

Atomic Terms, Hund's Rules, Atomic Spectroscopy

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I. Diatomic Molecules: Hydrogen

We now consider diatomic molecules, and the wavefunctions, energies, and spectroscopies associated with such systems. Naturally, we will build upon the approaches we have adopted in the past, as well as introduce new ideas to allow us to solve more complicated problems. The hydrogen molecule H_2 (or dihydrogen) contains 2 nuclei and 2 electrons. In order to discuss properties of molecules (dipole moment, polarizability, geometry, spectroscopic transitions related to bond stretching, rotations, etc.) we need to have wavefunctions and energetic states for molecules, i.e, molecule wavefunctions and energies. Thus, we must solve a Schrodinger wave equation for the molecular system. Some things to consider are the interactions involved in the Hamiltonian of such a system:

- Nuclear translation (kinetic energy)
- Electronic translation (kinetic energy)
- Nuclear-Nuclear repulsion
- Nuclear-electron attraction
- electron-electron repulsion
- spin-orbit coupling

The Hamiltonian is thus:

$$\hat{H} = \hat{K}E_N + \hat{K}E_e + \hat{V}_{NN} + \hat{V}_{Ne} + \hat{V}_{ee} + \hat{V}_{so}$$

Bear in mind the repulsions and attractions will contribute positively and negatively to the energy of the system. As in the Hydrogen atom case, we

can decompose this problem into a center of mass and relative motion problem.

- $mass_{electron} = \frac{mass_{proton}}{1836}$. Electrons treated as "massless"
- Center of mass of system thus defined by nuclear masses and their positions
- Center of mass problem is a quantum mechanical particle-in-a-box problem (not very interesting)
- Hamiltonian terms for center-of-mass problem: $\hat{H} = -\frac{\hbar^2}{2\mu}\nabla_n^2 - \frac{\hbar^2}{2M}\nabla_{COM}^2$
- $M = mass_{nucleus\ 1} + mass_{nucleus\ 2}$ and μ is the reduced mass,

$$\mu = \frac{(mass_{nucleus\ 1})(mass_{nucleus\ 2})}{M}$$

The relative motion problem

Separating out the center-of-mass motion leaves the problem of dealing with the relative motion of nuclei and electrons:

- Nuclear and electronic motion still relative to center of mass of system
- Cannot straightforwardly *separate* nuclear and electronic motions as done for hydrogen atom case: without simplifications/qualifications, Hamiltonian is not strictly separable into nuclear and electronic components.
- Coulomb interactions between nuclei and electrons "couple" the two systems and do not possess inherent symmetry (i.e. spherical symmetry with central force potential for hydrogen atom nucleus-electron interaction)

The way out of this dilemma is the **Born-Oppenheimer Approximation**.

:

- Nuclei are 10^3 times heavier than electrons. Electronic dynamics, being much faster, allows electrons to rapidly "equilibrate" to more slowly-varying nuclear geometries. Thus, consider nuclei fixed and determine electronic wavefunctions for a given nuclear geometry/configuration
- $\Psi \cong \Psi_e(R, r_e)\Psi_n(r_n, \theta_n, \phi_n)$
- Electronic wavefunctions effectively become "functions" of nuclear separation. For the nuclei, the electronic wavefunctions determine a potential, $E(R)$

- Repeatedly determining electronic wavefunctions and energies for multiple nuclear configurations yields apparent internuclear potential, $E(R)$.

Solution of Relative Nuclear Motion

Within the BO approximation, then, one obtains a Hamiltonian for the nuclei that includes the internuclear potential as discussed above:

$$\hat{H}_N(R)\Psi_N(R) = \left[\hat{K}E_N + E(R) \right] \Psi_N(R) = E\Psi_N(R)$$

Since it is evident in the case of the H_2 diatomic that we can consider the system analogous to a rotor, the explicit Hamiltonian will contain radial and spherical polar components (spherical polar coordinates were shown to be convenient reference for such calculations):

$$\hat{H}_N\Psi_N = \left[-\frac{\hbar^2}{2\mu} \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{1}{2\mu R^2} \hat{L}^2 + E(R) \right] \Psi_N = E\Psi_N$$

- Wavefunction is factorable into Radial and spherical harmonic functions as in hydrogen atom case
- $\Psi_N = \zeta(R)Y_{lm}(\theta_N, \phi_N)$
- solving for R requires we know E(R) explicitly
 - **Harmonic Approximation** Near Equilibrium Nuclear Separation
 - Taylor expand about equilibrium distance. Truncate at first term, giving Harmonic (quadratic) form.
 - $E(R) = E(R_e) + \frac{1}{2!} \left(\frac{\partial^2 E}{\partial R^2} \right)_{R_e} (R - R_e)^2 + \frac{1}{3!} \left(\frac{\partial^3 E}{\partial R^3} \right)_e (R - R_e)^3 + \dots$
 - Essentially a *harmonic oscillator* treatment of motion of nuclei.
 - Corrections can be added via *perturbative* treatments

The energies of the diatomic molecule one obtains thus mimic the vibrational and rotational counterparts for the hydrogen atom.

- Vibrational energy: associated with quantum number $n = 0, 1, 2, 3, \dots$
- Energy: $E_{vib} = \left(n + \frac{1}{2} \right) h\nu_o - \left(n + \frac{1}{2} \right)^2 R_e h\nu_o + \dots$

- The second term is a correction for the anharmonic contributions neglected in the above formulation using only the harmonic (quadratic) terms in $E(R)$
- Rotational Energies: treating the diatomic as a *rigid rotor*, the energy depends on the total angular momentum, J (recall for the hydrogen atom the energy for the rigid rotor was $\hbar l(l+1)$).
- Diatomic rotational energy: $E_{rot} = B_e h J(J+1)$
- Rotational Constant: $B_e = \frac{\hbar}{4\pi\mu R_e^2}$
- Coupling between rotation and vibration modulates B_e :
 $B_n: B_n = B_e - \alpha \left(n + \frac{1}{2}\right)$
- Real molecules are not rigid rotors; distortion due to centrifugal effects:
 $-D_c J^2(J+1)^2$
- Total rotational energy: $E_{rot} = B_n J(J+1) - D_c J^2(J+1)^2$

The total energy for a diatomic such as H_2 thus becomes (in the BO approximation with harmonic oscillator / rigid rotor treatment corrected for higher order effects):. The energy includes contributions from *vibration-rotation* coupling and *centrifugal distortion*.

$$E_{n,J} = \left(n + \frac{1}{2}\right) h\nu_o - \left(n + \frac{1}{2}\right)^2 R_e h\nu_o + \dots \\ + \left(B_e + \alpha_e \left(n + \frac{1}{2}\right)\right) J(J+1) - D_c J^2(J+1)^2$$

Spectroscopy of Diatomic Molecule

- Diatomics possess rotational - vibrational spectra (dynamical models included in the description)
- Selection Rules
 - $\Delta J = \pm 1$
 - $\Delta n = \pm 1$
- Infrared (vibrational stretching) frequencies

Summary

- H_2 problem can be formulated as harmonic oscillator / rigid rotor problem within the Born-Oppenheimer Approximation
- Perturbative corrections for coupling and higher-order dynamical effects (vibrational anharmonicity, centrifugal distortion)
- Energy depends on vibrational and rotational quantum numbers
- Have not specifically determined electronic wavefunction and states for this problem.
 - Explicit knowledge of electronic states important for describing reactivity (bond making and breaking), chemical bonding

Molecular Spectroscopy

Vibrational - Rotational

I. By applying the criterion of a non-vanishing transition dipole within the dipole approximation, the selection rules for vibrational and rotational spectroscopies for molecules can be determined. Here we state the results and a brief discussion.

- Vibration
 - Vibrational energy levels: $E_{vib} = \left(n + \frac{1}{2}\right) h\nu_o - \left(n + \frac{1}{2}\right)^2 R_e h\nu_o + \dots$
 - Wavefunctions are Hermite polynomials
 - Transition dipole criterion gives: $\Delta n = \pm 1$ for *vibrational transitions*. This is in the *infrared* region of EM spectrum.
 - Vibrational modes can be symmetric or antisymmetric (CO_2 stretching modes)
- Rotation
 - Recall energy levels for rotational energy levels for diatomic (rigid rotor including distortion effects)
 - $\left(B_e + \alpha_e \left(n + \frac{1}{2}\right)\right) J(J + 1) - D_c J^2(J + 1)^2$
 - Selection Rule: $\Delta J = \pm 1$

 - $\Delta E = E(J_{final}) - E(J_{initial})$
 - For $\Delta J = +1$, $\Delta E = 2hcB(J + 1)$
(R-branch, high frequencies in infrared spectrum)

- For $\Delta J = -1$, $\Delta E = -2hcBJ$
(P-branch, low frequencies, in infrared spectrum)
 - For $\Delta J = 0$ is a forbidden transition for infrared; $\Delta J = 0, \pm 2$ for Raman spectroscopy (scattering phenomenon)
 - Note that the energy differences for the two changes are not necessarily the same
- Information from vibrational-rotational spectroscopy: normal mode frequencies, normal modes, geometries

Molecular Orbitals

Having discussed qualitatively the nature of the energy states of a diatomic, we now discuss the wavefunctions associated with *molecular* states. Electronic wavefunctions for molecules are known as *molecular wavefunctions*. Just as the many-electron atomic wavefunction is built from 1-electron atomic orbitals, molecular wavefunctions are built from *molecular orbitals*.

- Molecular Orbitals approximated as
- Linear Combination of Atomic Orbitals (LCAO-MO)
- SCF Hartree-Fock orbitals
- Valence-bond orbitals
- Huckel orbitals (conjugated systems)

Recall that when given the *total wavefunction* of a system (i.e, linear superposition of eigenstates), the energy can be determined as an expectation value:

$$E = \int \Psi_{molecular}^* \hat{H} \Psi_{molecular} d^3 \mathbf{r}$$

Applying this relation in a variational sense allows us to arrive at important results for energies and associated wavefunctions.

We first consider the H_2^+ system. At infinite separation, we can imagine that the single electron is *localized* at one of the nuclei. As we bring the two nuclei closer together, it is plausible to consider the location of the electron (if we can speak in such deterministic terms) as being delocalized between the two nuclei. Thus, the molecular wavefunction can be written as a linear combination of molecular orbitals which are themselves combinations of atomic orbitals situated on individual nuclei.

- LCAO-MO formulation of wavefunction.
- Linear combination of 1s orbitals centered on each nuclei, A and B
 - $\Psi_{MO,\pm} = \frac{1}{\sqrt{2(1\pm S_{AB})}} (\phi_{1s,A} \pm \phi_{1s,B})$
 - In this case, the molecular wavefunction is equivalent to the molecular orbital since each molecular orbital holds 2 electrons
- The energy associated with the molecular wavefunction (orbital):

$$E_{MO,\pm} = \frac{1}{1\pm S_{AB}} (H_{AA} \pm H_{AB})$$
- The H and S are shorthand notations for the various integrals that arise from the calculation of the expectation value of the energy
 - $H_{ij} = \int \phi_i^*(\tau) \hat{H} \phi_j(\tau) d\tau$
 - Overlap integral: $S_{ij} = \int \phi_i^*(\tau) \phi_j(\tau) d\tau$
 - Note that for the overlap integral, the orbitals in the integrand are associated with different nuclei, and so the integral represent the amount of overlap of the orbitals. For the same type of orbital, this would be unity if the two orbitals were situated on the same nucleus.

Energetics of the H_2^+ system:

- There are two energy states associated with the wavefunctions defined above; moreover, they are associated with molecular orbitals.
- One is a **bonding state**, or bonding orbital, and the other an **anti-bonding state** or anti-bonding orbital.
- Relative to a hypothetical non-bonded state (where the hydrogen atom and proton are ∞ separated), the bonded state has an energy minimum at the equilibrium bond distance, R_e .

s

Note on molecular orbital symmetry:

- Molecular orbitals possess inherent symmetry properties. Consider the molecular wavefunction (orbital) for H_2^+ we are discussing.
- Symmetry is related to operators
- Symmetry under inversion: $\hat{I}\Psi(x, y, z) = \Psi(-x, -y, -z) = \pm\Psi(x, y, z)$

- Symmetry under reflection through a plane (x-y plane):
 $\hat{\sigma}\Psi(x, y, z) = \Psi(x, y, -z) = m\Psi(x, y, z)$
- Symmetry under rotation by an angle θ
 - * $\mathbb{R}_{z,\theta}\Psi(x, y, z) = \Psi(x \cos\theta + y \sin\theta, y \cos\theta - x \sin\theta, -z)$
 $= \pm\Psi(x, y, z)$

Considering the molecular wavefunction for the hydrogen molecule ion H_2^+ , we see that the wavefunctions, based on symmetry, are:

- symmetric
 $\Psi_g = \frac{1}{\sqrt{2(1+S_{AB})}} (\phi_{1s,A} + \phi_{1s,B})$
- anti-symmetric
 $\Psi_u = \frac{1}{\sqrt{2(1-S_{AB})}} (\phi_{1s,A} - \phi_{1s,B})$
- $E_g < E_u$. The bonding state must have a lower energy relative to the infinitely separated state compared to the anti-bonding state.

Chemical Bonding and the Molecular Wavefunction

- Molecular orbitals can help us understand a few concepts related to chemical bonding
- Bonding orbitals have no nodes; anti-bonding orbital has a node midway between the nuclei
 - * Probability of finding electron along the coordinate linking the two nuclei
 - * Non bonded case: electron equally likely found on either nucleus
 - * For both the bonding and anti-bonding orbitals, the **volume** accessible to the electron is **greater** than in the non-bonded case.
 - * Electron in bonded case is **delocalized**
 - * Differences in the probability for bonding and anti-bonding orbitals
 - Electron probability greater between nuclei for bonding orbital than anti-bonding orbital

- For bonding orbital, electron density moves closer to region between nuclei as well as closer to each nucleus.
- * Ingredients for chemical bond formation: electron density **delocalization** over entire molecule. Bonding orbital **increases** electron probability density between nuclei and closer to each nuclei; anti-bonding orbital increases electron probability density away from region between nuclei.

Linear Combination of Atomic Orbitals-Molecular Orbitals

For many-electron molecules, the problem of solving the **n-electron** problem is reduced to solving **n one-electron** problems via the Hartree approximation. The **one-electron molecular orbitals** are solved for via a Schrodinger equation of the form:

$$\hat{H}_{HF}\sigma_i(\mathbf{r}_i) = \epsilon_i\sigma_i(\mathbf{r}_i) \quad i = 1, 2, \dots, n$$

The **molecular orbitals** σ_i are expressed as *linear combinations* of atomic orbitals, hence the LCAO-MO approach. For an n-electron system, the Slater determinantal form of the wavefunction is :

$$\psi(1, 2, 3, \dots, n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \sigma_1(\mathbf{r}_1, \alpha_1) & \sigma_1(\mathbf{r}_1, \beta_1) & \dots & \sigma_m(\mathbf{r}_1, \beta_1) \\ \sigma_1(\mathbf{r}_2, \alpha_2) & \sigma_2(\mathbf{r}_2, \beta_2) & \dots & \sigma_m(\mathbf{r}_2, \beta_2) \\ \vdots & \vdots & & \vdots \\ \sigma_1(\mathbf{r}_n, \alpha_n) & \sigma_2(\mathbf{r}_n, \beta_n) & \dots & \sigma_m(\mathbf{r}_n, \beta_n) \end{vmatrix}$$

where $m = \frac{n}{2}$ if n is even and $m = \frac{n+1}{2}$ if n is odd. The molecular orbitals, σ_i are expressed as linear combinations of atomic orbitals (AO's) as:

$$\sigma_j(\mathbf{r}_1) = \sum_{i=1}^{\infty} c_{ij}\phi_i(\mathbf{r}_1)$$

The sum is over atomic orbitals on all atoms and the subscript "1" refers to the electron being considered. The set of AO's ϕ_i

are a basis, and since the infinite set forms a complete set, the MO's expressed as linear combinations of AO's are in practice approximate, since we cannot use an infinite expansion.

The coefficients (and variable exponents in the radial parts of the atomic orbitals) are optimized variationally using the Hartree-Fock method. In deriving the variational equations, one obtains the Secular equations, which in matrix form, are associated with the Secular determinant. The solutions of the c_{ij} are determined by solving for the zeroes of the secular determinant.

In general, n atomic orbitals used in defining the molecular orbitals yields n molecular orbitals.

We can use **molecular orbital diagrams** to visualize the energetics of molecular orbitals. Before we construct such diagrams for simple diatomic molecules (homonuclear and heteronuclear), we present some general ideas:

- * Only atomic orbitals of the same symmetry will combine with one another (maximize overlap)
- * Two interacting AO's give rise to two molecular orbitals.
 - The MO energies will be different relative to the AO energies. A necessary condition for this splitting is non-zero overlap of the AO's in the molecule.
- * The MO with the lower energy is the in-phase combination of AO's, and is called the bonding orbital.
- * The MO with the higher energy is the out-of-phase combination of AO's and is called the anti-bonding orbital.
- * The **energy splitting between MO** increases with overlap
- * The relative contribution of two AO's in a MO is determined by the **relative magnitude** of their coefficients.
 - AO's with equal energy will give equal coefficients for the MO
 - AO's with different energies: the magnitude of the coefficient of the lower-lying AO is greater in the bonding orbital and smaller in the anti-bonding orbital

Symmetry of molecular orbitals:

- * gerade(g): symmetric upon inversion
- * ungerade(u): antisymmetric upon inversion
- * σ symmetry: rotation about the molecular axis leaves MO unchanged

* π symmetry: nodal plane includes molecular axis

Molecular Orbitals for Homonuclear Diatomic Molecules

For the sequence of molecules H_2 to N_2 , the MO orbital energies (via Hartree-Fock) are:

$$1\sigma_g < 1\sigma_u^* < 2\sigma_g < 2\sigma_u^* < 1\pi_u < 3\sigma_g < 1\pi_g^* < 3\sigma_u^* \\ \sigma_g(1s) < \sigma_u^*(1s) < \sigma_g(2s) < \sigma_u^*(2s) < \pi_u(2px, 2py) < \sigma_g(2pz) < \\ \pi_g^*(2px, 2py) < \sigma_u^*(2pz)$$