Correlation effects in a relativistic calculation of the $6s^2\,^1S_0-6s\,6p\,^1P_1$ transition in ytterbium

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The energies and oscillator strength for the spin-allowed $6s^2\,^1S_0-6s\,6p\,^1P_1$ transition in neutral ytterbium have been determined by a relativistic Hartree-Fock calculation which includes both intravalence and valence-core correlation effects. The intravalence correlation is found by a multiconfiguration approach in which only configurations involving virtual excitations from the valence shell are admixed. The valence-core correlation is taken into account by a model to represent core polarization by the valence electrons. Intravalence correlation is found to be more important for the transition energy since core polarization lowers both $6\,^1S_0$ and $6\,^1P_1$ energies by roughly the same amount. Core polarization, however, is the stronger influence in determining the oscillator strength. The fact that the calculated transition energy agrees to within 1% with experiment, whereas the calculated oscillator strength is 10% to 20% too high, may indicate that the polarizability of the Yb^{2+} core calculated by Fraga, Karwowski, and Saxena, namely, $7.36a_0^3$, is too small.

I. INTRODUCTION

Correlation effects in atoms can often be conveniently split into intravalence, valence-core, and intracore contributions. In *ab initio* calculations, these contributions can, at least in principle, be evaluated by multiconfiguration techniques. In oscillator strength calculations, only the first two contributions are usually important. Inclusion of intravalence correlation poses mostly moderate problems, as one can usually get more than 90% of the intravalence correlation energy by mixing only a few configurations. However, for the valence-core correlation in many-electron atoms, there are usually too many configurations which make roughly equal contributions to permit an accurate multiconfiguration result.

As a practical solution, we have previously[1] suggested an approach in which most of the intravalence correlation is represented by limited configuration mixing, whereas the valence-core correlations are all represented approximately by a core-polarization model potential together with the corresponding modification to the dipole-moment operator in the oscillator strength calculations. We have already tested this approach successfully in calculations of relativistic oscillator strengths for the $6s^2\,^1S_0-6s\,6p\,^1P_1$ and $^3P_1$ transitions in neutral mercury[1] and its isoelectronic ions,[2] as well as in the cadmium isoelectronic sequence.[3] In the present study, we apply this method to the spin-allowed $4f^{14}6s^2\,^1S_0-4f^{14}6s\,6p\,^1P_1$ transition in neutral ytterbium. Yb differs from Hg in that the outermost orbital of the core consists of $4f_{7/2}$ electrons, and the $5d_{3/2}$ and $5d_{5/2}$ orbitals are vacant. As a result, in Yb the $6p\,5d$ configurations can make important contributions to the $6s\,6p\,^1P_1$ state. As far as we are aware, no previous Hartree-Fock calculations of Yb oscillator strengths have been reported.

II. CALCULATIONS

Three types of multiconfiguration relativistic Hartree-Fock (MC-RHF) calculations have been performed with a modified version of the code by Desclaux.[4] In the first type

(MC-RHF I), the ground state $^1S_0$ is the pure $6s_{1/2}^2$ state, whereas the upper state $^1P_1$ is described in intermediate coupling

$$|6\,^1S_0\rangle = |6s_{1/2}^2, J=0\rangle \ , \tag{1a}$$

$$|6\,^1P_1\rangle = b_1|6s_{1/2}6p_{1/2}, J=1\rangle + b_2|6s_{1/2}6p_{3/2}, J=1\rangle \ . \tag{1b}$$

The "frozen core" approximation is used with the core orbitals $\ldots 4f^{14}$ frozen in the ground state. For the excited state, convergence is achieved for the higher of the two states with $J=1$ corresponding to $^1P_1$. In the second type of calculation (MC-RHF II), the upper $^1P_1$ state is again represented in intermediate coupling, but additional configurations are included for the ground state $^1S_0$

$$|6\,^1S_0\rangle = a_1|6s_{1/2}^2, J=0\rangle + a_2|6p_{1/2}^2, J=0\rangle + a_3|6p_{3/2}^2, J=0\rangle \ . \tag{2}$$

In the third type of calculation (MC-RHF III), the ground state is represented as in MC-RHF II [Eq. (2)] but now additional configurations are included in the excited state $^1P_1$:

$$\begin{aligned}
|6\,^1P_1\rangle =\ & b_1|6s_{1/2}6p_{1/2}, J=1\rangle + b_2|6s_{1/2}6p_{3/2}, J=1\rangle \\
& + b_3|6p_{1/2}5d_{3/2}, J=1\rangle + b_4|6p_{3/2}5d_{3/2}, J=1\rangle \\
& + b_5|6p_{3/2}5d_{5/2}, J=1\rangle \ .
\end{aligned} \tag{3}$$

The coefficients a_i and b_i of Eqs. (1a), (1b), (2), and (3) are presented in Table I. The valence orbitals $6s_{1/2}$, $6p_{1/2,3/2}$ are different in the initial and final state and appropriate overlap integrals must be computed in oscillator strength calculations.

First, all three types of multiconfiguration calculations were performed with valence-core correlation entirely neglected in order to estimate the influence of intravalence correlation by itself. Then the third type of calculation (MC-RHF III) was repeated with valence-core correlation represented through the core-polarization approach (MC-RHF III + CP). The core-polarization potential adopt-

TABLE I. Configuration-mixing coefficients, ionization energies, and transition energies, together with oscillator strengths calculated with both experimental (E) and theoretical (T) transition energies for the $4f^{14}6s^2\,^1S_0$–$4f^{14}6s6p\,^1P_1$ transition in neutral ytterbium.

| State or transition | Intravalence correlation only | | | Intravalence correlation + core polarization | | | |
	MC-RHF I[a]	MC-RHF II[b]	MC-RHF III[c]	MC-RHF III+CP1[d]	MC-RHF III+CP2[e]	MC-RHF III+CP3[f]	Experiment
Configuration-mixing coefficients[g]							
$^1S_0$ a_1	1.0000	0.9638	0.9638	0.9738	0.9776	0.9782	
a_2		0.1715	0.1715	0.1459	0.1342	0.1320	
a_3		0.2044	0.2044	0.1746	0.1623	0.1601	
$^1P_1$ b_1	−0.5371	−0.5371	−0.4607	−0.4433	−0.4201	−0.4107	
b_2	0.8435	0.8435	0.8054	0.8123	0.8060	0.8029	
b_3			0.2315	0.2378	0.2673	0.2795	
b_4			−0.0879	−0.0884	−0.0964	−0.0994	
b_5			0.2789	0.2815	0.3053	0.3141	
Ionization energies[h] (hartrees)							
$^1S_0$	0.189 250	0.211 967	0.211 967	0.219 041	0.224 491	0.229 819	0.229 826[i]
$^1P_1$	0.083 779	0.083 799	0.099 035	0.105 344	0.109 121	0.115 580	0.115 607
Transition energies (hartrees)							
$^1S_0$–$^1P_1$	0.105 471	0.128 168	0.112 932	0.113 697	0.115 370	0.114 239	0.114 219[i]
Oscillator strengths							
$^1S_0$–$^1P_1$ (E)	2.24	1.53	2.01	1.69	1.54	1.50	1.30,[j] 1.27[k]
(T)	2.07	1.72	1.99	1.68	1.56	1.50	1.23,[l] 1.38[m] 1.40[n]

[a]Relativistic multiconfiguration Hartree-Fock calculations with the . . . $4f^{14}$ core frozen in the ground state and composition of the ground $^1S_0$ and excited $^1P_1$ states described by Eqs. (1a) and (1b), respectively. The core polarization is neglected here.

[b]As in footnote a but composition of $^1S_0$ and $^1P_1$ states given by Eqs. (2) and (1b), respectively.

[c]As in footnote a but composition of $^1S_0$ and $^1P_1$ states given by Eqs. (2) and (3), respectively.

[d]As in footnote c but core polarization is included for valence electrons. The cutoff radius r_0 set to the mean radius of the outermost orbital of the Yb^{2+} core ($r_0 = 1.492a_0$).

[e]As in footnote d but r_0 adjusted to match the experimental ionization energy of the ground $^2S_{1/2}$ state of Yb^+ ($r_0 = 1.148a_0$).

[f]As in footnote c but r_0 adjusted to match the experimental ionization energies of the $^1S_0$ and $^1P_1$ states (relative to ground state of Yb^{2+}) of the neutral ytterbium ($r_0 = 1.102$ and 1.086 for $^1S_0$ and $^1P_1$, respectively).

[g]Configuration-mixing coefficients for Eqs. (1b), (2), and (3).

[h]Ionization energies are computed as differences between the total energies of singly ionized and neutral ytterbium. If the core polarization is accounted for, it is appropriately included for valence electrons in both atom and ion. Because of the way the r_0 is adjusted in MC-RHF III+CP3 calculations, the total energy of Yb^+ is evaluated as total energy of Yb^{2+} increased by experimental ionization energy of Yb^+ (cf. footnote f).

[i]Reference 5.
[j]Reference 6.
[k]Reference 7.
[l]Reference 8.
[m]Reference 9.
[n]Reference 10.

ed, namely,

$$V_{CP} = -\tfrac{1}{2}\alpha\left(\sum_i \mathbf{F}_i\right)^2 \qquad (4)$$

represents the interaction of the ion core through its dipole polarizability α, with the sum of electric fields $\mathbf{F}_i$ produced by each valence electron at $\mathbf{r}_i$. Here $\mathbf{F}_i$, appropriately averaged over the core, is modeled[11] by $\mathbf{F}_i = \mathbf{r}_i(r_0^2 + r_i^2)^{-3/2}$ in a.u., where r_0 is a measure of the core radius. The one-electron terms in Eq. (4) are added to the one-electron Hartree-Fock Hamiltonian of each valence electron, whereas the cross or "dielectric" terms are computed together with the direct Coulomb repulsion r_{ij}^{-1} between valence elec-

trons. The "dielectric" terms affect the calculations of the excited $^1P_1$ state, but for the ground $^1S_0$ state they contribute only to off-diagonal matrix elements in type II and III calculations.

In calculations of transition moments, the dipole-length form is used with the dipole moment $\mathbf{d} = -\mathbf{r}$ of each valence electron replaced by $\mathbf{d} + \mathbf{d}_c$, where $\mathbf{d}_c = \alpha\mathbf{F}$ is the dipole moment induced in the core by the electron. The value of the core polarizability α was set to the static dipole polarizability calculated by Fraga, Karwowski, and Saxena[12] for Yb^{2+} ($7.363\ a_0^3$). Three different values of cutoff radius r_0 were used leading to three versions of MC-RHF + CP calculations. In version CP1, r_0 was set to the

mean radius of the outermost orbital of Yb^{2+} ($1.492a_0$). In the second version (CP2), the value of r_0 adjusted to match the experimental ionization energy of the ground $^2S_{1/2}$ state of Yb^+, relative to Yb^{2+}, was used ($r_0 = 1.148a_0$). Finally, in version CP3, r_0 was adjusted to match the experimental ionization energy of the ground $^1S_0$ and excited $^1P_1$ states of neutral Yb relative to Yb^{2+} ($r_0 = 1.102a_0$ and $1.086a_0$ for $^1S_0$ and $^1P_1$, respectively). The values of the ionization energies for the $^1S_0$ and $^1P_1$ states, the $^1S_0$–$^1P_1$ transition energies, and the oscillator strengths resulting from the different types of calculations are presented in Table I.

III. DISCUSSION AND CONCLUSIONS

Several conclusions can be drawn. Our "best" (MC-RHF III + CP3) calculation after transformation to the LS basis results in the following composition of the ground $^1S_0$ and excited $^1P_1$ states: The $^1S_0$ is 95.70% $6s^2$ $^1S_0$, 4.28% $6p^2$ $^1S_0$, and 0.02% $6p^2$ $^3P_0$, whereas the $^1P_1$ is 79.69% $6s6p$ $^1P_1$, 18.52% $6p5d$ $^1P_1$, 1.64% $6s6p$ $^3P_1$, 0.13% $6p5d$ $^3D_1$, and 0.02% $6p5d$ $^3P_1$. The large contribution of the $6p5d$ configuration is clearly visible for the $^1P_1$ state. This distinguishes the ytterbium case from that of mercury where the $5d$ shell is already filled so that no virtual transitions to it are possible and the contribution of the $6p6d$ configuration is expected to be much smaller. Unfortunately, we were unable to achieve the convergence for the $^1S_0$ state if the $4f^{14}5d^2$ configuration was included, but a semiempirical analysis of the Yb spectra performed by Nir and Gold-schmidt[13] suggests that the contribution of this configuration to the ground $^1S_0$ state is very small. The value of the g_J factor in the $^1P_1$ state calculated in the MC-RHF III + CP3 calculation is 1.008 and may be compared with the experimental value of 1.035 ± 0.005.[14] The experimental results indicate that the composition of this state should have a much larger component (roughly 7% of $^3P_1$ character) than predicted by our calculation.

Intravalence correlation plays a very important role in achieving a good agreement with experiment for the $^1S_0$–$^1P_1$ transition energy. Its inclusion reduces the discrepancy with experiment from 7.7% to 1.0%. As may be seen from Table I, the contribution of the $6p5d$ configuration to the $^1P_1$ state is of particular importance here. The influence of core polarization (valence-core correlation) on the transition energy is rather small as it lowers the energies of both states by roughly the same amount. This may seem surprising, since the roughly r^{-4} dependence of V_{CP} would lead one to expect a significantly larger polarization effect in the lower-lying $^1S_0$ state. However, the dielectric term $-\alpha \mathbf{F}_1 \cdot \mathbf{F}_2$ arising from V_{CP} has, as mentioned, a practically negligible effect in $^1S_0$ states but significantly *enhances* the polarization influence in ^1P states. The enhancement reflects the result that the expectation value $\langle \mathbf{F}_1 \cdot \mathbf{F}_2 \rangle_{1_P}$, hence the angular correlation $\langle \hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2 \rangle_{1_p}$ is positive in ^1P states: in simple pictorial terms, the two valence electrons are more likely than not to be found on the same "side" of the atom.

Such an angular correlation is easily demonstrated with simple zeroth-order nonrelativistic wave functions for the two valence electrons. With spatial wave functions of the form (labels 1 and 2 refer to the two valence electrons)

$$\Psi\{_P^{1,2)}\} = [\phi_s(1)\phi_p(2) + \phi_p(1)\phi_s(2)]/\sqrt{2} \ ,$$

$$\Psi\{_{3P}^{1,2)}\} = [\phi_s(1)\phi_p(2) - \phi_p(1)\phi_s(2)]/\sqrt{2} \tag{5}$$

for the ^1P and ^3P states, respectively, one easily derives

$$\langle \hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2 \rangle_{1_P} = -\langle \hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2 \rangle_{3_P} = \tfrac{1}{3} \left| \int_0^\infty dr \, R_s R_p \right|^2 \rangle 0 \ , \tag{6}$$

where R_s and R_p are the radial orbitals corresponding to the spatial one-electron functions ϕ_s and ϕ_p, respectively. Although the use of nondegenerate relativistic wave functions complicates the picture somewhat, our calculations here and for mercury[1] and cadmium[3] demonstrate the correctness of these trends.[15]

For oscillator strengths, core polarization seems to have a stronger influence than intravalence correlation. Clearly, better agreement with experiment for both ionization energies (remaining discrepancy 2.3% and 5.6% for $^1S_0$ and $^1P_1$, respectively) and oscillator strengths is achieved in MC-RHF III + CP2 calculation, where the value of r_0 is adjusted to match the experimental ionization energy of the valence electron in Yb^+, relative to Yb^{2+}, and is used instead of the mean radius of the outermost orbital of Yb^{2+}. The further adjustment of r_0 to match experimental ionization energies (relative to the ground state Yb^{2+}) of neutral ytterbium in the $^1S_0$ and $^1P_1$ states separately, leads to a small additional reduction in oscillator strength (below 4%). In our opinion, the latter approach (MG-RHF III + CP3) yields the most reliable oscillator strengths. The fact that they are 7%–22% higher than experimental values depending on the experimental data used for comparison (see Table I) may indicate that the value of α chosen is considerably too low. A higher polarizability (closer to $12a_0^3$ or $13a_0^3$) would move the oscillator strength into the experimental range and also increase our predicted value of g_J for the 6 $^1P_1$ state. One might well expect the value of α for Yb^{2+} from Fraga *et al.* to be too low, since it came from a Hartree-Fock calculation and ignores the relativistic dilation of the $4f$ orbitals which contribute most strongly to the polarizability. On the other hand, a recent calculation[16] with the relativistic random phase approximation of α for Yb^{2+} gives a somewhat lower ($6.39a_0^3$) than the value of Fraga *et al.*

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[1] J. Migdalek and W. E. Baylis, J. Phys. B 17, L459 (1984).
[2] J. Migdalek and W. E. Baylis, J. Phys. B 18, 1533 (1985).
[3] J. Migdalek and W. E. Baylis, J. Phys. B (to be published).
[4] J. P. Desclaux, Comput. Phys. Commun. 9, 31 (1975).
[5] W. C. Martin, R. Zalubas, and L. Hagan, *Atomic Energy Levels-The Rare-Earth Elements*, Nat. Stand. Ref. Data Ser. Nat. Bur. Stand.

No. 60 (National Bureau of Standards, Washington, DC, 1978).

[6]M. Baumann and G. Wandel, Phys. Lett. 22, 283 (1966).

[7]W. Lange, J. Luther, A. Stendel, and H. Walther, Phys. Lett. 20, 166 (1966).

[8]N. P. Penkin, K. B. Blagoev, and V. A. Komarovskii, in *Proceedings of the 6th International Conference on Atomic Physics*, edited by R. Damburg (Plenum, New York, 1979).

[9]T. Andersen, O. Poulsen, P. S. Ramanujam, and A. Petrakiev-Petkov, Sol. Phys. 44, 257 (1975).

[10]F. H. K. Rambow and L. D. Schearer, Phys. Rev. A 14, 738 (1976).

[11]J. Migdalek and W. E. Baylis, J. Phys. B 11, L497 (1978).

[12]S. Fraga, J. Karwowski, and K. M. S. Saxena, *Handbook of Atomic Data* (Elsevier, Amsterdam, 1976).

[13]S. Nir and Z. B. Goldschmidt (unpublished), quoted in Ref. 5.

[14]M. Baumann and G. Wandel, Phys. Lett. 28A, 200 (1968).

[15]H. Walther (private communication) has correctly suggested that such angular correlation can also explain the positive (negative) specific-mass shift in ^1P (^3P) states of two-electron spectra.

[16]D. Kolb, W. R. Johnson, and P. Shorer, Phys. Rev. A 26, 19 (1982).