

Oscillator strengths, Landé g values, and hyperfine structure for $3d^4 J=0 \rightarrow 3d^3 4p J=1$ transitions in Fe V

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Relativistic configuration-interaction (RCI) calculations with $\sim 15\,000$ vectors have been done for f values, Landé g values, and hyperfine structure constants for Fe v. There is at least a factor of 2 improvement over our earlier achievable accuracies (Nb II). The 21 largest f values (>0.01) have an average length-velocity gauge difference of 6.7%, and the average error in the energy differences between adjacent levels is $213\ (180)\ \text{cm}^{-1}$ for even- (odd-) parity levels. We find significant f value differences as compared to recent values from Breit-Pauli R -matrix calculations, and, to a lesser extent, as compared to older semiempirical f values. Oscillator strengths to three nearly degenerate odd-parity levels are sensitive to errors smaller than $200\ \text{cm}^{-1}$, but the sum is conserved, as expected.

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I. INTRODUCTION

As noted in a recent paper by Nahar and Pradhan on Fe V transition probabilities [1], there is a need for reliable Fe v results to aid analysis of spectra in hot stars [2] and young white dwarfs [3]. In fact, this lack is quite general—there are few reliable results for $d^n \rightarrow d^{n-1}p$ transitions available in the literature. A second reason to consider Fe v is the existence of substantial differences between some of the f value results of Nahar and Pradhan [1], and the semiempirical work of Fawcett [4], and it would be useful to see if any resolution can be achieved regarding which are the more accurate values. Similar discrepancies have been found [5] by experimenters for selected C I, N I, O I, and F I [6] f values. Finally, this work is a natural extension of our study of transition-metal atoms and ions, in particular of an earlier study we made of two $4d^3 5p$ lifetimes in Nb II [7].

From the theoretical viewpoint, studies of $(d+s)^n \rightarrow (d+s)^{n-1}p$ transitions require the inclusion of both relativistic and correlation effects, even for first-row transition-metal atoms or ions. This can be seen from the work of Martin and Hay [8], for example, where it was noted that relativistic effects for d and s electron energies differ by 0.1 eV or more. This difference may be important, because at least for lightly ionized species, levels associated with d^n , $d^{n-1}s$ and $d^{n-2}s^2$ levels can be quite close to each other, so that good wave functions must have the proper admixture of them. This is especially true of hyperfine structure (HFS) constants, where the amount of $d^{n-1}s$ admixture can often be crucial, since it can have such a large HFS constant, due to the open s electron (see, e.g., Ref. [9]). In this work, we show that for some closely spaced levels ($\Delta E < 900\ \text{cm}^{-1}$) that errors in ΔE [10] as small as $200\ \text{cm}^{-1}$ can change certain f values 30–50% (also see Ref. [11]). Based on these results, we suggest that if calculated f values are to be accurate, they must properly account for the ΔE 's to nearby levels (of the same parity and J). A quantitative estimate as to a specific f values sensitivity to these spacings can be determined by shifting diagonal matrix elements in the relativistic configuration-interaction (RCI) matrix, to bring the theoretical and experimental spac-

ings into agreement, as we describe in Sec. III. The sum of f values to a group of nearby levels may remain nearly constant [11,12], so that one is just transferring oscillator strength from one level to another. This is illustrated in Sec. III.

There are few *ab initio* relativistic correlation calculations for $d^n \rightarrow d^{n-1}p$ transitions, due to the considerable demand they make on present computational methodologies. The presence of open d -shell electrons means one may be dealing with very large N -electron basis sets (>1000 vectors for a configuration). Furthermore, there may be several nearby energy levels. These factors mean more excitation is needed from the core ($3s$ and $3p$ electrons here), and more second-order effects (triple and quadruple excitations), than for transitions just involving s and p electrons.

The study reported here is a considerably more challenging one than the two reported earlier for Cs II [11] and Nb II [7]. For Cs II, the transitions were considerably simpler, *viz* $5p^5 (5d/6s \rightarrow 6p)$. For Nb II, we computed $(d+s)^4 \rightarrow (d+s)^3p$ transitions, producing even-parity wave functions yielding average energy errors of $450\text{--}824\ \text{cm}^{-1}$, and, for the lowest four odd-parity levels, average errors of $271\ \text{cm}^{-1}$. The RCI matrices had orders <3500 , except for $J=2$ even, which had a basis of order ~ 6600 . For the largest transition, there was a 14% spread between the two gauges, although smaller f values were seen to have smaller spreads.

In the present calculation, we increased the RCI matrix limit from 7000 to 20 000, by redimensioning our algorithms [13]. The experience we gained since 1995 [7] in how to choose the excitations to include in the wave function was also invaluable. The decision process is given in Sec. II. As a consequence, we were able to uniformly reduce the average energy error to $\sim 200\ \text{cm}^{-1}$ ($\sim 0.025\ \text{eV}$) while treating more levels, and bring the average gauge agreement in f values to $\sim 6.7\%$. The order of the RCI matrices for FeV was $\sim 15\,000$, a fivefold increase from the typical Nb II size. It may be noted that due to its ionicity, Fe v is easier to deal with than Nb II, because d^n , $d^{n-1}s$, and $d^{n-2}s^2$ are well separated in Fe v, for equivalent accuracy levels.

Our approach is to use a Dirac-Coulomb Hamiltonian,

with Breit terms where necessary. Odd- and even-parity wave functions are obtained from separate RCI calculations, so that nonorthonormality effects must be included [7] in evaluating f values. We give results for both the length (Babuskin) and velocity gauges; agreement between the two gauges is a necessary, but not a sufficient condition for correctness, as is illustrated in Sec. III.

The only other *ab initio* calculations on $d^n \rightarrow d^{n-1}p$ transitions use a portion of the low- Z Pauli Hamiltonian. These have been done by Nahar and Pradhan [1], based on the R -matrix methodology of Berrington *et al.* [14], and Luke [15]. Fe v probably has a low enough Z , so calculations based on the two different relativistic Hamiltonians should yield the same answer in principle.

II. METHODOLOGY

Wave functions are calculated using the RCI method, the details of which can be found in a series of papers [16] and references therein. We begin with a Dirac-Coulomb or Dirac-Breit Hamiltonian, and a zeroth order, or reference function, is generated by solving multiconfigurational Dirac-Fock (MCDF) equations using Desclaux's program [17]. Our basis members (or parents) are eigenstates of J^2 and J_z and relativistic parity, formed from a linear combination of four component spinors (major and minor components). Once the MCDF reference (i.e., dominant) manifold is generated, first-order perturbation theory is formally applied (with the Coulomb operator as the normal perturbation) to generate the form for the correlated "first-order" wave function. This function is constituted by single and double subshell excitation from the reference. The amount of excitation from the core is determined by practicability, and past experience.

Generally, single and double excitations are made into subshells not occupied in the MCDF reference, and radial functions need to be generated for these "virtual" subshells (denoted vl). As has been recognized by most CI practitioners since the 1960s [18], these virtual radials are not "spectroscopic," but rather represent the compact portions of infinite Rydberg/continuum series (for bound states), when obtained within the CI (RCI) process. Our long-standing preference has been to use a few analytic functions to represent each virtual radial, which allows their easy adjustment (change of one parameter, called the effective charge, or Z^*), after which they are converted to the numerical mesh of Desclaux [17] to improve computational efficiency. For the RCI methodology, we have found the use of a relativistic screened (Z^*) hydrogenic function (SHF) to be an excellent choice. It is capable of acquiring about 90% of the correlation energy, while avoiding variational collapse into the positron sea as a result of the simultaneous choice of both major and minor components, once Z^* is fixed. As is typical of single-particle expansions, convergence is slow after one SHF, but in practice we find that no more than three SHF's are needed per virtual radial for each reference shell being excited. Good estimates for the initial Z^* s can be obtained by equating each $\langle r \rangle$ for the shell being excited, and its virtual replacement.

The first step in constructing our Fe v RCI bases is to

apply all possible single and double excitations out of the $3d^4$ and $3d^3 4p$ valence shells. The valence configurations consist of excitations into open subshells with orbital symmetries up to $l=4$ (g), as well as the moderately important (see Sec. III) excitation $3d^2 \rightarrow v h^2$ for both parities.

The second step in the basis construction involves opening the core, in this case down to $3s$. To keep the size of the bases manageable, we select only those excitations with differing contributions to the RCI energies of levels within the $3d^4$ and $3d^3 4p$ manifolds. Specifically, it is known [19] that the single excitations $nl \rightarrow n/v(l+2)$, e.g., $3p \rightarrow v f$, are important, as are excitations involving the exclusion effects [20] $nl \rightarrow n(l+2)$, e.g., $3s \rightarrow 3d$, and $nl nl' \rightarrow nl'' nl'''$, e.g., $3p^2 \rightarrow 3d^2$. Exclusion excitations may also include noncomplex preserving excitations like $3p^2 \rightarrow 3dvd$. Their common denominator is at least one excitation into an unfilled subshell of the same n . Core excitations with negligible (~ 1 meV) differential contributions within each manifold of five or 19 levels (even or odd cases) are omitted. This reduces any potential problems from the preferential (and artificial) pulling away of the reference manifolds from those of the less correlated nearby manifolds (see the discussion of second-order effects below).

Finally, we include any configurations not already present which are important for the atomic properties we wish to calculate. For hyperfine structures core excitations must include $ns \rightarrow s$ (because of potentially large contact contributions). For f values, the first-order theory of oscillator strengths, [21], gives us guidance. For electric dipole transitions, one applies the dipole operator (r) to each manifold of both parities. Applying $3p \rightarrow s+d$ to the even $3d^4$ manifold leads us to include $3s^2 3p^5 3d^5$ and $3s^2 3p^5 3d^4 (vs+vd)$, which correspond to $3p4p \rightarrow d^2 + sd$ in the odd calculation. Likewise, $3s \rightarrow p$, applied to $3d^4$, suggests inclusion of $3s3p^6 3d^4 (4p+vp)$ and $3s3p^6 3d^3 vpvvd$, which are already present in the odd calculation as $3s \rightarrow 3d$ and $3s4p \rightarrow 3dvp + vpvvd$. Considering the same $3p \rightarrow s+d$ and $3s \rightarrow p$ excitations with respect to the odd $3d^3 4p$ manifold, leads us to add $3s^2 3p^5 3d^3 (vsvp + vpvvd)$ and $3s3p^6 3d^3 vp^2$ (note that vp appears here because $4p$ is not present in the $3d^4$ DF manifold) to the even calculation, and suggests that some configurations already present, $3s^2 3p^5 3d^4 vp$ ($3p \rightarrow vp$) and $3s^2 3p^6 3d^3 vd$ ($3d \rightarrow vd$), are important contributors to the oscillator strength calculations. Our code [22] fully accounts for the nonorthonormality between basis sets of different parities.

Our approach to this problem is to position the levels within each manifold as accurately as possible. As previously stated, a proper positioning of levels leads to a more accurate mixing between levels, which was found [11] to be crucial to the calculation of some atomic properties, including HFS and possibly f values, our main objective in this case.

Recently, we placed a great deal of emphasis on the selection of radial basis sets in an effort to minimize the impact of core excitations. For example, in the case of Ce^- [23] we found that selecting radial bases created from single manifold Dirac-Fock calculations minimized differences between the neutral and negative $5d$ radial wave functions. This in turn minimized the need for core-valence pair excitations involving $5d$ due to the negligible difference of their energy

TABLE I. Energy contributions ($-meV$) to Fe v $3d^4J=0$ energy levels.

Excitation	${}^5D_0^e$	${}^3P_0^e[1]$	${}^1S_0^e[1]$	${}^3P_0^e[2]$	${}^1S_0^e[2]$
$3d \rightarrow s + d + g$	26.6	106.5	65.4	274.7	514.5
$3d^2 \rightarrow s^2 + p^2 + h^2 + sd + dg + pf$	45.0	145.2	193.9	150.6	266.3
$3d^2 \rightarrow d^2$	423.8	520.0	572.4	614.2	822.6
$3d^2 \rightarrow f^2$	581.7	749.0	825.4	873.7	1265.9
$3d^2 \rightarrow g^2$	70.4	105.4	123.6	126.5	212.7
$3p \rightarrow p$	67.9	41.3	33.4	52.7	37.8
$3p \rightarrow f$	2326.1	1936.4	1850.1	2049.5	1518.3
$3s \rightarrow s + d$	126.6	173.3	655.3	292.3	259.1
$3p^2 \rightarrow d^2$	1271.3	1742.9	1898.3	1863.9	2720.0
$3p^2 \rightarrow dg$	111.5	112.5	114.1	118.2	124.0
$3s^2 \rightarrow d^2$	31.7	66.2	88.8	87.6	222.6
$3p3d \rightarrow sp + pd$	1331.9	1334.3	1330.7	1328.0	1334.6
$3s3d \rightarrow p^2$	32.0	32.1	29.7	31.7	32.2
$3s3p \rightarrow pd + df$	456.4	471.9	479.2	478.9	518.6
Total	6903.0	7536.9	8260.5	8342.5	9849.1

contribution between the two species. With the quadruply ionized Fe v, however, we are dealing with much larger correlation contributions (see Tables I and II for energy contributions—totals are over 6 eV for all levels) than the typical negative ion species (usually 1–2 eV total contribution with the largest configurations adding a few hundreds of meV). Thus for Fe v, opening the core is essential for an accurate level positioning (with average errors of thousands of cm^{-1} for valence-only calculations). The relatively high ionization stage does yield some advantages, however. We note that the vd radials are sufficiently diffuse as to have little impact on exclusion-type configurations in a differential manner. For example, we may neglect the full saturation of $3p^2 \rightarrow d^2$, since $3p^2 \rightarrow vd^2$ makes nearly the same contribution to all of the levels within each manifold. Additionally, we note a negligible impact from the inclusion of a $4s$ subshell in our one-electron radial bases. We attribute this to the lack of s - d mixing in Fe v that is typical of transition metals and rare earths, where we have near degeneracy or even an intermixing of d^n , $d^{n-1}s$, and $d^{n-2}s^2$ manifolds. This can be seen experimentally [10] for the even $J=0$ Fe v case, where the nearest $3d^34s$ level is over 90 000 cm^{-1} above the uppermost $3d^4$ level, while our calculations suggest a similar gap between the uppermost level of the $3d^34p$ manifold and the next-nearest $J=1$ level. This lack of s - d mixing allows us to omit the corresponding $3d \rightarrow 4s$ and $3d^2 \rightarrow 4s^2$ excitations to all important correlation configurations, greatly reducing the potential number of basis members.

Also of interest is the importance of second-order effects on our latest calculations [23,24]. Often as correlation is added to the configuration of interest, we produce an artificial pulling away of the corresponding manifold from other configurations that are not as fully correlated. For nearby configurations (often identified by large weight factors since their coefficients are inversely proportional to the energy difference between the levels) the pulling away can be a significant fraction of the energy differences. Thus we may find

a few configurations whose contributions drop significantly as the calculation progresses. In Fe v we have two competing complications of this problem compared to our most recent work [23,24]. First we have the aforementioned fact that the nearest manifolds are far removed from the ones we are interested in, which works in our favor. In fact, in the odd $3d^34p$ case, we found little impact on valence configuration energy contributions as the core was opened up. On the other hand, we have a larger overall energy contribution in this quadruply ionized system, such that smaller percentage changes in the individual configurations coefficients can affect them to a non-negligible degree.

For both parities, we explore triple and quadruple excitations created by applying to each other those excitations most important in the manifolds of interest. For example, consideration of the importance of $3d^2 \rightarrow vd^2$, $3d^2 \rightarrow v f^2$, and $3p \rightarrow v f$ suggests potential second-order excitations $3d^4 \rightarrow vd^4 + vd^2 v f^2 + v f^4$ and $3p3d^2 \rightarrow vd^2 v f + v f^3$. We proceed by trial and error, including one such configuration at a time, and tracking its effect on the positioning of the upper roots. As expected, due to the high ionicity of the system and the remoteness of the next lowest manifolds of each parity, second-order effects play a much more subdued role compared to our earlier negative ion work [23,24]. Many of the triples and quadruples have negligible (few cm^{-1}) effects, though a few (including $3s^23p^2 \rightarrow 3d^4$ and $3p^3 \rightarrow 3d^2 v f$) are shifted some upper levels on the order of 20 cm^{-1} . When we consider adding second-order effects, we are concerned chiefly with adjustments in the 100- cm^{-1} range, and 20- cm^{-1} improvements are not substantial enough for inclusion considering the burden on our basis set of these more complex configurations. Our code [13] was recently expanded to include 20 000 basis members, but this limit can be easily surpassed since many of these second-order configurations contain 2500 parents or more (in cases where such large configurations are too important to neglect (e.g. Ref. [25]), our REDUCE method can be used to substantially

TABLE II. Energy contributions ($-meV$) to Fe v $3d^3 4pJ=1$ energy levels.

Excitation	$^5F_1^o$	$^5D_1^o[1]$	$^3D_1^o[1]$	$^5P_1^o$	$^5D_1^o[2]$	$^3P_1^o[1]$	$^3P_1^o[2]$	$^3D_1^o[2]$	$^1P_1^o[1]$	$^3S_1^o[1]$
$4p \rightarrow p+f$	15.0	12.3	20.6	7.0	26.1	23.6	25.2	48.0	48.9	25.7
$3d \rightarrow s+d+g$	37.7	23.3	39.2	54.0	67.6	65.5	120.3	137.6	108.0	133.3
$3d^2 \rightarrow s^2+p^2+h^2$	11.8	13.2	11.6	17.2	20.4	21.8	58.1	43.7	49.8	54.6
$sd+pf+dg$										
$3d^2 \rightarrow d^2$	198.0	196.3	198.7	233.4	234.2	236.1	266.9	251.9	257.4	260.0
$3d^2 \rightarrow f^2$	268.7	266.9	270.1	388.8	386.0	389.2	432.8	405.0	413.3	420.7
$3d^2 \rightarrow g^2$	30.8	30.5	31.0	49.6	49.4	50.3	60.5	53.0	56.9	56.6
$3d4p \rightarrow sp+pg+fg$	20.4	18.2	20.2	13.9	14.9	15.5	17.1	22.1	22.7	23.5
$3d4p \rightarrow sf$	23.8	14.7	26.6	28.6	49.0	46.1	24.7	58.5	55.3	31.7
$3d4p \rightarrow pd$	50.8	48.6	52.7	49.1	58.9	55.5	47.9	51.7	44.4	46.5
$3d4p \rightarrow df$	121.3	121.5	120.5	98.2	97.7	100.8	111.1	114.1	124.0	128.1
$3p \rightarrow p$	78.9	82.3	83.4	90.8	85.0	90.3	66.6	65.4	75.0	74.2
$3p \rightarrow f$	2112.0	2102.1	2112.7	2023.5	2057.4	2038.1	1802.5	1900.2	1897.4	1840.8
$3s \rightarrow s+d$	127.9	108.8	134.4	315.7	354.3	356.3	205.7	245.2	308.1	284.4
$3p^2 \rightarrow sd+dg$	146.0	146.0	145.9	148.8	148.7	148.5	146.4	145.9	147.0	145.9
$3p^2 \rightarrow d^2$	1902.8	1898.7	1903.8	2079.1	2084.0	2090.4	2287.0	2217.9	2220.5	2258.6
$3s^2 \rightarrow d^2$	58.5	58.3	58.4	62.2	63.0	64.8	71.8	55.7	71.2	59.9
$3p4p \rightarrow d^2+sd$	404.0	432.3	407.3	436.8	385.8	403.1	418.8	362.5	370.5	398.9
$3p3d \rightarrow pd+df+fg$	944.2	944.2	945.0	943.6	944.6	945.2	951.5	948.4	948.5	949.3
$3s4p \rightarrow pd+df$	16.9	19.4	17.2	20.4	16.8	17.4	19.3	15.9	16.1	17.3
Total	6569.6	6537.5	6599.3	7061.3	7143.7	7158.1	7134.3	7142.9	7234.8	7210.2
Excitation	$^3D_1^o[3]$	$^3D_1^o[4]$	$^3P_1^o[3]$	$^3S_1^o[2]$	$^1P_1^o[2]$	$^3D_1^o[5]$	$^3D_1^o[6]$	$^3P_1^o[4]$	$^1P_1^o[3]$	
$4p \rightarrow p+f$	52.0	50.8	58.6	185.6	98.2	70.8	44.7	39.1	157.1	
$3d \rightarrow s+d+g$	111.4	123.5	103.0	123.5	178.5	193.8	255.0	280.8	263.4	
$3d^2 \rightarrow s^2+p^2+h^2$	42.7	46.4	56.2	57.3	45.3	47.9	86.8	82.8	101.8	
$sd+pf+dg$										
$3d^2 \rightarrow d^2$	252.6	265.9	261.5	232.1	258.1	304.4	391.9	395.1	391.1	
$3d^2 \rightarrow f^2$	407.4	417.1	416.6	388.7	413.5	412.7	649.4	651.8	654.3	
$3d^2 \rightarrow g^2$	54.7	58.7	57.7	50.1	55.2	56.2	107.9	107.9	108.9	
$3d4p \rightarrow sp+pg+fg$	21.9	26.7	25.1	43.7	41.7	25.4	19.5	27.9	38.6	
$3d4p \rightarrow sf$	67.4	57.4	55.5	85.3	58.3	23.7	41.0	36.7	71.1	
$3d4p \rightarrow pd$	47.6	48.5	49.2	44.9	45.6	48.9	50.6	59.4	42.4	
$3d4p \rightarrow df$	118.8	133.6	136.7	185.1	174.8	148.5	119.7	154.2	182.6	
$3p \rightarrow p$	75.8	64.5	64.0	65.2	66.2	65.5	59.9	55.5	47.5	
$3p \rightarrow f$	1941.4	1899.4	1903.9	2081.5	1901.7	2107.4	1693.9	1760.5	1746.3	
$3s \rightarrow s+d$	328.0	322.4	366.0	344.9	288.1	308.5	224.6	299.6	274.3	
$3p^2 \rightarrow sd+dg$	147.2	147.3	147.0	149.1	146.1	150.1	152.9	153.3	153.4	
$3p^2 \rightarrow d^2$	2194.7	2238.7	2247.2	2120.6	2252.2	2155.6	2669.3	2681.3	2692.6	
$3s^2 \rightarrow d^2$	65.7	76.5	69.7	62.1	59.1	70.2	147.9	147.1	148.7	
$3p4p \rightarrow d^2+sd$	358.6	345.7	346.9	231.7	289.4	371.3	390.1	330.6	263.1	
$3p3d \rightarrow pd+df+fg$	947.2	949.2	948.9	944.6	948.5	942.7	959.8	960.0	959.7	
$3s4p \rightarrow pd+df$	16.0	15.6	15.1	10.0	11.1	16.4	17.6	13.3	11.1	
Total	7251.1	7287.8	7328.9	7377.5	7331.6	7519.8	8082.4	8236.6	8308.0	

reduce the basis size). There is one important second-order effect, however, that is essential to the final improvements in the spectra of both parities. The quadruple excitation $3p^4 \rightarrow 3d^4$ ($3p^2 \rightarrow 3d^2$ applied to itself) contributes $\sim 200\text{cm}^{-1}$ to many of the upper $J=1$ roots and over 300cm^{-1} to the lowering of the uppermost $J=0$ level with respect to the rest of the $3d^4$ manifold.

III. RESULTS

Correlation configuration contributions to the Fe v $3d^4 J=0$ and $3d^3 4p J=1$ energy levels are given in Tables I and II. Each table is generated from a single RCI run of 3609 and 15 889 vectors, respectively. The levels are presented increasing from the lowest energy of each parity, and less

important (smaller energy contribution) configurations are grouped together by the type of excitations.

The energy contribution of the i th parent to the j th level is computed using the intermediate normalization $\langle \Phi_j | \Psi \rangle = 1$ from

$$\Delta E(i) = \frac{c_i}{c_j} \langle \Phi_j | H | \chi_i \rangle, \quad (1)$$

where Φ_j is the reference function (the $3d^4$ or $3d^3 4p$ portion of the j th level), c_j is the RCI coefficient of Φ_j , χ_i is a correlation function basis member (parent), and c_i is the RCI coefficient of χ_i . Contributions are then summed over the parents of each nonrelativistic configuration, as presented in Tables I and II.

We find that in valence calculations for both parities, the positioning of the lower roots is in reasonable agreement with experiment [10], while the higher levels are off by as much as 5000 cm^{-1} with respect to the lowest level of each parity. Upon opening the core as discussed in Sec. II, we find that the relative positioning of levels within the references is dominated by two configurations: $3p \rightarrow vf$, which favors the lowest root for each parity, and $3p^2 \rightarrow 3d^2$, which is the main contributor to the relative lowering of the upper states. Other energetically important excitations are $3d^2 \rightarrow vd^2 + vf^2$ and $3s \rightarrow 3d$, and the $3d$ single excitations, which together account for the majority of the remaining contributions to the lowering of the upper states. Also of particular note is the collective impact of the $3d^2 \rightarrow vl^2$ excitations with large effects even for $l=4$ ($>25 \text{ meV}$ for some odd states and $>100 \text{ meV}$ in the uppermost even level). We therefore extend these $3d^2$ pair excitations to $3d^2 \rightarrow vh^2$, which provides a differential contribution of as much as 35 (20) meV for the even (odd) case.

Our choice of $3s$ as the limit for core excitations results from test calculations which partially open the $2p$ subshell. Inclusion of the exclusion effects $2p^2 \rightarrow 3d^2$ and $2p3d \rightarrow vpv d + vdv f$ indicate a potential differential contribution of less than 10 cm^{-1} . On a similar note, we also explored the inclusion of the Breit operator in a smaller test run (a full RCI calculation with magnetic Breit effects present in all matrix elements is possible, but about four times more expensive—current calculation times for final runs are $\sim 3\text{h}$ on a 500-MHz Alpha Station). To provide estimates of Breit effects on the full RCI run, we make use of our ability to artificially shift diagonal matrix elements of our final matrix. Often this option is used to explore changes in mixing between manifolds due to relative positioning. Here we apply individual shifts to each of the 19 diagonal elements of the $3d^3 4p J=1$ manifold, with the size of each shift corresponding to the relative change in the matrix elements with the magnetic Breit correction in the smaller run (the absolute change in the matrix elements, due to the Breit correction, is caused by a large common core contribution, while the relative changes are on the order of 100 cm^{-1}). Results indicate corrections to the lower $J=1$ levels on the order of $\sim 10 \text{ cm}^{-1}$. Many of the upper levels are lowered by $\sim 100 \text{ cm}^{-1}$ with respect to the lowest $J=1$ level, but the variation in the Breit corrections with each successive level

is gradual enough that the relative positioning between adjacent levels is affected to a much lesser degree, with levels whose mixing is most dependent on separation (see the discussion later in this section) adjusted by $\sim 10 \text{ cm}^{-1}$ with respect to each other. We find such small corrections to the mixing of levels (changes in LS composition are 1% or less for all levels) insufficient to warrant inclusion of Breit effects in the final matrix (see below for a discussion of shifts on the order of 200 cm^{-1} among nearby levels).

The most difficulty with level placement occurs for the bottom two $J=1$ levels. This gap is critical to the mixing of the two states (i.e., their LS composition) and their atomic properties (see the discussion below). Note that for most excitations the contributions to these two levels are nearly identical (see Table II). At the valence-excitation-only stage of our calculations, the energy gap between these levels is in good agreement with experiment [10]. Unfortunately, the gap is increased by $\sim 20 \text{ meV}$ (160 cm^{-1}), over a 10% change, with the opening of the core. This is due primarily to the difference in contribution of $3s \rightarrow 3d$, which is essential in placement of the higher levels. Agreement with experiment [10] (see Table III) is largely restored by inclusion of $3p4p$ pair excitations, which we would normally expect to be small. We attribute the importance of these exclusion effects to relative nearness of the $4p$ subshell to the $n=3$ shell in this quadruply ionized system. Here the $\langle r \rangle$ for the $3d$ and $4p$ radial functions are 0.9 and 2.3 a.u., respectively, whereas in a typical neutral or negative ion system, the $4p$ radial would be much more diffuse (4–6 a.u.).

In Table III we present our RCI energy spectrum with comparison to experiment [10] and the R -matrix calculations of Nahar and Pradhan [1]. While we track energy positions with respect to the lowest level of each parity as our calculations progress, our ultimate concern is with the relative positioning of nearby levels as it affects mixing between adjacent levels. Comparison with experiment [10] of each gap between adjacent levels, i.e., 18 gaps in the odd spectrum and four gaps in the even spectrum, shows an average error of 180 cm^{-1} (213 cm^{-1}), or 7.5% (0.7%), for the odd (even) RCI spectrum. We note that the corresponding errors in the R -matrix calculations [1] are 687 cm^{-1} (1459 cm^{-1}) or 26.7% (7.9%), for the odd (even) spectrum. Additionally, in cases where the dominant LS term of an R -matrix level disagrees with experiment, the authors of Ref. [1] reordered these levels for purposes of oscillator strength calculations. These levels are indicated in Table III, though we have presented the spectrum in direct order of increasing energy.

Also given in Table III are the HFS constants A and Landé g values, as well as our LS composition of the levels. The LS percentages are taken from the MCDF portion of the RCI wave functions. The original J^2 and J_z eigenstates of the dominant manifold for each parity are linearly transformed into a new set of L^2 , S^2 , and J_z parents with no loss of completeness. The rotation to the approximate LS basis uses the assumption that the minor components of the one-electron spinors are negligible and the major components are independent of j . The LS percentages are then calculated by summing the weights of the parents of a given LS term, normalized to the weight of the MCDF portion of the wave

TABLE III. Energy levels (cm^{-1}) for Fe v $3d^4J=0$ and $3d^34pJ=1$ levels and HFS (A in MHz) and Landé g values for the odd states. Energies are given with respect to the lowest state of the same parity.

Level	Expt [10]	Nahar and Pradhan [1]	RCI	A	g value
$^1P_1^o[3]$ (100)	84720	88888	85603	105.3	0.999
$^3P_1^o[4]$ (99, 3D 1)	77526	80691	78038	99.8	1.490
$^3D_1^o[6]$ (99, 3P 1)	69792	71968	70397	139.1	0.509
$^3D_1^o[5]$ (100)	50929	54160	51866	127.5	0.500
$^1P_1^o[2]$ (88, 3S 8, 3D 4)	38231	41586 ^a	38848	115.4	1.063
$^3S_1^o[2]$ (90, 1P 6, 3P 4)	36902	40302 ^a	37125	40.2	1.915
$^3P_1^o[3]$ (91, 3S 4, 1P 4, 3D 1)	32841	34914	33275	68.4	1.485
$^3D_1^o[4]$ (94, 1P 5, 3P 1)	30928	33104 ^a	31262	135.2	0.536
$^3D_1^o[3]$ (63, 1P 23, 3S 12, 3P 2)	29113	31535 ^a	29363	173.1	0.820
$^3S_1^o[1]$ (69, 1P 17, 3P 12, 3D 1)	28445	29680 ^a	28922	47.4	1.742
$^1P_1^o[1]$ (48, 3D 37, 3S 11, 3P 4)	28219	29110 ^a	28689	102.8	0.949
$^3D_1^o[2]$ (94, 1P 3, 3P 2)	26012	27036 ^a	26344	211.7	0.547
$^3P_1^o[2]$ (83, 1P 7, 3S 5, 3D 5)	24203	23799	24566	84.8	1.453
$^3P_1^o[1]$ (61, 5D 38, 5P 1)	19024	20409	18837	30.7	1.513
$^5D_1^o[2]$ (61, 3P 38, 3D 1)	17404	19180	17160	169.4	1.494
$^5P_1^o$ (97, 3P 2, 3S 1)	15901	17095	15721	-5.6	2.474
$^3D_1^o[1]$ (52, 5F 44, 5D 4)	2253	2041	2270	174.2	0.317
$^5D_1^o[1]$ (81, 5F 17, 3D 2)	1149	1042	1187	84.6	1.227
$^5F_1^o$ (39, 3D 46, 5D 15)	0	0	0	99.8	0.457
$^1S_0^e[2]$ (100)	121130	124197	121153		
$^3P_0^e[2]$ (100)	63420	65889	63821		
$^1S_0^e[1]$ (99, 3P 1)	39633	43023	39696		
$^3P_0^e[1]$ (99, 1S 1)	24055	23591	24180		
$^5D_0^e$ (100)	0	0	0		

^aIndicates levels which the authors of Ref. [1] reordered to match experimental LS designations [10].

function. All levels are over 97% pure $3d^4$ or $3d^34p$, which allows us to use these approximate compositions as a reasonable labeling system for the RCI levels. The number in brackets in our labeling of levels indicates the ordering of the level with respect to any other levels with the same dominant LS term. Landé g values, however, are calculated from the full RCI wave functions. This computation excludes the anomalous g value, which introduces an error probably ten times smaller than that associated with the RCI wave functions.

We find that the $J=1$ A and g values are most sensitive in those levels with low LS purity. Adjustments in energy gaps between nearby levels and corresponding changes in LS composition are thus the focus of the latter stages of the calculation. To this end we include some large (in the sense of number of basis members) configurations with relatively small differential energy contributions, as compared to those mentioned above. These include $3p^2 \rightarrow 3dvd + 3dvg$ and $3p3d \rightarrow vpv d + vdvf + vfv g$. As mentioned previously, we recently expanded our code to allow 20 000 basis members (from the previous limit of 7000 parents), and these calculations are some of the first to utilize this new capability. The final $J=1$ run contains 15 889 parents, ~ 6000 of which are added in these final stages where energies are shifted among the upper states on the order of a few 100 meV. Differences between MCDF and RCI values of the A 's are quite small,

with the largest being the low LS purity levels, which differ by ~ 20 MHz. For the g values, the largest impact is on the lowest level. Prior to inclusion of the $3p4p$ pair excitations discussed above, the placement of the second and third $J=1$ levels was off by $> 150\text{cm}^{-1}$. Changes in LS percentages of a few percent as these gaps are brought to their final positions result in a 20% increase in the g value of this level. This change is due to the larger mixing of 3D from the third level and 5D from the second level at the expense of 5F . For $J=1$, pure 3D and 5D states have g values of 0.5 and 1.5, respectively, while 5F contributes zero to a $J=1$ g value, which is why this mixing is crucial. We note that the leading LS term for the lowest level is actually 3D , though we have retained the 5F label to avoid confusion with earlier work [1,4,10]. The choice also reflects the fact that the $3d^34p$ manifold has six 3D parents and a single 5F parent, though consideration of leading terms of our LS analysis suggests seven 3D roots and no root with 5F as the leading term.

In Table IV we present the largest 21 of the 95 $E1$ f values (those > 0.01). Also presented here are the prior Breit-Pauli R -matrix values [1] and semiempirical values [4]. The "lowest" f value is strikingly different for all three methods. An independent, preferably experimental, determination seems warranted. For the largest f values we agree reasonably well with both of the other methods, but where

TABLE IV. Largest (>0.01) $E1$ f values for Fe v $3d^4J=0 \rightarrow 3d^34pJ=1$.

Transition	RCI (v)	RCI (l)	Fawcett [4]	Nahar and Pradhan [1]	
$^5D_0^e$	$\rightarrow ^5F_1^o$	0.116	0.110	0.163	0.2154
	$\rightarrow ^5D_1^o[1]$	0.064	0.060	0.041	5.5150×10^{-3}
	$\rightarrow ^3D_1^o[1]$	0.065	0.061	0.059	0.05744
$^3P_0^e[1]$	$\rightarrow ^5P_1^o$	0.073	0.072	0.076	0.08420
	$\rightarrow ^5F_1^o$	0.041	0.036	0.039	0.02317 ^a
	$\rightarrow ^3D_1^o[1]$	0.051	0.046	0.061	0.06702 ^a
	$\rightarrow ^3P_1^o[2]$	0.148	0.141	0.153	0.09377 ^a
	$\rightarrow ^3S_1^o[1]$	0.012	0.011	0.028	2.193×10^{-3} ^{a, b}
	$\rightarrow ^3D_1^o[4]$	0.020	0.020	0.024	7.067×10^{-3} ^{a, b}
$^1S_0^e[1]$	$\rightarrow ^3P_1^o[2]$	0.011	0.010	<0.010 ^c	7.035×10^{-3} ^a
	$\rightarrow ^1P_1^o[1]$ ^d	0.118	0.108	0.216	8.021×10^{-3} ^{a, b}
	$\rightarrow ^3S_1^o[1]$ ^d	0.045	0.042	<0.010 ^c	1.968×10^{-4} ^{a, b}
	$\rightarrow ^3D_1^o[3]$ ^d	0.059	0.054	0.029	2.048×10^{-3} ^{a, b}
	$\rightarrow ^3P_1^o[3]$	0.013	0.012	0.011	0.01148 ^a
$^3P_0^e[2]$	$\rightarrow ^1P_1^o[2]$	0.060	0.059	0.073	0.07864 ^{a, b}
	$\rightarrow ^3P_1^o[1]$	0.011	0.010	0.013	0.01009 ^a
	$\rightarrow ^3P_1^o[3]$	0.017	0.016	0.021	0.05201 ^a
	$\rightarrow ^3S_1^o[2]$	0.082	0.074	0.088	0.04824 ^{a, b}
	$\rightarrow ^3D_1^o[5]$	0.145	0.136	0.168	0.1648 ^a
	$\rightarrow ^3P_1^o[4]$	0.042	0.045	0.046	0.04867 ^a
	$\rightarrow ^1S_0^e[2]$	$\rightarrow ^1P_1^o[3]$	0.295	0.289	0.379

^aThese entries taken from the extended online table referenced in Ref. [1].

^bThese f values are for transitions to $J=1$ levels that the authors of Ref. [1] reordered to match experimental LS designations.

^cJust as we do here, the author of Ref. [4] presented only oscillator strengths ≥ 0.01 .

^dSemiempirically improved f values for these transitions may be found in Table V.

the two earlier works disagree our values are in better agreement with the semiempirical work. Our f values are fairly stable as our calculations progress. The largest changes (on the order of 10%) are made with the addition of the second set of virtuals to many of the larger configurations. Beyond this point the f values change by only a few percent (with the exceptions noted below), with the average agreement between gauges ranging from 6% to 8% in the latter stages of the calculation. For those transitions shown in Table IV, the average gauge agreement is 6.7% for our final run. In general, gauge agreement can be a good indicator of improved accuracy of f values. Often, however, for cases with large mixing between levels we find a transfer of oscillator strengths between corresponding levels with little consequence to gauge agreement. We are therefore most concerned with those levels which exhibit large LS mixing with nearby levels, particularly those which appear highly sensitive to relative positioning.

In general, we note two sets of $J=1$ levels whose LS composition are highly sensitive to relative positioning. The first and third levels (5F and $^3D[1]$) are fairly well positioned throughout the calculation, but are affected largely through mutual interaction with the intermediate $^5D[1]$ level. The other important set is the ninth, tenth, and 11th roots ($^1P[1]$, $^3S[1]$, and $^3D[3]$). Here the positioning of the $^1P[1]$ level with respect to the intermediate $^3S[1]$ level is in good agreement with experiment, and the largest changes in composition of the trio is due to improvements of

relative positions of these two levels with respect to the $^3D[3]$ level. Our RCI $^1P[1]$ - $^3D[3]$ gap is 674 cm^{-1} , compared with the experimental [10] value of 894 cm^{-1} . Small improvements in this gap in the end stages of the calculation were found to dramatically alter the mixing of these levels to the extent of flipping the leading LS term from 3D to 1P for the $^1P[1]$ root.

Though further improvements of relative positioning of these upper levels may be possible, they would likely come at the expense of the positioning of other levels within the manifold, and be insufficient to account for the $>200\text{-cm}^{-1}$ shift needed to widen the $^1P[1]$ - $^3D[3]$ gap to match the experimental [10] value. We therefore turn to the matrix element shifting discussed earlier. We wish to chose a set of shifts in diagonal matrix elements which forces relative positioning of the $^1P[1]$ / $^3S[1]$ / $^3D[3]$ trio to match experiment, while at the same time creating a minimum disturbance to the rest of the manifold. The rotated approximate LS parents we used for identifying the $3d^34p$ levels are useful here. Shifting of individual diagonal elements corresponding to these LS parents roughly simulates the missing differential correlation to these terms that would be required to bring the relative positioning of these levels into agreement with experiment. We note that of the three 1P parents, the $^1P[1]$ level is mostly comprised of two of them, with the third 1P parent contributing less than 2%. Similarly, the $^3S[1]$ level is dominated by one of the two 3S parents, with

TABLE V. Effects of positioning on properties of $3d^3 4pJ=1$ $^1P[1]$, $^3S[1]$, and $^3D[3]$ levels.

	Expt. [10]	Incomplete RCI	RCI	Shifted RCI	Fawcett [4]
$\Delta E^3D[3]-^3S[1](\text{cm}^{-1})$	668	404	441	668	509
$\Delta E^3S[1]-^1P[1](\text{cm}^{-1})$	226	255	233	226	367
$\Delta E^3D[3]-^1P[1](\text{cm}^{-1})$	894	659	674	894	876
$LS\% \ ^1P[1](^1P/^3S/^3D)$	61/-/-	37/15/44	48/11/37	67/10/18	79/-/9
$LS\% \ ^3S[1](^1P/^3S/^3D)$	-/83/-	21/64/1	17/69/1	10/76/2	-/87/5
$LS\% \ ^3D[3](^1P/^3S/^3D)$	-/-/73	30/13/56	23/12/63	10/6/83	-/7/77
$^1S_0^e[1] \rightarrow ^1P[1]f$ value (v/l)		0.091/0.083	0.118/0.108	0.167/0.153	0.216
$^1S_0^e[1] \rightarrow ^3S[1]f$ value (v/l)		0.056/0.052	0.045/0.042	0.025/0.023	<0.010
$^1S_0^e[1] \rightarrow ^3D[3]f$ value (v/l)		0.076/0.070	0.059/0.054	0.026/0.024	0.029

the other making a negligible contribution in this root. Our choice for the simplest shift is then to shift the two important 1P diagonal elements by one amount and the single 3S element by another amount. Shifts in diagonal elements do not translate linearly to changes in the energy spectrum, and the shifts must be arrived at through several iterative trials (the RCI matrix is re-diagonalized for each set of shifts, and the energies are compared to the experimental splittings). We find that shifting the 1P diagonal element by 535 cm^{-1} and the 3S elements by 393 cm^{-1} matches the relative positioning of these three levels to experiment [10]. Note that this shift is not unique as the same level spacing could be achieved by other means (e.g., by shifting 3D elements up), and in a sense we are forcing a certain LS composition on these levels. The goal here, however, is to obtain an idea of the size of the change in properties that might be expected were we able to make corresponding improvements to the calculation in an *ab initio* manner.

In Table V we present results for the effects of this shift on LS composition and important corresponding f values. We present values corresponding to the three levels of concern only, though it should be noted that our approach of shifting the three most important elements has the intended effect of minimally altering the rest of the spectrum (other nearby levels not shown in Table V show changes in LS composition of 1% or less compared to the $\sim 20\%$ changes in the three levels of interest). The shifted f values of Table V should be more accurate than the unshifted (but fully *ab initio*) RCI value. For comparison we include the relevant information from the final *ab initio* run as well as an earlier incomplete run. This earlier run excludes some of the final adjustments to our basis such as the large $3p^2$ and $3p3d$ pair excitations discussed earlier, as well as the second order $3p^4 \rightarrow 3d^4$ excitation. Also included in Table V are the corresponding experimental [10] and semiempirical [4] results. Note that the LS composition for these columns should be taken as lower bounds as leading terms only have been presented in these references [4,10]. The f values presented are those that change the most as our calculations progress. We note that with increasing improvements in the positioning of these levels our f values agree more with those of Fawcett [4].

One can make some general observations from these results. First, of the three LS terms, 1P , 3S , and 3D , an even-parity 1S level only has a nonzero oscillator strength with

the 1P level. The preshifted $^1S[1] \rightarrow ^3D[3]f$ value is too large, because it has too much 1P in it (Table V). In fact, the corrections for both $^1S \rightarrow ^3S[1]$, $^3D[3]f$ values are directly proportional to the changed 1P ratio in the two states. Moreover, the sum of the three oscillator strengths is the same, pre-shifted and post-shifted, as expected [12], since we have a group of nearly degenerate and isolated levels.

Since there is only one nonzero contribution, $^1S \rightarrow ^1P$, the three oscillator strengths are directly proportional to the (square) of the 1P coefficient which, to first order, is inversely proportional to the difference of the diagonal matrix elements, or nearly equivalently, to the experimental energy difference (e.g., $^1P[1]-^3D[3]$). The presence of a third state, $^3S[1]$, is a minor, not a conceptual, complication. The clear message is that the position of nearly degenerate levels needs to be accurately determined, particularly if the basis functions associated with the levels have very different oscillator strengths. Furthermore, the shift method is a good way to test an f value's sensitivity to the energy-level positioning, and can even lead to an improved estimate of the exact result.

It should be noted that the three levels presented in Table V are the levels most affected by relative positioning. The other group of the three lowest odd levels mentioned above, though similarly sensitive to LS mixing, were not shifted. These levels are already well positioned with respect to one another ($\sim 20\text{-}40\text{cm}^{-1}$), and shifts this small have too small an effect on LS mixing to significantly alter the corresponding f values. The remaining f values presented in Table IV are more isolated from adjacent levels than those mentioned above and thus much less affected by relative positioning (and LS mixing). For example, final adjustments on the order of 200 cm^{-1} in positioning of the upper $J=1$ states resulted in changes in the corresponding f values of 0.001 or less ($\sim 1\%$ vs the $\sim 50\%$ changes to the f values shown in Table V). The dramatic changes depicted in Table V illustrate why we find an accurate positioning of the energy spectrum, as well as tracking of cases of sensitive LS mixing between levels, to be crucial to a calculation of oscillator strengths.

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