

Oscillator Strengths for the Alkaline-Earth Atoms Using Rotor-Vibrator and Configuration-Interaction Wave Functions

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We have calculated oscillator strengths for transitions between low-lying states of the alkaline-earth atoms using both configuration-interaction (CI) and simple optimized molecular rotor-vibrator (RV) wave functions for the e -core- e system. Our CI results compare favorably with experimental and other accurate values, indicating that these functions used in previous studies of electron correlation are reliably accurate. Most RV results agree better with accurate values than do Hartree-Fock results, thus showing the success of the RV model in its first test of calculating an experimental observable.

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Research seeking to elucidate the nature of electron correlation in atoms has focused primarily on two-electron systems, particularly the doubly excited autoionizing states of helium (He^{**}). These were traditionally described by mixtures of independent-particle configurations, which express how the angular momenta of the individual electrons are spoiled. New approximate constants of motion were then sought, to give an alternative, and perhaps more accurate, intuitive physical interpretation and classification of these states. In the collective, moleculelike picture of electron correlation developed first for He^{**} ,¹ the characteristic quantum numbers are those describing collective vibrational and rotational excitations of the "linear triatomic molecule" e -nucleus- e . Watanabe and Lin² have recently made the first efforts toward extending this model to three-electron systems.

The molecular picture is strikingly apt for low-lying valence states of the more experimentally tractable quasi two-electron systems, the alkaline-earth atoms,³⁻⁵ and the alkali-metal negative ions.⁶ From core pseudopotentials and Sturmian basis functions, configuration-interaction (CI) wave functions were calculated for the valence electrons in these states and used to construct their conditional probability densities in the internal e -core- e frame. The densities for these systems show³ spatial behavior at least as moleculelike as that found by similar means for doubly excited He .⁷ These wave functions were used to calculate expectation values of the momentum correlation of the two valence electrons,⁸ $\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle$. The predictions from the molecular model of the sign and relative magnitude of this quantity for each state were borne out in almost all cases. Most recently, we⁵ calculated overlaps (S) of these wave functions with simple molecular rotor-vibrator wave functions in order to quantify the extent of validity of the molecular picture. By varying the parameters of the rotor-vibrator functions to maximize the overlaps, we constructed optimized approximate moleculelike wave functions for the correlated atomic states. Projections of the one-term

rotor-vibrator wave functions onto the corresponding many-configuration CI wave functions were large in many cases; S^2 is above 0.9 for most states.

In the present work, we test the accuracy of both the elaborate atomic wave functions used in the aforementioned studies and the simple molecular rotor-vibrator functions which approximate them by using each set of functions to calculate oscillator strengths for transitions in the alkaline-earth atoms. This represents the first calculation of an experimentally observable atomic property using electronic rotor-vibrator wave functions and in this way provides a first test of the utility and validity of the molecular model of electron correlation in atoms.

We first calculated oscillator strengths for the atomic transitions using the CI wave functions of Krause and Berry,³ obtained by treating the alkaline-earth atoms as two-electron atoms with the core pseudopotentials of Bachelet, Hamann, and Schlüter.⁹ These functions are of the form

$$\Psi = \mathcal{A} \sum_{l_1 n_1 l_2 n_2} C_{l_1 n_1 l_2 n_2} \phi_{n_1 l_1}(r_1) \phi_{n_2 l_2}(r_2) \mathcal{Y}_{l_1 l_2}^M(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2), \quad (1)$$

where the radial basis functions $\phi_{nl}(r) = \mathcal{N} r^{n-1} e^{-\xi r}$ are Sturmians and the $\mathcal{Y}_{l_1 l_2}^M(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)$ are coupled spherical harmonics. The absorption oscillator strength, in the dipole length form, is given by

$$f = \frac{2\Delta E}{3(2L_i + 1)} \sum_{M_i, M_f} |\langle \Psi_f | \mathbf{r}_1 + \mathbf{r}_2 | \Psi_i \rangle|^2, \quad (2)$$

where the subscripts i and f indicate respectively the initial and final states; we use atomic units. We took experimental values¹⁰ for ΔE since the dipole matrix element is the theoretically critical quantity. The calculation is straightforward and all the necessary integrals can be performed analytically.

We also calculated oscillator strengths using the Morse molecular wave functions obtained by Hunter and Berry⁵ for the alkaline-earth atoms. These are simple products of stretching, bending, and rotation functions

TABLE I. Oscillator strengths (f) are presented here for selected transitions in the alkaline-earth atoms. The ΔE values, in atomic units, are from Ref. 10. The configuration-interaction (f_{CI}) and rotor-vibrator (f_{RV}) values were calculated as described in the text. The values from accurate calculations (f_{ACC}), Hartree-Fock calculations (f_{HF}), and experiment (f_{EXPT}) were taken from the literature. All of the calculated values were obtained with use of the dipole length form of the transition matrix element.

Atom	Transition	ΔE	This work		Literature		
			f_{CI}	f_{RV}	f_{ACC}	f_{HF}	f_{EXPT}
Be	$2s2s\ ^1S^e \rightarrow 2s2p\ ^1P^o$	0.1939	1.31	1.15	1.36 ^a	1.68 ^b	1.34 ^c
Be	$2s2p\ ^1P^o \rightarrow 2p2p\ ^1D^e$	0.0632	0.015	0.064	0.0016 ^d	0.16 ^b	<0.048 ^c
Be	$2s2p\ ^1P^o \rightarrow 2s3s\ ^1S^e$	0.0552	0.111	0.064	0.141 ^a	—	—
Be	$2s2p\ ^3P^o \rightarrow 2p2p\ ^3P^e$	0.1718	0.442	0.484	0.452 ^f	0.53 ^g	0.46 ^h
Be	$2s2p\ ^3P^o \rightarrow 2s3s\ ^3S^e$	0.1371	0.074	0.041	0.091 ⁱ	0.06 ^g	0.086 ^j
Mg	$3s3s\ ^1S^e \rightarrow 3s3p\ ^1P^o$	0.1597	1.72	1.56	1.76 ^k	1.99 ^l	1.83 ^m
Mg	$3s3p\ ^1P^o \rightarrow 3s3d\ ^1D^e$	0.0517	0.135	0.056	0.246 ^k	1.01 ^l	0.24 ⁿ
Mg	$3s3p\ ^1P^o \rightarrow 3s4s\ ^1S^e$	0.0385	0.122	0.076	0.155 ^k	0.33 ^l	0.15 ⁿ
Mg	$3s3p\ ^3P^o \rightarrow 3p3p\ ^3P^e$	0.1639	0.617	0.770	0.641 ^k	0.81 ^l	0.61 ^o
Mg	$3s3p\ ^3P^o \rightarrow 3s4s\ ^3S^e$	0.0880	0.123	0.039	0.137 ^k	0.13 ^l	0.14 ^p
Ca	$4s4s\ ^1S^e \rightarrow 4s4p\ ^1P^o$	0.1078	1.84	1.67	1.88 ^q	2.26 ^q	1.71 ^p
Ca	$4s3d\ ^1D^e \rightarrow 4s4p\ ^1P^o$	0.0082	4.(-5)	0.004	0.001 ^r	0.011 ^s	—
Ca	$4s4p\ ^1P^o \rightarrow 4s5s\ ^1S^e$	0.0440	0.107	0.077	0.16 ^t	0.48 ^s	—
Ca	$4s4p\ ^3P^o \rightarrow 4p4p\ ^3P^e$	0.1059	0.593	0.699	0.622 ^r	0.87 ^s	0.53 ^u
Ca	$4s4p\ ^3P^o \rightarrow 4s5s\ ^3S^e$	0.0742	0.135	0.047	0.116 ^t	0.14 ^s	0.16 ^u
Sr	$5s5s\ ^1S^e \rightarrow 5s5p\ ^1P^o$	0.0989	1.85	1.73	2.10 ^v	2.45 ^v	1.94 ^m
Sr	$5s4d\ ^1D^e \rightarrow 5s5p\ ^1P^o$	0.0071	0.0001	0.006	0.001 ^v	0.018 ^v	—
Sr	$5s5p\ ^1P^o \rightarrow 5s6s\ ^1S^e$	0.0405	0.004	0.035	—	—	—
Sr	$5s5p\ ^3P^o \rightarrow 5p5p\ ^3P^e$	0.0949	0.490	0.562	—	—	0.55 ^w
Sr	$5s5p\ ^3P^o \rightarrow 5s6s\ ^3S^e$	0.0653	0.091	0.038	—	—	0.19 ^p
Ba	$6s6s\ ^1S^e \rightarrow 6s6p\ ^1P^o$	0.0823	1.55	1.56	1.68 ^x	2.64 ^q	1.64 ^y
Ba	$6s5d\ ^1D^e \rightarrow 6s6p\ ^1P^o$	0.0304	0.0005	0.033	0.0057 ^x	—	<0.0034 ^z
Ba	$6s6p\ ^1P^o \rightarrow 6s8s\ ^1S^e$	0.0743	0.148	0.094	0.037 ^t	—	—
Ba	$6s6p\ ^3P^o \rightarrow 5d5d\ ^3P^e$	0.0483	0.142	0.188	0.086 ^t	—	—
Ba	$6s6p\ ^3P^o \rightarrow 6s7s\ ^3S^e$	0.0596	0.106	0.041	0.13 ^t	—	0.18 ^{aa}

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for the e -core- e "triatomic molecule,"

$$\Psi = \mathcal{A} \frac{1}{r_1 r_2} R_{n_1 n_2}^{\pm}(r_1, r_2) \times G_{v_2}^k(\theta_{12}) \left[\frac{2L+1}{8\pi^2} \right]^{1/2} \mathcal{D}_{Mk}^{L*}(\alpha\beta\gamma). \quad (3)$$

The various terms are described in detail in Ref. 5. Briefly, $R_{n_1 n_2}^{\pm}(r_1, r_2)$ is a symmetrized (+) or antisymmetrized (-) product of Morse oscillator eigenfunctions with n_1 and n_2 quanta, respectively, in the two "bonds"; $G_{v_2}^k(\theta_{12})$ is a two-dimensional harmonic oscillator eigenfunction with v_2 bending quanta and k quanta of vibrational angular momentum about the axis of the linear configuration; and $\mathcal{D}_{Mk}^{L*}(\alpha\beta\gamma)$ is a rotation matrix and an eigenfunction for the rigid symmetric rotor. The parameters of these simple molecular wave functions were determined in Ref. 5 by our maximizing their overlaps with the corresponding CI wave functions. For completeness, we have included Ba here, even though the molecular assignments of some of its states are questionable.

The oscillator-strength calculation using these wave functions proceeds along the lines followed in calculations of molecular rotation-vibration line intensities.¹¹ We employ a body-fixed bisector frame⁵ $x'y'z'$, in which the e -core- e triangle lies in the $x'z'$ plane with the nucleus at the origin and the x' axis bisecting the interelectronic angle θ_{12} . The components of the dipole moment vector μ are

$$\mu_{x'} = (r_1 + r_2) \cos(\theta_{12}/2), \quad (4a)$$

$$\mu_{y'} = 0, \quad (4b)$$

$$\mu_{z'} = (r_1 - r_2) \sin(\theta_{12}/2). \quad (4c)$$

To transform μ into the space-fixed frame, we rewrite it as a spherical tensor¹² of rank one with components

$$\mu_q = \begin{cases} \mu_{z'}, & q=0, \\ \mp \frac{1}{2} \sqrt{2} (\mu_{x'} \pm i\mu_{y'}), & q = \pm 1. \end{cases} \quad (5)$$

Now,

$$\mu_m = \sum_q \mathcal{D}_{mq}^{1*}(\alpha\beta\gamma) \mu_q(r_1, r_2, \theta_{12}), \quad (6)$$

and the oscillator strength can be written as

$$f = \frac{2\Delta E}{3(2L_i+1)} \sum_{M_i, M_f, m} |\langle \Psi_f | \mu_m | \Psi_i \rangle|^2 \quad (7)$$

$$= \frac{2\Delta E}{2L_i+1} \sum_{M_i, M_f} |\langle \Psi_f | \mu_0 | \Psi_i \rangle|^2, \quad (8)$$

where again atomic units are employed. The integral over the Euler angles can be performed analytically; thus we are left with three separable one-dimensional integrations to perform numerically.

The results of our two calculations are presented in Table I together with various literature values of oscillator strengths for comparison: The most accurate calculated and experimental values we could find, and Hartree-Fock values. All the calculated values compared here were obtained by use of the dipole-length form of the matrix element, and wherever possible with experimental ΔE values. The same comparison is presented graphically in Fig. 1.

The agreement between our CI oscillator strengths and other accurate calculated and experimental values is quite good, particularly for the relatively strong transitions. This indicates that the pseudopotential-based CI wave functions are of reliable accuracy, especially for the S - P and P - P transitions. They appear to be less reliable for the transitions involving D states, most of which are extremely weak, where our results differ substantially from the accurate values on a relative basis. We attempted to improve these results by further optimization of the exponent ξ in the radial basis functions; this gave only slight improvement in the results.

The molecular wave functions used here represent a zero-order approximation, in the collective, moleculelike picture, to the true wave functions. Thus it seems appropriate to compare the oscillator strengths calculated from them with those calculated from a zero-order approximation of the independent-particle model, i.e., Hartree-Fock wave functions, as well as with the accu-

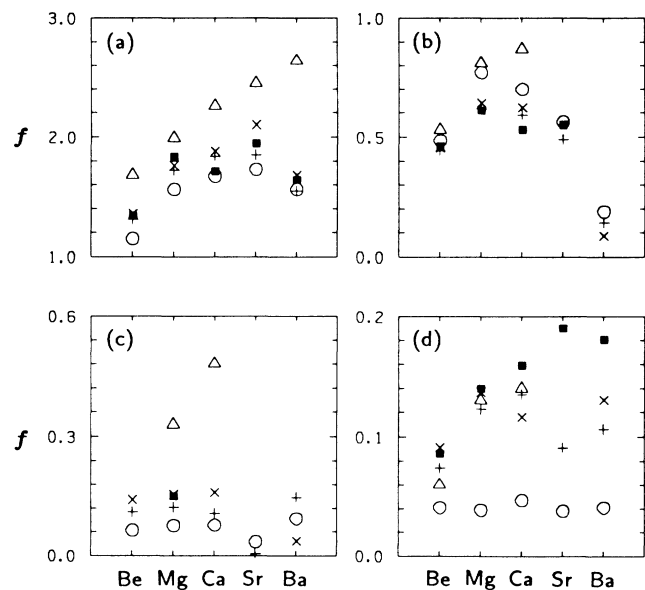


FIG. 1. Graphical representation of the oscillator strength values from Table I organized by transition: (a) $1S^e \rightarrow 1P^o$, (b) $3P^o \rightarrow 3P^e$, (c) $1P^o \rightarrow 1S^e$, and (d) $3P^o \rightarrow 3S^e$. The symbols are as follows: triangles, Hartree-Fock calculations; circles, rotor-vibrator; pluses, CI; crosses, accurate calculations; and filled squares, experiment.

rate values. Table I and Fig. 1 show that for most of the transitions the rotor-vibrator oscillator strengths agree better with the accurate values than do the Hartree-Fock oscillator strengths. The only case where Hartree-Fock appears to be consistently better is for the ${}^3P^o \rightarrow {}^3S^e$ transitions. The agreement between the rotor-vibrator oscillator strengths and the accurate values is best for intrashell transitions, as expected, since the molecular picture seems less applicable for intershell states.

All of the transitions we have considered are allowed based on electron spin, total angular momentum, and parity selection rules. Almost all of them are also allowed on the basis of the stricter selection rules of the independent-particle model. The one exception is the $6s6p\ {}^3P^o \rightarrow 5d^2\ {}^3P^e$ transition in Ba, which is forbidden in the independent-particle picture since it corresponds to a "two-electron jump." In the molecular picture, on the other hand, this transition corresponds to an allowed bending transition. We can see from the tabulated value that the oscillation strength for this transition is indeed small but substantial. Unfortunately, this example is clouded somewhat because the $5d^2\ {}^3P^e$ state of Ba appears to lie midway between the independent-particle and rotor-vibrator extremes.³ Nevertheless, it shows how the molecular picture might lend useful insight into atomic oscillator strengths.

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