

1.2: Matter (Component 2)

A typical molecule will have thousands of possible energy levels involving rotational, vibrational and electronic excitations and combinations thereof. However, relatively few transitions between these states will be allowed. Rules restricting transitions between states are called **Selection Rules**. They all have a basis in symmetry of the molecules. Thus, Group theory is a powerful tool to develop selection rules, and thus, to interpret the observed spectra.

From undergraduate quantum mechanics, you are familiar with the solutions to the time-independent Schrödinger Equation

$$H^{(0)}\psi_n(\vec{r}) = E_n\psi_n(\vec{r})$$

or in bra/ket notation

$$\hat{H}^{(0)}|n\rangle = E_n|n\rangle$$

which can be solved exactly for many systems, such as the harmonic oscillator, the rotating diatomic (rigid) molecule, and the H-atom and numerically for the rest. The wavefunctions, $\{|n\rangle\}$, are called **stationary** states with energies $\{E_n\}$. These are solutions to the time-independent Schrödinger equation.

If \hat{H} is absolutely independent of time, then a molecule described by a particular ψ_n will stay in that state forever. There will be no possibility for transitions between different ψ_n , which is the essence of spectroscopy. Transitions between stationary states can only happen in the presence of a time-dependent Hamiltonian. This is provided by the oscillating electric and magnetic fields of the radiation. So the total Hamiltonian is now

$$H_{tot} = H^{(0)} + H^{(1)}(t)$$

where $H^{(1)}(t)$ is the time-dependent Hamiltonian that describes the interaction with the electromagnetic radiation.

Electric Dipole Coupling

Ultraviolet and visible radiation interacts with matter which causes electronic transitions (promotion of electrons from the ground state to a high energy state). The ultraviolet region falls in the range between 190-380 nm, the visible region falls between 380-750 nm. For the interaction of the oscillating electric field, $\vec{E}(t)$ of monochromatic radiation of frequency, ν , with the electrons of the molecules,

$$H^{(1)}(t) = \vec{E} \cdot \vec{\mu} \cos(\pi\nu t) \quad (1.2.1)$$

where \vec{E} is the amplitude of the oscillating **electric field vector** and $\vec{\mu}$ is the **electric dipole moment** of the molecule and ν is the frequency of the radiation. The electric dipole moment is a summation of all charges in the species.

$$\vec{\mu} = -e \sum_i \vec{R}_i$$

\vec{E} is polarized in a plane to the direction of propagation. Generally, light is depolarized meaning that polarization is uniformly distributed in the XY plane for Z direction. Laser radiation, in contrast, is often plane polarized, with a simple polarization in the XY plane or at some angle.

For Reference

The energy of 285 nm photons is $6.97 \times 10^{-19} J$ and for one mole of photon 419.7 kJ/mol

The mean wavelength in visible is 565 nm. The energy of 565 nm photons is $3.52 \times 10^{-19} J$ and for one mole of photon 211.7 kJ/mol

If the radiation is not strong, then $H^{(1)}(t) \ll H^{(0)}$ and the change introduced by $H^{(1)}(t)$ can be treated as a perturbation, e.g., [1st order transition theory](#). We will not go through the steps here, which are covered in many standard textbooks in Quantum Mechanics.

From such approaches, we get an expression for the transition probability is often called "**Fermi's Golden Rule**"

$$W_{i \rightarrow f} = \left(\frac{4\pi}{h} \right) |H_{fi}^{(1)}|^2 \rho(\Delta E)$$

where

- i and f label the initial and final states in the transition
- $W_{i \rightarrow f}$ is the probability per unit time that a transition occurs.
- $\rho_N(\Delta E)$ is the density of final states and
- $\Delta E = \text{abs}(E_f - E_i)$ in dimensions of energy⁻¹. This important part of is $W_{i \rightarrow f}$ is $H_{fi}^{(1)}$

$$H_{fi}^{(1)} = \langle f | H^{(1)} | i \rangle \quad (1.2.2)$$

For example, for the **electric dipole-induced transition** (Equation 1.2.1), the coupling element is

$$H_{fi}^{(1)} = \vec{E} \cdot \langle f | \vec{\mu} | i \rangle \quad (1.2.3)$$

other transitions (e.g., electric quadrupole-induced transition, magnetic dipole-induced transitions, etc) will have different expressions.

If this matrix element of the perturbed Hamiltonian is non-zero, then transitions **CAN** be induced from $|i\rangle$ to $|f\rangle$. The importance of symmetry is that the integrals (Equation 1.2.2 or 1.2.3) can often be shown to be ZERO, using group theory arguments. **We will be getting to this later.** Transitions can be assigned because we know that some for them cannot occur or can only occur with some probability with a weak absorption from the applied radiation (within 1st order perturbation theory).

Separation of Eigenstates

Born-Oppenheimer approximation: energy separated into three types rotational levels superimposed on vibrational levels and vibrational levels superimposed on electronic levels.

$$\Delta E = \Delta E_{\text{electronic}} + \Delta E_{\text{vibration}} + \Delta E_{\text{rotation}}$$

And there is a strong separation of magnitude in these energies (Figure 1.2.1):

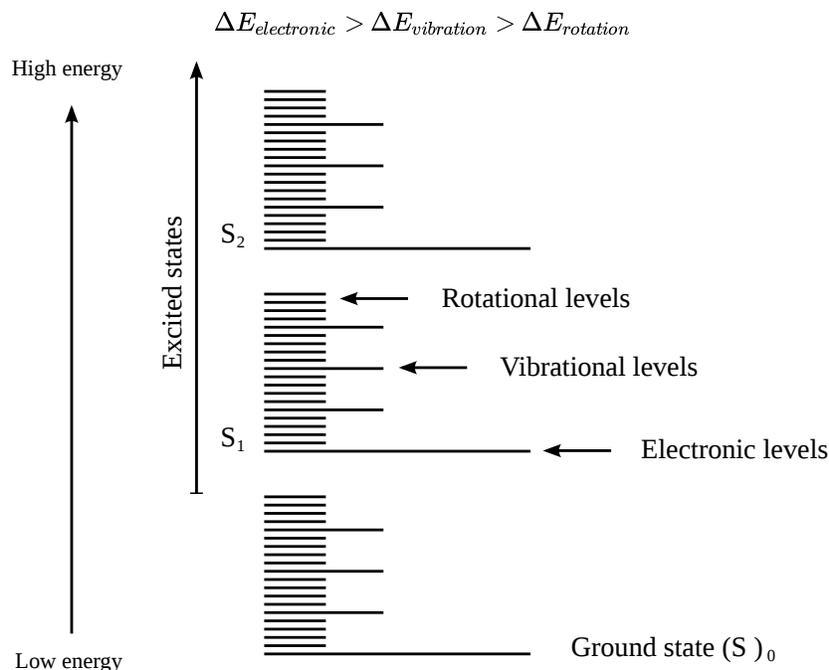


Figure 1.2.1: A diagram representing singlet energy-levels in a molecule to help explain the concept of electronic, rotational and vibrational energy-levels to my students. (CC BY-SA 3.0; Lvzon via [Wikipedia](https://en.wikipedia.org/wiki/Born-Oppenheimer_approximation))

The energy levels (eigenstates) can be rated in the following order **electronic > vibrational > rotational**. Each of these transitions differ by an order of magnitude. Rotational transitions occur at lower energies (longer wavelengths) and this energy is insufficient

and cannot cause vibrational and electronic transitions, but vibrational (near infra-red) and electronic transitions (ultraviolet region of the electromagnetic spectrum) require higher energies. The diagram below illustrates possible transitions that occur.

- transitions represents pure rotational changes (far infrared).
- transitions rotational-vibrational (rovibrational) transitions;
- transitions are rotational-vibrational-electronic transitions (visible and ultraviolet) S_0 is electronic ground state and S_1 and S_2 are electronic excited states.

For a transition to be spectroscopically observed

1. There must exist a coupling mechanism (via $H^{(1)}$) between initial and final eigenstates
2. The initial eigenstate ($|i\rangle$) must be **populated** (e.g., d^0 d-d electronic transition). Since most spectroscopies involve molecules/systems that are **thermally populated**, then the Boltzmann distribution is required

$$p_i = \frac{e^{-E_i/kT}}{Q}$$

with

$$Q = \sum_i^{\infty} e^{-E_i/kT}$$

(assuming non-degenerate eigenstates)

3. The final eigenstate ($|f\rangle$) must be **unpopulated** (e.g., d^{10} d-d electronic transitions)

Note

At room temperature ($kT = 200 \text{ cm}^{-1}$), most electronic transitions occur from $v = 0$, but not from $J = 0$ eigenstate. So potentially multiple excitation transitions typically coexist.

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