Chapter 12. Simple Applications

12.1 Motion in 1 dimension and tunneling

12.1.1 Linear motion

$\psi(x)'' = 2m\,(V(x)–E)\,\psi(x)$ (T = E-V , curvature ~ kinetic quantum energy)

$T = \int dx \cdot \psi^* \cdot (–1/2m)\,\psi'' = +(1/2m) \int dx \cdot |\psi'|^2 > 0$ (T ~ slope squared of ψ)
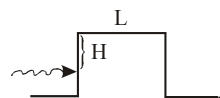
$E < V(x)$: classically forbidden: $\psi \sim \exp(\pm x\sqrt{2m\,(V–E)}\,)$ exp. decay (wave end)

$E > V(x)$: classically allowed: $\psi \sim \exp(\pm ix\sqrt{2m\,(E–V)}\,)$ oscillation (wave)

12.1.2 Tunneling through a barrier

Tunnel probability $\sim \exp(–\sqrt{8mHL^2}\,) = e^{-2L\sqrt{2mH}}$

m = mass of particle,   H and L = height and length of barrier   (Fig. 12.10)

12.2 Electrons in boxes

12.2.1 The one dimensional case

Second order linear D.E.: general solution with two parameters, $f(x) = c_1 \cdot f_1(x) + c_2 \cdot f_2(x)$.

Here, for $V(x) = $ const, $f = \cos(kx)$ and $\sin(kx)$ or $\exp(\pm ikx) = \cos(kx) \pm i \cdot \sin(kx)$

Eigenvalue equation: $D^2 \circ f = f \cdot \lambda$ has three variables c_1, c_2, λ

Physical boundary conditions for confined particles: f(left) = f(right) = 0

One boundary condition fixes $c_1 : c_2$ (shape of state function)

here: $f = 0$ at $x = 0$ $\rightarrow$ $c_1 : c_2 = 0 : 1$

Second boundary condition: discretizes the eigenvalues

numerate E_n, f_n by some consecutive numbers n ("quantum numbers") ,

here: $k = n\pi/L$,   n = 1, 2, 3, …

$\psi_n = \sin(n\pi x/L)$, $E_n = n^2\pi^2/2mL^2$ (Fig. 12.4)

12.2.2 Cyanine dyes

Conjugated carbon chains with nonalternating, equal bond lengths: The present orbital model has no problems, but the (localized 2e-2c)-Valence Bond-restriction cannot represent it: VBs loophole is "use two `resonating´ graphics" for the stationary state of this "mesomeric system".

For equal bond lengths, the nuclear attraction felt by electrons described by π orbitals is comparatively constant (does not apply for `σ-electrons´ or for alternating bond lengths).

Length of a box corresponding to chain "with d double bonds":

$L \approx (2d + 1) \cdot D$, where D = atomic distance (so-called bond length)

Highest occupied molecular orbital HOMO has quantum number n = d, lowest unoccupied molecular orbital LUMO has n = d + 1. Smallest excitation energy $\Delta E = E(L,d+1) - E(L,d) = \omega = h \cdot \nu = h \cdot c/\lambda$

Longest wave length (längstwellig) first absorption line $\lambda = hc / \Delta E$, $\Delta E = \pi^2/2\,m_e\,D \cdot L$

$\lambda_{\text{1st abs.}} \sim L$ (cyanine dyes)   See also the "German" Figs. page

12.2.3 Electron in a 3-dimensional box   (Figs. 12.7/8)

$\psi_{\vec{n}} = \sin(n_x\pi x/L_x) \cdot \sin(n_y\pi y/L_y) \cdot \sin(n_z\pi z/L_z)$

$E_{\vec{n}} = \pi^2/2m \cdot (n_x^2/L_x^2 + n_y^2/L_y^2 + n_z^2/L_z^2)$

$\vec{n}$ = quantum vector, reciprocal point, crystal momentum.

Symmetry leads to degeneracy! - σ and π states

• a) Electron in a cube (atom, CH_4)
$\vec{n}$ = (1,1,1): one "s-type" state
$\vec{n}$ = (2,1,1) or (1,2,1) or (1,1,2): triplet of degenerate "p-type" states
CH_4 valence shell of 4 bonds has *two* IPs at 14 (p-type) and 23 eV (s-type).

• b) Electron in a long box: different lengths give rise to different kinetic zero point energies and to different "energy ladders".

   b1) Linear molecule has 1 long and 2 short extensions - "σ-ladder" and a doubly degenerate "π-ladder" starting a higher energy, with only few σ-levels between the "dense π-band".

   b2) Planar molecule has 2 long and 1 short extensions - a "σ-net" and a higher "π-ladder or -net"
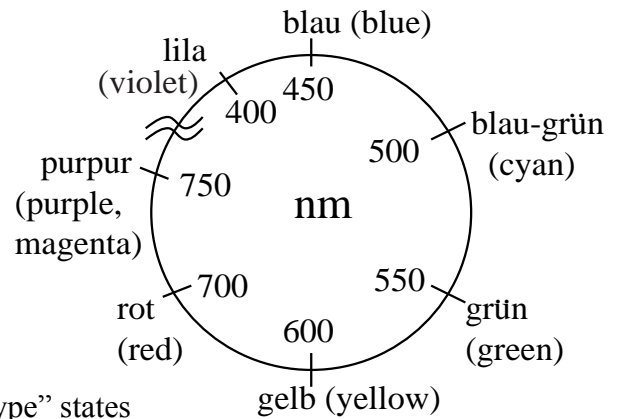
12.3 Harmonic oscillation (vibration)

$V = k/2 \cdot (\Delta R)^2$, $\psi_n = P_n(\Delta R) \cdot \exp(-1/2\,(\Delta R)^2\,\sqrt{\mu k})$, $E_n = (n+1/2)\,\omega$, $\omega = \sqrt{k/\mu}$, $n = 0, 1, \ldots$
P_n is a hermite polynomial:
$P_0 = 1$, $P_1(x) = x$, $P_2(x) = 2x^2 - 1$, $P_3(x) = 2x^3 - 3x$, $P_4(x) = 4x^4 - 12x^2 + 3$, etc.
P_n is gerade/ungerade for n even/odd. For large n, P_n^2 oscillates rapidly between 0 and twice
the classical probablity $1/v = \sqrt{\mu/(2E - k\Delta R^2)}$

Separation between 2 vibrational levels is just $\Delta E_{n,n+1} = \hbar\omega = \sqrt{k/\mu}$ (in au).

Selection rule for vibartions (see §15.5): absorption/emission of electromagnetic radiation is possible only between adjacent states of different g/u symmetry.
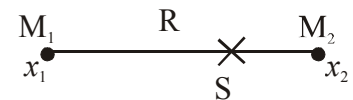
Several dimensions: $E_{\vec{n}} = \sum_i (n_i + 1/2)\,\sqrt{k_i/\mu_i}$

d-fold symmetry results in degeneracy; zero-point energy is $E_o = d/2 \cdot \omega$ (Fig. 12.13)

Coordinate Transformation and Reduced Mass

$(x_1, x_2) \rightarrow R = x_2 - x_1$, $S = (M_1 x_1 + M_2 x_2)/(M_1 + M_2)$
        (Relative separation) (Schwerpunkt, center of gravity)

In coordinates (x_1, x_2), kinetic energy is a simple sum of squares (according to Pythagoras), but potential energy depends simply on R, which is a complicated square root of x-coordinates in 3 dimensions, and is independent of S.   Therefore transform to (R, S)-coordinates:

$V \rightarrow \mathbf{V}(x_1,x_2)\bullet = \mathbf{0}(S) + \mathbf{V}(R)\bullet$ and

$$T \rightarrow -\frac{1}{2M_1} \cdot \frac{d^2}{dx_1^2} - \frac{1}{2M_2} \cdot \frac{d^2}{dx_2^2} = \ldots = \frac{-1}{2(M_1+M_2)} \cdot \frac{d^2}{dS^2} - \frac{M_1+M_2}{2M_1 \cdot M_2} \cdot \frac{d^2}{dR^2}$$

Reduced mass $\mu = (M_1 \cdot M_2)/(M_1 + M_2) < M_1, M_2$

If $M_1 = M_2$: $\mu = M/2$; if $m \ll M$, $\mu \leq m$

12.4 Rotation

12.4.1 Planar Rotation

Electron along a ring, rotation of a molecular group around an axis (CH_3; NH_3 in ammine complexes): *no* left and right *boundary, but* $\psi(0) = \psi(2\pi)$, $\psi'(0) = \psi'(2\pi)$ *connection* conditions.

Angle $\varphi = \varphi + 2n\pi$ is "infinitely indeterminate". Because of this mathematical subtlety, the physical $\Delta\ell$ and the physical T_0 can be zero.

$\psi_m = e^{im\varphi}$, $E_m = m^2/2\mu R^2$, $m = 0, \pm 1, \pm 2, \ldots$ (degeneracy!) $\ell_z = m\hbar$ $\boldsymbol{\ell_z} = -i\hbar\,\partial/\partial\varphi$
$I = \Sigma_i M_i R_i^2 = \mu R^2$ = moment of inertia

Aromatic Rings: π-electronic states along planar cyclic N-membered carbon chains with nonalternating bond distances D: $2\pi R = N \cdot D$.

1 electron per C: System $(C_N H_N)^q$ has (N-q) π-electrons. The HOMO has quantum number $m_{HOMO}=[(N-q+1)/4]$.

Accordingly the valence electron has energy $\varepsilon = (2\pi^2/D^2) \cdot (m_{HOMO}(N)/N)^2$.

Note: 1) One electron more than fitting into a closed shell according to the *Pauli principle* is loosely bond (examples: Na, $C_6H_6^-$).

2) A hole in a stable HOMO will be filled: stable orbital $\Rightarrow$ filled shell (not vice versa). An orbital is stable if it has low potential energy (C_6H_6, $C_5H_5^-$, but no longer $C_4H_4^{2-}$; Na^+, Ne, F^-, $(O^{2-})A_n^+$, but no longer O^{2-} in vacuum) and/or low kinetic energy (large ring: C_6H_6, but not C_4H_4).

A stable π-ring orbital will house up to 4n+2 electrons (*Hückel-Rule*), especially for n=0 and n=1.

12.4.2 Rotation in 3-dimensional space, angular momentum

$\ell = r \times p \rightarrow \boldsymbol{\ell = r \times p}$, $[\boldsymbol{\ell_x, \ell_y}] = i\,\boldsymbol{\ell_z}$

ℓ depends on r and p; while x, y, z are 'independent', x and p_x are 'interdependent' through Heisenberg's relations. Therefore ℓ_x and ℓ_y are also 'interdependent'. The 3-dimensional angular momentum vector has only 2 well-defined components, because $\ell = r \times p$ and Heisenberg's smearing $\Delta x \cdot \Delta p > \frac{1}{2} \cdot \hbar$

$|\boldsymbol{\ell}| = \hbar \cdot \sqrt{(l+1)l}$, $\ell_z = m \cdot \hbar$, $m = l,\ l-1,\ \ldots,\ -l$ (Fig. 12.25)
l = hole or half number: eigenfunction single or double valued ($\pm\sqrt{}$)

$|\boldsymbol{\ell}| \circ Y_{lm}(\theta,\varphi) = Y_{lm} \cdot \hbar \cdot \sqrt{l(l+1)}$, $\boldsymbol{\ell_z} \circ Y_{lm} = Y_{lm} \cdot \hbar \cdot m$, spherical harmonics $Y_{lm} \sim e^{im\varphi}$

The complex spherical harmonics have well-defined ℓ_z-component. They are the simplest basis for the discussion of angular momenta and magnetism in a magnetic field (note: electron has m and e, a rotating electron has ℓ and magnetism).

Combine two Y-functions with same l into real Z-functions: $Z_{e,\pm m} = (Y_{lm} \pm iY_{l-m}) / \sqrt{\pm 2}$. These are the simplest basis for discussion of electrons 'oriented in an electric field'. They have no sharp ℓ-component in any direction.

Rotational energy: $E_{l,m} = l(l+1) / 2I + m^2 \cdot \Delta(1/2I)$ (Tab. 12.3)

I = moment of inertia ; $\Delta(1/2I)$ = difference of `rotational constants´ for different sym. axes

For molecules: $l, j \rightarrow J$, and $m \rightarrow K$

12.5 Angular Momentum Vector Coupling

ℓ-vector lies somewhere on a cone , two ℓ-vectors have a fixed angle between them

Angle of (z-axis, ℓ): $\cos \theta = m / \sqrt{l(l+1)}$

For a p-electron: $l = 1$, $m = 0$ or ± 1: $\theta = 90°$ or $45°$ (Fig. 12.26)

For a spin: $l = |m| = 1/2$: $\theta = \text{acos} \sqrt{1/3} = 54.74° = $ magic angle

Pseudoparallel triplet-spins: ⚡ or   ⚡   or ⚡ (Fig. 12.29)

$\alpha(s_1) \alpha(s_2)$; $\alpha(s_1) \beta(s_2) + \beta(s_1) \alpha(s_2)$; $\beta(s_1) \beta(s_2)$

Spinvectors are not vertical! They cannot be really parallel! Pseudoparalleles spins point to "the same side", e.g. to `right up´ and `right down´!
Pseudoparallel spins have permutation-symmetric two-spin-functions.

An up-spin and a down-spin is half triplet (see above) , half antiparallel singlet (⚡): $\alpha(s_1)\beta(s_2) - \beta(s_1) \alpha(s_2) = $ "$\alpha\beta-\beta\alpha$" . This function is permutation-antisymmetric.

Charge position space and spin direction space refer to the same real 3D space.

Learning objectives

After careful study of this chapter you should be able to:

(1) Write down the Schrödinger equation for a *particle in a box*, eqn (14.1.3), justify and specify the boundary conditions, and find the allowed energies and wavefunctions, eqn (14.1.9).

(2) Describe the principal features of the solutions of a particle in a box, Section 14.1(b).

(3) Write down the Schrödinger equation for a particle confined to a rectangular surface, eqn (14.1.11), and use the *separation of variables* technique to find its solutions.

(4) State the meaning of *degeneracy*, Section 14.1(c).

(5) Describe the procedure for calculating the wavefunction of a particle in a system with *potential barriers*, Section 14.1(d), and find the wavefunctions in the case of a rectangular barrier, Example 14.2.

(6) Explain how *tunnelling* occurs, and state how the probability of tunnelling depends on the mass of the particle and the width of the barrier, Section 14.1(d).

(7) Write down the Schrödinger equation for a *harmonic oscillator*, eqn (14.2.1), obtain the form of its solutions at large displacements, and describe how the full equation is solved, Section 14.2(a).

(8) Write down an expression for the energy levels of a harmonic oscillator, eqn (14.2.4), and calculate their separation.

(9) Describe the wavefunctions of the harmonic oscillator, and use the properties of *Hermite polynomials* to calculate its properties, Example 14.4.

(10) State and apply the *virial theorem*, eqn (14.2.11).

(11) Calculate the probability that an oscillator will be found at classically forbidden displacements, eqn (14.2.12).

(12) Write down the Schrödinger equation for the motion of a *particle on a ring*, eqn (14.3.2), justify and specify the *cyclic boundary conditions*, and find the wavefunctions, eqn (14.3.4).

(13) Explain the origin of the *quantization of angular motion*, and write expressions for the permitted values of its z-component, eqn (14.3.6).

(14) Write down the operator for the z-component of angular momentum, eqn (14.3.9).

(15) Write down the Schrödinger equation for *rotation in three dimensions*, eqn (14.3.17).

(16) Show that the Schrödinger equation for rotation is separable, eqn (14.3.18).

(17) Write down the expression for the energy of a particle on a sphere in terms of its angular momentum quantum number, eqn (14.3.22).

(18) Write down expressions for the magnitude of the angular momentum, eqn (14.3.24), and the permitted values of its z-component, eqn (14.3.25). See also Box 14.3.

(19) State the meaning of *space quantization* and explain the significance of the *Stern–Gerlach experiment*, Section 14.3(g).

(20) Explain the meaning of *spin*, and state the spin properties of an electron, Section 14.3(h).

(21) Specify the *vector model* of angular momentum, Section 14.3(i).