PROBING THE COLLECTIVE AND INDEPENDENT-PARTICLE CHARACTER OF ATOMIC ELECTRONS

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1. Introduction

1.1. HISTORICAL BACKGROUND

Niels Bohr and Arnold Sommerfeld developed their model of the hydrogen atom and other one-electron atoms based on the concepts of discrete, stationary states and quantized energies and angular momenta of these atoms. Every stationary state carried its own constants of motion, to each of which corresponded a quantum number. Transitions between stationary states corresponded to sudden changes in the values of constants of the motion and of the corresponding quantum numbers, and to the absorption or emission of radiation to maintain conservation of energy.

Bohr, with Henrik Kramers, tried to extend this model to the helium atom and larger atoms\(^1,^2\). So did many of their contemporaries\(^3-^9\). Almost all of these efforts began with the assumption that each electron should have its own conserved energy and angular momentum, and its own corresponding quantum numbers. These assumptions became the constraints for a variety of mechanical models in which the two electrons of helium moved in orbits presumably stabilized by the attraction of the nucleus for the electrons and the repulsion of the electrons for each other. Only Irving Langmuir proposed a model, at that time, that did not preserve the individual angular momenta of each electron\(^6-^8\). Rather, Langmuir said\(^6\) "Bohr assumes that ... the angular momentum of every electron round the center of its orbit is \(h/2\pi\),... 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 which, by being transferred from electron to electron, circulates in each of two directions about the nucleus." (An amusing historical footnote to this was the objection raised by the young van Vleck to Langmuir's model, on the grounds that it did not quantize the angular momenta of each electron, as Bohr had proposed\(^9,^{10}\).) Then, beginning in 1925, came the quantum mechanics of Schrödinger, Heisenberg and Dirac, and its immediate, successful application to the hydrogen atom.

By 1928, quantum mechanics was well established and had become a powerful computational tool, especially because of the variational method with the proof that it
always gives convergence *from above* to the lowest state of any system\textsuperscript{11-13}. With only
desk calculators, Hylleraas applied this approach in what became a long series of ever more
accurate calculations of the ground state of the helium atom\textsuperscript{11}. Perhaps just because of the
accuracy that such calculations yield, interest faded, for many years, in any mechanistic
interpretation of the structure of the helium atom or of more complex atoms. Only
sporadically did works appear that treated mechanistic or structural aspects of the
correlation problem\textsuperscript{14, 15}.

Then, triggered by the discovery of a series of unusually-shaped spectral lines of doubly-
excited helium\textsuperscript{16, 17}, new interest sprang up in the mechanistic interpretation of such
species. Despite their lying in the ionization continuum, broad spectral lines of doubly-
excited helium atoms, He\textsuperscript{**}, had been expected\textsuperscript{18}, but the observations did not fit the first
predictions. Those predictions had been that two series of lines would appear; actually
only one was strong enough to show in the first spectra. The interpretation appeared
immediately\textsuperscript{17}: configuration mixing, representing electron correlation, made one of the
expected series extremely weak, while the other collected almost all of the oscillator
strength.

Several attacks soon appeared, dealing with accurate computation\textsuperscript{19-29} and with more
interpretive orientations. Of the latter, some were based on the use of hyperspherical
coordinates\textsuperscript{30-34}, usually chosen as \( R=(r_1^2 + r_2^2)^{1/2} \), \( \alpha=r_1/r_2 \) and \( \theta_{12} \), the angle between
the two electron-nucleus vectors. We shall discuss the hyperspherical coordinate approach
briefly. Other early attacks were based on symmetry considerations, notably on the
recognition that a) diagonalizing the electron-electron interaction operator \( e^2/r_{12} \) is very
much like (but not identical to) diagonalizing the (square of the) vector obtained as the
difference between the Runge-Lenz vectors of the two electrons, if they are each treated as
hydrogenic\textsuperscript{35, 36}. In classical terms, the Runge-Lenz vectors are essentially the semimajor
axes of the Kepler elliptical orbits. Making the quantum operator corresponding to this
length diagonal, so that it becomes at least approximately a constant of motion, corresponds
to tying the two Kepler orbits so that they precess together, keeping the *length* of the
vector between their semimajor axes constant. This approach was one of the threads that
leads to the interpretation we shall pursue in most detail.

### 1.2. ALTERNATIVE QUANTIZATIONS AND CONSTANTS OF MOTION

This concept, generalized, eventually has become a powerful organizing concept of the
quantum mechanics of complex systems: that the constants of motion and corresponding
quantum numbers are characteristic of specific systems and states. There is no simple,
universal criterion justifying identification of constants and quantum numbers with the real
component particles of an atom, molecule or larger system. In more positive terms, this
means that a central part of the analysis of any physical system is the identification of what
quantities are strictly conserved and what quantities are approximately conserved. The
strictly conserved quantities correspond to true fundamental symmetries of the system and
its Hamiltonian. The approximately conserved quantities correspond to approximate symmetries of the real system and usually to exact symmetries of model systems and model Hamiltonians. Energy is an exactly conserved quantity because of the time invariance of any isolated system and its Hamiltonian. Total momentum is an exactly conserved quantity for any system in field-free space because of the translational invariance of the system and its Hamiltonian. Total angular momentum is an exactly conserved quantity for any system isolated in a field-free space because of the angular invariance of the system and its Hamiltonian.

Orbital and spin angular momenta are approximately conserved quantities for light atoms because the exchange of angular momentum between them is weak: we can neglect the spin-orbit coupling of the electrons in light atoms in many situations. We express this by using approximate Hamiltonians in which spin-orbit coupling is simply omitted. Another familiar example of approximate quantization is the separation of normal modes of vibration of a molecule. The approximation here is that the vibrations are perfectly harmonic, which takes the potential energy of the Hamiltonian to be strictly quadratic in displacements of the atoms from positions of equilibrium. Such a Hamiltonian can always be separated by transformation to a sum of Hamiltonians of independent, noninteracting harmonic oscillators, the normal modes of vibration. This means that the energy of each normal mode is a constant of the motion, with its own quantum number, and there are as many constants of motion as there are oscillatory degrees of freedom. This model has been extremely effective for describing the lowest vibrational states of most molecules; only those nonrigid molecules whose atomic nuclei undergo large-amplitude motions fail to fit closely to the harmonic approximation. However states above the very lowest can display enough anharmonicity to make the harmonic model, separability and the corresponding approximate constancy of motion all fail. The water molecule is an example: the lowest quantum states of the stretching modes of its O-H bonds fit the harmonic model, and are well described as symmetric and antisymmetric stretching modes, with both O-H bonds stretching and contracting in synchrony in the former, and with one stretching while the other contracts synchronously in the other. However with three or more quanta in these bonds, the harmonic picture is a far less accurate representation of many of the states than is a local-mode picture, in which, at any instant, the quanta can be found localized in one O-H bond or the other, with only occasional transfer of the excitation between the two bonds. Eventually, this exchange must take place so that the two O-H bonds are indistinguishable on a sufficiently long time scale, but for times of order several vibrational periods, the molecule appears to have its quanta localized, so that if the numbers of quanta in the two bonds are unequal, the bonds appear inequivalent.

Still one other example of approximate quantization is the Hartree-Fock model. This is, in effect, a quantum mechanical formulation of the Bohr-Sommerfeld quantum theory, insofar as it is based on the assumption that each electron has its own well-defined energy and angular momentum. Only the azimuthal quantum numbers, i.e. the orientations of the individual angular momenta, are spoiled in this picture. The Hamiltonian for the Hartree-Fock system has a potential energy that represents the electron-electron interaction by the mean field of that interaction, as felt by each electron. This means that the Hamiltonian is separable into a sum of one-electron Hamiltonians, each with its own eigenvalues and eigenfunctions. This model is therefore also called an "independent-particle" model. The
Hartree-Fock approximation is accurate enough to give well over ninety percent of the binding energy of the electrons in most atoms, yet it fails to represent many of the properties of atoms, including their capacity to form stable negative ions and chemical bonds. Configuration mixing is the standard way to correct this model for the effects of electron-electron correlation, in either a variational or perturbational formalism. Robert Mulliken made the remark, "A little configuration mixing goes a long way," and indeed this is so, as the later discussion will show.

This analysis will examine some of the possible ways that two-electron atoms and quasi-two-electron atoms—the valence electrons of the alkaline earth atoms—are approximately quantized and how this quantization can be determined. Most of the discussion will focus on the choices among the Hartree-Fock and two collective models. The latter are based on quantization in which the constants of motion—exact constants in the simplified models, but presumably approximate constants in the real atoms—involves motion of both electrons.

1.3 THE TOOLS OF THE ANALYSIS

Several means have been employed to give insight into the quantization of two-electron and many-electron atoms, and into the extent and consequences of electron correlation. Many of these involve solving Schrödinger equations based on exact and model Hamiltonians and comparing the energy levels $E_j$, their intervals ($E_i - E_j$) (corresponding to spectral line frequencies) and sometimes the eigenfunctions $\psi_j$ or their absolute squares $|\psi_j|^2$. A powerful tool in the early stages of the analysis\textsuperscript{36, 41-46} and perhaps a very important one for ultimate understanding of these issues is the application of symmetry-based interpretations of the energy spectra and states of the atoms. Another has been the conditional probability distribution obtained by integrating $|\psi_j|^2$ over irrelevant variables and setting one variable equal to a significant value, such as its most probable; this allows us to study graphic representations of the spatial and momentum distribution of electron probability density\textsuperscript{14, 47-54}. Still another such tool is the overlap $S_{j\alpha}$ (or its absolute square), of an accurate wavefunction $\psi_j$ with an approximation $\psi_{j\alpha}$, based on the specific model $\alpha$ and its Hamiltonian $H_{\alpha}\textsuperscript{55}$.

Apart from the intervals between energy levels, all of these diagnostic tools are theoretical constructs. However much we may employ these abstract devices, it is of course absolutely necessary to use other diagnostic tools that are observable, to determine the validity of any interpretation we make. But even here, testing the validity of a model or approximation depends on comparing what we observe with what the model says we should observe. This means that we are obligated to evaluate the expectation values of each of the observables we measure, within each model we test. Observables that serve as probes of electron correlation and the nature of multi-electron quantization include the intensities of spectral lines\textsuperscript{56, 57}, atomic quadrupole moments\textsuperscript{58}, possibly the specific mass contribution to the isotope shift of spectral lines\textsuperscript{59} (a measure of the mean of the inner
product of pairs of electron momentum vectors, \( \langle p_1 \cdot p_2 \rangle \), probably useful only for He and other 2-electron atoms\(^{60}\), and angular correlations from \((\gamma, 2e)\) and \((e, 3e)\) processes, i.e. double-ionization processes initiated, respectively, by radiation\(^{61-65}\) and by electron impact\(^{66-78}\). As yet, most of these probes of electron correlation and quantization have hardly been exploited. The vigor of theoretical studies will, one can hope, stimulate their investigation.

2. Symmetry–Based Interpretations

2.1. INITIAL EXPLORATIONS

Wulfman\(^{35, 79, 80}\), Novaro and Freyre\(^{81}\) and Herrick and Sinanoglu\(^{36, 41}\) first suggested that the helium atom, particularly in its doubly-excited states, could be treated in terms of the hydrogen-like symmetry each electron would have in the absence of the other. This symmetry, the symmetry of the hydrogen atom consisting of two inequivalent, point-particles bound by their Coulomb attraction, is that of the rotations of a 4-dimensional sphere\(^{82-84}\). The symmetry group of this system is the orthogonal group \(O(4)\), and it has one constant of motion more than \(O(3)\), the corresponding rotation group in three dimensions. In addition to the orbital angular momentum with quantum number \(l\), and energy of the electron with quantum number \(n\), the length of the Runge-Lenz vector \(\mathbf{B}\), essentially the semimajor axis of the classical Kepler orbit of the electron, is the new constant of motion. This extra symmetry, characteristic specifically of the Coulomb potential, is what raises the degeneracy of the states of the hydrogen atom to \(n^2\), rather than only \(2l+1\).

Hence a natural approach to the doubly-excited states of the helium atom would be based on the direct product of the \(O(4)\) groups of the two electrons, \(O(4)_1 \times O(4)_2\). The states of the helium atom would then correspond approximately to bases of the irreducible representations of a suitable subgroup of \(\hat{O}(4)_1 \times O(4)_2\). A particularly attractive choice of subgroup is a new \(O(4)\) group: \(O(4) \subset O(4)_1 \times O(4)_2\). There are, however, several choices of the new \(O(4)\) group, corresponding to different choices of constants of motion. These are combinations of the constants of motion of the individual electrons. The choice selected by Wulfman and by Herrick and Sinanoglu takes as constants of motion the total orbital angular momentum, the vector sum \(l_1 + l_2\) of the angular momenta of the two electrons, and the length of the difference \(\mathbf{B}\) of the two Runge-Lenz vectors, \(|\mathbf{B}_1 - \mathbf{B}_2|\). Wulfman and Kumei made this selection on the basis that it corresponds approximately to diagonalizing the electron-electron repulsion, \(e^2/r_{12}\): Herrick and Sinanoglu found that this choice, diagonalizing \(|\mathbf{B}|^2\), gave the best agreement of limited-basis computations with experiments and with far more elaborate and accurate computations of the doubly-excited states of helium. Specifically, they used only the doubly-excited, Hartree-Fock-type states in which both electrons have the same principal quantum numbers, \(n_1 = n_2\), which they called the DESB or "doubly excited symmetry basis." The lowest-energy states of each manifold corresponding to a specific \(n\) are given remarkably well by this very approximate
procedure, both in terms of the energies, which Herrick and Sinanoglu studied, and in terms of the wave functions, examined by Rehmus et al.\textsuperscript{48, 50}. However the higher members were, in many cases, very poorly represented, as frequently happens in variational calculations carried out by expansion in a fixed basis set. More accurate calculations, with larger basis sets, corrected this\textsuperscript{51, 52}.

An interesting aside regarding the history of these ideas is the extent to which the idea of using O(4) $\subset$ O(4)\textsubscript{1}xO(4)\textsubscript{2} was stimulated by the notion that the two electrons of doubly-excited helium would be far from each other and therefore very hydrogen-like and not strongly correlated. This stimulus is totally irrelevant to the development of the group theoretical interpretation--fortunately, because it turns out to be a misconception. The electrons in doubly-excited helium are in fact extremely strongly correlated, far more correlated that the electrons of helium in its ground or singly-excited states. In fact, of all atoms in the periodic table, the electrons of helium are the least correlated of the valence shell electrons in their ground state. The physical basis for the increased correlation in the excited states is the low kinetic energies of the electrons in those states, making the electron-electron scattering far more important than in the ground state, particularly when the two electrons begin to approach each other.

Quantization based on O(4) $\subset$ O(4)\textsubscript{1}xO(4)\textsubscript{2} is more general than just the representations that involve strong electron-electron correlations. Nikitin and Ostrovsky showed that the same formal broken symmetry obtains in the case in which the two electrons have very different principal quantum numbers\textsuperscript{85, 86}. Here, however, the independent-particle picture is very much the appropriate one, because the two electrons have very different momenta and very different spatial distributions in this situation.

### 2.2. MULTIPLETS AND SUPERMULTIPLETS

The next step, and almost the whole picture as it now stands, came with the analysis of Kellman, Herrick and Poliak\textsuperscript{42-46}. First, in their 1978 paper, Kellman and Herrick found that subsets--multiplets--of the states of each manifold obtained with the DESB calculations correspond strikingly to rotor series, even more so than the rotor series encountered in nuclear structure\textsuperscript{87}. Then they found that entire sets of states constructed from the basis sets with $n_1 = n_2$ have patterns of energies and quantum numbers that correspond to states of a linear, ABA system like a linear triatomic molecule, with very light A-particles and a much heavier B-particle. These are supermultiplets, in the terminology used for classifying groups of levels sharing some common quantum numbers. In particular, the intra-shell manifolds correspond to states of the linear, light-heavy-light three-body system with quanta in the modes of rotation and doubly-degenerate bending. The lowest state of the manifold with $n_1 = n_2 = 2$, for example, corresponding to the 2s\textsuperscript{2} 1S\textsuperscript{e} state of doubly-excited helium, plays the role of the ground state. The next state on the energy scale, the 2s2p 3P\textsuperscript{0} state, is the first excited rotational state; the next is the 2s2p 1P\textsuperscript{0} state, which is one of the pair of states with one quantum in the bending-vibration mode. These would be degenerate if there were no Coriolis interaction, but its occurrence splits the energies of
these two states. The other member of the pair of bending states is the $2p^2 \, 1^P_e$ state. In the manifold of states with $n = 2$, there are only two others, the $2p^2 \, 1^D_e$, corresponding to the state with two quanta of rotation and no excitation of any bending, and the highest, the $2p^2 \, 1^S_e$ state, corresponding to two quanta in the bending mode, one in each of the states. A sketch of the symmetry-based pattern and the accurately-calculated levels for the manifold with $n_1 = n_2 = 3$ are shown in Figure 1. Herrick, Kellman and Poliak also speculated on the possibility of states of helium corresponding to stretching modes, but these lay outside their symmetry structures.

Figure 1. The pattern of energy levels (upper figure) based on the Herrick-Kellman supermultiplet pattern and the accurately calculated energy levels of doubly-excited helium with $n_1 = n_2 = 3$. The quantum numbers $I$, $K$ and $T$ correspond, respectively, to the rigid-rotor rotational quantum number, the number of bending quanta (but numbered up and down from the central value of the submanifold with $I=0$) and the number of units of angular momentum associated with the degenerate bending mode, angular momentum along the figure axis. These can be put in correspondence with the number of bending quanta, $\nu$, and the quantum number $L$ of total angular momentum (independent of spin), i.e. into correspondence with the quantum numbers familiar in the spectroscopy of triatomic molecules, as follows: $I = L - T$, $K = L_{\text{maximum}} - I_{\text{maximum}} = L_{\text{max}} - (n-1)$. 
A connection was made by Watanabe and Lin, between the supermultiplet approach of Herrick and Kellman and the representation of doubly-excited helium in terms of hyperspherical coordinates. A precursor to this appeared in a rediscovery of the quantization according to the quantum numbers I, K and T, with the addition of another very approximate two-valued quantum number A, that indicates an approximate odd-even kind of symmetry.

One further advance in the symmetry-based approach has just appeared. While the analysis just described provides a persuasive classification and a useful analogy to the linear triatomic molecule, it still left open the real physics associated with the collective O(4) symmetry of the helium atom. It also left untouched the question of possible extensions to systems of more than two electrons. In fact the only extensions to three or more electrons have been made in the context of hyperspherical coordinates and in models based on freezing the electrons onto spheres of fixed radii, much as had been done previously with two electrons. The new advance by Kellman appears to be a significant step toward finding a strong, approximate symmetry for the two-electron and potentially several-electron Hamiltonians, based on unitary rather than rotational or orthogonal symmetry. The rotational symmetry emerges as a subgroup of the higher, unitary symmetry. If this approach is successful, it may lead to the identification of new, approximate collective quantum numbers for many-electron atoms, and to their association with particular kinds of collective modes of motion.

3. Interpretations Based on Wave Functions

3.1. GRAPHIC REPRESENTATIONS OF HELIUM

The two-electron system, with its six degrees of freedom, seems at first too complicated to lend itself to graphical representation, for example in terms of \( \Psi(r_1, r_2) \) or \( |\Psi(r_1, r_2)|^2 \). However this is too pessimistic a view. First, for purposes of interpreting correlation and quantization, the spatial orientation of the system of two electrons and a nucleus is irrelevant, so that one can immediately eliminate three of the six variables by integrating \( |\Psi(r_1, r_2)|^2 \) over the three Euler angles that specify that orientation. At that stage, one has a choice of variables for representing the system in internal coordinates. The two most frequent choices are hyperspherical coordinates, usually taken to be \( R \equiv (r_1^2 + r_2^2)^{1/2} \), \( \alpha \equiv \arctan(r_1/r_2) \), and \( \theta_{12} \equiv \arccos((r_1 \cdot r_2)/r_1 r_2) \), and simply \( r_1, r_2 \) and \( \theta_{12} \). Both are useful, but the former tend to lock computations and interpretations to concepts in which \( R \) and \( \alpha \) are the relevant coordinates, which is not always the case as we shall see. Hence the following discussion is based largely on the representation of the three-variable reduced form of \( |\Psi(r_1, r_2)|^2 \), namely the density \( \rho \) in terms of \( r_1, r_2 \) and \( \theta_{12}, \rho(r_1, r_2, \theta_{12}) \).

This quantity is still too complicated to graph, even as a graph in three dimensions. One more reduction is required. We so this by constructing the conditional probability
distribution $\rho(r_2, \theta_{12}; r_1=a)$, with a specific choice or set of choices for the value $a$, such as the most probable value of $r_1$. This enables us to construct three-dimensional graphs of $\rho(r_2, \theta_{12}; r_1=a)$ or to generate entire sequences of images in the form of animations and thus make time a surrogate for the $r_1$ axis. In this way, the full behavior of $\rho(r_1, r_2, \theta_{12})$ can be represented graphically. Here, however, we are limited to discrete images, such as those shown in Fig.2. Note in this figure how similar are the three rotor states, in this internal-coordinate representation, and how alike are the two bending-mode states. The two distributions furthest to the right are those of the $2s3s\,^3S^e$ and $2s3s\,^1S^e$ states, corresponding respectively to the first excited antisymmetric and symmetric stretching modes. These, which will be discussed further, do not fit into the supermultiplet pattern but are expected on the basis of the analogy with the triatomic ABA molecule.

The conclusion we can draw from these distributions, completely consistent with the symmetry-based supermultiplet interpretation, is that the states of doubly excited helium, at least those in which the two electrons have the same or very similar quantum numbers, are well described by the same kind of collective quantization that describes the rotations and vibrations of a linear ABA triatomic molecule. When we look later at quantitative measures of validity of models, we will turn to the question of whether collective quantization gives a better description of this and other systems than does the traditional independent-particle model stemming from a mean-field, Hartree-Fock approach.

Before closing this section, we should mention the graphic representation of the ground state of the helium atom and of its isoelectronic counterpart, the H$^-$ ion. These have been discussed in reviews of the subject$^{98,99}$, as well as in the original articles based on very approximate$^{47,100,101}$ and accurate$^{49}$ wave functions. Because in these states the electrons are frequently near the nucleus, their kinetic energies are large relative to the potential energy of their repulsion, except when the electrons are very close together. Consequently electron correlation is not strong, especially in the ground state of helium, and its quantization is primarily independent-particle-like. The hydride ion is more an intermediate case; electron correlation is far more important than in He, but much of this correlation is radial, rather than angular. As a result, H$^-$ does not seem to fit well into the supermultiplet picture, but since it has only a single bound state, there is little motivation to use a symmetry-based model to describe it.

3.2. GRAPHICAL REPRESENTATIONS FOR OTHER ATOMS: ALKALINE EARTHS

The doubly excited helium atom is not the only example in which electron correlation and collective quantization have been invoked. The role that correlation might play in alkaline earth atoms was pointed out by Greene and O'Mahony$^{102-104}$. Krause$^{53}$ computed well-converged wave functions for the ground and low-lying excited states of the valence electrons of these atoms, using frozen-core effective potentials$^{105,106}$. Soon thereafter, he computed comparable functions for the alkali negative ions, also two-valence-electron atoms$^{54}$. The wave functions for the alkaline earth atoms were refined further by
Hunter. In fact the two valence electrons of the alkaline earth atoms, Be, Mg, Ca, Sr and Ba, are at least as interesting as the electrons of doubly excited helium, perhaps much more so because these atoms are far easier to study experimentally than the transient species we denote as He**. Moreover the ground states of the alkaline earth atoms display the same

Figure 2. Conditional probability distributions and energy levels for the doubly excited states of helium with $n_1 = n_2 = 2$. The distributions are shown in cylindrical coordinates, with the angle $\theta_1 = 0$ indicated by the leftmost vertical bar in each figure. In fact these distributions are all multiplied by the factor $r_2^2$ of the Jacobian, so that the concentration of probability density close to the nucleus is suppressed, making the angular distributions easier to see.
extreme angular correlation that the $2s^2 1S^e$ state of He** shows. The same holds for the entire pattern of low-lying excited states of these atoms: they are all strongly correlated, analogous to their He** counterparts, but lie in the energy range of bound states, rather that of the ionization continuum, where all states eventually autoionize.

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Figure 3. Conditional probability distributions for the ground and low-lying excited states of Ca. The central column of distributions are derived from well converged Sturmian configuration interaction expansions. The left column of distributions are based on single-term rotor-vibrator functions with harmonic bending modes and symmetric and antisymmetric combinations of localized Morse stretching modes. The right column of distributions is based on Hartree-Fock independent-particle wave functions.
The alkaline earth atoms offer a striking opportunity to compare the conditional probability distributions based on well-converged wave functions with those based on simple, independent-particle and rotor-vibrator models. Figure 3 illustrates such a comparison for states of the calcium atom, all with conditional probability distributions for the "fixed" electron taken at its most probable distance from the nucleus. While some states are represented about as well by both the independent-particle and collective, rotor-vibrator models, none is represented better in these graphs by the independent-particle model and several have collective, rotor-vibrator representations that are much more like the well converged functions than are the independent-particle, Hartree-Fock approximate functions. In short, this qualitative criterion implies that the collective model and collective quantization appears more realistic and therefore in some sense more accurate to describe the valence electrons of the alkaline earths than an independent-particle model and individual-electron quantization.

The role of configuration interaction in representing angular correlation is important and important to understand. Only a small fraction of the np\(^2\) \(^1\)S\(^e\) configuration need be added to the ns\(^2\) \(^1\)S\(^e\) principal configuration of the ground state to introduce so much angular correlation that the two electrons are virtually prohibited from being on the same side of the nucleus. Figure 4 shows two simplified models of the ground \(^1\)S\(^e\) state of Be composed of only those two configurations. The upper figure is based on a function containing 98% of the 2s\(^2\) configuration and the lower figure, on a function that is 90% 2s\(^2\), in the sense that the squares of the coefficients of the 2s\(^2\) functions are 0.98 and 0.90, respectively.

Figure 4. Illustrations of the effect on angular correlation of a small amount of configuration mixing. The left figure is a conditional probability distribution for a wave function of the ground state of the valence electrons of Be composed 98% of 2s\(^2\) and 2% of 2p\(^2\). The right figure is based on a function that is 90% 2s\(^2\) and 10% 2p\(^2\). The spikes indicate the position of the "fixed" electron in the conditional probability distribution.
3.3. OVERLAP CRITERIA

The next stage of comparing independent-particle and collective, rotor-vibrator quantization is a comparison of the overlaps, or more properly, the squares of the overlaps of the approximate functions with well-converged wave functions\textsuperscript{55, 57}. The results of this comparison are, in some instances, a little surprising insofar as some independent-particle wave functions have overlaps with accurate functions that are larger than the overlaps of the collective, rotor-vibrator functions, even when the graphs such as those in Fig.3 indicate that the angular correlation is better represented by the rotor-vibrator model. Nonetheless the rotor-vibrator model comes off as somewhat more reliable, overall, than the independent-particle model, although not nearly so clearly so as it does according to the qualitative criterion of visual similarity. Table 1 contains these overlaps.

Table 1. Squared overlaps between configuration interaction (CI), rotor-vibrator (RV) and Hartree-Fock (HF) wave functions. The CI-RV overlaps are taken from Hunter\textsuperscript{55} and the CI-HF and HF-RV overlaps, from Batka\textsuperscript{57}.

| Atom | configuration term | $|\langle \Psi_{CI} | \Psi_{RV} \rangle |^2$ | $|\langle \Psi_{CI} | \Psi_{HF} \rangle |^2$ | $|\langle \Psi_{HF} | \Psi_{RV} \rangle |^2$ |
|------|--------------------|----------------|----------------|----------------|
| Be   | $2s2s$ $1S_e$      | 0.9966         | 0.8948         | 0.8957         |
| Be   | $2s2p$ $3P^o$      | 0.9836         | 0.9869         | 0.9793         |
| Be   | $2s2p$ $1P^o$      | 0.9108         | 0.9173         | 0.9105         |
| Be   | $2s3s$ $3S_e$      | 0.9587         | 0.9719         | 0.9331         |
| Be   | $2s3s$ $1S_e$      | 0.9102         | 0.9545         | 0.9213         |
| Be   | $2p2p$ $1D^e$      | 0.8542         | 0.7157         | 0.6434         |
| Be   | $2p2p$ $3P_e$      | 0.9856         | 0.9872         | 0.9858         |
| Mg   | $3s3s$ $1S_e$      | 0.9973         | 0.9255         | 0.9275         |
| Mg   | $3s3p$ $3P^o$      | 0.9505         | 0.9840         | 0.9385         |
| Mg   | $3s3p$ $1P^o$      | 0.7970         | 0.9288         | 0.7952         |
| Mg   | $3s4s$ $3S_e$      | 0.9648         | 0.9782         | 0.9385         |
| Mg   | $3s4s$ $1S_e$      | 0.9241         | 0.9625         | 0.9211         |
| Mg   | $3s3d$ $1D^e$      | 0.6457         | 0.6902         | 0.1573         |
| Mg   | $3p3p$ $3P_e$      | 0.9928         | 0.9791         | 0.9783         |
| Ca   | $4s4s$ $1S_e$      | 0.9963         | 0.9177         | 0.9216         |
| Ca   | $4s4p$ $3P^o$      | 0.9551         | 0.9651         | 0.9221         |
| Ca   | $4s3d$ $1D^e$      | 0.5236         | 0.8541         | 0.2624         |
| Ca   | $4s4p$ $1P^o$      | 0.8649         | 0.8458         | 0.7198         |
| Ca   | $4s5s$ $3S_e$      | 0.9578         | 0.9594         | 0.9232         |
| Ca   | $4s5s$ $1S_e$      | 0.9233         | 0.9247         | 0.8919         |
| Ca   | $4p4p$ $3P_e$      | 0.9783         | 0.8784         | 0.8915         |
### Table 1, cont.

<table>
<thead>
<tr>
<th>Element</th>
<th>Orbital</th>
<th>Wave Function</th>
<th>(\text{CI}^e)</th>
<th>(\text{RV}^e)</th>
<th>(\text{HF}^e)</th>
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<td>(^1\text{Po})</td>
<td>0.9163</td>
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<td>0.6120</td>
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<tr>
<td>Sr</td>
<td>5s6s</td>
<td>(^3\text{Se})</td>
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</tr>
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<td>(^1\text{De})</td>
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<tr>
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<td>6s6p</td>
<td>(^3\text{po})</td>
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<td>0.8877</td>
<td>0.8541</td>
</tr>
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<td>6s6p</td>
<td>(^1\text{Po})</td>
<td>0.8329</td>
<td>0.5319</td>
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</tr>
<tr>
<td>Ba</td>
<td>5d5d</td>
<td>(^3\text{po})</td>
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<tr>
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<td>5d5d</td>
<td>(^1\text{Se})</td>
<td>(\text{no convergence})</td>
<td>0.7552</td>
<td>(\text{no convergence})</td>
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<tr>
<td>Ba</td>
<td>6s7s</td>
<td>(^3\text{Se})</td>
<td>0.9727</td>
<td>0.9232</td>
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<td>6s7s</td>
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<td>0.9362</td>
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<td>0.7101</td>
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<tr>
<td>He</td>
<td>2p2p</td>
<td>(^3\text{Pe})</td>
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<td>0.9870</td>
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<tr>
<td>He</td>
<td>2p2p</td>
<td>(^1\text{De})</td>
<td>0.8159</td>
<td>0.9204</td>
<td>0.6759</td>
</tr>
</tbody>
</table>

### 3.4. Oscillator Strength Criteria

The next quantitative criterion brings us to observable quantities, the values of oscillator strengths, as evaluated from the three kinds of wave functions--CI, RV and HF--and from experimental measurements. These are shown in Fig.5 for five allowed transitions. In the first four transitions, respectively the ground \(^1\text{Se} \rightarrow ^1\text{Po}\), \(^1\text{Po} \rightarrow ^1\text{De}\), \(^1\text{Po} \rightarrow ^1\text{Se}\) and \(^3\text{po} \rightarrow ^3\text{pe}\), the Hartree-Fock results are significantly further from both the accurately computed values and the experimental values, where they are available. For the fifth kind of transition, \(^3\text{po} \rightarrow ^3\text{Se}\), the Hartree-Fock is closest to the accurate calculations. In all but that last case, the accurate calculations and the experimental results agree quite satisfactorily.

### 3.5. Quadrupole Moments

The quadrupole moment of a charge distribution offers a measure of its nonspherical character. In nuclear physics, quadrupole moments have been standard probes of shapes, but few atomic quadrupole moments have been measured, and among these, the only excited states to be observed have been two Rydberg states of helium\(^{107,108}\), and the
metastable $^3\text{P}_2$ states of Ne, Ar, Kr and Xe$^{109}$. Previously, Angel, Sandars and Woodgate had measured the quadrupole moment of aluminum atoms in their $^2\text{P}_{3/2}$ ground state$^{110}$.

Although the charge distribution in, for example, the ground states of the alkaline earth atoms is nonspherical in its own internal, "inertial axis" coordinates, such nonspherical character is not an observable. The ground states of the alkaline earth atoms are all $^1\text{S}_\text{e}$ states, which simply have quadrupole moments of zero. However many excited states of doubly excited helium and of the more experimentally accessible alkaline earth atoms do have nonvanishing quadrupole moments, which could be measured. Values of these quadrupole moments have been computed with well-converged Sturmian CI functions, to indicate approximately what experimental values should be expected$^{58}$. Values have also been computed, as part of the same study, from unrestricted Hartree-Fock functions (for some of the states) and from rotor-vibrator functions. Typical expectation values of $Q_{zz} = -(e/2) \sum_i (3z_i^2 - r_i^2)$ are shown in Table 2. In most cases, the three wave functions yield similar values for the quadrupole moments. The resonance $^3\text{P}_\text{e}$ excited state of Ca is an exception, for which the three values differ considerably. The rotor-vibrator values of some of the states of Ba are also far from the values predicted by the well-converged functions.

Figure 5. Graphic summary of the oscillator strengths $f$ for five allowed transitions of the alkaline earth atoms: a) $^1\text{Se} \rightarrow ^1\text{Po}$; b) $^1\text{Po} \rightarrow ^1\text{De}$; c) $^1\text{Po} \rightarrow ^1\text{Se}$; d) $^3\text{Po} \rightarrow ^3\text{Pe}$, and e) $^3\text{Po} \rightarrow ^3\text{Se}$. The small circles represent $f_{CI}$, the large circles represent $f_{RV}$, the crosses represent $f_{HF}$, and the solid circles represent the experimental values, where they are available. Results are taken from Batka$^{57}$. 
While the quadrupole moments reflect the effects of correlation, it is not particularly easy to infer from simple models what these should be, or even what their signs should be. For example one might naively suppose that the pairs of "partner" states of the bending vibration would at least have quadrupole moments of the same sign, but this is not the case. The nsnp $^1P^0$ states have positive quadrupole moments and the npnp $^3P^e$ states have negative quadrupole moments, corresponding to prolate charge distributions, while the positive quadrupole moments indicate oblate distributions.

Table 2. Some typical values of atomic quadrupole moments based on Sturmian CI, on unrestricted Hartree-Fock and on rotor-vibrator wave functions. Values are in units of $ea_o^2$, the electron charge times the Bohr radius, squared.

<table>
<thead>
<tr>
<th>Atom</th>
<th>State</th>
<th>$Q_{zz}$(CI)</th>
<th>$Q_{zz}$(HF)</th>
<th>$Q_{zz}$(RV)</th>
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<tr>
<td>He</td>
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<td></td>
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<td>-4.332</td>
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3.6. ANGULAR CORRELATIONS IN DOUBLE IONIZATION

A promising direction is the measurement and prediction of the angular correlation of the electrons in a two-electron ionization process. This may be accomplished either by electromagnetic radiation, in what is called a (γ,2e) process, or by electron impact, in what is called an (e,3e) process. If, in an (e,3e) process, the incident electron has quite high energy, and the two electrons knocked out leave with energies high compared with their binding energy, then the electron-electron interactions in the final state are likely (but not guaranteed) to be small, so that the process measures predominantly a property of the initial state. In particular, it measures the distribution of angles $\theta_{12}$ between the two electron-nucleus vectors. This is an oversimplification, because there can always be some effect of the electron-electron interaction in the final state. Nevertheless with interpretation, these two approaches are probably the most direct ways to study electron correlation that we know.

Glassgold and Ialongo$^{111}$ pointed out in 1968 that the angular correlation of electrons ejected in a fast process, such as the (e,3e) process, would be a particularly direct way to observe correlation effects, but the technology was not yet ready for such a sophisticated problem. Theoretical calculations were appearing$^{112, 113}$, but the experiments were, at that time, simply too difficult to do. The mechanism of the double ionization had just been worked out$^{114}$—and was confirmed by a later analysis$^{115}$—to be predominantly a correlation effect that shows itself when one electron is suddenly knocked out, leaving the atom in a nonstationary superposition of new stationary states of the now-ionized system, a superposition that includes continuum states that correspond to a second ionization. This process, called "shake-off", dominates the double ionization when the incident electron has an energy of a few KeV and the ejected electrons carry kinetic energies of order a hundred or a few hundred eV.

Calculations continued to be done, largely for helium and other rare-gas atoms in their ground states$^{63, 64, 66-68, 73-77, 116-118}$ but also for alkaline earth atoms, for which correlation is much more important$^{65, 78}$. Experiments with the corresponding double photoionization were carried out, first to study the threshold law$^{119, 120}$ whose theory had been pursued previously$^{121-124}$. Then, angle- and energy resolved double photoionization studies were reported for the helium and argon atoms$^{61, 62}$. Shortly before, the first experiments on angular correlations in the (e,3e) process appeared$^{69-72}$. One set of experiments was done to study the simpler process abbreviated as (e,3−1e), i.e. only two of the three outgoing electrons are observed$^{125}$. It seems that a great deal of information is lost in this simplification, at least regarding the effects of correlation$^{78}$.

Until this kind of study is applied to a system, such as an alkaline earth or conceivably even doubly excited helium, the question remains open of how powerful (e,3e) experiments will
be to reveal effects of electron correlation and the nature of the quantization of two-electron and many-electron atoms. Such experiments are now underway with Mg atoms, but only the Auger double ionization process has been reported until now\textsuperscript{126, 127}. Of course a natural way to carry out the analysis when we have reliable experimental results will, as with other methods, to compare not only the predictions of accurate theoretical calculations but of approximate models as well, models for which specific quantities are constants of the motion.

3.7. OTHER CORRELATIONS AND DISPERSIONS

There is one other class of probes we can consider, which is based on analysis of wave functions. This is the set of quantities in the category of expectation values of distributions, correlations and dispersions. As yet, these do not reveal as much as one might hope, but they are potentially useful and should be introduced in this context. The first is simply the angular distribution, $p(q_{12})$, which was examined by Coulson and Neilson\textsuperscript{15} and by Banyard and Ellis\textsuperscript{100, 101}. In a sense, this is now superseded by the distributions in more than just a single variable, but such reduced distributions can still give insight into angular correlation.

The next to consider is the expectation value of the projection of the electron momenta onto each other, $\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle$, which is, in principle, measurable as the special mass effect of the isotope shift of atomic spectral lines. This is an attractive index to probe collective quantization because even its sign is a powerful indicator of the nature of correlation. In a rotationally excited state, insofar as the rigid rotor model is applicable, this quantity should be negative and moderately large because the electrons 1 and 2 should move along roughly antiparallel momentum vectors. Likewise, in a harmonic, symmetric stretch mode along the traditional normal mode for this motion, the projection should also be negative. For the antisymmetric stretch mode and for the bending modes, however, this quantity should be positive. This quantity was studied for doubly-excited helium, as well as for helium in its ground and singly-excited states, and the expectations of the model are indeed borne out\textsuperscript{59}. In some respects, this is the most reassuring justification currently available for collective, molecule-like quantization in doubly excited helium.

The use of $\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle$ as an easily-interpreted index of correlation is perhaps limited to helium and helium-like ions. The reason is that inner-shell electrons contribute significantly to this quantity\textsuperscript{60}. Even though their correlation is much less than that of valence electrons, their momenta are enough larger to compensate, so that their contributions to the expectation value are large enough to hide the contribution of the valence electrons. J. Morgan has suggested in private communication that, instead of $\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle$, one could use the pure angular quantity $\langle \mathbf{p}_1 \cdot \mathbf{p}_2 | \mathbf{p}_1 | \mathbf{p}_2 \rangle$, which would very much reduce the inner-shell contributions.
Still another kind of probe that goes beyond the mean interelectronic angle (or, as with $\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle$ or $\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle_{\text{rms}}$, simply the expectation value of the cosine of the momentum-space angle $\theta_{12}$) is the mean deviation of that angle. In general, Hartree-Fock functions have considerably larger values of the root-mean-square deviation $\Delta \theta_{12}$ than do either the collective, rotor-vibrator or configuration interaction wave functions. This is of course consistent with the Hartree-Fock being a mean field representation, so that there is little to create any angular focusing of the wave function.

Analyses of the momentum correlations of the valence electrons of correlated systems will continue to be a useful tool for theoretical investigation, and perhaps experiments with electrons, analogous to the Coulomb explosion imaging experiments with molecules, will eventually enable us to observe these momentum correlations.

4. Interpretations Based on Classical and Semiclassical Models

4.1. THE BOHR-SOMMERFELD APPROACH

This discussion opened with a historical review of efforts to apply Bohr-Sommerfeld quantization to some suitable model of the helium atom. In the period before quantum mechanics developed, this effort was notably unsuccessful. However the difficulties were surmountable, and in 1980 Leopold and Percival succeeded in creating a satisfactory description of the helium atom in its ground state within the old quantum theory. (Later these authors extended their work to treat the symmetric/antisymmetric symmetry of identical particles, in order to treat excited singlet and triplet states.) They achieved this by including zero-point motion, by using variational rather than perturbational methods wherever possible, and with the use of expansions for the interelectronic repulsion operator, angular momentum coupling and specific perturbation terms developed for this purpose. They also followed the strict imposition of the Einstein-Brillouin-Keller prescription that the motion should correspond to motion on invariant tori (but not to truly periodic orbits, because the different modes have incommensurate natural periods). This requires that the quantization be half-integral, not integral, as all the treatments of the 1920's would have had it. The outcome can be summarized by a comparison of the total energy of the ground state and the ionization potential, from experiment and from several calculations including that of Leopold and Percival. The experimental values are -2.9037 atomic units and 24.58 eV, respectively. The best quantum mechanical calculations give results identical with these, to as many figures as we have quoted. The variational results from Leopold and Percival's semiclassical calculation are -2.8407 a.u. and 22.88 eV, respectively. Their corresponding results based on perturbation methods are -2.741 a.u. and 20.16 eV. The classical results derived in 1922 by van Vleck were -2.765 a.u. and 20.70 eV. Kramers, with a model of inclined orbits, obtained a total binding energy of -2.762 a.u. and an ionization energy of 20.60 eV. The method is also applicable to
excited states, as demonstrated in the 1980 paper, particularly after particle symmetry is accounted for.

4.2. ORBITS, PLANETARY ATOMS, LANGMUIR STATES

The development of the semiclassical description was actually preceded by Percival's analysis of highly excited states in which the electrons have angular momenta approaching the maximum allowed by the principal quantum numbers. The classical analogue of these states has the electrons going around the nucleus in nearly-circular orbits, never approaching the nucleus. Percival introduced the term "planetary atoms" to describe such states in his first publication on this subject. Such states have very little overlap with the ground state and consequently are not easily produced by absorption of a single quantum. They are, however numerous and therefore may play important roles in situations in which atoms may be highly excited.

Quantitative methods for finding energies and classifying the planetary states emerged somewhat later. Richter and Wintgen found a means to regularize the three-body Coulomb system and then, with Tanner, implemented this to find the variety of categories of classical orbits of the helium-like system. These include the Langmuir orbits, which were shown to correspond to regions of stability, and were then computed by Müller, Burgdörfer and Noid. The quantum analogue of a Langmuir orbit has both electrons on the same side of the nucleus, corresponding to being at a turning point in a state in which the two electrons oscillate in synchrony, like two pendula on opposite sides of the nucleus.

The corresponding semiclassical explorations also proceeded successfully. Weidenmüller showed how to incorporate the Pauli principle into the sum (trace) of periodic orbits as derived by Gutzwiller. A particularly important advance was that of Ezra, Richter, Tanner and Wintgen, who studied the near-collinear states of helium, corresponding to the stretching vibrations in the collective, molecular picture. Arguments had been made for some time, based largely on the analyses done in hyperspherical coordinates, that the stationary states of such a system included states analogous to both the symmetric stretch and the antisymmetric stretch modes of a harmonic model of a molecule. The former would be the "ridge states" because they would have maximum probability on the ridge of the potential if it is represented in the hyperspherical coordinates described earlier. Ezra et al. quantized the dynamics of the model, which they showed is chaotic, and found evidence for the antisymmetric states but nothing at all like the symmetric stretch or "ridge" states. They concluded that such states do not exist. However the manifold developed as the states of the rotor-vibrator model virtually demands stretching-mode states that are totally symmetric with respect to the symmetry operations of the rotor-vibrator Hamiltonian. The answer is that they are indeed there, but do not look like the symmetric-stretch normal modes of a harmonic oscillator. Instead, they are the sums--symmetric combinations--of local-mode excitations, analogous to the local-mode states of the water molecule. They had been identified as such, or at least the lowest member of the series had, the 2s3s $^1\text{Se}$ state of He and its analogues in the alkaline earth atoms, in the
work of Hunter. Figure 6 shows conditional probability distributions for He in collinear geometry, for the 2s3s \(^1S^e\) and 2s3s \(^3S^e\) states, from well-converged Sturmian CI functions and from the three approximate functions: single-configuration, Hartree-Fock type functions (but based on hydrogenic orbitals), symmetric and antisymmetric combinations of local Morse oscillators with only one quantum in either one or the other of the local oscillators, and finally the symmetric and antisymmetric normal mode states.

(a) \[2s3s \, ^1S^e\]

(b) \[2s3s \, ^3S^e\]

(c)

(d)

10 \(r_1\) 0 \(r_2\) 10

Figure 6. Conditional probability distributions with \(\theta_{12}=\pi\), as functions of the distances \(r_1\) and \(r_2\) of the two electrons of helium from the nucleus, for the states that should be the first excited stretching-mode states, in a collective, molecular picture. The left column represents the probability for the 2s3s \(^1S^e\) state which should correspond to a state totally symmetric in the \(C_{\infty v}\) symmetry of the linear-molecule Hamiltonian, and the right column represents the corresponding triplet, which corresponds to the antisymmetric stretch. The top row shows the results from the CI functions, the second row are the single-configuration Hartree-Fock-like functions, the third row are the symmetric and antisymmetric combinations of Morse local-mode states and the fourth row are based on harmonic, normal-mode functions. Clearly all four of the triplet functions are similar to each other, but the normal-mode symmetric-stretch function gives results very different from the others, notably from either the well-converged CI function or the symmetric local-mode function.

While all the representations are similar for the triplet, the one which is clearly not at all like the accurate function is the harmonic, normal-mode symmetric stretch. This is borne out quantitatively for this state and the corresponding states of the alkaline earths, through the
comparison of the mean values of $\cos \theta_{12}$ and of $\cos^2 \theta_{12}$ for these states. While the former is very small, the latter is not, showing that the low value of the former is due to cancellation of significant contributions with opposite sign, not to orthogonality of the motion of the two electrons\textsuperscript{142}.

5. Summary and Conclusions

This discussion has begun with the early history of the attempts to find the nature of the quantization in simple, two-electron and few-electron atoms, then went into the means by which we can assess the extent of validity of one or another model, and then turned to the specific probes and findings. Finally, the discussion returned to a very brief survey of the progress that has been made in trying to solve the same classical and semiclassical forms of these problems that we used to introduce the Chapter. Many, perhaps most of the questions of what the best constants of motion are, and of how we can recognize them from experiments, remain unanswered. However we have far clearer ideas now than anyone had in the 1920's of how to get answers, and even more so of how rich and enlightening are the questions we have to ask along the way. The several-body problem is terribly, tantalizingly difficult, even in special cases such as the planetary and Langmuir orbits. Let us hope that this Chapter is a stimulus to some of its readers to help move us toward new answers.

References.


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