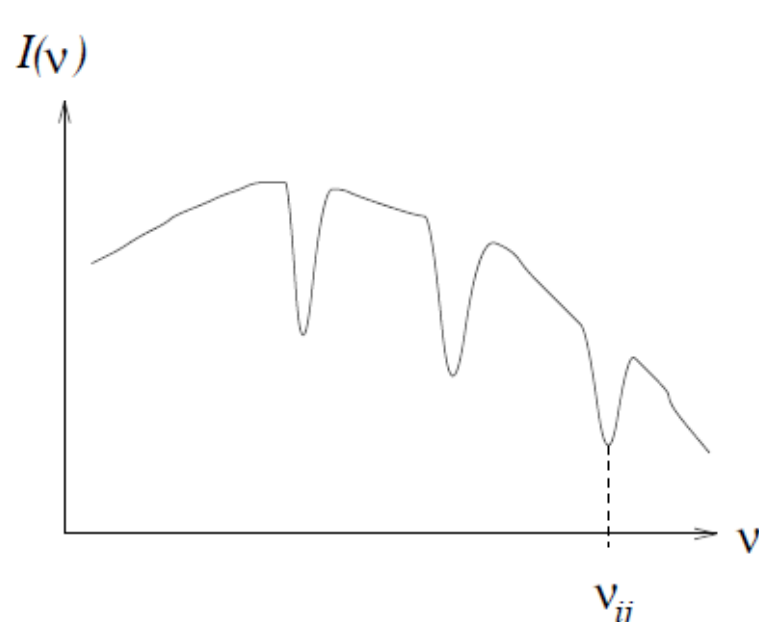
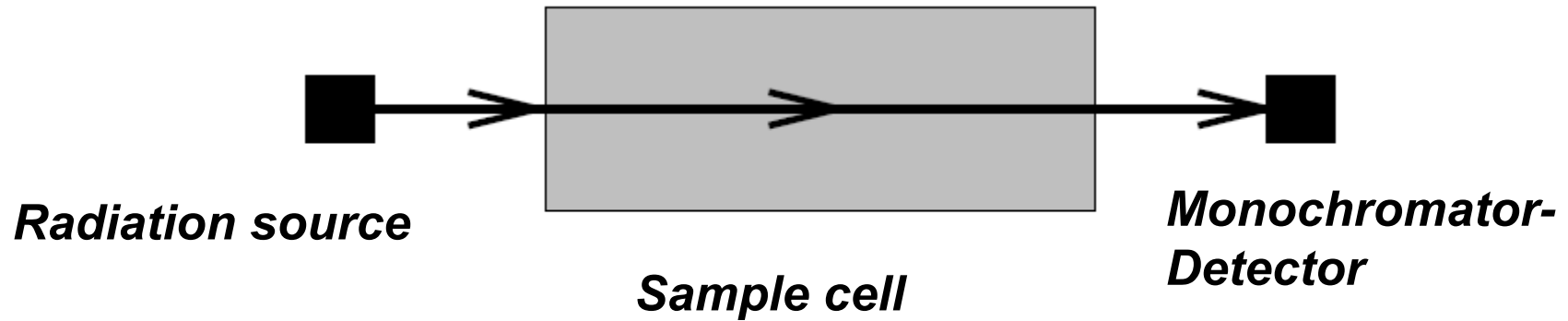
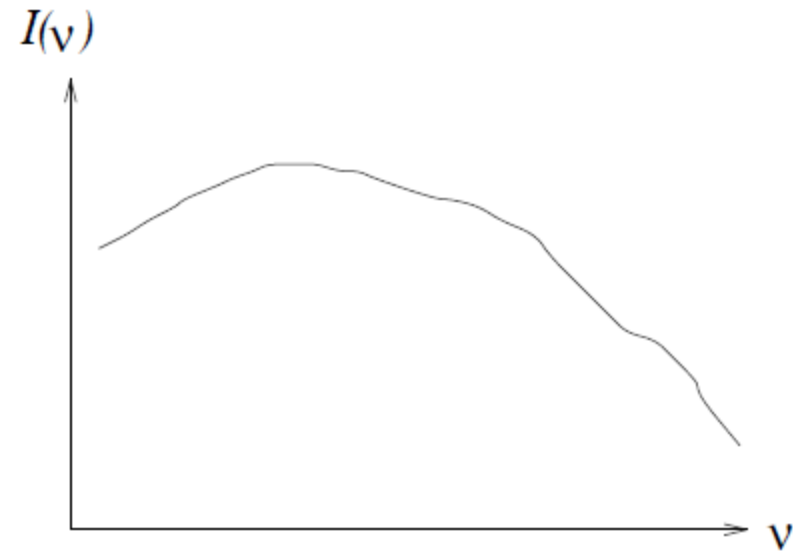


Spectroscopy in summary

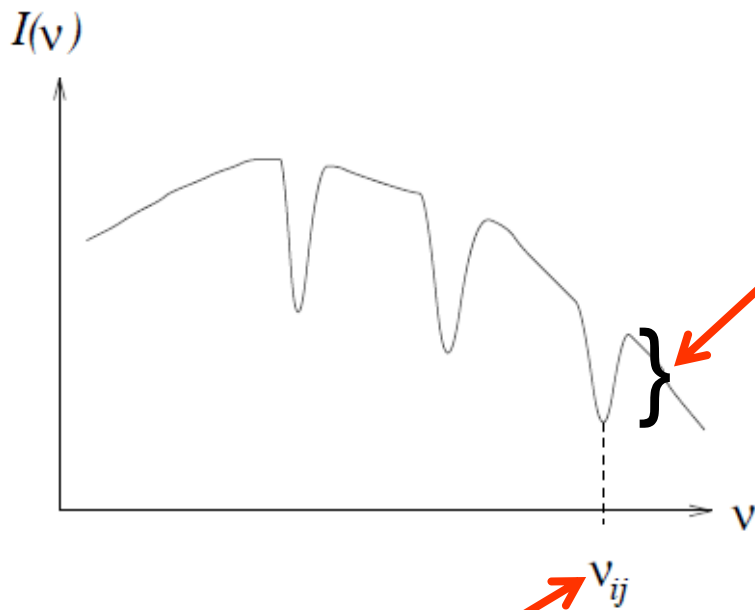
Simple absorption experiment



Absorption spectrum



Reference (background) spectrum



Intensities of spectral lines

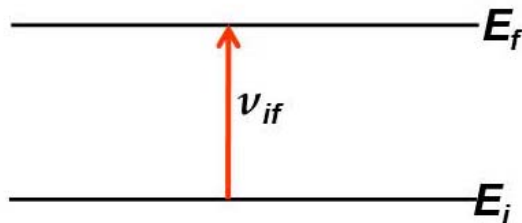
Integrated absorption coefficient (weak radiation)

$$I(f \leftarrow i) = \frac{8\pi^3 N_A \nu_{if}}{(4\pi\epsilon_0)3hc^2} F(E_i) R_{\text{stim}}(f \rightarrow i) S(f \leftarrow i)$$

Line strength

$$S(f \leftarrow i) = \sum_{A=X,Y,Z} |\langle \Phi_f^* \mu_A \Phi_i \rangle|^2$$

The positions of spectral lines



Bohr frequency condition

$$h\nu_{if} = E_f - E_i = \Delta E_{if}$$

We require the molecular energies E_j for the line positions and the wavefunctions Φ_j for the intensities.

Consequently, we must solve the time-independent Schrödinger equation:

$$\hat{H}\Phi_j = E_j \Phi_j$$

! ? ? ?

Quantum Mechanics

One-particle systems (I)

We consider a particle of mass m moving with kinetic energy T in a **time-independent** potential $V(\mathbf{r})$.

Classically, the total energy is:

$$(1) \quad E = T + V(\mathbf{r}) = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) + V(x, y, z)$$

Quantum-mechanically, the associated Hamiltonian \hat{H} is obtained by replacing the spatial and linear momentum coordinates in (1) by the corresponding operators:

$$(2) \quad \hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(x, y, z)$$

One-particle systems (II)

The possible energies E_n of the system are obtained by solving the **time-independent Schrödinger equation**:

$$(3) \quad \hat{H}(x, y, z)\Psi_n(x, y, z) = E_n\Psi_n(x, y, z)$$

In shorthand notation:

$$(4) \quad \hat{H}\Psi_n = E_n\Psi_n$$

Ψ_n is the wave function of the n -th state.

Summary: exact solutions

System	degrees of freedom	quantum numbers	energy eigenvalues	wave functions	nodes
Particle in a box, $V=0$	1	n	$\frac{\hbar^2}{8mL^2} n^2$	$\sqrt{2/L} \sin \frac{n\pi}{L} x$	$n-1$
Particle in a box, $V=0$	3	n_x, n_y, n_z	$\frac{\hbar^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$	$\Psi_{n_x}(x) \Psi_{n_y}(y) \Psi_{n_z}(z)$	$n_x + n_y + n_z - 3$
Harmonic oscillator, $V = \frac{1}{2} kx^2$	1	ν	$\hbar\omega(\nu + \frac{1}{2})$	$N_\nu H_\nu(y) e^{-y^2/2}$	ν
Rigid rotor, $V=0$	2	l, m	$\frac{\hbar^2}{2I} l(l+1)$	$Y_l^m(\theta, \varphi)$	l
H atom, $V = -Ze^2/r$	$6 \rightarrow 3$	n, l, m	$-\frac{Z^2 e^2}{2a} \frac{1}{n^2}$	$R_{nl}(r) Y_{lm}(\theta, \varphi)$	$n-1$

Exact solutions of the Schrödinger equation

Typical quantum effects:

- Quantization of the energy
- Quantization of the angular momentum
- Incomplete knowledge of angular momenta
- Zero-point energies
- Reach of classically forbidden areas

Applications:

- Spectroscopy
- Statistical thermodynamics
- Reference for approximate solutions

***How do we solve a
Schrödinger
equation?***

Variation method (I)

Variation theorem: The expectation value E_Ψ calculated with an arbitrary permissible wave function Ψ is an upper bound for the exact energy E_0 of the ground state of the system.

$$(9) \quad E_\Psi = \langle \Psi | \hat{H} \Psi \rangle \geq E_0 \quad (\Psi \text{ normalized})$$

Variation principle: Among all permissible wave functions Ψ for the ground state, look for the function resulting in the lowest expectation value E_Ψ .

$$(10) \quad E_\Psi \rightarrow \text{minimum}$$

Variation method (II)

Practical procedure:

A trial variation function with free parameters α_i is chosen for Ψ , and these parameters are determined according to the variation principle such that the best approximate solution is obtained with this type of trial function.

This corresponds to an **extreme-value** problem where the variation δE_Ψ must vanish for arbitrary variations of the parameters α_i .

$$(11) \delta E_\Psi(\alpha_1, \alpha_2, \dots) = \frac{\partial E_\Psi}{\partial \alpha_1} d\alpha_1 + \frac{\partial E_\Psi}{\partial \alpha_2} d\alpha_2 + \dots = 0$$

Since the variations $d\alpha_i$ are arbitrary, we have:

$$(12) \frac{\partial E_\Psi}{\partial \alpha_i} = 0 \quad \text{for all } i.$$

Linear variational calculations (I)

The variation function Ψ is written as a linear combination of n basis functions ϕ_i :

$$(13) \quad \Psi = \sum_{i=1}^n c_i \phi_i$$

The coefficients c_i are varied until the energy expectation value reaches a minimum.

$$(14) \quad E_{\Psi} = \frac{\langle \Psi | \hat{H} \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (\Psi \text{ not normalized})$$

$$(15) \quad \frac{\partial E_{\Psi}}{\partial c_i} = 0 \quad \text{for } i = 1, 2, \dots, n$$

Linear variational calculations (II)

The variational calculation leads to the **secular equations**:

$$(16) \quad \sum_j (H_{ij} - E_{\Psi} S_{ij}) c_j = 0 \quad \text{for } i = 1, 2, \dots, n$$

$$(17) \quad H_{ij} = \langle \phi_i | \hat{H} \phi_j \rangle = H_{ji} \quad (\text{matrix element of } \hat{H})$$

$$(18) \quad S_{ij} = \langle \phi_i | \phi_j \rangle = S_{ji} \quad (\text{overlap integral})$$

Known: integrals H_{ij} and S_{ij}

Unknown: coefficients c_j and associated energy E_{Ψ}

Linear variational calculations (III)

Linear algebra: nontrivial solution of the set of simultaneous, linear, homogeneous equations (16) if

$$(19) \quad | H_{ij} - E_{\Psi} S_{ij} | = 0$$

The solution of this secular determinant results in n energies E_k , the smallest one being the variational energy of the ground state. For every energy E_k , the corresponding coefficients c_{jk} and hence the wavefunction Ψ_k are determined from eqs.(16).

Linear variational calculations (IV)

Use of an additional index in order to distinguish between different solutions:

$$(20) \quad \Psi_k = \sum_{j=1}^n c_{jk} \phi_j$$

$$(21) \quad \sum_j H_{ij} c_{jk} = \sum_j S_{ij} c_{jk} E_k \quad \text{for } i, k = 1, 2, \dots, n$$

Matrix notation:

$$(22) \quad \mathbf{H} = \{H_{ij}\}, \mathbf{C} = \{c_{ij}\}, \mathbf{S} = \{S_{ij}\}, \mathbf{E} = \{E_i \delta_{ij}\}$$

$$(23) \quad \mathbf{HC} = \mathbf{SCE}$$

\mathbf{H} and \mathbf{S} are real and symmetric for real basis functions, \mathbf{E} is a diagonal matrix.

Linear variational calculations (V)

Important special case: Orthonormalized basis.

$$(24) \quad S_{ij} = \delta_{ij}$$

$$(25) \quad \mathbf{HC} = \mathbf{CE}$$

\mathbf{H} is the matrix representation of the Hamiltonian in the chosen orthonormalized basis. **Diagonalization** of \mathbf{H} yields the energy eigenvalues (diagonal elements of \mathbf{E}) and the eigenvectors (columns of \mathbf{C}). It is:

$$(26) \quad \mathbf{E} = \mathbf{C}^{-1}\mathbf{HC} = \mathbf{C}^T\mathbf{HC}$$

$$(27) \quad \mathbf{C}^T\mathbf{C} = \mathbf{I} \text{ resp. } \sum_j c_{jk}^2 = 1 \quad \text{for } k = 1, 2, \dots, n$$

The inverse and transpose of matrix \mathbf{C} are equal. The eigenvectors are orthonormalized.

***In practice:
convert Schrödinger
equation to matrix
eigenvalue equation***

***Diagonalize matrix with
computer***

Basis functions?

$$\Psi_k = \sum_{j=1}^n c_{jk} \phi_j$$

How do we choose these basis functions?

Wavefunctions and expansion coefficients are initially unknown – the basis functions must be chosen.

Example: Rotation-vibration problem:

Basis of eigenfunctions for „model“ molecule:

- Rigidly rotating molecule***
- Harmonically vibrating molecule***

Many-Particle Systems

Overview: many-particle systems

For systems with three or more interacting particles no exact solutions of the Schrödinger equation are available, but only approximate solutions.

Goal:

- Treatment of many-particle systems, consisting of M atomic nuclei (spatial coordinates \mathbf{R}_A , spin coordinates σ_A , nuclear charge numbers Z_A , masses M_A) and N electrons (spatial coordinates \mathbf{r}_i , spin coordinates s_i , mass m_e).
- Approximate solutions of the corresponding **nonrelativistic time-independent Schrödinger equation** $\hat{H}\Psi = E\Psi$.
- The **Hamiltonian** $\hat{H}(\mathbf{r},\mathbf{R})$ takes into account the kinetic energy of the nuclei and electrons as well as the potential energy of all Coulomb interactions.
- The **wave function** $\Psi(\mathbf{r},\mathbf{R},\mathbf{s},\boldsymbol{\sigma})$ depends on all spatial and spin coordinates.

Nonrelativistic Schrödinger equation

$$(1) \quad \hat{H}(\mathbf{r}, \mathbf{R}) \Psi_n(\mathbf{r}, \mathbf{s}, \mathbf{R}, \sigma) = E_n \Psi_n(\mathbf{r}, \mathbf{s}, \mathbf{R}, \sigma)$$

Notation:

- | | | |
|-----|--|---------------------------------------|
| (2) | $\mathbf{r}_i = (x_i, y_i, z_i)$ | spatial coordinates for electron i |
| (3) | s_i | spin coordinate for electron i |
| (4) | $\mathbf{R}_A = (x_A, y_A, z_A)$ | spatial coordinates for nucleus A |
| (5) | σ_A | spin coordinate for nucleus A |
| (6) | $\mathbf{r} = (\mathbf{r}_1, \dots, \mathbf{r}_N)$ | spatial coordinates for all electrons |
| (7) | $\mathbf{s} = (s_1, \dots, s_N)$ | spin coordinates for all electrons |
| (8) | $\mathbf{R} = (\mathbf{R}_A, \dots, \mathbf{R}_K)$ | spatial coordinates for all nuclei |
| (9) | $\sigma = (\sigma_A, \dots, \sigma_K)$ | spin coordinates for all nuclei |

Convention:

- | | | | |
|-------------------|--------------|-------------------------|--------------|
| Electrons: | number N ; | indices i, j, \dots ; | mass m . |
| Nuclei: | number K ; | indices A, B, \dots ; | mass M_A . |

Nonrelativistic Hamiltonian (I)

$$(10) \quad \hat{H}(\mathbf{r}, \mathbf{R}) = \hat{T}_N(\mathbf{R}) + \hat{T}_{\text{el}}(\mathbf{r}) + \hat{V}_{\text{Ne}}(\mathbf{r}, \mathbf{R}) + \hat{V}_{\text{ee}}(\mathbf{r}) + \hat{V}_{\text{NN}}(\mathbf{R})$$

Kinetic energy:

$$(11) \quad \hat{T}_N(\mathbf{R}) = - \sum_A \frac{\hbar^2}{2M_A} \left(\frac{\partial^2}{\partial x_A^2} + \frac{\partial^2}{\partial y_A^2} + \frac{\partial^2}{\partial z_A^2} \right) = - \sum_A \frac{\hbar^2}{2M_A} \Delta_A$$

$$(12) \quad \hat{T}_{\text{el}}(\mathbf{r}) = - \frac{\hbar^2}{2m} \sum_i \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) = - \frac{\hbar^2}{2m} \sum_i \Delta_i$$

Potential energy:

$$(13) \quad \hat{V}_{\text{Ne}}(\mathbf{r}, \mathbf{R}) = - \sum_A \sum_i Z_A e^2 / r_{Ai} / 4\pi\epsilon_0$$

$$(14) \quad \hat{V}_{\text{ee}}(\mathbf{r}) = + \sum_{i < j} \sum e^2 / r_{ij} / 4\pi\epsilon_0$$

$$(15) \quad \hat{V}_{\text{NN}}(\mathbf{R}) = + \sum_{A < B} \sum Z_A Z_B \cdot e^2 / R_{AB} / 4\pi\epsilon_0$$