PHYSICAL REVIEW A

GENERAL PHYSICS

THIRD SERIES, VOLUME 40, NUMBER 6 SEPTEMBER 15, 1989

Wavelength, oscillator strength, and fine structure for the $^4P \rightarrow {}^4S^\circ$ transition of Mg^-

Donald R. Beck

Department of Physics, Michigan Technological University, Houghton, Michigan 49931

(Received 8 May 1989)

We have calculated the electron affinities, including many-body and relativistic effects, of Mg^- ^4P and Mg^- $^4S^\circ$ to be 321 and 536 meV, respectively. The electric dipole f value for the $^4P \rightarrow {}^4S^\circ$ transition is 0.3087 (length) and 0.3000 (velocity), occurring at a theoretically predicted wavelength of 2921 Å. The $J=1/2 \rightarrow 3/2$ fine-structure splitting for Mg^- ^4P is predicted to be 11.8 cm^{-1}, and the $J=3/2 \rightarrow 5/2$ splitting 19.4 cm^{-1}. These results should help in the attempt being made by Andersen (private communiation) to observe the $^4P \rightarrow {}^4S^\circ$ transition in the laboratory.

I. INTRODUCTION

In the past few years, we have been using *ab initio* methods to predict excited bound states of negative ions for species as large as Zn^- [1]. Very recently, some bound excited states have begun to be observed by either time-of-flight methods used by Peterson and co-workers at SRI[2,3] and Pegg *et al.* at Oak Ridge[4] to detect Be^- and Ca^- ^4P states, or by direct observation of an optical transition connecting two bound states, such as was originally[5] done for the Li^- $1s2s2p^2\,{}^5P \rightarrow 1s2p^3\,{}^5S^\circ$ transition, and very recently by Andersen and co-workers at Aarhus for the Be^- $1s^22s2p^2\,{}^4P \rightarrow 1s^22p^3\,{}^4S^\circ$ transition.[6]

For the case of excited states of negative ions, it is fair to state, I believe, that theory has generally preceded experiment, and has been quite valuable in suggesting where to look, within a narrow wavelength range, how intense the transition was going to be, and what fine-structure effects were present. As far as the optical transitions are concerned, the work of Bunge[7] for the Li^- transition predated the measurement, as did the work of Beck and Nicolaides[8] for the Be^- transition. Specific examples which remain to be followed up include a transition in Zn^- (Ref. 1) and one in Mn^-,[9] both predicted by the last author.

In this paper, we wish to consider another example of an optical transition: that of Mg^- $3s3p^2\,{}^4P \rightarrow 3p^3\,{}^4S^\circ$. An incomplete analysis of only moderate accuracy of this transition was presented in 1984 by Beck.[10] Since the transition is now under investigation at Aarhus,[11] this is a good time to "complete" the analysis and improve the accuracy of the results. Simultaneously, we will provide results for the two Mg thresholds, Mg $3s3p\,{}^3P^\circ$ and Mg $3p^2\,{}^3P$, which will serve as a check, in addition to being of intrinsic interest in themselves.

II. NONRELATIVISTIC MANY-BODY CALCULATIONS

The methods we used to construct a many-body nonrelativistic wave function have been discussed in detail in previous articles.[1,8,12,13] Briefly, we begin with the nonrelativistic restricted Hartree-Fock (RHF) solution generated by the numerical program of Froese-Fisher.[14] We begin to correlate the outermost shell (M shell, here) first. These effects are differentially the largest, and often involve near degeneracies, which are hard to account for if inner shells are correlated first.[8] Our basic N-electron building block is the configuration. First-order perturbation theory dictates that configurations involving single and double excitations of the RHF subshells constitute the first-order correction to the RHF result. For the M shell, for the states of interest here, this means the excitations $3s \rightarrow s+d$, $3p \rightarrow p$, $3s3p \rightarrow sp+pd+df+fg+\ldots$, and $3p^2 \rightarrow p^2+d^2+f^2+g^2+\ldots$ form the first-order M-shell wave function. Here, only the angular characteristics are indicated and the dots indicate a nonterminating series. In practice, our calculations terminate with the written out terms; effects of higher-order terms can be subsequently simply added.[8] Next, it is necessary to represent the radial characteristics of the new orbitals (called "virtuals") appearing in the first-order wave function. Much evidence[1,8,12,13,15] suggests that this may be done efficiently through the use of a few well-chosen Slater-type orbitals (STO's); $r^n\exp(-\zeta^* r)$ are chosen through the use of the energy variational principle. Here we have used three such STO's for the largest contributors, and two for less important configurations. The STO power n is chosen to be the lowest value possible, which has not already appeared.

The results obtained using first-order M-shell correla-

TABLE I. Nonrelativistic contributions to the energies of Mg^- and its thresholds [in hartree ($=1$ a.u.$\cong 27.209\,76$ eV].

Type	Mg $^3P^\circ$	Mg^- ^4P	Mg ^3P	Mg^- $^4S^\circ$
RHF	$-199.546\,713$	$-199.550\,806$	$-199.384\,181$	$-199.390\,374$
Singles, doubles from M shell[a]	$-0.006\,412$	$-0.015\,551$	$-0.008\,632$	$-0.021\,241$
Triples from M shell[b]	0	$-0.000\,26$	0	$-0.001\,15$
Singles, doubles from L-M shell[b]	$-0.012\,678$	$-0.010\,989$	$-0.009\,979$	$-0.009\,072$
Total CI	$-199.565\,802$	$-199.577\,598$	$-199.402\,792$	$-199.421\,944$
Estimated error[c]	$0.000\,728$	$-0.000\,940$	$-0.000\,321$	$-0.000\,360$

[a] Computed by removing only this contribution and rediagonalizing the CI matrix.

[b] Computed by removing all other contributions and rediagonalizing the CI matrix.

[c] Includes estimate of effect (on M shell and L-M shell correlation) of truncating configuration and one electron spaces (see Sec. III).

tion are given in Table I. The next step is to explore higher-order M-shell effects (triples). We did this by forming all possible triply excited M-shell configurations that could be built out of the M-shell one-electron basis (see Table II). M-shell triples of course appear in the negative ion only. From Table I it can be seen that such effects [calculated by comparing the final configuration interaction (CI) energy obtained with and without triples] are significant—they contribute 7.2 meV to the electron affinity (EA) of the ^4P and 31.4 meV to the EA of the $^4S^\circ$.

TABLE II. Slater-type orbitals $nl(\zeta)$ used to represent virtual space (exponents ζ in parenthesis).

Mg $^3P^\circ$	Mg^- ^4P	Mg ^3P	Mg^- $^4S^\circ$
$4s(1.111)$	$4s(0.649)$	$3s(1.945)$	$3s(1.613)$
$5s(1.680)$	$3s(0.789)$	$4s(3.556)$	$4s(3.602)$
$3s(3.386)$	$5s(1.669)$		
$5s(3.950)$	$3s(3.556)$		
$4p(1.580)$	$4p(1.407)$	$4p(1.608)$	$4p(1.400)$
$5p(1.403)$	$3p(0.992)$	$3p(1.149)$	$3p(0.990)$
$3p(2.566)$	$5p(1.381)$	$5p(1.315)$	$5p(1.222)$
$5p(3.675)$	$3p(3.00)$	$3p(3.767)$	$3p(3.413)$
	$5p(4.082)$	$4p(4.403)$	$4p(3.754)$
$3d(0.813)$	$3d(0.684)$	$3d(0.813)$	$3d(0.697)$
$4d(1.365)$	$4d(1.27)$	$4d(1.437)$	$4d(1.197)$
$3d(3.150)$	$5d(1.23)$	$5d(1.421)$	$5d(1.089)$
$5d(3.859)$	$3d(3.15)$	$3d(2.843)$	$3d(2.948)$
	$5d(3.995)$	$4d(3.473)$	$4d(3.350)$
$4f(1.140)$	$4f(0.855)$	$4f(1.052)$	$4f(0.880)$
$5f(1.806)$	$5f(1.365)$	$5f(1.758)$	$5f(1.516)$
$4f(2.534)$	$4f(2.605)$	$4f(2.393)$	$4f(2.457)$
$5f(8.829)$	$5f(3.030)$	$5f(8.909)$	$5f(3.000)$
$5g(1.245)$	$5g(1.011)$	$5g(1.315)$	$5g(1.245)$
Average value of r (a.u.)			
$\langle r\rangle_{3p}=4.069$	$\langle r\rangle_{3p}=5.369$	$\langle r\rangle_{3p}=4.474$	$\langle r\rangle_{3p}=5.171$
$\langle r\rangle_{3s}=3.108$	$\langle r\rangle_{3s}=3.379$		
$\langle r\rangle_{2p}=0.684$	$\langle r\rangle_{2p}=0.684$	$\langle r\rangle_{2p}=0.682$	$\langle r\rangle_{2p}=0.682$
$\langle r\rangle_{2s}=0.691$	$\langle r\rangle_{2s}=0.691$	$\langle r\rangle_{2s}=0.691$	$\langle r\rangle_{2s}=0.691$

Our next step is to include the contributions from first-order L-M excitations, as these are expected to be differentially the largest. If we assumed no change in the radial functions in going from atom to ion (e.g., Mg $3s3p\ ^3P^\circ$ versus Mg^- $3s3p^2\ ^4P$), then application of first-order perturbation and angular momentum theory[16] would predict that the contributions of $2s3p$ and $2p3p$ pair excitations are 50% greater (this being the change in angular factors) in the negative ion than in the threshold, and that furthermore, all KK, KL, LL, as well as L, $3s$ correlation effects would be the same in atom and ion. In fact, as we shall see here and have seen in the past (e.g., Refs. 1 and 10), L $3p$ correlation effects do not differ nearly as much as predicted, and L $3s$ effects are substantially larger in the atom than in the negative ion. Both of these trends arise from the same cause: the more contracted nature of the M shell in the atom than in the negative ion (i.e., a radial change). It should be noted that L $3s$ effects, which will be seen to contribute significantly to the $^4P \rightarrow {}^4S^\circ$ wavelength and moderately to the EA for the ^4P, were not present in the original work[10] on Mg^-.

The necessity of including LM correlation effects, coupled with our desire of keeping the CI energy matrix small (<350 N-electron basis functions), led us to use our BCB method[1,17] to rapidly compute N-electron L^2,S^2 eigenstates (here, each configuration is broken into two parts; L^2,S^2 eigenstates are constructed for each part using standard diagonalization methods[16,18] and each part is then reassembled according to the prescription of Bartlett[1,17,19]). For configurations with 100–200 determinants this method is about 100 times faster than direct diagonalization. A given configuration may have several L^2,S^2 eigenfunctions, which, it might appear, must be kept in the energy matrix. But as Bunge[20] has discussed, within the context of first-order perturbation theory, one need only keep as many eigenvectors as there are independent radial integrals connecting the configuration to the RHF solution. We have automated this[1] in a procedure we call REDUCE, so that the original set of eigenvectors is orthonormally mapped to the minimal set. The savings (in energy matrix size) can be quite substantial, with little loss[1,21] in energy: To illustrate, for Mg^- $3s3p^2\,{}^4P$ a contribution to the $2p3p$ energy is the configuration (referenced to the RHF solution) $2p3p\rightarrow dd'$ (the prime distinguishes the fact that the two d functions are distinct in the Pauli sense). This configuration has 18 ${}^4P$ eigenvectors. Yet the interaction with the RHF solution can be written in terms of four two-electron radial integrals, viz., $R^K(2p3p;dd')$ and $R^K(2p3p;d'd)$ where $K=1,3$. Therefore, the original 18 vectors may be "REDUCED" to 4. This of course happens for all virtuals having this configuration type, and similar reductions occur for other types. For the calculations described here, reductions in the size of the CI matrix of 2–4 are routine; for the transition metals (e.g., Ref. 1) reductions by a factor of 10 are more normal.

Because the M shell was fairly localized, a common set of virtual STO's could be used to span the space. The L shell is also localized, but in a different region of space, which calls for the introduction of new virtual STO's (see Table II) to describe LM correlation effects. Generally these new functions, prior to orthogonalization, have an average radius near the geometric mean of the L- and M-shell radii.

The contributions of the LM correlation to the EA's is shown in Table I (obtained from the full CI matrix by retaining, then deleting, these effects). In Table III, we

TABLE III. Contributions to correlation and error estimates in μhartree. [Error in deleting specific configurations formed from the basis of Table I or (arbitrary 1) estimated error due to angular truncation (see text). When a second number appears in an error column, it corresponds to the energy gained by adding additional virtuals (see text for more details).]

Correlation type[a]	Mg ${}^3P^\circ$		Mg^- ${}^4P$		Mg ${}^3P$		Mg^- ${}^4S^\circ$	
	$-\varepsilon$	Error	$-\varepsilon$	Error	$-\varepsilon$	Error	$-\varepsilon$	Error
$3s\rightarrow s$	≈ 0	≈ 0	≈ 0	0.0				
$3s\rightarrow d$	4031	1	2466	1				
$3p\rightarrow p$	≈ 0	≈ 0	≈ 0	≈ 0	0	0	0	0
$3p^2\rightarrow p^2$			2245	0	1274	0	5911	0
$3p^2\rightarrow d^2$			4457	0	6567	0	14727	0
$3p^2\rightarrow f^2$			323	-2	382	0	1014	0
$3p^2\rightarrow g^2$			47		63	0	140	0
$3p^2\rightarrow l^2$ $(l>5)$				16		24		44
$3s3p\rightarrow sp$	866	0	2553	10				
$3s3p\rightarrow pd$	813	0	2330	2				
$3s3p\rightarrow df$	260	0	642	0				
$3s3p\rightarrow fg$	36	0	66	0				
$3s3p\rightarrow ll+1$ $(l>3)$		4		11				
$2p3s\rightarrow sp$	2165	2/12	1754	18/47				
$2p3s\rightarrow pd$	5576	7/63	4546	29/91				
$2p3s\rightarrow df$	694	6/67	564	38/80				
$2p3s\rightarrow l\ l+1$ $(l>2)$		121		122				
$2p3p\rightarrow s^2$	0	21	0	28	196	0	202	0
$2p3p\rightarrow p^2$	971	1/5	1187	18/12	1996	$-13/4$	1966	2/15
$2p3p\rightarrow d^2$	1740	10/50	2216	$-13/85$	3784	$-11/74$	3635	$-6/128$
$2p3p\rightarrow f^2$	146	20	153	12	314	9/22	264	6
$2p3p\rightarrow l^2$ $(l>3)$								
$2p3p\rightarrow sd$	386	32/16	494	26/30	2568	30/48	2541	0/83
$2p3p\rightarrow pf$	61	63	118	46	203	38/23	124	25/20
$2p3p\rightarrow l\ l+2$ $(l>1)$		33		23				
$2s3p\rightarrow sp$	188	43	243	23	527	7	567	9
$2s3p\rightarrow pd$	115	34	156	51	344	25	315	16
$2s3p\rightarrow df$	78	25	59	40	202	41	171	18
$2s3p\rightarrow l\ l+1$ $(l>2)$								
$2s3s\rightarrow s^2$	164	0	121	14				
$2s3s\rightarrow p^2$	248	12	201	21				
$2s3s\rightarrow d^2$	353	11	307	11				
$2s3s\rightarrow l^2$ $(l>2)$		69			44			

[a] E.g., $2p3p\rightarrow d^2$ means one $2p$ and one $3p$ electron are removed from the RHF function and replaced with two virtual functions which may be identical or different.

display the contributions to *LM* correlation by symmetry class. Comparing the $2p3p$ correlation between negative ion and threshold, we see that they are quite similar, except for $^4P/^3P^\circ$ where the vp^2 and vd^2 contributions are larger (more negative) in the negative ion; on the other hand, for $^4S^\circ/^3P$ the vd^2 contribution differs significantly (larger in the threshold). Obviously these effects involve competition between angular and radial effects. Very substantial differences, favoring the threshold, occur for $2p3s$ contributions; these differences are entirely radial in nature. For $2s3p$ correlation the threshold is favored but the difference is considerably smaller (there are fewer $2s$ than $2p$ electrons, and the $2s$ is more remote from the $3p$ than is the $2p$). For $2s3s$, the threshold is again favored, but the effects are also modest.

In carrying out the calculation for *LM* correlation, three further restrictions were imposed, to limit the size of the energy matrix: (1) no eigenvector was kept whose CI coefficient was below 0.001 in magnitude, (2) no eigenvector contributing less than 5 μhartree was kept, and (3) no higher-order effects (triples, quadruples) involving the *L* shell were introduced.

III. ERROR ANALYSIS FOR TOTAL ENERGIES

Table III also contains an error analysis for *M*-shell and *LM* correlation effects. Three sources of error are identified. (i) Deletion of configurations which can be formed from the existing basis (Table II) (contributions for all deleted configurations are included); (ii) estimates of the effect of truncating the radial space [this was made by adding an optimized virtual STO for excitations which contributed the most to the energy difference (threshold versus negative ion) and was done for *LM* excitations only, as the *M* shell is considered sufficiently well saturated—the absence of a contribution of this type in Table III means no error analysis was done]; and (iii) an estimate of the effects of higher values of l for the pairs contributing most to the EA. Except for the $3p^2$ pairs, this was done directly (inclusion of new configurations having higher angular momentum; viz., for $2p3s$ we included $fg+gh+hi+dg$, for $3s3p$ we included gh, and for $2s3s$ we included ff'). Again, contributions which are absent were not "tried." In the case of $3p^2$ pairs, the higher contributions were assumed to behave as $1/l^n$, the coefficient and the power being found by fitting to the highest two values of l contributions calculated, and the series explicitly summed.

The total estimated error for each state is then found by summing up the above contributions. For Mg $^3P^\circ$ we find the energy lowered by 728 μhartree, for Mg$^-$ ^4P by 940 μhartree, for Mg ^3P by 321 μhartree, and for Mg$^-$ $^4S^\circ$ by 360 μhartree. This increases the ^4P EA by 6.0 meV and the $^4S^\circ$ EA by only 1.1 meV. We note that these contributions should be highly additive, because each one (where applicable) was determined by subtracting the energies obtained by diagonalizing the full CI matrix (with and without the contribution). The computed contributions (columns 2, 4, 6, and 8 of Table III), on the other hand, are correct to first order only (this is why a few of them have the "wrong" sign). They are displayed for the purposes of analysis only; they were not used to obtain any of the results displayed in Table I.

There are, of course, other sources of error in the correlation contribution to the EA's which have not been estimated. Principally, these include configurations formed by double excitation from the *L* shell, those formed from one or two excitations from the *K* shell, and triple and quadrupole excitations involving at least one electron from the *L* or *K* shells. From this work, we can at most obtain some indirect measure of the size of these effects by comparing the wavelength obtained for the $^3P^\circ$-^3P transition with the experimental[22] value. In Sec. IV we see that the error is about 4 Å.

IV. RELATIVISTIC EFFECTS, EA's AND WAVELENGTHS

Relativistic effects were computed by doing Dirac-Fock calculations (for the single dominant nonrelativistic configuration) using the program of Desclaux[23] and comparing the EA's to those obtained from the nonrelativistic RHF calculations to get the relativistic corrections (shown in Table IV). For the EA's and wavelengths of Table IV, the relativistic corrections are associated with the lowest levels ($J=\frac{1}{2}$ for the ^4P, and $J=0$ for the $^3P^\circ$ and ^3P).

For the ^4P EA our new prediction, including the error estimate, is 321 meV, which we believe to be the best available value. While this is in excellent agreement with the value of Weiss,[24] his result (as well as that of Bunge *et al.*[25]) involves contributions from the *M* shell only. For comparison, our nonrelativistic *M*-shell result is 360 meV (no error estimate). Contrasting to our previous work, we see that the current EA is 39 meV smaller than the older[10] value. This is due to the more accurate treatment of *LM* correlation ($2p3s$, $2s3p$, and $2s3s$ excitations were added, and the description of $2p3p$ correlation improved), and to the inclusion of relativistic effects (they lower the EA by about 5 meV).

Our best current value for the $^4S^\circ$ EA, 536 meV, shows a modest change from the earlier[10] value of 514 meV. This is not very surprising, as relativistic effects are already included,[10] and there is no correlation of the type *L* $3s$ to be included.

Two wavelengths are also shown in Table IV. For the threshold transition (an f value is given in Sec. V), the best theoretical result we obtain (including the error estimate) is 36 016 cm^{-1}, while the experimental value[22] is 35 962 cm^{-1}, an error of about 4 Å. It is not surprising that we have an error this large, if one bears in mind that the focus of all calculations was to minimize the errors in the individual electron affinities; i.e., the correlation effects accounted for most accurately were those that differed the most between the negative ion and its threshold.

With this in mind, the most accurate predictions for the $^4P(J=1/2)$-$^4S^\circ(J=3/2)$ wavelength should be obtained by using the experimental wavelength for the $^3P_0^\circ$-$^3P_0$ transition, and the theoretical result for the difference of the two electron affinities. This result, given in Table IV, is 2921 Å. If the error estimate is not included, the

TABLE IV. Energetic properties.

Electron affinities E_a (in MeV)

	$^3P_0^\circ$-$^4P_{1/2}$	$^3P_0$-$^4S_{3/2}^\circ$
Calculated, nonrelativistic	321	539
Relativistic correction	−5	−3
Total, this work	316	536
Total, including error estimate	321	536
Our prior work[a]	360	514
Weiss[b]	320	
Bunge *et al.*[c]	390	

Wavelengths

	Mg $^3P_0^\circ$-$^3P_0$
Calculated, nonrelativistic	0.163 011 a.u.
Relativistic	6.248×10^{-4} a.u.
Total, this work	0.163 636 a.u.
Total, including error estimate	36 016 cm^{-1}
Experiment[d]	35 962 cm^{-1}

Wavelengths

	Mg $^4P_{1/2}$-$^4S_{3/2}^\circ$
$(^3P^\circ$-$^3P_0)_{\text{expt}}+(\Delta E_a)_{\text{theor}}$	2921 Å[e]
$(^3P^\circ$-$^3P_0)_{\text{expt}}+(\Delta E_a)_{\text{theor}}$	2925 Å[f]
$(^4P_{1/2}$-$^4S_{3/2}^\circ)_{\text{theor}}$	2917 Å[e]

[a] Reference 10.
[b] Reference 24.
[c] Reference 25.
[d] Reference 23.
[e] Includes error correction.
[f] No error correction.

result becomes 2925 Å. We might use this as a minimal indicator of the uncertainty in our wavelength prediction, viz., 2921±4 Å. For comparison, if completely theoretical results are used (including the error estimate), the transition wavelength is 2917 Å.

V. FINE STRUCTURE

Since Mg is an atom of rather low Z, use of the low-Z Pauli approximation and first-order perturbation theory should be adequate to evaluate the fine structure. The algebra associated with evaluation of the various matrix elements has been developed earlier[26,27,29] and is incorporated in our present nonrelativistic many-body code,[28] program BCB. Within the context of low-Z Pauli theory, fine-structure splittings occur due to three operators: the one-body spin-orbit, the two-body spin-orbit and spin-other-orbit, and the two-body spin-spin. For the configurations of interest here, these are listed in the order of their importance. Furthermore, as has been discussed,[26,27,29] frequently the dominant portion of the two-body spin-orbit and spin-other-orbit operators effectively behaves as a one-body spin-orbit operator, serving to shield a significant part of the nuclear charge.

This last is an important point, because it enables us to predict that the principal correlation corrections of the

TABLE V. Fine structure (in cm^{-1}).

State	Splitting	RHF	Correlated	Experiment[a]
Mg $3s3p\ ^3P^\circ$	$J=0\rightarrow J=1$	15.3	20.6	20.1
	$J=1\rightarrow J=2$	31.1	41.9	40.7
Mg $3p^2\ ^3P$	$J=0\rightarrow J=1$	15.4	22.1	20.6
	$J=1\rightarrow J=2$	30.4	41.6	40.6
Mg^- $3s3p^2\ ^4P$	$J=1/2\rightarrow J=3/2$	8.9	11.8	
	$J=3/2\rightarrow J=5/2$	14.6	19.4	

[a] Reference 22.

TABLE VI. Electric dipole oscillator strengths.

Transition	Source	Length	Velocity	Experiment
Mg $^3P^\circ \rightarrow {}^3P$	RHF, this work	0.8060	0.5034	
	Correlated, this work	0.6223	0.6397	
	Correlated, prior work[a]	0.639	0.604	
	Weiss[a]	0.61	0.61	
	Ref. 33			0.50±0.05
	Ref. 34			0.53±0.05
Mg$^-$ $^4P \rightarrow {}^4S^\circ$	RHF, this work	0.4617	0.2107	
	Correlated, this work	0.3087	0.3000	
	Correlated, prior work[c]	0.299	0.291	

[a] Reference 31.
[b] Reference 32.
[c] Reference 10.

fine structure are likely to be single excitations of the type $2p,3p \rightarrow p$ (only jumps of 0 or ±1 in l are permitted; the latter are excluded because parity must be preserved). Although excitations like $2p \rightarrow p$ can give rise to a lot (12 for the ^4P) of parents, a form of REDUCE can be applied to them, such that only one parent has a surviving off-diagonal matrix element with the RHF function (the operator involved is the one-body spin-orbit operator). This survivor can be expressed in the parental coupling scheme: for the ^4P, it is $[(2p^5vp{:}^3P)(3s3p^2{:}^4P)]^4P$. It is useful to note for the future, that if one wished to treat hyperfine structure simultaneously, then other parents would have to be kept as well.

The next question that arises is: which configurations determine the "radial" characteristics of these single excitations? This is a question not fully answered in the literature, that we shall examine in some detail here. The final question concerns completeness of the virtual p one-electron radial space. We cannot necessarily assume that a set which appears to be satisfactory for energy is automatically adequate for fine structure. Recognizing that any additional p functions are to describe fine structure rather than electrostatic energy, we optimized the exponents of these additional STO's by examining the absolute value of the product: $c(vp)^*\langle 2p/r^{**}-3/vp\rangle$, which corresponds to the radial portion of the off-diagonal matrix element connecting the RHF and single excitation (one-body spin-orbit operator). Here, $c(vp)$ is the CI coefficient determined by diagonalizing the electrostatic energy matrix (our process avoids having to evaluate the full fine structure for each exponent explored—a costly process). A new virtual is then added, and the process continued, until the last contribution is smaller than some present tolerance (e.g., fine-structure change less than 1 cm^{-1}).

Our first-structure calculations were made by augmenting the basis used to produce the electron affinities with the $2p,3p \rightarrow p$ excitations. An analysis of the energy matrix was made using perturbation theory (first and second order) to determine which configurations most influence the radial characteristics of the single excitations. We found a rather simple answer, at this level: these characteristics were determined by the RHF configuration, by the configuration resulting from the excitation $3p^2 \rightarrow vp^2$ (a large energy contributor), and by other $2p \rightarrow p$ single excitations. Our results appear in Table V. For the thresholds, experimental values[22] exist, and our many-body results are in good agreement with them, giving us some confidence in the predictions we made for the Mg$^-$ ^4P, which were not previously available. Finally, we made some attempt to explore the effects of contributions indirectly arising from double excitations out of the L shell. Our limited search uncovered no substantial changes in our results.

VI. OSCILLATOR STRENGTHS

In Table VI we give our results for the Mg $^3P^\circ \rightarrow {}^3P$ and Mg$^-$ $^4P \rightarrow {}^4S$ oscillator strengths. For the first transition, we used the experimental energy difference, and for the latter our best theoretical wavelength (2921 Å). The f values were evaluated using the same wave functions that produced the electron affinities, and all nonorthonormality effects were correctly evaluated using the methods of Ref. 30. It can be seen that for both transitions the length and velocity results are in excellent agreement; absence of such agreement is an indication of flaws in the wave functions (the converse is not true). For the Mg transition, "experimental" values have been obtained by the author from older lifetime measurements. The present results suggest that measurements for this transition might well be improved to be in conformity with presumed present theoretical accuracy.

ACKNOWLEDGMENTS

Support by the National Science Foundation (Grant No. PHY-87-15246) is gratefully acknowledged.

[1] D. R. Beck, Phys. Rev. A **37**, 1847 (1988).

[2] Y. K. Bae and J. R. Peterson, Phys. Rev. A **30**, 2145 (1984).

[3] T. J. Kvale *et al.*, Phys. Rev. Lett. **55**, 484 (1985).

[4] D. J. Pegg, J. Thompson, R. Compton, and G. Alton, Phys. Rev. Lett. **59**, 2267 (1987).

[5] S. Mannervik, G. Astner, and M. Kisielinski, J. Phys. B **13**, L441 (1980); R. L. Brooks *et al.*, Phys. Rev. Lett. **45**, 1318 (1980).

[6] J. O. Gaardsted and T. Andersen, J. Phys. B **22**, L51 (1989).

[7] C. F. Bunge, Phys. Rev. A **22**, 1 (1980).

[8] D. R. Beck and C. A. Nicolaides, Int. J. Quantum Chem. **S18**, 467 (1984).

[9] D. R. Beck and Z. Cai, Phys. Rev. A **37**, 4481 (1988).

[10] D. R. Beck, Phys. Rev. A **30**, 3305 (1984).

[11] T. Andersen (private communication).

[12] D. R. Beck and C. A. Nicolaides, Int. J. Quantum Chem. Symp. **8**, 17 (1974).

[13] D. R. Beck and C. A. Nicolaides, Int. J. Quantum Chem. Symp. **10**, 119 (1976).

[14] C. Froese-Fisher, Comput. Phys. Commun. **14**, 145 (1978).

[15] C. F. Bunge, Phys. Rev. A **14**, 1965 (1976).

[16] D. R. Beck and C. A. Nicolaides, in *Excited States in Quantum Chemistry,* edited by C. A. Nicolaides and D. R. Beck (Reidel, Dordrecht, 1979), p. 105.

[17] D. R. Beck, R. J. Key, A. R. Slaughter, R. D. Mathews, and M. S. Banna, Phys. Rev. A **28**, 2634 (1983).

[18] H. F. Schaefer and F. E. Harris, J. Comput. Phys. **3**, 217 (1968).

[19] J. H. Bartlett, Jr., Phys. Rev. **38**, 1623 (1931).

[20] A. Bunge, J. Chem. Phys. **53**, 20 (1970).

[21] D. R. Beck, Z. Cai, and G. Aspromallis, Int. J. Quant. Chem. Symp. **21**, 457 (1987).

[22] C. E. Moore, *Atomic Energy Levels,* Natl. Bur. Stand (U.S.) Circ. No. 467 (U.S. GPO, Washington, D.C. 1949), Vol. I.

[23] J. P. Desclaux, Comput. Phys. Commun. **9**, 31 (1975).

[24] A. W. Weiss, Phys. Rev. **166**, 70 (1986).

[25] C. F. Bunge, M. Galan, R. Jaurequi, and A. V. Bunge, Nucl. Inst. Meth. **202**, 299 (1982).

[26] D. R. Beck, J. Chem. Phys. **51**, 2171 (1969).

[27] D. R. Beck and H. Odabasi, Ann. Phys. (N.Y.) **67**, 274 (1971).

[28] Program BCB, D. R. Beck and G. Aspromallis (unpublished).

[29] M. Blume and R. E. Watson, Proc. R. Soc. London A **270**, 127 (1962).

[30] C. A. Nicolaides and D. R. Beck, in *Excited States in Quantum Chemistry,* edited by C. A. Nicolaides and D. R. Beck (Reidel, Dordrecht, 1979), p. 143.

[31] D. R. Beck and O. Sinanoglu, Phys. Rev. Lett. **28**, 945 (1972).

[32] A. W. Weiss, J. Chem. Phys. **47**, 3573 (1967).

[33] J. Bromander, H. G. Berry, and R. Buchta, Nucl. Instrum. Methods **90**, 55 (1970).

[34] T. Andersen, J. Desesquelles, K. A. Jessen, and G. Sorensen, J. Quant. Spectrosc. Radiat. Transfer **10**, 1143 (1970).