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Ro-vibrational collective interpretation of supermultiplet classifications of intrashell levels of two-electron atoms

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We investigate whether the intrashell portion of the double-excitation spectrum of the helium atom may be interpreted in terms of collective rotational and bending vibrational motion, analogous to the ro-vibrational motion of molecules. Earlier work by us had identified a few levels in each atomic shell as having a rotorlike spectrum cutoff at higher energies, analogous to the cutoff rotorlike spectra of some nuclei. In this paper we use the I and d supermultiplets of the preceding paper of this journal, to interpret the entire intrashell manifold for each principal quantum number N, as resembling cutoff rotational and bending vibrational levels of a highly nonrigid linear symmetric XYX "molecular" structure. We obtain a good qualitative fit of each intrashell spectrum using leading-order ro-vibrational energy formulas from molecular spectroscopy including anharmonicity, centrifugal distortion, and rotation-vibration coupling. We interpret these effects for low-lying intrashell states of two-electron atoms, and find them to be consistent with an average equilibrium configuration $\theta_{12}=180°$ for the interelectronic angle. Analysis of the time scales of the proposed rotational, bending, and other degrees of freedom suggests approximate separability. We also identify parts of the spectrum analogous to molecular l doubling, and indicate a possible link between the related Coriolis force and a recently proposed mechanism for decay by autoionization. Certain aspects of our collective interpretation of the atomic supermultiplets are discussed which have close parallels in nuclear physics, including the Elliott model and the SU(6) interacting boson model for nuclear collective motion.

I. INTRODUCTION

Previous papers[1,2] have established that intrashell spectra of doubly excited two-electron atoms have a useful, approximate classification with two novel types of "supermultiplets." We constructed those d and I supermultiplets by using quantum numbers originating in the O(4) group theoretical shell structure of the hydrogen atom. In the present paper we investigate the energy-level structure contained in the supermultiplets from a different point of view. We shall be concerned with aspects of the intrashell level spacings which reflect a novel "collective motion" interpretation of electron correlation in the two-electron atom. Earlier we had identified[3] a few of the levels in low-lying shells as having a rigid-rotor-like spectrum. Moreover, these spectra became more like those of a rigid rotor at low values of Z in the isoelectronic series, indicating a direct relationship between the rigidity of the structure and the electron correlation. We therefore postulated that the rotorlike spectra originated in motion of a highly nonrigid linear symmetric XYX structure for the atom, with X's electrons and Y the nucleus. The supermultiplets have now brought to light the even more startling possibility that a rotor-vibrator interpretation might be feasible for the entire intrashell manifold. We pursue the investigation of a rotor-vibrator interpretation herein. Certain aspects of the energy levels, their quantum numbers, and their stability against autoionization are found to be consistent with a rotor-vibrator model of the atom. The importance of our discovery lies in its possible implications for atomic structure theory, as well as its potential connections to chemistry and other parts of physics. The two-electron atom has long served as a model for understanding correlation in other systems. This connection is perhaps even stronger in the case of the doubly excited states, since their correlation involves $s, p, d, \ldots$ orbitals typical of the ones used to describe valence shells of atoms and molecules.

The importance of pair correlations in many-body problems and chemical bonding is well established. It is by no means obvious, however, that one should expect to find ro-vibrational progressions of levels in the doubly excited states, since the Schrödinger wave equation for two-electron atoms contains only Coulombic terms in the potential energy:

$$[-(\hbar^2/2m)(\nabla_1^2+\nabla_2^2)-Ze^2(1/r_1+1/r_2)+e^2/r_{12}-E]\Psi(\vec{r}_1,\vec{r}_2)=0\,. \quad (1.1)$$

Our interpretation therefore implies an approximate separability of coordinates of a type previously not thought to be realistic. Apparently this separation of levels in the intrashell supermultiplets involves three types of motion in the atom: (i) fast radial motion which accounts for the shell structure of the atom; (ii) relatively slow vibrational motion, probably involving the interelectronic angle θ_{12}; (iii) even slower rotational motion. The separability implied by the energy scales related to these motions is less than what is found in an *XYX* molecule. Nevertheless, our picture of the atom may allow one to treat radiative and nonradiative processes involving doubly excited states in a conceptually simple manner—without the usual detailed quantum-mechanical calculations. Our work in some ways resembles results in nuclear physics, and we also think it important to consider possible links which may lead to a mutual exploitation of concepts.

The organization of our paper is as follows. In Sec. II we discuss links between our work and various aspects of molecular, nuclear, and elementary particle physics. Although the precise origins differ in each case, ro-vibrational collective motion seems to be a common feature of molecular, nuclear, and now atomic few-body problems. Section III outlines molecular ro-vibration theory as we use it in the two-electron atom. The ro-vibrational interpretation of the atomic intrashell supermultiplets is then given in Sec. IV. We discuss our results in Sec. V.

II. COLLECTIVE MOTION, SHELL STRUCTURE, AND CLASSIFICATION SCHEMES

In this section we consider the possibility that a description of electron correlation in terms of collective motion underlies the phenomenological double-excitation supermultiplet schemes. Such a description would be pleasing in that it would greatly facilitate the qualitative understanding of correlated electron motion, and would help link the description of correlation in atoms with that in several other types of physical systems.

Perhaps the most obvious example of collective motion in quantum-mechanical systems is the motion of the nuclear framework of molecules. Here, the occurrence of nearly rigid structures makes such a description entirely natural and straightforward; the motion may be described as small amplitude vibration with nearly rigid rotation.[4] To a first approximation the vibrational and rotational motions are separable, with simple harmonic vibrations. This combination of near rigidity and separability results in spectra consisting of infinite sequences of vibrational levels, on each of which is built an infinite sequence of rotational levels.

The applicability of collective motion to other types of systems is much less straightforward. The basic reason is that most quantum-mechanical systems—individual nuclei and atoms are two examples—may be described with independent motion of the constituent particles within the shells of a central-field potential. This contrasts sharply with the usual description of molecules, where rigid bonds preclude such a description of the nuclear motion. Nonetheless, it has been known for years that nuclear spectra display features characteristic of rotation and vibration.[5] We shall briefly look into this problem here, to elucidate the apparent rotation-vibration levels in doubly excited states of two-electron atoms.

A good deal of effort has succeeded in clarifying the relationship between nuclear collective motion on the one hand, and shell structure on the other hand. Broadly speaking, nuclear collective motion occurs in shell systems when the independent particle motion gives rise to time-independent or time-dependent deformations of the system.[5] The first possibility is exemplified by nuclear rotation. The Hartree-Fock self-consistent field of the nucleus may give rise to a nonspherical equilibrium distribution of the constituent nucleons. A nonspherical shape breaks rotational invariance; the symmetry is restored by allowing all orientations of the system. Quantum mechanically, this is tantamount to allowing rotation of the system as a whole. The second possibility, time-dependent deformations of the structure, is exemplified by nuclear collective vibration. Variations in the independent-particle potential give rise to excitations of the single-particle motion, and collective vibrational motion results if the induced density changes are equal to those needed to drive the vibrating potential.

An aspect of nuclear collective motion which is strikingly different from the rotation-vibration motion of nearly rigid bodies arises when the nucleus has only a few particles outside a closed shell. In this situation coupling of single-particle orbitals gives rise to only a finite number of spectroscopic terms—in contrast to the infinite number of levels found in molecules.[6] The collective spectrum for particles in a shell is therefore necessarily *cut off* after a finite number of levels.[7] This paradoxical situation of a *cutoff* in a collective spectrum seems to have its origin in the disappearance at the cutoff of the deformation which gives rise to the collective excitations. The limitation to a finite number of levels thus does not preclude a collective spectrum.

One can also approach the problem of collective motion in nuclei group theoretically. We know of two such theories: the Elliott model[8] and the independent boson model of Arima and Iachello.[9] The Elliott model exploits SU(3) symmetry of the three-dimensional harmonic oscillator to describe rotational spectra of light nuclei. The spectra arise from perturbations of SU(3)-symmetric representations for shell model levels. In the independent boson model, used to describe heavy even-even nuclei, it is assumed that pairs of nuclei couple to form elementary representations of SU(6), which are taken to be the constituent bosons of the model. These in turn couple to give representations of SU(6) which are split by perturbations having the symmetry of various subgroups. Different kinds of collective spectra, including rotations and vibrations, are obtained depending on the SU(6) subgroup chosen. Both the independent boson model and the Elliott model account in elegant fashion for the collective-type spectra and the existence of cutoffs.

The applicability of collective motion to electrons in atoms is even more problematic than was the case with nuclei. This is because deformed nuclear shapes associated with collective motion are not inconsistent with the "liquid drop" model of the nucleus, whereas the electron cloud in atoms is usually thought of as a gas. Collective density oscillations similar to the plasmons of an electron gas have been investigated for heavy many-electron atoms.[10] However, the applicability of those ideas to understanding very small atoms is not clear.

Because of the usual orbital approach for atomic configurations, it may be thought that a collective motion interpretation is not to be expected for the two-electron atom. However, the electron correlation due to the Coulomb repulsion $1/r_{12}$ in Eq. (1.1) involves the atomic shell structure as well, and in an independent particle picture this is described by the group O(4) which accounts for the N^2-fold spatial degeneracy of hydrogen-atom levels. In a Hartree-Fock description of orbitals in the two-electron atom this degeneracy is broken slightly, and thus the applicability of O(4) to this system is only approximate. Nonetheless, the doubly excited intrashell states possess a relatively high degree of electron correlation, much of which may be attributed to near-degeneracy configuration mixing in the wave function. One sees this correlation clearly in spatial electron density distributions of the states, which show the interelectronic angle θ_{12} peaked at 180° in *some* of the doubly excited wave functions.[11] Thus the situation for doubly excited atoms seems closer to that for collective motion in nuclei, rather than a dilute gas.

In an earlier study we found evidence for a collective rotational interpretation of the doubly excited intrashell spectra of low-Z two-electron atoms.[3] As one sees from Eq. (1.1), the electron correlation due to $1/r_{12}$ is stronger at lower Z, since the central Coulomb field attraction is weaker. We found that if one considers the sequence of levels which corresponds to the lowest energy state for each value of the angular momentum $L=0,1,\ldots$ in a shell, the resulting spectrum looked very much like that of a rigid rotor. This was surprising because of the high degree of nonrigidity implied by spatial density distributions for the states. Those rotorlike spectra also included cutoffs, with the highest energy level in each series given by $L=2N-2$. This cutoff was described using a coupled O(4) representation for each shell. The collective interpretation was only partially successful in unravelling the intrashell spectrum, however, because it treated only a few levels from each intrashell manifold. Moreover, it did not address the question of what, if anything, constituted the "vibrational" motion of the electrons in the atom. It will be seen that the present work marks an extension of the results of Ref. 3, in that we now treat the entire intrashell manifold in terms of both rotational and bending motion vibrations.

We have discussed above the relation between a collective approach to electron correlation in atoms, with the more familiar collective motion in molecules and nuclei. We now discuss briefly links between the supermultiplet theory of the preceding paper, and similar work in other branches of physics. Examples which postulate continuous groups for many-body systems include the Elliott model[8] and the interacting boson model[9] for nuclear collective motion, as well as Wigner supermultiplet theory[12] and the eightfold way[13] in particle physics. Although continuous groups may be used as a mathematical tool for simplifying matrix elements and classifying term symbols for orbital configurations in atoms,[14] the applicability of the groups to understanding energy levels in many-electron atomic spectra including many different intrashell configurations is not clear. The supermultiplets we describe, on the other hand, offer concrete evidence of the need to understand better the relation of continuous groups to a nontrivial atomic spectrum. Details of the quantum numbers underlying the I and d supermultiplets are discussed thoroughly in Ref. 1. In spite of the partially *ad hoc* character of the supermultiplets, the approach is somewhat akin to that of the group-theoretical models found in nuclear and elementary particle physics.

III. THE LINEAR *XYX* MOLECULE AS A ROTOR VIBRATOR

In this section we give a brief survey of the structure and spectral theory of linear triatomic molecules, emphasizing aspects which have direct bearing on our interpretation of doubly excited intrashell states in Sec. IV. We therefore consider the case of a linear symmetric *XYX* structure, with the X's spin-$\frac{1}{2}$ fermions positioned equidistant from the central Y atom. Only the spin of the X's will be treated. We shall be concerned with the description of the motion of the atomic nuclei X_1, X_2, and Y. All internal degrees of freedom and associated quantum numbers for electronic motion are ignored. This is entirely reasonable, since in the Born-Oppenheimer approximation the molecular nuclear framework may be thought of as moving in a potential created by the much lighter electrons. Our concern is therefore with the geometry of the nuclear framework, molecular vibration and rotation and also their coupling; and associated quantum numbers. Readers unfamiliar with this subject, or with the conventional ro-vibrational concepts and symbols we use, should consult the references cited herein for a fuller treatment.

Molecular rotation is usually slow compared to vibration; hence the starting point of ro-vibration theory is with the separation of these degrees of freedom.[4] A linear triatomic molecule has a total of six degrees of freedom (excluding center-of-mass motion): four vibrations and two rotations. Figure 1(a) depicts the four vibrational normal modes, including the symmetric stretch (ν_1), two degenerate bending modes (ν_2), and an asymmetric stretch (ν_3). The rotational angular momentum of a three-body system may be described with three Euler angles. Only two degrees of freedom of the linear molecule are rotational, however, Since the symmetric and asymmetric stretches carry no angular momentum, it is evident that a portion of the angular momentum is carried by the degenerate bending modes ν_2. As Fig. 1(a) shows, when the degenerate modes are coupled 90° out of phase the resulting motion gives a component $\pm l$ of angular momentum directed along the molecular axis. (Here the symbol l for vibrational angular momentum should not be confused with the same symbol which is used for one-electron orbital angular momentum in atomic theory.) A set of four vibrational quantum numbers is designated by v_1, v_2, v_3, and l.

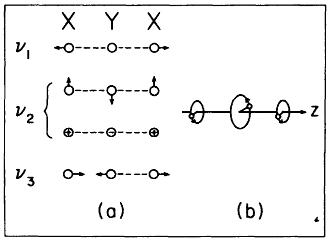

FIG. 1. (a) Normal modes of a linear symmetric XYX molecule. (b) Coupling of degenerate bending modes which gives a component of vibrational angular momentum along the molecular z axis.

The choice of a specific set of Euler angles is problematic for molecules, because of nonrigidity due to vibration.[15] Our molecule-fixed coordinates are chosen with the z axis taken to lie along the equilibrium configuration. Two Euler angles θ and ϕ give the orientation of the molecule axis, while the third Euler angle χ is related to the configuration of the bent structure relative to the equilibrium axis. χ is therefore related to the vibrational angular momentum, and hence to l. We make the usual assumption that molecular vibration is rapid compared to rotation, and that the vibrational amplitude is small compared to the molecular dimensions. In this case l is nearly a good quantum number for the magnitude of angular momentum along the molecule-fixed axis. The allowed values of l for each bending vibration quantum number v_2 are those of a two-dimensional oscillator:

$$l = v_2, v_2 - 2, \ldots, 1 \text{ or } 0 . \tag{3.1}$$

The remaining contribution to the angular momentum comes from rotation of the structure as it undergoes rapid, small-amplitude vibration.

To a good approximation then, the linear molecule is pictured as a symmetric top which undergoes separable, nearly rigid rotation and harmonic vibration. The corresponding zero-order wave function is given by[16]

$$\begin{aligned}\Psi(v_1 v_2 v_3, J \pm l M) = {} & C e^{-(\nu_1 \xi_1^2 + \nu_2 \rho_2^2 + \nu_3 \xi_3^2)/2} \rho_2^l L_{n_2}^l(\nu_2 \rho_2^2) \\ & \times H_{v_1}(\nu_1^{1/2} \xi_1) H_{v_3}(\nu_3^{1/2} \xi_3) D_{\pm l\, M}^J(\theta\phi\chi) .\end{aligned} \tag{3.2}$$

Here C is a normalization constant, ξ_1 and ξ_3 are normal vibration coordinates $-\infty \leqslant \xi_i \leqslant \infty$, ρ_2 is a radial bending coordinate $0 \leqslant \rho_2 \leqslant \infty$, $H_n(x)$ is a Hermite polynomial, and $L_{n_2}^l(x)$ is an associated Laguerre polynomial with $n_2 = \frac{1}{2}(v_2 - l)$. $D_{KM}^J(\alpha\beta\gamma)$ is the usual rotation wave function for a symmetric top, with quantum numbers J for total angular momentum, M for the projection along a space-fixed axis, and K for the projection along the molecule-fixed z axis. The six quantum numbers v_1, v_2, v_3, J, l, and M describe completely the six ro-vibrational degrees of freedom of the linear XYX molecule.

When describing the ro-vibrational energy and also the effects of nonrigidity, it is convenient to introduce alternate hierarchies of zero-order quantum numbers, each of which represents a different picture of the molecular motion. A related situation is encountered in the theory of diatomic molecules, where Hund's cases (a–e) describe different coupling schemes for the electronic and rotational angular momentum.[17] Here, for the linear XYX molecule, we will describe two hierarchies of ro-vibrational quantum numbers for labeling states in terms of angular momentum, parity, and permutation symmetry, taking into account the Pauli exclusion principle since the X nuclei are taken to be fermions. These hierarchies are certainly implicit in the standard theory of molecular spectroscopy, and have been used to clarify certain aspects of nonrigid triatomic molecules.[18] It will turn out that these molecular hierarchies have a salient parallel in the I and d supermultiplets of the doubly excited states of two-electron atoms. The hierarchies involve quantum numbers related to two complementary pictures of the system.

The first picture derives from the usual partition of molecular motion into vibrations and rotations. The molecule undergoes rotation which is essentially that of a simple linear rotor, since on the time scale of rotation the molecular vibration averages to a shape which has the symmetry of the linear equilibrium configuration. A hierarchy for this picture is the following (hierarchy 1):

$$\begin{aligned} &v_1=0,1,2,\ldots\;, \\ &v_3=0,1,2,\ldots\;, \\ &v_2=0,1,2,\ldots\;, \end{aligned} \tag{3.3a}$$

$$\begin{aligned} &l=v_2, v_2-2,\ldots,1 \text{ or } 0; \\ &J=l,l+1,\ldots\;, \\ &M=J,J-1,\ldots,-J, \\ &R=J-l=0,1,\ldots\;. \end{aligned} \tag{3.3b}$$

Recall that J is the total angular momentum excluding spin; M is the projection along the laboratory-fixed axis, and $\pm l$ is the projection along the molecule axis. The additional quantum number R is what one would naively associate with rotations about an axis perpendicular to the linear molecule axis. A quantum number R which behaves as a true angular momentum, unlike the R used here, occurs in the spectra of diatomic molecules in Hund's case (d). The linear XYX molecule treated here is more analogous to Hund's case (a).

The second hierarchy of quantum numbers we consider differs from the foregoing one in that it places less stress on the division between vibration and rotation. Rather, it emphasizes excitations which leave J unchanged ($\Delta J=0$, or "radial" excitation) and excitations which change J ($\Delta J>0$ excitations). In order to describe the degree of radial excitation of the system we define quantum numbers

$$\begin{aligned} &n_1=v_1\,, \\ &n_2=\tfrac{1}{2}(v_2-l)\,, \\ &n_3=v_3\,, \end{aligned} \tag{3.4}$$

which give the number of nodes in the radial wave functions [c.f. Eq. (3.2)] of the respective vibrations. The second hierarchy, which emphasizes the partition into radial excitation ($\Delta J=0$) and angular-momentum excitation ($\Delta J>0$) is (hierarchy 2):

$$\begin{aligned} &J=0,1,2,\ldots\;, \\ &M=J,J-1,\ldots,-J, \\ &l=J,J-1,\ldots,0\,, \\ &R=J-l=0,1,\ldots\,; \end{aligned} \tag{3.5a}$$

$$\begin{aligned} &n_1=0,1,2,\ldots\;, \\ &n_2=0,1,2,\ldots\;, \\ &n_3=0,1,2,\ldots\;. \end{aligned} \tag{3.5b}$$

We now analyze the ro-vibration states according to their angular momentum, parity (Π), and spatial exchange (P_{12}). The angular momentum classification is already contained in Eqs. (3.3) and (3.5) as the allowed values of J and l. The classification according to parity and exchange yields the following results[19-21]:

$$\Pi=\begin{cases} +1,-1, & l>0 \\ (-1)^J, & l=0 \end{cases} \tag{3.6}$$

and

$$P_{12}=(-1)^{l+v_3}\,. \tag{3.7}$$

Taking into account the Pauli principle, we may specify the angular momentum, parity, and permutation symmetry of allowed levels by the term symbol ${}^{2S+1}J^{\pi}$. A ro-vibrational level is then completely specified by the quantum labels ${}^{2S+1}J^{\pi}$, l, M, v_1, v_2, and v_3. These may be arranged according to either hierarchy 1 or 2, as illustrated in Figs. 2 and 3 for the case v_3 even, which turns out to be the case relevant for the atomic intrashell spectrum. Except for the absence of cutoffs, these hierarchies closely resemble the I and d supermultiplets of the preceding paper.[2]

We now consider energy level formulas for the XYX molecule. In zeroth order the energy formula is

$$\begin{aligned} E(v_1v_2v_3Jl)=\hbar\omega_1(v_1+\tfrac{1}{2})+\hbar\omega_2(v_2+1)+\hbar\omega_3(v_3+\tfrac{1}{2}) \\ +B_e[J(J+1)-l^2]\,, \end{aligned} \tag{3.8}$$

with $\omega_i=2\pi\nu_i$. B_e is the rotation constant,

$$B_e=\hbar^2/2I_e\,, \tag{3.9}$$

with I_e the moment of inertia based on the equilibrium values of the nuclear coordinates. The term $-l^2$ in Eq. (3.8) accounts for the portion of the angular momentum which is due to the bending vi-

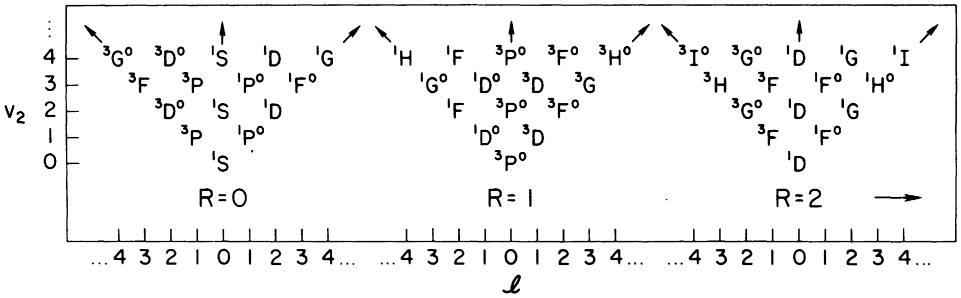

FIG. 2. Spectroscopic term symbols for molecular ro-vibrational levels described by quantum numbers in hierarchy 1, including only lower values of n_2, l, and R. This ordering is identical to that of "I supermultiplets" for doubly excited intrashell levels in Ref. 1, as described here in Secs. III and IV.

brations.

The theory of higher-order contributions to the ro-vibrational energy is well established, and takes into account nonrigidity of the XYX structure and anharmonicity in the potential energy. The leading-order contributions of these effects are usually described in terms of three separate energy corrections[4].

i. Anharmonicity. This introduces higher powers of $(v_i+\frac{1}{2}d_i)$ in the vibrational energy, where d_i is the degree of degeneracy of the ith normal mode. For molecules with singly and doubly degenerate vibrations the anharmonic contribution is seen in the following expression for the vibrational energy, neglecting terms higher than quadratic:

$$E_{\text{vib}}=\sum_i \hbar\omega_i(v_i+\tfrac{1}{2}d_i)+\sum_{i,k}x_{ik}(v_i+\tfrac{1}{2}d_i)(v_k+\tfrac{1}{2}d_k)+\sum_{i,k}G_{i,k}l_il_k\,. \tag{3.10}$$

The coefficients X_{ik} are usually negative, which corresponds to a lowering of the energy levels due to a potential less repulsive than the harmonic potential. In the XYX molecule the nondegenerate modes have $l_1=l_3=0$, and the last term in Eq. (3.10) may be written simply as Gl^2.

ii. Centrifugal Distortion. This affects the rotational constant. Rotation produces centrifugal forces which stretch the molecule, therefore increasing the moment of inertia and decreasing the rotational energy constant from its equilibrium value. A first correction which takes this into account is

$$B=B_e-D[J(J+1)-l^2]\,. \tag{3.11}$$

For molecules, the constant D is generally much smaller than B_e.

iii. Rotation-Vibration Coupling. This correction also affects the rotational constant, and is due to deviations of B from the equilibrium value B_e because of vibrations. Taking this into account, B_e is replaced by

$$B_v=B_e-\sum_i \alpha_i(v_i+\tfrac{1}{2}d_i)\,. \tag{3.12}$$

The constants α_i are usually positive for nondegenerate vibrations, but may be negative for the degenerate bending mode since this decreases the average moment of inertia.

Taking into account contributions from Eqs. (3.10)–(3.12), the ro-vibrational energy formula for the linear XYX molecule becomes

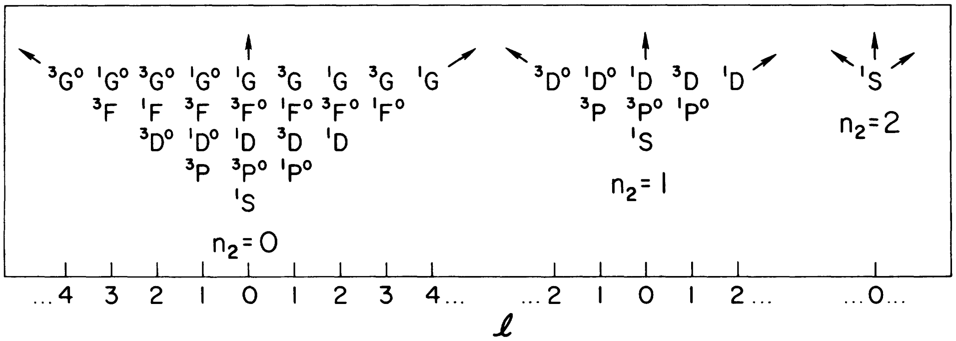

FIG. 3. Spectroscopic term symbols for molecular ro-vibrational levels described by quantum numbers in hierarchy 2, including only lower values of n_2, l, and R. This ordering is identical to that of "d supermultiplets" for doubly excited intrashell levels in Ref. 1, as described here in Secs. III and IV.

$$E(v_1v_2v_3Jl)=\sum_i \hbar\omega_i(v_i+\tfrac{1}{2}d_i)+\sum_{i,k}X_{ik}(v_i+\tfrac{1}{2}d_i)(v_k+\tfrac{1}{2}d_k)$$
$$+\Big(B_e-\sum_i \alpha_i(v_i+\tfrac{1}{2}d_i)\Big)[J(J+1)-l^2]+Gl^2-D[J(J+1)-l^2]^2\,. \qquad (3.13)$$

We shall not be concerned with higher-order contributions to the energy, except for a small splitting of the remaining $\pm l$ degeneracy implicit in the ro-vibrational energy formula Eq. (3.13). This effect, which is called "l doubling", is more difficult to describe quantitatively, and we defer discussion of this point until Sec. IV.

IV. RO-VIBRATIONAL INTERPRETATION OF INTRASHELL SPECTRA

In this section we use the results of Sec. III for the *XYX* molecule to give an interpretation of the qualitative behavior of the intrashell doubly excited states. This will be illustrated for the case of doubly excited helium. Specific conclusions we reach are the following. (i) The I and d supermultiplets originally formulated in a group theoretical approach also have a close correspondence to the ro-vibrational hierarchies of quantum numbers of an *XYX* molecule; (ii) intrashell energy levels of the doubly excited atom resemble those of rotational and bending vibrational motions of a highly nonrigid linear *XYX* molecule; and (iii) deviations of the intrashell atomic spectrum from that of a simple rotor-vibrator energy formula may, for the most part, be described with parameters appearing in Eq. (3.13) for the effects of anharmonicity, centrifugal distortion, and rotation-vibration coupling. Our presentation leading to these results is contained in Secs. IV A–V E. Section IV F then describes possible implications of molecularlike motions in the atom for effects not included in Eq. (3.13), namely splitting of the $\pm l$ degeneracy and autoionization of the doubly excited states.

A. Description of the model

The full rotor-vibrator picture, involving six degrees of freedom for the internal motion of an *XYX* structure, is not realistic for what is known about the two-electron atom. This is because the Coulomb potential energy in Eq. (1.1) has no stable equilibrium configuration comparable to that of a linear *XYX* molecule on a Born-Oppenheimer potential-energy surface. To see this clearly, we express the Coulomb potential energy using a symmetric radial coordinate $s=r_1+r_2$, an asymmetric radial coordinate $t=r_1-r_2$, and a bending angle θ_{12}. In the *XYX* molecule these are related to the normal modes ν_1, ν_3, and ν_2, respectively, shown earlier in Fig. 1. For each value of the coordinate s, we consider values of the other coordinates near the symmetric linear configuration defined by $t=0$ and $\theta_{12}=\pi$. A leading-order expansion of the Coulomb potential energy there is

$$V(r_1,r_2,\theta_{12})=-4(Z-\tfrac{1}{4})/s-(4Z/s^3)t^2+(1/8s)(\theta_{12}-\pi)^2+\cdots. \qquad (4.1)$$

Here we use atomic units $e=m=\hbar=1$; the unit of length is then the Bohr radius $a_0=\hbar^2/me^2$, and the atomic unit of energy is e^2/a_0. Thus s and t in Eq. (4.1) are dimensionless radial coordinates.

It is clearly not possible to carry out the usual molecular normal mode analysis with Eq. (4.1) because there is no minimum in the first term, which describes a symmetric Coulomb attraction of the electrons to the nucleus. ω_1 is therefore not defined. Similarly, radial motion along the coordinate t involves a maximum in the potential, rather than a stable minimum, and thus $\omega_3^2<0$. In contrast to these instabilities with s and t, bending motion along the coordinate θ_{12} does occur in a stable potential minimum. When treating the intrashell spectrum, we will therefore include in our interpretation only rotations and bending mode vibrations.

Implicit in the preceding description, and also in the usual treatment of autoionizing levels as quasibound states, is the notion of a potential energy surface for each double-excitation shell N. Bound states contained in each potential would include intrashell states as described herein, and also intershell states which describe Rydberg series leading to the dissociation limit $\mathrm{He}^{**}\to\mathrm{He}^{+}(N)+e^{-}$. The actual construction of such a potential energy surface is more problematic, since it would involve a set of collective coordinates taking into account properties of the Coulomb potential. One method which tries to come to grips with this problem uses hyperspherical radial coordinates in place of r_1 and r_2 (Refs. 22 and 23). However, that approach does not lend itself to a simple interpretation of the rotation-vibration structure we have found.

One might view our ro-vibrational interpretation of intrashell spectra as an attempt to understand the shape of an assumed potential energy surface for each double-excitation shell. Molecular spectroscopy provides a similar interpretation of Born-Oppenheimer potential energy surfaces. It is entirely possible, however, that other types of collective motion including both positions and momenta of the electrons could account for ro-vibrational structure in the intrashell spectra. We have noted in Ref. 1 for instance, that vibrational levels might be associated with motion of a vector like the Lenz vector in hydrogen-atom O(4) theory. The angle between two Lenz vectors describing electrons 1 and 2 would be analogous to the angle θ_{12}, and would lead to a similar interpretation of states. Reference 24 shows a configuration of two classical Lenz vectors which would correspond to a linear symmetric donfiguration of the type described herein for an *XYX* molecule. With this cautionary point about separability aside, we now turn to the ro-vibrational interpretation of levels.

B. Supermultiplet quantum numbers

The first point we consider is the relationship between the molecular hierarchies of quantum numbers and the corresponding supermultiplet hierarchies of quantum numbers for doubly excited states. We first consider molecular hierarchy 1, and the I super-multiplets of Ref. 1. We note that Fig. 2 of Ref. 1 for I supermultiplets, and Fig. 2 of this paper for hierarchy 1 are similar if one makes the following correspondence between atomic quantum numbers (left) and molecular quantum numbers (right):

$$\begin{aligned} &N-K-1 \leftrightarrow v_2,\\ &I \leftrightarrow R,\\ &T \leftrightarrow l. \end{aligned} \tag{4.2}$$

There is also the trivial identity between quantum numbers describing the total spatial angular momentum: $L=J$. The two schemes are then the same except that the I supermultiplets are finite in number, being cut off above a certain value of I. Furthermore, within each I supermultiplet there are additional cutoffs above certain values of T and K. Note that where an atomic term symbol is allowed in the I supermultiplet scheme, the same term symbol appears in the molecular hierarchy. Thus the properties of the corresponding atomic and molecular levels under rotation, parity, and permutation symmetries are the same.

An analogous correspondence of symmetry properties is found here between the d supermultiplets of Fig. 4 of Ref. 1, and hierarchy 2 of Fig. 3 of this paper. The correspondence between atomic quantum numbers (left) and molecular quantum numbers (right) is

$$\begin{aligned} &N-d-1 \leftrightarrow n_2,\\ &T \leftrightarrow l,\\ &I \leftrightarrow R. \end{aligned} \tag{4.3}$$

Again the analogy between the atomic and molecular schemes is exact except for cutoffs in the values of d, T, and I (or L) for the atomic d supermultiplets.

This identity of behavior of the corresponding atomic and molecular states under rotation, parity, and permutation symmetries is not a trivial point. In fact, it is extremely surprising since the two classifications were performed for two systems—atoms and molecules—having first approximations with very dissimilar physical bases. The identity of their symmetry properties encourages us to treat the correspondence between the two systems as more than a formal similarity. We therefore consider as a next step, whether the atomic intrashell energy levels resemble spectra of a bending, rotating *XYX* structure, taking into account cutoffs.

C. Simple rotor-vibrator supermultiplet energies

We now analyze the simple rotor-vibrator energy formula in Eq. (3.8) according to hierarchies 1 and 2, neglecting contributions of ω_1 and ω_3. We will see that the energy level progressions are indeed analogous to the corresponding atomic supermultiplet spectra.

i. Hierarchy 1. Energy levels in this scheme are described with one rotation quantum number R, and two bending-vibration quantum numbers v_2 and l (cf. Fig. 2). With these, the rotor-vibrator energy is cast into three terms:

$$E=B_eR(R+1)+\omega_2(v_2+1)+B_el(2R+1)\,. \tag{4.4}$$

The first term represents the rotational energy of the molecule in its ground vibrational state, $v_2=l=0$. It is the energy of a rigid dumbbell rotor. The second term accounts for bending of the rotor, and each level has the (v_2+1)-fold degeneracy of a two-dimensional oscillator. Thus for each value of R there is a complete spectrum of two-dimensional oscillator levels. The third term describes splitting of the oscillator degeneracy due to rotation; this splitting grows linearly with increasing vibrational angular momentum l.

The preceding sequence of ro-vibrational levels is similar to that of the I-supermultiplet spectra for each double-excitation shell N, if one makes the correspondence of quantum numbers in Eq. (4.2). From Ref. 3 we see that the dumbbell rotor quantum number R has the following cutoff values in each shell:

$$R=0,1,2,\ldots,2N-2. \tag{4.5}$$

For each value of R, we then have the following cutoff values for the vibrational quantum numbers:

$$l=\begin{cases} 0,1,\ldots,\frac{1}{2}(2N-2-R) & (R \text{ even}) \\ 0,1,\ldots,\frac{1}{2}(2N-3-R) & (R \text{ odd}) \end{cases} \tag{4.6a}$$

$$v_2=\begin{cases} l,l+2,\ldots,2N-2-R-l & (R \text{ even}) \\ l,l+2,\ldots,2N-3-R-l & (R \text{ odd}). \end{cases} \tag{4.6b}$$

Applying these cutoffs to the rotor-vibrator energy in Eq. (4.4), one sees from the first two terms diamondlike patterns of energy levels similar to ones described in Ref. 1 for I supermultiplets. The degeneracy across each row in a supermultiplet would be due to the oscillator degeneracy. The I supermultiplets in Ref. 1 do not have this exact degeneracy, but show splittings analogous to those of the third term of Eq. (4.4) when $R>0$. However, this does not always give the right direction of the very slight splitting found in the largest I supermultiplet ($I=R=0$) in each shell. Evidently if the XYX model is to apply to the doubly excited states, we will have to include higher-order effects in the energy. This is certainly not unreasonable, in view of the highly nonrigid structure of the atom, and anharmonicity due to the Coulomb potential. These effects will be treated in Sec. III D.

ii. Hierarchy 2. Energy levels in this scheme are described with one radial-bending quantum number n_2, and two rotation quantum numbers R and l. The rotor-vibrator energy formula in terms of these is

$$E=2\omega_2(n_2+\tfrac{1}{2})+l[\omega_2-B_e(2R+1)]+B_eR(R+1). \tag{4.8}$$

The energy levels predicted by this formula are the same ones predicted by Eq. (4.4), only viewed here in the different perspective provided by hierarchy 2. The first term in Eq. (4.8) represents radial bending ($\Delta J=0$). In Fig. 3 this corresponds to a progression of ${}^1S^e$ levels. Note that this energy contribution is essentially that of two one-dimensional oscillators, both having the same vibrational quantum number. The remaining terms in Eq. (4.8) describe energy contributions from rotational ($\Delta J>0$) excitation. Spectroscopic term symbols for these states are seen in Fig. 3 above each of the ${}^1S^e$ levels. These have been arranged to display an ordering similar to that of Eq. (4.8). The second energy term increases linearly with l and accounts for excitations involving rotations about the molecular z axis, as well as coupling with R. The third energy term describes a rotor series, with the quantum number R roughly analogous to what one expects for rotations about an axis perpendicular to the molecular axis, as discussed in Sec. III.

The energy levels for hierarchy 2 bear a close similarity to the d-supermultiplet spectrum for each double-excitation shell N if one makes the correspondence between quantum numbers in Eq. (4.3). The quantum numbers are found to have the following cutoff values:

$$\begin{aligned} &n_2=0,1,\ldots,N-1,\\ &l=0,1,\ldots,N-1-n_2,\\ &R=0,1,\ldots,2(N-1-n_2)-l. \end{aligned} \tag{4.9}$$

One sees from this that each ${}^1S^e$ level shown in Fig. 3 is the lowest member of a supermultiplet in the atom. It is also easy to see why the atomic d-supermultiplets shift to higher energies with decreasing d; this was not explained in Ref. 1. In the rotor-vibrator model decreasing d corresponds to increasing n_2—and hence to radial-bending excitation. This illustrates one advantage of the rotor-vibrator approach: It allows us to draw a simple qualitative picture of the doubly excited atom.

Overall, we have identified two hierarchies of ro-vibrational quantum numbers and cutoffs for a linear XYX molecule. These have an energy-level structure similar to the double-excitation supermultiplets. The present results therefore tentatively suggest a model of the atom as a linear XYX structure. We ask the reader to bear in mind that this may turn out to be merely a convenient metaphor, in view of the possibility that similar level structure could somehow also arise from more complicated collective motion of the electrons.

D. Higher-order contributions to supermultiplet energies

While the overall ro-vibrational supermultiplets contructed using cutoffs in the energy formulas Eqs. (4.4) and (4.8) are qualitatively similar to the atomic supermultiplets, individual levels show substantial deviations. As noted above, such deviations are to be expected. In this section we therefore carry the rotor-vibrator model one step further. We consider the possibility that higher-order corrections included in the usual molecular treatment of energies might be able to account better for details in the supermultiplet energy spectra.

The starting point of our analysis is Eq. (3.13), which gives the leading-order contributions of molecular nonrigidity and anharmonicity. We will continue to neglect all contributions of the stretching vibrations, since these do not apply to the atomic spectra. Our modified equation for intrashell energies is then

$$
\begin{aligned}
E = {} & E_N + W(v_2+1) + X(v_2+1)^2 + Gl^2 \\
& + [B - \alpha(v_2+1)][J(J+1) - l^2] \\
& - D[J(J+1) - l^2]^2 . \qquad (4.10)
\end{aligned}
$$

Here the phenomenological terms E_N and W allow us to circumvent our ignorance about the precise interpretation of the other degrees of freedom in relationship to the rotations and bending vibrations. One may regard E_N simply as an additive shell constant, and interpret W as an effective bending frequency. We do not expect that Eq. (4.10) will describe all of the levels exactly, and it is not our goal to fit the entire spectrum in a least-squares sense. Rather, if the rotor-vibrator model is realistic, a fit of several low-lying levels in each shell should reproduce the spectrum of higher states reasonably well. Equation (4.10) contains seven parameters for each shell, and therefore it is not possible for us to use it to fit the spectrum when $N = 2$, which contains fewer states. For higher shells we consider the following seven states, indicated by energy e_i and quantum numbers (${}^{2S+1}J^{\pi}$, v_2, l):

$$
\begin{aligned}
& e_0 = ({}^1S^e, 0, 0), \quad e_1 = ({}^3P^o, 0, 0), \\
& e_2 = ({}^1D^e, 0, 0), \quad e_3 = ({}^1P^o, 1, 1), \\
& e_4 = ({}^3D^e, 1, 1), \quad e_5 = ({}^1D^e, 2, 2), \qquad (4.11) \\
& e_6 = ({}^1S^e, 2, 0).
\end{aligned}
$$

One obtains for each of these levels an energy expression from Eq. (4.10) involving the seven ro-vibrational parameters. Inverting these equations we find the values of the parameters which fit the spectrum:

$$
\begin{aligned}
E_N &= \tfrac{1}{8}(16e_0 + 9e_1 - e_2 - 16e_3 + 6e_5 + 2e_6), \\
W &= \tfrac{1}{6}(-7e_0 - 9e_1 + e_2 + 24e_3 - 6e_5 - 3e_6), \\
X &= \tfrac{1}{24}(4e_0 + 9e_1 - e_2 - 24e_3 + 6e_5 + 6e_6), \\
B &= \tfrac{1}{12}(-10e_0 + 9e_1 + e_2 + 3e_3 - 3e_4), \qquad (4.12) \\
\alpha &= \tfrac{1}{12}(-2e_0 + 2e_2 + 3e_3 - 3e_4), \\
D &= \tfrac{1}{24}(-2e_0 + 3e_1 - e_2), \\
G &= \tfrac{1}{12}(e_0 - 3e_1 + 2e_2 + 3e_3 - 3e_4 + 3e_5 - 3e_6).
\end{aligned}
$$

Table I gives values of the ro-vibration parameters for intrashell doubly excited states of helium, $N = 3$–5. These were computed using data from Ref. 1. Similar values would be found for $N = 3$ using energies of Lipsky *et al.*,[25] and for $N = 3$ and 4 using Oberoi's energies.[26] The experimental data for these levels are not extensive enough for us to carry out a complete fit. Figures 4(a) and 4(b) show the I and d supermultiplets obtained from Eq. (4.11) with our parameters for $N = 4$. One may compare the fit with the corresponding supermultiplets in Figs. 3 and 5 of Ref. 1. Evidently the intrashell spectrum can be fit rather well with our ro-vibrational parametrization, although the agreement is clearly not exact. A noteworthy feature of Fig. 4 is the way it illustrates the importance of anharmonicity and rotation-vibration coupling in determining the degree of nondegeneracy, and the ordering of levels across each row in an I supermultiplet. The agreement weakens as one moves to higher levels within each supermultiplet, but this is to be expected since Eq. (4.11) only accounts for leading-order corrections to the ro-vibrational energy.

TABLE I. Ro-vibrational parameters determined from a fit of doubly excited helium energies in Ref. 1, using the parametrization in Eq. (4.10). Energy units are electron volts (eV).

	$N = 3$	$N = 4$	$N = 5$
W	3.62(−1)	1.38(−1)	6.81(−1)
X	4.56(−2)	1.45(−2)	5.59(−3)
G	−3.09(−2)	−6.96(−3)	−2.27(−3)
B	1.69(−2)	6.86(−3)	3.00(−3)
α	−1.66(−2)	−3.03(−4)	−8.19(−4)
D	−1.90(−3)	−3.18(−4)	−8.56(−5)

As we discussed in Sec. III, the parameters in the molecular-energy formula usually have definite signs corresponding to the physical effect being described. Each of our parameters in Table I has the same sign consistently for $N = 3$–5, possibly indicating a corresponding physical significance. We compare the signs of these atomic parameters with those typical of a linear triatomic molecule in Table II. W and B are positive in both cases, as they should be for stable vibrations and rotations of an XYX structure. The signs of the atomic parameters X, G, and D are reversed from those of their molecular counterparts; our negative α is consistent with the positive or negative values allowed in molecules.

A significant feature of the parameters in Table I is seen in the ratios X/W and G/W, which decrease in magnitude with higher N. This indicates that the vibrations are becoming more harmonic. Similarly, the values of D/B and α/B diminish at higher N, indicating more rigid rotation. Apparently the atomic intrashell spectrum behaves more like that of an XYX structure with rigid rotations and harmonic vibrations as one moves to higher shells.

We now derive simple estimates of the ro-vibrational constants one would expect for the two-

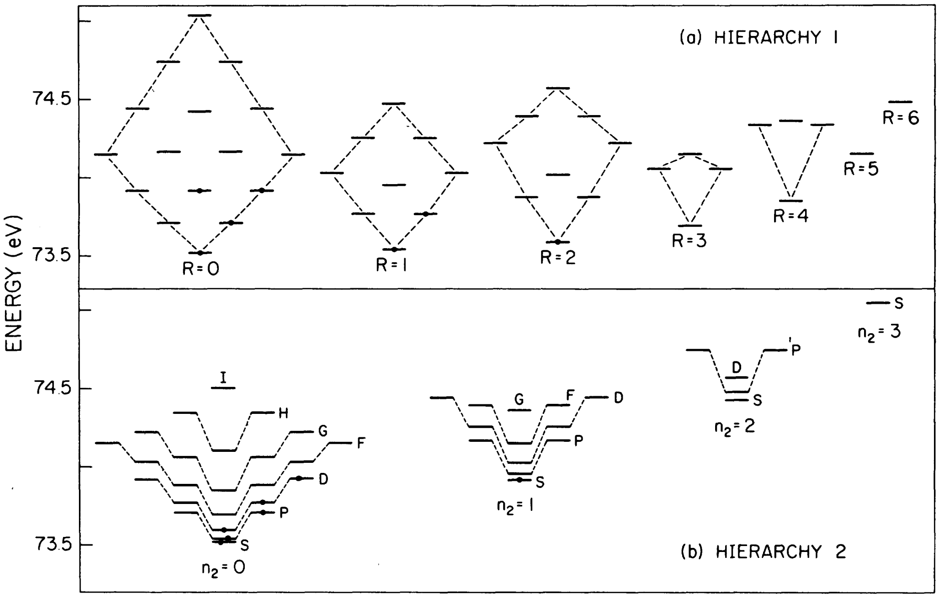

FIG. 4. Ro-vibrational energy levels from Eq. (4.10) with parameters from a fit of $N=4$ helium levels (cf. Table I), taking into account cutoffs. Fitted levels are indicated with a filled circle (●). The level orderings seen here for hierarchy 1 and 2 are similar to those of Ref. 1 for I supermultiplets and d supermultiplets, respectively. This illustrates the apparent collective rotation-vibration structure of the doubly excited helium spectrum when two electrons are in the same shell.

electron atom if it were in fact a rotating, vibrating linear XYX structure. We will compare these constants with the above trends for parameters from the helium spectra. The model assumes a constant X-Y bond length r, which corresponds roughly to the most probable radius for electrons in orbitals. Typically this scales as $r \propto N^2$ in atoms. The rotational constant for the XYX structure is

$$B_e = 1/4r^2\,, \tag{4.13}$$

and we remind the reader that we are using atomic units so that r is dimensionless. Values of ω_2, X, and G are now estimated from the behavior of the potential near the linear configuration, including only the bending coordinate. We describe this with an angle $\beta = \frac{1}{2}(\pi - \theta_{12})$, which gives the deviation of each electron from the linear configuration. The potential in the symmetric radial configuration is then

$$1/r_{12} = (1/2r)\sec\beta = 1/2r + (1/4r)\beta^2 + (5/48r)\beta^4 + \cdots\ . \tag{4.14}$$

We obtain the force constant from the usual normal mode analysis,[4] assuming an infinite mass for the nucleus:

$$\omega_2 = 1/2r^{3/2}\ . \tag{4.15}$$

We now derive expressions for X and G. From Eq. (3.2) the wave function for the radial bending vibration is

$$\Psi_{v_2 l} = C_0 \beta^l e^{-k\beta^2/2} L^l_{n_2}(k\beta^2)\,, \tag{4.16}$$

with normalization constant C_0, and a dimensionless constant $k = r^{1/2}$. We use this zero-order wave function to estimate the parameters X and G, by treating the quartic anharmonicity term in the potential with first-order perturbation theory. This yields a leading-order vibrational energy [cf. Eq. (3.10)]

$$E_{\rm vib} = \omega_2(v_2+1) + (5/96r^2)[3(v_2+1)^2 - l^2 + 1]\ . \tag{4.17}$$

From this we extract the following vibrational anharmonicity constants:

$$X = 15/96r^2\,, \tag{4.18a}$$

TABLE II. Comparison of signs of ro-vibrational parameters in Eq. (4.10) for a typical XYX linear symmetric molecule, with those found here for doubly excited intrashell levels of helium (cf. Table I).

	Molecule	Helium
W	+	+
X	−	+
G	+	−
B	+	+
α	+, −	−
D	+	−

$$G = -5/96r^2 . \qquad (4.18b)$$

The signs of these constants agree with those from the empirical fit of doubly excited helium levels in Table II. They differ from those typical of molecules. We note that the molecular formulas for X and G include a significant contribution from anharmonic coupling of the bending and symmetric stretch vibrations,[27] whereas the present treatment has assumed decoupling of these degrees of freedom.

It is less easy to rationalize the behavior of α and D from corresponding molecular formulas, since these involve stretching constants not included in our ro-vibrational model. However, the negative sign we find for α is not unreasonable for degenerate bending modes even in molecules, as we discussed in Sec. III. In molecules, D is positive due to stretching of the molecule as it rotates faster. The negative value we find for D in helium suggests a *contraction* of the system as it rotates faster. However, this is entirely consistent with atomic-shell theory, in which the peak radial probability of orbitals may decrease with increasing angular momentum. In the hydrogen atom, for example, the average radius of an orbital u_{Nlm} is $\bar{r} = [3N^2 - l(l+1)]/2Z$. We have searched for similar evidence for such a contraction of the two-electron radial distribution with increasing angular momentum in potential energy curves and radial distributions of doubly excited states computed[22] in the hyperspherical coordinate approach. To our satisfaction, we find that the lowest $^3P^o$ state is indeed bound at a slightly smaller radius than is the lowest $^1S^e$ state. The transition $^1S^e \rightarrow {}^3P^o$ for these intrashell states corresponds to the first rotational excitation in our rotor interpretation of the atom.

The above analysis showed that the signs of the atomic ro-vibrational constants are consistent with a picture of the atom as a rotating, vibrating, XYX structure. We now consider the relative magnitudes of some of these quantities to extend the picture further. First we consider the vibrational anharmonicity contribution to the energy, which was noted above to decrease at higher N relative to the harmonic contribution. This behavior is consistent with the XYX model with increasing radius r, since the above equations show the following scaling of anharmonic contributions relative to the harmonic vibration constant: $X/\omega_2 \propto r^{-1/2}$, and $G/\omega_2 \propto r^{-1/2}$. A similar r dependence is predicted for the ratio B_e/ω_2, but the empirical parameters in Table I in fact show very little change in this ratio with increasing N. This may be due to the fact that the empirical parameter W represents an effective vibrational constant which includes other contributions to the energy not described by Eq. (4.10).

It is difficult to compare the rotation versus vibration parts of the energy quantitatively, because empirical fits generally lead to different values of the shell radius r for these motions. This is one indication of the very high degree of nonrigidity and anharmonicity in helium when viewed from the ro-vibrational approach. It is possible to compare G and X directly, since they both describe vibrational energy contributions of the same order. We note Eq. (4.18) predicts the constant ratio

$$G/X = -\tfrac{1}{3} . \qquad (4.19)$$

Values of G and X for helium give a comparable value, but clearly the agreement is not exact. To illustrate better the degree of rigidity, we have investigated ro-vibrational parameters for other values of Z in the isoelectronic series, and we find the same qualitative behavior and signs as described above for helium. Previously we noted[3] a higher degree of rigidity for the XYX structure at low Z, based on a study of rotor spectra. In Table III we offer similar results for the vibrational ratio G/X as a function of Z. We do not attach too much significance to individual values in Table III, since the energies of Ref. 1 are not of highest accuracy. We are impressed, however, by the way the values of G/X for lower Z seem to be shifting towards the value predicted by the rotor-vibrator model with harmonic bending plus a quartic asymmetry. Similar trends are seen for other values of N and other computed data, although the precise numbers differ from the ones in Table III.

E. Energy separability and time scales

We now consider relative magntidues for the energies corresponding to rotational, vibrational, and shell excitation, and also their related time scales in connection with the degree of separability of the underlying electronic motions. Only the lowest excitations within a shell are treated; these involve the $^1S^e$, $^3P^o$, and $^1P^o$ states as contained in the following excitation energies:

TABLE III. Isoelectronic series behavior of empirical ro-vibrational parameter ratio from data in Ref. 1 with $N=4$ for the cases $Z=\infty$, $Z=2$ (He), and $Z=1$ (H^-). These are compared with the value predicted by the linear XYX rotor-vibrator model in Eq. (4.19), including a quartic perturbation of the bending vibration.

	$Z=\infty$	$Z=2$	$Z=1$	XYX
G/X	−1.22	−0.48	−0.36	−0.33

$$\begin{aligned} \Delta R &= e_1 - e_0 , \\ \Delta V &= e_3 - e_0 , \\ \Delta S &= e_0(N+1) - e_0(N) . \end{aligned} \tag{4.20}$$

In Table IV we list ratios of these energy differences, and also the time scales for corresponding motion computed from the formula $\tau = \hbar/\Delta E$. These are compared with the estimated autoionization lifetime of each state, from values appearing in Ref. 28. Three features are apparent from the data. *First*, the energies for rotational, bending, and other excitations are significantly different, showing consistency with the notion of approximate separability; *second*, the magnitude of the separation increases with higher N, for example, the vibration-rotation splittings satisfy an approximate relation $\Delta V/\Delta R \simeq 2N+1$; *third*, the time scale for the lowest rotational excitation $^1S^e \rightarrow {}^3P^o$ is roughly comparable to estimated autoionization lifetimes of those states. The first two of these observations suggest the rotor-vibrator picture grows better at higher N. The third point indicates a possible link between rotations and autoionization; this will be explored briefly in Sec. IV F.

F. *T* doubling and autoionization

Thus far, our analysis has looked for evidence in the supermultiplet spectra which would bear on a possible ro-vibrational interpretation. The results of this study have shown consistency between the spectra and the model energy formula in Eq. (4.10). It is more difficult to account for even higher-order effects in the energy, but such an analysis would not be warranted here in view of the limited accuracy of the available intrashell spectra. In addition, one would like to compare radiative transitions for the rotor-vibrator with corresponding transitions between doubly excited states in the same shell. However, detailed computations of those transitions are not within the scope of this paper.

TABLE IV. Rotation-vibration separability parameters for increasing principal quantum number in doubly excited states of helium. τ_Q is the time scale for lowest energy excitation of rotations ($\tau_{\Delta R}$), vibrations ($\tau_{\Delta V}$), and radial intershell transitions ($\tau_{\Delta S}$) $N \rightarrow N+1$. $\tau(^{2S+1}L^{\pi})$ is the corresponding autoionization lifetime of these lowest states, from data in Ref. 28. Notation and units are $2(-3) = 2\times 10^{-3}$ sec.

	Atomic shell N			
	2	3	4	5
$\Delta V/\Delta R$	5.1	7.0	8.9	10.9
$\Delta S/\Delta V$	5.1	8.0	10.4	
$\Delta S/\Delta R$	26	56	92	
$\tau_{\Delta R}$	15(−16)	88(−16)	312(−16)	823(−16)
$\tau_{\Delta V}$	3(−16)	13(−16)	35(−16)	75(−16)
$\tau_{\Delta S}$	6(−17)	16(−17)	34(−17)	
$\tau(^1S^e)$	47(−16)	80(−16)	44(−14)	
$\tau(^3P^o)$	78(−16)	67(−16)	26(−15)	
$\tau(^1P^o)$	18(−15)	44(−16)	14(−15)	12(−14)

One additional effect we can look into, and which is not described by Eq. (4.10), is the splitting of the $\pm l$ degeneracy known as "l doubling".[4] This has an analog in the structure of diatomic molecules known as "Λ doubling" of electronic levels due to rotational coupling.[17] The effect we wish to account for in the atomic supermultiplets was called "T doubling", and the computed energies for helium were observed to have several regular trends[1]: (i) T doubling increases with I for fixed K and T in the I-supermultiplet scheme; (ii) T doubling decreases with increasing T in each d supermultiplet; and (iii) for each T-doubled pair of levels, the one with $\Pi(-1)^L = -1$ has the lower energy. Reference 1 could not account for these trends, nor could it explain the near-degeneracy of each T-doubled pair to begin with.

One advantage of the rotor-vibrator approach is that it accounts for the degeneracy at the outset. Whether or not the same mechanism which causes l doubling in molecules could also account for T doubling in the atom is not at all clear, however. In particular, it is possible that the T doubling results partially from effects not as important in the molecule, such as the behavior of the wave function near the Coulomb singularity at $\theta_{12} = 0$. Nonetheless, we cite two known trends for the l doubling and Λ doubling which are consistent with trends (i) and (ii) for T doubling: (i) The molecular doubling increases in magnitude with increasing values of J, and (ii) molecular l doubling falls off rapidly with increasing l. Although there is confusion in the literature as to the proper description of molecular doubling, there seems to be agreement that it results from a combination of two effects.[29] First, the bending vibration may take place in a plane parallel or perpendicular to the axis of molecular rotation. As a result of the bending, the effective moment of inertia is different in the two cases. Second, when the bending vibration takes place perpendicular to the axis of rotation, the Coriolis force excites the asymmetric stretch. The Coriolis force is zero when the vibration is parallel to the rotation axis. The combination of these effects gives rise to the l doubling.

Coriolis coupling in an XYX model of the atom would have some bearing on the simple autoionization mechanism proposed by Rehmus and Berry,[30]

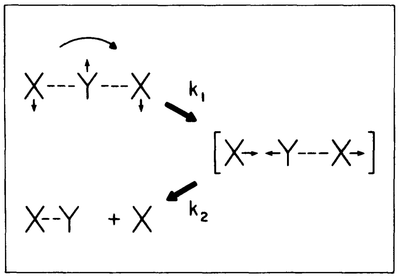

FIG. 5. Illustration of one possible rotation-vibration mechanism leading to the linear asymmetric stretch pathway for autoionization proposed by Rehmus and Berry (Ref. 30). We show this in two steps: (1) The *XYX* structure undergoes rotation and bending vibration, and the Coriolis interaction between rotation and bending activates the asymmetric stretch mode; and (2) this leads to further coupling with the autoionization continuum. Overall, such a route would describe the decay of a doubly excited state: $\mathrm{He}^{**} \rightarrow \mathrm{He}^{+} + e^{-}$.

in which one electron approaches the nucleus while the other electron exists on the opposite side. This decay route would involve coupling of an initially stable electronic motion to large-amplitude asymmetric stretching. As we show in Fig. 5, it is possible that the Coriolis force is partially responsible for excitation of this asymmetric mode, but the precise extent of this interaction is not known. We have already noted that autoionization lifetimes of low-lying intrashell levels are comparable to the rotational time scale, and this suggests a possible link. We have investigated autoionization lifetimes of levels with $N \leq 4$, and have found the noteworthy trend that in a T-doubled pair the width of the state with $\Pi(-1)^L = -1$ is generally smaller (longer lifetime). This is the same trend noted above for T-doubling energies of the states. Evidently the possible connection of T doubling, autoionization, and the Coriolis interaction should be more closely studied in the future.

V. DISCUSSION

Our presentation of evidence for a ro-vibrational interpretation of doubly excited intrashell levels in He is nearly complete. Our starting point was the I and d supermultiplets of the preceding paper. We pointed out that they resembled manifolds of ro-vibrational levels of linear *XYX* molecules, using two hierarchies of molecular quantum numbers. We drew a correspondence between the O(4)-based quantum numbers I, d, and T on the one hand, and the molecular quantum numbers R, n_2, and l on the other. In order to make this analogy it was necessary to accept cutoffs in the postulated intrashell collective spectra. This situation is reminiscent of that which obtains in nuclear spectra due to limitations of shell structure. From investigation of computed levels of the I and d supermultiplets, we established that the intrashell energy patterns resemble rotational and bending vibrational spectra of a highly nonrigid, linear triatomic molecule. We found that a parametrization of the intrashell spectra in terms of an energy level expression from molecular spectroscopy succeeded well in accounting for many of the qualitative features of the supermultiplets of Ref. 1. We then investigated the degree of separability between the apparent rotational and vibrational collective modes and the remaining degrees of freedom, and found that a good measure of separability is implied by differences in magnitude of the energy scales involved. The apparent degree of separability increases with N, although it does not approach the degree of separability typically in molecules, at least for $N \leq 5$. An investigation of the dependence of ratios of parameters used in our fit of the spectra showed that deviations from naive rotor-vibrator behavior decrease with higher N, consistent with apparent increasing rotation-vibration separability.

The use of supermultiplets to organize the intrashell spectra has an obvious affinity to efforts to use group theoretical methods to understand complicated phenomena in other areas of physics. By exploiting the organizing power of the supermultiplets and the suggestive energy patterns of Ref. 1, we have been able to greatly extend earlier work to give a ro-vibrational interpretation of the entire intrashell manifold for each N. This is most gratifying, since the group theory underlying the supermultiplets bears no obvious relationship to ro-vibrational theory. Their utility in drawing the ro-vibrational interpretation thus shows the efficacy of the supermultiplets for linking apparently unrelated physical models. In this sense our work has a parallel in the Elliott SU(3) model and the SU(6) interacting boson model, both of which use classification schemes to elucidate collective interpretations of nuclear spectra.

There are several points which we would like to address concerning our findings. Broadly speaking, these have to do with completing the ro-vibrational picture for the two-electron atom. This requires that we consider the extension of the model so that it can encompass Rydberg series, and thus the entire two-electron spectrum; the nature of the degrees of freedom corresponding to symmetric and antisymmetric stretching modes; and the definition of atomic wave functions in coordinates which explicitly show the collective nature of the problem.

We have shown that rotations and bending vibrations of an *XYX* structure give an adequate picture of the intrashell spectrum, which includes only states *NN* having electrons in orbitals with the same principal quantum number *N*. As we discussed at the beginning of Section IV, it is difficult to account for the stretching motions in the two-electron atom since these are not locally stable at the symmetric configuration when one considers the Coulomb potential energy surface. Moreover, both the spectrum of double excitations between shells, and also the intershell states (Nn) with $n > N$, contain Rydberg progressions rather than harmonic stretching levels. Naively, one might think that the former series $N=1,2,3,\ldots$ corresponds to symmetric stretching, and that the latter series with $n>N$ corresponds to asymmetric stretching. Unfortunately, this is contradicted by the fact that molecular stretching motions carry no angular momentum, while the Rydberg excitations certainly can. There are also important considerations of matching the permutation symmetry and parity labels of states for the putative atomic stretches with those of atomic terms. This complication was dealt with most satisfactorily for the intrashell spectrum through the dovetailing of the symmetry labels of the atomic supermultiplets with those of the molecular hierarchies.

Related to the question of interpreting the symmetric and asymmetric stretching in the two-electron atom is the problem of explaining the wave functions in a way which manifests collective features of the spectra. If rotational and bending vibrational motion is really responsible for the overall spectral features of intrashell states, it should prove possible to write the corresponding portions of the wave functions in terms of collective coordinates defined in a body-fixed frame. The counterpart of this idea in the study of collective motion in nuclei invokes the concept of "intrinsic" states and intrinsic collective coordinates.[5] The intrinsic state describes in a body-fixed coordinate system a "structure" which undergoes collective motion as described by the collective coordinates. One starting point for investigating a similar possibility in two-electron atoms is the internal frame described by Bhatia and Temkin,[31] although it is not obvious how one should identify a collective vibrational motion in that approach. Although hyperspherical coordinates of the type used recently for two-electron atoms involve one type of collective radial motion,[22] collective bending vibrations are not a part of that treatment. In this connection, hyperspherical coordinates which might prove more enlightening for two-electron collective bendings and rotations, are those of Whitten and Smith.[32]

Ultimately, one would like to derive the collective picture from the two-electron Schrödinger wave equation (Eq. 1). This seems hard to do at present, but consideration of the many points raised herein may eventually lead to a more satisfying description of the doubly excited states. In any case, should the present collective ro-vibrational model only turn out to be a metaphor, it has so far provided us with an extremely useful and appealing way of describing what is otherwise a very difficult problem to grasp.

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