PHYSICAL REVIEW A VOLUME 37, NUMBER 6 MARCH 15, 1988

Corrected fine-structure energy levels and oscillator strengths for Ne I – Si V in the neon sequence

T. M. Luke
Department of Applied Mathematics and Centre for Chemical Physics, University of Western Ontario, London, Ontario, Canada N6A 5B9

(Received 27 July 1987)

The problem of calculating transition rates between atomic fine-structure levels is considered. Nonrelativistic configuration-interaction calculations of terms of interest are performed and the terms are then mixed by the relativistic couplings of the Breit-Pauli Hamiltonian. Frequently it turns out that the mixing components of the Breit-Pauli matrix are larger than the relative term energies. This leads to sensitivity of the level eigenvectors to small errors in the energies and thus to errors in the transition rates among the levels. A nonperturbative method for correcting the level vectors for cases involving any number of strongly mixed terms is developed. The method is based on solving the inverse eigenvalue problem for a matrix using the observed spectrum to correct the diagonal matrix elements of the Breit-Pauli matrix. It is applied in the present work to calculate level wave functions and transition rates for the $1s^2 2s^2 2p^5 3s$, $3p$, and $3d$ levels of the Ne I–Si V ions of the neon isoelectronic sequence.

I. INTRODUCTION

It has been recognized for some time that calculated fine-structure oscillator strengths may be in serious error when there are errors in the nonrelativistic energy separations of the terms that mix to form the fine-structure levels and that it is important to correct for such errors. The importance of these points is mentioned briefly by Eissner *et al.*[1] and more extensively by Hibbert[2] and by Zeippen *et al.*[3] These authors are interested particularly in cases of forbidden transitions involving levels with only small admixtures of terms that allow the dipole transitions to occur. Because the admixtures are small, very simple corrections to mixing coefficients based on perturbation theory work well.

In Ref. 2 Hibbert gives an example that shows the dramatic effect that mixing coefficient corrections derived from observed energy splittings can have on rates. He considers the $2s3p\,^3P_1$-$2s^2\,^1S_0$ electric dipole transition in O V. A simple raw calculation of the rate gives a result that is in error by a factor of 3 compared to both observation and large-scale configuration-interaction (CI) calculations. Adjustment of the $^1P_1$-$^3P_1$ splitting to the observed value corrects the mixing coefficient of the ^1P term in the $^3P_1$ level and brings the new calculated decay rate to the observed (and large scale CI) values.

A new correction method was presented in Refs. 4 and 5 which does not depend on being able to treat the relativistic mixing using perturbation theory and observed splittings but rather obtains corrections by solving an inverse eigenvalue problem for the Breit-Pauli matrix with the observed level spectrum as input. The method was applied to correct a calculation that used fairly elaborate multiconfiguration wave functions for the four $3s$ levels and the ten $3p$ levels of neutral neon where we have situations involving 2, 3, and 4 strongly mixed terms. As in Hibbert's work, some striking improvements in rates were obtained, the most substantial being a change by a factor of almost 20 which brought the calculated p_4-s_5 rate into line with the observed result. Also, the Landé g factors for the levels, which depend on the mixing coefficients, were strikingly improved to agree with experiment.

In the present article, we extend the method of Refs. 4 and 5 and we give the results of a calculation of all the excited $n=3$ levels for the first five elements of the neon sequence. We obtain corrected level mixing coefficients and transition rates for all electric dipole transitions among these levels. We purposely use a small number of configurations for the calculation and find nevertheless that the corrected results are good where comparison with observation or more elaborate calculations are possible. Further, we show that a requirement of the earlier scheme, that we make use of observed g factors to resolve an ambiguity in choice of solution, can be removed so that their values are predicted rather than assumed. This is important since these factors may well not be available from observations. Also, where the g factors do exist, their accurate prediction demonstrates the effectiveness of the correction method in its objective of producing good mixing coefficients.

This calculation introduces other elements to the problem that were not previously encountered in this approach. One is the occurrence in Na II of two $J\Pi$ spaces where five terms are significantly mixed. The situation is the prototype for much more severe cases such as in the transition elements, where there is the potential for many more terms being mixed more or less strongly. The original analysis was readily applied to up to four strongly mixed terms; as the dimensions increase, the direct extension of this approach is not practicable so we modify it. In addition, there may be several strongly mixed terms from the same $SL\Pi$ subspace—a complication not previously encountered.

We describe in Sec. II the particular calculation at hand and discuss a modified method of correcting the levels which is algebraically straightforward, handles the general problem, including the case where several terms of a given $SL\Pi$ subspace are strongly mixed, and obviates the need for additional information to remove ambiguity. Thus the extended techniques developed here are applicable to the correction of any CI calculation of any ion provided accurate spectral observations are available. In Sec. III we report and discuss the results of the present calculations, and we make some concluding remarks in Sec. IV. Mathematical details are treated in the Appendixes.

II. DESCRIPTION OF THE CALCULATION AND CORRECTION METHOD

The calculation proceeds in four stages: (1) calculation of nonrelativistic wave functions for the relevant terms of the ion; (2) construction of the Breit-Pauli matrix in the fixed basis of these terms; (3) solution of the inverse eigenvalue problem using observed eigenvalue input to obtain a corrected Breit-Pauli matrix; (4) use of this this corrected matrix to obtain corrected level wave functions and transition rates. Details on each follow.

(1) The structure of the ion levels of interest in this work was obtained using the multiconfiguration optimized potential model[6] (MCOPM). This is an *ab initio* ion-structure calculation which is then to be corrected by the present techniques. We use the configuration set $1s^22s^22p^6$, $1s^22s^22p^53s$, $3p$, $3d$, $4s$, $4p$, $4d$. (For Na II, the $1s^22s^22p^55s$ configuration is added.) This "minimal" set allows the outer orbitals to satisfy both spectroscopic and correlation roles.[7]

In this calculation we minimize an equally weighted sum of excited $3s$-, $3p$-, and $3d$-term energies together with the energy of the ground state using the full nonrelativistic Hamiltonian and CI wave functions for the terms. As described in Ref. 7, for example, the orbitals are calculated in a set of central potentials and the energy sum is minimized with respect to variations of these numerically evaluated potentials. The resulting terms are then used for a first-order treatment of the relativistic interactions in the Breit-Pauli Hamiltonian to yield the fine-structure levels. (This is the essence of the calculation. The computer code actually performs all calculations using as basis the *algebraic* terms corresponding to the various configurations. For the sake of clarity we discuss the problem using the more physical basis of the configuration-mixed terms that are the eigenvectors of the nonrelativistic Hamiltonian. In the following we will refer, as appropriate, to "algebraic" and "physical" bases.)

(2) A typical matrix in this physical term basis has the form given in Eq. (1):

$$H_{\mathrm{BP}}=\begin{bmatrix} -57.4373 & 0.0060 & 0.0073 & -10^{-6} \\ (0.0006) & & & \\ 0.0060 & -57.4196 & -0.0032 & 0.0089 \\ & (0.0014) & & \\ 0.0073 & -0.0032 & -57.4209 & -0.0072 \\ & & (-0.0001) & \\ -10^{-6} & 0.0089 & -0.0072 & -57.4583 \\ & & & (-0.0019) \end{bmatrix} . \tag{1}$$

This is the matrix for the $3d$ ($J\Pi=2-$) space of Si V. The rows and columns are labeled by the strongly coupled $3d$ terms $^3F^\circ$, $^3D^\circ$, $^1D^\circ$, and $^3P^\circ$. (The 2 space is actually spanned by 11 either algebraic or physical terms in the present calculation, but in the physical basis these four terms of interest are, to an excellent approximation, decoupled from the rest of the space and can be treated separately.) The matrix elements are expressed in hartrees. The diagonal elements are in large part the nonrelativistic term energies while the off-diagonal elements are the spin orbit and other relativistic couplings. We give in parentheses, below the diagonal elements, the corrections that are made in this particular case to the diagonal elements as a result of solving the inverse eigenvalue problem.

Diagonalizing this matrix yields the relativistically mixed fine-structure levels, the elements of the eigenvectors being the mixing coefficients in this basis while the eigenvalues are the level energies. An important point to note in Eq. (1) is that the diagonal energy differences are in some instances comparable or small relative to the off-diagonal elements. This leads to strongly mixed levels. Furthermore, even in a very sophisticated calculation, although the term wave functions and *absolute* term energies may be very good, errors in the small *differences* between diagonal elements are likely to be significant. As a result, the raw level mixing coefficients may be in serious error.

(3) At this stage, the earlier correction procedure or its present extensions may be applied to each of the $J\Pi$ spaces. The inverse eigenvalue problem actually yields up to $N!$ sets of mixing coefficients for each space, where

N is the number of strongly mixed terms. From this set, the correct set must be chosen as we describe below. The outcome is then usually that one obtains a correction to the diagonal elements only of each $SL\Pi$ block of the Breit-Pauli matrix. Examples of the shifts are given in Eq. (1). There are more complicated cases where there is more than one strongly mixed vector from a given $SL\Pi$ space; these are discussed below and in Appendix B.

Using the earlier approach, the $N=2$ case is trivial, while the $N=3$ and $N=4$ cases encountered in this work can be reduced to the solution of pairs of nonlinear algebraic equations—graphically this amounts to obtaining the intersections of two multibranched curves in a plane. (The positions of these curves depend only on the eigenvalues and the off-diagonal matrix elements. The curves corresponding to the observed eigenvalues will be somewhat shifted from those corresponding to the raw or calculated eigenvalues.) The Landé g factors can be calculated for each solution (intersection point) that results from the observed eigenvalue input, and by comparison with the observed g factors the correct solution is easily identified as the one with the best g-factor match.

In practice, few observed g factors are available. However, one finds, in the case of neon where one can check using observed g factors, that the patterns of intersection points on the graphs for raw and corrected solutions do not differ radically. Consequently, after one performs a reasonable raw calculation and finds the intersection point that, using the raw spectrum yields the input raw diagonal matrix elements, then the corresponding "nearby" intersection point in the corrected calculation yields the physically correct solution as indicated by the g factors. Thus it appears to be only a slight though unproven conjecture that one can dispense with the g-factor criterion if the raw calculation is at all reasonable and simply use the corrected solution corresponding to the raw one for each $J\Pi$ space. This is what has been done here with the result that the calculation predicts the g factors instead of requiring them as input.

In addition to these cases, which involve up to a 4×4 problem to invert, a more complicated situation arises in the case of the $J\Pi=1-$, $2-$ spaces of the $3d$ levels in Na II. At this stage in the sequence, the $3d$ levels are plunging down past the $4s$ levels; as a result, there is rather strong mixing of the $3d$ levels with the $4s$ levels at that ion and we encounter 5×5 Breit-Pauli matrices. This requires us to extend the method to higher dimensions. A description of the solution method used for this case is given in Appendix A.

A couple of points distinguish this problem and higher-dimension problems from those looked at earlier. One is that they clearly become algebraically more cumbersome so that it may be most efficient to simply solve Eqs. (A3)–(A7) numerically for the corrected diagonal elements $\{H_i\}$ rather than attempt substantial algebraic simplification as was done in earlier work. The other is an associated practical difficulty in solving several (more than two) nonlinear algebraic equations without graphical assistance: namely, the problem of finding good starting estimates that converge to the desired physical solution. The "numerical continuation" scheme sketched in Appendix A is very effective in this regard and was used in this work.

Another feature of this calculation of $3d$ levels in Na II that differs from previous work is that both the 5×5 cases of the previous paragraphs involve more than one strongly mixed term from a given $SL\Pi$ subspace, so we require a correction scheme that is somewhat more complicated than the previous one where we just apply common shifts to the diagonal elements of each $SL\Pi$ block of the $J\Pi$ space matrix. We describe in Appendix B how this is to be done.

(4) Finally, when the new diagonal elements $\{H_i\}$ have been determined, suitable corrections are made to the Breit-Pauli matrix and we then recalculate the level wave functions. Using the corrected levels we calculate the electric dipole transition rates which are reported in Sec. III. The relativistic calculation of the fine structure and the transition rate calculations are performed using the SUPERSTRUCTURE program of Eissner *et al.*[1] with the Thomas-Fermi-Dirac potentials replaced by the MCOPM potentials.

III. RESULTS AND DISCUSSION

We have carried out the program of calculations for the ions Ne I, Na II, Mg III, Al IV, and Si V using either seven or eight configurations as described in Sec. II. Beyond that point in the sequence not all the observed energies required for making corrections are, at present, available for the set of levels under consideration. In the following, we discuss separately the L-S compositions of the levels and the transition rates.

A. L-S compositions

In Table I we give the compositions and Landé g factors of the 21 mixed levels for each of the five ions. We also give comparison values from elsewhere for the compositions and g factors where available. In the case of neon, the comparison compositions of the $3s$ and $3p$ levels are from previous larger-scale calculations[4,5] and the g factors are taken from observations.[8] For the other ions, the comparison compositions have been calculated by various authors using a method based on the Hartree-Fock model in which the radial integrals and spin-orbit parameters are varied to fit the observed spectrum. Generally, the compositions are fairly similar though there are certainly disparities. In the case of Mg III, Al IV, and Si V, for example, the Hartree-Fock values for the L-S compositions of the $3p(1+)$ and $3d(2-)$ levels are very close to the raw values obtained in the present calculation but rather far displaced from the corrected values in the present work.

The g_L values' dependence on these compositions is given by

$$g_L=\sum_{S'L'}\omega_{S'L'}g(S'L'J)\ , \tag{2}$$

where

$$g(SLJ)=1+\frac{J(J+1)-L(L+1)+S(S+1)}{2J(J+1)} \tag{3}$$

TABLE I. L-S compositions and Landé g factors g_L for relativistically mixed levels in the neon sequence. The levels are designated by the notation $nl(J\Pi)^m$, where m designates the order in energy from lowest to highest of the level characterized by the outer electron in orbital nl and overall angular momentum and parity J,Π. Present results are given as the first entry for each element while the second entries are from observations in the case of the neon g_L values and from other calculations in the case of L-S compositions. Observed values of g_L are from Ref. 8. Calculations are from various sources as noted.

Level compositions (%) and Landé factors

	$3s(1-)^1$			$3s(1-)^2$		
Ion	$^3P_1$	$^1P_1$	g_L	$^3P_1$	$^3P_1$	g_L
Ne I	93	7	1.465	7	93	1.035
	93[a]	7	1.464[b]	7	93	1.037
Na II	95	5	1.477	5	95	1.023
	96[c]				96	
Mg III	95	5	1.474	5	95	1.026
	95[d]	5		5	95	
Al IV	93	7	1.465	7	93	1.035
Si V	90	10	1.451	10	90	1.049
	90[e]	10		10	90	

	$3p(2+)^1$				$3p(2+)^2$				$3p(2+)^3$			
	$^3D_2$	$^1D_2$	$^3P_2$	g_L	$^3D_2$	$^1D_2$	$^3P_2$	g_L	$^3D_2$	$^1D_2$	$^3P_2$	g_L
Ne I	76	22	2	1.138	7	49	44	1.233	17	30	53	1.296
	75	22	2	1.137	7	48	45	1.232	18	29	53	1.298
Na II	89	9	2	1.157	3	65	31	1.162	8	25	67	1.348
	88					65					67	
Mg III	90	8	2	1.159	2	64	33	1.170	8	28	65	1.337
	89					61	36			30	62	
Al IV	89	9	2	1.159	2	58	40	1.201	9	33	58	1.306
	88[f]	10				56	42		10	35	55	
Si V	86	11	3	1.158	2	53	45	1.227	12	36	52	1.282
	86[g]	11				50	48			39	48	

	$3p(1+)^1$					$3p(1+)^2$					$3p(1+)^3$					$3p(1+)^4$				
	$^3D_1$	$^3P_1$	$^1P_1$	$^3S_1$	g_L	$^3D_1$	$^3P_1$	$^1P_1$	$^3S_1$	g_L	$^3D_1$	$^3P_1$	$^1P_1$	$^3S_1$	g_L	$^3D_1$	$^3P_1$	$^1P_1$	$^3S_1$	g_L
Ne I	0	1	1	98	1.988	73	9	18	0	0.681	27	24	49	0	0.984	0	66	32	2	1.347
	0	1	1	98	1.989					0.678					0.994					1.340
Na II	0	1	0	99	1.995	91	3	6	0	0.563	9	26	65	0	1.083	0	70	29	1	1.359
				99		91							60				66			
Mg III	0	1	0	99	1.995	92	3	5	0	0.557	8	23	68	0	1.075	0	73	26	1	1.373
				99		91						30	61				65	34		
Al IV	0	1	0	99	1.994	89	4	7	0	0.572	10	22	68	0	1.057	0	74	25	1	1.377
				99		89		6			10	29	60				65	34		
Si V	0	1	0	99	1.992	86	5	9	0	0.598	14	21	65	0	1.032	0	73	25	1	1.377
				99		86		8				28	58				65	33		

TABLE I. (*Continued*).

Level compositions (%) and Landé factors

Ion	$3p(0+)^1$		$3p(0+)^2$	
	$^3P_0$	$^1S_0$	$^3P_0$	$^1S_0$
Ne I	97	3	3	97
	97	3	3	97
Na II	100	0	0	100
	100			100
Mg III	100	0	0	100
	100			100
Al IV	100	0	0	100
	100			100
Si V	100	0	0	100
	100			100

	$3d(3-)^1$				$3d(3-)^2$				$3d(3-)^3$			
	$^3F_3$	$^1F_3$	$^3D_3$	g_L	$^3F_3$	$^1F_3$	$^3D_3$	g_L	$^3F_3$	$^1F_3$	$^3D_3$	g_L
Ne I	40	60	0	1.034	19	11	71	1.250	41	30	30	1.133
				1.034				1.250				1.125
Na II	53	47	0	1.045	22	31	47	1.175	25	22	53	1.197
	53						46				54	
Mg III	62	37	1	1.053	23	46	31	1.121	15	16	69	1.242
	68	32			19	52	29			16	70	
Al IV	71	28	1	1.063	16	57	27	1.103	12	16	72	1.251
	76	22			13	62	34		10	15	75	
Si V	76	23	1	1.068	12	59	28	1.104	12	18	70	1.245
	79	19				65	24			16	74	

	$3d(2-)^1$					$3d(2-)^2$					$3d(2-)^3$					$3d(2-)^4$				
	$^3F_2$	$^3D_2$	$^1D_2$	$^3P_2$	g_L	$^3F_2$	$^3D_2$	$^1D_2$	$^3P_2$	g_L	$^3F_2$	$^3D_2$	$^1D_2$	$^3P_2$	g_L	$^3F_2$	$^3D_2$	$^1D_2$	$^3P_2$	g_L
Ne I	0	19	17	64	1.352	29	30	41	0	0.953	64	2	31	4	0.810	7	49	12	32	1.219
					1.356					0.949					0.781					1.242
Na II[h]																				
Mg III	0	4	3	93	1.470	73	10	17	0	0.775	27	20	53	0	0.944	0	65	27	7	1.144
				93		77		14			23	31	46				56	37		
Al IV	0	3	2	94	1.477	78	8	13	0	0.752	21	20	58	0	0.964	0	68	26	6	1.141
				95		83	6	10			16	30	50				57	38	5	
Si V	0	3	2	94	1.477	79	8	13	0	0.750	21	21	58	0	0.967	0	68	26	6	1.140
				95		84	6	9			15	34	51				57	38	5	

TABLE I. (*Continued*).

Level compositions (%) and Landé factors

Ion		$3d(1-)^1$				$3d(1-)^2$				$3d(1-)^3$		
	$^3D_1$	$^3P_1$	$^1P_1$	g_L	$^3D_1$	$^3P_1$	$^1P_1$	g_L	$^3D_1$	$^3P_1$	$^1P_1$	g_L
Ne I	1	80	19	1.394	37	9	55	0.859	62	12	26	0.747
				1.397				0.860				0.752
Na II[i]												
Mg III	2	98	1	1.481	60	0	40	0.703	39	2	59	0.816
		98			60		40		39		59	
Al IV	1	98	0	1.485	83	0	16	0.588	16	1	83	0.926
		98			85		15		14		85	
Si V	1	98	0	1.486	90	1	9	0.554	9	1	91	0.960
		99			91		8		8		92	

[a] References 4 and 5.
[b] Reference 8.
[c] Reference 12.
[d] Reference 13.
[e] Reference 14.
[f] Reference 15.
[g] Reference 16.
[h] See Table III.
[i] See Table II.

is the g factor for an L-S coupled term occurring with weight ω_{SL} given by the square of the mixing coefficient.

We are aware of published observations of g_L values only for neon. We recall that they are predicted rather than fitted in this approach and they appear to be very satisfactory in neon. This leads to some confidence in the mixing coefficients of the other corrected levels.

A problem in applying the correction scheme arose in only one case and that was in calculating the five $3d,4s$ levels of the $J\Pi = 1-$ space. As we describe in Appendix B, the approach is to start with corresponding raw values of $\{H_i\}$ and $\{\lambda_i\}$ and numerically continue to the physical values. In this case, despite proceeding in rather small steps, there comes a point in the process where the Newton's method calculation fails to converge, indicating there is no longer a solution to Eqs. (A3)–(A7). This likely implies one of two things: either the observed values for the λ_i are in error or the off-diagonal elements δ_{ij} are not sufficiently accurately calculated. The observations are from the recent compilation of Martin and Zalubas,[9] who quote the thesis of Wu.[10] In the absence of information that these observations are in error, it appears that larger-scale calculations to yield more accurate off-diagonal elements should be undertaken to see if the difficulty lies there.

To further deal with this particular case we give in Table II two sets of L-S compositions—one from the raw calculation and one, denoted best, which is from the last calculation that converged in the numerical continuation process towards the observed energies. The energies, all adjusted to have the same lowest value of zero for convenience, are tabulated and it can be seen that the "best" energy is rather close to the observed. Indeed, all three energies for a given level do not differ greatly. Nevertheless, the raw and best mixing coefficients differ substantially in several instances. Thus, apart from the fact that an exact solution is not quite possible, this case is also unusual inasmuch as the coefficients vary rather strongly with modest changes in the set of eigenvalues.

A more typical case is illustrated in Table III, where the raw and corrected coefficients for the $3d(2-)$ case in Na II are displayed. They show the behavior that usually occurs when the energy shifts are modest. We plan to further investigate the $3d(1-)$ case of Na II and report on it when the reasons for sensitivity and nonsolution are understood. For the present, no transition rates will be reported for these levels. The rates from the raw calculation may turn out to be reasonable but the questions concerning this case should be understood first.

B. Transition rates

We report in Tables IV and V the computed transition rates for all the electric dipole transitions among the $n = 3$ levels for these ions. Included with the neon values are the observed rates for the $3p$ levels. The calculated rates are virtually all within 10% of the observations. Judging from the g_L values, the $3d$ transition rates should be equally good, though we do not have observational data for comparison. As we proceed along the sequence, except for the case of the Na II $3d$ $(1-)$ levels which we

TABLE II. L-S compositions for the incomplete calculation of $3d$, $4s(1-)$ levels in Na II. "Best" results are the energies and compositions from the last calculation in numerical continuation from raw to observed energies before breakdown in Newton's method occurred.

				L-S composition (%)									
	E_{raw}	E_{best}	E_{obs}[a]	Raw levels					Best levels				
Level		(cm^{-1})		$3d\,{}^3D_1$	$3d\,{}^3P_1$	$4s\,{}^3P_1$	$3d\,{}^1P_1$	$4s\,{}^1P_1$	$3d\,{}^3D_1$	$3d\,{}^3P_1$	$4s\,{}^3P_1$	$3d\,{}^1P_1$	$4s\,{}^1P_1$
$3d(1-)^1$	0	0	0	3	94	1	1	1	2	94	2	1	1
$3d(1-)^2$	1014	1020	1070	14	0	20	62	3	6	1	40	44	9
$4s(1-)^1$	1225	1232	1236	22	1	41	8	29	30	0	25	24	21
$3d(1-)^3$	2388	2394	2470	48	1	19	28	3	31	0	26	25	18
$4s(1-)^2$	2509	2515	2525	14	4	18	1	64	31	5	7	6	51

[a]Reference 9.

TABLE III. L-S compositions for calculations of $3d$, $4s(2-)$ levels in Na II. Raw and obs refer to calculated results with raw and observed energies for the levels.

			L-S composition (%)									
	E_{raw}	E_{obs}[a]	Raw levels					Obs levels				
Level	(cm^{-1})		$3d\,{}^3F_2$	$3d\,{}^3D_2$	$3d\,{}^1D_2$	$3d\,{}^3P_2$	$4s\,{}^3P_2$	$3d\,{}^3F_2$	$3d\,{}^3D_2$	$3d\,{}^1D_2$	$3d\,{}^3P_2$	$4s\,{}^3P_2$
$3d(2-)^1$	0	0	0	6	4	85	4	0	5	3	88	4
$4s(2-)$	627	708	0	4	3	1	92	0	3	2	1	94
$3d(2-)^2$	728	876	53	19	28	0	0	56	17	26	0	0
$3d(2-)^3$	1856	2013	47	21	32	0	0	44	21	36	0	0
$3d(2-)^4$	2005	2174	0	50	33	13	4	0	54	32	11	4

[a]Reference 9.

TABLE IV. Transition rates for $3p$-$3s$ levels in Ne I–Si V ions. The first line for each transition gives the calculated result with the exponent in parentheses. The second line, for Ne I only, gives observed results. These have the same exponent as the calculations and the quoted experimental error is given in parentheses. The notation for the levels uses the energy ordering system of Table I. Results of other recent calculations for Si V are included.

	Transition rate (sec^{-1})					
Transition	Ne I	Na II	Mg III	Al IV	Si V	Si V[a]
$3p(3+)$-$3s(2-)$	5.620(7) 5.15(.01)[b]	2.274(8)	4.546(8)	7.219(8)	1.015(9)	9.340(8)
$3p(2+)^1$-$3s(2-)$	1.830(7) 1.79(.07)	8.078(7)	1.648(8)	2.696(8)	3.894(8)	3.740(8)
$3p(2+)^1$-$3s(1-)^1$	3.313(7) 3.01(.12)	1.404(8)	2.804(8)	4.362(8)	5.927(8)	5.340(8)
$3p(2+)^1$-$3s(1-)^2$	3.134(6) 3.07(.13)	3.415(6)	3.921(6)	4.716(6)	5.797(6)	5.190(6)
$3p(2+)^2$-$3s(2-)$	3.062(7) 2.93(.10)	8.654(7)	1.798(8)	3.304(8)	5.230(8)	5.210(8)
$3p(2+)^2$-$3s(1-)^1$	4.929(6) 4.49(.16)	2.141(7)	5.693(7)	1.244(8)	2.164(8)	2.350(8)
$3p(2+)^2$-$3s(1-)^2$	1.984(7) 1.78(.06)	1.168(8)	2.277(8)	3.062(8)	3.516(8)	2.530(8)
$3p(2+)^3$-$3s(2-)$	1.198(7) 1.21(.04)	9.005(7)	1.809(8)	2.438(8)	2.833(8)	1.980(8)
$3p(2+)^3$-$3s(1-)^1$	1.898(7) 1.78(.06)	7.357(7)	1.364(8)	1.925(8)	2.392(8)	2.040(8)
$3p(2+)^3$-$3s(1-)^2$	2.643(7) 2.36(.08)	8.495(7)	1.901(8)	3.668(8)	5.931(8)	5.840(8)
$3p(1+)^1$-$3s(2-)$	2.920(7) 2.66(.11)[c]	1.001(8)	1.905(8)	2.990(8)	4.228(8)	4.400(8)
$3p(1+)^1$-$3s(1-)^1$	1.120(7) 1.01(.04)	4.284(7)	8.011(7)	1.190(8)	1.538(8)	1.560(8)
$3p(1+)^1$-$3s(0-)$	2.796(6) 2.47(.11)	1.181(7)	2.213(7)	3.215(7)	4.064(7)	4.000(7)

TABLE IV. (*Continued*).

Transition	Ne I	Na II	Mg III	Al IV	Si V	Si V[a]
			Transition rate (sec^{-1})			
$3p(1+)^1$-$3s(1-)^2$	1.326(5) 1.3(.1)	4.894(5)	1.240(6)	2.687(6)	5.143(6)	3.600(6)
$3p(1+)^2$-$3s(2-)$	6.755(6) 6.17(.3)[b]	1.814(7)	3.522(7)	6.109(7)	9.746(7)	8.840(7)
$3p(1+)^2$-$3s(1-)^1$	3.526(7) 3.26(.15)	1.267(8)	2.515(8)	4.139(8)	6.095(8)	5.620(8)
$3p(1+)^2$-$3s(0-)$	1.148(7) 1.06(.5)	8.061(7)	1.636(8)	2.387(8)	2.892(8)	2.680(8)
$3p(1+)^2$-$3s(1-)^2$	2.190(6) 1.87(.09)	1.478(6)	1.467(6)	1.925(6)	2.536(6)	1.960(6)
$3p(1+)^3$-$3s(2-)$	3.394(6) 3.75(.15)	2.138(7)	3.981(7)	5.670(7)	6.925(7)	8.760(7)
$3p(1+)^3$-$3s(1-)^1$	5.902(5) 6.8(.3)	1.339(7)	3.103(7)	4.966(7)	6.640(7)	6.910(7)
$3p(1+)^3$-$3s(0-)$	2.636(7) 2.59(.10)	6.792(7)	1.234(7)	2.075(8)	3.270(8)	3.470(8)
$3p(1+)^3$-$3s(1-)^2$	2.452(7) 2.22(.08)	1.230(8)	2.587(8)	4.034(8)	5.356(8)	4.140(8)
$3p(1+)^4$-$3s(2-)$	1.213(7) 1.10(.05)[b]	6.403(7)	1.375(8)	2.192(8)	2.988(8)	2.310(8)
$3p(1+)^4$-$3s(1-)^1$	6.151(6) 4.68(.24)	3.032(7)	6.066(7)	8.742(7)	1.016(8)	9.150(7)
$3p(1+)^4$-$3s(0-)$	1.622(7) 1.51(.07)	7.262(7)	1.583(8)	2.659(8)	3.906(8)	3.150(8)
$3p(1+)^4$-$3s(1-)^2$	2.382(7) 2.40(.11)	8.388(7)	1.596(8)	2.584(8)	3.806(8)	4.010(8)
$3p(0+)^1$-$3s(1-)^1$	6.276(7) 5.72(.25)	2.653(8)	5.386(8)	8.583(8)	1.190(9)	1.100(9)
$3p(0+)^1$-$3s(1-)^2$	3.336(5) 3.5(.4)	4.106(6)	1.248(7)	2.986(7)	6.155(7)	5.200(7)
$3p(0+)^2$-$3s(1-)^1$	1.096(6)	1.292(7)	4.734(7)	1.267(8)	2.894(8)	4.080(8)
$3p(0+)^2$-$3s(1-)^2$	7.846(7)	4.558(8)	1.152(9)	2.081(9)	3.138(9)	5.060(9)

[a] Reference 11.

[b] Reference 17.

[c] Reference 18.

TABLE V. Transition rates for $3d$-$3p$ levels in Ne I–Si V ions. The exponent for each rate is given in parentheses. The notation for the levels uses the energy ordering system of Table I. Results of other recent calculations for Si V are included.

Transition	Ne I	Na II	Mg III	Al IV	Si V	Si V[a]
			Transition rate (sec^{-1})			
$3d(4-)$-$3p(3+)$	4.560(7)	4.727(8)	1.215(9)	2.107(9)	2.954(9)	2.960(9)
$3d(3-)^1$-$3p(3+)$	1.778(6)	3.390(7)	1.084(8)	2.332(8)	3.629(8)	
$3d(3-)^1$-$3p(2+)^1$	3.410(7)	3.342(8)	9.196(8)	1.716(9)	2.495(9)	2.490(9)
$3d(3-)^1$-$3p(2+)^2$	6.338(6)	6.857(7)	1.230(8)	1.034(8)	7.667(7)	4.280(7)
$3d(3-)^1$-$3p(2+)^3$	8.217(5)	1.456(7)	2.942(7)	2.918(7)	1.828(7)	1.500(7)
$3d(3-)^2$-$3p(3+)$	1.354(7)	1.139(8)	2.308(8)	3.346(8)	4.513(8)	4.450(8)
$3d(3-)^2$-$3p(2+)^1$	1.679(6)	2.492(7)	5.652(7)	3.245(7)	7.309(6)	7.180(4)
$3d(3-)^2$-$3p(2+)^2$	2.432(7)	3.014(8)	8.658(8)	1.604(9)	2.317(9)	2.240(9)
$3d(3-)^2$-$3p(2+)^3$	1.974(6)	4.538(6)	5.103(6)	5.706(7)	1.144(8)	1.420(8)
$3d(3-)^3$-$3p(3+)$	9.198(4)	1.747(7)	9.885(7)	2.106(8)	2.976(8)	2.540(8)
$3d(3-)^3$-$3p(2+)^1$	4.250(6)	5.658(7)	9.639(7)	1.100(8)	1.036(8)	1.010(8)
$3d(3-)^3$-$3p(2+)^2$	2.936(6)	7.954(6)	2.589(5)	1.940(7)	4.304(7)	6.450(7)
$3d(3-)^3$-$3p(2+)^3$	3.555(7)	3.654(8)	9.899(8)	1.773(9)	2.576(9)	2.520(9)

TABLE V. (*Continued*).

	Transition rate (sec^{-1})					
Transition	Ne I	Na II	Mg III	Al IV	Si V	Si V[a]
$3d(2-)^1$-$3p(1+)^1$	2.390(7)	1.297(8)	7.600(8)	1.308(9)	1.802(9)	1.790(9)
$3d(2-)^1$-$3p(3+)$	1.742(6)	8.282(6)	2.972(7)	4.850(7)	6.631(7)	7.710(7)
$3d(2-)^1$-$3p(2+)^1$	5.549(5)	2.504(7)	1.112(7)	1.895(7)	3.115(7)	4.000(7)
$3d(2-)^1$-$3p(1+)^2$	1.780(6)	8.408(6)	9.853(6)	1.803(7)	3.220(7)	3.180(7)
$3d(2-)^1$-$3p(2+)^2$	1.437(7)	1.158(8)	2.032(8)	3.714(8)	5.630(8)	6.420(8)
$3d(2-)^1$-$3p(1+)^3$	9.816(5)	1.874(7)	3.686(7)	5.837(7)	7.573(7)	8.690(7)
$3d(2-)^1$-$3p(2+)^3$	3.277(6)	1.079(8)	2.017(8)	2.988(8)	3.580(8)	2.750(8)
$3d(2-)^1$-$3p(1+)^4$	9.696(5)	7.251(6)	1.378(7)	3.804(7)	5.972(7)	4.440(7)
$3d(2-)^2$-$3p(1+)^1$	5.858(4)	3.005(4)	8.830(4)	1.842(5)	3.622(5)	2.640(5)
$3d(2-)^2$-$3p(3+)$	1.030(6)	9.034(6)	1.900(7)	3.045(7)	4.284(7)	4.320(7)
$3d(2-)^2$-$3p(2+)^1$	1.448(7)	1.405(8)	3.450(8)	5.825(8)	8.283(8)	8.330(8)
$3d(2-)^2$-$3p(1+)^2$	1.972(7)	2.511(8)	7.926(8)	1.477(9)	2.114(9)	2.100(9)
$3d(2-)^2$-$3p(2+)^2$	1.566(5)	2.458(5)	8.652(4)	5.309(4)	6.567(5)	2.650(5)
$3d(2-)^2$-$3p(1+)^3$	4.976(6)	4.446(7)	4.387(7)	2.609(7)	1.110(7)	1.420(7)
$3d(2-)^2$-$3p(2+)^3$	1.135(6)	8.606(6)	9.452(6)	6.578(6)	3.864(6)	2.850(6)
$3d(2-)^2$-$3p(1+)^4$	0.0	5.431(4)	1.780(3)	1.168(5)	6.416(5)	1.220(6)
$3d(2-)^3$-$3p(1+)^1$	8.806(5)	5.894(4)	7.209(5)	1.410(6)	1.848(6)	4.590(5)
$3d(2-)^3$-$3p(3+)$	0.0	1.275(6)	4.801(6)	9.837(6)	1.526(7)	2.380(7)
$3d(2-)^3$-$3p(2+)^1$	3.908(5)	1.238(6)	1.839(7)	5.678(7)	1.080(8)	1.450(8)
$3d(2-)^3$-$3p(1+)^2$	9.173(6)	1.116(8)	1.471(8)	1.388(8)	1.206(8)	1.750(8)
$3d(2-)^3$-$3p(2+)^2$	1.136(6)	9.423(6)	3.618(7)	5.493(7)	5.540(7)	8.780(6)
$3d(2-)^3$-$3p(1+)^3$	2.331(7)	2.767(8)	8.221(8)	1.546(9)	2.295(9)	2.240(9)
$3d(2-)^3$-$3p(2+)^3$	6.179(6)	4.878(7)	1.559(8)	2.972(8)	4.252(8)	3.870(8)
$3d(2-)^3$-$3p(1+)^4$	2.815(6)	8.868(4)	1.028(6)	3.331(6)	2.131(6)	4.830(5)
$3d(2-)^4$-$3p(1+)^1$	7.275(6)	3.498(7)	2.790(7)	2.783(7)	2.873(7)	3.430(7)
$3d(2-)^4$-$3p(3+)$	9.401(4)	1.224(6)	2.194(7)	4.479(7)	6.516(7)	4.990(7)
$3d(2-)^4$-$3p(2+)^1$	6.226(5)	3.388(7)	9.910(7)	1.915(8)	2.577(8)	2.150(8)
$3d(2-)^4$-$3p(1+)^2$	2.861(6)	1.372(7)	4.578(7)	7.851(7)	9.731(7)	6.450(7)
$3d(2-)^4$-$3p(2+)^2$	1.211(6)	6.301(7)	1.743(8)	3.240(8)	4.741(8)	4.210(8)
$3d(2-)^4$-$3p(1+)^3$	5.043(6)	6.414(4)	6.163(5)	2.991(6)	3.817(6)	1.180(5)
$3d(2-)^4$-$3p(2+)^3$	1.643(6)	6.553(6)	5.889(6)	1.194(7)	3.466(7)	1.140(8)
$3d(2-)^4$-$3p(1+)^4$	2.560(7)	2.950(8)	8.152(8)	1.447(9)	2.090(9)	2.060(9)
$3d(1-)^1$-$3p(1+)^1$	3.132(7)	b	8.705(8)	1.501(9)	2.099(9)	2.130(9)
$3d(1-)^1$-$3p(2+)^1$	9.855(5)	b	4.298(7)	7.599(7)	1.105(8)	1.290(8)
$3d(1-)^1$-$3p(1+)^2$	5.041(4)	b	1.960(6)	4.090(6)	8.863(6)	9.150(6)
$3d(1-)^1$-$3p(2+)^2$	4.632(6)	b	8.083(7)	1.533(8)	2.333(8)	2.580(8)
$3d(1-)^1$-$3p(1+)^3$	9.187(3)	b	2.192(7)	3.913(7)	5.291(7)	7.220(7)
$3d(1-)^1$-$3p(2+)^3$	1.262(6)	b	8.866(7)	1.288(8)	1.494(8)	1.130(8)
$3d(1-)^1$-$3p(0+)^1$	3.562(6)	b	8.182(7)	1.431(8)	1.947(8)	1.810(8)
$3d(1-)^1$-$3p(1+)^4$	4.129(6)	b	8.279(7)	1.241(8)	1.529(8)	1.240(8)
$3d(1-)^1$-$3p(0+)^2$	1.418(6)	b	5.781(5)	3.219(5)	2.069(5)	2.360(4)
$3d(1-)^2$-$3p(1+)^1$	3.165(6)	b	8.025(5)	3.126(6)	3.956(6)	5.090(6)
$3d(1-)^2$-$3p(2+)^1$	2.747(6)	b	6.232(7)	1.377(8)	2.050(8)	2.050(8)
$3d(1-)^2$-$3p(1+)^2$	1.201(7)	b	3.176(8)	7.025(8)	1.097(9)	1.060(9)
$3d(1-)^2$-$3p(2+)^2$	4.761(5)	b	2.593(5)	5.991(6)	1.564(7)	1.360(7)
$3d(1-)^2$-$3p(1+)^3$	6.396(6)	b	2.369(8)	2.196(8)	1.731(8)	1.450(8)
$3d(1-)^2$-$3p(2+)^3$	6.616(5)	b	5.004(6)	2.779(6)	5.279(5)	1.060(3)
$3d(1-)^2$-$3p(0+)^1$	4.670(6)	b	3.182(8)	7.982(8)	1.250(9)	1.280(9)
$3d(1-)^2$-$3p(1+)^4$	6.902(4)	b	1.853(7)	1.379(8)	2.688(8)	2.850(8)
$3d(1-)^2$-$3p(0+)^2$	4.822(6)	b	7.857(7)	4.612(7)	2.927(7)	2.470(6)
$3d(1-)^3$-$3p(1+)^1$	2.606(6)	b	5.889(6)	2.225(6)	4.148(5)	4.220(4)
$3d(1-)^3$-$3p(2+)^1$	4.348(5)	b	1.692(7)	7.027(6)	2.640(6)	7.860(3)
$3d(1-)^3$-$3p(1+)^2$	3.573(6)	b	5.572(7)	5.231(6)	8.499(6)	2.370(7)
$3d(1-)^3$-$3p(2+)^2$	2.540(5)	b	1.914(7)	3.020(7)	3.384(7)	3.600(7)
$3d(1-)^3$-$3p(1+)^3$	3.015(6)	b	1.635(8)	5.525(8)	1.004(9)	9.310(8)
$3d(1-)^3$-$3p(2+)^3$	6.985(5)	b	5.730(6)	1.548(7)	2.435(7)	3.980(7)
$3d(1-)^3$-$3p(0+)^1$	1.286(7)	b	2.161(8)	1.520(8)	1.160(8)	6.740(7)
$3d(1-)^3$-$3p(1+)^4$	9.498(6)	b	3.241(8)	5.074(8)	7.003(8)	7.590(8)
$3d(1-)^3$-$3p(0+)^2$	5.876(6)	b	1.634(8)	3.790(8)	5.900(8)	1.550(8)

TABLE V. (*Continued*).

Transition	Transition rate (sec^{-1}) Ne I	Na II	Mg III	Al IV	Si V	Si V[a]
$3d(0-)\text{-}3p(1+)^1$	3.958(7)	2.781(8)	9.216(8)	1.590(9)	2.240(9)	2.290(9)
$3d(0-)\text{-}3p(1+)^2$	4.279(6)	1.076(7)	6.141(7)	1.137(8)	1.778(8)	1.860(8)
$3d(0-)\text{-}3p(1+)^3$	2.034(6)	3.634(7)	7.542(7)	1.134(8)	1.360(8)	1.770(8)
$3d(0-)\text{-}3p(1+)^4$	6.045(6)	8.126(7)	2.193(8)	3.576(8)	4.574(8)	3.770(8)

[a] Reference 11.

[b] These values are not calculated; see text.

have discussed earlier, we would expect the results to be at least of comparable quality since correlation effects are generally of less importance.

Bhatia *et al.*[11] have recently published a large set of computed data, including transition rates for more highly ionized ions in the sequence beginning with Si V. Their results are also included in Tables IV and V. Their calculations use the program SUPERSTRUCTURE with a configuration set that includes only up to $n=3$ orbitals. This will, in part, account for differences between the two sets of results.

More important than small differences in effective orbital wave functions is the fact that the mixing coefficients for the levels are almost certainly rather different in several cases between the two calculations; this can have a substantial effect on the transition rates. We use the $3d(2-)$ levels of Si V to illustrate. In Table VI we list our raw and corrected energy splittings along with those of Ref. 11. Their level splittings are close to our raw results, as we would expect. In addition, we given present raw and corrected L-S compositions and see that for the two higher $3d(2-)$ levels the raw and corrected results differ considerably.

In Table VII we give the transition rates from all these $3d(2-)$ levels, quoting Ref. 11, as well as the present raw and corrected results. We note two points. One is that among the "less allowed" rates, the results of Ref. 11 are generally closer to the present raw results than to the corrected ones. The other is that there can be substantial differences between the raw and corrected results. (Of course there are also many transitions where the differences are negligible since these are not sensitive to energy-splitting errors.) It is clearly important to make the corrections for some transitions.

Finally, we give in Table VIII lifetimes derived from our Na II transition rates and compare them with recent observations by Pinnington.[19] With one or two exceptions, these results are within 10% or so of the observations. A large number of other observed and computed results are quoted in Ref. 19 and the reader is referred to that paper for these other results.

IV. CONCLUSIONS

In atomic spectroscopy, energy levels are frequently well known, with rather high accuracy from observation, whereas accurate experimental transition rates are much more difficult to come by. This work takes advantage of this fact by making use of the former to assist in the calculation of the latter.

The technique can be applied to configuration-interaction calculations involving any reasonable number of mixed terms to produce accurate wave functions, providing always that the observed energies for the mixed levels of interest are available. Once again the point of these empirical correction methods is that they provide

TABLE VI. Splittings and L-S compositions for $3d(2-)$ levels in Si V. Present work designated as raw or corrected. The second and third entries for the L-S composition of each level are present raw and corrected results, respectively.

Level	E_{other}[a]	E_{raw} (cm^{-1})	E_{corr}	L-S compositions (%) ^3F	^3D	^1D	^3P
$3d(2-)^1$	0	0	0				95[b]
				0	4	2	94
				0	3	2	94
$3d(2-)^2$	4101	4203	4703	84[b]	6[b]	9[b]	0[b]
				79	8	12	0
				79	8	13	0
$3d(2-)^3$	9302	9343	9803	15[b]	34[b]	51[b]	0[b]
				20	32	48	0
				21	21	58	0
$3d(2-)^4$	10 352	10 353	10 877	0[b]	57[b]	38[b]	5[b]
				0	56	37	6
				0	68	26	6

[a] Reference 11.

[b] Reference 16.

TABLE VII. Transition rates for $3d(2-)$ levels in Si V: comparison of present raw and corrected results with those of Ref. 11.

	Transition rate (sec^{-1})		
Transition	Other[a]	Raw	Corr
$3d(2-)^1$-$3p(1+)^1$	1.790(9)	1.685(9)	1.802(9)
$3d(2-)^1$-$3p(3+)$	7.710(7)	6.909(7)	6.631(7)
$3d(2-)^1$-$3p(2+)^1$	4.000(7)	3.836(7)	3.115(7)
$3d(2-)^1$-$3p(1+)^2$	3.180(7)	3.658(7)	3.220(7)
$3d(2-)^1$-$3p(2+)^2$	6.420(8)	6.280(8)	5.630(8)
$3d(2-)^1$-$3p(1+)^3$	8.690(7)	8.536(7)	7.573(7)
$3d(2-)^1$-$3p(2+)^3$	2.750(8)	3.272(8)	3.580(8)
$3d(2-)^1$-$3p(1+)^4$	4.440(7)	4.977(7)	5.972(7)
$3d(2-)^2$-$3p(1+)^1$	2.640(5)	2.532(5)	3.622(5)
$3d(2-)^2$-$3p(3+)$	4.320(7)	4.313(7)	4.284(7)
$3d(2-)^2$-$3p(2+)^1$	8.330(8)	8.318(8)	8.283(8)
$3d(2-)^2$-$3p(1+)^2$	2.100(9)	2.108(9)	2.114(9)
$3d(2-)^2$-$3p(2+)^2$	2.650(5)	1.322(6)	6.567(5)
$3d(2-)^2$-$3p(1+)^3$	1.420(7)	5.615(6)	1.110(7)
$3d(2-)^2$-$3p(2+)^3$	2.850(6)	1.479(6)	3.864(6)
$3d(2-)^2$-$3p(1+)^4$	1.220(6)	1.111(6)	6.416(5)
$3d(2-)^3$-$3p(1+)^1$	4.590(5)	3.642(5)	1.848(6)
$3d(2-)^3$-$3p(3+)$	2.380(7)	2.413(7)	1.526(7)
$3d(2-)^3$-$3p(2+)^1$	1.450(8)	1.663(8)	1.080(8)
$3d(2-)^3$-$3p(1+)^2$	1.750(8)	1.216(8)	1.206(8)
$3d(2-)^3$-$3p(2+)^2$	8.780(6)	1.430(7)	5.540(7)
$3d(2-)^3$-$3p(1+)^3$	2.240(9)	2.329(9)	2.295(9)
$3d(2-)^3$-$3p(2+)^3$	3.870(8)	3.853(8)	4.252(8)
$3d(2-)^3$-$3p(1+)^4$	4.830(5)	8.951(5)	2.131(6)
$3d(2-)^4$-$3p(1+)^1$	3.430(7)	2.486(7)	2.873(7)
$3d(2-)^4$-$3p(3+)$	4.990(7)	5.269(7)	6.516(7)
$3d(2-)^4$-$3p(2+)^1$	2.150(8)	1.883(8)	2.577(8)
$3d(2-)^4$-$3p(1+)^2$	6.450(7)	6.658(7)	9.731(7)
$3d(2-)^4$-$3p(2+)^2$	4.210(8)	4.822(8)	4.741(8)
$3d(2-)^4$-$3p(1+)^3$	1.180(5)	1.848(5)	3.817(6)
$3d(2-)^4$-$3p(2+)^3$	1.140(8)	1.005(8)	3.466(7)
$3d(2-)^4$-$3p(1+)^4$	2.060(9)	2.128(9)	2.090(9)

[a] Reference 11.

an efficient method of correcting the unsatisfactory aspect of the level wave function, namely, the mixing coefficients, while leaving reasonably accurate orbitals and term wave functions unchanged. Alternatively, one can also, in principle, construct accurately mixed-level wave functions with accurate energy splittings by using a very large CI calculation. However this may be expensive, and if the level functions are required for other purposes, such as in subsequent scattering or photoionization calculations, computer resources may not be readily available for the scale of calculation required. Simpler, empirically corrected wave functions may be better suited to such a situation.

ACKNOWLEDGMENTS

This work was supported by a grant from the Natural Sciences and Engineering Research Council of Canada. A contribution by Mr. H. Wu for technical assistance is also acknowledged.

APPENDIX A

In this appendix we summarize details pertaining to the 5×5 matrix eigenvalue inversion problem. This same approach applies to higher dimensions though, of course, the algebra is more complicated. In the following, we work in the physical basis and denote the diagonal matrix elements by H_i and the off-diagonal elements by δ_{ij}. The secular equation can be written in terms of the eigenvalues λ_i or in terms of the elements of the Hamiltonian matrix H as

$$(\lambda-\lambda_1)(\lambda-\lambda_2)(\lambda-\lambda_3)(\lambda-\lambda_4)(\lambda-\lambda_5)=0\ , \tag{A1}$$

$$\mathrm{Det}(H-\lambda I)=0\ . \tag{A2}$$

Expanding these and equating coefficients of like powers of λ we obtain the following five equations:

$$\sum H_i=\sum \lambda_i\ , \tag{A3}$$

$$\sum H_iH_j=\sum(\lambda_i\lambda_j+\delta_{ij}^2)\ , \tag{A4}$$

$$\sum H_iH_jH_k-\sum\delta_{ij}^2(H_k+H_l+H_m)$$

$$=\sum(\lambda_i\lambda_j\lambda_k-2\delta_{ij}\delta_{ik}\delta_{jk})\ , \tag{A5}$$

TABLE VIII. Lifetimes of 3*p* and 3*d* levels in Na II: comparison of present corrected results with observed values.

Level	Lifetime (nsec) Calculated	Observed[a]
$3p(3+)$	4.40	4.98±0.15
$3p(2+)^1$	4.45	5.34±0.20
$3p(2+)^2$	4.45	4.59±0.20
$3p(2+)^3$	4.02	4.20±0.15
$3p(1+)^1$	6.44	6.20±0.24
$3p(1+)^2$	4.41	
$3p(1+)^3$	4.43	4.84±0.20
$3p(1+)^4$	3.99	
$3p(0+)^1$	3.71	3.76±0.15
$3p(0+)^2$	2.13	
$3d(4-)$	2.14	2.7±0.3
$3d(3-)^1$	2.26	2.6±0.3
$3d(3-)^2$	2.25	2.9±0.4
$3d(3-)^3$	2.24	
$3d(2-)^1$	2.37	3.0±0.4
$3d(2-)^2$	2.20	
$3d(2-)^3$	2.23	2.1±0.3
$3d(2-)^4$	2.23	
$4s(2-)$	2.28	2.4±0.4

[a]Reference 19.

$$\begin{aligned}\sum H_iH_jH_kH_l &- \sum \delta_{ij}^2(H_kH_l+H_lH_m+H_mH_k) \\ &+2\sum \delta_{ij}\delta_{ik}\delta_{jk}(H_l+H_m) \\ &= \sum(\delta_{ij}^2\delta_{kl}^2+\lambda_i\lambda_j\lambda_k\lambda_l)-\sum \delta_{ij}\delta_{ik}\delta_{lj}\delta_{lk}\ , \qquad \text{(A6)}\end{aligned}$$

$$\mathrm{Det}H=\lambda_1\lambda_2\lambda_3\lambda_4\lambda_5\ . \qquad \text{(A7)}$$

Obvious restrictions apply to the foregoing summations along the lines $i<j$, etc. to ensure that a given term appears only once in a given sum.

We seek to solve these equations for the diagonal elements H_i in terms of the observed eigenvalues λ_i and the off-diagonal elements δ_{ij}, all of which are assumed to be accurately known.

There are up to 5! solution sets $\{H_i\}$ to these equations. We will not go into a detailed discussion of their solution. Simplifications are possible and they can then be solved numerically using Newton's method. An important practical matter can be mentioned usefully, however. This concerns the related questions of choosing good starting estimates for the H_i, in order to obtain convergence and selecting the desired physical solution from the 5! possible ones. We seek the intersection of five hypersurfaces unless we attempt a messy and perhaps not very rewarding algebraic reduction of the equations to yield a lower-dimension problem. We have no graphical aid, as we had in previously published work, to show us where the intersection points lie, but the following approach has been found to work very effectively.

We seek the solution set $\{H_i\}$ for the physical $\{\lambda_i\}$ with the $\{\delta_{ij}\}$ remaining fixed throughout the calculation. The problem is that a multidimensional Newton's method calculation will converge only if the starting estimates for the H_i are reasonably good. We achieve this by moving in a sequence of, say, five or ten steps from the raw, calculated set of λ_i to the observed set, using as a starting estimate at each step the exact solution of the previous step; and, of course, the point is that we have the exact raw solution as the zeroth step to begin the procedure. In practice, after the first step, we improve convergence markedly by using as starting estimates for the H_i linear extrapolations of the previous iterations. By this process of "numerical continuation," under the (unproved) assumption that no other solution set is nearby so that one accidently converges in error to that wrong solution, we solve the starting estimate-convergence problem and predict rather than require as input the Landé *g* factors g_L.

APPENDIX B

In this appendix we give some technical details concerning the corrections made to the actual code in use under various circumstances. This includes some discussion on correcting the Breit-Pauli matrix in the more general case when there is more than one strongly mixed term for a given $SL\Pi$ subspace.

Hitherto, in Appendix A, we have implicitly used the physical nonrelativistic terms that are coupled by the magnetic interactions as basis set. In practice one is likely to be computing in the algebraic basis of terms from the various configurations. A $J\Pi$ block of the Breit-Pauli matrix has, in this algebraic basis, a much larger dimension than 5×5, say, reflecting the fact that there is in general a number of correlation terms.

In the frequently occurring case where each $SL\Pi$ subspace of the $J\Pi$ space contains only one strongly coupled term of physical interest, each H_i correction is achieved by applying a common shift to all the diagonal elements of the corresponding $SL\Pi$ block of the Breit-Pauli matrix. This will appear as a special case of the analysis later in this appendix. If there is more than one strongly coupled term from a given $SL\Pi$ block, this procedure would result in the same correction of the terms in the same block, whereas the corrections will be different, in general. For example, we recall that in Na II the 3*d* and 4*s* terms in the ^3P block are strongly mixed but do not share a common correction so one cannot apply a common shift to the diagonal elements of the ^3P block in the algebraic basis.

The following discussion shows how the corrections are handled where there are several terms in a given block and where the code uses the algebraic basis of terms from the various configurations, as in the case of SUPERSTRUCTURE. We designate the Breit-Pauli matrix in the physical basis by **H** and in the algebraic basis by $\mathbf{H}^A$ and designate the matrix whose columns are the eigenvectors of the nonrelativistic Hamiltonian by **V**. The connection is then simply

$$\mathbf{H}^A=\mathbf{V}\mathbf{H}\mathbf{V}^T\ . \qquad \text{(B1)}$$

Correcting for the observed eigenvalue input means a shift in the diagonal elements of **H**:

$$\mathbf{H}\rightarrow\mathbf{H}+\boldsymbol{\epsilon}\ , \qquad \text{(B2)}$$

where $\epsilon_{ij}=\delta_{ij}\epsilon_i$ are the calculated diagonal element corrections and δ_{ij} is the Kroenecker symbol. The effect in the algebraic basis in which the calculation is actually performed is to shift all the elements of the Hamiltonian matrix in general according to

$$\mathbf{H}^A \rightarrow \mathbf{H}^A + \mathbf{E} , \tag{B3}$$

where $\mathbf{E}=\mathbf{V}\epsilon\mathbf{V}^T$ or, in terms of components, $E_{ij}=\epsilon_l V_{il} V_{jl}$.

There are simplifications under various circumstances. One that is always present is that the matrix **V** is block diagonal, having components in only one $SL\Pi$ subspace of a given $J\Pi$ space. Consequently, the algebraic correction matrix **E** is also block diagonal. Also, if only one vector of a given $SL\Pi$ subspace is of physical interest and strongly coupled to the other subspaces of interest, we can shift all energies of the corresponding $SL\Pi$ block of **H** by a common amount ϵ. Then using the fact that **V** is an orthogonal matrix, $E_{ij}=\epsilon\delta_{ij}$ is the common correction shift for the diagonal elements in the algebraic basis, as we noted earlier in this appendix.

On the other hand, if several vectors in a given block are strongly mixed in the level of interest, they will, in general, have different nonzero shifts and the full correction expression (B3) is to be used to adjust all the elements of the corresponding block of $\mathbf{H}^A$. For example, in a given subspace, we might have three nonzero corrections ϵ_α, ϵ_β, and ϵ_γ for terms of physical interest. In this case, the correction to the Breit-Pauli matrix in the algebraic basis is given by

$$E_{ij}=\epsilon_\alpha V_{i\alpha}V_{j\alpha}+\epsilon_\beta V_{i\beta}V_{j\beta}+\epsilon_\gamma V_{i\gamma}V_{j\gamma} \quad (\alpha,\beta,\gamma \text{ not summed}) . \tag{B4}$$

---

[1] W. Eissner, M. Jones, and H. Nussbaumer, Comput. Phys. Commun. **8**, 270 (1974).

[2] A. Hibbert, J. Phys. B **12**, L661 (1979).

[3] C. J. Zeippen, M. J. Seaton, and D. C. Morton, Mon. Not. R. Astron. Soc. **181**, 527 (1977).

[4] T. M. Luke, J. Phys. B **18**, 589 (1985).

[5] T. M. Luke, J. Phys. B **19**, 843 (1986).

[6] K. Aashamar, T. M. Luke, and J. D. Talman, J. Phys. B **12**, 3455 (1979).

[7] T. M. Luke, Phys. Scr. **23**, 1066 (1981).

[8] E. H. Pinnington, J. Opt. Soc. Am. **57**, 271 (1967).

[9] W. C. Martin and B. Zalubas, J. Phys. Chem. Ref. Data **10**, 164 (1981).

[10] C.-M. Wu, Ph.D. thesis, University of British Columbia, 1971.

[11] A. K. Bhatia, U. Feldman, and J. F. Seely, Atom. Data Nucl. Data Tables **32**, 435 (1985).

[12] J. E. Hansen, unpublished material referred to in Ref. 9.

[13] E. Andersson and G.-A. Johannesson, Phys. Scr. **3**, 203 (1971).

[14] P. W. Murphy, Astrophys. J. **153**, 301 (1968).

[15] V. Kaufman, M.-C. Artru, and W. L. Brillet, J. Opt. Soc. Am. **64**, 197 (1974).

[16] W. L. Brillet, Phys. Scr. **13**, 289 (1976).

[17] P. Hartmetz and H. Schmoranzer, Phys. Lett. **93A**, 405 (1983).

[18] P. Hartmetz and H. Schmoranzer, Z. Phys. A **317**, 1 (1984).

[19] E. H. Pinnington, W. Ansbacher, and P. Meenakshi Raja Rao, Phys. Lett. **97A**, 337 (1983).