Collective and Planetary Motion in Atoms

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Abstract

The evolution of the conception of electron correlation is sketched, particularly the ideas that emerged in the late 1970s. Those ideas have led to a deep reexamination of the behavior of electrons sharing a valence shell. Doubly-excited helium was the first case in which it could be clearly established that the electronic states exhibit collective rotations and vibrations, rather than predominantly independent-particle-like behavior. More recently, it has appeared that the ground states and most but not all of the low-lying excited states of the alkaline-earth atoms are also much more like collective rotor-vibrators than like quantum analogues of solar systems. The appearance of such molecule-like characteristics for the electrons in atoms leads to a search for independent-particle-like behavior for atoms in highly excited vibrational states of small molecules such as H$_2$O, NH$_3$, and CH$_4$. Together, the two kinds of systems potentially exhibiting characteristics traditionally associated with the other suggest trying to find a more unified formulation of few-body problems that makes collective and independent-particle behavior into related but complementary manifestations of some more general characterization of the states of few-body systems.

1. Introduction

The dazzling success of the planetary model of Niels Bohr's 1913 trilogy, in reproducing the known spectral lines of hydrogen and predicting others and in explaining the lines found by Pickering (1897) in the spectrum of β-Puppis and by Fowler (1912) in laboratory discharges, stimulated attempts to interpret the spectrum of neutral helium atoms with an extension of the same model. The solution to
this problem was far subtler than suspected [except perhaps by Einstein (1917)] and was not solved in terms of Bohr–Sommerfeld quantization until the work by Leopold and Percival (1980), and then only for the ground state. [See also Percival (1977) for a review, and Coveney and Child (1984) for the next development.] However by 1920, in his address to the German Physical Society, Bohr expressed an expectation whose fulfillment is beginning to emerge with the ideas we shall explore here. [See Nielsen (1976).] Bohr said, regarding the attempt to extend the results for the hydrogen atom to other atoms and to molecules,

“It appears no longer possible to justify the assumption that in the normal states the electrons move in orbits of special geometric simplicity like ‘electron rings’. Considerations relating to the stability of atoms and molecules against external influences and concerning the possibility of the formation of an atom by successive addition of the individual electrons compel us to claim, first that the configurations of electrons are not only in mechanical equilibrium, but also possess a certain stability in the sense required by ordinary mechanics, and secondly that the configurations employed must be of such a nature that transitions to these from other stationary states of the atom are possible. These requirements are not in general fulfilled by such simple configurations as electron rings and they force us to look for possibilities of more complicated motions.”

These sentences presage not only the shell structure of atoms; we can even read into them the seeds of our contemporary ideas regarding collective behavior of electrons in atoms, and it is to this topic that this essay is primarily devoted. We shall, however, look a bit beyond, toward some generalizations to which those ideas inevitably lead us.

Certainly the accepted picture today of atomic structure supposes that the best first approximation is the independent-particle model in which each electron has an energy and an angular momentum of its own. The orientations of those angular momenta cannot be even modestly good constants of the motion, but we suppose that one-electron energies and angular momenta can be treated as approximate constants of the motion with corresponding “pretty good” quantum numbers. This behavior is in sharp contrast to the collective rigid-body rotations and normal-mode vibrations we use as the first approximation for describing the behavior of atoms in simple molecules. Bohr himself recognized this difference in 1913, in the third paper of the trilogy (Bohr 1913).

We shall see here how some of those distinctions between the two classes of systems break down when we scrutinize them with the tools now available to us. As the distinctions begin to blur, we find atomic states that are characterized by molecule-like quantization and perhaps molecular states for which independent-particle atom-like quantum numbers are appropriate. The systems begin to seem like the armadillos of Rudyard Kipling (1946), neither tortoises nor hedgesnogs but a blending of the two. Nuclear physics has long had to confront systems that exhibit both sorts of characteristics and concepts from this field have been important in influencing what has happened recently in atomic physics. It is tantalizing to conjecture that the cross fertilization might lead eventually to a formulation of the few-body problem that puts nuclei, atoms and molecules on a common footing, so that we can recognize their commonalities as easily as their differences.
The slowness with which the interpretation of electron correlation in atoms has emerged might be associated with the history of computation. In the earliest days, back-of-the-envelope hand calculations were all one could do, and suffered very nicely for the original model of Bohr. With the advent of hand-operated desk calculators, it became possible to do self-consistent field calculations at the level of Hartree and Hartree–Fock methods, and to interpret the results of these calculations. When electronic computers became available, elaborate, many-electron variational wave functions could be and were generated, for example of the multiconfiguration type. However, during the period when these functions, often quite accurate, were first being generated, their interpretation was apparently a computation problem just a step more complicated than their generation, so that the interpretive phase for wave functions of present accuracy waited until the powerful microprocessor-based computers of today. Ironically, the task of extracting the relevant information to interpret even very complicated wave functions turns out to be not much more difficult than carrying out the calculations that produce those functions.

The recent history relevant here begins with the approaches that treated the electrons of doubly-excited helium atoms like almost-hydrogenic electrons interacting weakly via their mutual repulsion. The special symmetry of the hydrogen atom that makes its $n$th level $n^2$-fold degenerate is the symmetry of rotation of a sphere in four dimensions, $O(4)$, so that the starting point used for calculating energy levels and wave functions of doubly-excited helium takes the zero-order Hamiltonian as $O(4) \times O(4)$. This is just the approach Herrick and Sinnenoglu (1975) followed and was also followed independently by Wulfman (1973). The electron–electron interaction breaks this symmetry; the problem was to find what smaller group gives a proper picture of the approximate symmetry of the full Hamiltonian with the electron repulsion included. The answer they found is a single $O(4)$ whose extra invariant is the square of the length of the difference of the two electrons’ Runge–Lenz vectors, $A_1$ and $A_2$. Since each Runge–Lenz vector is essentially the semi-major axis of the classical Kepler ellipse, the invariance of $|A_1 - A_2|^2$ indicates that the two classical ellipses precess together. Wulfman (1973) showed that diagonalizing the operator corresponding to this invariant is approximately but not exactly equivalent to diagonalizing the operator $1/R_{12}$, so things seemed to be starting to fall into place. However, the quantum-mechanical counterpart of the precession of the ellipses was very much a mystery: it did suggest that helium in a state well described by the $O(4)$ model might show some tendency toward maintaining a geometric structure to its probability distribution.

Pursuing this idea, Rehmus, Kellman, Roothaan and the present author in 1978 (Rehmus et al. 1978a, b) presented suitable probability distributions from the wave functions generated by Herrick and Sinnenoglu to look for spatial correlations, particularly angular correlations that would give the atom a persistent “shape”. There was little question of what was wanted: mean deviations of the symmetry of the probability distribution with respect to the mean interelectronic angle $\theta_{12}$ would be the very least. Fortunately it was possible to extract vastly more information by not reducing the data nearly so far. Beginning with the full probability distribution for the two electrons $|\Psi(R_1, R_2)|^2$, a function of six variables, one can remove the dependence of this distribution on its orientation in the space of the laboratory
coordinates by integrating it over the Euler angles that specify that orientation. This leaves a reduced distribution in three variables; what three variables ought one to use? Clearly one must be $\theta_{12}$; for the interpretive purposes we had in mind, the others ought to be the distances $R_1$ and $R_2$ of the two electrons from the nucleus. Figure 1 shows these variables. But this is still not quite sufficient; one cannot readily graph a function of three independent variables. However, one can graph a function of two independent variables and even represent such a graph as a projection on a sheet of paper. The reduction is natural: one reduces the already reduced probability distribution or density $\rho(R_1, R_2, \theta_{12})$ to the conditional probability distribution $\rho(R_2, \theta_{12}; R_1 = a)$ which is the probability distribution for the distance $R_2$ and the angle $\theta_{12}$, provided that the distance $R_1$ has the value $a$. With the reduced density or probability distribution based on these variables, it is straightforward to construct the distribution from a variety of conventional forms for wave functions, and it is equally straightforward to interpret the distributions. (See Rehmus et al. 1978a, b and Rehmus and Berry 1979.) We discovered a bit later that exactly this choice had been made by Shim and Dahl (1978) to help them interpret the physical basis of Hund's rule, and in 1959 by Munsch and Phuvinage (1963) to explore the correlation in the ground state of helium. Computational tools were not yet powerful enough in 1963 to make the appropriate computations feasible for more than one simple graph. Now one can construct the graphs readily, and much of the subsequent discussion focuses on examining and interpreting such graphs. Figure 2 illustrates the probability distributions for the ground and first two excited states of the helium atom, specifically the distributions for $R_2$ and $\theta_{12}$ when $R_1$ takes on its most probable value. (Strictly, all the distributions shown here are multiplied by the factor $R_2^2$ from the Jacobian; without this factor, it is difficult to see clearly the asymmetry in the lower states, particularly the S states.) These and some of the subsequent illustrations are done in a Cartesian representation; others are done in cylindrical polar representation. The former spreads out the region near the origin, which is helpful for seeing that region. However, the polar representation seems closer to reality because it shows the nucleus as a singular point at the origin, not as a line at the bottom of a trough. Both fig. 2a and 2c exhibit some polarization of the distribution toward $\theta_{12} = \pi$; that is, electron 2 does indeed show some tendency to be on the side of the nucleus away from electron 1. However this tendency is not strong. We can expect more correlation of the electron distribution.
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Fig. 2. Cartesian representations of the conditional probability distributions \( p(R_2, \theta_{12}; R_1 = a) \) for the three lowest states of the helium atom with \( a \) at the most probable value of \( R_1 \). In all three cases (a, b, c) some angular correlation is evident, but the large amplitude of the distributions near \( \theta_{12} = 0 \) is indicative that the behavior is dominated by independent-particle character. The star indicates the value of \( R_1 \).

in coordinate space in the two-electron H\(^-\) ion. Figure 3 shows the conditional probability distribution for this species, again in Cartesian representation, for several values of \( R_1 \), from a very small and improbable value through the most probable region out to a very large and very improbable value. The H\(^-\) ion does show more asymmetry in \( \theta_{12} \) than do the states of He in fig. 2, but still electron 2 can appear at any value of \( \theta_{12} \) and \( R_2 \), as one expects of an electron that can be moderately well described as occupying its own atomic orbital.

Section 2 reviews the current concept of correlation in doubly-excited helium, beginning with the recognition of rotor series and then supermultiplets. Section 3 describes some of the recent findings regarding the atoms of the alkaline earth
elements. Section 4 peeks a bit through some of the doors opened by the new conceptions described in sections 2 and 3.

2. Doubly-excited helium atoms

In 1978, Kellman and Herrick (1978) pointed out that the observed and calculated levels of helium in which both electrons have the same quantum number (greater than 1) contain sets of levels that correspond remarkably well to rotor series. That is, in each of the known groups of levels for which \( n_1 = n_2 \), there is a terminating set of levels with angular momentum quantum numbers \( J = 0, 1, 2, \ldots \), alternating even and odd, with energies approximately \( \hbar^2 J(J + 1) \) above the level of the lowest for which \( J = 0 \) in that group. This was followed by three much longer papers in 1980 (Herrick and Kellman 1980, Herrick, Kellman and Poliak 1980 and Kellman and Herrick 1980) in which the authors showed that the rotor series could be fit into supermultiplets corresponding to symmetry broken from that of the \( \mathrm{O}(4) \) of the two interacting electrons. Kellman and Herrick, in the third of the 1980 papers, showed
that the particular supermultiplet pattern of He**, the doubly-excited helium atom, is the O(3) × SU(2) of a rotor in three dimensions and a two-dimensional harmonic oscillator. The ideal supermultiplet pattern and the corresponding states of He** for \( n_1 = n_2 = 3 \) are shown in fig. 4. The papers culminate with the identification of this symmetry as equivalent to that of the rotations and bending vibrations of a linear e-He-e rotor-vibrator like a linear ABA triatomic molecule. Kellman and Herrick speculated that the level pattern might well reveal symmetric and antisymmetric stretching vibrations as well. This analysis, it must be remembered, was done from phenomenological and symmetry arguments; the interpretation in terms of molecule-like collective rotation and vibration came afterward, and was not put intentionally into the model. The molecular interpretation came only when the analysis was complete.

We had of course been in fairly close touch with Herrick and Kellman as this work took shape, and it did indeed stimulate our thinking. If their assignments were
Fig. 5. (a, bottom) The levels of the helium atom for which \( n_1 = n_2 = 2 \) and, at the right upper corner, the four lowest levels of the manifold with \( n_1 = 2, n_2 = 3 \), \( v_3 \), \( v_4 \), \( J \) of the Linear three-body system, corresponding respectively to the symmetric stretch, the doubly degenerate bend, the asymmetric stretch and the total rotational angular momentum (spin is neglected in the designations at the bottom). The spin, orbital angular momentum and parity are indicated for each level. The quantum number \( J \) of fig. 4 corresponds to \( J \) here; \( K \) of fig. 4 is \( v_2 + 2 \) of this figure, and \( T \) of fig. 4 denotes the magnitude of angular momentum along the figure axis associated with the doubly degenerate bending mode. (b, top) Cylindrical polar representations of the conditional probability distributions for the levels whose energies are shown in fig. 5a), the two highest P levels excepted. The distributions shown here exhibit very strong angular correlation, of the degree expected for strongly collective behavior; for example, the three states of the rotor series at the left differ only very slightly when viewed in the intrinsic coordinate frame this way, although they obviously differ in their overall rotational distributions in the laboratory frame. Similarly, the partners of the degenerate bending mode have very similar distributions expected for independent-particle behavior. In this polar representation, the position of the “fixed” electron is shown by the vertical that falls from the surface of the distribution to a point within the indicator circle below. The other four “legs” indicate the positions on that circle of \( \theta_{12} = 0, \pi/2, \pi \) and \( 3\pi/2 \).
correct, then we reasoned that the conditional probability distributions for the states of He** in the supermultiplets should look like the distributions for rotors and vibrators, not like those of independent-particle systems. In the intrinsic coordinates \( R_1, R_2, \theta_{12} \), the members of a rotor series should have distributions that look very much alike; the differences among them should be primarily in their behavior with respect to the Euler angles whose time variation corresponds to rotation in the laboratory frame. By the same token, the degeneracies of the ideal harmonic two-dimensional oscillator should be reflected in the distributions of the corresponding nearly-degenerate states of the supermultiplet model. And there should be states corresponding to combinations of rotational and vibrational excitation, rotational ladders built on excited vibrational states.

Yuh et al. (1981) constructed probability distributions of the electrons of the \( 2s^2 \ 1S^e, 2s2p \ 3P^o, 2s2p \ 1P^o \) and \( 2s3s \ 3S^e \) states of He**, using a functional basis with the electron–electron distance \( R_{12} \) as one of the variables. The first two of these ought to be the first two members of a rotor series—the third should be the \( 2p^2 \ 1D^e \)—the \( 1P^o \) should be one of the two partners of the first excited level of the bending vibration, and the last should be the first excited state of the antisymmetric stretching mode. (The designations such as \( 2s2p \) refer of course to an independent-particle picture and are strictly inappropriate labels for states characterized by collective behavior. However, there is no ambiguity here in using the independent-particle labels and the observed levels are generally designated in the literature such that way. Hence, we shall refer to the states in terms of the orbital labels for convenience with the understanding that the single-particle quantum numbers must not be taken literally.) Indeed, the distributions do have the expected forms. This was strong persuasive support for the collective molecular model but its validity depended on all the states of the manifold with \( \nu_1 = \nu_2 = 2 \) fitting the molecular pattern.

The full picture was established for the states of this lowest set of states of He** by the calculations of Ezra and Berry (1983). The energy level pattern for these states, organized according to the quantum numbers of the normal modes of vibration \( \nu_1, \nu_2 \) and \( \nu_3 \) (symmetric stretch, bend and antisymmetric stretch, respectively) and \( J \), the quantum number for rigid-body rotation, is shown in fig. 5a. (An additional approximate quantum number \( \lambda \), designating angular momentum along the figure axis associated with the doubly degenerate bending vibration, is also useful, but is not indicated in fig. 5a.) The conditional probability distributions for the corresponding eigenstates are shown in fig. 5b, for one electron at its most probable distance from the nucleus. The three members of the rotor series—the \( \2s^2 \ 1S^e \), \( 2s2p \ 3P^o \) and the \( 2p^2 \ 1D^e \)—do appear very much the same in this intrinsic-coordinate picture, although in the independent particle model there is no particular reason why they should be similar. The partner states corresponding to one quantum of bending—the \( 2s2p \ 1P^o \) and the \( 2p^2 \ 3P^e \)—are also very much alike despite their differences in (presumed) configuration, spin and parity. The \( 2p^2 \ 1S^e \) state corresponds to two quanta of bending vibration but no angular momentum. The first states above this manifold are also shown; the \( 2s3s \ 3S^e \) does correspond to the one-quantum state of the antisymmetric stretch mode and the corresponding singlet, to the one-quantum state of the symmetric stretch mode. The molecular model seems well justified, at least for some of the doubly excited states of helium.
Fig. 6. Cartesian representations of the conditional probability distributions of the "2s\(^2\)\(^1\)S (lower row) and "2p\(^2\)\(^1\)D levels (upper row) of He, Be\(^{++}\) and Ne\(^{++}\), respectively from left to right. The \(^1\)S levels retain their strong angular correlation as the nuclear charge \(Z\) increases but the distributions for the \(^1\)D levels become progressively more symmetrical about \(\theta_{12} = \pi/2\), so that in the helium-like neon ion, the distribution indicates that each electron carries its own nearly constant angular momentum.

The model does have its limits. Nikitin and Ostrovsky (1976, 1978) showed that if the principal quantum numbers \(n_1\) and \(n_2\) are very different, then as intuition suggests, the independent-particle model becomes the more appropriate one. Furthermore, because it is the large Coulomb repulsion of the electrons relative to their kinetic energy that causes the extreme molecule-like collective behavior, one suspects that if the kinetic energy were made large enough, the strong collective behavior would give way to independent-particle behavior. This can be done by increasing the nuclear charge; figure 6 shows conditional probability distributions for the \(2s\(^2\)\(^1\)S and 2p\(^2\)\(^1\)D levels of He, Be\(^{++}\) and Ne\(^{++}\). The \(^1\)S levels retain their highly correlated form, independent of the nuclear charge \(Z\), but the \(^1\)D levels transform from rotor-like in He to independent-particle-like, almost symmetrical about \(\theta_{12} = \pi/2\), in Ne\(^{++}\). The explanation for the persistence of correlation in the \(2s\(^2\)\(^1\)S and 2s2p\(^1\)P as well) has been interpreted by Navarro and Freyre (1971) and much more systematically by Ho and Wulfman (1983) and by Wulfman and Levine (1984). In effect, the increase of kinetic energy in these states arising from increases in \(Z\) is compensated by the accompanying decrease in the spacing and ease of mixing of the configurational levels that must take place to generate the highly correlated rotor character. The \(^1\)D levels, on the other hand, do reflect the unexplained effect of increasing \(Z\) by becoming truly 2p\(^2\)-like as \(Z\) increases. Hence the correlated, molecule-like picture clearly has only a limited range of validity; it is by no means a universal model for states of many-electron atoms. It might even seem presumptuous at this point to suppose that the collective molecular model is applicable to anything except doubly-excited two-electron species.

A technical point needs to be mentioned here. All the doubly-excited states of helium are indeed at energies above the first ionization limit and are therefore
strictly resonances, not bound states. The method used to calculate the states described above is a variational procedure with only square-integrable functions in the basis. Hence, the calculation was equivalent to one based on a Feshbach projection in which the continuum was projected away. The coupling to the continuum can then be made, e.g. by Fano’s bound state-continuum mixing procedure (Fano 1961); Rehmus and Berry (1981) used just such an approach to evaluate the lifetime of two of the $^1S$ states of He**.

3. The atoms of the alkaline-earth elements

The next natural step was to ask whether any states of other atoms exhibit any tendencies toward the kind of collective behavior found in He**. Are there any more common species, easier to study in the laboratory than the exotic, short-lived doubly excited helium, in which collective rotations and vibrations might be found? The obvious targets of this question were the quasi-two-electron atoms and ions, those with two electrons in their valence shell outside a closed core. This meant studying the alkaline-earth atoms Be, Mg, Ca, Sr and Ba, and the negative ions of the alkali atoms, Li$^-$ through Cs$^-$
. To carry out systematic calculations of the full electronic structure for even a modest number of states for all of these would be a major project. Moreover, such an effort would develop far more information than is needed to answer the questions at hand. It would suffice to have the results of a model calculation for those states of interest: provided the results are well-converged and robust to small changes in the core potential, it would be enough to study the electron distributions of the two valence electrons in the effective potential due to the field of the nucleus and all the core electrons. It is only the correlation between the valence electrons that we investigate at this point, not the valence-core correlations, which are certainly far the smaller in the alkaline-earth atoms and alkali negative ions. Following this course, Krause and Berry (1985a, b) constructed two-electron wave functions for the ground states and a variety of bound excited states of all the alkaline-earth atoms, and the ground states and stable excited states or resonances of the alkali negative ions, using effective core potentials of several types, most extensively those of Bachelet et al. (1982), but also those of Weeks and Rice (1968) and of Barthelat et al. (1977). Figure 7 shows conditional probability distributions of the ground states of the alkaline earths, for four values of the “fixed” electron–nucleus distance. The distributions are a little broader in $\theta_{12}$ than those of the rotor states of He** but are clearly far more like those rotor states than like the ground state of the helium atom.

Collective behavior seems to be the rule for most of the low-lying excited states of these atoms as well. Figure 8 contains distributions for all the alkaline-earth atoms with one electron–nuclear distance at approximately its most probable value, for most of the states analogous to the He** states with $n_1 = n_2$, plus the two states of each corresponding to the “$2s3s$” $^1S$ and $^1S$ levels of He**. As with He**, the $^1S$, $^3P^0$ and $^1D^0$ levels in the three left columns have the similar shapes expected of the members of a rotor series; the next $^1P$ and $^3P$ levels, odd and even respectively, have their maxima at values of $\theta_{12}$ much less than $\pi$ and have zeros at $\theta_{12} = \pi$, as the first
Fig. 7. Cartesian representations of the conditional probabilities of the valence electrons of the alkaline-earth elements in their ground states, for four values of the "fixed" electron–nuclear distance. While broader in the direction of $\phi_{z}$ than the corresponding distributions for the "2s$^2$" state of He, these all exhibit much more angular correlation and therefore more collective character than the distributions for the bound excited states of He or the ground state of H$^-$. 
Fig. 8. Cartesian representations of the conditional probability distributions for all the states of the alkaline-earth atoms (analogous to those of He** shown in fig. 5h), the analogues of the "2p^2" 3S excepted. The collective quantum numbers \( v_1, v_2, v_3, J \) are indicated below, so that the first three columns correspond to the roto states and the next two to the first excited states of the bending mode. The 1P levels of Ba and Mg show moderately large probability densities at \( \theta_{12} = 0 \), and the 1P state of Ba exhibits a distribution intermediate between the single maximum characterizing a first-excited bending state and the symmetrical double maxima of a d^3P^0 state which would correspond to independent-particle behavior. All these distributions are constructed with \( R_1 \) at its most probable value, indicated by a star.
Fig. 9. Cartesian representations of the conditional probability distributions for the S states of Mg that correspond to the symmetric stretch ($^1S^e$) and the antisymmetric stretch ($^3S^e$) state, respectively, for five values of the electron-nuclear distance $R_1$, indicated by a star, showing how these do indeed correspond to the appropriate classical models. The symmetric stretch picture fails if $R_1$ is very small or very large; in the former case, its effective force is almost as if it is part of the nucleus, and in the latter case, it behaves like a Rydberg electron. Both these extreme cases correspond to situations of very low probability.
excited partner states of a doubly-degenerate bending vibration should. The $^1P^o$ levels of Be and Mg are somewhat more independent-particle-like than the "2s2p" $^1P^o$ level of He; it seems, from their moderately high probability densities at $\theta_{12} = 0$. The probability density of the lowest $^3P^o$ level of Ba does not look at all like that of a first excited state of a bending vibration; we shall return to this state shortly. The $^3S$ levels all have the forms expected of antisymmetric stretching vibrations. This is even more apparent in fig. 9 where the probability densities for the presumed excited stretching-mode states of Mg are shown for several values of the fixed electron-nucleus distance. The $^1S$ state of this pair seems a bit less of a pure stretching mode than the triplet; however, one must keep in mind that if one electron is very close to the nucleus, the other electron is subject to a nearly centrosymmetric potential, and if one electron is very far from the nucleus, it must behave as a Rydberg-like, independent particle. Hence, we should expect symmetric-stretch character for the $^1S$ state only for intermediate values, the most probable values of course, of the fixed electron-nucleus distance. And this is what we find from the calculations.

The energy levels of the low-lying states of the alkaline-earth atoms seem to show patterns characteristic of three-particle rotor-vibrators, with rotor series and bending-mode states, according to Kellman’s (1985) analysis. The splittings of the vibrational partner-states are considerably larger than in He**, and in a few instances, states identified by Krause and Berry (1985a, b, c) as belonging to the vibrator-rotor manifold are not the same as those Kellman assigned to the same niche in the manifold. Nevertheless, the energy-level pattern is largely interpretable in terms of the collective model.

The distributions for the ground states of the alkali negative ions are very similar to those of their iso-electronic counterparts in the alkaline earths. The "$np^2$" $^3P^o$ states of the alkali negative ions are, with the exception of Li-, stable with respect to spontaneous detachment, according to the calculations of Norcross (1974). These states have energies below the energies of the corresponding excited $^2P$ levels of the neutral alkalis, and have no allowed decay mechanism to the ground states of the neutrals, plus a free electron. These triplets, like the "$np^2$" $^3P^o$ levels of the alkaline earths, have nodes at $\theta_{12} = \pi$ and maxima at angles corresponding to bent structures. The alkali negative ions have been discussed by Krause and Berry (1985c).

A few additional points need to be made to give a balanced assessment of the case for collective, molecule-like behavior in two-electron atoms. First, one of the most persuasive points is the make-up of the $^1D$ functions whose distributions appear in fig. 8. For Be and Mg, these are, respectively, dominated by the $2p^2$ and $3p^2$ configurations. For the heavier elements of this group, sd configurations are more important; for Sr and Ba, respectively, the dominant configurations in their lowest $^1D$ levels are 5s4d and 6s5d. Despite this major difference, the spatial distributions of the full variational wave functions are extremely similar. This inevitably suggests that a common characteristic responsible for that similarity is more fundamental to the behavior of the $^1D$ states than is the dominant configuration. The rotor character seems to serve as that common characteristic.

In some cases, notably the "$np^2$" $^3P^o$ and $ns(n + 1)s$ $^3S^o$ levels, approximately the same distribution emerges whether the independent-particle or collective picture
is used. In both these kinds of states, the constraints imposed by particle symmetry, the exclusion principle and the spatial symmetry force the distribution to be like a first excited bending state in the case of the $^3P$ and like an antisymmetric stretch-state in the case of the $^3S$. One can only say from these examples that they do not contradict the expectations based on the collective model. By contrast, some few states conform to neither model. The lowest $^3P^o$ level of Ba is not based on the $6p^6$ configuration, but on the $5d^{10}$, in an independent-particle picture or in a configuration-based variational calculation. A pure bending-vibration form for this state would give a single maximum in the probability distribution at some angle $\theta_1$ less than $\pi$; a pure $d^2\,^3P^o$ level would give a distribution with two equal maxima at $\pi/4$ and $3\pi/4$. The distribution shown for this level in fig. 8 has two maxima of very unequal heights. This state seems to fall between the two extreme models.

All in all, while the collective molecular picture is clearly not universally applicable for the description of the states of two-electron and quasi-two-electron atoms, it seems to be a more appropriate description for many of the states of these species than is the alternative independent-particle model. The physical basis for this behavior in the quasi-two-electron systems is not very different from that in He$^{**}$. In both kinds of systems, the valence electrons are kept from the region near the nucleus, so that they never have very high kinetic energy, and their spatial distributions are consequently very much affected by the electron-electron repulsion. In the alkaline-earth atoms, the ion core keeps the valence electrons away from the nucleus; in He$^{**}$ and the iso-electronic ions, orthogonality of the 1s orbitals to all the higher orbitals serves the same function. In both kinds of systems, we see a kind of behavior that can be simply characterized and is in no way particularly startling, yet is quite different from what we have traditionally associated with the character of two-electron atoms.

Some unanswered questions are obvious at this stage. Is it possible to quantify the extent of validity of the molecular model by projecting well-converged variational functions onto simple vibrator.rotor functions to determine the amplitude and total contribution of the basic collective states to the stationary states? Would variational expansions in series of rotor-vibrator functions converge significantly faster than series expansions in the traditional configurational, independent-particle basis? The effective force constant and moment of inertia of a rotor-vibrator model can be treated as variational parameters to maximize the overlap of a rotor-vibrator function with an accurate function; are the optimizing values of those parameters sensible, and consistent with the properties of atoms? Do the valence electrons of the atoms of the third and fourth groups of the periodic table exhibit collective, molecule-like behavior? Do all the electrons with the same principal quantum number participate on an equal footing in the correlation in the valence shell, or does the separation of $s$- and $p$-subshells emerge in the form of a separation or distinction between the probability distributions of $ns$-$mp$-subshells? If the collective, molecular picture is correct at least for the ground states of some atoms, then should we not think of these atoms as having internal geometric structure which only needs to be oriented in order to form directional chemical bonds? Traditionally, we envision directional bonds being formed by the distortions and polarizations of the atomic charge distribution due to the fields of neighboring
atoms or ions. Whether there would be observable consequences associated specifically with this phenomenon remains to be investigated.

4. Independent-particle behavior in small molecules

Suppose we turn around the question “Can electrons in atoms exhibit collective rotations and vibrations like those of atoms in small molecules?” and ask instead, “Can the atoms in a small molecule such as the hydrogens in H$_2$O or CH$_4$ exhibit independent-particle-like behavior comparable to that of electrons in the ground state of the helium atom?” Could we find states in which the hydrogens of H$_2$O each have their own pretty good orbital angular momentum quantum numbers? Why do the hydrogens in a water molecule not have independent orbital angular momentum? The reason, crudely but accurately put, is that they bump into each other. If they could be kept out of each other’s way, then instead of bending vibrations, H$_2$O would show hindered but rather independent rotation of the hydrogen atoms.

It has been apparent since the work of Henry [see Henry (1977) for a summary and review of the early development] that when enough quanta are put into a bond, it can happen that the quanta remain there in a local stretching mode. Lawton and Child (1979, 1980, 1981) and then Child and Lawton (1981) showed how a water molecule excited by four or five or more quanta in its stretching modes would be capable of exhibiting local O–H stretching; the benzene molecule exhibits local C–H stretching when it absorbs a quantum of visible radiation from a helium–neon laser, a phenomenon found by Swofford et al. (1976). Of course the effective potential for a local stretching mode is much like a Morse potential, steeply repulsive at short distances, with a deep well, and tailing out to a weakly attractive long-distance portion as the bond stretches toward dissociation. In a highly excited state in such a well, the probability distribution is much more concentrated in the long-distance parts where the kinetic energy is low than in the region over the deep well. In other words it is much more probable to find a bond stretched nearly to its classical turning point in such a state than at a distance near its equilibrium distance. It is imaginable that a water molecule, highly excited in a local stretching mode so that the two hydrogen atoms are most probably at very different internuclear distances, could also be excited in its bending mode. If the distances of the two hydrogens from the oxygen are different enough, they would not “bump into each other.” Rather, they would be capable of passing so that the bending mode would have turned into an internal rotation of the inner hydrogen about the oxygen nucleus.

It is not yet known whether or not such a transformation from bending, stretching and overall rotation into independent atomic motions can take place in highly excited vibration–rotation states of H$_2$O. Some very simple calculations by Berry, Ezra and Natanson (1983) were based on fixing one O–H distance at its equilibrium value and the other at classical turning points for several local stretching modes. Then the wave function for the angular motion of this system was determined with two different potential surfaces then available for the H$_2$O mole-
cule, one by Sorbie and Murrell (1978) and the other by Murrell, Carter, Mills and Guest (1981). The former potential supported independent-particle rotations below the dissociation limit; the latter did not. Figure 10 shows the effective potential for the angular motion and three of the probability densities $\rho(\theta_{12})$ for $S$ states, one with energy well below the barrier, one also with energy below the barrier but close enough that tunneling is important, and one with energy above the barrier; these are of course based on the Sorbie–Murrell potential. More sophisticated methods are nearly ready to be applied to this problem, such as that of Natanson et al. (1984, 1986), and a better answer should be available soon. However it is more likely that the greatest bottleneck to getting an unambiguous theoretical prediction of this phenomenon is the generation of a reliable potential surface for the water molecule.

5. Concluding remarks

What can we expect to observe of these phenomena, of molecule-like atoms and independent-particle-like molecules? There are several possibilities. Very nonrigid molecules appear to have the characteristics of liquids, with well-defined diffusion
coefficients based on the rate of increase with time of mean displacements; with liquid-like pair distribution functions; with spectral distributions containing modes at frequencies close to zero. Hence measurements capable of showing these properties, particularly measurements showing angular distributions, may tell us of non-rigid, independent-particle-like character in small molecules. Diffraction experiments may well give us strong persuasive indications, but diffraction results do not distinguish disordered rigid forms from fluids. We shall need to study excited molecules with other techniques such as Raman–Brillouin scattering to probe for soft modes, and perhaps examination of angular and energy correlations of fragments from Coulomb explosions of molecules previously excited to known states of interest. Mean angles will be less interesting in this context than their next moment, the mean deviations of the bond angles from their means.

To look for strong correlations of electrons, several techniques come to mind. Electron diffraction is now capable, in favorable cases, of yielding mean values of the interelectronic distance (strictly, of its inverse); with a little more resolving power, it may be possible to evaluate the mean deviation of 1/r_{ij}, which is a measure of the correlation of the two electrons. A method more tractable now but requiring some new theory for its interpretation is the measurement of angular and energy distributions of photoelectrons from atoms photoexcited to the state of interest. Still another method, in a sense the counterpart of the Coulomb-explosion experiment for molecules insofar as it is a sudden process, is an (e, 3e) double ionization with very fast incoming electrons. This method will give a snapshot of the two-electron distribution in the atom, and since the alkaline earths seem to exhibit molecule-like correlation of their valence electrons, coincidence experiments to detect the angular correlation of the two slow electrons following a fast (e, 3e) process can be carried out with vapor of Ca, Sr or Ba. Here, however, as with the Coulomb explosions, the mean deviation in the angular distributions will be much more interesting than the mean angles.

These speculations are meant to give assurance that the phenomena of correlation and independent-particle character are more than games for a computer exerciser. They are observables, and we are only beginning to conceive laboratory probes to test their extent and importance. The experiments just suggested may well be more difficult or more complex than others that readers can invent.

Finally, we may ask whether it might be possible to find a unifying way to describe few-body systems that will encompass electrons in atoms, atoms in molecules, nucleons in nuclei and perhaps other few-body systems as well. Can we find a formulation from which the collective or independent-particle character of each state will emerge naturally before, rather than after each problem is solved on an ad hoc basis? Niels Bohr was right that we must look for possibilities of more complicated motions than co-planar orbits; the search to find those motions gives us the stimulus to look for a new level of unity for our ideas concerning the dynamics of simple systems.

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Discussion, session chairman T.A. Bak

Broglia: Can one view the results you have shown as being the transition densities associated with some of the elementary modes of excitation of the few-electron systems under study?

Berry: Not the pictures I have shown here; they are all truly reduced densities of either stationary states for the alkaline earths and the ground and singly-excited states of He, or projected quasi-stationary parts of the scattering resonances of doubly excited helium. However Paul Rehmus and I have examined a few transition densities for bound-free auto-ionizing transitions in doubly-excited He in order to find what parts of configuration-space and what operators are most important for generating the transitions amplitude. This was an extremely productive line, and we are planning to study transition densities systematically for the atoms and states I have been discussing here.

Temmer: Has the time not come to do experiments which, in nuclear physics, are called “pickup” and “stripping” reactions to highlight the single-particle aspects of these molecules? I mean reactions of the type $H^- + X \rightarrow H^0 + X^-$, where $X$ is the atom or molecule whose excited “single-particle” states we wish to characterize? The negative hydrogen ion is merely an example of the type of ion one can use. The spectroscopy is done on the outgoing $H^0$ with high resolution which is now technically possible.

Berry: Charge-transfer processes have, of course, been studied for a long time in atomic collision experiments, but most of these used positive ions on neutrals. The analogue of your suggestion would be, for example, $Be$ (instead of $H^-$) + $He^- \rightarrow Be^+ + He$. I cannot recall whether $Be$ has been used for such experiments but I believe Ca has been. The (negative ion + neutral) electron-transfer reactions are more difficult because some collisions $A^- + B \rightarrow A + B^-$ are dominated by detachment processes, $A^- + B \rightarrow A + B + e$. However, one could study $F^- + Cl$, or $H^- + Na$, or $Li^- + Na$, to pursue the process you suggest; one might even be able to make the predicted $^3P^o$ state of $Na^-$ by colliding excited Na(3p) with Cs$^-$ or with Cs in a high Rydberg state.