Chapter 2
Structure of ^{88}Sr and $^{88}Sr_2$

Molecules are *complicated*, much more so than atoms. As Art Schawlow famously once said, "a diatomic molecule is a molecule with one atom too many." This complexity over atomic structure arises due to the new degrees of freedom available to molecules in the form of vibration and rotation, which causes the energy spectra for even relatively simple homonuclear diatomic molecules to become fabulously complex. In order to make sense of this chaos, physicists like to make simplifying approximations about molecular structure so that different species of molecules can be discussed using a common language.

Unfortunately, learning this common language is much like learning any language, in that you really need to absorb through immersion and osmosis: targeted questions can only take you so far. One difficulty is that some of the most important, seminal work laying the foundations for characterizing molecular structure was written in the 1920s and 1930s... and in German [4, 7]. The great, synthesizing textbooks [1–3] cite these important papers and work out special cases, and the best strategy for understanding molecular structure is to absorb these books and the relevant papers they cite. It might perhaps also be a good idea to learn German...

It would be foolish to attempt in one chapter of an experimental thesis to reproduce a body of knowledge which in reality takes a lifetime to master. Instead, this chapter will specifically focus on the structural features of $^{88}Sr_2$. Specifically, a brief overview of the physics responsible for deciding which quantum numbers are "good" will be presented, as well as a discussion of the symmetries which restrict the set of allowed quantum numbers in both the electronic ground and excited states.

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2.1 Rotational Structure

In theory, the full energy structure of a molecule can be ascertained by writing down its Hamiltonian and then solving the Schroedinger equation. We can start the process of simplification by first recognizing that the Hamiltonian $\hat{H}$ for a diatomic molecule can be divided into three different parts:

$$\hat{H} = \hat{H}_e + \hat{H}_v + \hat{H}_R, \tag{2.1}$$

where $\hat{H}_e$, $\hat{H}_v$, and $\hat{H}_R$ denote the electronic, vibrational, and rotational degrees of freedom of the molecule, respectively [6].

These three terms are fairly well decoupled from one another. The electronic energy of the molecule can be approximated as the total electronic energies of the atomic states forming the molecule (either $^1S_0$ or $^3P_1$ for the molecules considered in this thesis), and the vibrational energy can be characterized by a single number describing how quickly the nuclei vibrate with respect to one another (e.g., v can take any value between 1 and 62 for $^{88}Sr_2$ in the electronic ground state). The rotational part of the Hamiltonian is most complicated, however, because of the many different forms of angular momentum (spin and orbital, nuclear and electronic) which must be accounted for and properly added together to produce a total rotational energy. It is consideration of the rotational part of the Hamiltonian which will influence our choice for how to properly label the rovibrational levels of $^{88}Sr_2$.

The rotational Hamiltonian can be written in terms of the total rotational angular momentum $\hat{R}$ in the following way:

$$\hat{H}_R = B\hat{R}^2, \tag{2.2}$$

where the rotational constant $B = \frac{\hbar^2}{2\mu R^2}$ is related to the size (i.e., bond length) of the molecule R and its reduced mass μ, and will generally be a function of the vibrational state. However, the Hamiltonian above glosses over the fact that electronic momentum $\hat{J}_a = \hat{L} + \hat{S}$ can be carried by one or both of the Sr atoms, where $\hat{L}$ and $\hat{S}$ are the total orbital and spin electronic angular momenta, respectively. Since we are interested in how these various angular momenta interact, we should rewrite Eq. (2.2) as

$$\hat{H}_R = B\hat{R}^2 = B(\hat{J} - \hat{L} - \hat{S})^2, \tag{2.3}$$

where $\hat{J} = \hat{R} + \hat{J}_a$ is the total (rotational plus electronic) angular momentum of the molecule (excluding nuclear spin in this case because the ^{88}Sr nucleus is spinless).

Determining how to summarize the rotational energy of our molecule depends on which terms in the above Hamiltonian are most important, which is a complicated question to answer. Whether or not spin and orbital angular momentum can be

considered separately, and how strongly they couple to the total rotational angular momentum, will depend upon the size and structure of the atoms comprising a particular molecule.

2.1.1 Hund's Cases

The standard language used for characterizing different coupling types is to classify molecules according to different *Hund's cases*, which assign "good" quantum numbers based upon the relative strengths of coupling between different angular momenta. The $^{88}Sr_2$ molecule is best described by either Hund's case (a) or (c), depending on whether we are discussing the electronic ground state or excited state. An excellent description of when and why various Hund's cases apply in different situations is given by Stepanov and Zhilinskii [5]. Here we'll just make a few brief remarks.

2.1.1.1 Hund's Case (a)

In Hund's case (a), it is assumed that the orbital angular momentum $\hat{L}$ is strongly coupled to the internuclear axis, while the electronic spin $\hat{S}$ is strongly coupled to $\hat{L}$ [2]. The result is a situation in which we have a maximal number of "good" quantum numbers:

- Λ, the projection of the electronic orbital angular momentum $\hat{L}$ onto the internuclear axis.
- Σ, the projection of the electronic spin angular momentum $\hat{S}$ onto the internuclear axis.
- S, the total electronic spin angular momentum of the system.
- J, the total angular momentum (rotational plus electronic).
- Ω, the projection of the electronic angular momentum $\hat{L}+\hat{S}$ onto the internuclear axis.

Hund's case (a) is a good description of the electronic ground state of $^{88}Sr_2$, which possesses no electronic angular momentum at all. However, it turns out that strontium molecules comprised of a ground state atom plus an excited atom will be better described by a different approximation.

2.1.1.2 Hund's Case (c)

In Hund's case (c), it is assumed that the spin-orbit coupling between $\hat{L}$ and $\hat{S}$ is stronger than that of either to the internuclear axis. In this case, the $\hat{L}$ and $\hat{S}$ operators combine to form a total electronic angular momentum operator $\hat{J}_a$ which is

only weakly coupled to the rotational motion of the nuclei. Rewriting the rotational Hamiltonian as

$$\hat{H}_R = B(\hat{J} - \hat{J}_a)^2 = B(\hat{J}^2 + \hat{J}_a^2 - 2\hat{J} \cdot \hat{J}_a), \tag{2.4}$$

assuming Hund's case (c) is a valid description then amounts to assuming that the term $-2B\hat{J} \cdot \hat{J}_a$ is small [6]. The Hamiltonian then consists of two parts: a "zeroth-order" contribution $\hat{H}_R^0 = B(\hat{J}^2 + \hat{J}_a^2)$, which informs which labels we choose to describe our molecule's rotational levels; and a "perturbation" contribution $\hat{H}_R^1 = -2B\hat{J} \cdot \hat{J}_a$, which will cause mixing between the zeroth-order basis states.

The operators which commute with $\hat{H}_R^0$ should serve as the labels for our Hund's case (c) basis states, since their eigenfunctions will diagonalize the Hamiltonian. Upon inspection, it's clear that $\hat{J}^2$, $\hat{J}_a^2$, and their projections will commute with $\hat{H}_R^0$, and so we will label our Hund's case (c) basis states with four quantum numbers J, J_a, M_J, and Ω, as well as a catch-all label $\eta(\Omega)$ describing electronic and vibrational degrees of freedom (itself labeled by Ω for purposes of bookkeeping):

$$|\Psi\rangle_{\text{Hund's case (c)}} = |\eta(\Omega), J_a; J, M_J, \Omega\rangle \tag{2.5}$$

A semicolon separates the labels J_a and J to indicate that these two vector spaces are decoupled from one another. This assumption amounts to requiring the perturbation $\hat{H}_R^1 = -2B\hat{J} \cdot \hat{J}_a$ to be small. Cases for which $\hat{H}_R^1$ is not small result in *Coriolis coupling*, whereby states with different Ω can be mixed together. See Sect. 4.2.2.2 for details.

Given this set of possible quantum numbers to work with, let's now consider what possibilities are allowed for $^{88}Sr_2$ molecules in both the electronic ground and singly-excited $^1S_0 + ^3P_1$ states.

2.1.2 Electronic Ground State

In the $^1S_0 + ^1S_0$ electronic ground state, the situation is relatively simple. Neither component atom of the strontium molecule carries either spin or orbital angular momentum (i.e., $L = S = 0$), implying that both the total electronic angular momentum J_a and its projection along the internuclear axis Ω must equal 0.

We can also make some general statements about the symmetry required of such a molecule. Because the ^{88}Sr nucleus is bosonic, it *must* be true that upon exchange of the two nuclei, the total molecular wavefunction should retain the same sign.

However, whether or not the molecular wavefunction acquires a minus sign can also be determined from the symmetries of the electronic wavefunctions and the molecular wavefunction's quantum numbers. According to Herzberg (Section V,2c, p. 238) [3], nuclear exchange for a molecular wavefunction comprised of two even, electronic ground state atomic wavefunctions will remain unchanged for *even* values

of J, and acquire a minus sign for *odd* values of J. (Why exactly this is so is *complicated*. A hint is that the nuclear exchange operator is equivalent to a reflection of all particles [electrons plus nuclei] at the origin, followed by a reflection of only the electrons at the origin. Each of these operations has a well-defined effect on the rotational, vibrational, and electronic wavefunctions whose product comprises the total molecular wavefunction. Determining the sign behavior of nuclear exchange is then a matter of evaluating the effect of each inversion on each component of the wavefunction.)

This result leads to dramatic consequences. If odd-J states acquire a minus sign upon nuclear exchange, but bosonic nuclei require that the wavefunction remain unchanged, then it must be true that *only even J levels are allowed in the electronic ground state*. Sure enough, we have so far only observed even-J in the ground state. See Table 3.2 for details.

There is one additional symmetry which must be true of ground state molecules. The inversion symmetry of the total ground state molecular wavefunction must be *even* since it is composed of two atoms in identical states. Odd symmetry is impossible because symmetrization would force the wavefunction to equal zero. This can also be thought of as a result of the Wigner-Witmer rules [3, 7]. The name we give this inversion symmetry is *gerade* for even and *ungerade* for odd.

2.1.3 Electronic Excited State

The electronic state is naturally more complicated. First, because the atomic wavefunctions of each of the component atoms are different, the molecular wavefunction can have either *ungerade* or *gerade* symmetry. However, bosonic symmetry upon exchange of the nuclei must still be respected.

Because the $^3P_1$ atom carries 1 unit of electronic angular momentum J_a, the total projection Ω of $\hat{J}_a$ onto the internuclear axis can take on the value of either 0 or 1. This leads to four distinct possible combinations of inversion symmetry ($= u, g$) and Ω ($= 0, 1$) which serve as labels for our singly excited rovibrational levels: 1_u, 0_u, 1_g, and 0_g. And by considering once again how each component of the wavefunction transforms under different symmetry rules, we arrive at the following restrictions for the quantum numbers of singly-excited rovibrational levels:

- 1_u supports $J \geq 1$
- 0_u supports $J \geq 1$ and *odd*
- 1_g supports $J \geq 1$
- 0_g supports $J \geq 0$ and *even*

These restrictions on the possible combinations of J, g/u, and Ω will have dramatic implications for both the interpretation of linear Zeeman shifts and our ability to control all quantum numbers in both the initial and final state of photodissociation experiments. See Fig. 2.1 for an illustration of the various potentials describing $^{88}Sr_2$ molecules in the electronic ground and singly excited states.

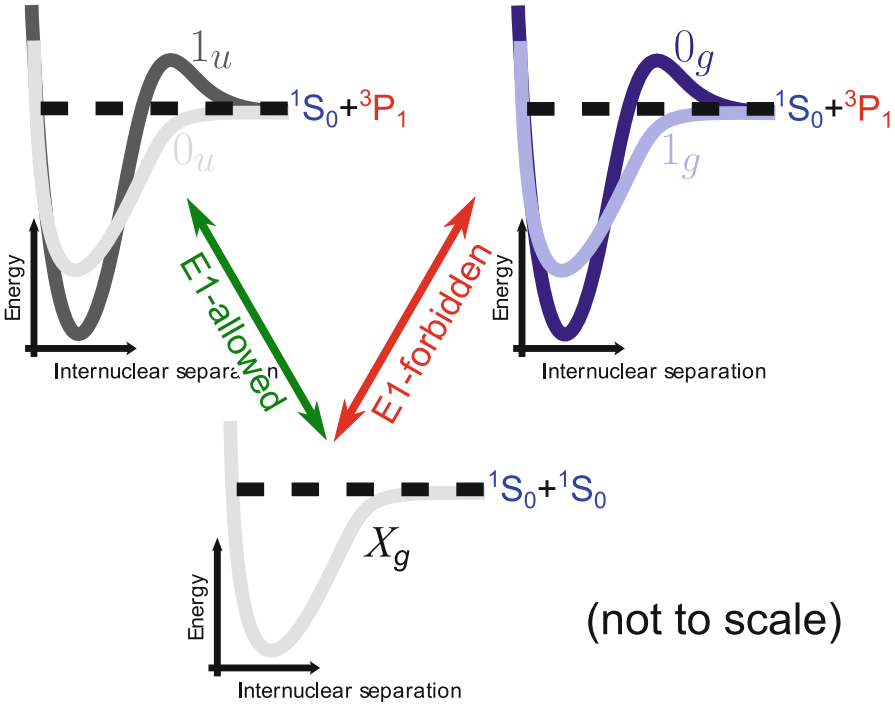


Fig. 2.1 Qualitative potential curves (not to scale) are drawn illustrating the structure of $^{88}Sr_2$ molecules in both the electronic ground and singly excited states for different values of inversion symmetry and Ω. E1 transitions connect states of opposite inversion symmetry and $\Delta J = 0, \pm 1$. E1, M1, and E2 selection rules combined with the restriction of J to either even or odd values for different potentials enable observations of pure Hund's case (c) linear Zeeman shifts (Chap. 4), precise measurements of strongly forbidden transition strengths (Chap. 5), precise determinations of transition strengths to and lifetimes of highly subradiant states (Chap. 6), and explorations of quantum state resolved photochemistry (Chap. 8 and attached publication)

2.1.3.1 Aside: On Parity-Adapted Wavefunctions

In Hund's case (a) and (c), the rotational energy for a molecule with total rotational angular momentum J and projection along the internuclear axis Ω is given by the following expression [3]:

$$E_{\text{rot}} = B_v[J(J+1) - \Omega^2], \tag{2.6}$$

where B_v is a vibrational level-dependent rotational constant. What's interesting about this equation is that *rotational energy doesn't depend on the sign of* Ω. This means that $\Omega = \pm 1$ are energy-degenerate. Therefore to truly diagonalize our Hamiltonian, we should use parity-adapted superpositions of positive and negative Ω [8]:

$$|\Psi\rangle_{\text{Hund's case (c)}} = \frac{1}{\sqrt{2}}\big(|\eta(\Omega), J_a; J, M_J, \Omega\rangle + (-1)^p|\eta(-\Omega), J_a; J, M_J, -\Omega\rangle\big), \tag{2.7}$$

where p is the parity of the state being considered. This fact will have implications for how we interpret the state mixing responsible for linear Zeeman shifts of 0_u levels, and may additionally have something to do with the mystery of magnetic field dependence of the $1_u/0_u$ potential alluded to in Chap. 8.

References

1. Atkins, P., Friedman, R.: Molecular Quantum Mechanics. Oxford University Press, Oxford (2011)
2. Brown, J., Carrington, A.: Rotational Spectroscopy of Diatomic Molecules. Cambridge University Press, Cambridge (2003)
3. Herzberg, G. *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules*. Princeton: D Van Nostrand Company, Inc., 1950
4. Hund, F.: Allgemeine Quantenmechanik des Atom- und Molekelbaues. Handbuch der Physik, vol. 24, p. 561. Springer, Berlin (1933)
5. Stepanov, N., Zhilinskii, B.: When and why Hund's cases arise. J. Mol. Spectrosc. **52**(2), 277–286 (1974)
6. Veseth, L.: Hund's coupling case (c) in diatomic molecules. I. Theory. J. Phys. B At. Mol. Phys. **6**(8), 1473 (1973)
7. Wigner, E., Witmer, E.: Über die Struktur der zweiatomigen Molekelspektren nach der Quantenmechanik. Z. Phys. **51**, 859 (1928)
8. Xie, J., Zare, R.: Selection rules for the photoionization of diatomic molecules. J. Chem. Phys. **93**(5), 3033–3038 (1990)

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McDonald, M.P.

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