Theoretical lifetimes of Nb II $z\ 4d^3\ 5p\ {}^5G^o_3$ and ${}^3D^o_3$ levels

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Using relativistic configuration-interaction wave functions, we have obtained length and velocity f values for all lower $J=2,3,4$ $(4d+5s)^4$ levels connected to the $z\ 4d^3 5p\ {}^5G^o_3$, and ${}^3D^o_3$ levels. Our lifetime results for length and velocity operators are $\tau({}^5G^o_3)=5.16$ and 6.53 ns, respectively, and $\tau({}^3D^o_3)=4.67$ and 5.60 ns, respectively. These are in good agreement with the experimental values of 5.8–6.2 and 5.0 ns. As we find for hyperfine structure, the $4d^4$, $4d^3 5s$ interactions are important in generating accurate lifetime and f-value results.

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I. INTRODUCTION AND THEORY

Recently, we have begun work on $(d+s)^n$ transition-metal states, using relativistic configuration-interaction methods to generate hyperfine structure (hfs) for the $J=2$ Nb II states [1], for example. For many states d^n and $d^{(n-1)}s$ eigenfunctions interact strongly, due to near degeneracy effects. This was found to have important consequences for hfs [1,2], and here we investigate just what the impact on the f values might be. There are three reasons for choosing to investigate Nb II lifetimes: (i) They are important in determining the solar abundance of Nb II: (ii) measurements of its excited-state lifetimes have already been made [3,4]; and (iii) we had already [1] created accurate wave functions for the $J=2$ states.

When there is near degeneracy of d^n and $d^{(n-1)}s$ states, it is important that relativistic effects be included from the start, because they can contribute differentially [5] up to several tenths of an eV. Some time ago, we made the decision to implement a fully relativistic many-body theory, instead of a perturbation-based one. This distinction begins with the choice of the Hamiltonian—we use the Dirac-Coulomb (Breit) Hamiltonian rather than the low-Z Pauli approximation. We feel that this simplifies the algebra and is valid for all Z. It may not be quite as competitive for very low-Z species, where relativistic effects are so small that perturbation theory can be more appropriate. We begin by constructing a zeroth-order wave function, from a multiconfiguration Dirac-Fock solution, using Desclaux's program [6]. These are antisymmetrized eigenstates of J^2 and J_z, built from relativistic one-electron functions, i.e., spinors.

We improve this wave function by using first-order perturbation theory to select its form (configurations, one-electron symmetries) and the relativistic configuration interaction (RCI) to determine its parameters—configuration coefficients and effective charges (Z^*) for the extra ("virtual") radial functions. The virtuals are chosen to be relativistic screened hydrogenic functions to avoid potential problems [7] of variational collapse. With the choice $n=l+1$, a single function can represent up to 90% of the correlation energy associated with a specific symmetry (κ).

The RCI function is thus built by making single and double excitations from the zeroth-order function. In the case of near degeneracy, several zeroth-order functions [e.g., all the $(d+s)^4$ eigenvectors] may have to be used, and the process is a multireference one [2,8]. Here the $(d+s)^4$ $J=2,3,4$ states require a multireference treatment, which is detailed elsewhere [1,8]. From observation [9] the $z\ 4d^3 5p\ {}^5G^o_3$ and ${}^3D^o_3$ states are fairly well isolated from $(4d^2 5s+4d5s^2)5p$ states, and the $4d^3$ electrons are mainly coupled to ${}^4F$. The MCDF solution is 96% ${}^4F$ for ${}^5G^o_3$ and 85% ${}^4F$ for ${}^3D^o_3$. We thus have used the six $4d^3({}^4F)5p\ J=3$ states as reference functions when creating the RCI functions [10].

The presence of so many open d electrons, followed by single and double excitations from closed-core subshells, gives rise to configurations each having as many as several thousand vectors. If not controlled, this could give rise to RCI matrices of order $\approx 10^5$—too large to be manageable in this context. To handle this efficiently, we rotate these functions [11] to maximize the number of zero interactions with all reference functions, and then discard all vectors producing these zeros. This reduces our RCI matrices to order 7000 or less.

Once the wave functions are created, the electric dipole transition probabilities between levels are obtained using the formalism outlined earlier [7] which is based on the work of Grant [12]. We calculate in both the length and the velocity gauges, using the experimental [9] excitation energies. These results would be equal, if the Ψ's were exact. Since each wave function is calculated independently, the wave functions for different states are not orthornormal. We take the nonorthornormality effects completely into account by using methods given elsewhere [7]. Since the Nb II wave functions are large (see the next section), calculation times can be significant. Though we have speeded up our f-value program [13] ≈ 100 times from the original version, calculation times as long as 2 h per f value were found on a Sparc 10.

II. RESULTS AND ANALYSIS

The Nb II $(4d+5s)^4$ $J=2,3,4$ wave functions are the largest and energetically most accurate. In addition to

TABLE I. Calculated f values for $(d+s)^4$ $J=2,3,4$ to $z\,4d^3 5p\,{}^5G^o_3$, ${}^3D^o_3$ transitions. Only f values >0.005 are shown. Results obtained using experimental excitation energies. The present "Dirac-Fock" results are obtained using the renormalized coefficients of the MCDF vectors occurring in the RCI calculations. The RCI results are from the present work also.

	RCI		Dirac-Fock	
Transition	Velocity	Length	Velocity	Length
$a\ 4d^4\,{}^5D_2 \rightarrow {}^3D^o_3$	0.054	0.068	0.069	0.081
$a\ 4d^3 5s\,{}^5F_2 \rightarrow {}^3D^o_3$	0.020	0.027	0.028	0.050
$a\ 4d^3 5s\,{}^5F_3 \rightarrow {}^3D^o_3$	0.026	0.031	0.041	0.054
$a\ 4d^3 5s\,{}^5F_4 \rightarrow {}^3D^o_3$	0.052	0.068	0.084	0.113
$a\ 4d^4\,{}^3P_2 \rightarrow {}^3D^o_3$	0.065	0.069	0.045	0.035
$a\ 4d^3 5s\,{}^3F_3 \rightarrow {}^3D^o_3$	0.008	0.009	0.024	0.024
$a\ 4d^3 5s\,{}^3F_4 \rightarrow {}^3D^o_3$	0.038	0.041	0.008	0.006
$b\ 4d^4\,{}^3F_4 \rightarrow {}^3D^o_3$	0.009	0.009	0.008	0.004
$a\ 4d^3 5s\,{}^5F_2 \rightarrow {}^5G^o_3$	0.239	0.315	0.276	0.433
$a\ 4d^3 5s\,{}^5F_3 \rightarrow {}^5G^o_3$	0.065	0.074	0.085	0.099

single and double excitations from the $4d$ and $5s$ valence shells, they include $4p4d$, $4p5s$ pair correlations, as well as single excitations from $4s$ and $4p$. These excitations are into previously unoccupied subshells (i.e., virtuals, denoted v) with $l \leq 4$, allowing two to three radial functions for each l. Additional details concerning the valence and core-valence correlation has been given in Ref. [1] for the case of Nb II $J=2$. The "Brillouin"-type symmetry preserving single excitations are particularly important in correcting for the variation of the $4p$, $4d$, and $5s$ radial functions with levels. There are also important "Pauli exclusion" effects present, associated with the core pair excitations $4p^2 \rightarrow 4d^2 + 4d\,vd$, which can differ as much as a few tenths of an eV from level to level. These must be included, if accurate results for all the $(d+s)^n$ levels are to be obtained, as is being recognized [2,14].

The even $J=2$ levels have an average error of only 450 cm^{-1} for the bottom ten levels, using a CI matrix of order 6559. The $J=3$ and $J=4$ levels are less well determined, with average energy errors of 539 cm^{-1} and 824 cm^{-1} for their lowest six levels, with CI expansion sizes of 3333 and 3342, respectively. Further details for the even-parity levels can be found in Refs. [1,8].

For the $(4d+5s)^3 5p$ states, we have included single and double excitations from the $4d$, $5s$, $5p$ valence electrons and the $4p^2 \rightarrow 4d^2 + 4d\,vd$ Pauli exclusion effects. As is the case with the even-parity states, the virtual space has been restricted to $l \leq 4$. At this stage, the average energy error was 271 cm^{-1} for the bottom four levels, which includes the $z\,{}^5G^o_3$ and the $z\,{}^3D^o_3$, with matrix of order 2069. We do not include the $4p \rightarrow vp, vf$ excitations, nor the $4p\,4d$ pair correlation. These involve a large number of coefficients and determinants and to a substantial extent, they energetically cancel. We have performed an LS analysis [15] of the odd-parity multiconfigurational Dirac-Fock (MCDF) solutions and find that the ${}^5G^o_3$ is 95% pure whereas the ${}^3D^o_3$ is 43% ${}^3D^o_3$, 42% ${}^5F^o_3$, and 7% ${}^5D^o_3$.

In Table I, we present our results for all possible absorption oscillator strengths ≥ 0.005. We can see that the RCI length and velocity results are closer than are the Dirac-Fock values. Experimentally, only lifetime values are available. For $\tau({}^5G^o_3)$ there are two values [3,4], 6.2 ns and 5.8 ns, and for $\tau({}^3D^o_3)$ a common value [3,4] of 5.0 ns.

Lifetimes are given [16] in terms of the spontaneous-emission transition probability A_{ki} as (in s):

$$\tau_k = \frac{1}{\sum_i A_{ki}} , \tag{1}$$

where

$$A_{ki} = \frac{6.670 \times 10^{15}}{\lambda^2(J_i, J_k)} \frac{g_i}{g_k} f_{ik} , \tag{2}$$

where $g = 2J+1$ is the statistical weight for the lower (i) and upper (k) states, λ is in Å, and f_{ik} is given in Table I. Our lifetimes are given in Table II. The RCI results agree quite well with experiment and with each other (spread $\approx 10\%$). The Dirac-Fock velocity results are also good, but the corresponding length results are poor.

The results in Tables I and II give us the ordering for

TABLE II. Lifetimes $\tau(ns)$, for $z4d^3 5p\,{}^5G^o_3$ and ${}^3D^o_3$.

		RCI		Dirac-Fock	
Lifetime	Expt.	Velocity	Length	Velocity	Length
$\tau({}^5G^o_3)$	6.2(4) 5.8(5)	6.53	5.16	5.47	3.78
$\tau({}^3D^o_3)$	5.0(4-5)	5.60	4.67	4.74	3.86

the decay channels for $^5G^o_3$ $J=2>J=3>J=4$ and for $^3D^o_3$ $J=4\approx J=2>J=3$. If we could know *a priori* which were the important lower states, this could save much computation. Since the length operator is proportional to ΔE [7], the lowest states are favored, if radial and angular characteristics are similar.

Nb II is a moderate Z atom and the $^5G^o_3$ and $4d^35s\ ^5F$ states are $>90\%$ LS pure. At least for these, LSJ analyses may yield useful results. Nonrelativistically, $\Delta S=0$, $|\Delta L|\leq 1$; given [9] the distribution of lower levels, only decays to $4d^35s\ ^5F_J$ may be important for the $^5G^o_3$. Next, we consider the J dependence of the $^5G^o_3$ f values.

Nonrelativistically, we may show that the f value between two levels has the proportionality

$$f_{ik}\approx\frac{(2J_i+1)}{\lambda^3(J_i,J_k)}\begin{Bmatrix}J_i & 1 & J_k\\ J_k & S & L_i\end{Bmatrix}^2. \tag{3}$$

Since λ only depends weakly on J for $^5G^0_3\rightarrow{}^5F_J$, angular factors should predominate. Equation (3) predicts $f(J_i=2)\approx\frac{25}{6}$, $f(J_i=3)\approx\frac{25}{16}$, $f(J_i=4)\approx\frac{1}{16}$; proportions which are pretty well borne out by Table I results.

The situation for $^3D^o_3$ is considerably more complicated. First, the state is nearly an equal mixture of $^3D^o$ and $^5F^o$. Second, using LS rules, each can decay to a variety of lower states, *viz.*[3] (PDF) and $^5(DF)$, some of which may not be so pure themselves (especially $S=1$ [1]). We may use Eq. (3) to correctly predict that $^3D^o_3\rightarrow{}^3L_2$ decay is largest for $L=1$ (see Table I) and that $^5F^o_3\rightarrow{}^5D_J$ decay is largest for $J=2$. However, the $^5F^o_3\rightarrow{}^5F_J$ decays are not ordered (in J) as predicted.

The remaining length-velocity discrepancies are likely mainly due to the failure to include $4p\rightarrow vp, vf$, and $4p4d$ pair correlations in the odd-parity states. Secondarily, improvements in the $J=3,4$ states may also be warranted. Such improvements are computationally expensive and must be postponed to the future.

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