On the effects of the two-body non-fine-structure operators of the Breit–Pauli Hamiltonian

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Abstract. We have incorporated the two-body non-fine-structure operators of the Breit–Pauli Hamiltonian, namely contact spin–spin, two-body Darwin and orbit–orbit, into the program AUTOSTRUCTURE. Illustrative results are presented, including some for reactions involving the process of autoionization.

1. Introduction

The advent and continuing development of highly charged ion sources and heavy-ion storage rings utilizing electron coolers provides a challenge to theorists to describe the statics and dynamics of high-Z ions, see for example Bosch (1987), Levine *et al* (1989) and Müller (1995). Furthermore, the demands by spectroscopic modellers of laboratory plasmas (e.g. magnetic fusion plasmas—Sheffield (1994), see also the Joint European Torus at `http://www.jet.uk`) and astrophysical plasmas (e.g. the Solar Corona and the Solar Heliospheric Observatory satellite—Fleck *et al* (1995), see also `http://sohowww.nascom.nasa.gov`) are for ever more accurate atomic data for highly charged ions. The computation of such atomic data requires that relativistic effects be taken into account. This can be achieved through the use of the Dirac equation and Breit interaction (a fully relativistic approach) or through the use of the Dirac equation and Breit interaction in the Pauli approximation (a relativistic correction approach, using non-relativistic wavefunctions). The latter approach is the subject of this paper, it being still in widespread use. Also, this paper completes the work on the Breit–Pauli Hamiltonian started by Jones (1970, 1971).

The Breit–Pauli Hamiltonian (see Bethe and Salpeter 1977) can be written as

$$H_{\mathrm{BP}} = H_{\mathrm{nr}} + H_{\mathrm{rc}} \tag{1}$$

where H_{nr} contains the usual non-relativistic operators, namely electrostatic and kinetic plus nuclear, and H_{rc} contains the relativistic correction operators which can be grouped as

$$H_{\mathrm{rc}} = H_{\mathrm{rc1}} + H_{\mathrm{rc2}} \tag{2}$$

where H_{rc1} contains the one-body operators, namely mass–velocity, Darwin and nuclear spin–orbit, and H_{rc2} contains the two-body operators. The two-body operators can be subdivided further, namely

$$H_{\mathrm{rc2}} = H_{\mathrm{fs2}} + H_{\mathrm{nfs2}} \tag{3}$$

where H_{fs2} contains the (two-body) fine-structure operators, namely spin–orbit, spin–other-orbit and spin–spin, and H_{nfs2} contains the (two-body) non-fine-structure operators, namely contact spin–spin, Darwin and orbit–orbit.

The reasons for these groupings are as follows. The one-body operators scale roughly as $Z^4\alpha^2$ while the two-body operators scale roughly as $Z^3\alpha^2$. Thus, the one-body operators dominate in high-Z ions. Of course, when summed-over a number of electrons e.g. a closed-shell, then some of the two-body operators behave and scale as a one-body operator (Blume and Watson 1962). The non-fine-structure operators commute with the L^2 and S^2 operators while the fine-structure operators do not and so the latter are responsible for departures from LS-coupling. So far as atomic structure is concerned the two-body non-fine-structure operators are deemed to be of little interest, except perhaps for ionization potentials (Eissner *et al* 1974). In low-Z ions where their size is comparable with the one-body operators the uncertainty in the LS-coupling problem due to the use of a finite configuration interaction expansion dominates while in high-Z ions the one-body operators dominate. However, atomic collisions take place via a two-body interaction and in highly charged ions configuration interaction is dominated by that within a complex. Furthermore, the incorporation of the Breit or Breit–Pauli operators into general collision codes is less well developed. For example, the Breit–Pauli R-matrix code (see Berrington *et al* 1995) that is used by the Iron Project (see Hummer *et al* 1993) only includes the one-body (relativistic) operators. Thus, it is of interest to be able to evaluate the likely effect of neglecting the two-body operators.

Our principal interest is that of the resonance contribution to electron–ion excitation, ionization and recombination. This we explore within the independent processes and isolated resonance approximations using the AUTOSTRUCTURE code (see Badnell 1986). We note that there has been considerable development of the code since the original publication and the most recent release of the code is available via (the World Wide Web or) anonymous FTP from (`ftp://`) `patiala.phys.strath.ac.uk`. Since AUTOSTRUCTURE incorporates SUPERSTRUCTURE (see Eissner *et al* 1974) it already includes all of the one-body operators plus the two-body fine-structure operators. We now extend it to include the two-body non-fine-structure operators. The Darwin and contact spin–spin operators are trivial to include and are present in the BREIT program of Hibbert *et al* (1991) which is part of the MCHF package of Froese Fischer (1991) and which can be incorporated into the CIV3 program of Hibbert (1975) as well. The orbit–orbit operator is a different beast and little has been done in the way of a general treatment. References to earlier work and tabulations of matrix elements for configurations with at most one open-shell have been given by Walker (1971), Saxena *et al* (1972) and Dankwort (1977). Saxena *et al* (1972) also tabulated the complete orbit–orbit energy for the ground term of all singly-charged ions, neutral atoms and negative ions from He to Kr, as well as for excited terms of the ground configuration for several atoms. But an automatic treatment by a 'general' structure code appears to be lacking. Of course, the inclusion of the (generalized) Breit interaction by the GRASP code (see Dyall *et al* 1989), for example, means that its effect is not ignored by fully relativistic approaches but a Breit–Pauli treatment is required to best assess the effect of the inclusion or omission of two-body non-fine (and fine-) structure operators by Breit–Pauli collision codes.

Many authors have given expressions for the orbit–orbit matrix elements that arise from including the orbit–orbit operator in the Hamiltonian, not necessarily completely general and often in a form amenable to a particular implementation (in principle). The closest prescription to that we have implemented is that due to Eissner *et al* (1974) in

their original SUPERSTRUCTURE theory paper. However, in practice we found that their prescription was not quite the most convenient to implement and also that our re-derivation and subsequent numerical results indicated a number of (typographical) errors in their original work. Thus, in section 2 we present the expressions that we actually used while in section 3 we make comparisons with the results of other authors for various two-body non-fine-structure interactions as well as present some illustrative results of our own in section 4. We finish with a short conclusion.

2. Theory

The two-body non-fine-structure Hamiltonian is given by

$$H_{\text{nfs2}} = \sum_{i>j} [g_{ij}(\text{css}') + g_{ij}(\text{d}) + g_{ij}(\text{oo}')] \tag{4}$$

where the contact spin–spin, Darwin and orbit–orbit operators are given by

$$g_{ij}(\text{css}') = -\frac{16\pi}{3}\alpha^2 s(i) \cdot s(j)\delta(r_{ij}) \tag{5}$$

$$g_{ij}(\text{d}) = \frac{1}{2}\alpha^2 \nabla_i^2 \left(\frac{1}{r_{ij}}\right) \tag{6}$$

and

$$g_{ij}(\text{oo}') = -\frac{\alpha^2}{r_{ij}}\left[p_i \cdot p_j + \frac{r_{ij} \cdot (r_{ij} \cdot p_j)p_i}{r_{ij}^3} \right] \tag{7}$$

respectively, where p_i, r_{ij}, s etc have their usual meaning (see e.g. Eissner *et al* 1974).

2.1. Contact spin–spin plus Darwin

The contact spin–spin and Darwin two-body operators can be re-written so that their total contribution to the Breit–Pauli Hamiltonian is given by (Eissner *et al* 1974),

$$g_{ij}(\text{css}') + g_{ij}(\text{d}) = -g_{ij}(\text{d}) \qquad \text{for all } i \neq j. \tag{8}$$

The corresponding matrix elements, for Slater states $a \equiv n_a l_a \mu_a m_a$, b etc, in the uncoupled representation of Eissner *et al* (1974) are given by

$$-\langle ab|g_{ij}(\text{d})|cd\rangle = \delta(\mu_a, \mu_c)\,\delta(\mu_b, \mu_d)\delta(m_a + m_b, m_c + m_d)$$

$$\times \sum_{\lambda}(-1)^{m_a - m_d}(2\lambda + 1)c_\lambda(l_a m_a, l_c m_c)\,c_\lambda(l_b m_b, l_d m_d)X_2(ab, cd) \tag{9}$$

where

$$c_\lambda(lm, l', m') = \frac{[(2l + 1)(2l' + 1)]^{\frac{1}{2}}}{2\lambda + 1}\mathbf{C}\begin{matrix} l & l' & \lambda \\ 0 & 0 & 0 \end{matrix}\mathbf{C}\begin{matrix} l & l' & \lambda \\ -m & m' & m' - m \end{matrix}, \tag{10}$$

the $\mathbf{C}^{\cdots}_{\cdots}$ being Clebsch–Gordan coefficients, and

$$X_2(ab, cd) = \frac{\alpha^2}{2}\int_0^\infty \left(\frac{1}{r^2}\right)P_{n_a l_a}P_{n_b l_b}P_{n_c l_c}P_{n_d l_d}\,\text{d}r, \tag{11}$$

P_{nl} being the radial component of a one-electron wavefunction. Following Eissner *et al* (1974), the algebraic coefficient in equation (9) differs only by a factor $(2\lambda + 1)$ from that

of the Coulomb electrostatic matrix element (see equation (18) of Eissner *et al* 1974) and so the combined effect of the contact spin–spin plus Darwin operators can be obtained by replacing each Slater integral R_λ as follows:

$$R_\lambda(ab, cd) \leftarrow - R_\lambda(ab, cd) + (2\lambda + 1)X_2(ab, cd). \tag{12}$$

2.2. Orbit–orbit

The matrix elements of the orbit–orbit interaction are given by

$$\langle ab|g_{ij}(\mathrm{oo}')|cd\rangle = \delta(\mu_a, \mu_c)\delta(\mu_b, \mu_d)\delta(m_a + m_b, m_c + m_d)(-1)^{m_a - m_d}$$
$$\times \left\{ \sum_\lambda [1 - \delta(\lambda, 0)]c_\lambda(l_a m_a, l_c m_c)c_\lambda(l_b m_b, l_d m_d)Z_\lambda(ab, cd) \right.$$
$$\left. + \sum_\lambda d_\lambda(l_a m_a, l_c m_c)d_\lambda(l_b m_b, l_d m_d)O_\lambda(ab, cd) \right\} \tag{13}$$

where

$$Z_\lambda(ab, cd) = \lambda(\lambda + 1)[T_{\lambda+1}(ab, cd) - T_{\lambda-1}(ab, cd)]$$
$$+[l_a(l_a + 1) - l_c(l_c + 1) - \lambda(\lambda + 1)][U_{\lambda+1}(ab, cd) - U_{\lambda-1}(ab, cd)]$$
$$+[l_b(l_b + 1) - l_d(l_d + 1) - \lambda(\lambda + 1)][U_{\lambda+1}(ba, dc) - U_{\lambda-1}(ba, dc)]$$
$$+[l_a(l_a + 1) - l_c(l_c + 1) - \lambda(\lambda + 1)][l_b(l_b + 1) - l_d(l_d + 1) - \lambda(\lambda + 1)]$$
$$\times \left\{ \frac{\lambda - 2}{\lambda(2\lambda - 1)}\overline{V}_{\lambda-2}(ab, cd) - \frac{\lambda + 3}{(\lambda + 1)(2\lambda + 3)}\overline{V}_\lambda(ab, cd) \right\} \tag{14}$$

and

$$O_\lambda(ab, cd) = 2[(\lambda + 1)(\lambda + 2)(2\lambda + 1)(2\lambda + 3)]^{-1}\ [(l_a + l_c + \lambda + 2)$$
$$\times(l_c - l_a + \lambda + 1)(l_a - l_c + \lambda + 1)(l_a + l_c - \lambda)(l_b + l_d + \lambda + 2)$$
$$\times(l_d - l_b + \lambda + 1)(l_b - l_d + \lambda + 1)(l_b + l_d - \lambda)]^{\frac{1}{2}}\ \overline{V}_\lambda(ab, cd). \tag{15}$$

The integrals T_λ, U_λ and N_λ are defined by equations (86), (87)† and (71) of Eissner *et al* (1974). It is the N_λ integrals that our $\overline{V}_\lambda$ are defined in terms of, namely

$$\overline{V}_\lambda(ab, cd) = N_\lambda(ab, cd) + N_\lambda(ba, dc). \tag{16}$$

Again, as noted by Eissner *et al* (1974), the algebraic coefficient in front of the Z_λ integral differs only by the factor $[1 - \delta(\lambda, 0)]$ from that of the Coulomb electrostatic matrix element and so can also absorbed into a generalized R_λ integral. The problem lies with the coefficient in front of the O_λ integral which involves the coefficients d_λ, which are of a similar form to the c_λ coefficients namely

$$d_\lambda(lm, l'm') = \left[(2l + 1)(2l' + 1)\right]^{\frac{1}{2}} \mathbf{C}\begin{matrix} l & l' & \lambda \\ 0 & 0 & 0 \end{matrix} \mathbf{C}\begin{matrix} l & l' & \lambda + 1 \\ -m & m' & m' - m \end{matrix}, \tag{17}$$

but cannot be completely absorbed into a generalized R_λ integral. One can make some progress, as did Eissner *et al* (1974), by separating-out the interactions between valence electrons from those between valence electrons and closed-shell electrons. Summing over all

† There is a factor of r_2 missing from this equation.

common closed-shell electron states denoted by b, the valence–closed-shell matrix elements (see equation (13)) are given by

$$\sum_b \langle ab|g_{ij}(\text{oo}')|bc\rangle = \delta(\mu_a, \mu_c)\delta(m_a, m_c)\delta(l_a, l_c)\xi(a, c) \tag{18}$$

where

$$\xi(a, c) = \sum_b [1 - \delta(l_b, 0)][1 - \delta(l_c, 0)] \sum_{\lambda=1}^{l_a+l_b+1} \frac{2}{\lambda(\lambda + 1)} \left[\mathbf{C} \begin{array}{ccc} l_a & \lambda - 1 & l_b \\ 0 & 0 & 0 \end{array} \right]^2$$
$$\times (l_a + l_b + \lambda + 1)(l_a - l_b + \lambda)(l_b - l_a + \lambda)(l_a + l_b - \lambda + 1)\overline{V}_{\lambda-1}(ab, bc). \tag{19}$$

This equation (19) differs by several factors from equation (92) of Eissner *et al* (1974). We will make use of it as part of our testing procedure in section 3. The point of this reduction is that the algebraic coefficient in equation (18) is the same as that for the matrix elements of the one-body kinetic plus nuclear operators (see equation (17) of Eissner *et al* (1974)) and so the ξ integral could be absorbed into the one-body non-relativistic integral. This approach, however, is a dead-end. Eissner *et al* (1974) state that the valence–valence *algebraic* factor can be absorbed into their $E_{UU'}$ factor (see Eissner *et al* (1974), equation (51)) but this is just a redefinition of the problem, it does not solve it. The interactions between valence electrons remain and appear at first to be non-trivial to deal with.

2.2.1. Solution. We first note that the algebraic coefficients of the Z_λ and O_λ integrals differ only trivially, apart from the d_λ instead of c_λ coefficients. Secondly, we recognize that the d_λ coefficients are *already* being evaluated for the generation of the spin–orbit plus spin–other-orbit algebra, specifically the $\langle ab|V_{ij}^{(2)}|cd\rangle$ term—see equation (75) of Eissner *et al* (1974). It is a simple matter to store them and combine them with newly generated O_λ integrals using the indexing that has already been set-up for the generation of the electrostatic matrix elements. In effect we are absorbing the $d_\lambda(a, c)d_\lambda(b, d)O_\lambda(ab, cd)$ contribution into the $c_\lambda(a, c)c_\lambda(b, d)R_\lambda(ab, cd)$ contribution. Thus, we do not specifically separate-out the valence–closed-shell and valence–valence interactions. They are automatically dealt with as the various electrostatic contributions arise, including the interactions *between* closed-shells. We see that in fact little extra computational effort is required to include the complete orbit–orbit interaction *provided* that the corresponding two-body fine-structure interactions have been included. It is there that the computational effort resides. Since the two-body fine-structure and non-fine-structure interactions are of the same order (in Z) it can be argued that it makes little sense to omit the fine-structure while including the non-fine-structure. It should be noted however that since the non-fine-structure operators (one- and two-body) commute with the $\mathbf{L}^2$ and $\mathbf{S}^2$ operators one could include their effect while remaining in LS-coupling rather than resorting to the more computationally demanding intermediate coupling scheme. This is particularly relevant to the collision problem where it is common to include the one-body non-fine-structure operators in LS-coupling calculations.

For the case of autoionization one of the atomic orbitals P_{nl} is replaced by a continuum orbital. This presents no new numerical difficulties. The matrix elements of the interaction now scale one power of Z lower (as do the one-body bound–continuum elements) as a result though. The non-relativistic two-body bound–continuum autoionization matrix elements scale as Z^0 while the corresponding two-body (fine- and) non-fine-structure elements scale roughly as $Z^2\alpha^2$.

2.3. Validity of the Breit–Pauli Hamiltonian

The Breit–Pauli Hamiltonian is a 'low-Z' approximation that is valid when the expansion parameter satisfies $\alpha^2 Z^2 \ll 1$. As we have noted, it contains (in fact all) interactions of order $\alpha^2 Z^3$ and $\alpha^2 Z^4$ while the leading (radiative correction) term that is omitted is of order $\alpha^3 Z^4$ (see Bethe and Salpeter 1977, section 39α). Just how high in Z we can apply the Breit–Pauli Hamiltonian depends on a number of points. We list a few: whether we require spectroscopic accuracy of energy levels or just cross sections to 30% say; the relative size of the coefficients of the $\alpha^m Z^n$ terms; whether Z is in fact the nuclear charge or whether the quantity in question depends more on a screened value. The main problem that we encounter as we move to ever higher Z is that the one-body mass–velocity and Darwin terms become too large to be treated as a perturbation (Cowan and Griffin 1976). More precisely, better accord with experiment and Dirac–Fock–Breit theory is obtained when the mass–velocity and Darwin terms are included in the solution of the radial equation, see for example Pindzola and Badnell (1990), Spies *et al* (1992) and Lampert *et al* (1996). In principle the relativistic correction terms of the Breit–Pauli Hamiltonian should be evaluated using non-relativistic wavefunctions (Bethe and Salpeter 1977). However, in practice the benefit of using semi-relativistic radial functions to evaluate the remaining relativistic corrections outweighs either their omission or the use of non-relativistic radial functions.

3. Tests

Unless stated otherwise, the atomic orbitals were evaluated in a Thomas–Fermi–Dirac–Amaldi model potential with the *nl*-dependent scaling parameters being determined by minimization of the ground term energy for each atom.

3.1. Contact spin–spin plus Darwin

The contact spin–spin energies of the ground term of the eight neutral atoms Na–Ar were evaluated and compared with the results of Walker (1971, table 3). The two sets of results differed by 1% or less, except for S for which we obtain 0.068 13 au compared with the 0.060 64 au obtained by Walker (1971). Walker (1971) used Hartree–Fock radial functions. Also, the contact spin–spin (plus Darwin) contributions to the energy levels of Fe^{14+} for selected levels of the $3l3l'$ configurations were compared with those obtained (Griffin 1996) from the MCHF_BREIT program of Hibbert *et al* (1991) *using the same* radial functions. Agreement to 4 significant figures was found in general.

3.2. Orbit–orbit

The angular algebra coefficients of the radial integrals were spot checked against those found in the equations and tables of Walker (1971), Saxena *et al* (1972) and Dankwort (1977). Furthermore, our results for the complete orbit–orbit contribution to the ground term energy of the eight neutral atoms Na–Ar was compared with the results of Saxena *et al* (1972, table 2) and Walker (1971, table 3). Again we obtained agreement with both sets of results to better than 1%, except for Mg where we obtained 0.005 493 au compared to the 0.004 628 au obtained by Walker (1971) and the 0.005 570 au obtained by Saxena *et al* (1972). This disagreement for Mg was noted by Saxena *et al* (1972), who also used Hartree–Fock radial functions, otherwise their results differed from those of Walker (1971) typically by less than 0.1%. As a check on the d^q configurations, as opposed to the p^q, we also

calculated similar results for neutral Fe and obtained 0.115 88 au compared to 0.124 61 au obtained by Saxena *et al* (1972, table 1). We attribute the greater difference in this case to the greater sensitivity of the atomic radial functions. For Cu^+ the percentage difference has halved (0.189 73 au versus 0.184 53 au) Finally, we cross-checked our two different methods for calculating the valence–closed-shell contribution, as discussed in section 3.2, and obtained the same results from both of them.

4. Results

We provide some illustrative results for a variety of processes sampling a wide range of Z so as to demonstrate the likely effects of including or omitting the two-body non-fine-structure operators in a given problem.

4.1. Level energies and ionization potentials of some He-like ions

Jones (1974) compared term and level energies of the He-like ions Si^{12+}, Ca^{18+} and Fe^{24+}, calculated with SUPERSTRUCTURE, with those of Ermolaev and Jones (1974) who obtained essentially exact non-relativistic term energies, using Hylleraas functions, as well as level energies that included all relativistic corrections through α^2 and α^3 plus some important α^4 terms. Jones (1974) found that the agreement for the level energies (0.1%) was much worse than for the term energies (0.01%) and attributed it to the omission of the non-fine-structure operators by SUPERSTRUCTURE. Furthermore, the ionization potentials differed greatly, by 1%.

We focus first on Fe^{24+}. We use the l-dependent Thomas–Fermi model potential available to SUPERSTRUCTURE then. On taking the scaling parameters $\lambda_s = 0.98$ and $\lambda_p = 1.0$ (Jones did not specify the values of λ_l that he used) we can reproduce his term energies (Jones 1974, table 1) to within 0.002 Rydberg, which is much smaller than any differences that we need to compare. The level energies obtained by Jones (1974, table 2) were typically 0.65 Rydberg too high, relative to the ground level, compared to those of Ermolaev and Jones (1974). On including the two-body non-fine-structure operators in our calculations (the contact spin–spin plus Darwin dominate) we find that our excited levels are lowered by about 0.20 Rydberg, relative to the ground level, reducing but not eliminating the discrepancy. With regards to the ionization potentials, we present our results that were obtained both with and without the contribution from the two-body non-fine-structure operators in table 1 and compare them with the results of Jones (1974) and Ermolaev and Jones (1974). We see that our results which omit the two-body non-fine-structure operators differ hugely (1%) from those of Jones—we can offer no explanation for this—but they are in close agreement with those of Ermolaev and Jones (1974). We see also that the inclusion of the two-body non-fine-structure operators further improves the agreement for Fe^{24+}, but the contribution is small. For the lower-charged ions it is likely that this contribution is less than the uncertainty in the ionization potential due to inaccuracies in the wavefunctions. What our results do demonstrate is that AUTOSTRUCTURE, and in fact SUPERSTRUCTURE, can calculate a much more accurate ionization potential than is implied by Jones (1974) and thus, the key discussion on the accuracy of SUPERSTRUCTURE by Eissner *et al* (1974, section 3.4.2).

Table 1. Ionization potentials for the ground 1^1S_0 level of some He-like ions.

Ion	Ermolaev and Jones (1974)	This work		Jones (1974) without nfs2
		With nfs2	Without nfs2	
Fe^{24+}	648.8993	648.921	649.148	653.228
Ca^{18+}	376.9832	376.942	377.044	373.172
Si^{12+}	179.1692	179.093	179.127	178.359

4.2. Dielectronic recombination of Na-like Se^{23+}

We consider the LMn resonances that arise in the dielectronic recombination of Se^{23+}. The possible reaction pathways can be summarized schematically by

$$e^- + 2p^63s \rightarrow 2p^53s3lnl' \rightarrow \left\{ \begin{array}{l} 2p^63s \\ 2p^63l \\ 2p^6nl' \end{array} \right\} + e^-$$

$$\rightarrow \left\{ \begin{array}{l} 2p^63s3l \\ 2p^63snl' \\ 2p^63lnl' \end{array} \right\} + \hbar\omega \qquad (20)$$

and

$$\rightarrow 2p^53p^2nl' \rightarrow \left\{ \begin{array}{l} 2p^63p \\ 2p^6nl' \end{array} \right\} + e^-$$

$$\rightarrow \{2p^63p^2\} + \hbar\omega. \qquad (21)$$

The direct pathway is given by equation (21) while the indirect pathway (equation (21)) can only take place through configuration interaction with the direct pathway. Gorczyca and Badnell (1996) have shown that the mixing of the direct and indirect pathways has a very large effect on the *total* dielectronic recombination cross section reducing it by up to a factor of two, depending on the energy. In figure 1 we show how the (energy-averaged) dielectronic recombination cross section is affected, as a function of principal quantum number n for the $l = 1$ Rydberg states, by the effect of the two-body non-fine-structure operators perturbing the mixing. We observe a 5–10% reduction depending on n. Note, the absolute dielectronic recombination cross section (in Mb) can be obtained by multiplying the cross section in figure 1 by the bin-width $-$ 1.75 eV.

4.3. Resonant excitation of Ne-like Xe^{44+}

Next, we look at the LMM resonances that arise in the elastic scattering of electrons from Xe^{44+}. This can be described by

$$e^- + 2p^6 \rightarrow 2p^53l3l' \rightarrow 2p^6 + e^-$$

$$\rightarrow 2p^63l'' + \hbar\omega,$$

where we note that we have allowed for radiation damping of the resonances.

We see from figure 2 that the main effect of the two-body non-fine-structure operators is to shift the cross section in energy. We have chosen a broad distribution function so as to aid the comparison. A typical (experimental) electron-cooler distribution would be an order of magnitude finer in energy resolution and then small relative shifts in the positions of resonances would change the resonance structure more noticeably. Here, the total integrated LMM resonant-excitation cross section is only reduced by about 2%. If we focus on
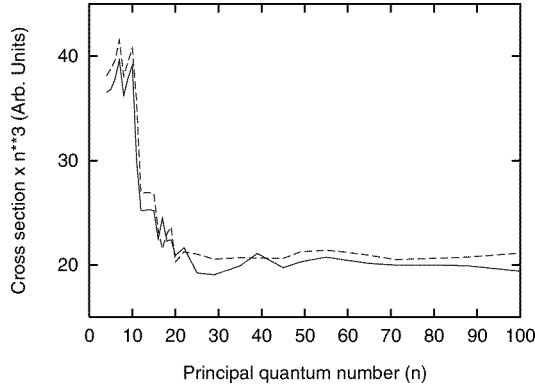
Figure 1. *LMn* energy-averaged dielectronic recombination cross sections $\times n^3$ as a function of principal quantum number *n* for the $l = 1$ Rydberg states of $Se^{23+}+e^-$. $- - -$, including two-body fine-structure operators only; ——, including both two-body fine-structure and non-fine-structure operators.
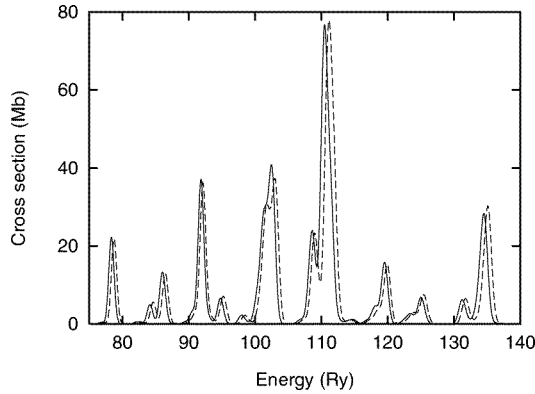

Figure 2. *LMM* elastic resonant-excitation cross sections for Xe^{44+}, convoluted with a 0.5 Rydberg FWHM Gaussian function. $- - -$, including two-body fine-structure operators only; ——, including both two-body fine-structure and non-fine-structure operators.

individual $J\pi$ symmetries we find that the even parity cross sections are hardly affected while all but one of the odd symmetry cross sections are reduced by about 5%. Within a given $J\pi$ symmetry the autoionization rates can change quite considerably, strong and weak rates being redistributed by mixing, but this only has a large effect on the cross section, summed-over all resonances of a symmetry, when it affects competition between 'forbidden' and 'allowed' channels—which is not the case here—see Badnell *et al* (1994, table 1) for an example.

4.4. Resonant transfer and excitation of He-like U^{90+}

Finally, we consider an extreme case—that of the dielectronic recombination of U^{90+}—for which we observe that not only is there no catastrophic breakdown of the Breit–Pauli approximation at high-Z but also that the correct qualitative behaviour is obtained. Actually, the quantity we view is the dielectronic recombination cross section convoluted with the Compton profile for the H_2 molecule (see Pindzola and Badnell 1990) for which
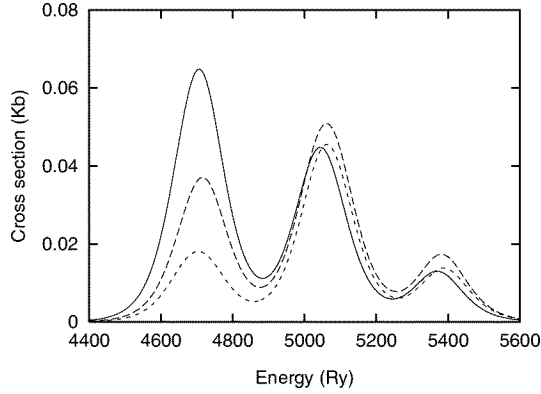
Figure 3. KLL resonant transfer and excitation cross sections for collisions of U^{90+} with H_2.
- - - -, no two-body operators; – – –, including two-body fine-structure operators only; ——,
including both two-body fine-structure and non-fine-structure operators.

measurements have been made by Graham *et al* (1990). Because of their Z^4 dependence the
radiative rates are so large that the cross section is directly proportional to the autoionization
rates. In figure 3 we present results for the KLL resonances, which fall into three broad
groups as discussed by Pindzola and Badnell (1990).

We see that the lowest energy peak is progressively increased in height as both the
two-body fine-structure operators and then the two-body non-fine-structure operators are
switched-on. This enhancement mirrors that observed by Pindzola and Badnell (1990) with
their Dirac–Fock results obtained both with and without the inclusion of the Breit operator.
The magnitude of the Breit–Pauli cross section (including all of the two-body operators) is
about 30% less than the Dirac–Fock–Breit cross section of Pindzola and Badnell (1990)—
which itself is in quite good agreement with the measurements made by Graham *et al*
(1990).

5. Conclusion

We have incorporated the two-body non-fine-structure operators of the Breit–Pauli
Hamiltonian, namely contact spin–spin, two-body Darwin and orbit–orbit, into the program
AUTOSTRUCTURE. We have shown that this entails little extra in the way of computer
resources provided that the two-body fine-structure operators are also included at the same
time, as they should be. We have provided some illustrative examples which show
that their effect is 'small' in general, as expected, but interesting nevertheless. It is
now possible to assess routinely the effect of the full Breit–Pauli Hamiltonian on energy
levels, radiative rates, autoionization rates and, via the correspondence principle, threshold
excitation collision cross sections. This should prove useful in assessing the likely error that
will arise due to the omission of the two-body operators (both fine- and non-fine-structure)
by Breit–Pauli collision codes, such as the R-matrix code used by the IRON Project.

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