Ab Initio Electric Dipole f values for Fe II (3d^{6}4s+3d^7) $J = 9/2 \rightarrow$ 3d^{6}4p $J = 9/2$ Transitions

Donald R. Beck

Physics Department, Michigan Technological University, Houghton, MI USA 49931

PACS Ref: 31.25.Eb, 31.25.Jf, 32.70.Cs, 32.10.Fn

Abstract

Relativistic configuration interaction f values have been obtained for 264 transitions between the lowest 12 $J = 9/2$ and 22 $J = 9/2^o$ levels. Length and velocity gauges agree to 3.8% for the in-shell transitions, and 10.0% for the shell jump transitions. Two of the $J = 9/2^o$ levels are so nearly degenerate that it was necessary to introduce a semiempirical correction to produce the proper level ordering. Landé g values are calculated for all levels, and a more efficient way of adding magnetic Breit effects to the energy matrix is given.

1. Introduction

Fe II is one of the most astrophysically important of the transition metal atoms, yet is so complex that few *ab initio* calculations have been done for it, and only a few experimental f values, determined from lifetime combined with branching fraction ratios, are available. Recently there has been much renewed interest in Fe II, such as that associated with the FERRUM project as described in a 2002 review article [1]. An updated review should be available in 2005 [2]. A more extensive list of Fe II references can be found in the NIST data base [3].

In this work, we apply the relativistic configuration interaction (RCI) methodology to the low lying $9/2 \rightarrow 9/2^o$ transitions in Fe II. This application is a follow up to our earlier work on the homologous configurations of Tc I [4]. Among the complications that need to be addressed are: (1) the need to simultaneously treat relativity and correlation effects, due to the near degeneracy of $(n+1)$s and nd electrons (relativistic effects differ by as much as 0.1 eV/electron between s and d symmetries [5]); (2) the large number of complicated basis functions needed to deal with open nd subshell configurations, complications which reach their peak at the $n = 7$ case considered here; (3) the greater significance of core-valence interactions for d electrons as compared to s or p valence electrons; (4) accounting for the radial variation of d functions with level, which arises from the incomplete collapse of the d's into the core (this increases the need to include second order correlation effects); (5) the close energy spacing (e.g. < 2000 cm^{-1}) of excited states, particularly those closer than 200 cm^{-1} which currently represents the approximate theoretical accuracy limit for *ab initio* treatments of the transition metals (failure to account well for energy differences between closely spaced levels can mean that basis functions are not properly "mixed" into computed wavefunctions, which can lead to erroneous predictions for other properties such as f values).

Since our approach is fully relativistic, a new calculation must be done for each J and parity. Each calculation can currently yield up to 30 energy levels (a restriction of convenience). In this work we wished to include the ground state 3d^{6}4s ^{6}D$_{9/2}$, which means (for an electric dipole processes), we would be interested in odd parity $J = 11/2$, 9/2, 7/2 states. Calculation complexity increases with decreasing J in this example (e.g. cpu times depend on the number of determinants). By picking $J = 9/2^o$ we comprised between complexity and the number of energy levels a single calculation would yield. The $J = 9/2^o$ states are less well studied than are the $J = 7/2^o$ states [3].

In Section 2 we will lay out the methodology of our approach. A new method of speeding up calculations 4-5 times will be emphasized. An older method (DSM) for correctly positioning two nearby levels will be discussed, and some (*ab initio*) justification for its use will be given.

In Section 3 we will present our results for energy differences among Fe II J=9/2 (12) and $9/2^o$ (22) levels, as well as Fe III $J = 4$ levels, studied as a precursor to improve our knowledge of how to accurately treat correlation for 3d^6 electrons. Average errors between adjacent energy levels are 319 cm^{-1} (17.3%) for $J = 9/2$, 164 cm^{-1} (20.0%) for $J = 9/2^o$, and 452 cm^{-1} (12.2%) for $J = 4$. The "high" percentage indicates the adjacent levels are closely spaced on average. For the 30 transitions with f values greater than 0.01 there exist two semi-empirical calculations from Kurucz [6] and Raassen [7] with which to compare. For five of the f values, there also exist experimental results. Generally, we are in good agreement with all of these. In the absence of near degeneracy problems, based on past experience [8], we would expect the in-shell transitions, viz $3d^64s \rightarrow 3d^64p$, to be more accurate than the shell jump transitions, viz $3d^7 \rightarrow 3d^64p$. There seems to be some evidence of this in Fe II, where the average spread between the length and velocity gauges is 3.8% for in shell transitions, and 10.0% for shell jump transitions.

2. Methodology

The Hamiltonian used is the Dirac-Breit with the uniform charge distribution nuclear model. The Breit operator is often divided into two parts, the magnetic and the retardation [9] for purposes of theoretical and computational ease, i.e. the magnetic operator, $\sum_{i,j} -\vec{\alpha}_i \cdot \vec{\alpha}_j / r_{ij}$, is easier to treat, with the retardation part appearing to be negligible, at least for Fe II (see Section 3.1).

It is from the Dirac-Breit Hamiltonian that the low Z Pauli Hamiltonian is derived [10] that has been used by Hibbert and co-workers [11]. Their work is of considerable interest in that it employs a similar strategy to RCI. For Fe II, it is likely that both Hamiltonians are capable of yielding accurate results.

In RCI, the wavefunctions are eigenstates of J^2, J_z, and parity, and are separated into a reference and correlation part. Usually, the reference part consists of the single non-relativistic manifold which dominates the level of interest [12]. A manifold consists of all relativistic configurations reducing to the same non-relativistic configuration in the $c \rightarrow \infty$ limit. A few additional configurations may be added to the reference list for wavefunctions with strong interactions (e.g. $n\mathrm{s}^2 + n\mathrm{p}^2$, at times, or the anions [13]). As a first step, it is important to determine how many and which energy levels are desired for each J, parity, as this determines the reference space.

Each reference function is a linear combination of Slater determinants, whose coefficients are chosen to generate the desired eigenvalues of J^2, J_z, and parity. Determinantal elements are spinors-products of radial functions (major and minor components) to be determined and spin-angular functions which are eigenstates of j^2, j_z, and parity. The unknown radial functions and coefficients are determined by application of the energy variational principle, which produces the multi-configurational Dirac(Hartree)-Fock (MCDF) equations. These are solved using Desclaux's algorithm [14]. Normally, it is not necessary to include the Breit operator at this stage. This is added later, while correlating the wavefunctions.

To introduce correlation effects, we apply perturbation theory to suggest what additional manifolds are needed in the wavefunction. To first order, correlation manifolds would be created by single or double excitation from the appropriate outer subshells of each of the reference functions. The additional radial functions needed, called virtuals (vl), are represented by relativistic screened hydrogenic (RSH) functions, with a single parameter Z^*, the effective charge. These virtuals represent the compact portion of an entire Rydberg and continuum series, and 1-2 per symmetry (κ) per shell are sufficient to capture ~90% of the correlation energy.

In perturbation theory, the second order energy is given by $-|H_{0i}|^2/|H_{00} - H_{ii}|$ where $|0\rangle$ is a reference function, and $|i\rangle$ is a correlation function. While small denominators (near degeneracy) need careful treatment, maximizing the numerator is usually more important. The is done by using virtuals which have a $\langle r\rangle$ similar to that of the reference radial being replaced. This gives us an estimate for each Z^*, which is fine tuned during the RCI diagonalization process. Virtuals of the same symmetry (κ) originating from two different shells will clearly need different Z^*. It is now clear why the d^7 configuration is more complicated than d^5 – double excitation into a fixed virtual pair leaves the most "complicated" core in the former (d^5 "core").

In the present work, virtual orbital symmetries higher than $l = 5$ seem unnecessary, and even $l = 5$ energetically differentially contributes less than 100 cm^{-1} as seen in Table I for Fe III. By using intermediate normalization, whereby the reference function is normalized, each correlation function, $|i\rangle$, contributes $\epsilon_i = (c_i/c_0)H_{i0}$ to the correlation energy. It is the collected negative sum (in eV) that is given in Table I for each manifold.

Table I contains additional items of interest: (1) no excitations are made from the deeper core electrons: 1s, 2s, 2p, as there is no current evidence they are needed, (2) the variation of the 3d radial function with level can clearly be seen in the 3d^5vd entry which is much larger for the two uppermost levels. This is correcting the 3d radial which was generated for the ^{5}D level.

There are also no second order correlation manifolds present in Table I. These correspond to triple and quadruple excitations from the reference (here only 3d^6). The largest of these would be formally constructed from products of the most important single and double excitations. Illustrations would be 3d^4 $\rightarrow$ vd^4 + vd^2vf^2 + vf^4; 3p3d^2 $\rightarrow$ vd^2vf + vf^3. The need for their presence can be partially monitored by observing how much energy is lost in the nearly degenerate correlation manifolds (e.g. 3d $\rightarrow$ vd) as the large single and doubles are added. Such effects do not appear to be needed. Finally, the 3p^4 $\rightarrow$ 3d^4 second order "exclusion" effect is absent because it can not produce $J = 4$.

Restricting the RCI energy matrix to a "moderate" size improves computational efficiency, ease of analysis, and helps to systematize our understanding of correlation effects. This does have the down side of putting more pressure on the user not to miss any important correlation effects. With open d subshell electrons, it is easy to generate configurations having thousands of basis functions, so the current limit of 20 000 could be quickly reached. The 3p3d $\rightarrow$ vpvd configuration in Table I has 1838 basis functions for example. For Fe II, the $J = 9/2^o$ matrix order could easily exceed 50 000, if nothing were done.

The RCI matrix size can be substantially lowered by employing a formally first order procedure which we call REDUCE [4, 15]. Essentially, one rotates the full basis set for the correlation manifold to maximize the number of zero matrix elements the rotated basis makes with the reference functions. These rotated functions are then discarded. Using only the Dirac-Coulomb Hamiltonian and assuming the major radial components are independent of j and the minor components are zero, each matrix element can be expressed as a linear combination of a small number (N) of radial integrals. For the rotated basis, the coefficient of each radial integral must vanish for as many functions as possible, subject to the condition that the basis remains orthonormal. Mathematically, one solves N equations in M unknowns (M is the number of basis functions, usually $M \gg N$). This underdetermined problem is solved by the singular value decomposition procedure of Press *et al.* [16]. The size reduction can be very great – for example, it was ~7× smaller for the important $3d^2 \rightarrow v f^2$ excitations in $(4d+5s)^6 5p$ $J = 7/2$ in Tc I [4], and ~10× smaller for Fe II $J = 9/2^o$.

RCI computational costs are primarily (>70%) associated with the generation of the structure for each matrix element, which is done explicitly using determinants. Dirac-Coulomb calculation costs are several hours on a SUN Blade 2000 for the full matrix. With the magnetic portion of the Breit operator included, computational costs increase by factors of 4-11. For Fe II, the increase is 11, which means calculations may well span two days (single user). In this work, we remove this bottleneck, decreasing the incremental cost to less than a factor of 2 as follows: we recognize that Breit effects are generally small in most of the applications we undertake, and that they should only need to be calculated for the reference configurations (e.g. $3d^6$), the nearly degenerate configurations (e.g. $3d \rightarrow vd$), and all diagonal matrix elements. Thus we exclude magnetic Breit effects for all matrix elements involving two different correlation manifolds. All diagonal elements must be included to prevent the energetic "pulling away" of the reference diagonal elements from the correlation diagonal elements, which might substantially effect the denominators in the second order energy. Implementation within the RCI code [17] was straightforward – magnetic Breit structure was simply not calculated when not needed. Provisions are made to have a separate (larger) Breit reference space. The net effect was to introduce an error below 1 cm^{-1} for all the Fe II $J = 9/2^o$ energy differences.

Sometimes it is not possible to include enough correlation to adequately position the levels, and the prediction of properties is insufficiently accurate. This can stem from several causes: (1) nearly degenerate configurations (e.g. $3d \rightarrow vd$, $4p \rightarrow vf$) which are incompletely correlated with respect to the reference space; (2) interactions between a valence basis function and those representing a Rydberg series, e.g. $4p^5 4d^2$ interacting with $4p^6 nf$ [18]; (3) levels "just too close together" (say < 300 cm^{-1}), such as the z ^{2}G and y ^{4}F $9/2^o$ Fe II levels. A crude, but reasonably effective way improve the situation is to shift the energy of one (or a very few) of the basis functions a small amount, i.e. the diagonal matrix element for the basis function is changed by less than twice the desired change. For cases (1) and (2) above, the shift amount can either be determined semi-empirically (if the spectra is known) or by a separate *ab initio* calculation on the basis function as reference, which includes the missing correlation, which because of size limitations can not be included in the combined RCI energy matrix. This method has been employed for B I [19], Tc I [4] f values, and La II hyperfine structure [20].

The approach has also been tested in Zr III and Nb IV [21] by explicitly including some of the missing correlation (and reducing the amount of the shift correspondingly) without fundamentally changing the result. In Fe II $9/2^o$, however, the two levels (z ^{2}G and y ^{4}F) are too close (~75 cm^{-1}) to to allow adjustment by means other than semi-empirical. Frequently, the sum of f values from one level to a group of closely spaced levels may be nearly conserved while shifting, as has been shown formally [22]. This is indeed the case for Fe II, as we shall see.

Calculation of the f values requires that non-orthogonality be properly evaluated. This is done using the methods of King *et al.* [23], which over the years have been made several thousand times more efficient by the author [24] by making maximum use of symmetry [25]. The latest step has to been to implement a "one-pass" calculation which computes all $12 \times 22 = 264$ Fe II transitions for the cost of one (for optical transitions). Total calculation time for the Fe II transitions is ∼2 hours (SUN Blade 2000).

Our f values are calculated in two gauges, length and velocity [26], using the experimental energy difference between the states of different parity. We have two formal means of identifying which configurations are (or may be) important contributors to the f values. First is the first order theory of oscillator strengths [27], or FOTOS, which applies the transition operator, r, to the reference levels of one parity to predict what needs to be present in the other parity. This is particularly useful for excitations from the shallow core which are expensive to include in any large number (e.g. 3p3d → vpvd was added to $J = 9/2$ this way). Such excitations normally affect the velocity operator more. Second, the f value program [24] supplies an analysis table which lists the most important contributors to the transition matrix element. These generally involve at least one reference function. This is used to identify which are the important virtual radial functions. The radial basis is then examined to make sure it is sufficiently well saturated for these contributions.

3. Results

Correlation is added in "layers", beginning with the outermost (valence) electrons and single and double excitations. Initially, we focus on the energetically differential correlation effects. For shallow core (3s,3p) excitations, exclusion effects (involving 3d) and symmetry changing single excitations are the first concern. Excitations $3p^2 \rightarrow 3d^2$ and 3p → vf are the principle contributors in these categories. A series of "medium size" calculations are done to make sure the radial and angular space is sufficiently saturated. Once this is achieved, the most important triple and quadruple excitations may be included if energy contributions from nearly degenerate configurations (e.g. 3d → vd) are significantly diminished during the correlation process. More crudely, these second order effects may be (partially) represented via shifts. Finally, any necessary FOTOS configurations are added.

3.1 Fe III $3d^6$ $J = 4$ Energy Levels

Calculations were done on Fe III ($J = 4$) to make sure we had a good understanding of how to correlate the $3d^6$ core, before we undertook the Fe II calculations. From Table II, we see that the average error [12] between adjacent energy levels is 452 cm^{-1} (12.2%). The final wavefunctions use ∼6000 basis functions, and include the magnetic Breit effect. A separate calculation of retardation contributions to energy differences yields a maximum of ∼1 cm^{-1}, entirely negligible.

Only the differentially significant (> 100 cm^{-1}) contributions are retained in Table I. We did look at exclusion effects from opening 2p, viz 2p3p → $3d^2$, $2p^2$ → $3d^2$, and the symmetry changing 2p → vf, as well as some of the easier to include second order effects, e.g. $3d^3$ → $v d^3$ and $3d^4$ → $v d^4$, but these all fell below the significant threshold.

The 3d → vd diagonal matrix elements have been shifted downwards 0.18 a.u. to represent missing correlation effects (second order with respect to $3d^6$). The total correlation in the $3d^5$ ^{5}D state is ∼ −0.28 a.u., and the author feels the −0.18 a.u. shift, which mainly affects the two uppermost levels, is a good compromise value. The shift should be less, of course, because there is less correlation in five 3d electrons than in six. The shifted 3d → vd contributions (Table I) are in good agreement with results obtained from a calculation using only $3d^6$ and $3d^5 v$d.

Table II also contains our prediction for the Landé g values of the levels, computed as described elsewhere [4], as well as the LS composition of the levels. Also shown are Landé g values taken from Kurucz's data [6] which are described elsewhere [28]. JLS eigenstates are produced by diagonalizing the combined $J^2 + L^2 + S^2$ matrix formed from the determinantal basis, subject to the assumptions that the minor component can be neglected and the radial part of the major component is independent of j. All but the ^{3}H, ^{3}F (lower), and ^{3}G levels are quite pure. The ^{3}H (^{3}F) has a significant mixture of ^{3}F (^{3}H) which may appear somewhat odd ($\Delta L = 2$), but there is a significant ^{3}G presence (∼1.3%) in these levels, so we are probably observing a second order effect. It also should be noted that the ^{3}H and (lower) ^{3}F energy levels are quite close (∼1000 cm^{-1}) which also enhances the interactions. Comparison of these Landé g values indicate the RCI levels are less LS pure than those of Kurucz [6].

3.2 Fe II Energy Levels

In Table III, we present results for energy differences and Landé g values for the lowest $J = 9/2$ Fe II $3d^6 4s$ + $3d^7$ levels. Supplementary RCI calculations show that the missing $3d^5 4s^2$ ^{4}G level at 54 264 cm^{-1} [12] does not significantly impact the results of Table III. The level is relatively isolated, so interaction with basis functions representing nearby levels should be weak. The average error between adjacent energy levels is 319 cm^{-1} (17.3%). The final wavefunction includes magnetic Breit effects, and is built from 14 200 basis functions. Without use of REDUCE [15] the energy matrix order would have been ∼34 000. Excitations from 3s, 3p, and 3d important for Fe III (see Table I) have also been included in the Fe II calculations. The Landé g values are in good agreement with experimental results [12] and the semi-empirical values of Kurucz [6].

Table IV contains the energy differences and Landé g values for the Fe II $J = 9/2^o$ levels. Small but important shifts have been introduced for the $3d^6 4p$ ^{2}G and ^{2}H basis functions. The ^{2}G shift (∼110 cm^{-1}) serves to flip the z ^{2}G and y ^{4}F 9/2 levels into their observed [12] positions (75 cm^{-1} apart). Prior to the shift they are separated (and flipped) by 94 cm^{-1}. As noted earlier, *ab initio* methods can not be expected to routinely account for such small splittings. With this shift, the Landé g values (Table IV) are also in good agreement with experiment [12]. The main effect of the ^{2}H shift is to reduce the three spin change f values to less than 0.01.

Correlating the Fe II $J = 9/2^o$ levels is somewhat easier than what was necessary for Tc I [4] because in the 22 energetically lowest levels, all reference configurations are the same, except for $3d^5 4s4p$ z ^8P. This level interacts only weakly with the nearby $3d^6 4p$ levels, and in fact is less well correlated than they are (a shift of -0.11 a.u. for 3d $\rightarrow$ vd is introduced to partially compensate). In Tc I, one must carefully deal with all three reference configurations, $(4d{+}5s)^6 5p$ [4].

The Table IV Landé g values are also in good agreement with experiment [12] and the semi-empirical values of Kurucz [6]. Predictions are made for 8 of the 22 levels. Magnetic Breit effects are included, and final calculation time is ~19.5 hours, the longest of any here. The energy matrix size is 10 200 which is effectively equivalent to a matrix of order 52 700 through use of REDUCE [15]. The average adjacent energy splitting error is 164 cm^{-1} or 20.0%. The "large" percentage associated with the "small" energy error gives some indication of the near degeneracy present.

3.3 Fe II f values

For every transition shown in Table V, there are at least three sets of values, two semi-empirical, from the data bases of Kurucz [6] and Raassen [7], and the RCI results. Generally, all three sets are in good agreement. The Kurucz f values are computed by determining basis function mixing from fitting the observed spectrum [12] in a Cowan-like procedure and obtaining the radial functions for the transition integral from a relativistic Thomas-Fermi calculation [28]. Raassen and co-workers use the method of orthogonal operators to determine the basis set mixing, and extract the transition probability radial integrals (length form) from an *ab initio* source [29].

For the first three transitions, there are several additional sources, one *ab initio* calculation [30] and three experiments [31, 32, 33] where results are obtained from a combination of lifetime and relative transition probability (branching fractions) measurements. For the first transition, our value seems a bit low, whereas for the third one we are in excellent agreement with experiment [32]. Experimental values [34, 35] also exist for two other transitions in Table V.

Because of the near degeneracy of many of the odd levels, as indicated by the large (>10%) error in energy differences between some adjacent energy levels and the sometimes very different f values associated with these levels, we have introduced further "small" shifts. For the odd parity calculation we have shifted the y ^4H diagonal matrix element down 75 cm^{-1} and the w ^2G diagonal matrix element down 305 cm^{-1}. This reduces the average adjacent odd parity energy level error to 5.0%.

For the even parity calculation we have shifted the a ^4H (b ^2H) diagonal matrix elements down 310 (200) cm^{-1} reducing the error to 7.5%. By LS coupling the $3d^6$ electrons we are able to shift only one basis function. Only the odd parity shifts had a noticeable impact on some of the f values (see Table V). The main changes are for transitions to the x ^4G and x ^4F states, which for transitions from the even a ^4G increases the difference between the RCI and semi-empirical results. This is also mirrored in the difference between the computed Landé *g* values – the RCI values tend to be more LS pure than those of Kurucz. We tentatively conclude that these three levels: x ^{4}G, x ^{4}F, and y ^{4}H (all odd) deserve further investigation.

The RCI results of Table V illustrate two points: (1) the sum of *f* values to a group of nearby levels from a single common level is nearly constant as a diagonal matrix element is shifted a moderate amount, (2) gauge agreement does not imply correctness, i.e. we have transitions which have good gauge agreement pre- and post-shift, but whose values are outside the gauge range.

Our results suggest that the merit of all *ab initio* *f* values involving nearly degenerate levels be partially judged on how accurately the adjacent energy spacings are obtained. In doubtful cases (e.g. $> 10\%$ error between two adjacent levels with quite different *f* values), the levels should be "manually" shifted to see how the individual *f* values change (the sum should be approximately conserved). Such shifts should be done even in the absence of experimental data. Finally, differences between RCI and the semi-empirical values may partially arise from our inclusion of the magnetic part of the Breit operator, non-orthonormality effects, or the more extensive inclusion of correlation effects.

Acknowledgements

This work is supported by the Division of Chemical Sciences, Office of Energy Research, U.S. Department of Energy, Grant # DE-FG02-92-ER14282.

Table I. *Fe III* $3s^2 3p^6 3d^6$ $J = 4$ *energy contributions (in* $-eV$*).*

	Energy Levels						
Configuration	^{1}G	^{3}F	^{1}G	^{3}G	^{3}F	^{3}H	^{5}D
3s^2 3p^6 3d^5 vs	0.000	0.000	0.001	0.001	0.000	0.000	0.000
3s^2 3p^6 3d^5 vd	0.250	0.277	0.069	0.106	0.086	0.092	0.103
3s^2 3p^6 3d^5 vg	0.238	0.226	0.114	0.157	0.098	0.121	0.072
3s^2 3p^6 3d^4 vs^2	0.019	0.021	0.011	0.006	0.009	0.006	0.006
3s^2 3p^6 3d^4 vp^2	0.129	0.134	0.116	0.087	0.107	0.077	0.082
3s^2 3p^6 3d^4 vd^2	1.698	1.676	1.596	1.554	1.553	1.547	1.458
3s^2 3p^6 3d^4 vf^2	1.498	1.541	1.395	1.332	1.391	1.264	1.345
3s^2 3p^6 3d^4 vg^2	0.164	0.170	0.149	0.137	0.147	0.129	0.139
3s^2 3p^6 3d^4 vh^2	0.041	0.043	0.036	0.032	0.035	0.030	0.032
3s^2 3p^6 3d^4 vs vd	0.018	0.013	0.030	0.020	0.026	0.017	0.012
3s^2 3p^6 3d^4 vs vg	0.017	0.014	0.013	0.013	0.011	0.014	0.008
3s^2 3p^6 3d^4 vp vf	0.106	0.090	0.101	0.095	0.088	0.101	0.066
3s^2 3p^6 3d^4 vd vg	0.004	0.003	0.005	0.004	0.004	0.004	0.003
3s^2 3p^6 3d^4 vf vh	0.059	0.051	0.067	0.058	0.059	0.059	0.044
3s^2 3p^5 3d^6 vf	1.933	1.828	1.908	2.119	1.941	2.236	2.013
3s^2 3p^5 3d^5 vp vd	1.683	1.685	1.689	1.684	1.688	1.685	1.690
3s^2 3p^4 3d^8	0.653	0.722	0.525	0.311	0.466	0.181	0.312
3s 3p^5 3d^7 vf	0.212	0.215	0.204	0.196	0.202	0.193	0.197
3s 3p^6 3d^7	0.106	0.018	0.017	0.045	0.111	0.025	0.000
3s 3p^6 3d^6 vd	0.037	0.037	0.025	0.029	0.026	0.022	0.026
3p^6 3d^8	0.049	0.058	0.025	0.000	0.016	0.001	0.000

Table II. *Fe III* $3d^6$ $J = 4$ *energy levels (in cm*$^{-1}$*). Error is measured with respect to the* ^{5}*D level. The average adjacent energy difference error is 452* cm^{-1} *(12.2%). This is the better figure of merit.*

				Landé g value	
LS %	Expt [12]	RCI	Error	RCI	Kurucz [6]
^{5}D 100	0	0	0	1.499	1.501
^{3}H 92 + ^{3}F 5	20 482	21 718	1236	0.830	0.810
^{3}F 91 + ^{3}H 6	21 462	22 224	762	1.217	1.236
^{3}G 97	24 941	26 053	1112	1.051	1.053
^{1}G 99	30 886	32 156	1270	1.000	1.001
^{3}F 99	50 276	51 652	1376	1.249	1.250
^{1}G 99	57 222	58 986	1764	1.000	1.001

Table III. *Fe II* $3d^6 4s + 3d^7$ $J = 9/2$ *energy levels (in* cm^{-1}*). Error is measured from the ground state. The average adjacent energy difference error is 319* cm^{-1} *(17.3%). This is the better figure of merit.*

	Energy (cm^{-1})			Landé g value	
Label	Expt [12]	RCI	Error	RCI	Other
$3d^6 4s$ a ^6D	0	0	0	1.555	1.580[a]
$3d^7$ a ^4F	1873	1734	−139	1.333	1.330[a]
$3d^7$ a ^2G	15 845	16 471	626	1.109	1.109[b]
$3d^7$ a ^2H	20 806	21 827	1021	0.911	0.920[a]
$3d^6 4s$ a ^4H	21 582	23 051	1469	0.975	0.950[a]
$3d^6 4s$ b ^4F	22 637	23 863	1226	1.326	1.301[a]
$3d^6 4s$ a ^4G	25 805	27 308	1503	1.167	1.150[a]
$3d^6 4s$ b ^2H	26 353	28 198	1845	0.917	0.927[a]
$3d^6 4s$ b ^2G	30 389	32 251	1862	1.109	1.100[a]
$3d^6 4s$ c ^2G	33 467	35 405	1938	1.110	1.099[a]
$3d^6 4s$ c ^4F	50 158	52 673	2515	1.333	1.334[b]
$3d^6 4s$ d ^2G	58 632	61 653	3021	1.111	1.112[b]

[a] Experimental values from Sugar and Corliss [12].

[b] Semi-empirical values of Kurucz [6], presented where no experimental values are available.

Table IV. *Fe II $3d^6 4p$ + $3d^5 4s4p$ $J = 9/2$ Energy Levels (in cm^{-1}). Error is measured from the ground state. The average adjacent energy difference error is 164 cm^{-1} (20%). This is the better figure of merit. Includes shifts of ^2G and ^2H levels (see text).*

	Energy (cm^{-1})			Landé g value	
Label	Expt [12]	RCI	Error	RCI	Other
$3d^6 4p$ z ^6D	0	0	0	1.554	1.542[a]
$3d^6 4p$ z ^6F	3656	3781	125	1.433	1.430[a]
$3d^6 4p$ z ^4F	5774	5985	211	1.335	1.320[a]
$3d^5 4s4p$ z ^8P	14 507	14 298	−209	1.777	1.779[b]
$3d^6 4p$ z ^4G	22 348	23 663	1315	1.168	1.155[a]
$3d^6 4p$ z ^4H	22 530	23 838	1308	0.920	0.895[b]
$3d^6 4p$ z ^4I	23 054	24 366	1312	0.815	0.857[b]
$3d^6 4p$ z ^2G	23 624	24 890	1266	1.090	1.097[a]
$3d^6 4p$ y ^4F	23 699	24 966	1267	1.316	1.330[a]
$3d^6 4p$ y ^4G	25 490	26 833	1343	1.168	1.150[a]
$3d^6 4p$ y ^2G	26 373	27 691	1318	1.105	1.101[a]
$3d^6 4p$ z ^2H	27 097	28 459	1362	0.919	0.913[a]
$3d^6 4p$ x ^4G	27 237	28 653	1416	1.226	1.243[b]
$3d^6 4p$ x ^4F	27 554	28 931	1377	1.268	1.250[b]
$3d^6 4p$ y ^4H	28 130	29 543	1413	0.973	0.959[a]
$3d^6 4p$ y ^2H	29 542	30 849	1307	0.917	0.907[a]
$3d^6 4p$ x ^2G	31 856	33 229	1373	1.109	1.110[a]
$3d^6 4p$ x ^2H	33 671	35 208	1537	0.915	0.910[a]
$3d^6 4p$ w ^4F	34 192	35 734	1542	1.331	1.331[b]
$3d^6 4p$ w ^2G	34 633	36 423	1610	1.087	1.099[b]
$3d^6 4p$ w ^2H	35 292	36 856	1564	0.925	0.916[b]
$3d^6 4p$ v ^2G	45 412	47 486	2074	1.111	1.112[b]

[a] Experimental values from Sugar and Corliss [12].

[b] Semi-empirical values of Kurucz [6], presented where no experimental values are available.

Table V. *Fe II (3d^{6}4s + 3d^7) J = 9/2 → 3d^{6}4p J = 9/2 RCI f values (using experimental [12] ΔE; only values greater than 0.01 shown). The "spread" in gauges is defined by* $|f_L - f_V|/f_{avg} \times 50$. *Entries in italics are the shifted RCI values discussed in Section 3.3.*

Transition			Vel	Len	Spread	Other Calculations	Experiment
3d^{6}4s a ^{6}D	→ 3d^{6}4p	z ^{6}D	0.276	0.265	2.0%	0.258^{a}, 0.242^{b}, 0.240^{c}	0.220^{d}, 0.239^{e}, 0.213^{f}
	→	z ^{6}F	0.040	0.038	2.7%	0.034^{a}, 0.033^{b}, 0.053^{c}	0.028^{d}, 0.031^{e}, 0.033^{f}
3d^7 a ^{4}F	→ 3d^{6}4p	z ^{4}F	0.038	0.028	15.2%	0.044^{a}, 0.023^{b}, 0.040^{c}	0.020^{d}, 0.0275^{e}
	→	x ^{4}G	0.017	0.017	0.6%	0.038^{a}, 0.019^{b}	
	→	*x ^{4}G*	*0.011*	*0.011*			
	→	x ^{4}F	0.046	0.042	4.6%	0.055^{a}, 0.039^{b}	
	→	*x ^{4}F*	*0.053*	*0.048*			
3d^7 a ^{2}G	→ 3d^{6}4p	z ^{2}G	0.026	0.019	15.6%	0.036^{a}, 0.018^{b}	
	→	y ^{2}G	0.044	0.035	11.4%	0.046^{a}, 0.029^{b}	
	→	x ^{2}G	0.014	0.014	1.8%	0.021^{a}, 0.011^{b}	
	→	w ^{2}G	0.065	0.054	8.9%	0.092^{a}, 0.055^{b}	
3d^7 a ^{2}H	→ 3d^{6}4p	z ^{2}H	0.046	0.031	19.5%	0.055^{a}, 0.030^{b}	
	→	w ^{2}H	0.100	0.078	12.4%	0.134^{a}, 0.076^{b}	
3d^{6}4s a ^{4}H	→ 3d^{6}4p	z ^{4}G	0.029	0.028	1.1%	0.051^{a}, 0.026^{b}	
	→	z ^{4}H	0.205	0.195	2.6%	0.135^{a}, 0.163^{b}	
	→	z ^{4}I	0.015	0.015	2.4%	0.037^{a}, 0.027^{b}	0.024^{g}
	→	z ^{2}G	0.011	0.011	0.2%	0.013^{a}, 0.009^{b}	
	→	y ^{4}G	0.021	0.021	0.5%	0.023^{a}, 0.020^{b}	0.019^{h}
	→	y ^{4}H	0.018	0.018	0.8%	0.020^{a}, 0.018^{b}	
3d^{6}4s b ^{4}F	→ 3d^{6}4p	z ^{4}G	0.028	0.025	5.0%	0.027^{a}, 0.026^{b}	
	→	y ^{4}F	0.238	0.229	1.8%	0.219^{a}, 0.212^{b}	
3d^{6}4s a ^{4}G	→ 3d^{6}4p	x ^{4}G	0.113	0.107	2.6%	0.066^{a}, 0.093^{b}	
	→	*x ^{4}G*	*0.143*	*0.136*			
	→	x ^{4}F	0.153	0.151	0.6%	0.165^{a}, 0.143^{b}	
	→	*x ^{4}F*	*0.120*	*0.118*			
	→	y ^{4}H	0.015	0.013	6.6%	0.019^{a}, 0.011^{b}	
3d^{6}4s b ^{2}H	→ 3d^{6}4p	z ^{2}H	0.216	0.188	7.0%	0.189^{a}, 0.169^{b}	
	→	y ^{2}H	0.085	0.076	5.7%	0.069^{a}, 0.070^{b}	
	→	w ^{2}H	0.016	0.014	7.6%	0.016^{a}, 0.013^{b}	
3d^{6}4s b ^{2}G	→ 3d^{6}4p	z ^{2}G	0.038	0.031	10.1%	0.033^{a}, 0.031^{b}	
	→	x ^{2}G	0.254	0.227	5.7%	0.217^{a}, 0.210^{b}	

3d^{6}4s c ^{2}G	→ 3d^{6}4p	x ^{2}H	0.025	0.022	5.1%	0.028[a], 0.031[b]
	→	*x ^{2}H*	*0.032*	*0.028*		
	→	w ^{2}G	0.230	0.214	3.6%	0.220[a], 0.203[b]
	→	*w ^{2}G*	*0.243*	*0.223*		
	→	w ^{2}H	0.041	0.038	3.7%	0.016[a], 0.015[b]
	→	*w ^{2}H*	*0.022*	*0.020*		

---

[a] Semi-empirical calculations of Kurucz [6].

[b] Semi-empirical calculations of Raassen [7].

[c] *Ab initio* calculations of Nahar and Pradhan [30].

[d] Experimental values from Fuhr *et al.* [31].

[e] Experimental values of Bergeson [32].

[f] Experimental values of Cardelli [33].

[g] Experimental value of Sikstrom [34].

[h] Experimental value of Pickering *et al.* [35].

References

[1] Johansson, S. *et al.* in "Proceedings of the 7th International Colloquium on Atomic Spectra and Oscillator Strengths", edited by Hibbert, A. and Wiese, W. L., Phys. Scr. **T100**, 71 (2002).

[2] ASOS8, Madison, Wisconsin (2004). Invited talks to be published as a technical report in Physica Scripta (2005).

[3] Fuhr, J. R., Felrice, H. R., Olsen, K., and Hwang, J., Atomic Transition Probability Bibliographic Database (http://physics.nist.gov/PhysRefData/Fvalbib/html/reffrm0.html).

[4] O'Malley, S. M. and Beck, D. R., Phys. Scr. **68**, 244 (2003).

[5] Martin, R. L. and Hay, P. J., J. Chem. Phys. **75**, 4539 (1981).

[6] Kurucz, R. L., online database (files in http://kurucz.harvard.edu/atoms/2601/). Older published values by the same author appear in Kurucz, R. L., "Semi-empirical calculation of gf values: Fe II," Smithsonian Astrophysical Observatory Special Report **390**, Cambridge, MA (1981).

[7] Raassen, A. J. J., online database (ftp://ftp.wins.uva.nl/pub/orth/iron/FeII.E1) (1999).

[8] e.g. Beck, D. R. and Nicolaides, C. A., J. Quant. Spectrosc. Radiat. Transfer **16**, 297 (1976).

[9] Grant, I. P., Adv. Phys. **19**, 747 (1970).

[10] Bethe, H. A. and Salpeter, E. E., "Quantum Mechanics of One- and Two- Electron Atoms", Academic Press (1957), p. 181.

[11] Donnelly, M. P. and Hibbert, A., Mon. Not. R. Astron. Soc. **321**, 247 (2001).

[12] Sugar, J. and Corliss, C., J. Phys. Chem. Ref. Data **14**, Suppl. 2 (1985).

[13] O'Malley, S. M., and Beck, D. R., Phys. Rev. A **61**, 034501 (2000).

[14] Desclaux, J. P., Comput. Phys. Commun. **9**, 31 (1975).

[15] Beck, D. R., program REDUCE (unpublished).

[16] Press, W. H. *et al.* "Numerical Recipes in Fortran 77," Second Edition, Cambridge Press, New York (1992).

[17] Beck, D. R., program RCI (unpublished).

[18] Pan, L. and Beck, D. R., to be submitted for publication.

[19] Beck, D. R. and Nicolaides, C. A., Phys. Letts. A **61**, 227 (1977).

[20] Datta, D. and Beck, D. R., Phys. Rev. A **52**, 3622 (1995).

[21] Beck, D. R. and Pan, L., Phys. Scr. **69**. 91 (2004).

[22] Nicolaides, C. A. and Beck, D. R., Chem. Phys. Letts. **53**, 87 (1978).

[23] King, H. F. *et al.*, J. Chem. Phys. **47**, 1926 (1967).

[24] Beck, D. R., program RFV1S (unpublished).

[25] Beck, D. R. and Cai, Z., Phys. Rev. A **41**, 301 (1990).

[26] Grant, I. P., J. Phys. B **7**, 1458 (1974).

[27] Nicolaides, C. A. and Beck, D. R., Chem. Phys. Letts. **36**, 79 (1975).

[28] Kurucz, R. L., in *Trans. Internat. Astron. Union* **XXB**, edited by McNally, M., Kluwer, Dordrecht, 168 (1988). See also, Kurucz, R. L., in *Atomic and Molecular Data and Their Applications: 3rd Int'l. Conf.*, edited by Schultz, D. R. *et al.*, American Institute of Physics, 134 (2002).

[29] Raassen, A. J. J. and Uylings, P. H. M., J. Phys. B **31**, 3137 (1998).

[30] Nahar, S. N. and Pradhan, A. K., J. Phys. B **27**, 429 (1994).

[31] Fuhr, J. R., Martin, G. A. and Wiese, W. L., J. Phys. Chem. Ref. Data **17**, Suppl. 4 (1988).

[32] Bergeson, S. D. *et al.*, Ap. J. **464**, 1044 (1996).

[33] Cardelli, J. A. and Savage, B. D., Ap. J. **452**, 275 (1995).

[34] Sikstrom, C. M. *et al.*, J. Phys. B. **32**, 5687 (1999).

[35] Pickering, J. C., Johansson, S., and Smith, P. L., Astron. Astrophys. **377**, 361 (2001).