# Configuration $1s^2 2s3p$ in the sequence Ne VII–Fe XXIII: Level energies and lifetimes

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Energies were computed for the $2s3p$ levels in the Be isoelectronic sequence from $Z=10$ to 26. Multiconfiguration wave functions of form $(2s3p,2p3s,2p3d)$ were obtained from the program MCHF77. The Pauli relativistic corrections were calculated and the $2\times2$ spin-orbit-interaction matrix was diagonalized to obtain the $^1P_1$-$^3P_1$ interval and mixing coefficient. Results agree with observations and with other self-consistent-field calculations at $Z=10$, 23, and 26. The avoided crossing of the two $J=1$ levels is found to occur at $Z=21$. Finally, the radiative-decay probabilities of the mixed $J=1$ levels were calculated; results are compared with other calculations and checked against a recent experiment in Ne VII.

## I. INTRODUCTION

Recent experiments[1,2] and calculations[3–5] have called attention to the mixing of the $^1P$ and $^3P$ terms of the $2s\,3p$ configuration in the beryllium isoelectronic sequence. For moderate stages of ionization (C III–Ne VII) the $(2s\,3p)^1P_1$ level is known to be lower in energy than the $(2s\,3p)^3P_1$, with the mixing of the two levels being small but increasing with nuclear charge $Z$. For these ions, Russell-Saunders coupling is still generally very good; correlation is more important than relativity. However, for the $(2s\,3p)P$ terms, the configuration-interaction (CI) effects result in an exceptionally small electrostatic splitting, so that the spin-orbit interaction, although relatively weak, can produce appreciable singlet-triplet mixing.[5,6] As $Z$ increases, the mixing becomes very strong, the two levels cross, and for Fe XXIII the lower $J=1$ level has a larger triplet than singlet amplitude.[3,7–9]

Self-consistent-field calculations, including CI, have been carried out on the $2s\,3p$ states of the beryllium sequence for nuclear charge $Z=6$–$15$,[4–6,10,11] $Z=23$ (Ref. 8), and $Z=26$.[8,9] Two sets of $1/Z$ perturbation calculations have been done, which give different predictions for the location of the avoided crossing; that is, for the value of $Z$ above which the $^3P_1$ lies below the $^1P_1$. Also, Refs. 3 and 8 are in disagreement about the ordering of these two levels in V XX ($Z=23$).

An experimental signature of this singlet-triplet mixing is of course the difference between the mean lives of the levels of the $(2s\,3p)^3P$ term; the singlet component of the $J=1$ level produces the relatively strong intercombination lines connecting it to singlet levels of the $n=2$ complex thus shortening its mean life compared to that of the $J=0,2$ levels.[1] Thus comparison between calculated and measured values of this mean-life difference provides an interesting test of theory: the system is simple enough to be tractable and yet the calculation must involve CI, intermediate coupling (IC), and relativistic effects. For N, O, and F this comparison has been done by Hibbert[5] and the results are quite satisfactory: the observed[1] mean-life difference can be understood as arising primarily from the $(2s^2)^1S_0$-$(2s\,3p)^3P_1$ intercombination line, with about a 10% contribution from decay to the $(2p^2)^1D_2$ level.[5] For Ne VII on the other hand, existing theoretical work is insufficient to provide a precise comparison with the recent experimental results of Hardis *et al.*[2]

This paper describes a series of *a priori* calculations of the $(2s\,3p)^{1,3}P$ levels in the Be sequence for $Z=8$–$26$. The results include energy levels, mixing coefficients, and radiative decay modes. Wave functions and nonrelativistic energies were obtained for the $2s\,3p$ and $2s^2$ levels from the multiconfiguration Hartree-Fock (MCHF) program MCHF77 of Froese Fischer[12]; relativistic (Pauli) corrections were calculated from these wave functions by perturbation theory. As the final step in obtaining the $2s\,3p$ level energies, the mixing of the singlet and triplet $J=1$ levels produced by the spin-orbit interaction was computed, again using the MCHF wave functions. The $2s\,3p$ excitation energies calculated in this way compare well with observations[2,3,8,13–16] and CI calculations[4–6,8,11] at both the low- and high-$Z$ limits of the present study, as shown in Table I. Finally the electric dipole ($E1$) radiative decay probabilities were calculated from the resulting mixed MCHF states via the standard dipole length operator.

## II. CALCULATIONS

The MCHF approach requires fewer basis states than the CI method, because the radial wave functions are recomputed to minimize each term energy. This of course requires more computer time per interacting configuration and complicates the task of calculating relativistic corrections and transition probabilities because similar orbitals belonging to different states have no orthonormality properties. For the ions considered here the strong nuclear Coulomb potential produces a clear separation in energy of states belonging to different complexes (states having a different set of principal quantum numbers). Thus, in a MCHF representation of the $^1P$ and $^3P$ states under consideration here, it is sufficient to use only the odd-parity configurations of the "$K^2LM$" complex: $2s\,3p$, $2p\,3s$, and $2p\,3d$. Similarly the ground state was computed via the

 

TABLE I. Excitation energies of $2s\,3p$ levels ($10^3$ cm$^{-1}$).

| Spectrum | Term | $J$ | MCHF | Observed | CI Calculations |
|---|---|---|---|---|---|
| O V | $^3P$ | 2 | 582.5 | 582.92[a] | 582.39[b] |
| | | 1 | 582.4 | 582.84[a] | 582.31[h] 581.44[i] |
| | | 0 | 582.4 | 582.80[a] | 582.28[h] |
| | $^1P$ | 1 | 580.5 | 580.83[a] | 580.48[h] 579.50[i] |
| Ne VII | $^3P$ | 2 | 1028.4 | 1028.8[b] | |
| | | 1 | 1028.1 | 1028.5[b] | 1027.3[j] 1026.0[i] |
| | | 0 | 1028.0 | 1028.4[b] | |
| | $^1P$ | 1 | 1025.3 | 1025.6[c] | 1025.4[j] 1023.1[i] |
| Mg IX | $^3P$ | 2 | 1597.4 | | |
| | | 1 | 1596.8 | | |
| | | 0 | 1596.4 | | |
| | $^1P$ | 1 | 1593.4 | 1593.6[d] | |
| S XIII | $^3P$ | 2 | 3108.4 | | |
| | | 1 | 3106.4 | | |
| | | 0 | 3104.4 | | |
| | $^1P$ | 1 | 3101.8 | | |
| Ca XVII | $^3P$ | 2 | 5122.7 | | |
| | | 1 | 5119.5 | | |
| | | 0 | 5111.8 | | |
| | $^1P$ | 1 | 5110.4 | 5113[e] | |
| V XX | $^3P$ | 2 | 6969.5 | | |
| | | 1 | 6948.9 | 6944.0[f] | 6947.8[f] |
| | | 0 | 6949.3 | | |
| | $^1P$ | 1 | 6966.0 | 6963.8[f] | 6967.7[f] |
| Fe XXIII | $^3P$ | 2 | 9109.9 | | |
| | | 1 | 9076.4 | 9076.1[g] | 9075.2[f] |
| | | 0 | 9075.4 | | |
| | $^1P$ | 1 | 9106.7 | 9107.5[g] | 9110.0[f] |

[a]Bockasten and Johansson (Ref. 13).
[b]Hardis *et al.* (Ref. 2).
[c]Tondello and Paget (Ref. 14).
[d]Soderqvist (Ref. 15).
[e]Fawcett and Hayes (Ref. 16).
[f]Bromage *et al.* (Ref. 8).
[g]Boiko *et al.* (Ref. 3).
[h]Hibbert (Ref. 11).
[i]Glass (Ref. 4).
[j]Hibbert (Ref. 5).

MCHF representation $(2s^2,2p^2)^1S$. The configuration-mixing coefficients which result are significantly different for the $^1P$ and $^3P$ cases, but in each case they vary quite slowly and smoothly as $Z$ increases from 8—26, as shown in Table II. Unlike the case of intershell correlations, we expect the coefficients for mixing within a complex to be roughly independent of $Z$.

In order to identify the contribution of electron correlations to the level intervals, single-configuration Hartree-Fock (HF) calculations were also performed for the $2s\,3p$ levels. As expected, the HF interval is normal ($^3P$ below $^1P$) in all cases; it is the correlation contribution which in-

TABLE II. Mixing coefficients for $(2s\,3p)^{1,3}P$ levels in the Be isoelectronic sequence.

| | O | Ne | Mg | S | Ca | V | Fe |
|---|---|---|---|---|---|---|---|
| $\langle 2s\,3p \mid {}^1P\rangle$ | 0.9502 | 0.9476 | 0.9467 | 0.9440 | 0.9424 | 0.9415 | 0.9409 |
| $\langle 2p\,3s \mid {}^1P\rangle$ | −0.2961 | −0.3035 | −0.3069 | −0.3143 | −0.3188 | −0.3211 | −0.3229 |
| $\langle 2p\,3d \mid {}^1P\rangle$ | 0.0966 | 0.0999 | 0.0983 | 0.1005 | 0.1015 | 0.1020 | 0.1024 |
| $\langle 2s\,3p \mid {}^3P\rangle$ | 0.9908 | 0.9908 | 0.9913 | 0.9914 | 0.9915 | 0.9916 | 0.9916 |
| $\langle 2p\,3s \mid {}^3P\rangle$ | −0.0803 | −0.0791 | −0.0780 | −0.0754 | −0.0735 | −0.0724 | −0.0716 |
| $\langle 2p\,3d \mid {}^3P\rangle$ | 0.1088 | 0.1094 | 0.1062 | 0.1069 | 0.1072 | 0.1074 | 0.1075 |
| IC coefficient $\alpha$ | 0.0257 | 0.0584 | 0.1203 | 0.3826 | 0.6675 | −0.6447 | −0.5882 |

TABLE III. Contributions to the level interval $^3P_1$-$^1P_1$ ($10^3$ cm$^{-1}$), where A is the HF term interval, B is the correlation energy difference (MCHF-HF), C is the relativistic mass correction, D is the Darwin relativistic correction, E is the diagonal spin-orbit interaction, F is the spin-orbit mixing, and G is the total predicted interval.

| | O | Ne | Mg | S | Ca | V | Fe |
|---|---|---|---|---|---|---|---|
| A | −6.250 | −8.339 | −10.58 | −15.27 | −20.09 | −23.75 | −27.42 |
| B | 8.248 | 11.359 | 14.46 | 20.58 | 26.68 | 31.27 | 35.84 |
| C | −0.160 | −0.412 | −0.90 | −3.18 | −8.40 | −15.33 | −25.86 |
| D | 0.125 | 0.321 | 0.69 | 2.44 | 6.41 | 11.68 | 19.66 |
| E | −0.038 | −0.130 | −0.33 | −1.31 | −3.62 | −6.74 | −11.55 |
| F | 0.003 | 0.019 | 0.10 | 1.36 | 8.10 | −14.21 | −21.02 |
| G | 1.927 | 2.818 | 3.44 | 4.61 | 9.09 | −17.09 | −30.35 |

verts these terms for intermediate $Z$.

Diagonal relativistic corrections were computed as the expectation values of the standard Pauli Hamiltonian (Darwin and "mass" terms) treated as a one-electron operator.[17] The desired $^1P_1$-$^3P_1$ mixing coefficient $\alpha$ and predicted level energies were obtained by computing all the spin-orbit matrix elements between the MCHF states $(2s\,3p,2p\,3s,2p\,3d)^1P_1$ and $(2s\,3p,2p\,3s,2p\,3d)^3P_1$, and then diagonalizing the resulting $2\times 2$ energy matrix.

Table III lists the various contributions to the $^3P_1$-$^1P_1$ energy difference. Note that the "correlation" contribution (defined as the difference between the MCHF and HF term intervals) is the dominant one at low $Z$, and even for Fe XXIII is the largest single contribution. If this were not true, the present method would be of questionable validity, since it treats the CI self-consistently, but only introduces IC between the two $J=1$ levels after the MCHF wave functions have been determined. Table II lists the coefficients $C_{sp}$, $C_{ps}$, and $C_{pd}$, which give the amplitudes of the $2s\,3p$, $2p\,3s$, and $2p\,3d$ configurations in the separate MCHF solutions for the triplet and singlet levels, along with the predicted singlet-triplet mixing coefficient $\alpha$.

In order to predict the shortening of the $^3P_1$ mean life, relative to the $J=0,2$ levels, as a result of the singlet-triplet mixing, the radiative transition probabilities to all the even-parity singlets in the ground complex $(K^2L^2)$ are needed. Therefore in addition to the ground state $(2s^2,2p^2)^1S$, the MCHF states $(2p^2,2s^2)^1S$ and $(2p^2 2s\,3d)^1D$ were also calculated. The MCHF wave functions obtained for the latter two states are regarded as first approximations only; no attempt has been made to do a careful study of intershell correlations or achieve good agreement with the very well-known energy levels of the ground complex. However, for the present purpose these wave functions should be adequate, particularly as the two corresponding intercombination lines are considerably weaker than the one to the ground state and so make minor contributions to the mean-life decrease of the $(2s\,3p)^3P_1$ level. Finally, the required triplet transition probabilities were calculated approximately using for the lower states wave functions of the form $(2s\,3s,2p\,3p)^3S$ and $(2p^2)^3P$.

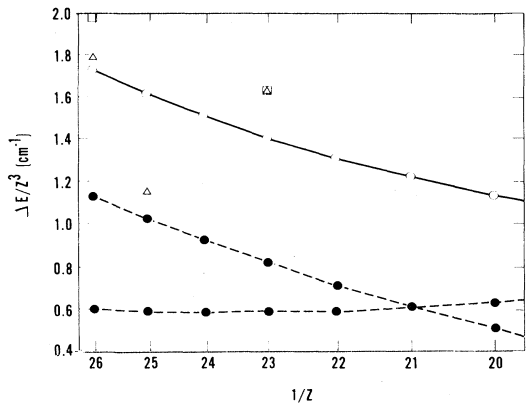


FIG. 1. $Z$ dependence of $(2s\,3p)^3P_1$-$^1P_1$ level interval. Dashed lines are the two unmixed levels; note crossing at $Z=21$. Solid line, MCHF level interval (present calculation); squares, relativistic CI calculations (Ref. 8); triangles, observed intervals ($Z=25$ and 26, Ref. 3; $Z=23$, Ref. 8).

## III. RESULTS

The relatively straightforward *a priori* MCHF calculations of the $2s\,3p$ levels reported here use only a small number of configurations and treat the relativistic contributions perturbatively; nevertheless, they give excitation energies which agree well with experiment and with CI calculations at both ends of the sequence O V—Fe XXIII, as shown by Table I. Thus it seems that this MCHF method provides reasonably reliable predictions of the energies and mean lives of the $2s\,3p$ levels for this portion of the Be sequence. The present results confirm the general trend of previous calculations in the range $Z=14$—26, which have used $1/Z$ perturbation theory. However, there are quanti-

TABLE IV. $E1$ decays of the $(2s\,3p)^3P$ levels in Ne VII. Listed are transition probabilities in $ns^{-1}$.

| Lower term | Wavelength | MCHF | Expt.[a] | Other calculations | | | |
|---|---|---|---|---|---|---|---|
| $(2s\,3s)^3S$ | 1992 Å | 0.213 | | 0.209[b] | 0.211[c] | 0.209[d] | 0.208[e] |
| $(2p^2)^3P$ | 136 | 0.319 | | 0.217[b] | 0.397[c] | | 0.4[e] |
| Total from $J=0,2$ levels | | 0.532 | 0.56 | 0.42[b] | 0.61[c] | | 0.6[e] |
| $(2s^2)^1S$ | 97 | 0.3865 | | | 0.275[f] | 0.80[g] | |
| $(2p^2)^1S$ | 161 | 0.0006 | | | | | |
| $(2p^2)^1D$ | 142 | 0.0225 | | | | | |
| | | 0.410 | 0.43 | | | | |
| Total from $J=1$ level | | 0.942 | 1.0 | | | | |

[a]Hardis *et al.* (Ref. 2).
[b]Nussbaumer (Ref. 18).
[c]Hummer and Norcross (Ref. 10).
[d]Hibbert (Ref. 19).
[e]Glass (Ref. 4).
[f]Hibbert (Ref. 5).
[g]Odabasi (Ref. 6).

tative differences as should be expected considering the importance of the correlation effects. An example of this is the location of the avoided crossing. Boiko *et al.*[3] find the crossing between $Z=24$ and 25, while Sampson *et al.*[7] find it between 14 and 18. Figure 1 shows the MCHF-predicted interval between the two $J=1$ levels plotted as a function of $1/Z$, both with and without singlet-triplet mixing; the crossing is clearly predicted to be at $Z=21$ (Sc XVIII). Also plotted in Fig. 1 for comparison are the observed intervals[3,8] and the predictions of relativistic CI calculations.[8]

Another specific result is the calculation of theoretical mean lives for the $(2s\,3p)^3P$ levels in Ne VII for comparison with the recent experiment of Hardis *et al.*[2] Table IV shows the computed $E1$ transition probabilities and compares them with experiment and other calculations. The agreement with experiment seems good enough to support the view that the observed reduction in mean life of the $J=1$ level is indeed caused by the calculated intercombination lines, and that the MCHF wave functions and singlet-triplet mixing coefficients found here give a reasonable description of these levels.

Having achieved good results for $Z=10$, 23, and 26, it then seems reasonable to use the present method to predict the energies and radiative decay probabilities of the $(2s\,3p)^3P$ levels for intermediate $Z$. The energies have already been discussed and are listed in Table I; Table V gives the predicted $E1$ transition probabilities and approximate wavelengths for the spectra Mg IX, S XIII, and

TABLE V. Predicted $E1$ decays of the $(2s\,3p)^3P$ levels. Wavelengths are in angstroms; transition probabilities $A$ are in $ns^{-1}$.

| Transition | Mg IX | | S XIII | | Ca XVII | |
|---|---|---|---|---|---|---|
| | Wavelength | $A$ | Wavelength | $A$ | Wavelength | $A$ |
| $^3P_{0,2}$-$(2s\,3s)^3S$ | 1522, 1545 | 0.283 | 1028, 1071 | 0.443 | 751, 817 | 0.67 |
| $^3P_{0,2}$-$(2p^2)^3P$ | 82 | 0.946 | 39 | 5.96 | 23 | 21.0 |
| $^3P_1$-$(2s\,3s)^3S$ | 1536 | 0.279 | 1049 | 0.378 | 769 | 0.373 |
| $^3P_1$-$(2p^2)^3P$ | 82 | 0.932 | 39 | 5.09 | 23 | 11.62 |
| $^3P_1$-$(2p^2)^1S$ | 92 | 0.009 | 42 | 0.33 | 24 | 2.5 |
| $^3P_1$-$(2p^2)^1D$ | 84 | 0.215 | 40 | 7.89 | 23 | 63.0 |
| $^3P_1$-$(2s^2)^1S$ | 63 | 4.43 | 32 | 192 | 20 | 1694 |

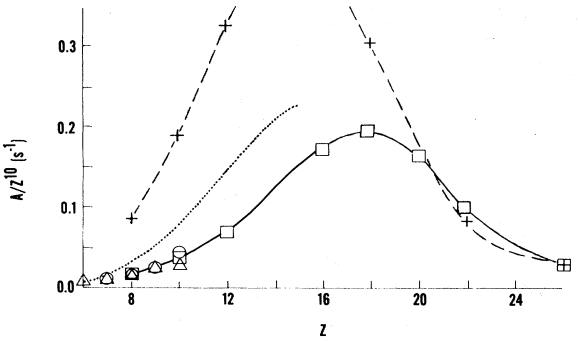


FIG. 2. $Z$ dependence of transition probability $A$ for intercombination line $(2s^2)^1S_0$-$(2s\,3p)^3P_1$. Solid line (squares), present MCHF calculations; dashed line (crosses), $1/Z$ perturbation calculation (Refs. 7 and 20); dotted line, CI calculations of Odabasi (Ref. 6); triangles, CI calculations of Hibbert (Ref. 5); open circles, experiments (Refs. 1 and 2).

Ca XVII. Finally, the predicted $A$ value for the intercombination line $(2s^2)^1S_0$-$(2s\,3p)^3P_1$ is plotted against $Z$ in Fig. 2, and compared with experiments.[1,2] and other calculations.[5–7,20] The present result agrees with CI calculations and experiments at low $Z$ and approaches the $(1/Z)$-expansion, IC results of Sampson *et al.*[7] at high $Z$ as is expected. If an experimental determination of this transition probability could be made for a value of $Z$ in the range 14—18 it would be a nice test of the present computational approach.

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[1]L. Engstrom, B. Denne, S. Huldt, J. O. Ekberg, L. J. Curtis, E. Veje, and I. Martinson, Phys. Scr. 20, 88 (1979).
[2]J. E. Hardis, L. J. Curtis, P. S. Ramanujam, A. E. Livingston, and R. L. Brooks, Phys. Rev. A 27, 257 (1983).
[3]V. A. Boiko, S. A. Pikuz, U. I. Safronova, and A. Ya. Faenov, J. Phys. B 10, 1253 (1977).
[4]R. Glass, J. Phys. B 12, 1633 (1979).
[5]A. Hibbert, J. Phys. B 12, L661 (1979).
[6]H. Odabasi, J. Opt. Soc. Am. 59, 583 (1969).
[7]D. H. Sampson, R. E. H. Clark, and S. J. Goett, Phys. Rev. A 24, 2979 (1981).
[8]G. E. Bromage, R. D. Cowan, B. C. Fawcett, and A. Ridgeley, J. Opt. Soc. Am. 68, 48 (1978).
[9]A. K. Bhatia and H. E. Mason, Astron. Astrophys. 103, 324 (1981).
[10]D. G. Hummer and D. W. Norcross, Mon. Not. R. Astron. Soc. 168, 263 (1974).
[11]A. Hibbert, J. Phys. B 13, 1721 (1980).
[12]C. Froese Fischer, Comput. Phys. Commun. 1, 151 (1969); 14, 145 (1978).
[13]K. Bockasten and K. B. Johansson, Ark. Fys. 37, 563 (1968).
[14]G. Tondello and T. M. Paget, J. Phys. B 3, 1757 (1970).
[15]W. C. Martin and R. Zalubas, J. Phys. Chem. Ref. Data 9, 1 (1980); J. Soderqvist, Ark. Mat. Astr. Fys. 30A, 1 (1944).
[16]B. C. Fawcett and R. W. Hayes, Mon. Not. R. Astron. Soc. 170, 185 (1975).
[17]H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer, Berlin, 1957), Sec. 13.
[18]H. Nussbaumer, Astron. Astrophys. 16, 77 (1972).
[19]A. Hibbert, J. Phys. B 9, 2805 (1976).
[20]D. H. Sampson (private communication).