

Astrophys. **28**, 589 (1965).

²For example, see O. Bely, *Ann. Astrophys.* **30**, 953 (1967); Y. Hahn, *Phys. Rev. Lett.* **39**, 82 (1977), and *Phys. Rev. A* **18**, 1028 (1978); R. D. Cowan and J. B. Mann, *Astrophys. J.* **232**, 940 (1978).

³For example, see J. W. Allen and A. K. Dupree, *Astrophys. J.* **155**, 27 (1969); C. Jordan, *Mon. Not. R. Astron. Soc.* **142**, 501 (1969); H. Nussbaumer and P. J. Storey, *Astron. Astrophys.* **44**, 321 (1975); V. L. Jacobs, J. Davis, P. C. Kepple, and M. Blaha, *Astrophys. J.* **211**, 605 (1977).

⁴R. E. Fox, W. M. Hickam, and T. Kjeldaas, Jr., *Phys. Rev.* **89**, 555 (1953).

⁵H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford Univ. Press London, 1969), Vol. I, Chap. 3; see also L. J. Kieffer and G. H. Dunn, *Rev. Mod. Phys.* **38**, 1 (1966).

⁶B. Peart and K. Dolder, *J. Phys. B* **1**, 872 (1968), and **8**, 56 (1975); see also work on Ba^+ by B. Peart, J. G. Stevenson, and K. Dolder, *J. Phys. B* **6**, 146 (1973); R. K. Feeney, J. W. Hooper, and M. T. Elford, *Phys. Rev. A* **6**, 1469 (1972).

⁷D. H. Crandall, R. A. Phaneuf, B. E. Hasselquist, and D. C. Gregory, *J. Phys. B* **12**, L249 (1979); R. J. W. Henry, *J. Phys. B* **12**, L309 (1979); R. A. Falk and

G. H. Dunn, to be published.

⁸D. H. Crandall, R. A. Phaneuf, and P. O. Taylor, *Phys. Rev. A* **18**, 1911 (1978).

⁹W. Lotz, *Z. Phys.* **220**, 466 (1969), and **216**, 241 (1968). The Lotz formula has been found to provide an upper limit to the direct ionization cross section in most cases. See, e.g., Refs. 7 and 8.

¹⁰Systematic uncertainties judged to have a possible correlation were added linearly after which a quadrature sum of systematic uncertainties was made. One-sided systematic uncertainties were added linearly to the resultant quadrature sum. The total absolute uncertainty estimated at high confidence level is less than $\pm 10\%$ for these data.

¹¹The atomic-structure program is described in R. D. Cowan, *The Theory of Atomic Structure and Spectra* (Univ. California Press, Berkeley, 1981).

¹²R. D. Cowan and D. C. Griffin, *J. Opt. Soc. Am.* **66**, 1010 (1976).

¹³C. H. H. Van Deurzen, *J. Opt. Soc. Am.* **67**, 476 (1977).

¹⁴L. B. Golden and D. H. Sampson, *J. Phys. B* **13**, 2645 (1980).

¹⁵M. E. Riley and D. G. Truhlar, *J. Chem. Phys.* **63**, 2182 (1975).

Electron Correlation and Kellman-Herrick Quantization in Doubly Excited Helium

Huoy-Jen Yuh, Gregory Ezra, Paul Rehmus,^(a) and R. Stephen Berry

Department of Chemistry and the James Franck Institute, The University of Chicago, Chicago, Illinois 60637

(Received 26 May 1981)

Conditional probability distributions based on accurate wave functions for He^{**} confirm the proposal that electron correlation in doubly excited atoms leads to quantization like that of a linear triatomic molecule.

PACS numbers: 31.20.Tz, 31.50.+w

Kellman and Herrick have proposed recently¹⁻⁴ that the quantization in some states of doubly excited helium is much more like that of a linear triatomic molecule than of the atomic shell model. Basing their inference primarily on the energy levels in approximate $O(4)$ symmetry derived from a broken $O(4) \times O(4)$ symmetry of two hydrogenlike electrons, they suggest that the approximate constants of the motion of states normally designated by configurations $(nl nl')$ correspond to the rotational and vibrational motions of a linear ABA molecule. Configuration mixing is considerable in these states, so that the orbital angular momentum of each electron is in no way a good constant of the motion; i.e., a "solar system" model is a poor model for states of He^{**} with $n_1 = n_2$.

However until the proposal of Kellman and Her-

rick, we had no physical picture to supplant that of orbiting electrons, each with nearly constant angular momentum. Their new molecular model offers a conceptual picture dramatically different from anything previously accepted as a description of electrons in an atom. (Moleculelike models had occasionally been proposed⁵ but never with a logical or quantitative basis comparable to or related to that of Refs. 1-4.) The arguments given by Kellman and Herrick are persuasive, but their model overturns our traditional conceptions at such a deep level that we are immediately obliged to put that model to test. If their suggestion survives such a test, it opens the possibility for identifying hitherto unexplored commonalities of microscopic few-body systems generally, including molecules, nuclei, and possibly even hadrons.

This report is precisely such a test. By examining accurate wave functions for several states of He**, we are able to confirm the essential validity of the Kellman-Herrick picture, and to show how the nonrigidity of the system introduces some minor modifications of an intuitively plausible sort.

The Herrick-Kellman supermultiplet model of He** identifies each atomic "intrashell" term, that is each atomic term of the manifold of (nl , nl') configurations, with quantum numbers R for rigid rotation, ν_2 for the doubly degenerate bending mode ν_2 , and J for total angular momentum. The quantum numbers ν_1 and ν_3 of the symmetric stretching vibration and the antisymmetric stretching vibration are contained in the model but were not invoked by Herrick and Kellman in their analysis of intrashell manifolds. The initial stimulus for the molecular model came from the recognition¹ that the intrashell manifolds of He** contain sets of states $^1S^e$, $^3P^o$, $^1D^e$, ..., characteristic of a rigid rotor: that these states correspond⁶ to large and frequently to maximum values of the operator $B^2 = (A_1 - A_2)^2$, where A_1 and A_2 are the Runge-Lenz vectors of electrons 1 and 2. Maximum B^2 corresponds to the largest possible distances between the classical Kepler ellipses of the separate electrons. Furthermore the spatial distribution of electrons in the lowest $^1S^e$ state of the $n_1 = n_2 = 2$ manifold does look like that of a rigid rotor.⁷ This was inferred from a configuration-interaction mixture of $2s^2$ and $2p^2^1S^e$ functions but later confirmed with an accurate function⁸; and that the energy levels of the rotor series conform closely to the pattern of a rigid rotor, much like the levels of nuclear rotor states.⁹

The rotor model was generalized to a supermultiplet model²⁻⁴ with the prediction that many

states of He** can be classified according to the quantization of a semirigid triatomic molecule $e-\alpha-e$.

If the states of He** obey Kellman-Herrick quantization, their wave functions should resemble the corresponding molecular rovibrational wave functions. We have found accurate Hylleraas-Kinoshita wave functions (to be given in a fuller report) for the states designated as $2s^2^1S^e$, $2s2p^3P^o$, $2s2p^1P^o$, $2p^2^1S^e$, and $2s3s^3S^e$ for He and Li^+ , and some states for H^- as well.

Kellman-Herrick quantization would have the first of these states be the ground $^1S^e$ state of its manifold, the $^3P^o$ be the first excited rotor state of that manifold, the $^1P^o$ be the first excited state of the bending mode ν_2 , and the $2p^2^1S^e$ be the rotationless state with two quanta of bending. The $2s3s^3S^e$ must be the first excited state of the antisymmetric stretching mode ν_3 , if we extend the model to accommodate stretching modes as well as bending and rotation.

From the accurate wave functions we have computed the conditional probability densities for these states in the variables r_1 , r_2 , and θ_{12} :

$$\rho(r_2, \theta_{12} | r_1 = \alpha) = \frac{\rho(r_1 = \alpha, r_2, \theta_{12})}{\left[\int dr_2 \int d\theta_{12} \rho(r_1, r_2, \theta_{12}) \right]_{r_1 = \alpha}} \quad (1)$$

is the probability that electron 2 be at the distance r_2 from the nucleus and at angle θ_{12} from the line between the nucleus and electron 1, when electron 1 is at distance r_1 from the nucleus. We had previously examined approximate wave functions for several states of He**,⁷ accurate ground states of He and He-like ions,¹⁰ and some accurate excited S states of He, including the $2s^2^1S^e$ and $2p^2^1S^e$ states.⁸ However accurate electron distributions in the states most crucial for testing Kellman-Herrick quantization have not been

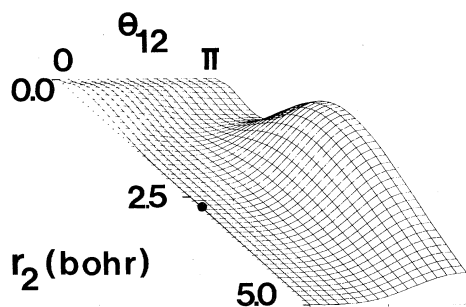


FIG. 1. Conditional probability density $\rho(r_2, \theta_{12})$ for the " $2s^2^1S^e$ " state of He** with $r_1 = 2.74$ bohrs, its most probable value. The heavy dot indicates the position of electron 1.

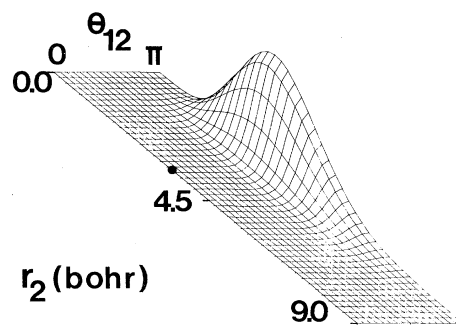


FIG. 2. Conditional probability density $\rho(r_2, \theta_{12})$ for the " $2s2p^3P^o$ " state of He** with $r_1 = 3.5$ bohrs, its most probable value.

examined previously.

Figure 1 shows the density (1) for the " $2s^2$ " $^1S^e$ state, based on the wave function of Ref. 8, with r_1 fixed at its most probable value. The most probable value for r_2 is equal to that of r_1 , and the charge density is clearly localized around $\theta_{12} = \pi$, precisely as one expects for a linear triatomic molecule in its ground state. The cross-sectional slice through $\rho(r_2, \theta_{12}; r_1)$ at $r_2 = 2.745$ bohrs is Gaussian, as one expects for the ground state of a bending mode.

Figure 2 shows the conditional probability density for the $2s2p$ $^3P^o$ state, for the most probable value of r_1 , 3.5 bohrs, based on a six-term Hylleraas function. Over the entire range of r_1 , the conditional probability for this state has its maximum at $\theta_{12} = \pi$ and the most probable value of r_2 occurs when $r_1 = r_2 \cong 3.5$ bohrs. The cross section of $\rho(r_2, \theta_{12}; 3.5)$ at $r_2 = 3.5$ is again a Gaussian. The most probable r value for the $^3P^o$ state is larger than that for the $2s^2$ $^1S^e$ state, which is qualitatively what one expects from centrifugal distortion.

Conditional probability densities for two values of r_1 of the $2s2p$ $^1P^o$ state are shown in Figs. 3(a) and 3(b). The wave function is a thirteen-term

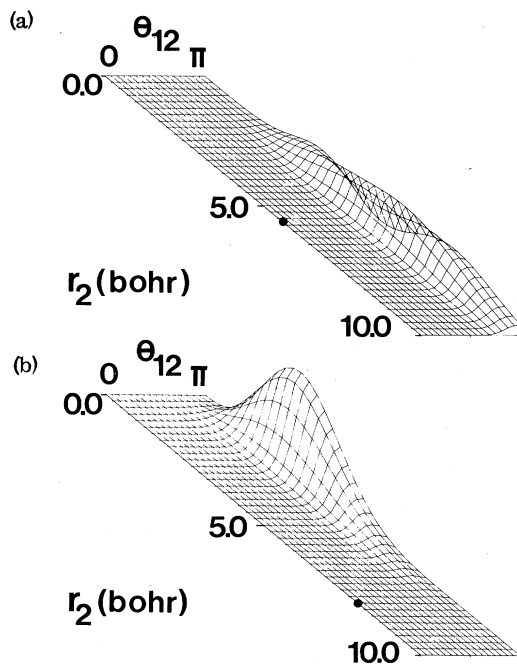


FIG. 3. (a) Conditional probability density $\rho(r_2, \theta_{12})$ for the " $2s2p$ " $^1P^o$ state of He^{**} with $r_1 = 5.6$ bohrs, where the marginal probability for r_1 has a *local* minimum. (b) As for (a), but $r_1 = 8.0$ bohrs.

Hylleraas function, which appears to be a more dramatic confirmation of Kellman-Herrick quantization than the states discussed previously. In Fig. 3(a), with r_1 at approximately 5.6 bohrs, the density shows a clear minimum, actually a nodal point, at the same value of r_2 and $\theta_{12} = \pi$. The cross-sectional curve at this r_1 and r_2 is very nearly the function for the first excited state for a two-dimensional harmonic bending mode. The bimodal distribution along the ray $\theta_{12} = \pi$ can be interpreted as coupling of the bending mode with the antisymmetric stretching mode. The most probable configuration for $\theta_{12} = \pi$, over the range of r_2 , occurs when one electron is at about 3.3 and the other at 8.6 bohrs [Fig. 3(b)]. The mixing of bending motion and antisymmetric stretch is a normal consequence of Coriolis interactions, which we presume to be responsible for the mixing here, due to the *nonrigidity* of the helium atom. In molecules, Coriolis interactions are one of the most common expressions of nonrigidity, spoiling the constancy of the rigid-rotor angular momentum. In He^{**} , vibration-vibration coupling seems to be their most visible consequence, at least with the Hylleraas functions used here.

An unscaled 83-term configurational wave function for the $^1P^o$ state with an energy 0.009 hartree higher than the Hylleraas function has its most probable value of r_1 at about 3 bohrs, considerably less than the Hylleraas-function value. The configurational function shows the bending character but exhibits very little interaction with the antisymmetric stretch. A comparison of the distributions derived from different wave functions will be presented in a fuller development.

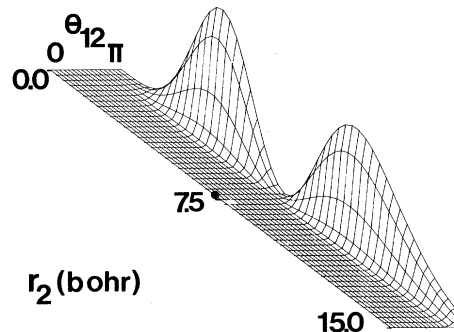


FIG. 4. Conditional probability density $\rho(r_2, \theta_{12})$ for the " $2s3s$ " $^3S^e$ state of He^{**} , with $r_1 = 7.2$ bohrs, the location of the local minimum of its marginal probability distribution.

The bending mode of a linear three-body system is, of course, doubly degenerate. The companion state to the $2s2p\ ^1P^o$ state is the $2p^2\ ^3P^e$ state, which we have not computed with Hylleraas-Kinoshita functions. However its distribution was computed from the hydrogenic one-term configurational function,⁷ giving a form in qualitative agreement with that of Fig. 3. Better evidence comes from calculations (by G. Ezra and R. S. Berry, to be published elsewhere) of the states of two electrons on a sphere, which yield fully converged wave functions for the partner states $^1P^o$ and $^3P^e$ that are indistinguishable.

The $2p^2\ ^1S^e$ function has been examined previously.⁸ This state has the qualitative angular behavior of a two-dimensional vibrator with two quanta in its bending motion, and a consequent maximum at $\theta_{12} = \pi$. The electron-electron repulsion makes itself evident as a cusp in the center of a large depression around $r_1 = r_2$ and $\theta_{12} = 0$.

The last state to be considered here is the $2s3s\ ^3S^e$ state. In Kellman-Herrick quantization, this is the state with one quantum of vibration in the antisymmetric stretching mode. Figure 4, based on a six-term Hylleraas-Kinoshita function, shows that this is precisely the nature of the first $^3S^e$ state. The most probable configuration has $r_1 \cong 2.5$ bohrs, $r_2 \cong 12$ bohrs, and $\theta_{12} = \pi$. When r_1 is at 7.2 bohrs, the other electron is most probably found at $\theta_{12} = \pi$, but at a distance either much shorter or much longer than r_1 .

It is significant that Hylleraas and Hylleraas-Kinoshita functions have been used here. With a limited configurational basis, it appears that the $2p^2\ ^1S^e$ state has a maximum at $\theta_{12} = 0$ when r_1 is near its most probable value. The minimal "DESB" basis^{6,7} gave this impression. However with the flexibility of larger and better basis,⁸ this state appears correctly, with its angular maximum at $\theta_{12} = \pi$.

We conclude that the Kellman-Herrick model is well supported by the spatial forms of the wave

functions of the lowest $^1S^e$, $^3P^o$, $^1P^o$, and $^3S^e$ states of He**. Consequently we infer that the quantization of doubly excited states of two-electron atoms with principal quantum numbers $n_1 \cong n_2$ is indeed well described by taking the approximate constants of the motion to be those of a linear triatomic molecule, i.e., of rigid-body rotation and of stretching and bending vibration.

We make one prediction: the " $2p^2\ ^3P^e$ " state should be the vibrational partner of the " $2s2p\ ^1P^o$ " state. Together they form the basis of a two-dimensional representation of SU(2). The sum and difference of these two functions should have identical charge distributions if the molecular model is exact.

One of us (G.E.) would like to acknowledge the support of a NATO Science Research Council (United Kingdom) fellowship. The research was carried out with the assistance of a grant from the National Science Foundation.

^(a)Present address: Department of Chemistry, Stanford University, Stanford, Cal. 94305.

¹M. E. Kellman and D. R. Herrick, *J. Phys. B* **11**, L755 (1978).

²D. R. Herrick and M. E. Kellman, *Phys. Rev. A* **21**, 418 (1980).

³D. R. Herrick, M. E. Kellman, and R. D. Poliak, *Phys. Rev. A* **22**, 1517 (1980).

⁴M. E. Kellman and D. R. Herrick, *Phys. Rev. A* **22**, 1536 (1980).

⁵B. F. Gray and H. O. Pritchard, *J. Chem. Soc.* **1957**, 3578.

⁶O. Sinanoglu and D. R. Herrick, *J. Chem. Phys.* **62**, 886 (1975).

⁷P. Rehmus, M. E. Kellman, and R. S. Berry, *Chem. Phys.* **31**, 239 (1978).

⁸P. Rehmus and R. S. Berry, *Chem. Phys.* **38**, 257 (1979).

⁹A. Bohr, *Rev. Mod. Phys.* **48**, 365 (1976).

¹⁰P. Rehmus, C. C. J. Roothaan, and R. S. Berry, *Chem. Phys. Lett.* **58**, 321 (1978).