1 Electronic Energy Levels of a Helium Atom (He)

The helium atom consists of a nucleus (with 2 protons) and 2 electrons. The energy levels are determined by the quantum states of the electrons under the influence of both the Coulomb attraction to the nucleus and the electron-electron repulsion.

1.1 Energy Levels and Configuration

In a neutral helium atom (He), the two electrons are expected to fill the lowest available energy levels in accordance with quantum mechanics.

Ground State (Fundamental State):

In the ground state, both electrons occupy the 1s orbital, the lowest energy state available. Thus, the configuration of the ground state is $1s^2$, meaning both electrons have the principal quantum number $n = 1$, orbital quantum number $l = 0$, and they occupy the 1s orbital.
The energy of the system depends on both the individual energies of the electrons and their interaction with each other. The total energy of the helium atom in the ground state is *lower* than the sum of the two independent electron energies due to electron-electron repulsion, but the repulsion also shifts the energy slightly upwards.

1.2 Role of the Pauli Exclusion Principle

The Pauli Exclusion Principle states that no two electrons can occupy the same quantum state simultaneously (i.e., they cannot have the same set of quantum numbers).
In helium, the Pauli principle forces the two electrons in the 1s orbital (which have the same spatial quantum numbers n and l) to have opposite spins. One electron has the spin quantum number $m_s = +\frac{1}{2}$, and the other has $m_s = -\frac{1}{2}$. This leads to a *singlet state* in the ground state configuration, ensuring that the Pauli Exclusion Principle is not violated.

1.3 Approach to Evaluate the Ground State Energy

One approach to evaluate the energy of the fundamental state is using *variational methods*. The helium atom is a three-body problem (two electrons and one nucleus), which cannot be solved exactly. However, approximations can be made:

Hartree-Fock Approximation:

In this approach, the wavefunctions of the electrons are approximated, assuming that each electron moves in an average potential due to the nucleus and the other electron. The energy of the system is minimized by varying the wavefunction parameters.

Thomas-Fermi Approximation:

A more basic approach that treats the electrons as a statistical cloud, giving an estimate of the ground state energy based on the charge density.

Exact Non-Relativistic Energy:

For helium, the exact non-relativistic energy of the ground state (from experimental data or more advanced calculations like Configuration Interaction) is approximately $-79\,\text{eV}$.

1.4 Excited States and Discrete Energy Levels

The excited states of helium correspond to configurations where one or both electrons occupy orbitals with $n > 1$.

Excited States:

In the excited states, the electrons can move to higher orbitals, such as 1s2s or 1s2p configurations. For example:

- In the $1s2s$ configuration, one electron remains in the 1s orbital, and the other is promoted to the 2s orbital.

- In the $1s2p$ configuration, the second electron moves to a 2p orbital.

These excited states form a *discrete energy spectrum*. The Pauli Exclusion Principle still applies, so the spin of the electrons in these states can lead to *singlet* or *triplet* states, depending on whether their spins are paired or parallel.

- *Singlet states:* Electrons have opposite spins, giving a total spin $S = 0$.

- *Triplet states:* Electrons have parallel spins, giving a total spin $S = 1$. Triplet states are lower in energy than singlet states due to *exchange interaction*.

1.5 Considerations on Excited States

The *discrete excited states* represent bound states where the electrons are still bound to the nucleus. The energy difference between the ground state and an excited state corresponds to the photon energy emitted or absorbed when the electron transitions between these states.

For higher excitations, the energy levels converge towards the *ionization energy*, after which the electron is no longer bound to the atom and the energy levels become continuous.

2 Schrödinger Equation for the H_2^+ Molecule in the Born-Oppenheimer Approximation

The H_2^+ molecule is the simplest molecular system, consisting of two protons and one electron. To solve the Schrödinger equation for this system, we commonly use the Born-Oppenheimer approximation. This approximation assumes that the nuclei (protons) are much heavier than the electron and thus move much more slowly. As a result, the electronic wavefunction can be solved separately, assuming fixed nuclei positions.

The Schrödinger equation for the H_2^+ molecule can be written as:

$$\hat{H}\Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R}),$$

where: - $\mathbf{r}$ represents the electronic coordinates, - $\mathbf{R}$ represents the internuclear distance between the two protons, - $\hat{H}$ is the Hamiltonian, and - $\Psi(\mathbf{r}, \mathbf{R})$ is the total wavefunction of the system.

In the Born-Oppenheimer approximation, we treat the nuclei as fixed, so the total wavefunction can be separated into an electronic wavefunction and a nuclear wavefunction:

$$\Psi(\mathbf{r}, \mathbf{R}) = \psi_e(\mathbf{r}; \mathbf{R})\chi(\mathbf{R}),$$

where: - $\psi_e(\mathbf{r}; \mathbf{R})$ is the electronic wavefunction for fixed nuclei, - $\chi(\mathbf{R})$ is the nuclear wavefunction.

The Hamiltonian can be split into two parts:

$$\hat{H} = \hat{H}_e + \hat{T}_N,$$

where: - $\hat{H}_e$ is the electronic Hamiltonian, and - $\hat{T}_N$ is the nuclear kinetic energy operator, which we initially ignore under the Born-Oppenheimer approximation.

The electronic Hamiltonian is given by:

$$\hat{H}_e = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{|\mathbf{r} - \mathbf{R}_1|} - \frac{e^2}{|\mathbf{r} - \mathbf{R}_2|} + \frac{e^2}{|\mathbf{R}_1 - \mathbf{R}_2|},$$

where: - m_e is the electron mass, - e is the elementary charge, - $\mathbf{R}_1$ and $\mathbf{R}_2$ are the positions of the two protons.

2.1 Electronic Fundamental State Energy

To evaluate the energy of the electronic fundamental state, we solve the electronic Schrödinger equation:

$$\hat{H}_e\psi_e(\mathbf{r}; \mathbf{R}) = E_e(\mathbf{R})\psi_e(\mathbf{r}; \mathbf{R}),$$

where $E_e(\mathbf{R})$ is the energy of the electronic ground state as a function of the internuclear distance $\mathbf{R}$.

This equation is solved using variational methods or numerical approaches, as an analytical solution is generally not possible for the H_2^+ molecule. The result of this calculation gives the electronic potential energy curve, $E_e(\mathbf{R})$, which represents the energy of the electron as a function of the internuclear distance.

2.2 Relation Between Fundamental State Energy and Internuclear Distance

The total energy of the system in the Born-Oppenheimer approximation is:

$$E(\mathbf{R}) = E_e(\mathbf{R}) + \frac{e^2}{|\mathbf{R}_1 - \mathbf{R}_2|},$$

where the second term accounts for the Coulomb repulsion between the two protons.

By minimizing the total energy $E(\mathbf{R})$ with respect to the internuclear distance $\mathbf{R}$, we can find the equilibrium distance R_0, which corresponds to the most stable configuration of the H_2^+ molecule. This distance is where the attractive forces between the electron and the nuclei balance the repulsive forces between the two protons.

At equilibrium, the molecule reaches its lowest energy configuration, and the corresponding value of $E_e(R_0)$ is the energy of the electronic fundamental state at the equilibrium internuclear distance.

2.3 Conclusion

In summary, the Schrödinger equation for the H_2^+ molecule can be approximately solved using the Born-Oppenheimer approximation. This involves fixing the nuclei and solving the electronic Schrödinger equation to obtain the electronic energy as a function of the internuclear distance. The equilibrium distance is determined by minimizing the total energy, which reflects the balance between attractive and repulsive forces in the molecule.

3 Spectral Line Shape and Width of a Radiative Transition Between Two Bounded States

When a radiative transition occurs between two bounded atomic or molecular states, the emitted or absorbed radiation has a specific spectral line associated with it. The shape and width of this spectral line are influenced by several factors. Understanding these factors is essential in fields such as spectroscopy, where precise information about energy levels, transition probabilities, and environmental effects is extracted from spectral lines.

3.1 Spectral Line Shape

The spectral line shape refers to the distribution of the intensity of radiation as a function of frequency (or wavelength) around the central frequency ν_0 corresponding to the energy difference between the two quantum states. Ideally, in the absence of perturbations, the spectral line would be a sharp Dirac delta function centered at ν_0. However, several phenomena lead to the broadening and shaping of the spectral line.

The shape of a spectral line can be modeled using different profiles, depending on the broadening mechanisms at play. The most common line shapes are:

- **Lorentzian line shape:** Arises from natural broadening due to the finite lifetime of the excited state.

- **Gaussian line shape:** Results from Doppler broadening due to the thermal motion of particles.

- **Voigt profile:** A convolution of Lorentzian and Gaussian profiles, representing a combination of broadening mechanisms.

3.2 Spectral Line Broadening Mechanisms

The width of a spectral line can be affected by several broadening mechanisms. These mechanisms fall into two broad categories: homogeneous broadening, where all atoms or molecules experience the same broadening, and inhomogeneous broadening, where the broadening varies between particles.

Natural Broadening

Natural broadening, also known as lifetime broadening, occurs due to the uncertainty principle. The uncertainty in the energy of the excited state is inversely related to its lifetime τ. The relationship between the spectral width $\Delta\nu_{\text{nat}}$ and the lifetime is given by:

$$\Delta\nu_{\text{nat}} = \frac{1}{2\pi\tau}.$$

This leads to a Lorentzian line shape, where the intensity $I(\nu)$ as a function of frequency ν is given by:

$$I(\nu) = \frac{I_0}{1 + \left(\frac{\nu - \nu_0}{\Delta\nu_{\text{nat}}/2}\right)^2}.$$

Natural broadening is typically small unless the lifetime of the excited state is extremely short.

Doppler Broadening

Doppler broadening arises due to the relative motion between the radiating atoms or molecules and the observer. Atoms in thermal motion will have velocities following a Maxwell-Boltzmann distribution, and their motion shifts the observed frequency due to the Doppler effect. The Doppler-broadened line shape is Gaussian, and the width is given by:

$$\Delta\nu_{\text{Doppler}} = \nu_0 \frac{v_{\text{rms}}}{c} = \nu_0 \frac{\sqrt{\frac{2k_B T}{m}}}{c},$$

where:

- v_{rms} is the root mean square velocity of the particles,

- k_B is the Boltzmann constant,

- T is the temperature,

- m is the mass of the atom or molecule,

- c is the speed of light.

Doppler broadening is more significant at higher temperatures and for lighter particles. The intensity distribution follows a Gaussian profile:

$$I(\nu) = I_0 \exp\left(-\frac{(\nu - \nu_0)^2}{2\sigma_\nu^2}\right),$$

where σ_ν is the standard deviation of the frequency distribution.

Pressure (Collisional) Broadening

Pressure broadening, also known as collisional broadening, occurs when collisions between atoms or molecules perturb the energy levels, leading to a shift and broadening of the spectral lines. The width of the spectral line due to pressure broadening is proportional to the pressure P:

$$\Delta\nu_{\text{pressure}} = \gamma P,$$

where γ is a constant that depends on the type of interaction (e.g., Van der Waals, Stark effect) and the type of colliding particles. The line shape for pressure broadening is typically Lorentzian.
Pressure broadening is significant at high gas densities, such as in stellar atmospheres or in gas discharges.

Stark and Zeeman Broadening

External electric or magnetic fields can also broaden spectral lines:

- **Stark broadening:** Occurs due to the presence of an external electric field, which causes energy level splitting or shifting (the Stark effect). This leads to both broadening and splitting of spectral lines.

- **Zeeman broadening:** Occurs in the presence of an external magnetic field (the Zeeman effect). The magnetic field causes the splitting of energy levels into multiple components, leading to a broadened spectral line.

3.3 Conditions for Relevance of Different Phenomena

The relevance of each broadening mechanism depends on various factors:

- **Natural broadening** dominates when the lifetime of the excited state is short, leading to significant uncertainty in energy.

- **Doppler broadening** becomes important at higher temperatures and for lighter atoms or molecules due to increased thermal motion.

- **Pressure broadening** is most relevant in high-density environments, such as gases under high pressure or stellar atmospheres.

- **Stark and Zeeman broadening** are significant when the system is subjected to strong external electric or magnetic fields.

In many cases, multiple broadening mechanisms are at play simultaneously. For example, Doppler broadening and pressure broadening often occur together, and the resulting line shape is modeled using a Voigt profile, which is a convolution of Gaussian (Doppler) and Lorentzian (pressure) profiles.

3.4 Conclusion

The spectral line shape and width of a radiative transition between two bounded states are determined by various broadening mechanisms. Each mechanism contributes to the final observed line shape, depending on the physical conditions of the system. Understanding these broadening effects allows for the interpretation of spectral lines and the determination of important physical properties such as temperature, pressure, and the presence of external fields.

4 Fine Structure of One-Electron Atoms: The Role of the Electron Magnetic Moment

The fine structure of one-electron atoms, such as hydrogen or hydrogen-like ions, refers to small corrections to the energy levels of the atom, which arise from relativistic and quantum mechanical effects. These corrections cause the splitting of energy levels that would otherwise be degenerate in the non-relativistic Schrödinger theory. The key components contributing to the fine structure include the relativistic correction to the kinetic energy, the spin-orbit interaction, and the Darwin term. A central aspect of the fine structure is the role played by the electron's magnetic moment due to its intrinsic spin.

4.1 Hamiltonian for Fine Structure

The fine structure of one-electron atoms can be described by adding relativistic corrections to the non-relativistic Hamiltonian. The full Hamiltonian including fine structure terms is:

$$\hat{H}_{\text{fs}} = \hat{H}_{\text{NR}} + \hat{H}_{\text{rel}} + \hat{H}_{\text{SO}} + \hat{H}_{\text{Darwin}},$$

where:

- $\hat{H}_{\text{NR}}$ is the non-relativistic Hamiltonian,

- $\hat{H}_{\text{rel}}$ is the relativistic correction to the kinetic energy,

- $\hat{H}_{\text{SO}}$ represents the spin-orbit interaction, and

- $\hat{H}_{\text{Darwin}}$ is the Darwin term, a relativistic correction accounting for the interaction between the electron and the nucleus.

4.2 Relativistic Correction to Kinetic Energy

The relativistic correction to the kinetic energy arises from the expansion of the relativistic expression for energy:

$$E = \sqrt{p^2c^2 + m_e^2c^4} \approx m_ec^2 + \frac{p^2}{2m_e} - \frac{p^4}{8m_e^3c^2}.$$

The first term is the rest mass energy, the second term is the non-relativistic kinetic energy, and the third term represents the relativistic correction. The relativistic correction to the Hamiltonian is given by:

$$\hat{H}_{\text{rel}} = -\frac{p^4}{8m_e^3c^2}.$$

This correction leads to a small shift in the energy levels, particularly for electrons in states with high quantum numbers.

4.3 Spin-Orbit Interaction

The spin-orbit interaction arises from the interaction between the electron's magnetic moment and the magnetic field generated by its motion around the nucleus. In the rest frame of the electron, the nucleus appears to generate a magnetic field due to its motion. The magnetic moment of the electron interacts with this magnetic field, leading to a coupling between the electron's spin $\mathbf{S}$ and its orbital angular momentum $\mathbf{L}$.

The spin-orbit interaction Hamiltonian is given by:

$$\hat{H}_{\text{SO}} = \frac{1}{2m_e^2c^2}\frac{1}{r}\frac{dV}{dr}\mathbf{L} \cdot \mathbf{S},$$

where $V(r)$ is the Coulomb potential of the nucleus, and $\mathbf{L} \cdot \mathbf{S}$ is the dot product of the orbital angular momentum and the spin angular momentum. This term splits the energy levels based on the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$, causing fine structure splitting.

The spin-orbit interaction leads to a splitting of states with the same orbital angular momentum quantum number l, but different total angular momentum quantum number $j = l \pm \frac{1}{2}$. The energy shift due to the spin-orbit interaction is proportional to:

$$\Delta E_{\text{SO}} \propto \frac{Z^4}{n^3}\left(j(j+1) - l(l+1) - \frac{3}{4}\right),$$

where Z is the atomic number and n is the principal quantum number.

4.4 The Role of the Electron Magnetic Moment

The electron has an intrinsic magnetic moment due to its spin, given by:

$$\boldsymbol{\mu}_S = -g_s\mu_B\mathbf{S},$$

where:

- $g_s \approx 2$ is the electron spin g-factor,

- $\mu_B = \frac{e\hbar}{2m_e}$ is the Bohr magneton, and

- $\mathbf{S}$ is the spin angular momentum of the electron.

The electron's magnetic moment interacts with the magnetic field generated by its orbital motion (leading to the spin-orbit interaction), as well as with external magnetic fields. This interaction is a key aspect of the fine structure splitting.

4.5 Darwin Term

The Darwin term arises from the Zitterbewegung (trembling motion) of the electron, which is a consequence of relativistic quantum mechanics. It accounts for the fact that the electron does not follow a simple classical trajectory but instead exhibits rapid fluctuations. The Darwin term modifies the potential at small distances and is important for states where the electron is close to the nucleus (i.e., s-states, where $l = 0$).
The Darwin term is given by:

$$\hat{H}_{\text{Darwin}} = \frac{\hbar^2}{8m_e^2c^2}\nabla^2 V(r).$$

This term contributes to the fine structure by slightly shifting the energy of s-orbitals, which have non-zero probability density at the nucleus.

4.6 Total Fine Structure Correction

The total fine structure energy shift is the sum of the relativistic kinetic energy correction, spin-orbit interaction, and the Darwin term. The fine structure correction to the energy levels is given by:

$$\Delta E_{\text{fs}} = \Delta E_{\text{rel}} + \Delta E_{\text{SO}} + \Delta E_{\text{Darwin}}.$$

In terms of quantum numbers, the total fine structure energy shift for a hydrogen-like atom is approximately:

$$\Delta E_{\text{fs}} \propto \frac{Z^4}{n^3}\left(1 + \frac{j(j+1) - l(l+1) - \frac{3}{4}}{l(l+1)}\right).$$

This splitting causes energy levels that are degenerate in the Schrödinger theory to split into multiple closely spaced levels, leading to the fine structure observed in atomic spectra.

4.7 Conclusion

The fine structure of one-electron atoms results from several relativistic effects, including the relativistic correction to the kinetic energy, the spin-orbit interaction, and the Darwin term. A key factor in fine structure splitting is the interaction of the electron's magnetic moment with the magnetic field arising from its orbital motion. These corrections lead to a splitting of atomic energy levels, which can be observed in high-resolution spectroscopy. Understanding fine structure is crucial for accurately describing the energy levels of hydrogen-like atoms and for interpreting their spectral lines.

5 Effect of a Uniform Electric Field on the Electronic Energy Levels of a One-Electron Atom: First-Order Perturbation Theory

The effect of an external electric field on the electronic energy levels of a one-electron atom can be studied using perturbation theory. In this discussion, we analyze the first-order perturbation theory to understand how a uniform and constant electric field influences the energy levels of an atom, such as the hydrogen atom. We also examine the validity range of this approximation.

5.1 Perturbation Theory Framework

In the presence of an external electric field, the Hamiltonian of the system is modified. The total Hamiltonian $\hat{H}$ of the one-electron atom is given by:

$$\hat{H} = \hat{H}_0 + \hat{H}'.$$

Here:

- $\hat{H}_0$ is the unperturbed Hamiltonian of the atom (e.g., the hydrogen atom without an external field),

- $\hat{H}'$ is the perturbing Hamiltonian due to the external electric field.

5.2 Perturbing Hamiltonian in an Electric Field

Consider a uniform and constant electric field $\mathbf{E}$ in the z-direction. The perturbing Hamiltonian $\hat{H}'$ is given by:

$$\hat{H}' = -e\mathbf{E} \cdot \mathbf{r},$$

where e is the charge of the electron and $\mathbf{r}$ is the position operator of the electron. For an electric field in the z-direction, this simplifies to:

$$\hat{H}' = -eE_z z.$$

5.3 First-Order Energy Corrections

In first-order perturbation theory, the correction to the energy of the n-th state is given by the expectation value of the perturbing Hamiltonian in that state. Let ψ_n denote the unperturbed eigenstate of the Hamiltonian $\hat{H}_0$, with energy E_n^0. The first-order energy correction $E_n^{(1)}$ is:

$$E_n^{(1)} = \langle \psi_n | \hat{H}' | \psi_n \rangle.$$

Substituting the perturbing Hamiltonian $\hat{H}'$, we get:

$$E_n^{(1)} = \langle \psi_n | -eE_z z | \psi_n \rangle = -eE_z \langle \psi_n | z | \psi_n \rangle.$$

Since the expectation value $\langle \psi_n | z | \psi_n \rangle$ depends on the parity of the wavefunction, the result is:

- For states with even parity, $\langle \psi_n | z | \psi_n \rangle = 0$. Therefore, the first-order energy correction is zero.

- For states with odd parity, $\langle \psi_n | z | \psi_n \rangle \neq 0$. In this case, the first-order energy correction is non-zero and proportional to E_z.

For example, in the hydrogen atom, the $2p$ states have odd parity, and the first-order energy shift due to the electric field is:

$$E_{2p}^{(1)} = -eE_z \langle 2p | z | 2p \rangle.$$

5.4 Validity of First-Order Perturbation Theory

The first-order perturbation theory is valid under the following conditions:

- **Weak Field Approximation:** The external electric field must be sufficiently weak so that the perturbing Hamiltonian $\hat{H}'$ is small compared to the unperturbed Hamiltonian $\hat{H}_0$. This means the electric field should be small enough that the linear approximation holds true.

- **Non-Degenerate States:** The theory assumes that the states involved are non-degenerate. If degeneracy occurs, higher-order perturbation theory might be required to account for interactions between degenerate states.

- **Validity Range:** The approximation is generally valid if the electric field strength is such that $eE_z z$ is much smaller than the characteristic energy scales of the atom. This is often quantified as $eE_z z \ll E_n^0$, where E_n^0 is the energy of the unperturbed state.

If these conditions are not met, higher-order perturbation theory or a non-perturbative approach might be necessary.

5.5 Conclusion

In first-order perturbation theory, a uniform and constant electric field modifies the energy levels of a one-electron atom by introducing a shift proportional to the expectation value of the position operator along the field direction. This perturbation results in energy shifts only for states with odd parity. The validity of this approximation depends on the strength of the electric field and the degeneracy of the states. For strong fields or degenerate states, higher-order corrections or alternative methods may be required.

6   Effects of a Strong Magnetic Field on the Electronic Energy Levels of One-Electron Atoms

In the presence of a strong magnetic field, the electronic energy levels of one-electron atoms experience significant modifications. This effect is known as the Zeeman effect, which arises from the interaction between the magnetic field and the magnetic moment of the electron. This discussion explores the impact of a strong magnetic field on the electronic energy levels and the properties of the emission spectrum. We will also discuss the conditions under which the strong-field approximation is valid and how it depends on the electronic energy level and the atomic number.

6.1   Effect of a Strong Magnetic Field on Electronic Energy Levels

Zeeman Effect

The Zeeman effect describes the splitting of atomic energy levels in the presence of a magnetic field. For a one-electron atom, the total Hamiltonian in the presence of a magnetic field $\mathbf{B}$ is given by:

$$\hat{H} = \hat{H}_0 + \hat{H}_B,$$

where:

- $\hat{H}_0$ is the unperturbed Hamiltonian of the one-electron atom,

- $\hat{H}_B$ is the Hamiltonian describing the interaction with the magnetic field.

The perturbing Hamiltonian due to the magnetic field is:

$$\hat{H}_B = -\mu \cdot \mathbf{B},$$

where μ is the magnetic moment of the electron. In a uniform magnetic field $\mathbf{B}$ along the z-axis, this can be written as:

$$\hat{H}_B = -\mu_B g \mathbf{S}_z B,$$

where:

- μ_B is the Bohr magneton,

- g is the Landé g-factor, and

- $\mathbf{S}_z$ is the z-component of the electron spin.

For one-electron atoms, the Landé g-factor g is approximately 2. This simplifies the perturbing Hamiltonian to:

$$\hat{H}_B = -2\mu_B \mathbf{S}_z B.$$

Energy Level Splitting

The presence of the magnetic field causes the splitting of the degenerate energy levels into multiple components. The energy shift due to the magnetic field is given by:

$$\Delta E_m = -g\mu_B m_s B,$$

where m_s is the magnetic quantum number associated with the electron spin. For a strong magnetic field, the energy levels split according to the values of m_s, leading to:

$$E_{n,m_s} = E_n^0 + \Delta E_{m_s},$$

where E_n^0 is the unperturbed energy level and ΔE_{m_s} is the shift due to the magnetic field. The splitting increases linearly with the magnetic field strength.

Properties of the Emission Spectrum

In the emission spectrum, the lines corresponding to transitions between different energy levels are split into multiple components due to the magnetic field. The number of components and their separation depend on the strength of the magnetic field and the magnetic quantum numbers of the initial and final states.

- **Multiplet Structure:** The splitting of spectral lines into multiple components creates a multiplet structure. For a given transition, the number of lines observed corresponds to the number of allowed transitions between the split energy levels.

- **Zeeman Splitting Patterns:** The pattern of the splitting depends on the magnetic quantum numbers involved in the transition. For weak fields, the splitting follows the normal Zeeman pattern, while in strong fields, the pattern can become more complex.

- **Intensity Distribution:** The relative intensities of the split components may vary depending on the polarization and selection rules of the transitions.

6.2 Strong-Field Approximation

The strong-field approximation is valid when the magnetic field is sufficiently strong compared to the energy scale of the electronic transitions. The conditions for validity are:

- **Field Strength:** The magnetic field strength B should be large enough so that the Zeeman splitting exceeds the intrinsic energy differences between the magnetic sublevels of the electron. In other words, $\mu_B B \gg \Delta E_n$, where ΔE_n is the energy difference between the electronic levels.

- **Dependence on Electronic Energy Level:** The strong-field approximation depends on the electronic energy level because the Zeeman splitting is proportional to the magnetic moment, which is influenced by the electron's quantum numbers and energy levels. Higher energy levels with larger magnetic quantum numbers exhibit more pronounced splitting.

- **Dependence on Atomic Number:** For one-electron atoms, the magnetic field strength necessary for the strong-field approximation is generally independent of the atomic number since the system involves only one electron. However, for multi-electron atoms, the effective field experienced by the electrons may be influenced by the atomic number.

6.3 Polarization Properties

The polarization properties of the emitted radiation are influenced by the selection rules and the nature of the transitions:

- **Linear Polarization:** The π-transitions (where $\Delta m_J = 0$) are polarized parallel to the magnetic field. They correspond to transitions where the magnetic quantum number m_J remains unchanged.

- **Circular Polarization:** The σ-transitions (where $\Delta m_J = \pm 1$) are polarized perpendicular to the magnetic field. These transitions correspond to changes in the magnetic quantum number m_J by ± 1.

The polarization of the emitted light can be observed by analyzing the light with polarizers aligned along and perpendicular to the magnetic field. The relative intensities of π and σ components provide information about the magnetic field and the atomic transitions.

6.4 Conclusion

A strong magnetic field significantly alters the electronic energy levels of one-electron atoms by inducing a Zeeman splitting that depends linearly on the field strength. This results in a complex emission spectrum with multiple components corresponding to the split energy levels. The strong-field approximation is valid when the magnetic field strength is much larger than the energy scale of the electronic transitions and depends on the specific energy levels and quantum numbers involved. The approximation is typically applicable to both high magnetic field strengths and higher electronic energy levels, with less dependence on the atomic number in the case of one-electron atoms.

7 Properties of an Ideal Gas of Fermions and Application to a Specific Physical System

An ideal gas of fermions is a system of particles that obey the Pauli exclusion principle, which states that no two fermions can occupy the same quantum state simultaneously. This has important implications for the statistical mechanics of such a system. In this discussion, we will outline the key properties of an ideal Fermi gas and then provide an example of a physical system that can be described as a Fermi gas.

7.1 Properties of an Ideal Fermi Gas

An ideal Fermi gas is characterized by the following properties:

1. Fermi-Dirac Statistics

Fermions are particles with half-integer spin and obey Fermi-Dirac statistics. The distribution function for fermions is given by the Fermi-Dirac distribution:

$$f(\epsilon) = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1},$$

where:

- ϵ is the energy of a state,

- μ is the chemical potential (Fermi level),

- k_B is the Boltzmann constant, and

- T is the temperature.

At absolute zero temperature ($T = 0$), all states with energy less than the Fermi energy E_F are occupied, and all states with energy greater than E_F are empty.

2. Fermi Energy and Fermi Temperature

The Fermi energy E_F is the highest occupied energy level at $T = 0$ K. It is given by:

$$E_F = \frac{\hbar^2}{2m} \left(\frac{6\pi^2 N}{V} \right)^{2/3},$$

where:

- $\hbar$ is the reduced Planck constant,

- m is the mass of a fermion,

- N is the number of particles, and

- V is the volume of the gas.

The Fermi temperature T_F is defined as:

$$T_F = \frac{E_F}{k_B}.$$

3. Density of States

The density of states $g(\epsilon)$ for an ideal Fermi gas in three dimensions is:

$$g(\epsilon) = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\epsilon}.$$

This expression represents the number of available quantum states per unit energy interval.

4. Heat Capacity

At low temperatures $(T \ll T_F)$, the heat capacity C_V of a Fermi gas is proportional to T^3 due to the small number of thermally accessible states. At temperatures much higher than the Fermi temperature $(T \gg T_F)$, the heat capacity approaches the classical value given by the equipartition theorem:

$$C_V = \frac{3}{2} N k_B.$$

5. Pauli Exclusion Principle

The Pauli exclusion principle plays a critical role in defining the properties of the Fermi gas. It prevents fermions from occupying the same quantum state, which leads to the phenomenon of Fermi pressure, a consequence of the Pauli exclusion principle.

7.2   Application to a Specific Physical System

A classic example of a physical system that can be described as a Fermi gas is **electrons in a metal**. In metals, the conduction electrons can be treated as a Fermi gas due to their high density and the fact that they obey Fermi-Dirac statistics.

Properties of Electrons in Metals

- **Fermi Energy:** For metals, the Fermi energy is typically in the range of a few electron volts (eV).

- **Low Temperature Behavior:** At low temperatures, the electronic heat capacity of a metal is proportional to T^3, as described above.

- **Electrical Conductivity:** The behavior of conduction electrons in metals can be described by the free electron model, which assumes that electrons form a degenerate Fermi gas.

In this context, the Fermi energy and the temperature dependence of various properties are crucial for understanding the electronic behavior of metals, including their conductivity and heat capacity.

7.3   Conclusion

An ideal Fermi gas exhibits several unique properties due to the Pauli exclusion principle and Fermi-Dirac statistics. Key features include the Fermi energy, the density of states, and the temperature-dependent heat capacity. Electrons in metals serve as a prominent example of a system that can be effectively described by the Fermi gas model, illustrating the practical application of these theoretical concepts in understanding the behavior of conduction electrons.

8 Rotational and Vibrational Transitions of Diatomic Molecules

In diatomic molecules, rotational and vibrational transitions occur due to the quantized nature of molecular rotation and vibration. These transitions are studied within the framework of the Born-Oppenheimer approximation, which separates the electronic, vibrational, and rotational motions. This document explains the rotational and vibrational transitions, their energy ranges, and the observed absorption spectra.

8.1 Born-Oppenheimer Approximation

The Born-Oppenheimer approximation assumes that the electronic and nuclear motions in a molecule can be separated. According to this approximation:

- **Electronic Motion:** The electronic motion is treated as if the nuclei are fixed in space. This simplifies the problem to solving the electronic Schrödinger equation for a fixed nuclear configuration.

- **Vibrational and Rotational Motion:** Given the electronic energy levels, the vibrational and rotational motions of the nuclei are treated as separate, with their own quantized energy levels.

This approximation allows us to decouple the electronic, vibrational, and rotational contributions to the total energy of the molecule.

8.2 Rotational Transitions

Energy Levels

The rotational energy levels of a diatomic molecule are given by:

$$E_J = \frac{\hbar^2}{2I} J(J+1),$$

where:

- J is the rotational quantum number (non-negative integer),

- I is the moment of inertia of the molecule, and

- $\hbar$ is the reduced Planck constant.

The rotational energy levels are typically in the microwave region of the electromagnetic spectrum.

Absorption Spectrum

Rotational transitions occur between different rotational levels. The transition frequency between levels J and J' is:

$$\nu_{J \to J'} = \frac{E_{J'} - E_J}{h},$$

where h is the Planck constant. For a rigid rotor model, this frequency is given by:

$$\nu_{J \to J'} = \frac{\hbar^2}{2Ih} \left[J'(J'+1) - J(J+1) \right].$$

The absorption spectrum in the microwave region shows a series of lines corresponding to these transitions.

8.3 Vibrational Transitions

Energy Levels

The vibrational energy levels of a diatomic molecule are given by the harmonic oscillator model (assuming the molecule behaves like a quantum harmonic oscillator):

$$E_v = \left(v + \frac{1}{2} \right) h\nu_e,$$

where:

- v is the vibrational quantum number (non-negative integer),

- ν_e is the vibrational frequency of the molecule,

- h is the Planck constant.

For more accurate descriptions, anharmonic oscillators are used, leading to:

$$E_v = \left(v + \frac{1}{2}\right) h\nu_e - \left(v + \frac{1}{2}\right)^2 h\omega_e x_e,$$

where $\omega_e x_e$ is the anharmonicity constant.

Absorption Spectrum

Vibrational transitions occur between different vibrational levels and typically fall in the infrared region of the spectrum. The transition frequency between vibrational levels v and v' is:

$$\nu_{v \to v'} = \frac{E_{v'} - E_v}{h}.$$

For a harmonic oscillator, this is:

$$\nu_{v \to v'} = \nu_e \left|v' - v\right|.$$

The absorption spectrum in the infrared region shows a series of lines corresponding to these vibrational transitions.

8.4 Combined Rotational-Vibrational Transitions

In a real diatomic molecule, both rotational and vibrational transitions can occur simultaneously, leading to a combined spectrum. The total energy of the molecule can be expressed as:

$$E_{v,J} = \left(v + \frac{1}{2}\right) h\nu_e - \left(v + \frac{1}{2}\right)^2 h\omega_e x_e + \frac{\hbar^2}{2I} J(J+1).$$

Absorption spectra show features that correspond to transitions between different rotational and vibrational levels. The combined spectra are more complex and are observed as bands in the infrared and microwave regions.

8.5 Conclusion

The rotational and vibrational transitions of diatomic molecules are crucial for understanding molecular spectroscopy. The Born-Oppenheimer approximation simplifies the study of these transitions by separating electronic, vibrational, and rotational motions. Rotational transitions are typically observed in the microwave region, while vibrational transitions are observed in the infrared region. The absorption spectra provide insights into the molecular structure and dynamics, with combined rotational-vibrational spectra offering a more detailed view.

9 Fine Structure Correction in One-Electron Atoms

The energy levels of one-electron atoms (such as hydrogen-like atoms) are determined using the non-relativistic Schrödinger equation. However, fine structure corrections, which account for relativistic effects, further modify these energy levels. These corrections arise from three main phenomena: (1) the relativistic correction to the kinetic energy, (2) spin-orbit coupling, and (3) the Darwin term. In this document, we will provide a phenomenological explanation of each of these corrections, discuss the relevant quantum numbers, and outline the corrections for the unperturbed energy level corresponding to $n = 2$.

The fine structure correction can be understood as a sum of contributions from various relativistic effects. The fine structure energy correction, ΔE_{fs}, for a hydrogen-like atom is given by:

$$\Delta E_{fs} = \Delta E_{\mathrm{rel}} + \Delta E_{\mathrm{SO}} + \Delta E_{\mathrm{D}}.$$

These terms are explained below:

*

(i) Phenomenological Explanation of Different Terms

Relativistic Correction to Kinetic Energy

In non-relativistic quantum mechanics, the kinetic energy of an electron is given by $T = \frac{p^2}{2m}$, where p is the momentum and m is the mass of the electron. However, special relativity modifies this relation. The total energy of an electron moving with momentum p is:

$$E = \sqrt{p^2 c^2 + m^2 c^4},$$

which, in the non-relativistic limit, can be expanded as:

$$E \approx mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2}.$$

The last term in this expansion represents the relativistic correction to the electron's kinetic energy. For an electron in a Coulomb potential, this correction results in a modification to the energy levels, which depends on the principal quantum number n.

Spin-Orbit Coupling

The electron has intrinsic angular momentum, or spin, which interacts with the magnetic field generated by its motion around the nucleus. This interaction, known as spin-orbit coupling, is given by:

$$\Delta E_{\mathrm{SO}} = \frac{1}{2m^2 c^2 r} \frac{1}{r} \frac{dV}{dr} \mathbf{L} \cdot \mathbf{S},$$

where $\mathbf{L}$ is the orbital angular momentum, $\mathbf{S}$ is the spin angular momentum, and $V(r)$ is the Coulomb potential. The spin-orbit term results in a splitting of energy levels depending on the total angular momentum quantum number j, which is related to the orbital l and spin s angular momentum via $\mathbf{j} = \mathbf{l} + \mathbf{s}$.

The Darwin Term

The Darwin term arises from the fact that the electron is not a point particle, but has a spatial extent due to the uncertainty principle. This leads to a small correction in the potential energy for s-states (where $l = 0$). The Darwin correction is given by:

$$\Delta E_{\mathrm{D}} = \frac{\hbar^2}{8m^2 c^2} \nabla^2 V(r).$$

Since $V(r) = -\frac{Ze^2}{r}$, this term only contributes for $l = 0$ states.

Relevant Quantum Numbers

The fine structure correction depends on the following quantum numbers:

- The principal quantum number n, which determines the overall energy level of the electron in the absence of fine structure corrections.

- The orbital angular momentum quantum number l, which influences both the relativistic correction to the kinetic energy and the spin-orbit coupling.

- The total angular momentum quantum number j, which arises from the combination of the electron's spin and orbital angular momentum. It is given by $j = l \pm \frac{1}{2}$.

The fine structure correction to the energy levels is given by the following formula:

$$\Delta E_{fs} = \frac{Z^4 \alpha^2}{n^3} \left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) mc^2,$$

where Z is the atomic number, α is the fine structure constant, and m is the electron mass. This correction leads to a splitting of the energy levels, with different energies for states with different values of j.

Fine Structure for $n = 2$

For $n = 2$, the possible values of the quantum numbers are:

$$l = 0, 1 \quad \text{and} \quad j = \frac{1}{2}, \frac{3}{2}.$$

The unperturbed energy for $n = 2$ is given by the Bohr formula:

$$E_n = -\frac{Z^2}{n^2} mc^2.$$

For $n = 2$, we have:

$$E_2 = -\frac{Z^2}{4} mc^2.$$

After accounting for fine structure, the energy levels split into different values depending on j. For $l = 1$, we have two possible states with $j = \frac{1}{2}$ and $j = \frac{3}{2}$. For $l = 0$, there is only one state with $j = \frac{1}{2}$.

Energy Splitting for $n = 2$

The energy corrections for $n = 2$ are given by:

$$\Delta E_{n=2} = \frac{Z^4 \alpha^2}{2^3} \left(\frac{2}{j + \frac{1}{2}} - \frac{3}{4} \right) mc^2.$$

For $l = 0$ and $j = \frac{1}{2}$, the correction is:

$$\Delta E_{l=0, j=\frac{1}{2}} = \frac{Z^4 \alpha^2}{8} \left(2 - \frac{3}{4} \right) mc^2 = \frac{5 Z^4 \alpha^2}{32} mc^2.$$

For $l = 1$, the corrections are:

$$\Delta E_{l=1, j=\frac{1}{2}} = \frac{Z^4 \alpha^2}{8} \left(\frac{2}{1} - \frac{3}{4} \right) mc^2 = \frac{5 Z^4 \alpha^2}{32} mc^2,$$

$$\Delta E_{l=1, j=\frac{3}{2}} = \frac{Z^4 \alpha^2}{8} \left(\frac{2}{2} - \frac{3}{4} \right) mc^2 = \frac{Z^4 \alpha^2}{32} mc^2.$$

Conclusion

The fine structure correction to the energy levels of one-electron atoms accounts for relativistic effects such as the relativistic correction to kinetic energy, spin-orbit coupling, and the Darwin term. These corrections depend on the quantum numbers n, l, and j, and lead to a splitting of the energy levels. For $n = 2$, the energy levels split into three distinct levels due to spin-orbit interaction and other relativistic effects.

10 Selection Rules for the Absorption of Radiation by Atoms

The absorption of radiation by atoms is governed by quantum mechanical selection rules, which dictate the allowed transitions between atomic energy levels. These selection rules are derived under the low-intensity field and dipole approximations, where the electromagnetic field interacts weakly with the atom, and the dominant interaction is through the electric dipole moment. In this discussion, we explore the selection rules for both one-electron and multi-electron atoms.

10.1 Dipole Approximation

In the dipole approximation, the interaction between an atom and an electromagnetic field is treated by assuming that the wavelength of the radiation is much larger than the size of the atom. The Hamiltonian describing the interaction is simplified to:

$$\hat{H}_{\text{int}} = -\mathbf{d} \cdot \mathbf{E},$$

where:

- $\mathbf{d}$ is the electric dipole moment of the atom,

- $\mathbf{E}$ is the electric field of the radiation.

The transition probability between two states is proportional to the square of the matrix element of the dipole operator between the initial and final states:

$$\langle \psi_f | \hat{\mathbf{d}} | \psi_i \rangle.$$

Non-zero matrix elements indicate allowed transitions, while zero matrix elements indicate forbidden transitions. The selection rules arise from evaluating these matrix elements based on the symmetries of the atomic states.

10.2 Selection Rules for One-Electron Atoms

In one-electron atoms (such as hydrogen-like atoms), the quantum numbers involved are:

- n — principal quantum number,

- l — orbital angular momentum quantum number,

- m_l — magnetic quantum number (projection of l along the z-axis),

- $s = 1/2$ — spin quantum number,

- $m_s = \pm 1/2$ — spin magnetic quantum number.

For electric dipole transitions, the selection rules are as follows:

Orbital Angular Momentum

The electric dipole operator is a vector operator and can change the orbital angular momentum by $\Delta l = \pm 1$. Thus, the selection rule for the orbital angular momentum quantum number is:

$$\Delta l = \pm 1.$$

This means that an electron can only transition between states where the orbital angular momentum changes by 1. For example, a transition from a p-state ($l = 1$) to an s-state ($l = 0$) or a d-state ($l = 2$) is allowed, but a transition between two s-states ($l = 0$) is forbidden.

Magnetic Quantum Number

The magnetic quantum number m_l can change by $\Delta m_l = 0, \pm 1$ during a dipole transition. Therefore, the selection rule for the magnetic quantum number is:

$$\Delta m_l = 0, \pm 1.$$

This governs the orientation of the angular momentum in space during the transition. The $\Delta m_l = 0$ transitions are often referred to as π-transitions, while $\Delta m_l = \pm 1$ transitions are σ-transitions.

Spin Quantum Number

The electric dipole operator does not affect the spin of the electron, so the spin quantum number remains unchanged. The selection rule for the spin quantum number is:

$$\Delta s = 0.$$

10.3   Selection Rules for Multi-Electron Atoms

In multi-electron atoms, the situation becomes more complex due to electron-electron interactions. The quantum numbers involved are:

- L — total orbital angular momentum,

- S — total spin angular momentum,

- J — total angular momentum ($J = L + S$),

- M_J — projection of J along the z-axis.

The selection rules for electric dipole transitions in multi-electron atoms are based on similar principles as for one-electron atoms, but they apply to the total quantum numbers.

Total Orbital Angular Momentum

The selection rule for the total orbital angular momentum quantum number L is:

$$\Delta L = \pm 1.$$

This rule governs the change in the total orbital angular momentum during a transition.

Total Spin Angular Momentum

As with one-electron atoms, the electric dipole operator does not change the spin of the atom. The selection rule for the total spin angular momentum quantum number S is:

$$\Delta S = 0.$$

This rule implies that electric dipole transitions cannot change the total spin of the atom.

Total Angular Momentum

The total angular momentum quantum number J is the sum of the total orbital angular momentum and the total spin angular momentum. The selection rule for J is:

$$\Delta J = 0, \pm 1, \quad \text{but} \quad J = 0 \rightarrow J = 0.$$

This rule means that J can change by 0 or ± 1, except that a transition between two states with $J = 0$ is forbidden.

Magnetic Quantum Number

Similar to one-electron atoms, the magnetic quantum number M_J can change by:

$$\Delta M_J = 0, \pm 1.$$

This governs the change in the projection of the total angular momentum during the transition.

10.4   Conclusion

The selection rules for the absorption of radiation by atoms are determined by the symmetries of the atomic states and the properties of the electric dipole operator. In both one-electron and multi-electron atoms, these rules govern the allowed transitions between energy levels. For one-electron atoms, the key rules involve changes in the orbital angular momentum and the magnetic quantum number, while the spin remains unchanged. In multi-electron atoms, the total angular momentum, total spin, and magnetic quantum number determine the allowed transitions, with similar restrictions on the changes in quantum numbers.

11 Solution of the Schrödinger Equation for the H$_2$ Molecule in the Born-Oppenheimer Approximation

The hydrogen molecule (H$_2$) is the simplest neutral molecule, consisting of two protons and two electrons. Solving the Schrödinger equation for the H$_2$ molecule is a fundamental problem in molecular quantum mechanics. The Born-Oppenheimer approximation is a widely used method that simplifies the solution by separating the electronic and nuclear (proton) motions. This document discusses the solution of the Schrödinger equation for H$_2$ within this approximation, focusing on the evaluation of the electronic ground state energy and its dependence on the internuclear distance.

11.1 Born-Oppenheimer Approximation

The Born-Oppenheimer approximation exploits the fact that the protons, being much heavier than the electrons, move much more slowly. Thus, the electronic and nuclear motions can be treated separately. The total wave function of the system $\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}_1, \mathbf{R}_2)$, where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the coordinates of the electrons and $\mathbf{R}_1$, $\mathbf{R}_2$ are the coordinates of the nuclei, is expressed as:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}_1, \mathbf{R}_2) = \psi_{\text{elec}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}_1, \mathbf{R}_2)\chi_{\text{nuc}}(\mathbf{R}_1, \mathbf{R}_2),$$

where:

- $\psi_{\text{elec}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}_1, \mathbf{R}_2)$ is the electronic wave function for fixed nuclei,

- $\chi_{\text{nuc}}(\mathbf{R}_1, \mathbf{R}_2)$ is the nuclear wave function.

In the Born-Oppenheimer approximation, we first solve the electronic Schrödinger equation for fixed positions of the nuclei and then use the resulting electronic energy to solve the nuclear motion problem.

11.2 Electronic Schrödinger Equation

For fixed nuclear positions, the electronic Schrödinger equation for the H$_2$ molecule is:

$$\hat{H}_{\text{elec}}\psi_{\text{elec}} = E_{\text{elec}}(R)\psi_{\text{elec}},$$

where $\hat{H}_{\text{elec}}$ is the electronic Hamiltonian, and $R = |\mathbf{R}_1 - \mathbf{R}_2|$ is the internuclear distance. The electronic Hamiltonian is given by:

$$\hat{H}_{\text{elec}} = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{|\mathbf{r}_1 - \mathbf{R}_1|} - \frac{e^2}{|\mathbf{r}_1 - \mathbf{R}_2|} - \frac{e^2}{|\mathbf{r}_2 - \mathbf{R}_1|} - \frac{e^2}{|\mathbf{r}_2 - \mathbf{R}_2|} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}.$$

Here, the terms correspond to the kinetic energy of the two electrons, the Coulomb attraction between the electrons and the nuclei, and the electron-electron repulsion. The repulsion between the two nuclei $\frac{e^2}{R}$ is treated as a constant for fixed internuclear distance.

11.3 Ground State Energy Evaluation

To determine the ground state energy, we solve the electronic Schrödinger equation for the lowest energy state (the electronic ground state). The exact solution of this equation is not feasible analytically, but it can be approximated using methods such as the variational method or molecular orbital theory.

In the simplest approximation, the molecular orbitals are constructed as linear combinations of atomic orbitals (LCAO approximation). For the hydrogen molecule, the molecular wave function is approximated as:

$$\psi_{\text{elec}} \approx \psi_{1s}(\mathbf{r}_1 - \mathbf{R}_1)\psi_{1s}(\mathbf{r}_2 - \mathbf{R}_2) + \psi_{1s}(\mathbf{r}_1 - \mathbf{R}_2)\psi_{1s}(\mathbf{r}_2 - \mathbf{R}_1).$$

Using this approximation, the total electronic energy $E_{\text{elec}}(R)$ as a function of the internuclear distance R can be estimated. The energy typically has the form:

$$E_{\text{elec}}(R) = -\frac{e^2}{R} + \frac{A}{R^2} - Be^{-\alpha R},$$

where A, B, and α are parameters determined from the electronic wave function and interaction terms.

11.4 Relation Between Fundamental State Energy and Internuclear Distance

The total energy of the H_2 molecule as a function of the internuclear distance R consists of the electronic energy $E_{elec}(R)$ and the repulsive Coulomb energy between the two nuclei:

$$E_{tot}(R) = E_{elec}(R) + \frac{e^2}{R}.$$

At large distances $R \to \infty$, the energy approaches the dissociation limit, which corresponds to two separate hydrogen atoms with energy:

$$E_{diss} = 2E_H = -27.2\,\text{eV}.$$

At smaller distances, the attractive interaction between the electrons and nuclei dominates, leading to a minimum in the potential energy curve. This minimum corresponds to the equilibrium bond length R_{eq} and the binding energy of the molecule.

The equilibrium bond length R_{eq} is the distance where the total energy $E_{tot}(R)$ is minimized:

$$\frac{dE_{tot}(R)}{dR} = 0 \quad \text{at} \quad R = R_{eq}.$$

For H_2, the equilibrium bond length is approximately $R_{eq} \approx 0.74\,\text{Å}$, and the binding energy is about $4.52\,\text{eV}$.

11.5 Conclusion

In the Born-Oppenheimer approximation, the Schrödinger equation for the H_2 molecule is solved by first determining the electronic energy for fixed nuclear positions. The total energy as a function of the internuclear distance R reveals a minimum at the equilibrium bond length, which corresponds to the binding energy of the molecule. The approximation allows for a clear separation of electronic and nuclear motions, simplifying the problem significantly.

12   The Born-Oppenheimer Approximation and Its Effect on the Absorption Spectra of Diatomic Molecules

The Born-Oppenheimer approximation is a fundamental approach in molecular quantum mechanics that simplifies the complex problem of solving the molecular Schrödinger equation by separating the nuclear and electronic motions. This approximation is especially useful in studying diatomic molecules, where the interaction between two atoms leads to distinct vibrational and rotational energy levels. The Born-Oppenheimer approximation has significant implications for the absorption spectra of diatomic molecules, particularly in the way electronic, vibrational, and rotational transitions are treated. This document discusses the Born-Oppenheimer approximation and its effects on the absorption spectra of diatomic molecules.

12.1   Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is based on the observation that nuclei are much heavier than electrons, and therefore their motion occurs on very different timescales. The approximation separates the molecular wave function into electronic and nuclear components. The total molecular wave function $\Psi(\mathbf{r}, \mathbf{R})$, where $\mathbf{r}$ are the electronic coordinates and $\mathbf{R}$ are the nuclear coordinates, is written as:

$$\Psi(\mathbf{r}, \mathbf{R}) = \psi_{\text{elec}}(\mathbf{r}; \mathbf{R})\chi_{\text{nuc}}(\mathbf{R}),$$

where:

- $\psi_{\text{elec}}(\mathbf{r}; \mathbf{R})$ is the electronic wave function for fixed nuclear positions,

- $\chi_{\text{nuc}}(\mathbf{R})$ is the nuclear wave function, which includes vibrational and rotational components.

The approximation involves solving the electronic Schrödinger equation for a fixed nuclear configuration:

$$\hat{H}_{\text{elec}}\psi_{\text{elec}}(\mathbf{r}; \mathbf{R}) = E_{\text{elec}}(\mathbf{R})\psi_{\text{elec}}(\mathbf{r}; \mathbf{R}),$$

where $\hat{H}_{\text{elec}}$ is the electronic Hamiltonian. The result is an electronic energy $E_{\text{elec}}(\mathbf{R})$ that depends parametrically on the nuclear positions. This energy then acts as a potential in the nuclear Schrödinger equation, which governs the vibrational and rotational motion of the nuclei:

$$\left[-\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 + E_{\text{elec}}(\mathbf{R}) \right] \chi_{\text{nuc}}(\mathbf{R}) = E_{\text{tot}}\chi_{\text{nuc}}(\mathbf{R}),$$

where M is the reduced mass of the nuclei, and E_{tot} is the total energy of the molecule.

12.2   Effect on the Energy Levels

In diatomic molecules, the total energy levels are composed of three distinct contributions:

- **Electronic energy** E_{elec},

- **Vibrational energy** E_{vib},

- **Rotational energy** E_{rot}.

The total energy is approximately the sum of these contributions:

$$E_{\text{tot}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}}.$$

12.2.1   Vibrational Energy Levels

The vibrational energy levels correspond to the quantized motion of the nuclei along the internuclear axis, treated as a harmonic or anharmonic oscillator. The vibrational energy levels are given by:

$$E_{\text{vib}}(v) = \left(v + \frac{1}{2} \right) h\nu_{\text{vib}},$$

where $v = 0, 1, 2, \ldots$ is the vibrational quantum number, and ν_{vib} is the vibrational frequency of the molecule.

12.2.2 Rotational Energy Levels

The rotational energy levels arise from the quantized rotational motion of the molecule as a rigid rotor. The rotational energy levels are given by:

$$E_{\mathrm{rot}}(J) = BJ(J+1),$$

where $J = 0, 1, 2, \ldots$ is the rotational quantum number, and B is the rotational constant, which depends on the moment of inertia of the molecule.

12.3 Absorption Spectra of Diatomic Molecules

The absorption spectra of diatomic molecules are determined by transitions between the quantized energy levels associated with the electronic, vibrational, and rotational states. In the Born-Oppenheimer approximation, these transitions are treated independently, although they can be coupled in practice.

12.3.1 Electronic Transitions

Electronic transitions involve the promotion of an electron from one molecular orbital to another. The energy difference between electronic states typically corresponds to the ultraviolet (UV) or visible regions of the electromagnetic spectrum. The selection rules for electric dipole transitions between electronic states are:

$$\Delta\Lambda = 0, \pm 1, \quad \Delta S = 0, \quad \Delta\Sigma = 0.$$

Here, Λ is the projection of the orbital angular momentum along the internuclear axis, S is the total spin quantum number, and Σ is the spin projection quantum number.

12.3.2 Vibrational Transitions

Within each electronic state, the molecule can undergo vibrational transitions between different vibrational energy levels. These transitions typically occur in the infrared (IR) region of the spectrum. The selection rule for vibrational transitions is:

$$\Delta v = \pm 1.$$

12.3.3 Rotational Transitions

The molecule can also undergo rotational transitions between different rotational energy levels. Rotational transitions occur within both electronic and vibrational states and are observed in the microwave or far-infrared region. The selection rule for rotational transitions is:

$$\Delta J = \pm 1.$$

12.3.4 Combined Transitions

In practice, vibrational and rotational transitions often occur simultaneously with electronic transitions. The absorption spectrum of a diatomic molecule thus consists of a series of closely spaced lines, corresponding to combined electronic, vibrational, and rotational transitions. The total transition energy is given by:

$$\Delta E = \Delta E_{\mathrm{elec}} + \Delta E_{\mathrm{vib}} + \Delta E_{\mathrm{rot}}.$$

This leads to the characteristic band structure observed in the absorption spectra of diatomic molecules, where each electronic transition is accompanied by a progression of vibrational and rotational transitions.

12.4 Temperature Dependence of the Spectra

The temperature of the gas affects the population distribution among the vibrational and rotational energy levels, according to the Boltzmann distribution. At higher temperatures, a larger number of molecules occupy higher vibrational and rotational states, leading to more intense transitions involving these higher energy levels. This results in a broadening of the absorption spectrum.

12.5   Conclusion

The Born-Oppenheimer approximation provides a powerful framework for understanding the structure and spectra of diatomic molecules by separating electronic, vibrational, and rotational motions. In the absorption spectra of diatomic molecules, transitions between these energy levels lead to distinct spectral features. Electronic transitions typically occur in the UV or visible regions, vibrational transitions in the infrared, and rotational transitions in the microwave or far-infrared regions. The combination of these transitions gives rise to the complex band structures observed in molecular absorption spectra, and the temperature of the gas influences the population of these energy levels and the resulting spectral lines.