

Advanced Quantum Mechanics & Spectroscopy (CHEM 7520)

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Week 10-11: Electronic spectroscopy of atoms and molecules

IV. DIATOMIC MOLECULES

1) In diatomic molecules, $\hat{H}$ no longer commutes with $\hat{L}^2$ and we only have three good quantum numbers:

$$\hat{S}^2 |\Psi\rangle = S(S+1) |\Psi\rangle \quad (1)$$

$$\hat{S}_z |\Psi\rangle = M_S |\Psi\rangle \quad (2)$$

$$\hat{L}_z |\Psi\rangle = \Lambda |\Psi\rangle \quad (3)$$

As before, S is a positive integer number and $-S \leq M_S \leq S$. The $\hat{L}_z$ quantum number is a good quantum number, but it is labeled as Λ for diatomics.

2) To obtain Λ for any electronic state of a diatomic molecule, we recall that each atomic orbital can be classified using a one-electron m_l quantum number. In diatomics, the same one-electron quantum number is labeled as λ . For example, for p_{+1} orbital $m_l = \lambda = +1$. Orbitals with $\lambda = 0, \pm 1, \pm 2, \pm 3, \dots$ are labeled as $\sigma, \pi, \delta, \phi, \dots$, respectively. To calculate Λ , all we need is to sum over all one-electron λ_i of spin-orbitals ψ_i that appear in the electronic wavefunction:

$$\Lambda = \sum_i^N \lambda_i \quad (4)$$

3) In diatomic molecules, the energy depends on S and $|\Lambda|$. Each state with a distinct electronic energy can be represented using the diatomic term symbol $^{2S+1}\Lambda$, where Λ is labeled as $\Sigma, \Pi, \Delta, \Phi, \dots$ for $\Lambda = 0, \pm 1, \pm 2, \pm 3, \dots$, respectively. We recall that for each state there is $2S+1$ degeneracy associated with spin. Thus, the Σ states are $2S+1$ degenerate, while $\Pi, \Delta, \Phi, \dots$ are $2 \times (2S+1) = 4S+2$ degenerate.

4) The Σ states have additional symmetry. We recall that the Hamiltonian must commute with the symmetry operators of the point group that the diatomic molecules belong to ($D_{\infty h}$ or $C_{\infty v}$). Therefore, the electronic wavefunction has

to be an eigenfunction of these operators. In particular, for the σ_v operation, the corresponding eigenvalue problem can be written as:

$$\hat{\sigma}_v |\Psi\rangle = \pm |\Psi\rangle \quad (5)$$

where $+1$ and -1 are the two possible eigenvalues. The Σ states corresponding to $+1$ and -1 eigenvalues are labeled as Σ^+ and Σ^- , respectively. In this case, the energies of the Σ^+ and Σ^- states will generally be different. To find the eigenvalues of the $\hat{\sigma}_v$ operator, we must act this operator on every orbital in a determinant. The following results can be used: $\hat{\sigma}_v |\sigma\rangle = |\sigma\rangle$, $\hat{\sigma}_v |\pi_{+1}\rangle = |\pi_{-1}\rangle$, $\hat{\sigma}_v |\delta_{+1}\rangle = |\delta_{-1}\rangle$, and so on.

5) One of the simplest diatomic molecules that we consider is BeH. The ground-state electronic configuration is $(1\sigma)^2(2\sigma)^2(3\sigma)^1$ and the electronic wavefunction can be written as:

$$|\Psi_{\text{BeH}}\rangle = \mathcal{A} 1\sigma\alpha(1)1\sigma\beta(2)2\sigma\alpha(3)2\sigma\beta(4)3\sigma\alpha(5) \quad M_L = 0, M_S = \frac{1}{2} \quad (6)$$

There is also a determinant with $M_S = -\frac{1}{2}$. This wavefunction corresponds to the $^2\Sigma^+$ state.

6) For BH, the ground-state electronic configuration is $(1\sigma)^2(2\sigma)^2(3\sigma)^2$, the electronic wavefunction can be written as:

$$|\Psi_{\text{BH}}\rangle = \mathcal{A} [\text{core}^4] 3\sigma\alpha(5)3\sigma\beta(6) \quad (7)$$

This wavefunction corresponds to the $^1\Sigma^+$ state.

7) For CH, the ground-state electronic configuration is $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^1$, the electronic wavefunction can be written as:

$$|\Psi_{\text{CH}}\rangle = \mathcal{A} [\text{core}^4] 3\sigma\alpha(5)3\sigma\beta(6)1\pi\alpha(7) \quad (8)$$

This wavefunction corresponds to the $^2\Pi$ state.

8) The NH molecule has the $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^2$ ground-state electronic configuration. This electronic configuration gives rise to several determinants. For each determinant, we can obtain the value of Λ by summing the values of λ_i corresponding to individual spin-orbitals. To determine the possible term symbols, we can use the rules similar to the ones we used before:

Rule 1: For each Slater determinant with given values of Λ and M_S , there is an

eigenfunction of $\hat{S}^2$ with $S \geq |M_S|$.

Rule 2: The quantum number S satisfies the property: $S \leq \frac{N}{2}$.

9) By starting with $\Lambda = 2$ and $M_S = 1$, and considering all of the Λ and M_S combinations with lower values, we obtain that the term symbols arising from the ground-state electronic configuration of the NH molecule are: $^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^+$.

10) The term symbols of diatomic molecules are equivalent for the following electronic configurations: $(\sigma)^n \equiv (\sigma)^{2-n}$, $(\pi)^n \equiv (\pi)^{4-n}$, $(\delta)^n \equiv (\delta)^{4-n}$, etc.

11) All homonuclear diatomics have a center of inversion. As a result, their wavefunctions must be the eigenfunctions of the *inversion operator*:

$$\hat{i}|\Psi\rangle = \pm |\Psi\rangle \quad (9)$$

Wavefunctions corresponding to $+1$ and -1 eigenvalues are labeled as g (gerade) and u (ungerade), respectively. Similarly, spin-orbitals $|\sigma\rangle$, $|\pi\rangle$, $|\delta\rangle$, ... are also the eigenfunctions of the inversion operator $\hat{i}$. The $|\sigma_g\rangle$ spin-orbitals correspond to the bonding σ -orbitals, while $|\sigma_u\rangle$ are the anti-bonding σ -orbitals. For π -orbitals, $|\pi_u\rangle$ is the bonding spin-orbital and $|\pi_g\rangle$ is the anti-bonding. This determines the relative energy ordering of these orbitals.

12) Examples of homonuclear diatomics and their electronic configurations:

- H_2 : $(1\sigma_g)^2$ ($^1\Sigma_g^+$ state)
- He_2 : $(1\sigma_g)^2(1\sigma_u)^2$ ($^1\Sigma_g^+$ state)
- Li_2 : $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2$ ($^1\Sigma_g^+$ state)
- Be_2 : $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2$ ($^1\Sigma_g^+$ state)
- N_2 : $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2$ ($^1\Sigma_g^+$ state)
- O_2 : $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2(1\pi_g)^2$ ($^3\Sigma_g^-$ state)
- F_2 : $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2(1\pi_g)^4$ ($^1\Sigma_g^+$ state)

13) Let's consider a difficult case: C_2 molecule. It's electronic structure is complicated because the $3\sigma_g$ and $1\pi_u$ orbitals are very close in energy. There are three possible electronic configurations that give rise to several electronic states that lie close to each other in energy:

- $(1\pi_u)^4 \equiv ^1\Sigma_g^+$
- $(1\pi_u)^3(3\sigma_g)^1 \equiv ^1\Pi_u \oplus ^3\Pi_u$

- $(1\pi_u)^2(3\sigma_g)^2 \equiv {}^3\Sigma_g^- \oplus {}^1\Delta_g \oplus {}^1\Sigma_g^+$

The relative energies of these states obtained from the experiment:

- $X^1\Sigma_g^+$: 0.00 eV
- $a^3\Pi_u$: 0.09 eV
- $b^3\Sigma_g^-$: 0.80 eV
- $A^1\Pi_u$: 1.04 eV
- $B^1\Delta_g$: 1.50 eV
- $B'^1\Sigma_g^+$: 1.91 eV

14) Now, let's discuss the effect of spin-orbit coupling in the electronic spectra of diatomics. Since $\hat{H}$ does not commute with $\hat{L}^2$, it also doesn't commute with the total angular momentum operator $\hat{J}^2$. The diatomic electronic wavefunction is an eigenfunction of the $\hat{J}_z$ operator, a *z-component of the total angular momentum operator*:

$$\hat{J}_z |\Psi\rangle = \Omega |\Psi\rangle \quad (10)$$

The range of the eigenvalues is given by $\Omega = \Lambda + S, \Lambda + S - 1, \dots, \Lambda - S$. When spin-orbit coupling is taken into account, the electronic energy depends on the value of Ω . The diatomic energy levels are labeled as ${}^{2S+1}\Lambda_\Omega$. For example, for the ${}^3\Delta$ state, there are three levels: ${}^3\Delta_1, {}^3\Delta_2, {}^3\Delta_3$.

15) Finally, we consider selection rules for diatomic molecules. The following transitions are allowed (dipole approximation):

- Must not change the projection of the orbital angular momentum by more than one unit: $\Delta\Lambda = 0, \pm 1$
- Must not change the projection of the total angular momentum by more than one unit: $\Delta\Omega = 0, \pm 1$
- Must not change the total spin: $\Delta S = 0$

These selection rules indicate that there are two types of allowed transitions: (i) those that do not change Λ ($\Sigma \rightarrow \Sigma, \Pi \rightarrow \Pi$, etc), and (ii) those that change Λ by one ($\Sigma \rightarrow \Pi, \Pi \rightarrow \Delta$, etc). As for the many-electron atoms, the $\Delta S = 0$ selection rule becomes less firm as the strength of the spin-orbit coupling increases. When spin-orbit coupling becomes strong, $\Delta\Omega = 0, \pm 1$ becomes the main selection rule.

V. POLYATOMIC MOLECULES

1) In polyatomic molecules, the only two operators that commute with $\hat{H}$ are $\hat{S}^2$ and $\hat{S}_z$. To distinguish different electronic states, we can use the fact that the symmetry operators $\hat{R}$ of the point group of the molecule commute with $\hat{H}$. Thus, for polyatomic molecules, electronic wavefunction must be the eigenfunction of $\hat{R}$ and, therefore, can be transformed according to the corresponding irreducible representation.

2) For atoms and diatomics, we used complex orbitals. For polyatomics, it is generally more convenient to use real orbitals. For example, for water molecule in the minimal basis, there are seven orbitals that transform according to irreps of the C_{2v} point group: $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2(4a_1)^0(2b_2)^0$. The Hartree-Fock wavefunction will have the form:

$$|\Psi_{\text{H}_2\text{O}}\rangle = \mathcal{A}[\text{core}^4]1b_2\alpha(5)1b_2\beta(6)3a_1\alpha(7)3a_1\beta(8)1b_1\alpha(9)1b_1\beta(10) \quad (11)$$

The symmetry of the wavefunction is determined as the direct product of the symmetries of the individual spin-orbitals. Thus, any closed-shell electronic wavefunction transforms according to the totally symmetric irrep in the point group. The symmetry of $|\Psi_{\text{H}_2\text{O}}\rangle$ is A_1 . Therefore, the ground electronic state of water is labeled as 1A_1 .

3) For the lowest-energy excited state of water, the electronic configuration is $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^1(4a_1)^1(2b_2)^0$. There are three determinants with $M_S = 0$ and 1 that correspond to this electronic configuration:

$$|\Psi\rangle = \mathcal{A}[\text{core}^4]1b_2\alpha(5)1b_2\beta(6)3a_1\alpha(7)3a_1\beta(8)1b_1\alpha(9)4a_1\alpha(10) \quad (12)$$

$$|\Psi\rangle = \mathcal{A}[\text{core}^4]1b_2\alpha(5)1b_2\beta(6)3a_1\alpha(7)3a_1\beta(8)1b_1\alpha(9)4a_1\beta(10) \quad (13)$$

$$|\Psi\rangle = \mathcal{A}[\text{core}^4]1b_2\alpha(5)1b_2\beta(6)3a_1\alpha(7)3a_1\beta(8)1b_1\beta(9)4a_1\alpha(10) \quad (14)$$

These determinants correspond to two electronic states: 3B_1 and 1B_1 . According to the experiment, the excitation energies of these two states are 7.0 and 7.4 eV, respectively.

4) The ground-state electronic configuration of benzene is $(a_{2u})^2(e_{1g})^4(e_{2u})^0(b_{2g})^0$. The Hartree-Fock ground-state wavefunction has the form:

$$|\Psi\rangle = \mathcal{A}[\text{core}]a_{2u}\alpha a_{2u}\beta e_{1gx}\alpha e_{1gx}\beta e_{1gy}\alpha e_{1gy}\beta \quad (15)$$

This wavefunction corresponds to the ${}^1A_{1g}$ state. The lowest excited state of benzene has the $(a_{2u})^2(e_{1g})^3(e_{2u})^1(b_{2g})^0$ configuration. This configuration gives rise to six electronic states: ${}^3E_{1u}$, ${}^3B_{2u}$, ${}^3B_{1u}$, ${}^1E_{1u}$, ${}^1B_{2u}$, and ${}^1B_{1u}$.

5) For the polyatomic molecules, the following selection rules apply in absorption/emission spectroscopy:

- $\Gamma(\Psi_{g.s.}) \otimes \Gamma(\mu) \otimes \Gamma(\Psi_{e.s.})$ must contain totally symmetric irrep
- Must not change the total spin: $\Delta S = 0$

For example, for water the ${}^1A_1 \rightarrow {}^1B_1$ transition is allowed. For benzene, the only allowed transition among the ones we considered is ${}^1A_{1g} \rightarrow {}^1E_{1u}$.