Pauli
$3s^2\ ^1S_0 \to 3s3p\ ^3P_1$	30	2.05	2.67	5.47	5.65
$3s^2\ ^1S_0 \to 3s3p\ ^1P_1$	50	114	115	114	115
$3s3p\ ^3P_2 \to 3s3p\ ^1P_1$	15	2.69	2.68	9.72	9.55
$3s3p\ ^3P_2 \to 3p^2\ ^1D_2$	40	4.01	0.61	4.40	4.48

The fact that the rate coefficient for the $3s^2\ ^1S_0 \to 3s3p\ ^3P_1$ transition, determined using the GFT method, is more than a factor of two lower than the rate coefficient for this transition determined from the full Breit–Pauli R-matrix calculation might seem surprising, especially in the light of the relatively good agreement between the results of these two methods for the resonance contributions to this transition. However, this difference is due primarily to the approximate factor of two discrepancy between the results of these two methods for the background cross section.

The importance of TCCs to the $3s3p\ ^3P_2 \to 3s3p\ ^1P_1$ excitation is seen quite clearly in table 2 from the fact that the rate coefficient for this transition is about 3.5 times larger when determined from a full Breit–Pauli calculation than when determined using the GFT method or JAJOM. On the other hand, the JAJOM result is only about 10% lower for the $3s3p\ ^3P_2 \to 3p^2\ ^1D_2$ transition, while the GFT method gives a rate coefficient more than a factor of seven too low. It is pleasing to see that the rate coefficients calculated from the ICFT method are in excellent agreement with the full Breit–Pauli R-matrix calculation for all transitions, the largest discrepancy being just over 3%.

We have also examined other transitions in this ion and found similar results with respect to these comparisons. The results of the ICFT calculation agree extremely well with the results of the full Breit–Pauli calculation; however, calculations based on the transformation of physical S-matrices, or the GFT method, yield results that are in good agreement with those obtained from the full Breit–Pauli R-matrix calculation only when the spin–orbit mixing of terms is relatively small.

For the small model calculations considered here, the saving in total computational time for the ICFT method over the full Breit–Pauli R-matrix method was modest, and it was realized almost entirely in solving the coupled equations in the asymptotic region between terms rather than between levels. However, for large complex systems, the speed of ICFT calculations over full Breit–Pauli R-matrix calculations will be quite substantial, especially with regard to the diagonalization of the $(N+1)$-electron Hamiltonian inside the R-matrix box. Furthermore, the additional overhead in performing ICFT calculations is small when compared to the initial LS-coupling calculation.

4. Conclusions

Additional work is needed to study the accuracy of the ICFT method for other cases where the effects of spin–orbit mixing are more pronounced than in this case. However, this ICFT method shows great promise in allowing for the determination of accurate level-to-level excitation cross sections in those systems for which the Breit–Pauli approximation yields accurate bound-state energy levels, and should make such calculations possible for systems where a full Breit–Pauli R-matrix calculation would be prohibitively large and time

consuming. It also enables new inner-region codes such as RMATRX II (see Burke *et al* 1994), that have been developed initially in *LS* coupling, to be applied more widely.

It remains to be seen what role there is for Breit–Pauli scattering codes. It may be that when the spin–orbit interaction is sufficiently large so as to cause the ICFT method to fail then it will be necessary to use a fully relativistic approach. We plan to develop the ICFT code further so that it can be applied to photoionization, while the extension to allow for radiation damping in electron-impact excitation and, hence, (total) photorecombination is straightforward.

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