

# Relativistic configuration interaction calculations of lifetimes of $\text{Si}^- 3p^3$ bound excited states

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**Abstract.** Relativistic configuration interaction lifetimes of  $\text{Si}^- 3p^3$   $^2D_{3/2}$ ,  $^2P_{1/2}$  and  $^2D_{5/2}$  states are calculated (using M1 and E2 length gauge transition probabilities) to be 162 s, 23.6 s and 27.3 h, respectively. Detailed analysis of individual configurational contributions to transition probabilities are used to improve the bases of the  $^4S_{3/2}$  and  $^2D_{3/2}$  calculations resulting in excellent E2 gauge agreement and a final M1 transition probability that is nearly three orders of magnitude larger than its initial Dirac-Fock value. Relatively poor E2 gauge agreement for transitions between the two  $J = 3/2$  states and  $^2P_{1/2}$  are found to have negligible impact on the  $^2P_{1/2}$  lifetime, as length gauge transition probabilities remain stable in the final stages of the calculation (changing only by a few percent while the velocity value shifts by 30% or more).

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## 1. Introduction

$\text{Si}^-$  is a difficult system, computationally, primarily due to the fact that L and S are “nearly good” quantum numbers for such a light, nonrelativistic system. Forbidden transitions between the  $^4\text{S}_{3/2}$  ground state (binding energy of  $11\,207\text{ cm}^{-1}$  [1, 2]) and the three bound excited doublet states –  $^2\text{D}_{3/2}$ ,  $^2\text{D}_{5/2}$  and  $^2\text{P}_{1/2}$  at  $6955$  [1, 2],  $6969$  [2] and  $10\,977$  [1, 3]  $\text{cm}^{-1}$  above the ground state, respectively – are complicated by the fact that contributions to transition probabilities from correlation configurations can be as important as interactions between terms within the  $3\text{p}^3$  Dirac-Fock (DF) manifold. For example, in our final  $J = 3/2$  calculation in  $\text{Si}^-$ , correlation configurations have a total weight of  $\sim 4.8\%$  in the  $^2\text{D}_{3/2}$  level while mixing within the  $3\text{p}^3$  configuration shows this state to be just  $0.00036\%$   $^4\text{S}$  and  $0.082\%$   $^2\text{P}$ . By comparison the homologous  $^2\text{D}_{3/2}$  level in our earlier work [4] on  $\text{Sn}^-$  binding energies was  $0.51\%$   $^4\text{S}$  and  $7.8\%$   $^2\text{P}$  within the  $5\text{p}^3$  DF manifold.

Since DF contributions to the transition probabilities are limited by the small coefficients of the allowed terms (e.g. the  $^4\text{S}_{3/2}$  state interacting with the tiny fraction of  $^4\text{S}$  in the  $^2\text{D}_{3/2}$  state), we expect correlation configurations to have contributions to the calculated transition probabilities on the same order as (or larger than) the DF portion of the wavefunction. This necessitates added attention to saturation of our one-electron basis sets within the important correlation configurations as well as inclusion of second order effects to properly position these configurations relative to the DF levels. Both of these factors are generally focused on several of the most energetically important configurations, but in this case we must apply them to large contributors to the transition probabilities as well.

## 2. Methodology

Our relativistic configuration interaction (RCI) calculations begin with a solution of the multiconfigurational Dirac-Fock (MCDF) equations using Desclaux's MCDF code [5]. To these DF radial solutions ( $1s_{1/2}$ ,  $2s_{1/2}$ , ...,  $3p_{3/2}$ ) we add a series of "virtual" radials, designated  $vl$ ,  $vl'$ ,  $vl''$ , etc. These virtual radials are introduced as relativistic screened hydrogenic functions (RSH) chosen with  $n = l + 1$  (zero nodes) to ensure greatest overlap with the DF orbital whose  $\langle r \rangle$  we are attempting to match. The effective charge,  $Z^*$ , is iterated in an energy minimization procedure, and each virtual is necessarily orthogonalized to any DF radial function (or virtual radial from a previous set) of the same symmetry. The virtual radials are present in correlation configurations that represent excitations into subshells not occupied in the  $3p^3$  DF configuration. With careful attention to saturation of important correlation configurations we find that a few RSH virtuals are generally sufficient to represent the corresponding unoccupied Rydberg series and continuum orbitals, e.g.  $vp + vp' + vp'' \approx 4p + 5p + 6p + 7p + 8p + \dots + \epsilon p$ .

In the case of  $\text{Si}^-$  our first ( $vs$  to  $vh$ ) and second ( $vs'$  to  $vg'$ ) sets of virtuals are added and iterated in the presence of single and double excitations from the  $3p^3$  configuration (with one exception discussed below). Typically, we would add the second set of virtuals as we open the first core subshell,  $3s$ , but we find that saturation of the valence excitation requires two sets of diffuse virtuals ( $\langle r \rangle \approx \langle r \rangle_{3p}$ ), particularly in the case of  $3p^2 \rightarrow vp^2$  and  $3p^2 \rightarrow vd^2$ . The third set of virtuals ( $vs''$  to  $vf''$ ) is iterated in the presence of single and double excitations out of  $3s^2$  as well as  $3s3p$  double excitations. Finally, our fourth set of virtuals is added primarily to saturate the  $2p3p$  pair excitations and contains only  $vp'''$ ,  $vd'''$ , and  $vf'''$  subshells.

The layering of the virtual sets discussed above follows our typical algorithm for producing our RCI bases. One important change to this process is the selection of the effective charge  $Z^*$  of our initial  $vp$ . We find that the valence single excitations  $3p \rightarrow vp$  and  $3p \rightarrow vf$  are important contributors in all the  $\text{Si}^-$  transition probability calculations (see section 3 for detailed discussion). In particular, the  $3p \rightarrow vp$  excitation is found to be critical in the early stages of the calculation as details of our bases are being worked out, e.g.  $3p \rightarrow vp$  contributions vary dramatically in calculations with only a single set of valence virtual orbitals vs a valence calculation with a second set as described above. The fact that the  $3p \rightarrow vp'$  excitation contributes nearly as much to the RCI energies as  $3p \rightarrow vp$  in the latter suggests that our initial  $vp$  is a poor choice for this particular configuration. Also, in a few test calculations, we find that the  $vp''$   $Z^*$  falls below that of  $vp$  ( $Z^* \sim 1.15$ ) and  $vp'$  ( $Z^* \sim 1.35$ ) to  $Z^* \sim 0.85$ . Both of these factors suggest a lack of saturation of the set of virtual p's in the diffuse portion of the radial space.

The cause of this missing large  $r$  portion of the  $vp$  radials is the much larger energy contribution arising from the  $3p^2 \rightarrow vp^2$  excitation. In this case small test calculations show, in fact, that the single excitation is optimized by a  $Z^*$  much smaller than the one that optimizes the double excitation. Since the latter contributes much more to

the RCI energy (e.g. 323 meV vs 19 meV in the  ${}^2P_{1/2}$  case), the energy minimization procedure selects the optimal  $Z^*$  for the double excitation. Subsequent sets of virtuals are optimized to core excitations and do not “pick up” this large  $r$  portion of the radial space. For this reason we set our initial  $vp$   $Z^*$  to the smaller value given in our single excitation test calculations:  $\sim 0.50$  for  ${}^2P_{1/2}$ ,  $\sim 0.65$  for both  ${}^2D$ ’s and  $\sim 0.80$  for the  ${}^4S_{3/2}$  calculation. Subsequent energy losses in the  $3p^2 \rightarrow vp^2 + vpvf$  excitations are regained by inclusion of the second set of valence virtual functions, with each of the  $vp'$  optimized  $Z^*$ ’s approximately equal to the value from the  $3p^2 \rightarrow vp^2$  test calculations.

Since our RCI wavefunctions are eigenstates of  $J^2$ ,  $J_z$  and parity, the  ${}^4S_{3/2}$  and  ${}^2D_{3/2}$  wavefunctions would normally be taken from a single  $J = 3/2$  calculation. However, with the difficulties with the  $3p$  single excitations we choose to perform a separate calculation optimized to each of the  $J = 3/2$  states. In addition to using differently optimized virtual functions as described above, we create a second set of DF radial wavefunctions optimized to the  ${}^2D$  level (by performing the energy optimization in the MCDF calculation [5] with respect to the second  $3p^3$  level). This result is a better zeroth order approximation for the  ${}^2D_{3/2}$  state, which decreases the impact of the valence single excitations on transition probabilities involving the  ${}^2D_{3/2}$  level, effectively absorbing part of the  $3p \rightarrow vp$  excitation into the  $3p^3$  DF configuration (i.e. the  ${}^2D_{3/2}$  energy contribution of  $3p \rightarrow vp$  in the  ${}^2D_{3/2}$  optimized calculation is less than half its value from a calculation which uses the  ${}^4S_{3/2}$  optimized DF radial functions).

Our bases involve single and double excitations out of  $2p^63s^23p^3$ , with  $3s$  single excitations and  $3s3p$  and  $3p^2$  double excitations providing the bulk of the correlation energy. Many of the  $2p$  subshell’s single excitations and core-valence pair excitations are small (tens of meV) and differentially small (less than 1 meV difference in energy contribution to each of the four levels) and would thus normally be excluded from a calculation based primarily on energy positioning and mixing between levels. However, the  $2p$  single excitations do contribute up to a few percent of some transition probabilities, and more importantly it is found that  $2p3s$  pair excitations contribute a few percent to some M1 transition probabilities and can affect some E2 values by as much as 10% through interaction with other configurations, even though they do not appear directly as even moderate contributors to any E2 transition probability. The impact on the other configurations they affect (as seen by changes in their own contributions in the E2 analysis) are unexpected: they are effectively  $2p3s \rightarrow 3pvl$  applied to the  $3p$  single excitations and  $2p \rightarrow 3p$  applied to the  $3s3p$  pair excitations, and since both  $2p3s \rightarrow 3pvl$  and  $2p \rightarrow 3p$  are fairly small contributors to the  $3p^3$  energies it is unusual that they have a sizable affect on some correlation configurations (compared to, for example, some of the second order triple and quadruple excitations discussed below).

Our final additions to our RCI bases involve second order effects created from products of important single and double excitations which result in triple and quadruple excitations relative to  $3p^3$ . Inclusion of these second order effects is intended to correct overcorrelation of  $3p^3$  with respect to nearby correlation configurations.

We can express the wavefunction,  $\Psi_i$ , of one of our final RCI levels as a linear

combination of the DF function,  $\phi_i$ , and the correlation configuration basis functions,  $\psi_j$ :

$$\Psi_i = a_i\phi_i + \sum_j b_{ij}\psi_j \quad (1)$$

Using the intermediate normalization  $\langle\phi_i|\Psi_i\rangle = 1$ , we can then express the energy contribution of basis member  $\psi_j$  to the  $\Psi_i$  state as:

$$E_{ij} = \frac{b_{ij}}{a_i}\langle\phi_i|H|\psi_j\rangle \quad (2)$$

Since the  $b_{ij}$  for single and double excitations are approximately inversely proportional to the diagonal energy matrix element difference,  $H_{jj} - H_{ii}$ , we see that an increase in the energy difference between our DF manifold and a correlation configuration decreases the energy contribution of that configuration. In cases where energy positioning is crucial, e.g. electron affinity studies or cases of mixing between multiple DF manifolds, such energy losses are tracked for their own sake in positioning of the levels of interest. In this case, however, this relationship is made most useful by using losses in energy as an indicator of changes in correlation configuration coefficients (which are in turn important in the transition probability calculations), and selecting which configurations are included when considering second order correlation.

For example, in opening the 3s subshell we include the  $3s \rightarrow vd$  excitation (which contributes as much as 0.8 eV) for  $3p^3$ , lowering it with respect to  $3p^2 \rightarrow vl^2$  which does not have the effective  $3s \rightarrow vd$  excitation applied to it. Continuing this example, the  $3p \rightarrow vl$  single excitations do have  $3s \rightarrow vd$  present in the form of the  $3s3p$  pair excitations. While the single valence excitations are thus more correlated than the double excitations, the DF manifold is still more correlated since the single excitations have neither  $3s^2$  nor  $3s3p$  pair excitations applied to them. The process is further complicated by the fact that the more nearby correlation configurations are more selectively affected by this overcorrelation of the DF manifold, since the change in position is a greater fraction of the difference between the diagonal energy matrix elements. In the case of  $Si^-$  many of the valence configurations exhibit losses of 10-25%, necessitating inclusion of some of the same excitations that are applied to  $3p^3$ .

Typically when adding second order effects formed by multiplying large first order energy contributors with each other, we determine their impact through a test RCI calculation by tracking changes in the energy contributions of single or double excitations that are part of the triple or quadruple excitation. For  $Si^-$  we also need to make a corresponding transition probability calculation since we find several second order configurations (particularly those involving  $3p$  single excitations) that have very little impact on energies (few tens of  $cm^{-1}$ ) that can change an E2 velocity value by a few percent. The sensitivity is due, as mentioned in section 1, to the fact that we have forbidden transitions in a light system with very little LS mixing between levels,

such that many of the correlation configurations can be as important to transition probabilities as the interaction between basis members of the  $3p^3$  configuration. For example, the transition probability matrix element between the  $^4\text{S}$  basis member in the initial and final state of  $^4\text{S}_{3/2} \rightarrow ^2\text{D}_{3/2}$  is multiplied by both the large coefficient in  $^4\text{S}_{3/2}$  ( $\sim 0.98$ ) and the tiny  $^4\text{S}$  coefficient in the  $^2\text{D}_{3/2}$  level ( $\sim 0.002$ ). A correlation configuration with coefficients in both states of  $\sim 0.05$  can then have a product of coefficients similar to that of the DF  $3p^3$  configuration interacting with itself. This product would be at least an order of magnitude smaller than the DF product in a heavier system where DF LS terms mix with coefficients themselves of  $\sim 0.05$  or greater.

Ultimately, we include in our final calculations the following second order configurations based on formally multiplying  $3p$  single excitations (for importance in transitions probabilities), the  $3s \rightarrow vd$  single excitation (the largest energy contributor), and the energetically important  $3p^2$ ,  $3s^2$  and  $3s3p$  double excitations:

$$\begin{aligned} 3p^3 &\rightarrow vp^3 + vpv d^2 + vpv f^2 + vp^2vf + vd^2vf + vf^3 \\ 3s3p^2 &\rightarrow vsup^2 + vp^2vd + vdvf^2 + vf^2vg + vsupvf + vpvdf + vpvfvg \\ 3s^23p &\rightarrow vsupvd + vpv d^2 + vd^2vf + vdvfvg \\ 3s3p^3 &\rightarrow vsup^3 + vsupvd^2 + vsupvf^2 + vp^3vd + vpv d^3 + vpvdf^2 \end{aligned}$$

with many of the above including virtuals from both the first and second sets (e.g.  $3p^3 \rightarrow vp^3 + vp^2vp' + vpv p'^2 + vp'^3$ ).

With our bases carefully constructed as described above, there are two additional tools that are useful in our analysis of transition probability calculations: the creation of approximate LS functions for critical excitations and a newly improved analysis subroutine for our transition probability code. Our basis members are relativistic eigenstates of  $J^2$ ,  $J_z$  and parity, but it possible to create approximate LS basis members through linear rotation of the  $jj$  basis members. This is done by simply diagonalizing the  $L^2 + S^2$  matrix subject to the approximation that the minor component of the one electron wavefunctions is negligible and the radial part of the major component is independent of  $j$ . Typically we apply this LS rotation to the DF basis members only, as our LS construction is less well developed than that of  $jj$  functions. We use this analysis primarily for level identification and comparison to experimental LS designations. For  $\text{Si}^-$  we also apply these rotations to the  $3p$  single excitations for the detailed analysis as discussed in section 3.

The general form of a transition probability is given by the following expression:

$$A_{ki} = \frac{2\alpha\Delta E}{2J_k + 1} \left| \sum_l \sum_m a_{il} a_{km} \langle \psi_{il} | \Phi + c\vec{\alpha} \cdot \vec{A} | \psi_{km} \rangle \right|^2 \quad (3)$$

where  $\Phi$  (scalar potential) and  $\vec{A}$  (vector potential) are determined by the gauge (velocity or length) and pole (E2 or M1 in the case of  $\text{Si}^-$ ) [6]. For purposes of analysis of contributions to transition probabilities, we collect terms in the double sum above at an intermediate stage of our calculations. We have recently modified this analysis package to allow for partial sums over individual configurations or groups of configurations. For our discussion here we collect contributions by the type of excitation from  $2p^6 3s^2 3p^3$  in

both the bra and the ket. As an example of our notation,  $\langle 3p | \dots | 3p^2 \rangle$  would represent the portion of the above double sum where the  $\psi_{il}$  in the bra is a basis member from a 3p single excitation and  $\psi_{km}$  in the ket is from a 3p<sup>2</sup> double excitation.

### 3. Results

Our RCI basis set construction focuses on configurations important to the  ${}^2D_{3/2}$  lifetime, primarily because the  ${}^4S_{3/2} \rightarrow {}^2D_{3/2}$  M1 transition is the most affected by correlation configurations. At the DF level (and early valence stage of the RCI calculations) this M1 transition probability is approximately an order of magnitude smaller than the corresponding E2 transition probability, but in our final calculations the M1 value dominates the  ${}^2D_{3/2}$  lifetime at over two orders of magnitude larger than the E2 transition probability. Tables 1 and 2 provide a summary of contributions to the the  ${}^4S_{3/2} \rightarrow {}^2D_{3/2}$  E2 and M1 transition probabilities, respectively. These contributions are presented as a fraction of the total (complete double sum in equation 3) from the final calculation, so that relative sizes of contributions can be compared as the calculations progress. Contributions are grouped by type of excitation as explained in the tables.

Several points can be taken from each table. For the E2 contributions in table 1 we note that the length gauge transition probability at each stage of our calculation is only about 10% higher in the DF portion of the sum than the total correlated value (recall, however, that the quantity tabulated here is proportional to the square root of the transition probability). The corresponding DF velocity gauge transition probabilities are  $\sim 1.5$  to  $\sim 2.5$  times larger than the fully correlated value, illustrating the greater importance of correlation in the velocity gauge calculations.

The columns of table 1 denote increasingly complex calculations at important stages of the basis set construction. The “Valence” column is from a calculation with all single and double excitations out of  $3p^3$  into two sets of virtual orbitals. The “3s open” column is taken from a calculation in which the third set of virtuals is added as discussed in section 2. Note the loss of contribution of the  $3p$  single excitations between the “Valence” and “3s open” due to the addition of  $\sim 1.9$  eV of correlation to  $3p^3$ , approximately half of which is from  $3s \rightarrow vd$  (also present in  $3p \rightarrow vp + vf$  in the double excitations  $3s3p \rightarrow vpv d + vdvf$ ), resulting in an increase in separation of  $3p^3$  and  $3p \rightarrow vp + vf$  of  $\sim 0.9$  eV. The “2p open” column represents inclusion of  $2p$  single excitations,  $2p^2$  core-core excitations and  $2p3p$  core-valence excitations. The next two columns are included to illustrate the individual contributions of the  $2p3s$  pair excitations and the second order triple and quadruple excitations. Though the  $2p3s$  excitations increase the difference between length and velocity transition probabilities, they are essential since a calculation with only second order effects added at this stage (“2p + TQ”) results in the velocity value falling below the length value. It is the combination of both these later additions that results in the excellent gauge agreement as seen in the “Final” calculation, largely through the correction of the  $3p$  single excitations’ positions and the resulting increase in their transition probability contribution to approximately the same amounts as in the “Valence” calculation.

Also presented in table 1 are the ratios of the velocity and length gauge transitions probabilities ( $A_{ki}^v/A_{ki}^l$ ), identical to the square of the ratio of the double sums from equation 3. This ratio is presented to illustrate the difficulty of obtaining accurate

velocity gauge values for transition probabilities of this size (i.e. forbidden transitions). The valence stage ratio of 2.13 represents an error in gauge agreement of 72.2%, while the final RCI transition probabilities agree to 0.2%. Since our general goal is to obtain gauge agreements to a few percent, or perhaps just less than 10% error for forbidden transitions, agreement of 0.2% appears ideal at first glance. We note, however, that with the extreme sensitivity of the velocity gauge (cf. difference between the “2p open” and “2p + TQ” calculations of table 1, for example), exploration of a few more small core-valence second order effects (or even accidental omission of a few of the triple excitations already included) could easily disturb this delicate balance. Still, we consider the value obtained for the E2 transition probability ( $4.37 \times 10^{-5} \text{ s}^{-1}$ ) to be an accurate one due to the stability of the length gauge value throughout the latter stages of our calculations.

In table 2, the breakdown of the  $^4\text{S}_{3/2} \rightarrow ^2\text{D}_{3/2}$  M1 transition probability clearly shows the progressive dominance of the M1 value to the  $^2\text{D}_{3/2}$  lifetime. The “3s open” column marks the stage of the calculation at which the E2 and M1 transition probabilities are of approximately the same order ( $\text{M1} \approx 2 \times \text{E2}$ ). The impact of opening the 2p subshell is seen to be the most important contribution to the M1 transition probability, principally through correlation of the 3s3p pair excitations from 2p3p and 2p3s pairs, effectively  $2pvl \rightarrow 3svl'$  and  $2pvl \rightarrow 3pvl'$ , which serve to compensate for the absence of 2p3p pair excitations in the 3s3p configurations, which would require the complex quadruple  $2p3s3p^2$  excitations (with respect to  $2p^63s^23p^3$ ).

Recalling the careful treatment of our first  $vp$   $Z^*$ , we note that the impact of that choice is not seen fully until the later stages of our calculations, at which point the 3s3p pairs dominate, partly due to better optimization of  $3s3p \rightarrow vsvp$  and  $vpvd$ , e.g. the  $Z^*$ 's that optimize  $3s3p \rightarrow vpvd$  are very close to those that individually optimize  $3s \rightarrow vd$  and  $3p \rightarrow vp$ . As a test of the actual impact of our approach to basis set construction, we rebuild our final  $^4\text{S}_{3/2} \rightarrow ^2\text{D}_{3/2}$  calculations without the improvements mentioned in section 2. With a single  $J = 3/2$  calculation optimized to  $^4\text{S}$ , no 2p3s pair excitations or second order effects, and  $vp$  optimized to the valence double rather than single excitation, our final  $^2\text{D}_{3/2}$  lifetime is increased from 162 s to over 8300 s. The bulk of the difference of this comparison calculation comes from near complete loss of contribution of core-valence correlation in the M1 transition probability, i.e. the analysis of contributions without the stated improvements is similar to that of the “3s open” column in table 2.

In table 3 we present all E2 and M1 transition probabilities among the  $\text{Si}^-$  bound states. For  $^2\text{D}_{5/2}$ , we present only the length gauge E2 transition probabilities, since the length gauge value is the more stable of the two, and given such small transition probabilities velocity gauge values often vary by an order of magnitude with minor changes in the basis set.

For the  $^2\text{P}_{1/2}$  transitions, there are several points that suggest problems with LS mixing. The most notable is the excellent E2 gauge agreement in the  $^2\text{D}_{5/2} \rightarrow ^2\text{P}_{1/2}$  transition probability. This is somewhat expected given that the  $J = 1/2$  and  $J = 5/2$  calculations each have a single basis member for the  $3p^3$  configuration and are both

doublet states, so we have none of the issues of LS mixing and small coefficients among terms of the same  $J$  as we do with the forbidden transitions involving  $J = 3/2$ .

In contrast, our gauge agreement for the other two  ${}^2P_{1/2}$  transitions is quite poor, but the summation of each of the gauges for the  ${}^4S_{3/2} \rightarrow {}^2P_{1/2}$  and  ${}^2D_{3/2} \rightarrow {}^2P_{1/2}$  transitions agrees to  $\sim 1\%$  (resulting in good agreement between the two lifetime values). Normally this would be an indication of heavy mixing between two DF manifolds [9], e.g. between configurations with differing d shell occupancy in a system with  $d^n$ ,  $d^{n-1}s$  and  $d^{n-2}s^2$  interleaved DF manifolds, or simply between LS terms of a single manifold in a heavier system with greater mixing. Given that our  ${}^2D$  levels are approximately  $700 \text{ cm}^{-1}$  above the experimental values [1, 2] and the  ${}^2P_{1/2}$  level is about  $1500 \text{ cm}^{-1}$  above the experimental position [1, 3], LS mixing within the  $3p^3$  manifold is a suspect for the cause of the gauge discrepancy in the  ${}^2P_{1/2}$  transitions. To check dependency of LS mixing on these energy differences, we shift the diagonal energy matrix elements of the  ${}^2D$  and  ${}^2P$  functions in the  $J = 3/2$  calculations (separate shifts in the  ${}^4S_{3/2}$  and  ${}^2D_{3/2}$  optimized cases) such that the  ${}^4S_{3/2} - {}^2D_{3/2}$  energy difference matches the experimental value [1, 2]. Changes in the  ${}^2P_{1/2}$  transition probabilities due to these shifts are on the order of a few percent individually and negligible with regard to the sum (the  ${}^2P_{1/2}$  lifetime is increased by less than  $1\%$ ). A similar calculation using these same energy shifts shows a change in the  ${}^2D_{3/2}$  lifetime of  $\sim 1$  second. Both these results (and direct comparison of coefficients of the three  $J = 3/2$  basis functions within the DF portion of the wavefunction) suggest the  $3p^3$   $J = 3/2$  LS mixing is largely insensitive to relative energy positioning. So, while our RCI energy errors are much larger than the  $2\text{-}300 \text{ cm}^{-1}$  we would prefer for a system of this complexity (three open shell electrons), we find that the effect of this error on the properties of interest to be minimal.

Analysis similar to that of table 1 shows, in fact, the problems in  $J = 3/2 \rightarrow J = 1/2$  gauge agreement arise from the critical mixing of the  $3p$  single excitations, as evidence in their large contributions to the final RCI velocity gauge values, increasing the  ${}^2D_{3/2} \rightarrow {}^2P_{1/2}$  velocity transition probability and decreasing the  ${}^4S_{3/2} \rightarrow {}^2P_{1/2}$  value. For example, in the DF portion,  $\langle DF | \dots | DF \rangle$ , of our intermediate analysis of  ${}^4S_{3/2} \rightarrow {}^2P_{1/2}$ , the E2 velocity gauge contribution is  $\sim 4.9$  times that of the length contribution, while the ratio of the totals (square root of the transition probabilities ratio,  $v/l$ ) is  $\sim 1.8$ . Though not sufficient to lower the velocity gauge to equal the length gauge,  $\sim 75\%$  of this correction comes from the  $3p \rightarrow vp$  ( ${}^4D_{1/2}$ ) contribution to the  $\langle DF | \dots | 3p \rangle$  portion of the sum. We note that as in the other E2 cases, the length value is much more stable as we construct our bases with the actual velocity transition probability being reduced by a factor of 7 from the DF to the final calculations while the  ${}^4S_{3/2} \rightarrow {}^2P_{1/2}$  final length gauge value is about half the DF value. Given that the ratio of these transition probabilities ( $v/l$ ) is  $\sim 24$  at the DF stage (again squaring the ratio from the contributions to the sums), the ratio  $\sim 3$  for our final calculation is more understandable.

The correction in the velocity gauge calculation is even more pronounced in the  ${}^2D_{3/2} \rightarrow {}^2P_{1/2}$  transition, where the  $\langle DF | \dots | DF \rangle$  contribution is  $\sim 30$  times smaller in the velocity calculation than in the length one, i.e. the DF transition probability ratio

( $v/l$ ) is  $\sim 0.0011$  compared to  $\sim 0.71$  in the final calculation. Approximately 90% of this correction is due to mixing of the  $3p \rightarrow vf$  ( ${}^2D_{3/2}$ ) excitation as part of the  $\langle 3p|\dots|DF\rangle$  portion of the intermediate transition probability analysis.

A similar breakdown of the LS contributions within the single excitations in the  ${}^4S_{3/2} \rightarrow {}^2D_{3/2}$  transition shows that the most important contributions within the  $\langle DF|\dots|3p\rangle$  and  $\langle 3p|\dots|DF\rangle$  portions of the intermediate analysis are  $3p \rightarrow vp$  ( ${}^4D_{3/2}$ ) +  $vf$  ( ${}^4D_{3/2}$ ) in the ket and  $3p \rightarrow vp$  ( ${}^2P_{3/2}$ ) +  $vf$  ( ${}^2D_{3/2}$ ) in the bra (44% and 15% of the total correction to the DF difference between gauges, respectively).

Given that we know the major contributors to the improved gauge agreement in each of the transitions with apparent mixing trouble, and we have LS approximate basis functions for these configurations, it is possible to attempt to tailor our bases to further improve the velocity gauge values of these  ${}^2P_{1/2}$  transitions. For example, we can add additional correlation to  $3p \rightarrow vp$  in the  $J = 1/2$  calculation, to improve  ${}^4S_{3/2} \rightarrow {}^2P_{1/2}$ , and likewise we can further correlate  $3p \rightarrow vf$  in the  $J = 3/2$  calculations to improve  ${}^2D_{3/2} \rightarrow {}^2P_{1/2}$ . The difficulty we encounter, however, is the fact that in each of these cases, where the  $3p \rightarrow vp$  excitation helps gauge agreement the  $3p \rightarrow vf$  excitation hurts, or vice versa. Also, at this stage we have no *ab initio* justification for treating such configurations separately, especially since we have paid particular attention to treating them equally all through the basis set construction; same configurations in all  $J$ 's, same types of second order effects added to all configurations of the same type, etc. Targeted adjustments can be useful, however, as a means of analyzing our final calculations. The LS approximate functions created for the  $3p$  single excitations are useful for shifting of the diagonal matrix elements of specific terms, i.e. those identified above as important to corrections only in the transitions to the  ${}^2P_{1/2}$  level (and excluding those important in the  ${}^4S_{3/2} \rightarrow {}^2D_{3/2}$  transition, which already has good gauge agreement). With such shifts we are able to improve gauge agreement for the  ${}^2D_{3/2} \rightarrow {}^2P_{1/2}$  transition from 34% to 10%, while simultaneously decreasing the difference in the  ${}^4S_{3/2} \rightarrow {}^2P_{1/2}$  gauge agreement by about a third. Even with such targeted shifts there is a disruption of our  ${}^4S_{3/2} \rightarrow {}^2D_{3/2}$  gauge agreement as its velocity gauge returns approximately to its value prior to the inclusion of second order effects. The importance of such a calculation, however, is that we find that even if we were able to create similar improvements in an *ab initio* manner, the summation over the transition probability gauges for  ${}^2D_{3/2} \rightarrow {}^2P_{1/2}$  and  ${}^4S_{3/2} \rightarrow {}^2P_{1/2}$  is preserved to the point that changes in either gauge of the  ${}^2P_{1/2}$  lifetime are on the order of 1%.

In a final series of test calculations, we find that inclusion of the Breit operator (often a concern for its tendency to alter LS mixing between levels) in all RCI calculations affects the final lifetimes by less than 1%.

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**Table 1.** Contributions (velocity/length gauge) to E2  $\langle {}^4S_{3/2} | \Phi + c\vec{\alpha} \cdot \vec{A} | {}^2D_{3/2} \rangle$  presented as fraction of the total sum in the final RCI calculation. Contributions other than “DF” include the sum over matrix elements that include that configuration in the bra (ket) and DF in the ket (bra), e.g. “3p<sup>2</sup>” entries are the sum of  $\langle 3p^2 | \dots | 3p^2 \rangle$ ,  $\langle 3p^2 | \dots | DF \rangle$ , and  $\langle DF | \dots | 3p^2 \rangle$ .

Config.	Valence	3s open	2p open	2p + 2p3s	2p + TQ	Final
DF	2.88/ 1.13	2.75/ 1.10	2.75/ 1.10	2.75/ 1.10	2.74/ 1.11	2.74/ 1.11
3p	-1.77/-0.29	-1.43/-0.15	-1.35/-0.14	-1.23/-0.11	-1.93/-0.24	-1.76/-0.20
3p <sup>2</sup>	0.08/ 0.07	0.13/ 0.07	0.15/ 0.05	0.14/ 0.05	0.11/ 0.06	0.11/ 0.06
3s	NA <sup>a</sup>	0.14/ 0.02	0.17/ 0.10	0.13/ 0.10	0.08/ 0.10	0.07/ 0.09
3s <sup>2</sup>	NA	0.00/ 0.08	0.02/ 0.02	0.03/ 0.02	0.06/ 0.02	0.05/ 0.02
3s3p <sup>b</sup>	NA	-0.02/ 0.03	-0.14/-0.03	-0.12/-0.02	-0.24/-0.05	-0.20/-0.05
2p	NA	NA	0.12/ 0.00	0.11/ 0.00	0.02/ 0.00	0.03/ 0.00
Other	0.09/-0.03	-0.01/-0.02	0.02/-0.02	0.02/-0.01	-0.04/ 0.00	-0.04/-0.03
Total	1.28/ 0.88	1.56/ 1.13	1.70/ 1.08	1.83/ 1.09	0.78/ 0.97	1.00/ 1.00
$A_{ki}^v/A_{ki}^l$	2.13	1.91	2.49	2.83	0.66	1.00

<sup>a</sup> Not applicable. These excitations are not present at this stage of the calculation.

<sup>b</sup> Also includes  $\langle 3s3p | \dots | 3s \rangle$ ,  $\langle 3s | \dots | 3s3p \rangle$ ,  $\langle 3s3p | \dots | TQ \rangle$ , and  $\langle TQ | \dots | 3s3p \rangle$  contributions where present. These are the largest terms in the sum that do not include the DF functions or the same type of excitation in both bra and ket.

**Table 2.** Contributions to M1  $\langle {}^4S_{3/2} | \Phi + c\vec{\alpha} \cdot \vec{A} | {}^2D_{3/2} \rangle$  presented as fraction of the total sum in the final RCI calculation. Since the M1 operator does not change configurations, these contributions represent a sum over the same configuration in the bra and ket, e.g. “3p<sup>2</sup>” entries are  $\langle 3p^2 | \dots | 3p^2 \rangle$  only.

Config.	Valence	3s open	2p open	Final
DF	0.04	0.14	0.09	0.11
3p	-0.02	-0.01	0.03	0.03
3p <sup>2</sup>	0.02	0.01	0.20	0.21
3s	NA <sup>a</sup>	0.00	0.11	0.11
3s <sup>2</sup>	NA	0.00	0.01	0.01
3s3p	NA	0.01	0.47	0.50
2p3p	NA	NA	0.02	0.02
2p3s	NA	NA	NA	0.02
Other	0.00	-0.01	0.01	-0.01
Total	0.04	0.14	0.94	1.00
${}^2D_{3/2} \tau^b$	23 000 s	5900 s	185 s	162 s

<sup>a</sup> Not applicable. These configurations are not present at this stage of the calculation.

<sup>b</sup> Includes corresponding E2 length gauge.

**Table 3.**  $\text{Si}^-$  transition probabilities ( $\text{s}^{-1}$ ) and lifetimes. The  $A_{ki}$  are given for E2 (velocity/length gauge) and M1 calculations ( $\text{n.nm-X} = \text{n.nm} \times 10^{-\text{X}}$ ). Lifetimes which are given for both gauges use the single M1 value in combination with each of the E2 values.

Transition	E2 $A_{ki}$ ( $\text{s}^{-1}$ )	M1 $A_{ki}$ ( $\text{s}^{-1}$ )	$\tau$
$^4\text{S}_{3/2} \rightarrow ^2\text{D}_{3/2}$	4.38-5/4.37-5	6.04-3	162 s / 162 s
$^4\text{S}_{3/2} \rightarrow ^2\text{D}_{5/2}$	/9.70-7	9.17-6	/ 27.3 h
$^2\text{D}_{3/2} \rightarrow ^2\text{D}_{5/2}$	/7.13-18	3.02-8	
$^4\text{S}_{3/2} \rightarrow ^2\text{P}_{1/2}$	9.30-3/2.85-3	2.50-3	23.5 s / 23.6 s
$^2\text{D}_{3/2} \rightarrow ^2\text{P}_{1/2}$	1.51-2/2.13-2	9.23-4	
$^2\text{D}_{5/2} \rightarrow ^2\text{P}_{1/2}$	1.48-2/1.48-2		