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## Electron correlation in alkaline-earth atoms

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Conditional probability distributions for the valence electrons of alkaline-earth atoms in their ground and valence excited states are constructed using large-basis Sturmian configuration-interaction wave functions for two electrons in frozen, effective-core potentials. The distributions indicate that the ground states of Be, Mg, Ca, Sr, and Ba, and the valence excited states of Be, are much more like linear triatomic molecules, akin to doubly excited He, than like independent-particle systems such as the ground states of He and He-like ions.

In many doubly excited states of helium ( $\text{He}^{**}$ ) and heliumlike ions, it is now well established that electron correlation is so strong that the quantization of the electrons corresponds much more to that of a vibrator rotator like a linear  $e\text{-}\alpha\text{-}e$  "triatomic molecule" than it does to independent-particle-like orbital quantization.<sup>1</sup> This is borne out in the spatial distributions of the electrons, especially as calculated in an internal ("intrinsic") coordinate system with accurate wave functions.<sup>2-5</sup> Certain key relationships make the collective, molecular picture not only seem preferable, but they emerge as specific consequences of that model.<sup>1,3,5</sup> In particular, these relationships include (a) the similarity of the spatial distributions of the electron probability densities for states belonging to a rotor series, such as the " $2s^2$ "<sup>1</sup> $S^e$ , " $2s2p$ "<sup>3</sup> $P^o$ , " $2p^2$ "<sup>1</sup> $D^e$  rotor series of  $\text{He}^{**}$ ; (b) the similarity of the spatial distributions of the probability densities for nearly degenerate levels belonging to states of the bending vibration, such as the " $2s2p$ "<sup>1</sup> $P^o$  and " $2p^2$ "<sup>3</sup> $P^e$  states of  $\text{He}^{**}$ ; (c) the persistence of rotor series and of corresponding spatial distributions for states clearly identifiable as rotationally excited series built on specific vibrationally excited states.

In this paper, we extend the previous work on helium and heliumlike ions to study the atoms of the alkaline earths. We have used the effective potentials of frozen  $M^{+2}$  cores<sup>6</sup> to construct Hamiltonians, Schrödinger equations, eigenfunctions, and eigenstates for the ground and several excited states of Be, Mg, Ca, Sr, and Ba. The two-electron wave functions for these atoms have been constructed with elaborate Sturmian basis sets of up to 92 independent functions and angular quantum numbers  $l_1$  and  $l_2$  as high as 6. This was done in order to make the accuracy of the two-electron wave functions produced for the alkaline earths comparable to that of the functions used to interpret the degree of correlated, molecularlike behavior in  $\text{He}^{**}$ .<sup>3</sup> It has since been shown that properties such as electron distributions, predicted by Sturmian wave functions of this accuracy,

are indistinguishable from those predicted by the most accurate  $\text{He}^{**}$  Hylleraas-Kinoshita functions of Bhatia and Temkin,<sup>7</sup> except in the cusp region of  $r_{12} \rightarrow 0$ .<sup>8</sup>

The functions we have generated for the alkaline earths are, therefore, presumably accurate enough to represent the principal features of the correlation of the valence electrons in the alkaline earths. We have checked the robustness of the calculations by employing frozen core potentials of varying form and complexity, and by verifying test cases with a hydrogenic basis in addition to the Sturmian basis. A future test will be done with all-electron multiconfiguration self-consistent field wave functions.

To interpret the physical character of the states of the alkaline earths under study, we have (a) examined the patterns of spectroscopic terms in analogy to Herrick and Kellman's study of He which led to the recognition of supermultiplets, (b) examined the configurational composition of the eigenfunctions,<sup>9,10</sup> and (c) constructed conditional probability distributions  $\rho(r_2, \theta_{12}|r_1)$  of the sort used to examine many states of helium and heliumlike ions.<sup>2,3,11-13</sup>

Of these three diagnostics, the third proves by far the most useful for the alkaline earths. Historically, the first was the basis of the breakthrough by Herrick and Kellman leading to the proposal of moleculelike collective rotations and vibrations in  $\text{He}^{**}$ . The  $\text{He}^{**}$  system, however, conforms rather well to the harmonic oscillator, rigid-rotor picture, so that the chain  $O(4) \times O(4) \supset O(4) \supset O(3) \times SU(2)$  could be recognized by its signature in the pattern of term values. In the alkaline earths, the ground and low-lying excited states have characteristics almost as moleculelike as  $\text{He}^{**}$  in terms of the collective behavior of their electrons, yet the patterns of their term values do not conform at all well to a harmonic oscillator model and only moderately well to a rigid-rotor model.

Now let us examine conditional probability distributions for the ground states of Be, Mg, Ca, Sr, and Ba (Fig. 1). These distributions,  $\rho(r_2, \theta_{12}|r_1)$ , are the probability densi-

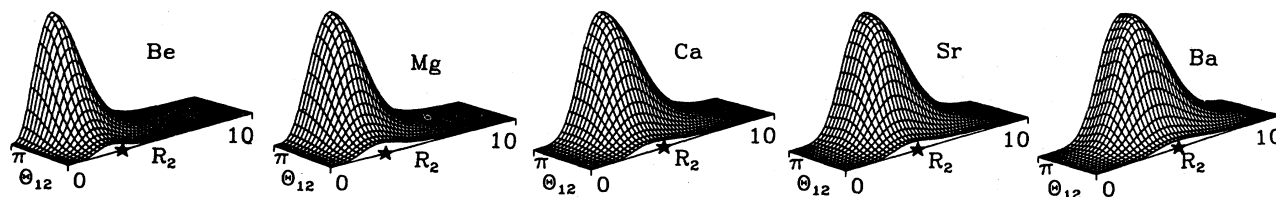


FIG. 1. Conditional probability distributions  $\rho(r_2, \theta_{12}|r_1)$  for Be, Mg, Ca, Sr, and Ba in their ground states, with  $r_1$  at approximately its most probable value in each case. These distributions indicate how the electrons, at their most probable positions, form "linear molecules" with their nuclei.  $R$  is measured in bohrs, and the distributions are scaled to a constant maximum height. The star denotes the position of electron 1.

ties for finding electron 2 at the distance  $r_2$  from the nucleus, while making an angle  $\theta_{12}$  with  $r_1$  at the nucleus if electron 1 is fixed at a distance  $r_1$  from the nucleus. The graphs of Fig. 1 show  $\rho(r_2, \theta_{12}|r_1)$  with  $r_1$  at its most probable value for the ground states of each of the alkaline earths discussed here.

The three most important aspects to recognize in Fig. 1 are (a) the strong peaking of  $\rho$  at  $\theta_{12} = \pi$ ; (b) the very small value of  $\rho$  for angles  $\theta_{12} < \pi/2$ , especially for very small  $\theta_{12}$ ; and (c) the near-Gaussian cross sections of  $\rho$ , both as a function of  $\theta_{12}$  when  $r_2$  is at or near its most probable value, and as a function of  $r_2$  peaked at  $r_1 = r_2$  for  $r_1$  at or near its most probable value. These are characteristics of the wave functions of the ground state of a two-dimensional oscillator. In fact, they are characteristics of an oscillator harmonic enough in the bottom of its potential well to have near-Gaussian probability distribution along its two principal directions. This behavior is in contrast to the distributions of the ground states of He and heliumlike ions. These species do show some correlation, angular more than radial, and the maxima do occur at  $\theta_{12} = \pi$ , but the values of  $\rho(r_2, 0|r_1)$  are not much lower than the values of  $\rho(r_2, \pi|r_1)$ , for the same  $r_1$  and  $r_2$ . The overall picture of the ground states of helium and heliumlike ions,<sup>12</sup> and even, to a lesser extent,  $H^-$ , is of states that are dominated by independent-particle behavior. These states are slightly perturbed from independent-particle behavior by correlation effects. By contrast, the " $2s^2$ "  $1S^e$  state of  $He^{**}$  and its isolectronic ions<sup>2</sup> show strong correlation and collective, moleculelike behavior.

Comparison of the distributions of Fig. 1 with those of Refs. 3 and 12 immediately tells us that the dominant feature in the *ground states* of the alkaline-earth atoms is a moleculelike electron distribution, rather than an independent-particle-like distribution. These distributions are not as extreme in their moleculelike character as the " $2s^2$ "  $1S^e$  state of  $He^{**}$ , of course. The zero-point amplitudes of angular and radial motion are larger than those of He, and, for the larger ions Ca, Sr, and Ba, the regions of  $\rho$  around their maxima are much flatter functions of  $\theta_{12}$  than for  $He^{**}$ . Furthermore, when  $r_1$  is very large, electron 2 can, with reasonable probability, execute full orbits in the  $\theta_{12}$  circle by "sneaking past" electron 1 at small  $r_2$  values.

The low-lying excited states of the alkaline earths also show strong collective behavior. Here, we present only a small subset of our results to illustrate the degree of moleculelike behavior in their valence excited states. We do not yet know where in the ladder of excited states, as the states become more Rydberg-like, independent-particle

quantization takes over, as it must for sufficiently different principal quantum numbers  $n_1$  and  $n_2$ .<sup>14</sup> The conditional probability distributions for the " $2s2p$ "  $3P^o$ , " $2s2p$ "  $1P^o$ , " $2p^2$ "  $3P^e$ , " $2p^2$ "  $1D^e$ , " $2s^2$ "  $1S^e$ , " $2s3s$ "  $3S^e$ , and " $2s3s$ "  $1S^e$  states of Be are shown in Fig. 2, arrayed and identified according to moleculelike quantization. As with He, the persistent similarities of the rotor series  $1S^e$ ,  $3P^o$ ,  $1D^e$ , and of the "near-degenerate"  $1P^o$  and  $3P^e$  partner states of the bending vibration are persuasive indicators of moleculelike correlation. The distributions for the higher  $1S^e$  state corresponds to a state with one quantum of symmetric stretch. The " $2s3s$ "  $3S^e$  state has the distribution of a state with one quantum of the antisymmetric stretching mode. However, it should be noted that the  $3S^e$  state is constrained by symmetry to have the same nodal structure as the first excited state of the antisymmetric stretch. A closer examination of the  $3S^e$  state shows that as one electron moves further from the nucleus, the other moves strictly closer and conversely, thus confirming the antisymmetric stretch or giant dipole character of this state. Similarly, the  $3P^e$  member of the first excited pair of states of the bending mode is constrained to have nodes at  $\theta_{12} = 0$  and  $\pi$ , so the node at  $\pi$  cannot be used as evidence for moleculelike behavior. It is the similarity of the  $1P^o$  distribution to that of the  $3P^e$ , and a nonzero *slope* for the  $3P^e$  distribution through  $\theta_{12} = \pi$  which are the persuasive indicators of molecular behavior. Figure 2 shows us that, though the rotations may be nonrigid and the vibrations anharmonic, the presence of an inner core is sufficient to reduce the extreme value of the kinetic energy of the valence electrons, so that their Coulomb repulsion enforces a highly correlated "structure" even in the low-lying states of the Be atom.

This report is, in a sense, only a first step toward obtaining new insights into the structure of open-shell atoms. The alkaline earths still pose many questions. For example, while  $He^{**}$  shows clear shell structure with well-defined maximum values of  $L$  and  $S$  for each  $n_1, n_2$  pair, it is not at all obvious whether the alkaline earths exhibit such shell structure. Perhaps the very concept of shell structure is unique to hydrogen and helium, while in systems such as the alkaline earths, the bound states are more properly labeled as members of recognizable vibrator-rotator series. There are also states that do not fit into the simple molecular model. One example is the " $4s3d$ "  $3D^e$  state of Ca, which seems to have no place at all in the molecular scheme. A future publication will explore such "interloper" states in greater detail. The application of group-theoretical models designed for anharmonic oscillators and nonrigid rotors is clearly an attractive direction to explore.<sup>15</sup> And, fi-

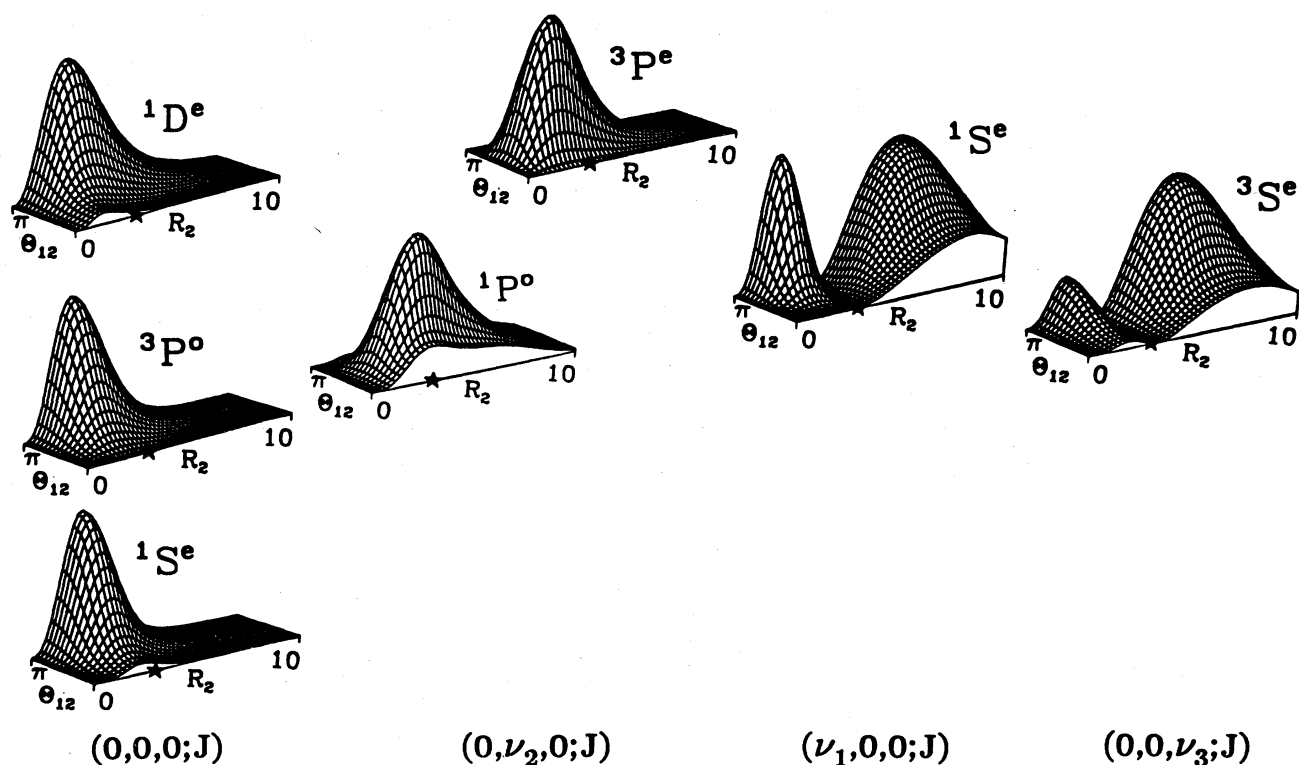


FIG. 2. Conditional probability distributions for low-lying excited states of Be, with the "fixed" electron at approximately its most probable position. These distributions should be compared with those of Ref. 3. The labels  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  refer, respectively, to the symmetric stretching, bending, and antisymmetric stretching modes of a linear triatomic molecule.  $J$  refers to the rotational excitation.

nally, elucidating the question of the structure of atoms with more than two valence electrons remains a more interesting challenge than ever.<sup>16</sup>

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