How good is Niels Bohr’s atomic model?

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Since 1913, Bohr’s planetary model for atomic structure has been predominant, but recent analyses suggest that collective quantization of atomic valence shells containing two electrons may be more valid. The history and evidence for these two extreme paradigms are presented and some of the potentially observable consequences are discussed briefly.

1. Introduction
With the compelling success of his planetary model of the hydrogen atom and the He⁺ ion (Bohr 1913) and the interpretation of the Periodic Table in terms of shell structure of planetary orbits (c.f. Bohr 1922a, 1922), Niels Bohr established a paradigm that has ever since then permeated our thinking about atoms and molecules. Our contemporary description is of course a translation of Bohr’s ideas into their quantum mechanical counterparts. The underlying physical concept of Bohr’s model which persists is that each electron has its own approximate constants of the motion and its own ‘pretty good quantum numbers’. This meant that the principal quantum number \( n \) and the orbital angular momentum quantum number \( l \), respectively, specify an approximately constant energy and angular momentum for each electron individually. If the atom were like a little solar system or its quantum mechanical analogue, then each electron would indeed have its own nearly constant energy and angular momentum.

A sequence of experimental and theoretical advances have brought the Bohr model first into scrutiny and then into question, as a suitable model for the valence electrons of some atoms. Specifically, many of the autoionizing, doubly-excited states of the He atom, the ground and many excited states of the alkaline earth atoms, the ground states and only expected bound excited states of the alkali negative ions, and, to a lesser degree, the ground and low-lying excited states of positive ions isoelectronic with the alkaline earth atoms, all conform closer to a collective, molecule-like model than to the independent particle model of Bohr. Here, we review how the Bohr model became an ingrained part of our thinking for many-electron atoms and then how that model came to be challenged. The story is not yet complete because we do not yet know how the valence electrons behave in atoms with three or more electrons in their valence shell. Nevertheless the story as far as it now goes gives us some interesting insights into how science moves ahead; we shall see how it is sometimes more important that new ideas be introduced than that those ideas be correct.

2. The old quantum theory and its legacy
Bohr surely must have started quickly to try to extend his model from one-electron atoms to helium, with its two electrons. He sometimes felt quite sanguine about making that extension, expressing these feelings in statements such as ‘This problem has been attacked by Kramers and the speaker; the results obtained so far have not yet been published; here I should like to give, in simple outline a survey of the mode of attack and the results obtained’ (Bohr 1922b, p. 979).

However, in 1920 he felt otherwise, at least when he spoke to the German Physical Society (Bohr 1922b, p. 241):

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 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 [italics mine].

Bohr began with a model for helium that placed the two electrons at opposite ends of a diameter of a circle, with the electrons rotating in the same direction. This was not successful, nor were any of the other mechanical
models introduced during the years 1919–1923. These included: Landé’s models (Landé 1919, 1920) of circular orbits of different radii, coplanar for the ground state and other states of what we now call the singlet states and inclined for what we now call triplets; Langmuir’s (1921a,b,c) parallel circular orbits (which Langmuir himself rejected); Langmuir’s other model, of electrons oscillating on circular arcs (Langmuir 1921a,b,c), to which we shall return; Kemble’s (1921) model of electrons rotating in opposite directions in coplanar circular orbits of unequal radii; van Vleck’s (1922) axially symmetric model of inclined, precessing orbits which is very similar to the one eventually published by Kramers (1923)—without Bohr. Langmuir’s second model was thought initially to give an accurate first ionization potential of He, but the experimental value then available proved to be in error. Figure 1 shows sketches of the orbits of the electrons in these models.

The most striking thing about these models is that all of them, save only Langmuir’s second model, require that the individual electrons have constant, quantized angular momenta. Langmuir (1921a) states:

Bohr assumes that the ‘permanent’ state of any atomic system is determined by the condition that the angular momentum of every electron round the center of its orbit is equal to $h/2\pi \ldots$. However it is an attractive hypothesis to assume that in the case of coupled electrons, the quantum theory is concerned not with the angular momentum possessed by one electron but rather with the angular momentum possessed, be transferred from electron to electron, circulates in each of two directions about the nucleus.

This model was rejected a year later by van Vleck who focused his attention on Langmuir’s introduction of a quantized maximum angular momentum for each electron and therefore decided that Langmuir’s approach contradicted, rather than generalized, the orbital quantization condition of Sommerfeld. van Vleck did not recognize that Langmuir had proposed quantizing only the total orbital angular momentum rather than the orbital angular momenta of all the individual electrons. It seems now that the doctrine of quantizing the individual angular momenta was so firmly fixed that it was almost unthinkable for a young man like van Vleck to challenge Bohr’s ideas. A brief, interesting insight into this history was given by Percival (1980) and a striking new, Langmuir-style approach was made recently by Dimitrijević and Grujić (1985).

The history of the theory of the helium atom breaks off in 1923 and, soon after the introduction of quantum mechanics, reemerges as a problem of accurate—and therefore elaborate—variational calculations. These began in 1928 (Hylleraas 1928) and continued, for the ground state of He, at least through the benchmark calculations of Morgan et al. (Freund et al. 1984). During the years from 1928 until 1980, little attention was given to mechanical pictures, to semiclassical Bohr–Sommerfeld approaches or even to mechanical interpretations of accurate variational wave functions for helium. The emergence of hand-operated and electric calculators and then of computers, and increasing insight into how to carry out convergent variational calculations efficiently all stimulated efforts to go in the direction of calculations of greater complexity, yielding more accurate expectation values of observables.

Two lines of recent work broke this pattern of ever greater emphasis on large-scale computation. One was the success of a semiclassical representation of the ground state of the helium atom (Leopold and Percival 1980, Leopold et al. 1980, 1982) in the tradition of Bohr and Sommerfeld, after most of the community had given up any hope for such a solution. The method has been pushed further to include effects of spin and exchange (Coveney and Child 1984) and an analogous solution of the other classic three-body problem, the ground state of the $\text{H}_2^+$ molecule, was independently achieved at almost the same time (Strand and Reinhardt 1984). These represent an approach whose implications are still uncertain, and which diverges from the topic to which the rest of this article is devoted. Before leaving it, we might take note of what made the new attacks successful when numerous earlier attempts were not: both pairs of workers, Leopold and Percival on $\text{He}$ and Strand and Reinhardt on $\text{H}_2^+$, realized the importance of following Einstein’s prescription of choosing coordinates and momenta which are truly canonical conjugates, a prescription which makes the calculation more cumbersome than if one merely chose the variables in the traditional way. More cumbersome, but right.

3. $\text{He}^*$: a new stimulus

The origin of the direction we shall pursue here can be traced to a theoretical paper by Fano (1961) and a fortuitous, entirely unexpected experimental result found and correctly interpreted by Madden and Codling (1963). The experiment was the first observation of the absorption spectrum due to excitation of both electrons of the helium atom. Madden and Codling had set out to conduct some absolute radiometric measurements by using synchrotron radiation from the relatively small electron synchrotron at the National Bureau of Standards. Helium was presumed to be transparent, causing only a little scattering, but this presumption turned out to be wrong. Instead, a series of intense absorption lines with unusual, dispersion-like shapes appeared. These were photographed and interpreted in terms laid down in 1961 by Fano as lines buried in a continuum with which the excited, ‘bound’ upper states interact. Cooper, Fano and Prats (1963) then showed that the weakness or
Mr. J. H. Van Vleck on the normal Helium Atom

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

(a) (b) (c)

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Oscillating or semi-circular model for the helium atom.

H. A. KRAMERS, Über das Modell des Heliumatoms.

Figure 1. Sketches of some of the models for the helium atom within the context of the old quantum theory: (a), from van Vleck (1922); (b), from Langmuir (1921a); (c), from Kramers (1923). Bohr's original model is at the top left, with both electrons in the same circular path. The one beneath it, Landé's model, puts the electrons in coplanar orbits for what is now called the singlet series and in orbits tipped out of the plane for what is now called the triplet series.

The nonappearance of two other series one might expect to see is due to electron correlation which can be described in terms of configuration interaction, for example between a dominant 2snp configuration and a secondary 2pns configuration. Doubly-excited helium, written \( \text{He}^{**} \), quickly captured the interest of many atomic theorists; the pursuit of that species leads us directly into the modern developments of our subject. Note that all the doubly-excited states of He lie at energies above the first ionization limit, so all such states may, in principle, auto-ionize to \( \text{He}^+ \) in its ground state and a free electron.

The line most relevant for us is the one in which techniques based on continuous symmetries and Lie groups were used to classify states of \( \text{He}^{**} \) and to guide
the calculation of very approximate wave functions for those states. However another line of attack, based on a particular choice of coordinates, namely one type of hyperspherical coordinates, was also being pursued (Macek 1968, Greene 1981, Lin 1982, 1983, 1985, and, for a recent review Fano 1983) and the connection between that line and the one we are pursuing here has begun to be made recently (Watanabe and Lin 1986).

The phenomenological, symmetry-based approach pursued by Herrick and Sinanoglu and Wulfman seems to have its origins in a plausible and attractive notion which, quite independent of its crucial contribution to the evolution of the concepts of atomic structure, turns out to be altogether wrong (Herrick and Sinanoglu 1975, Sinanoglu and Herrick 1975, 1976, Herrick 1975). Its wrongness is irrelevant, from hindsight, but its novelty, like the observation of the spectrum of He** and even Bohr’s original model, made it into a key idea. The notion was this: both electrons in doubly-excited He are very far away from the nucleus, therefore far from each other and therefore very much like electrons in hydrogen atoms, only weakly perturbed by the other electron.

If this picture were correct, then one could begin a description of He** by neglecting the electron–electron repulsion and consider the atom as a pair of hydrogenic electrons. This would mean that each electron would have the special degeneracy and corresponding high symmetry of the hydrogenic electron, a degeneracy of n^2 for the states with principal quantum number n, independent of the orbital angular momentum quantum number l (instead of a degeneracy of 2l + 1) and a symmetry corresponding to invariance under rotation in four dimensions instead of only in three. The Hamiltonian for the hydrogen atom is invariant under the orthogonal transformations (rotations) of the four-dimensional rotation group O(4), rather than of the three-dimensional rotation group O(3). (Strictly, instead of O(4) we should use the direct product O(3) × O(3).) Hence the Hamiltonian for the two electrons, with the electron–electron interaction neglected, is O(4) × O(4). If there were no electron–electron interaction, the degeneracy of a state in which the principal quantum numbers are n1 and n2 would be n1^2 × n2^2. The electron–electron interaction then acts as a symmetry-breaking operation, lowering the symmetry and splitting the degeneracies.

How do the degeneracies split? Are any degeneracies or near-degeneracies left, apart from the (2L + 1) × (2S + 1) degeneracy of a state with good orbital and spin quantum numbers L and S for the two electrons? If so, one can search for some group smaller than O(4) × O(4), but larger than the pure rotation group in 3 dimensions (and the spin rotation group) to describe the symmetry of the Hamiltonian of doubly-excited helium. Wulfman showed that a good approximate intermediate symmetry, corresponding to approximate but not exact diagonalization of e^2/r_{12} is an overall O(4) subgroup of O(4) × O(4) based on the three components of angular momentum L and the three components of the difference B of the Runge–Lenz vectors of the two electrons. (The Runge–Lenz vector of a classical Coulombic or Keplerian 2-body system is essentially the semimajor axis of the elliptical orbit.) The invariants of the system, apart from energy, are L^2, the square of the orbital angular momentum, and B^2, and one component of each of these vectors. The constancy of B^2 means, in classical terms, that the Kepler ellipses of the two electrons precess together, preserving the vector connecting the semimajor axes of these ellipses.

Herrick and Sinanoglu showed that diagonalizing B^2 with just a small basis, only the set of functions composed of products of two one-electron functions with the same principal quantum number, the ‘intrashell’ states, reproduced rather well the energies and quantum numbers of the corresponding doubly-excited states as found spectroscopically or from much more elaborate calculations. The physical interpretation of the states and the approximate quantum numbers of the O(4) group remained to be given. When the wave functions generated by Herrick and Sinanoglu were studied to see how they place the electrons in space (Rehmus et al. 1978a), we found that in some of the states, such as the nominal 2s^2 1S, the two electrons have a strong tendency to be on opposite sides of the nucleus. This is particularly apparent when the doubly-excited states are compared with the ground and singly-excited states (Rehmus 1978b, Rehmus and Berry 1979). However, no pattern was apparent in the spatial distributions of probability found for states of He** at that time, partly because of inaccuracies in the higher states due to the very small basis and partly because only a very limited set of states could be examined graphically, due to the large amount of time required to do the construction of the distributions by hand. It was not long before we were motivated to replace these methods with efficient, computerized construction of spatial distributions of electrons determined from well-converged wave functions, far more reliable than the early ones generated by Herrick and Sinanoglu with their (deliberately) extremely limited basis sets.

4. A collective model for He**
Herrick and Kellman began a collaboration in 1977, bringing together two viewpoints which, when brought to bear on the problem, led to a proposal and eventually to a resolution of what He** is like, in terms both of analogy to a classical model and in terms of the best set of approximate constants of motion. Their first paper together (Kellman and Herrick 1978) was a note pointing
out that the manifolds of ‘intrashell’ states of He** contain subsets of levels that are very much like the levels of a rigid rotor or the rotor series found in nuclei (deShalit and Feshbach 1974, pp. 377 ff). That is, the levels of these series fit rather closely to the formula \( E \propto J(J + 1) \), beginning with the lowest members of each series (\( J \) is an integer), and the states of each series have total angular momenta increasing in unit steps, with even parity for the levels with even \( J \) and odd parity for the levels with odd \( J \). The series all terminated, of course, because the sets of intrashell states are all finite.

Two years later, the picture had become much more elegant and comprehensive. Three papers laid out the full pattern (Herrick and Kellman 1980, Herrick et al., 1980, Kellman and Herrick 1980). Each set of intrashell states forms a supermultiplet which contains its rotor series as a particular subset. The states within a supermultiplet can be characterized by three quantum numbers, which Herrick and Kellman called \( K \), \( T \) and \( I \) by analogy with the parallel nuclear examples; the rotor series have the same value for two of these, \( K \) and \( T \), and values from 0 to the maximum value of \( J \) (the sum of the maximum values of \( I_1 \) and \( I_2 \)) for the third. The supermultiplet pattern has just the number of states, and the parities, spins and orbital angular momenta allowed by the shell model for each set of intrashell states, as figure 2 shows.

Moreover the underlying symmetry from which the supermultiplet pattern arises is indeed the O(4) of Wulfman and Herrick and Sinanoglu, the symmetry-preserving \( B^2 \) and approximately making \( e^2/r_{12} \) diagonal. But the physical significance of the quantum numbers, particularly of \( K \) and \( T \), was not yet apparent from the supermultiplet structure. Exposing the physics of the approximate constants corresponding to the quantum numbers required one further reduction of the symmetry. Kellman and Herrick (1980) showed that the particular O(4) of He** contains an isomorphism to a linear triatomic molecule of the form ABA with the electrons playing the roles of the very light A atoms and the nucleus, the role of the heavy B atom. The O(4) group contains a three-dimensional rotation group O(3) and the unitary group SU(2) of the two-dimensional harmonic oscillator. These are precisely the symmetries associated with the rigid rotation of the three-body system and the two-dimensional harmonic oscillator of the bending motion of the A–B–A angle, a doubly-degenerate vibration. In other words the approximate constants of motion of the intrashell states of He** could be identified with the excitations of the rotation and the doubly-degenerate bending mode of the symmetric, linear triatomic molecule. Viewed in terms of the O(4) group, the termination of the pattern of rotational and
vibrational levels is an automatic consequence of the supermultiplet structure; from the viewpoint associated with the separate rotational \(O(3)\) and vibrational \(SU(2)\) groups, there is no reason to expect the series to end. And, in fact, the series of rotational and vibrational levels in real triatomic molecules do run on, terminating only with the breakup of the molecule by dissociation. Induced by the Coulomb interaction, the shell structure remains important enough in \(\text{He}^{**}\) to make its \(O(4)\) supermultiplet character persist.

At this stage, the evidence for collective, molecule-like behaviour was entirely based on the correspondences between the actual levels, observed or calculated from elaborate variational or multichannel treatments, and the levels of the supermultiplet pattern, and between the symmetries associated with the supermultiplets and the symmetric, linear triatomic molecule. The decision to pursue the possibility of a collective, molecule-like model was stimulated (Herrick and Kellman 1980) by the forms of the spatial distributions of electrons found (Rehmus et al. 1978a) from some of the wave functions derived by Herrick and Sinanoglu (Herrick and Sinanoglu 1975, Sinanoglu and Herrick 1975, 1976, Herrick 1975). However one could not infer from those distributions any systematic molecule-like character of the states of \(\text{He}^{**}\); some of the key functions were simply so crude that even though their energies were reasonably good, their spatial distributions were misleading from the standpoint of exhibiting systematic, molecule-like relationships among the states. This was just the time when it became apparent that much better wave functions were needed, and that if a molecular model for \(\text{He}^{**}\) were correct, a reliable set of well-converged two-electron wave functions would show forms and systematic relationships characteristic of molecule-like rotation-vibration wave functions.

Furthermore, Kellman and Herrick had speculated that \(\text{He}^{**}\) might exhibit states analogous to excited states of symmetric and antisymmetric stretching modes. One could look for such modes among the excited states, but they would have to fall outside the sets of intrashell states, because there was no room in the supermultiplet patterns for such excited states of stretching modes.

The next stages were the substantiation of the collective, molecule-like model by examination of the probability distributions from well-converged wave functions for \(\text{He}^{**}\), the identification of stretching modes, the extended application of the model to describe the ground and low-lying excited states of the alkaline earth atoms, the quantification of the validity of the collective model and the beginnings of exploration of the observable implications of the model. Reviewing these will bring us to the present state of the subject.

5. Conditional probability distributions in coordinate space

The way electrons are correlated can be inferred to a remarkable degree by studying the probability distribution implied by the wave function. To carry this out, however, we must be a bit thoughtful about how we present this distribution. For a three-body system such as \(\text{He}^{**}\) one natural way presents itself; for systems of more particles, we have yet to find a comparably powerful approach because too much information is contained in the wave function and we do not know how to extract what is relevant in a manner adaptable to pictures. The three-body system has nine coordinates, of which three can be assigned to the location of the centre of mass and therefore need not be considered in studying correlation within the system. Likewise, the three coordinates describing the instantaneous orientation of the three particles in the laboratory coordinate system are also irrelevant to correlation. Fortunately both the centre-of-mass coordinates and the orientation coordinates, the Euler angles, can be removed from the full probability density \(|\Psi|^2\), the former by choice of origin and the latter by integration. We are then left with a reduced probability distribution in just three independent variables.

This puts us in a very comfortable position because a function of three variables can be exhibited as a series of graphs, each for a fixed value of one of the coordinates, showing how the density \(\rho\) depends on the other two independent variables. We can go even further and use time as a surrogate for one coordinate and plot the density as a function of the other two in a series of frames constituting a motion picture. In other words a movie can be used to display all the information contained in the reduced probability distribution depending on only three variables. It is impractical to display a movie in a journal but it is entirely feasible to show individual frames, and a number of these are presented in the figures that follow.

Before examining some of the plots, we must first consider more precisely what we wish to plot in our three-dimensional graphs. Specifically, what coordinates should we choose? For a two-electron atom, we might use the distances \(r_1\), \(r_2\) and \(r_{12}\), the so-called perimetric coordinates \((r_1, r_2)\) are the distances of electrons 1 and 2 from the nucleus and \(r_{12}\) is the distance between electrons); we might use the coordinates of Hylleraas, \(r_1 + r_2, (r_1 - r_2)/(r_1 + r_2)\), and \(r_{12}/(r_1 - r_2)\), which are one example of hyperspherical coordinates; we might use a form of hyperspherical coordinates more popular in recent years, \((r_1^2 + r_2^2)^{1/2}, \tan^{-1}(r_1/r_2)\) and \(\theta_{12}\). We ourselves have used Hylleraas coordinates for wave functions but not for displaying probability densities; we have used the latter choice of hyperspherical coordinates occasionally for displaying probability densities, but much less than have others (Cooper et al. 1963). Most of
our graphic representations have been done with \( r_1, r_2 \) and \( \theta_{12} \) as the independent coordinates because they are closest to a set with direct intuitive implications; that is, we consider, for the most part, distributions of the form \( \rho(r_1, r_2, \theta_{12}) \). However, hyperspherical representations also can give additional insights in a number of cases.

The technique required for examining probability distributions was in hand (Rehmus et al. 1978) when the results of Herrick and Kellman appeared. In fact one contour plot had been given in 1963 (Munsch and Pluvinage 1963) of the equivalent of \( \rho(r_1 = a; r_2, \theta_{12}) \), the conditional probability distribution for finding \( r_2 \) and \( \sigma_{12} \) if \( r_1 \) has the value \( a \), for a single value of \( a \), for the ground state of helium. The implications of the Herrick–Kellman work were notable: if the collective, molecular model were correct, then the probability distributions of specific states should look like molecular probability distributions, and, even more compelling if true, there would have to be relationships among the probability distributions of different but related states appropriate to the relationships among molecular probability distributions. For example the states constituting a rotor series should have very similar probability distributions when seen in the internal or intrinsic coordinate system, even though they would look very different from one another in the laboratory frame. Similarly, the nearly degenerate partner states of the bending vibration should also look very much like one another—not identical, because Coriolis forces spoil their degeneracy and physical equivalence. Such close relationships are not to be expected of the probability distributions for states that are primarily independent-particle like.

Some examples illustrate these implications. The lowest state of the doubly-excited He atom is a \(^1S^e\) state designated as \( 2s^2 \) in the usual configurational notation appropriate to the independent particle picture. In the collective, molecule-like picture, this is the rotationless, vibrationless ‘ground state’ of the manifold of doubly excited states. The first excited state of this manifold is an excited rotational state with rotational quantum number \( J = 1 \), so it must be a \(^1P^e\) state, and its wave function must have odd parity. Furthermore the wave function must be spatially antisymmetric to correspond to a rotor with \( J = 1 \), so, being a state of two electrons, the spin function must be symmetric so the state must be a \(^3P^o\) state. Its configurational designation would be \( 2s^2p \). The second rotor state must be a \(^1D^e\) by the same kind of reasoning, whose configurational designation for He would be \( 2p^2 \). These should have probability distributions that resemble one another strongly if the molecular model has any validity. Similarly, the first excited states of the bending vibration must be the \(^1P^e\) and \(^3P^o\) states with configurational designations \( 2s^2p \) and \( 2p^2 \), respectively. Clearly, if the molecular picture were valid, the first excited states of the bending mode would be similar, but if the independent particle were better, there would be no reason for such states to resemble one another.

To show what can be learned from such displays, we first show in figure 3(a) an example of the potential acting instantaneously on one electron, due to the nucleus and the other electron (Krause and Berry 1986). This has been constructed with one electron, the one responsible for the sharp repulsive spike in the potential surface, at its most probable distance from the nucleus for the ground state of He. In the cylindrical polar plot, the nucleus is at the origin and the axis for which \( \theta_{12} = 0 \) is defined by the electron at a specified distance. Then, in figure 3(b), we

![Figure 3](image_url)

Figure 3. (a) The potential acting on one electron of a helium atom when the other electron is at its most probable distance from the nucleus, with the atom in its ground state. The graph is in cylindrical polar coordinates, with the nucleus at the origin and the axis \( \theta_{12} = 0 \) defined by the radius vector of the 'fixed' electron, \( 1 \), with \( r_1 \) at its most probable value for the ground state of He, \( 0.5a_0 \). (b) The probability distribution for the ground state of helium, \( r_2^2 \rho(r_1 = 0.5a_0; r_2, \theta_{12}) \), with \( r_1 = 0.5a_0 \) as above.
see superposed on the potential the probability distribution for the other electron, if the first electron is at the position corresponding to the potential shown. In fact, this distribution is not \( p(r_1, r_2, \theta_{12}) \) with \( r_1 \) at its most probable value, but \( r_2^2 \rho(r_1, r_2, \theta_{12}) \), i.e. the probability distribution multiplied by the \( r_2^2 \) of the Jacobian. The reason for this is that the density for an s-orbital is so peaked at the nucleus that it is difficult to see the asymmetry of the distribution if it looks like a witch’s hat, but displays whatever asymmetry it has when converted into a volcano shape by the \( r_2^2 \) factor. After seeing a few pictures such as figures 3(a) and (b), one no longer needs to see the potential if one knows the position of the ‘fixed’ electron, and most of the probability distributions that follow are drawn without the corresponding potential.

The shape of the distribution for the ground state of helium is not symmetrical around the origin; the probability is a little higher near \( \theta_{12} = \pi \) than near 0. However the distribution of figure 3(b) shows clearly that electron 2 can get past electron 1 and thereby maintain its own angular momentum around the nucleus moderately well. This is true for the ordinary excited states of helium as well; in other words those states are rather well described by their configurational designations 1snl.

When we come to the doubly-excited states of He, as exhibited in figure 4 (Ezra and Berry 1983, 1986)†, the distributions no longer look even a little bit symmetric around the origin in the representation based on \( r_1, r_2 \) and \( \theta_{12} \) that we are using. Rather, we see in figure 4(a) that the \( 1S^e \) state we would designate traditionally as the \( 2s^2 \) is highly distorted so that electron 2 has essentially zero probability of ever being on the same side of the nucleus as electron 1, at least when electron 1 is near its most probable distance from the nucleus. This distribution, as well as the coefficients of the individual configurational terms in the variational expansion of the wave function, tell us that designating this state as \( '2s^2' \) may be misleading, even if the most important single term in the expansion corresponds to the \( 2s^2 \) configuration. But we do not yet have enough evidence to call upon collective, molecule-like quantization. To do that we must examine other doubly-excited states of He to see whether they exhibit the similarities and other relationships we now expect of molecular states.

Figures 4(b,c) show the probability distributions for the lowest doubly-excited states of He designated \( '2p^e' \) and \( '1D^e' \), which, in the Kellman–Herrick supermultiplet scheme are the first and second excited pure rotational states of He**. In independent-particle or configurational notation, these states would be called \( '2s2p' \) and \( '2p^2' \) respectively. We see that indeed the similarities of their spatial distributions are striking when seen in the internal coordinate system. The other \( '2s2p' \) state, the \( '2s2p' \) state, is an excited state of the nearly-degenerate bending mode; its partner is the \( '2p^2' \) state. These states, shown as figures 4(d,e), obviously have the double-humped shapes of first excited states of bending vibrations and are rather similar. However the triplet has a mandatory node along the axis of \( \theta_{12} = 0 \) while the singlet does not. The singlet is the state that can mix with the antisymmetric stretch by Coriolis interactions. The only other state of the ‘intrashell’ set with \( n_1 = n_2 = 2 \) is the \( 1S^e \) state which corresponds to that second excited state of the bending vibrations which has no angular momentum, and to the configuration \( 2p^2 \) in the independent particle picture. The probability distribution for this state is shown in figure 4(f); it has the maximum at \( \theta_{12} = \pi \) and the two subsidiary maxima expected of a second excited bending state.

The evidence becomes persuasive at this point, that the doubly-excited states of He, or at least those with \( n_1 = n_2 = 2 \) are like molecular states, with the rotational and bending modes available for excitation up to the limit allowed by the states satisfying the conditions on the \( n \).

The argument can be pushed a bit further when we recognize that the first excited states of the stretching modes, symmetric and antisymmetric, must correspond to the \( '2s3s' \) and \( '2s3s' \) states, respectively (see figure 4(g,h)). The degree of validity of such an assignment can be assessed qualitatively by again comparing well-converged probability distributions of these states with simple but optimized oscillator distributions and with independent-particle distributions. Because we are dealing here with stretching modes whose characteristics are most apparent if \( \theta_{12} = \pi \), it is most useful to plot the distributions of the stretching modes as functions of \( r_1 \) and \( r_2 \) with \( \theta_{12} \) fixed at \( \pi \), i.e. to plot \( r_1^2 \rho(r_1, r_2, \pi) \). This is done in figure 5 (Hunter and Berry 1987). Two molecule-like models are used for that figure; one, used for figure 5(a), is a harmonic, normal mode form. The other, used for figure 5(c), is a symmetrized or antisymmetrized combination of local, Morse-type vibrations. Figure 5(b) shows the independent-particle, single-configuration results and figure 5(a) shows the distributions for well-converged CI expansions. We learn a considerable amount from these examples. Most obvious is that the harmonic model does not work at all well to describe these states. The potentials for stretching are so anharmonic that the concept of a normal mode is hardly applicable. The triplet is very well fit by the antisymmetric combination of local modes and moderately well represented by the independent particle model except very near \( r_1 = 0 \) and \( r_2 = 0 \), probably least well to the eye at least by the harmonic model. The antisymmetric

† These are based on CI expansions in products of Sturmian functions. An earlier incomplete set, based on Hylleraas-Kinoshita functions, was given by Yu et al. (1981).

** These are based on CI expansions in products of Sturmian functions. An earlier incomplete set, based on Hylleraas-Kinoshita functions, was given by Yu et al. (1981).
Figure 4. Above: the probability distributions for one electron of He** when the other electron is at its most probable distance from the nucleus. As in figure 3(b), the distributions have been multiplied by the factor of $r_3^2$ which appears in the Jacobian, so that the distributions look like volcanoes rather than like witch’s hats; in the left column, reading up, the rotor series consisting of the ‘2s2' 1S' state, the ‘2s2p' 3P' state, and the ‘2p2' 1D' state; next, from left to right, the ‘2p2' 3P' state, the ‘2s2p' 1P' state, the ‘2p2' 1S' state, the ‘2s3s' 3S' state and the ‘2s2p' 1S' state. Below: the energy levels for these states arranged according to conventional molecule-like quantization according to $v_1$, the symmetric stretch, $v_2$, the doubly-degenerate band, $v_3$, the antisymmetric stretch and $J$, the total angular momentum (neglecting spin). The observed levels of the states corresponding to one quantum of rotation and one quantum of antisymmetric or symmetric stretch are shown at far right above the corresponding rotationless S' levels. The energy units of Rydbergs (Ry) are the units of the ionization energy of the hydrogen atom; Ry is approximately 13.6 eV.
Figure 5. The probability distributions for the '2s2p' states of He as functions of \( r_1 \) and \( r_2 \) with \( \theta_{12} = \pi \): (a) from well converged functions; (b) from single-configuration hydrogenic functions; (c) from symmetric and antisymmetric combinations of optimized local Morde oscillators; (d) from optimized harmonic normal modes, symmetric and antisymmetric (taken with permission from Ezra and Berry (1986)).
Niels Bohr's atomic model

stretch of course has a node along \( r_1 = r_2 \). The symmetric stretch, which we might expect naively to have a large density only around the line of \( r_1 = r_2 \), clearly has a large probability for \( r_1 \neq r_2 \), especially so long as one distance is large. Again, the inner antinodes make the independent particle function less like the accurate function than is the local mode function, but both these approximate functions have significantly higher peaks on the \( r_1 = r_2 \) line than does the accurate distribution. Again, and even more than for the antisymmetric stretch, the least accurate is the harmonic, normal mode description.

The physical basis of the strong correlation apparent in figures 4 and 5, and the much smaller effects of correlation in the ground and singly-excited states is this. For correlation to be unimportant, the electrons must not scatter each other strongly. To do this, they must have rather high relative kinetic energy, which requires that at least one of them be near the nucleus. This can be accomplished readily in the ground and singly-excited states but not at all readily in the doubly-excited states. This is because the orbitals with \( n > 1 \) are orthogonal to the 1s orbital and have only small amplitudes in the region near the nucleus. One implication of this reasoning is that states of atoms with higher nuclear charge might be expected to show less correlation than the same states of atoms with smaller nuclear charge. This is in fact true for some but not all states; the \( ^1D^e \) second excited rottor states become more and more symmetrical around \( \theta_{12} = \pi/2 \) as the nuclear charge \( Z \) increases from 2 in He\(^{**} \) to 10 in (Ne\(^{+8}\))\(^{**} \) so that the distribution in the latter is essentially that of a 2p electron. However, the lowest and first excited states, \( ^1S^e \) and \( ^3P^o \), remain essentially the same for all \( Z \). This is because as \( Z \) increases and the states of the two-electron system become more hydrogen-like, the 2s-2p separation decreases, allowing easier mixing of these two, and this effect just balances the effect of the higher kinetic energy. The demonstration that the effects of correlation persist for all \( Z \) in these states was made rigorous by Wulfman and his collaborators (Wulfman 1983, Ho and Wulfman 1983, Wulfman and Levine 1984).

6. The alkaline earth atoms and the alkali negative ions

The case for molecule-like quantization becomes plausible enough at this stage to make it worth searching for experimental tests, but He\(^{**} \) is not an easy species to study. If other, quasi-two-electron systems were to exhibit similar correlation in the valence shells, perhaps they might be studied for the observable effects of strong e-e interaction. The alkaline earth atoms and the alkali negative ions are the obvious choices for this. Krause and Berry (1985a,b) used the effective potentials of frozen cores (Bachelet et al. 1982, Weeks and Rice, 1968, Barthe-
7. Quantifying and observing the extent of collective behaviour

Having the graphic demonstrations of strong, molecule-like correlation we have just examined, we must next ask whether it is possible to compare the degree of validity of different models, whether we can find any experimental means for demonstrating such collective behaviour, and whether there are any new insights we gain which have observable consequences. Here we shall review one powerful means of quantifying the validity of the collective model, or any other model for that matter, and the results when that method is applied to He** and the alkaline earth atoms. Then we shall review two kinds of experimental consequences for which calculations have been made. In the closing section, we shall look at possible experimental consequences of molecule-like correlation and the directions this line of investigation is likely to take in the future.

The quantitative diagnostic tool for measuring the degree of validity of a model in quantum mechanics is the projection of the wave function of the state one wants to study onto the wave function corresponding to the model whose applicability is being questioned. Suppose \( \Psi \) is the exact wave function for the state of interest and the set \( \Phi_1, \Phi_2, \ldots \) are the eigenfunctions of the Hamiltonian \( \mathcal{H}_0 \) of the model system. Then if the model is particularly apt, some \( \Phi_j \) is expected to dominate \( \Psi \) in the sense that if the '2s2p \(^3\)P' state of Be is very much like the first excited rotor state, \( \Phi \) for that \(^3\)P state has a large projection onto the \( \Phi \) which solves the model rotor-vibrator Schrödinger equation for the first excited rotor state. We can assume safely that the \( \Phi \)s form a complete set so that

Figure 6. The probability distributions for one valence electron, in the ground states of the alkaline earth atoms, with the other valence electron at various distances from the nucleus. The smallest and largest distances are very improbable, so the distributions at these extrema are found only with low probability (taken with permission from Ezra and Berry (1986)).
Niels Bohr's atomic model

Figure 7. The probability distributions for one valence electron in the alkaline earth atoms, in their ground and low-lying excited states, with the other valence electron at its most probable distance from the nucleus (taken with permission from Ezra and Berry (1986)).
we can expand $\Psi$ in terms of the $\Phi$s; in the notation of the abstract states,

$$|\Psi\rangle = \sum_i |\Phi_i\rangle \langle \Phi_i | \Psi\rangle,$$

so that the numerical coefficient $\langle \Phi_i | \Psi\rangle$ is the projection of $\Psi$ onto $\Phi_i$ and $|\langle \Phi_i | \Psi\rangle|^2$ is the fraction of $\Psi$ which is $\Phi_i$. In carrying out a variational calculation such as a configuration interaction expansion, if the $\Phi$s are the pure configurational functions, the coefficients $\langle \Phi_i | \Psi\rangle$ are determined directly in the process of finding the eigenvectors of the exact Hamiltonian $H$. We need only examine the unitary matrix that diagonalizes the matrix of $H$ in the $\Phi$-representation, $\langle \Phi_i | H | \Phi_j\rangle$, to find the $\langle \Phi_i | \Psi\rangle$'s. If the model of interest is not the one to which the basis corresponds, one must put the desired model functions and the exact functions into the same coordinates and do the integrations directly. In the situation at hand, we are interested in both the independent particle model, based on a configurational representation, and the collective molecular model, based on rotor–vibrator functions.

The calculations of Ezra and Berry (1983), Berry and Krause (1988) and Krause and Berry (1985a,b) are variational, configurational expansions but in Sturmian-type rather than Slater-type basis functions so that the coefficients in those expansions are not really accurate measures of the validity of the Hartree–Fock model, the proper independent particle model for electrons in atoms or molecules. Strictly, one should use solutions to the Hartree–Fock equations for the system of interest. Next best is to use single-configuration functions with hydrogenic or Slater-type functions as their basis. This was done for the states of He** to which we refer here, and which have been compared with the analogous projections onto rotor–vibrator functions; in the same study, projections of the well-converged functions for the alkaline earth atoms used for figures 6 and 7 were made onto rotor–vibrator functions, Hunter and Berry (1987a).

To evaluate the projections of accurate functions onto rotor–vibrator functions, one must specify the rotor–vibrator functions. The stretching mode functions may, as we mentioned previously, be chosen to satisfy the Schrödinger equation for any oscillator one chooses, the most common and natural of which are the harmonic and Morse oscillators. It would be best for the two-electron atoms to choose potentials for the stretching modes which are asymptotically Coulombic, but no such oscillator functions are available so no attempt has yet been made to use them. The bending modes may also be represented by harmonic or other oscillators; in this instance the harmonic oscillator seems to be quite adequate, after comparison with an anharmonic model. The obvious choice for the rotor is the usual representa-

<table>
<thead>
<tr>
<th>State</th>
<th>Hydrogenic with configurational designation $n\ell\ell'$</th>
<th>Molecule-like with vibrator-rotor designation $v_1$, $v_2$, $v_3$, $J$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1S^*$</td>
<td>$2\ell$</td>
<td>0.688</td>
</tr>
<tr>
<td>$^3P^*$</td>
<td>$2\ell\pi$</td>
<td>0.908</td>
</tr>
<tr>
<td>$^1D^*$</td>
<td>$2\ell$</td>
<td>0.760</td>
</tr>
<tr>
<td>$^1P^*$</td>
<td>$2\ell\pi$</td>
<td>0.765</td>
</tr>
<tr>
<td>$^3P^*$</td>
<td>$2\ell$</td>
<td>0.865</td>
</tr>
<tr>
<td>$^1S^*$</td>
<td>$2\ell$</td>
<td>0.452</td>
</tr>
<tr>
<td>$^3S^*$</td>
<td>$2\ell\pi$</td>
<td>0.591</td>
</tr>
<tr>
<td>$^1S^*$</td>
<td>$2\ell\pi$</td>
<td>0.392</td>
</tr>
</tbody>
</table>
Table 2 Squares of overlaps of well-converged functions of various states of alkaline earth atoms onto optimized rotor-vibrator functions (suitably symmetrized and antisymmetrized combinations of local Morse oscillators are used for the stretching modes).

<table>
<thead>
<tr>
<th>Atom</th>
<th>State</th>
<th>Configurational designation</th>
<th>Collective designation</th>
<th>Square of overlap*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>1S'</td>
<td>2s^2</td>
<td>0.0; 0; 0</td>
<td>0.997</td>
</tr>
<tr>
<td></td>
<td>3p'</td>
<td>2s2p</td>
<td>0.0; 1</td>
<td>0.984</td>
</tr>
<tr>
<td></td>
<td>1D'</td>
<td>2p^2</td>
<td>0.0; 0; 2</td>
<td>0.854</td>
</tr>
<tr>
<td></td>
<td>1p'</td>
<td>2s2p</td>
<td>0.1; 1; 0</td>
<td>0.911</td>
</tr>
<tr>
<td></td>
<td>3p'</td>
<td>2p^2</td>
<td>0.1; 0; 0</td>
<td>0.986</td>
</tr>
<tr>
<td></td>
<td>5S'</td>
<td>2s3s</td>
<td>0.0; 1; 0</td>
<td>0.959</td>
</tr>
<tr>
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<td>1S'</td>
<td>2s3s</td>
<td>1.0; 0; 0</td>
<td>0.910</td>
</tr>
<tr>
<td>Mg</td>
<td>1S'</td>
<td>3s^2</td>
<td>0.0; 0; 0</td>
<td>0.997</td>
</tr>
<tr>
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<td>3p'</td>
<td>3s3p</td>
<td>0.0; 1</td>
<td>0.951</td>
</tr>
<tr>
<td></td>
<td>1D'</td>
<td>3p^2</td>
<td>0.0; 0; 2</td>
<td>0.646</td>
</tr>
<tr>
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<td>0.993</td>
</tr>
<tr>
<td></td>
<td>5S'</td>
<td>3s4s</td>
<td>0.0; 1; 0</td>
<td>0.965</td>
</tr>
<tr>
<td></td>
<td>1S'</td>
<td>3s4s</td>
<td>1.0; 0; 0</td>
<td>0.924</td>
</tr>
<tr>
<td>Ca</td>
<td>1S'</td>
<td>4s^2</td>
<td>0.0; 0; 0</td>
<td>0.996</td>
</tr>
<tr>
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<td>4s4p</td>
<td>0.0; 1</td>
<td>0.955</td>
</tr>
<tr>
<td></td>
<td>1D'</td>
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<td>0.524</td>
</tr>
<tr>
<td></td>
<td>1p'</td>
<td>4s4p</td>
<td>0.1; 0; 0</td>
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</tr>
<tr>
<td></td>
<td>3p'</td>
<td>4p^2</td>
<td>0.1; 0; 0</td>
<td>0.978</td>
</tr>
<tr>
<td></td>
<td>5S'</td>
<td>4s5s</td>
<td>0.0; 1; 0</td>
<td>0.958</td>
</tr>
<tr>
<td></td>
<td>1S'</td>
<td>4s5s</td>
<td>1.0; 0; 0</td>
<td>0.923</td>
</tr>
<tr>
<td>Sr</td>
<td>1S'</td>
<td>5s^2</td>
<td>0.0; 0; 0</td>
<td>0.994</td>
</tr>
<tr>
<td></td>
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<td>5s5p</td>
<td>0.0; 1; 0</td>
<td>0.963</td>
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<tr>
<td></td>
<td>1D'</td>
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<td>0.706</td>
</tr>
<tr>
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<td>1p'</td>
<td>5s5p</td>
<td>0.1; 0; 0</td>
<td>0.916</td>
</tr>
<tr>
<td></td>
<td>3p'</td>
<td>5p^2</td>
<td>0.1; 0; 0</td>
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<tr>
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<td>5S'</td>
<td>5s6s</td>
<td>0.0; 1; 0</td>
<td>0.968</td>
</tr>
<tr>
<td></td>
<td>1S'</td>
<td>5s6s</td>
<td>1.0; 0; 0</td>
<td>0.767</td>
</tr>
</tbody>
</table>

* Hunter and Berry (1987a).

Other possible ways to measure the momentum correlation may be via the distribution of oscillator strength over energies, or the inelastic and ionizing collisions of fast charged particles with atoms. The expectation value of the momentum correlation has been evaluated for the ground state and a number of singly-excited states (Kono and Hattori 1986) and, more recently, of several doubly-excited states of He and for the ground and several excited states of Mg (Krause et al. 1987). Without delving into the quantitative results, we can examine the results for He** and Mg to interpret their implications for a collective, molecule-like picture.

Figure 8 shows the classical model for some seven states and illustrates the predominant momenta expected for these states. The signs of the momentum correlation expected from this picture, whose values were calculated from well converged wave functions for He** and Mg, are given in the last column. Only one of the 14 examples fails to have the expected sign. The relative magnitudes are not inconsistent with the collective model, but are more difficult to interpret than their signs (Krause et al. 1987).

The final kind of information we wish to introduce is the evaluation of a number of oscillator strengths for alkaline earth atoms, specifically for allowed transitions. This was done recently (Hunter and Berry 1987b) for five transitions of each of the five alkaline earths with both the well-converged Sturmian CI functions used for the projections described above, and with the optimized rotor-vibrator functions that maximized the overlap of the model functions with the CI functions. The Sturmian CI functions were studied to check their validity and reliability. The rotor-vibrator functions were used for the first time to calculate a property already known from experiment and to allow a comparison of the results from this model with those already available for the independent particle model, i.e. with oscillator strengths calculated from Hartree-Fock functions. The Sturmian results were very gratifying, except for the transitions involving 1D states. However, the point of importance here is the comparison of the approximate values based on Hartree-Fock and molecule-like rotor-vibrator functions. These results are shown in figure 9 for 1S' → 1P', 3P' → 3P', 1P' → 1S' and 3P' → 3S' transitions. The circles, indicating the rotor-vibrator results, are Hartree-Fock and molecule-like rotor-vibrator functions. These results are shown in figure 9 for 1S' → 1P', 3P' → 3P', 1P' → 1S' and 3P' → 3S' transitions. The circles, indicating the rotor-vibrator results, are systematically closer than the triangles of the Hartree-Fock calculations to the crosses of the accurate calculations, the plusses of the Sturmian CI calculations and the filled squares of the experimental results although neither approximate method is terribly accurate for computing oscillator strengths.

...
<table>
<thead>
<tr>
<th>State</th>
<th>Term</th>
<th>Assignment</th>
<th>Classical picture</th>
<th>Sign $\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2s^2$</td>
<td>$1S^e$</td>
<td>Vibrationless ground state</td>
<td><img src="image" alt="Classical picture" /></td>
<td>Expected $He$ $Mg$</td>
</tr>
<tr>
<td>$2s2p$</td>
<td>$3p^o$</td>
<td>One quantum rigid rotor excitation</td>
<td><img src="image" alt="Classical picture" /></td>
<td>$- - -$</td>
</tr>
<tr>
<td>$2p^2$</td>
<td>$1D^e$</td>
<td>Two quanta rigid rotor excitation</td>
<td><img src="image" alt="Classical picture" /></td>
<td>$- - -$</td>
</tr>
<tr>
<td>$2s2p$</td>
<td>$1p^o$</td>
<td>One quantum bending vibration</td>
<td><img src="image" alt="Classical picture" /></td>
<td>$+ + +$</td>
</tr>
<tr>
<td>$2p^2$</td>
<td>$3p^e$</td>
<td>One quantum bending vibration</td>
<td><img src="image" alt="Classical picture" /></td>
<td>$+ + +$</td>
</tr>
<tr>
<td>$2p^2$</td>
<td>$1S^e$</td>
<td>Two quanta bending vibration</td>
<td><img src="image" alt="Classical picture" /></td>
<td>$- - +$</td>
</tr>
<tr>
<td>$2s3s$</td>
<td>$1S^e$</td>
<td>One quantum symmetric stretching vibration</td>
<td><img src="image" alt="Classical picture" /></td>
<td>$+ + +$</td>
</tr>
<tr>
<td>$2s3s$</td>
<td>$3S^e$</td>
<td>One quantum antisymmetric stretching vibration</td>
<td><img src="image" alt="Classical picture" /></td>
<td>$+ + +$</td>
</tr>
</tbody>
</table>

Figure 8. The signs, calculated from well converged wave functions and expected from the molecular picture, of the momentum correlation $\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle$ for various states of He$^{**}$ and Mg. The first column indicate the states and illustrate the classical expectation of the momentum vectors for these seven states. (The principal quantum numbers 2 and 3 should be replaced with 3 and 4 for Mg.)

8. Conclusions and outlook

Our first, most obvious and most important conclusion is that two atomic electrons, kept out of the deep potential well close to the nucleus but in the same or neighboring shells, behave in most states like a collective, molecule-like system more than they behave like a quantum mechanical analogue of a solar system. Energies and, in the applicable cases, angular momenta are approximate constants of the motion for collective modes of vibration and rotation—better approximate constants in most instances than the energies and angular momenta we would attribute to individual electrons in the orbitals appropriate to an independent particle model. The corresponding rotational and vibrational quantum numbers $v_1$, $v_2$, $v_3$ of the symmetric stretch mode, the doubly-degenerate bending mode and the antisymmetric stretch mode of a linear, three-particle system, and $J$, the rotational quantum number of the 'rigid' body, are better quantum numbers than $n_1$, $l_1$, $n_2$ and $l_2$, the independent particle quantum numbers—at least insofar as $n_1$ and $n_2$ specify the energies of the individual electrons.

In the ground and singly excited states of helium, as well as in many states of two-electron systems with high nuclear charge, the independent particle picture is the more appropriate. The independent particle picture is also the correct one for two electrons with very different principal quantum numbers (Nikitin and Ostrovsky 1976, 1978). In physical terms, these mean that if the relative kinetic energy of the two electrons allows them to pass each other within the atom without scattering each
Niels Bohr’s atomic model

other severely, the independent particle picture applies; this is the situation when either or both has a kinetic energy large compared with the electron–electron repulsion even at the shortest of the probable interelectronic distances the electrons may reach. If the kinetic energy of relative motion is not large compared with the electron-electron repulsive potential at moderate or short electron–electron distances, then these distances cannot be attained and the correlation of the electrons must be strong. Consequently if one or both electrons is in a 1s level, or if the two electrons are in very different Rydberg orbitals, they behave independently; if they are in the same shell, not the 1s, then their correlation is strong enough to make them behave collectively.

Many questions open when we recognize this situation. One is the matter of observable consequences. Some that are just now being explored are the possibilities of observing the correlation fairly directly. An implication of the collective model is that the alkaline earth atoms have permanent quadrupole moments even in their ground states, in their internal coordinate systems. They are like CO₂ molecules in this respect. It may be possible to observe these quadrupoles. A second implication is that if the two valence electrons of an alkaline earth atom are knocked out simultaneously and suddenly, their correlated angular distribution should reveal the angular correlation of the initial state. This process, called the (e, 3e) process when fast incident electrons do the knocking out, is being proposed to study correlation in alkaline earth and other atoms. It may be possible to infer the degree of correlation in initial states from angular distributions of photoelectrons produced by resonant, two-photon and multiphoton ionization (sometimes called REMPI).

An interesting conceptual consequence of the collective picture arises in the context of the formation of chemical bonds. Traditionally, one supposed that an alkaline earth atom in its ground state is spherical in any coordinate system. Hence the formation of one or, better, two bonds requires the polarization of the electron distribution in order to produce a linear structure of the form X–M–X. The collective picture implies that the alkaline earth atoms are only spherical in the laboratory coordinates, not in their internal coordinates, so that the formation of a linear structure requires only the orientation of the alkaline earth to form the linear structure with two substituents, and not (at least not very much) polarization. It remains to be seen whether we can find observable consequences of this notion.

The collective picture has some significant implications for the computation of atomic wave functions. One is the importance of including a CI basis orbitals of angular momentum ℓ at least twice as high as the highest

Figure 9. The oscillator strengths for four kinds of transition in the alkaline earth atoms, as calculated by Hartree–Fock functions (triangles), rotor–vibrator functions (open circles), Sturmian CI functions (plusses) and other accurate calculations (crosses), and as determined by experiment (closed squares). (a) 'ns² ¹S → 'nsnp ¹P'; (b) 'nsnp ³P → ³P'; (c) 'nsnp ¹P → 'ns(n+1)s ¹S'; (d) 'nsnp ³P → 'ns(n+1)s ³S'.
nominal $l$ of the orbitals in the dominant configuration. The reason is that in the collective picture of a two-electron system, there are times when one electron carries all the angular momentum and the other has none. One may even have more than 2$!$ if the other's angular momentum partly cancels that of the first electron. The second implication is one still unexplored. That is the likelihood that an expansion in rotor–vibrator functions would converge to an accurate wave function much faster than the CI expansions we are so accustomed to using. Such an expansion was not possible previously because we did not know what rotor–vibrator set to choose. Now, with the optimum dominant functions determined (Hunter and Berry 1987a), we know at least how to start.

The applicability of a collective model to three-electron and more complex atoms is a completely open question. Is the boron atom trigonal or the carbon atom tetrahedral in the ground state? Does the carbon atom suffer a Jahn–Teller distortion? Is the result of such a distortion, if any, significantly different from the effect of the splitting of the 2$s$ and 2$p$ subshells? Equally open is the question of the applicability of molecule-like correlation to molecules. The simplest molecule to test this would be LiH, in which the core electrons of the Li can be frozen into an effective potential and only the two electrons of the perturbed H$^-$ need be treated. And surely we will soon realize other ways to examine the limitations of the Bohr model of independent electrons, as we refine our understanding of the behavior of electrons in atoms and molecules.

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R. Stephen Berry, Professor in the Department of Chemistry and The James Franck Institute of The University of Chicago, was born in Colorado in 1931, and attended Harvard University as an undergraduate and graduate student. After leaving Harvard, he taught at The University of Michigan and at Yale before going to Chicago in 1964. His research has touched on spectra of negative ions, flash photolysis and shock wave studies of transient species and their reactions, resonant multiphoton ionization, theory of electronic and atomic collisions, coupling of electronic and re-vibrational motion, autoionization and predissociation, the theory of nonrigid systems and the phase changes of clusters. His interest in nonrigid systems, initially just of nonrigid molecules, led to curiosity about whether doubly-excited states of helium might show correlation strong enough to make the probability distributions show molecule-like structure. This helped to trigger Herrick and Kellman's systematic study of energy levels and supermultiplet structure of those levels, which in turn stimulated Berry's systematic study of the probability distributions not only for helium but for the alkaline earth atoms and alkali negative ions as well.

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