Table 1.3. Physical quantities in atomic units with $\hbar = e = m_e = 4\pi\epsilon_0 = 1$, and $\alpha^{-1} = 137.035\,989\,5\,(61)$.

Quantity	Unit	Value
length	a_0	$0.529\,177\,249\,(24) \times 10^{-10}$ m
mass	m_e	$0.910\,938\,97\,(54) \times 10^{-30}$ kg
time	$\hbar/E_h$	$2.418\,884\,326\,555\,(53) \times 10^{-17}$ s
velocity	$v_B \equiv \alpha c$	$2.187\,691\,42(10) \times 10^{6}$ m/s
energy	E_h	$4.359\,748\,2(26) \times 10^{-18}$ J
action	$\hbar$	$1.054\,572\,66\,(63) \times 10^{-34}$ J s
force	E_h/a_0	$0.823\,872\,95\,(49) \times 10^{-7}$ N
power	$E_h^2/\hbar$	$0.180\,237\,98\,(11)$ W
intensity	$\dfrac{E_h^2}{\hbar a_0^2}$	$64.364\,142\,(39) \times 10^{18}$W/m^2
charge	e	$1.602\,177\,33\,(49) \times 10^{-19}$ C
potential	E_h/e	$27.211\,396\,1\,(81)$ V
electric field	$\dfrac{E_h}{ea_0}$	$0.514\,220\,82\,(15) \times 10^{12}$ V/m
magnetic field	$\dfrac{E_h}{ea_0\alpha c}$	$2.350\,518\,09\,(71) \times 10^{5}$ tesla

2004.09.02/table-at-units1.pdf

1.3 ATOMIC UNITS

Atomic and molecular calculations based on the Schrödinger equation are most conveniently done in atomic units (a.u.), and then the final result converted to the correct SI units as listed in Table 1.3. In atomic units, $\hbar = m_e = e = 4\pi\epsilon_0 = 1$. The atomic units of length, velocity, time, and energy are then

$$\begin{aligned}
\text{length}: \quad & a_0 = \frac{\hbar^2}{m_e e^2} = \frac{\hbar}{\alpha m_e c}\,, \\
\text{velocity}: \quad & v_B = e^2/\hbar = \alpha c\,, \\
\text{time}: \quad & \tau_0 = \frac{\hbar^3}{m_e e^4} = \frac{\hbar}{\alpha^2 m_e c^2}\,, \\
\text{energy}: \quad & E_h = e^2/a_0 = \alpha^2 m_e c^2\,,
\end{aligned}$$

where, from the definition (1.8), the numerical value of c is $\alpha^{-1} = 137.035\,9895(61)$ a.u. For the lowest $1s$ state of hydrogen (with infinite nuclear mass), a_0 is the Bohr radius, v_B is the Bohr velocity, $2\pi\tau_0$ is the time to complete a Bohr orbit, and E_h (the Hartree energy) is twice the ionization energy. To include finite nuclear

2004.09.02/table-at-units2.pdf

Table 1.1. Table of physical constants. Uncertainties are given in parentheses.

Quantity	Symbol	Value	Units
speed of light in vacuum	c	2.997 924 58	10^{8} m s^{-1}
gravitational constant	G	6.672 59(85)	10^{-11} m^{3}kg^{-1}m^{-2}
Planck constant	h	6.626 075 5(40)	10^{-34} J s
	$\hbar = h/2\pi$	1.054 572 66(63)	10^{-34} J s
elementary charge	e	1.602 177 33(49)	10^{-19} C
		4.803 206 8(15)	10^{-10} esu
inverse fine structure constant, $4\pi\epsilon_0\hbar c/e^2$	α^{-1}	137.035 989 5(61)	
magnetic flux quantum, $h/2e$	Φ_0	2.067 834 61(61)	10^{-15} Wb
atomic mass unit, $\frac{1}{12}m(^{12}\mathrm{C})$	$m_{\mathrm{u}} = u$	1.660 540 2(10)	10^{-27} kg
	$m_{\mathrm{u}}c^2$	931.494 32(28)	MeV
electron mass	m_{e}	9.109 389 7(54)	10^{-31} kg
		5.485 799 03(13)	10^{-4} u
muon mass	m_μ	0.113 428 913(17)	u
proton mass	m_{p}	1.007 276 470(12)	u
neutron mass	m_{n}	1.008 664 904(14)	u
deuteron mass	m_{d}	2.013 553 214(24)	u
α-particle mass	m_α	4.001 506 178(84)	u
Rydberg constant, $m_{\mathrm{e}}c\alpha^2/2h$	R_∞	1.097 373 156 834(24)	10^{7} m^{-1}
	$R_\infty c$	3.289 841 960 305(72)	10^{15} Hz
	$R_\infty hc$	13.605 698 1(40)	eV
		2.179 874 1(13)	10^{-18} J
Bohr radius, $\alpha/4\pi R_\infty$	a_0	0.529 177 249(24)	10^{-10} m
Hartree energy, $e^2/[4\pi\epsilon_0]a_0 = 2R_\infty hc$	E_{h}	27.211 396 1(81)	eV
	E_{h}/h	6.579 683 920 61(14)	10^{15}Hz
	E_{h}/hc	2.194 746 313 668(48)	10^{7} m^{-1}
Compton wavelength, αa_0	$\lambdabar_{\mathrm{C}} = \lambda_{\mathrm{C}}/2\pi$	3.861 593 23(35)	10^{-13} m
classical electron radius, $\alpha^2 a_0$	r_{e}	2.817 940 92(38)	10^{-15} m
Thomson cross section, $8\pi r_{\mathrm{e}}^2/3$	σ_{e}	0.665 246 16(18)	10^{-28} m^2
Bohr magneton, $e\hbar/2m_{\mathrm{e}}$	μ_{B}	9.274 015 4(31)	10^{-24} J T^{-1}
		5.788 382 63(52)	10^{-5} eV T^{-1}
electron magnetic moment	$\mu_{\mathrm{e}}/\mu_{\mathrm{B}}$	1.001 159 652 193(10)	
muon magnetic moment	μ_μ/μ_{B}	4.841 970 97(71)	10^{-3}
proton magnetic moment	$\mu_{\mathrm{p}}/\mu_{\mathrm{B}}$	1.521 032 202(15)	10^{-3}
neutron magnetic moment	$\mu_{\mathrm{n}}/\mu_{\mathrm{B}}$	1.041 875 63(25)	10^{-3}
deuteron magnetic moment	$\mu_{\mathrm{d}}/\mu_{\mathrm{B}}$	0.466 975 447(91)	10^{-3}
electron g factor $2(1+a_{\mathrm{e}})$	g_μ	2.002 319 304 386(20)	
muon g factor $2(1+a_\mu)$	g_μ	2.002 331 846(17)	
proton gyromagnetic ratio	γ_{p}	2.675 221 28(81)	10^{8} s^{-1}T^{-1}
Avogadro constant	N_{A}	6.022 136 7(36)	10^{23} mol^{-1}
Faraday constant, $N_{\mathrm{A}}e$	F	9.648 530 9(29)	10^{4} C mol^{-1}
Boltzmann constant	k_{B}	1.380 658(12)	10^{-23} J K^{-1}
		8.617 385(73)	10^{-5} eV K^{-1}
	$k_{\mathrm{B}}/E_{\mathrm{h}}$	3.166 830(27)	10^{-6} K^{-1}
molar gas constant	R	8.314 510(70)	J mol^{-1} K^{-1}
molar volume (ideal gas), RT/P			
$T = 273.15$ K, $P = 101.325$ kPa	V_{m}	0.022 414 10(19)	m^3 mol^{-1}
$T = 273.15$ K, $P = 100$ kPa	V_{m}	0.022 711 08(19)	m^3 mol^{-1}
Stefan-Boltzmann constant $\pi^2 k_{\mathrm{B}}^4/(60\hbar^3 c^2)$	σ	5.670 51(19)	10^{-8} W m^{-2} K^{-4}
first radiation constant, $2\pi hc^2$	c_1	3.741 774 9(22)	10^{-16} W m^2
second radiation constant, hc/k_{B}	c_2	0.014 387 69(12)	m K
Wien displacement constant, $\lambda_{\max}T = c_2/4.965\,114\,23$	b	2.897 756(24)	10^{-3} m K

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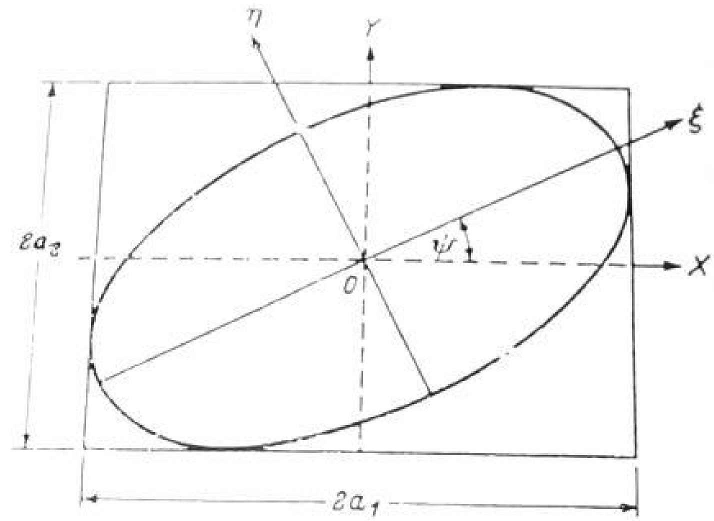
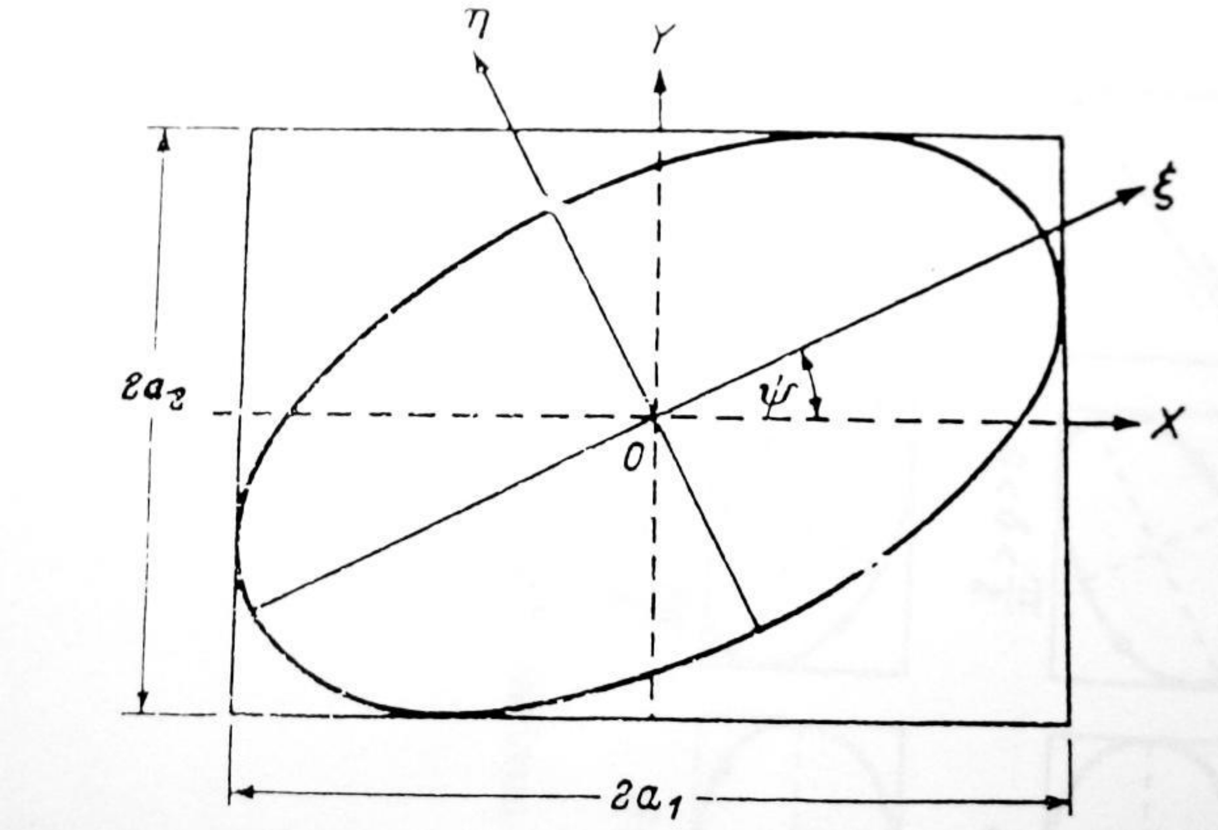


Fig. 1.6. Elliptically polarized wave. The vibrational ellipse for the electric vector.

The ellipse is inscribed into a rectangle whose sides are parallel to the co-or
axes and whose lengths are $2a_1$ and $2a_2$ (Fig. 1.6). The ellipse touches the si
the points ($\pm\, a_1$, $\pm\, a_2 \cos\delta$) and ($\pm\, a_1 \cos\delta$, $\pm\, a_2$).

2004.09.08/ellipse2.pdf



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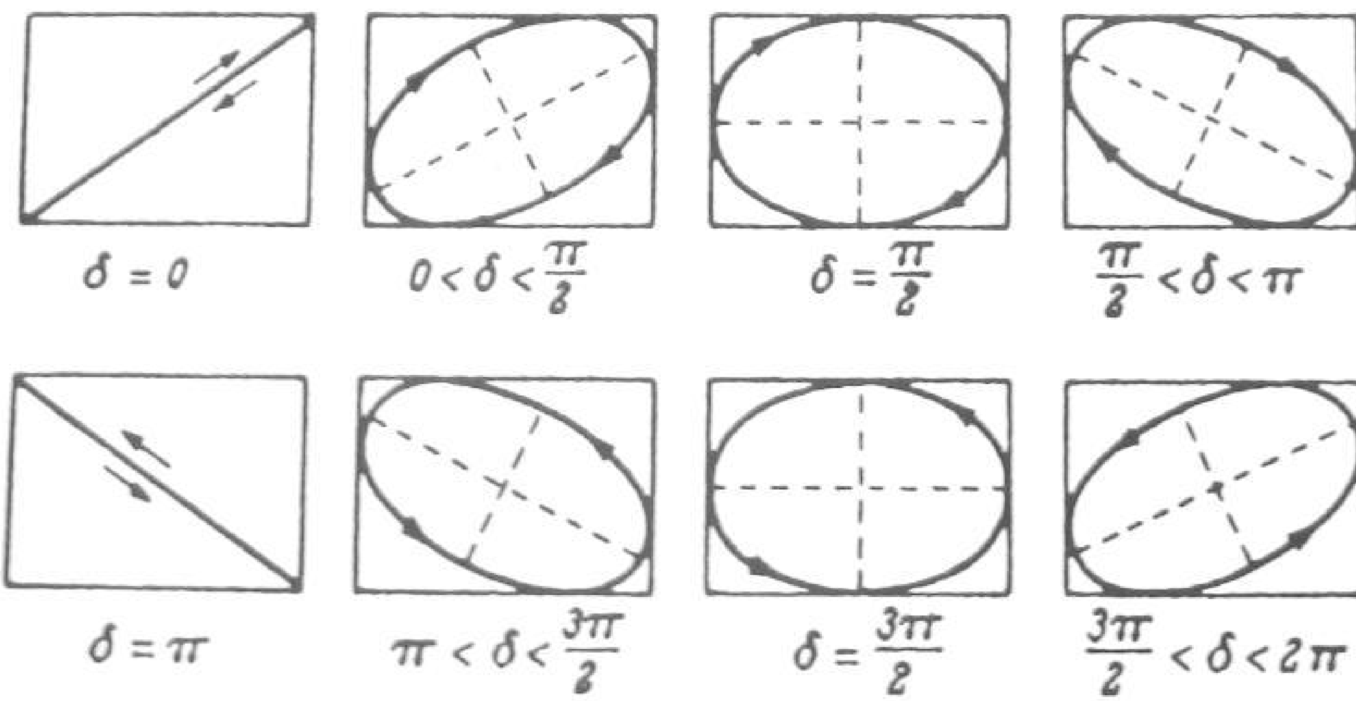

. Elliptical polarization with various values of the phase d

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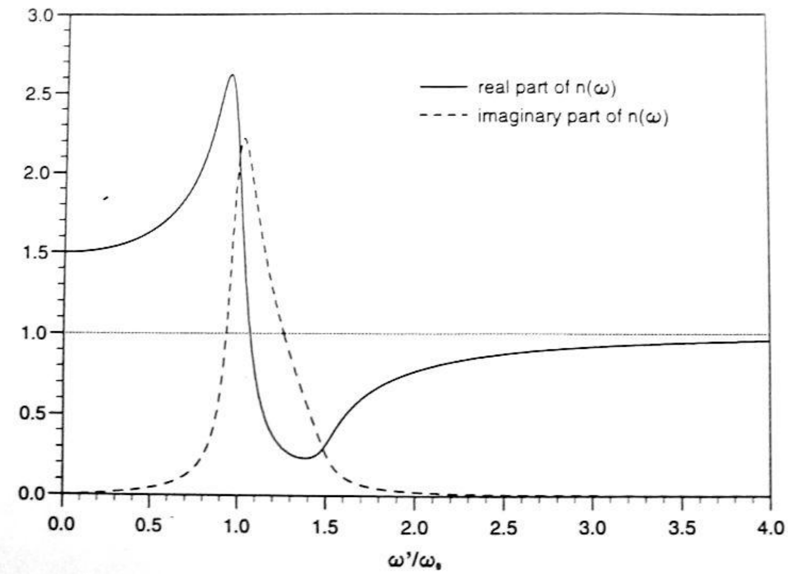

Fig. 1.1: *The real and imaginary part of* $n(\omega)$ *for real frequencies* $\omega = \omega'$.

where n is the refractive index of the medium and $\boldsymbol{E}$ is the spatial part of the observed, mean electric field vector. By using Eqs. (1.9)–(1.11) and the relation between the polarisation, the effective field, and the observed field given in [6, p.86]:

$$\boldsymbol{E}' = \boldsymbol{E} + \frac{4\pi}{3}\boldsymbol{P}, \tag{1.12}$$

we get the relation between n and the medium parameters given as

$$\frac{n^2-1}{n^2+2} = \frac{1}{3}\frac{-b^2}{\omega^2 - \omega_0'^2 + 2i\delta\omega}. \tag{1.13}$$

By solving this equation for n, we find the final expression for the complex index of refraction of the single resonance linear dispersive medium as

$$n^2(\omega) = 1 - \frac{b^2}{\omega^2 - \omega_0^2 + 2i\delta\omega}, \tag{1.14}$$

where $\omega_0^2 = \omega_0'^2 - \frac{1}{3}b^2$. Often the frequency ω_0 is called the undamped resonance frequency and not ω_0', as noted above. However, for practical use of Eq. (1.14), the resonance frequency is estimated empirically for the medium in matter. The interchange of ω_0 and ω_0' therefore only affect the physical explanation of the resonance frequency in terms of atomic theory which is beyond the scope of this thesis. The plasma frequency b is defined as :

$$b^2 = \frac{4\pi N e^2}{m}. \tag{1.15}$$

2004.09.08/lorentz.pdf

Table 2

Definitions of ϵ_0, μ_0, D, H, Macroscopic Maxwell Equations, and Lorentz Force Equation in Various Systems of Units

Where necessary the dimensions of quantities are given in parentheses. The symbol c stands for the velocity of light in vacuum with dimensions (lt^{-1}).

System	ϵ_0	μ_0	D, H	Macroscopic Maxwell Equations				Lorentz Force per Unit charge
Electrostatic (esu)	1	c^{-2} (t^2l^{-2})	$\mathbf{D}=\mathbf{E}+4\pi\mathbf{P}$ $\mathbf{H}=c^2\mathbf{B}-4\pi\mathbf{M}$	$\nabla\cdot\mathbf{D}=4\pi\rho$	$\nabla\times\mathbf{H}=4\pi\mathbf{J}+\frac{\partial\mathbf{D}}{\partial t}$	$\nabla\times\mathbf{E}+\frac{\partial\mathbf{B}}{\partial t}=0$	$\nabla\cdot\mathbf{B}=0$	$\mathbf{E}+\mathbf{v}\times\mathbf{B}$
Electromagnetic (emu)	c^{-2} (t^2l^{-2})	1	$\mathbf{D}=\frac{1}{c^2}\mathbf{E}+4\pi\mathbf{P}$ $\mathbf{H}=\mathbf{B}-4\pi\mathbf{M}$	$\nabla\cdot\mathbf{D}=4\pi\rho$	$\nabla\times\mathbf{H}=4\pi\mathbf{J}+\frac{\partial\mathbf{D}}{\partial t}$	$\nabla\times\mathbf{E}+\frac{\partial\mathbf{B}}{\partial t}=0$	$\nabla\cdot\mathbf{B}=0$	$\mathbf{E}+\mathbf{v}\times\mathbf{B}$
Gaussian	1	1	$\mathbf{D}=\mathbf{E}+4\pi\mathbf{P}$ $\mathbf{H}=\mathbf{B}-4\pi\mathbf{M}$	$\nabla\cdot\mathbf{D}=4\pi\rho$	$\nabla\times\mathbf{H}=\frac{4\pi}{c}\mathbf{J}+\frac{1}{c}\frac{\partial\mathbf{D}}{\partial t}$	$\nabla\times\mathbf{E}+\frac{1}{c}\frac{\partial\mathbf{B}}{\partial t}=0$	$\nabla\cdot\mathbf{B}=0$	$\mathbf{E}+\frac{\mathbf{v}}{c}\times\mathbf{B}$
Heaviside-Lorentz	1	1	$\mathbf{D}=\mathbf{E}+\mathbf{P}$ $\mathbf{H}=\mathbf{B}-\mathbf{M}$	$\nabla\cdot\mathbf{D}=\rho$	$\nabla\times\mathbf{H}=\frac{1}{c}\left(\mathbf{J}+\frac{\partial\mathbf{D}}{\partial t}\right)$	$\nabla\times\mathbf{E}+\frac{1}{c}\frac{\partial\mathbf{B}}{\partial t}=0$	$\nabla\cdot\mathbf{B}=0$	$\mathbf{E}+\frac{\mathbf{v}}{c}\times\mathbf{B}$
Rationalized MKSA	$\frac{10^7}{4\pi c^2}$ $(I^2t^4m^{-1}l^{-3})$	$4\pi\times10^{-7}$ $(mlI^{-2}t^{-2})$	$\mathbf{D}=\epsilon_0\mathbf{E}+\mathbf{P}$ $\mathbf{H}=\frac{1}{\mu_0}\mathbf{B}-\mathbf{M}$	$\nabla\cdot\mathbf{D}=\rho$	$\nabla\times\mathbf{H}=\mathbf{J}+\frac{\partial\mathbf{D}}{\partial t}$	$\nabla\times\mathbf{E}+\frac{\partial\mathbf{B}}{\partial t}=0$	$\nabla\cdot\mathbf{B}=0$	$\mathbf{E}+\mathbf{v}\times\mathbf{B}$

Table 3
Conversion Table for Symbols and Formulas

The symbols for mass, length, time, force, and other not specifically electromagnetic quantities are unchanged. To convert any equation in Gaussian variables to the corresponding equation in MKSA quantities, on both sides of the equation replace the relevant symbols listed below under "Gaussian" by the corresponding "MKSA" symbols listed on the right. The reverse transformation is also allowed. Since the length and time symbols are unchanged, quantities which differ dimensionally from one another only by powers of length and/or time are grouped together where possible.

Quantity	Gaussian	MKSA
Velocity of light	c	$(\mu_0\epsilon_0)^{-1/2}$
Electric field (potential, voltage)	$\mathbf{E}(\Phi, V)$	$\sqrt{4\pi\epsilon_0}\,\mathbf{E}(\Phi, V)$
Displacement	$\mathbf{D}$	$\sqrt{\frac{4\pi}{\epsilon_0}}\,\mathbf{D}$
Charge density (charge, current density, current, polarization)	$\rho(q, \mathbf{J}, I, \mathbf{P})$	$\frac{1}{\sqrt{4\pi\epsilon_0}}\rho(q, \mathbf{J}, I, \mathbf{P})$
Magnetic induction	$\mathbf{B}$	$\sqrt{\frac{4\pi}{\mu_0}}\,\mathbf{B}$
Magnetic field	$\mathbf{H}$	$\sqrt{4\pi\mu_0}\,\mathbf{H}$
Magnetization	$\mathbf{M}$	$\sqrt{\frac{\mu_0}{4\pi}}\,\mathbf{M}$
Conductivity	σ	$\frac{\sigma}{4\pi\epsilon_0}$
Dielectric constant	ϵ	$\frac{\epsilon}{\epsilon_0}$
Permeability	μ	$\frac{\mu}{\mu_0}$
Resistance (impedance)	$R(Z)$	$4\pi\epsilon_0 R(Z)$
Inductance	L	$4\pi\epsilon_0 L$
Capacitance	C	$\frac{1}{4\pi\epsilon_0}C$

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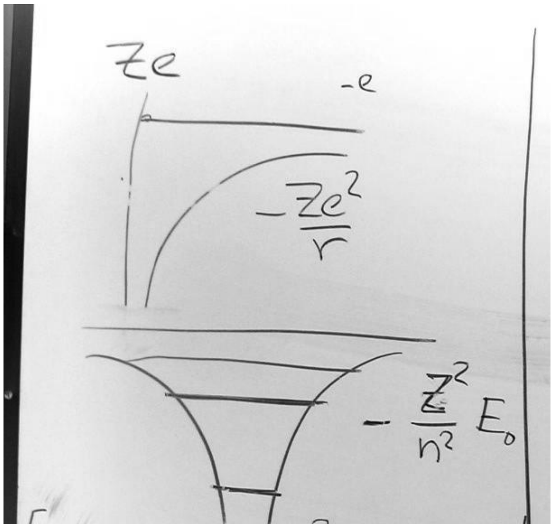

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}\right]\psi(\vec{r}) = E\psi(\vec{r})$$

$$\psi_{nlm} = R_{nl}(r)\,Y_{lm}(\vartheta,\varphi)$$

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Spherical Harmonics

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2}\underbrace{L^2}$$

$r, \vartheta, \varphi \qquad \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}$

Eigenfunctions of "certain operators" $\longrightarrow$ complete sets

$\Rightarrow$ Expansions; orthogonality

Fourier series

$$\psi(r) = \sum_{i=1}^{\infty} a_i\,\varphi_i(r)$$

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Taylor series

$$f(x) = \sum{}' a_n x^n$$

$x^n \longrightarrow$ orthogonal polynomials

$$f(x,y,z) = \sum{}' a_{mnk}\, x^m y^n z^l$$

$$= \sum_{N\ldots}{}' r^N \left(\frac{x}{r}\right)\left(\frac{y}{r}\right)\left(\frac{z}{r}\right)$$

$\cos\vartheta, \sin\vartheta \; \cos\varphi \sin\varphi$

"Nice combinations"

$\longrightarrow$ spherical harmonics

$$Y_{00} = \sqrt{\frac{1}{4\pi}} \qquad Y_{10} = \sqrt{\frac{3}{4\pi}}\,\frac{z}{r}$$

$$Y_{1\pm1} = \sqrt{\frac{3}{8\pi}} - \frac{x}{r} \mp i\frac{y}{r} \Rightarrow e^{i\varphi m}$$

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$\frac{a_0}{Z}$ 2-electron problem

$$\left\{-\frac{\hbar^2}{2m}\nabla_{r_1}^2 - \frac{\hbar^2}{2m}\nabla_{r_2}^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}\right\}\psi(\vec{r}_1, \vec{r}_2) = E\,\psi(\vec{r}_1, \vec{r}_2)$$

if no electron repulsion:
separation of variable

because of repulsion
separation of variables not possible

independen electron
approximation $\longrightarrow$ starting point for further work

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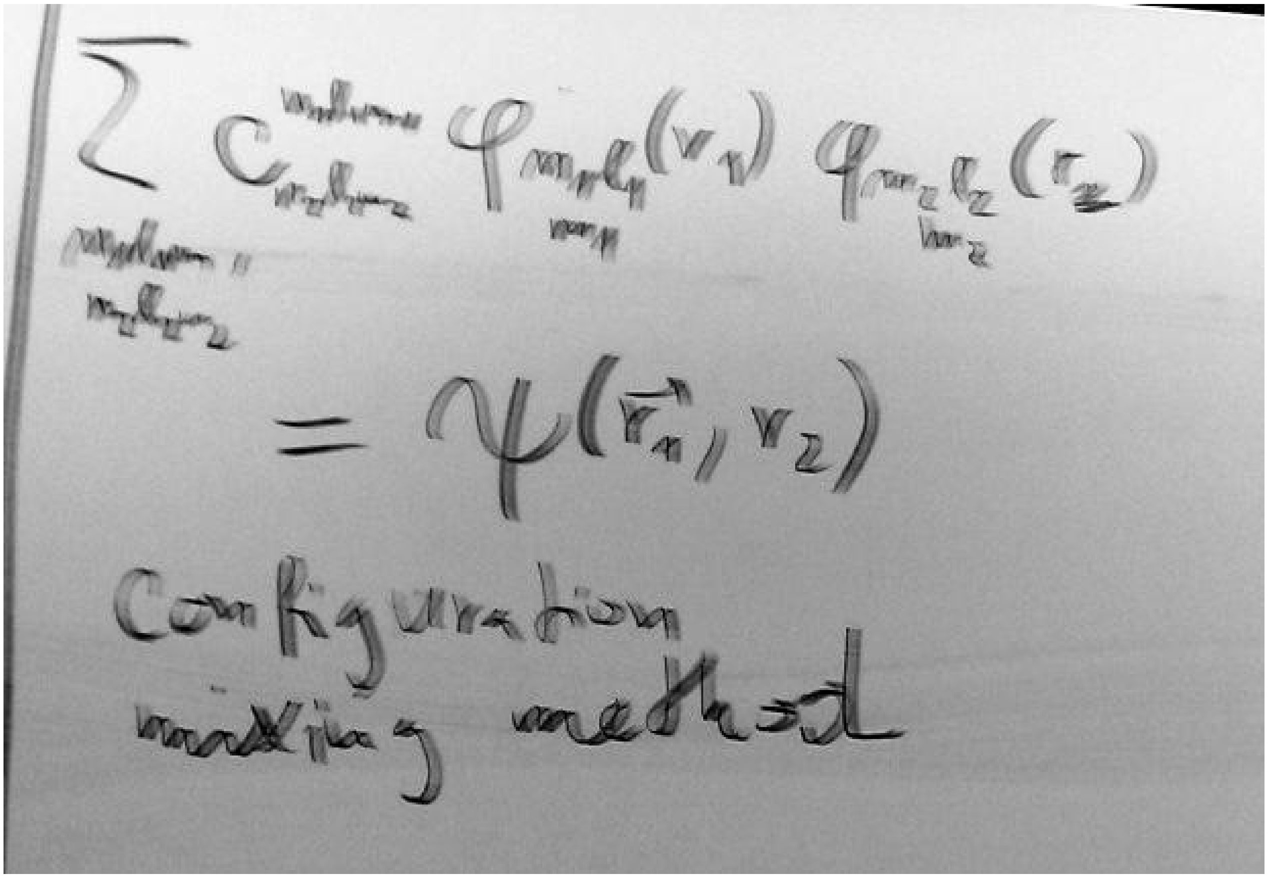

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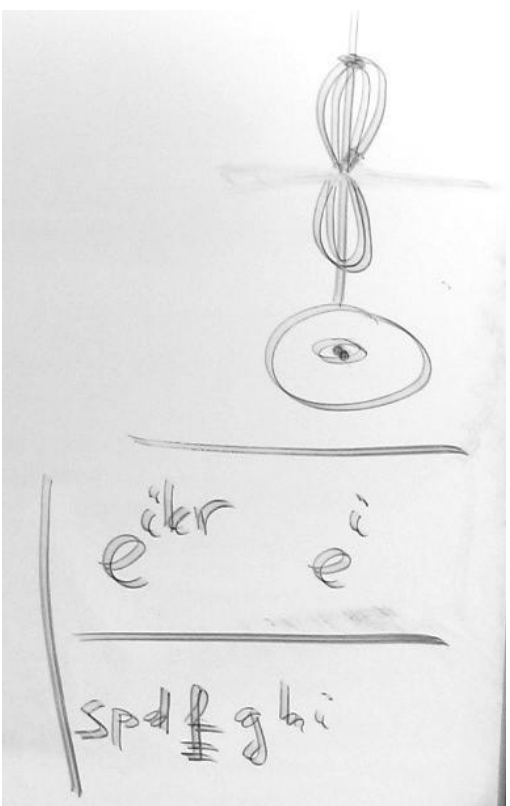

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$$\sum_{\substack{n_1 l_1 m_1,\\ n_2 l_2 m_2}} C^{n_1 l_1 m_1}_{n_2 l_2 m_2}\, \varphi_{n_1 l_1 m_1}(r_1)\, \varphi_{n_2 l_2 m_2}(r_2)$$

$$= \psi(\vec r_1, r_2)$$

Configuration mixing method

Ground state helium

$$\psi(\vec r_1, \vec r_2) \approx \varphi^{(Z=2)}_{1s}(r_1)\, \varphi^{(Z=2)}_{1s}(r_2)$$

SPIN

~~$l = 0, 1, 2 \ldots$~~

$\boxed{\text{two states}}$

$s = 1/2 \quad (3/2 \ldots)$

$S_z = \begin{cases} +1/2 \\ -1/2 \end{cases}$

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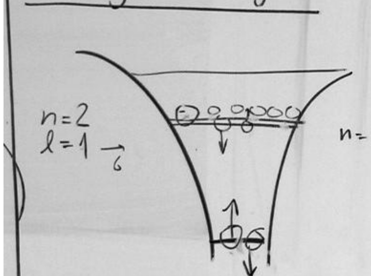
Pauli principle

In each "state" (orbital) can be only one electron (2 electrons differ by spin state)

Pauli principle from Symmetry



Ze?

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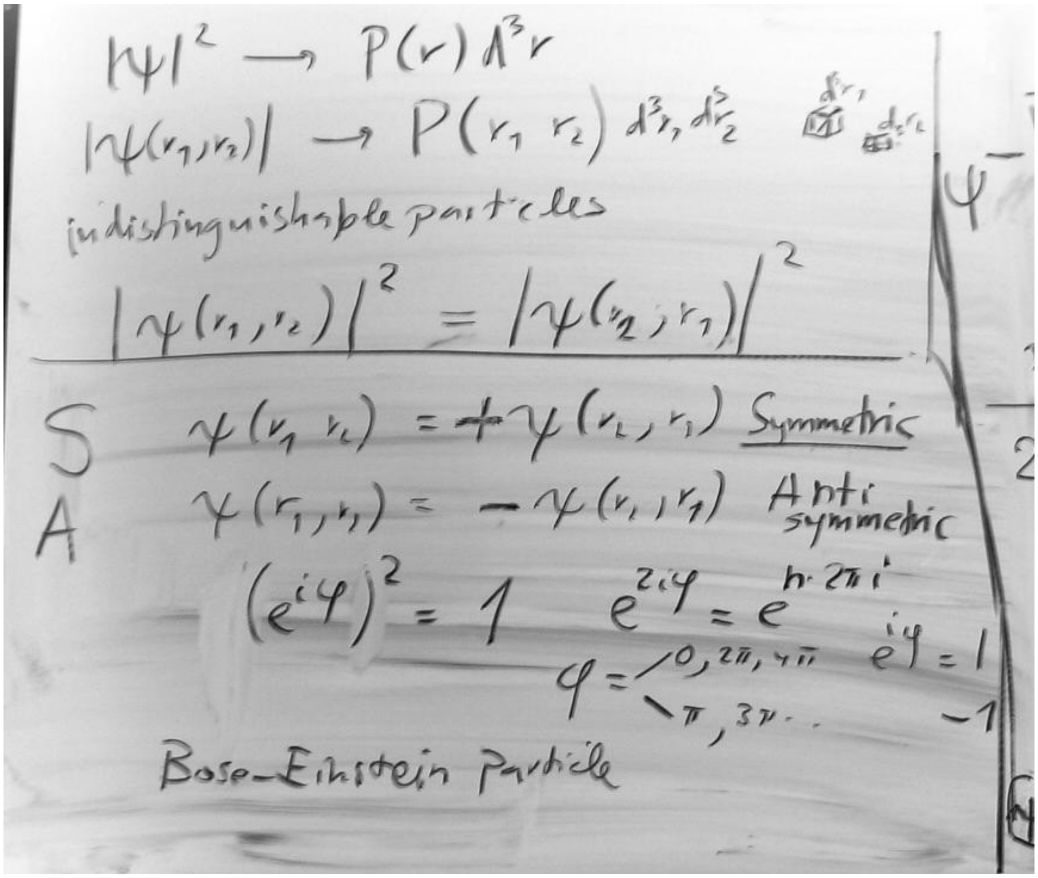

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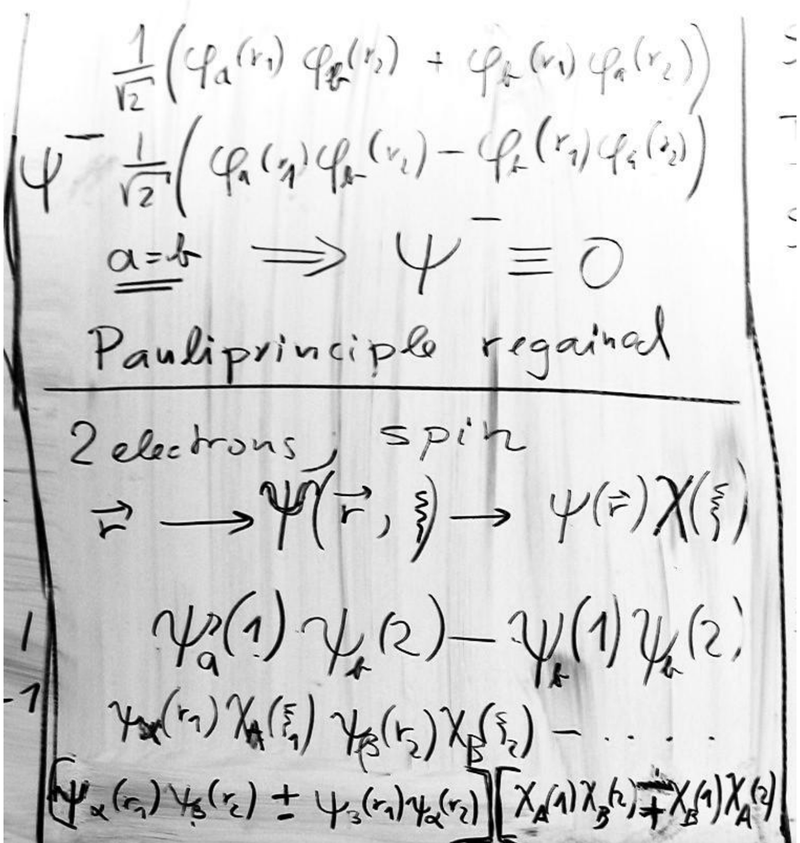

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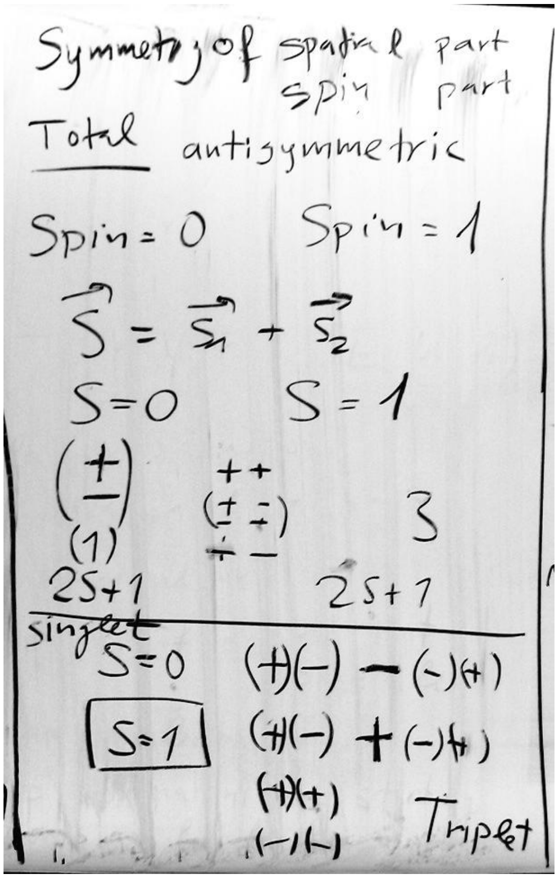

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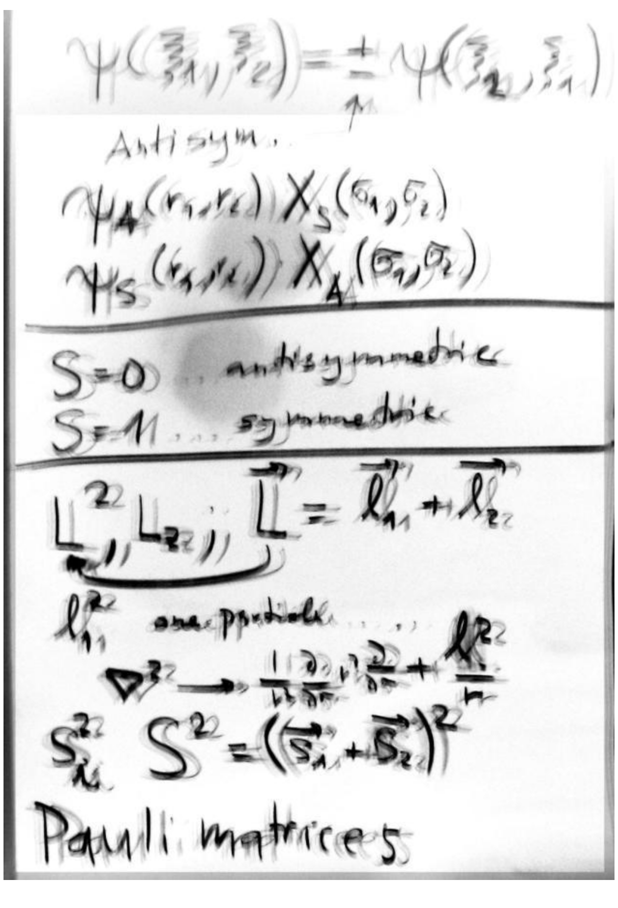

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$$\frac{\hbar^2}{2^2}\left(\sigma_1^2+\sigma_2^2+\sigma_3^2\right) \Longrightarrow \frac{1}{2}\left(1+\frac{1}{2}\right)\hbar^2$$

$$\sigma_i^2 = 1 \qquad [\sigma_i, \sigma_j] = \sigma_i\sigma_j - \sigma_j\sigma_i = i\,\varepsilon_{ijk}\sigma_k$$

Levi-Civita ε (Summation, Einstein)

$$\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} = \sigma_z \qquad \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} = \sigma_y \qquad \begin{pmatrix}0 & i\\ -i & 0\end{pmatrix}$$

$$S^2 = \left(\sigma_{1x}+\sigma_{2x}\right)^2 + \left(\sigma_{1y}+\sigma_{2y}\right)^2 + \ldots$$

$$\chi \longrightarrow \begin{pmatrix}1\\0\end{pmatrix}, \begin{pmatrix}0\\1\end{pmatrix} \qquad \chi_+ \quad \chi_- \qquad \chi_+ = \chi_\uparrow \quad \chi_- = \chi_\downarrow$$

$$|\chi_{1,2}\rangle = \frac{1}{\sqrt{2}}\left[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right] \qquad S=0$$

$$|\uparrow\uparrow\rangle, \quad |\downarrow\downarrow\rangle, \quad \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)$$

$$S_z = 1 \qquad S_z = -1 \qquad S_z = 0$$

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Summation of ang momenta

$$\vec{L} = \vec{\ell}_1 + \vec{\ell}_2$$

independent electrons

$$L: \quad |\ell_1 - \ell_2| \le L \le \ell_1 + \ell_2$$

$$S: \quad \left|\frac{1}{2} - \frac{1}{2}\right| \le S \le \frac{1}{2} + \frac{1}{2}$$

$\ell_1 = 2$ (d) $\quad \ell_2 = 1$ (p)

$$L: \quad |1-2| \le L \le 1+2$$

$$1 \le L \le 3$$

$2S+1$ … $S=0$ … singlett antisym

(3) $S=1$ … triplett sym.

$2^1S \qquad 2^3S$

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Triplett → space part antisymmetric

$\langle \psi | H | \psi \rangle$ expect. value

space antisymmetric

$T_1 + T_2 + V_1 + V_2 + \underline{\underline{V_{12}}}$

$+\dfrac{e^2}{\|r_1 - r_2\|}$ $\vec{r}_1 \approx \vec{r}_2$ largest

$\varphi_1(r_1)\varphi_2(2) - \varphi_2(1)\varphi_2(2)$

$r_1 = r_2$ $\varphi_1(r)\varphi_2(r) - \varphi_2(r)\varphi_1(r$

$\longrightarrow 0$

Spin triplett → smallest repulsion

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For parallel spins repulsion smallest

Effective spin-spin interaction

$\dfrac{e^2}{|r_1 - r_2|}$ gives smallest values

Ferromagnetism

Indepent particle model with repulsion

Evaluation of

$$\int |\varphi_1(\vec{r}_1)|^2 |\varphi_2(\vec{r}_2)|^2 \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} d^3r_1 d^3r_2$$

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$$Y_{lm}(\vartheta,\varphi) \qquad \left(\frac{x}{r}\right)^m \left(\frac{y}{r}\right)^n \left(\frac{z}{r}\right)^k$$

$$\frac{1}{|\vec r_1 - \vec r_2|} = \frac{1}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\vartheta_{12}}}$$

Legendre polynomials of $\cos\vartheta_{12}$ $\quad \vartheta_1\varphi_1,\ \vartheta_2\varphi_2$

$$\frac{1}{|\vec r_1 - \vec r_2|} = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} \frac{4\pi}{2l+1}\frac{r_<^l}{r_>^{l+1}} \cdot Y_{lm}^*(\vartheta_1\varphi_1)\, Y_{lm}(\vartheta_2\varphi_2) \qquad \boxed{d\Omega \quad \sin\vartheta\, d\vartheta\, d\varphi}$$

$r_< = r_1$ if $r_1 < r_2$

$\phantom{r_< =} r_2$ $\quad r_2 < r_1$

Spherical harmonic integrals

$$\int Y_{lm}^*(\Omega)\, Y_{l'm'}(\Omega)\, d\Omega = \delta_{ll'}\delta_{mm'}$$

2004.09.22/img$_1$088.*pdf*

$$\int Y_{lm}^*(\Omega)\, Y_{LM}(\Omega)\, Y_{l'm'}(\Omega)\, d\Omega$$

$$\int Y_{00}^*\ Y_{LM}\ Y_{00}\, d\Omega = \delta_{L0}\,\delta_{M0}\,..$$

$$\varphi_{1s}(\vec r) = R_{1s}(r)\, Y_{00}(\Omega)$$

$$R_{1s} = 2N_r\, e^{-Zr/a_0} \quad \frac{1}{\sqrt{4\pi}} \quad \Bigg|\ N_r = \sqrt{\left(\frac{Z}{a_0}\right)^3}$$

$$\int \psi_{100}^*(\vec r_1)\, \psi_{100}^*(\vec r_2)\, \frac{1}{|\vec r_1 - \vec r_2|}\, \psi_{100}(\vec r_1)\, \psi_{100}(\vec r_2)\, d^3r_1\, d^3r_2$$

$$\int |R_{1s}(r_1)|^2 |R_{1s}(r_2)|^2\, \frac{1}{r_>}\, \frac{1}{\cancel{4\pi}}\, \cancel{4\pi}\ r_1^2 dr_1\, r_2^2 dr_2$$

$$\int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \left(\frac{Z}{a_0}\right)^6 16\, e^{-2Zr_1 - 2Zr_2}\ \frac{1}{r_>}$$

2004.09.22/img$_1$089.*pdf*

$$\int_0^\infty r_1^2 dr_1 \frac{e^{-2Zr_1}}{r_1}\int_0^{r_1} dr_2\, r_2^2\, e^{-2Zr_2}$$

$$+\int_0^\infty r_1^2 dr_1 \left(\int_{r_1}^{\infty} dr_2\, r_2\, e^{-2Zr_2}\right) e^{-2Zr_1}$$

$$\int e^{-\alpha r}\, r\, dr = I_1 = -\frac{d}{d\alpha} I_0 \qquad -\left(\frac{1}{\alpha^2}+\frac{r}{\alpha}\right)e^{-\alpha r}$$

$$I_0 = \int e^{-\alpha r} dr = -\frac{1}{\alpha} e^{-\alpha r}$$

$$I_2 = -\frac{d}{d\alpha} I_1 = \frac{e^{-\alpha r}}{\alpha^3}\left[2+2r\alpha+(r\alpha)^2\right]$$

$$\frac{5}{4}\cdot\frac{1}{\alpha^5} \qquad \alpha \to 2Z$$

$$16\cdot\frac{5}{4} Z^6 \frac{1}{Z^5\cdot 2^5} = \frac{5}{8} Z \left(\frac{5}{8}\frac{Z}{a_0}\right)$$

2004.09.22/img$_1$090.*pdf*

$$\left\langle \varphi^Z_{1s}\varphi^Z_{1s} \left| \frac{1}{|\vec r_1-\vec r_2|} \right| \varphi^Z_{1s}\varphi^Z_{1s}\right\rangle$$

$$= \frac{5}{8} Z$$

$$\varphi_{1s}(\vec r) = 2\cdot e^{-\frac{Z}{a}r}\cdot\sqrt{\left(\frac{Z}{a_0}\right)^3}\; Y_{00}$$

$$Y_{00} = \frac{1}{\sqrt{4\pi}}$$

$$\frac{1}{|\vec r_1-\vec r_2|} = \sum_l{}' \sum_m{}' \frac{4\pi}{2l+1}\frac{r_<^l}{r_>^{l+1}} Y^*_{lm}(\hat r_1) Y_{lm}(\hat r_2)$$

Product of hydrogen-like (Z) orbitals $\psi_{nlm}\left(\frac{Z\vec r}{a_0}\right)$;

$$\left\langle T_1 + T_2 + V_1 + V_2 + \frac{e^2}{|\vec r_1-\vec r_2|}\right\rangle \left(\frac{e^2}{a_0}\right)$$

$$\frac{Z^2}{n_1^2}E_0 + \frac{Z^2}{n_2}E_0 + R_{n_1l_1m_1,n_2l_2m_2}\, Z Z E_0$$

2004.09.23/ph26x$_0$020.*pdf*

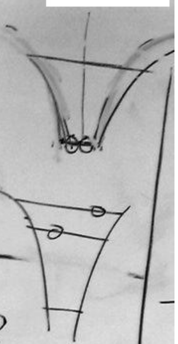
in a.u $E_0 = -\frac{1}{2}$ au

G.S of Helium

represented as

$\varphi_{1s}^{Z=2} \cdot \varphi_{1s}^{Z=2}$

$-\frac{Z^2}{2} - \frac{Z^2}{2} + \frac{5}{8} Z$



1 a.u. $\Rightarrow$ 27.2 eV

$-4 * 27.2 = -108.8$

$+ 5/8 \cdot 2 \cdot 27.2$ 54.4

$-4 + \frac{5}{8} \cdot 2 \longrightarrow -74.8$ eV

Vary Z

H^- He Li^+ Be^{++} B^{3+} C^{4+}

2004.09.23/ph26x$_0$021.*pdf*

$E_{ie} \propto Z^2$

$E_{rep} \propto Z$

$\frac{E_{rep}}{E_{ie}} \propto \frac{1}{Z}$

$-Z^2 + \frac{5}{8} Z = E_{2el}(Z)$

Perturbation theories

$H_0 \varphi_i = E_i \varphi_i$ $\{\varphi_i \quad i=1 \ldots \infty\}$

this is a complete set of functions

(Looks like Fourier Series

in F.S. $N_m e^{imk_0 \cdot x} = \varphi_m$

$\psi(x) = \sum_{m=1}^{\infty} c_m \varphi_m(x)$ $\langle \varphi_i | \varphi_1 \rangle$

$\int \psi_i O \psi_j = \langle \varphi_i | O | \varphi_j \rangle$

2004.09.23/ph26x$_0$022.*pdf*

$$\psi(r_1, r_2) = \sum_m{}' c_m(r_1)\varphi_m(r_2)$$

[parametric function,
r_1 looked at as a parameter

$$c_m(r_1) = \sum_m{}' d_{nm}\,\varphi_m(r_1)$$

$$\psi(r_1 r_2) = \sum_{r_1}\sum_{r_2}{}' d_{nm}\,\varphi_m(r_1)\varphi_m(r_2)$$

$\alpha \quad (m\,m)$

$$\psi(r_1, r_2) = \sum_\alpha{}' \underline{d_\alpha}\,\phi_\alpha(r_1 r_2)$$

$$\phi_\alpha(r_1 r_2) = \varphi_n(r_1)\varphi_m(r_2)$$

$$H\psi = E\psi$$

2004.09.23/ph26x$_0$023.*pdf*

$\langle \varphi_\alpha | \varphi_\beta \rangle = \delta_{\alpha\beta}$
orthonormal sets
scalar product → zero

$$H\psi = E\psi$$

$$H\sum{}' d_\alpha \phi_\alpha = E\sum{}' d_\alpha \phi_\alpha$$

$$\langle \phi_\beta | H | \sum d_\alpha \phi_\alpha \rangle$$

$$= E\sum{}' d_\alpha \langle \phi_\beta | \phi_\alpha \rangle$$

for each β many equations

$$\sum_\alpha H_{\beta\alpha} d_\alpha = E d_\beta$$

$$\left[\, H_{\beta\alpha} \,\right]\begin{bmatrix} d_1 \\ \vdots \\ d \end{bmatrix} = E\begin{bmatrix} d_1 \\ \vdots \\ d_\alpha \end{bmatrix}$$

Configuration mixing

2004.09.23/ph26x$_0$025.*pdf*

$$\left\langle \varphi_{1s}^{Z}\, \varphi_{1s}^{Z} \right| \frac{1}{|\vec{r}_1 - \vec{r}_2|} \left| \varphi_{1s}^{Z}\, \varphi_{1s}^{Z} \right\rangle = \frac{5}{8} Z$$

Variational methods

$$\mathcal{E} = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle}$$ has minimum

for the TRUE Ground state

any other ϕ than $\psi_{GS} \equiv \varphi_0$

$$\phi = \sum_{n=0}^{\infty}{}' c_n \varphi_n$$

assume we know all the φ_n

$H \varphi_n = E_n \varphi_n$

$E_0 < E_n$ where $n > 0$

2004.09.23/ph26x$_0$027.*pdf*

in a.u. $E_0 = -\frac{1}{2}$ au

G.S of Helium represented as

$\varphi_{1s}^{Z=2} \cdot \varphi_{1s}^{Z=2}$

$$-\frac{Z^2}{2} - \frac{Z^2}{2} + \frac{5}{8} Z$$

E_{ie}

E_{re}

$-Z^2$

$$\langle \phi | H | \phi \rangle = \sum_m{}' \sum_n{}' c_n^* c_m \langle \varphi_n | H | \varphi_m \rangle$$

$$H | \varphi_m \rangle = E_m | \varphi_m \rangle ; \quad \langle \varphi_n | \varphi_m \rangle = \delta_{nm}$$

$$\to \sum_m{}' \sum_n{}' \delta_{mn} E_m c_n^* c_m = \sum_n{}' E_n |c_n|^2$$

$$\langle \phi | \phi \rangle = \sum_n{}' |c_n|^2$$ [shorter if assumed $\langle \phi | \phi \rangle = 1$]

$$\frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\sum' E_n |c_n|^2}{\sum' |c_n|^2} \leqslant \frac{E_0 \cdot \sum' |c_n|^2}{\sum' |c_n|^2}$$

2004.09.23/ph26x$_0$029.*pdf*

$$Z^2 + \frac{5}{8} Z = E_{2el}(Z)$$

$\mathcal{E}(z) \qquad Z = 2$

$$H = T^{z^2} \quad \frac{Ze^2}{r}^{z} \quad \frac{e^2}{|r_1 - r_2|}^{Z}$$

wave function given by z

$$\mathcal{E}(z) = z^2 - 2zZ + \frac{5}{8} z$$

$z = Z$ agrees with above;

Hydrogen-like functions with variable $z \to \mathcal{E}(z)$

2004.09.23/ph26x$_0$030.*pdf*

$$\frac{d\mathcal{E}(z)}{dz} = 0$$

$$\frac{d}{dz}\left(z^2 - 2Zz + \frac{5}{8} z\right) = 0$$

$$2z - 2Z + \frac{5}{8} = 0$$

$$z = Z - \frac{5}{16}$$

$$\approx \; z \approx Z - 0.3$$

another, better approach

z_1, z_2

one electron z_1

second -"- z_2

$$N\{\varphi_{z_1}(1)\,\varphi_{z_2}(2) + \varphi_{z_2}(1)\,\varphi_{z_1}(2)\}$$

$$e^{-(z_1 r_1 + z_2 r_2)} + e^{-(z_2 r_1 + z_1 r_2)}$$

elementary correlation

Elementary Correlation

$$N\left(e^{-Z_1 r_1 - Z_2 r_2} + e^{-Z_2 r_1 - Z_1 r_2}\right)$$

2004.09.23/ph26x$_0$031.*pdf*

configuration mixing
explores correlation

independent $\varphi_1(r_1)\ \varphi_2(r_2)$

$\longrightarrow$ Probability $|\varphi_1(r_1)|^2 \cdot |\varphi_2(r_2)|^2$

$\sum_{mn} c_{mn}\ \varphi_m(r_1)\,\varphi_n(r_2)$

correlation $\psi(r_1, r_2)$

Hylleraas

$s = r_1 + r_2$

$t = r_1 - r_2 \quad T = (r_1 - r_2)^2$

$u = |\vec{r}_1 - \vec{r}_2|$

$\phi(s,t,u) = e^{-ks} \sum c_{\ell,2m,n}\, t^{2m} u^n$

Pekeris

2004.09.23/ph26x$_0$032.*pdf*

$T_1 + T_2 + V_1 + V_2 + \frac{e^2}{|r_1 - r_2|}$ $\frac{1}{2}$

Triplet $\rightarrow$ spatial antisym

$\frac{1}{\sqrt{2}}\left(\varphi_a(r_1)\,\varphi_b(r_2) - \varphi_b(r_1)\,\varphi_a(r_2)\right) = \psi$

$\int \psi^* \psi \, dr_1 dr_2 \rightarrow 2$

$\int \varphi_a T \varphi_b \, d\tau \rightarrow \langle \varphi_a | T | \varphi_b \rangle$

$\langle \varphi_a \varphi_b | T_1 | \varphi_c \varphi_d \rangle = \langle \varphi_a | T_1 | \varphi_c \rangle \langle \varphi_b | \varphi_d \rangle$

$= \langle \varphi_a | T_1 | \varphi_c \rangle \, \delta_{bd}$

$\langle \varphi_a \varphi_b | T_1 + V_1 | \varphi_c \varphi_d \rangle$

$= \delta_{bd} \cdot E_c \, \delta_{ac}$

$\langle \psi_{12} | H | \psi_{12} \rangle$

(2 terms) (3 terms) (2 terms)

2004.09.29/img$_1$135.*pdf*

$2 \quad \langle ab | T_1+V_1 | ab \rangle \quad E_a$

$\langle ab | T_2+V_2 | ab \rangle \quad E_b$

$\langle ab | \frac{e^2}{|r_1-r_2|} | ab \rangle$ keep

$- \langle ab | T_1+V_1 | ba \rangle \quad 0$

$- \langle ab | T_2+V_2 | ba \rangle \quad 0$

$- \langle ab | \frac{e^2}{r_1-r_2} | ba \rangle$ keep

$- \langle ba | T_1+V_1 | ab \rangle \quad 0$

$- \langle ba | T_2+V_2 | ab \rangle \quad 0$

$- \langle ba | \frac{e^2}{r_1-r_2} | ab \rangle$ keep

$\langle ba | T_1+V_1 | ba \rangle \quad E_b$

$\langle ba | T_2+V_2 | ba \rangle \quad E_a$

$\langle ba | \frac{e^2}{|r_1-r_2|} | ba \rangle$ keep

2004.09.29/img$_1$136.*pdf*

$$\frac{1}{2}\Big[E_a + E_b + \langle ab|V_{12}|ab\rangle - \langle ab|V_{12}|ba\rangle - \langle ba|V_{12}|ab\rangle + E_b + E_a + \langle ba|V_{12}|ba\rangle \Big]$$

$\langle ab | V_{12} | ab \rangle = \langle ba | V_{12} | ba \rangle$

(exchange - symmetric ...)

$\langle ab | V_{12} | ba \rangle = \langle ba | V_{12} | ab \rangle$

BECAUSE

$$\int \psi_a(1)\psi_b(2) \frac{e^2}{|r_1-r_2|} \psi_b(1)\psi_a(2)\, d\tau$$

$$= \int \psi_a(2')\psi_b(1') \frac{1}{|r_2'-r_1'|} \psi_b(2')\psi_a(1')\, d\tau'$$

$\langle \psi_{ab} | H | \psi_{ab} \rangle$

$$= E_a + E_b + \langle \varphi_a \varphi_b | \frac{e^2}{|r_1-r_2|} | \varphi_a \varphi_b \rangle$$

$$\xrightarrow{\text{DIRECT}} \qquad - \langle \varphi_a \varphi_b | \frac{e^2}{|r_1-r_2|} | \varphi_b \varphi_a \rangle$$

EXCHANGE

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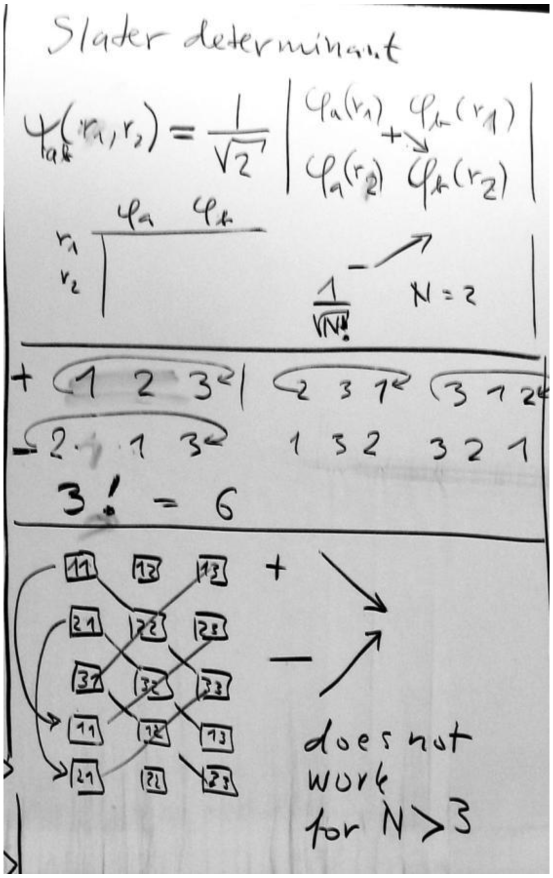

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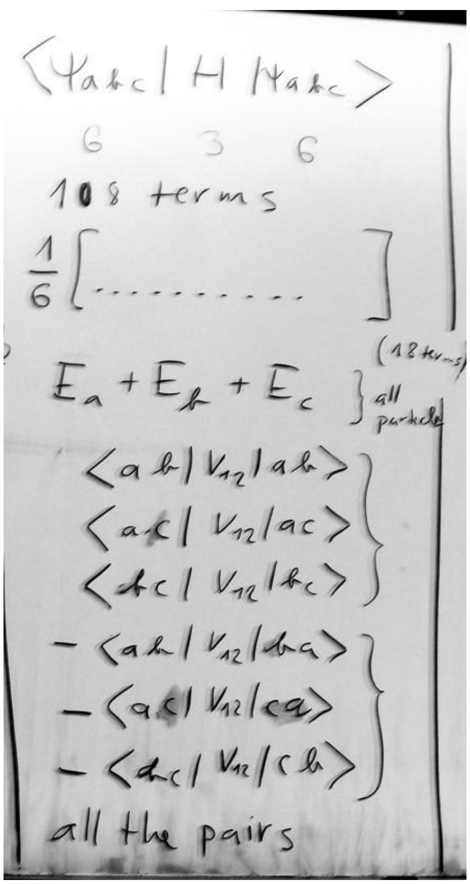

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Hartree-Fock

Hartree & Hartree

$$\int \psi_a^*(r_1) \underbrace{\sum_{i\neq a} \left[\int \psi_i^*(r_2) \frac{e^2}{|r_1-r_2|}\psi_i(r_2)\,dr_2\right]}\psi_a(r_1)\,dr_1$$

$e\rho(r) \leftarrow$ charge density

$\rho(r) \leftarrow$ particle density

$$\psi_i^*(r)\psi_i(r) \equiv |\psi_i(r)|^2 = P(r)$$

$$e\rho \longrightarrow eP \longrightarrow e|\psi_i(r)|^2$$

$$\sum_{i=1}^{N} e|\psi_i(r)|^2 \;;$$ interaction with a charge density di

2004.09.29/$\text{img}_1$151.*pdf*

$$\frac{q_1 q_2}{|r_1 - r_2|} \qquad q_2 = e\rho\,dV \equiv = eP\,dV$$

$$q_1 \frac{e\rho(r)\,dV}{|r_1 - r|}$$

with the whole "cloud"

$$q_1(r_1) \int \frac{e\rho(r)}{|r_1 - r|}\,dV$$

$$-\frac{Ze^2}{r} + e^2 \int \frac{\sum_{i=1}^{N} |\varphi_i(r')|^2}{|r - r'|}$$

an extra electron sees an atom

$$W(r) = -\frac{Ze^2}{r} + e\int \frac{\sum_i |\varphi_i(r')|^2}{|r - r'|}\,dr'$$

φ_i ... hydrogen-like orbitals??

2004.09.29/$\text{img}_1$154.*pdf*

$$\sum_i{}' (T_i + V_i) + \sum_{\text{pairs}}{}' \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

$$\to \sum_i{}' T_i + W_i(r)$$

$\varphi_i^{(0)}(r)$ guess

$$W^{(1)}(r) = -\frac{Ze^2}{r} \int \sum_{i=1}^{N} \frac{|\varphi_i^{(0)}(r)|}{|r-r'|} dr'$$

$$(T + W^{(1)})\,\varphi_i^{(1)} = E^{(1)} \varphi_i^{(1)}$$

$$\varphi_1^{(1)}, \varphi_2^{(1)} \dots \varphi_N^{(1)}$$

$$\hookrightarrow W^{(2)}(r) = -\frac{Ze^2}{r} + \int \sum_{i=1}^{N}{}' \frac{|\varphi_i^{(1)}(r')|^2}{|r-r'|} dr'$$

$$\left[T + W^{(2)}\right] \varphi_i^{(2)} = E_i^{(2)} \varphi_i^{(2)}$$

$$W^{(3)}$$

??

2004.09.29/img$_1$155.*pdf*

$$\varphi_i^{(0)} \longrightarrow W^{(1)}$$

$$W_1 \to \text{Schr} \to \varphi^{(1)}$$

$$\varphi^{(1)} \longrightarrow W^{(2)}$$

$$W_2 \to \text{Schr} \to \varphi^{(2)}$$

$$\varphi^{(2)} \longrightarrow W^{(3)}$$

$$\vdots$$

$$\varphi^{(n)} \longrightarrow W^{(n+1)}$$

Self-consistent

$$W^{(n+1)} - W^{(n)} \to 0$$

$$\int |\varphi_i^{(n+1)} - \varphi_i^{(n)}|^2 d^3r \leq \varepsilon$$

$$\varepsilon = 10^{-10}$$

Why should it converge??

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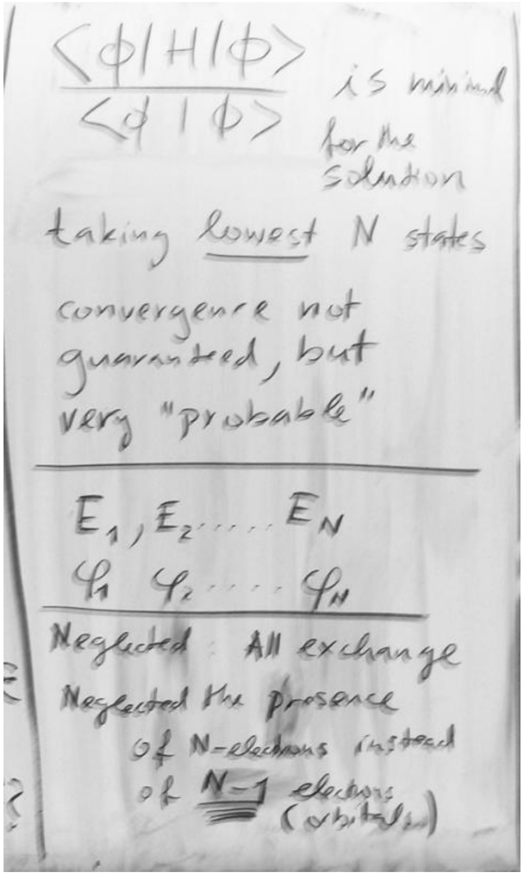

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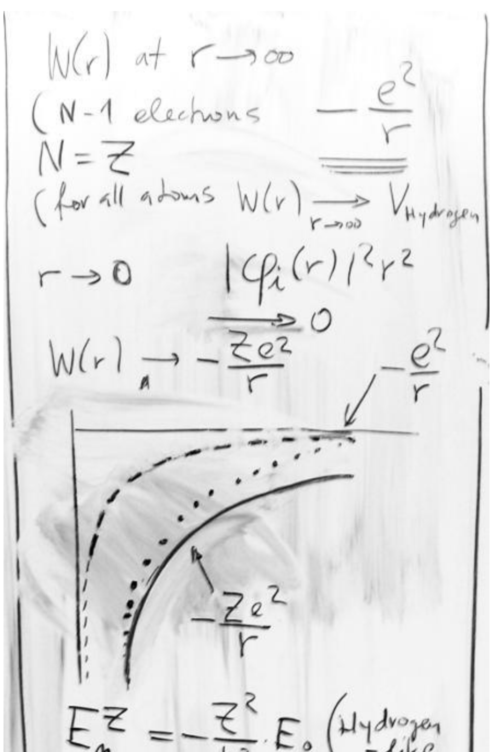

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Minimum with a constraint

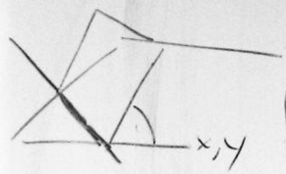
why:

$$\frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle}$$

$$f(x) = f(x_0) + \frac{1}{2} C (x-x_0)^2$$

$$a(x-x_0)^2 + f(x-x_c)$$

2 dim. ... minimum on a line



the line is an intersection

$$\boxed{g(x,y)=0}$$

$$ax+by+c = (cz)$$

$$f(x,y) - \lambda g(x,y)$$

2004.09.30/black0013.pdf

2 equations

$$\nabla\left[f(x,y) - \lambda g(x,y)\right] = 0$$

$$g(x,y) = 0$$

$\to x_0, y_0, \lambda$ 3 unknowns

λ moves minimum of the $f+\lambda g$ at the $g(x,y)=0$ the function REMAINS THE SAME ($f+\lambda g \equiv f$ at $g=0$

$$\langle\phi|H|\phi\rangle - \lambda\langle\phi|\phi\rangle$$

$$g = \langle\phi|\phi\rangle - 1, \; |\phi\rangle, \langle\phi|$$

i.e. $\phi^*(x)$ $\phi(x)$

$$\int\phi^* H\phi\, d\tau - \lambda\int\phi^*\phi \;\Big|\; \delta\phi^*$$

extremum

$$\int\delta\phi^*(H\phi - \lambda\phi)\,d\tau = 0$$

$$\boxed{H\phi - \lambda\phi = 0}$$

2004.09.30/black0014.pdf

Slater determinant
with N-orbitals

$N!$ terms

$(N!)^2$ .. all zero except of $N!$ terms

each with "itself"

$$\sum_{i,j} \frac{e^2}{|r_i - r_j|} + H_0 = H$$

$$\langle \phi | H | \phi \rangle$$

$$\sum_{\text{orbitals}}' \langle i | H_0 | i \rangle$$

$$+ \sum_{\text{pairs}}' \left[J_{ij,ij} - K_{ij,ji} \right]$$

$$J_{ij} - K_{ij}$$

2004.09.30/black0015.pdf

$\langle \phi | \phi \rangle \rightarrow$? Each of the orbitals is normalized?

$\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$?

$N \times N$ Lagrange multipliers

$\lambda_{ij} \rightarrow \lambda_{ii} \equiv \lambda_i$ by diagonalize

$$\langle \delta\varphi_i | H_0 | \varphi_i \rangle$$

$$+ \sum_k \langle \delta\varphi_i \varphi_k | H_1 | \varphi_i \varphi_k \rangle$$

$$= \sum_k \langle \delta\varphi_i(r) \varphi_k(r') | H_1 | \varphi_k(r) \varphi_i(r') \rangle = \lambda_i \langle \delta\varphi_i | \varphi_i \rangle$$

$$H_0 | \varphi_i \rangle + \sum_k \left(\langle \varphi_k(r') | H_1(r, r') | \varphi_k(r') \rangle \right) | \varphi_i \rangle$$

$$- \left[\sum_k' \int \varphi_k(r') V(r, r') \varphi_i(r') \, dr' \right] \varphi_k(r)$$

$$= \lambda_i | \varphi_i \rangle$$

2004.09.30/black0016.pdf

$$\left[\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} + \sum_{k\neq i} \int \frac{|\varphi_k(r')|^2 e^2}{|r-r'|} d^3r'\right]\varphi_i(r)$$

$$- \sum_{k\neq i} \int \frac{\varphi_k(r)\,\varphi_k^*(r')}{|r-r'|} e^2\, \varphi_i(r') = \lambda_i \varphi_i(r)$$

$$\underbrace{\left[T + V_0 + W\right]}_{\text{local potentials}}\varphi(r) + \int \underbrace{V(r,r')}_{\text{nonlocal potential}}\varphi(r')\, d^3r' = \lambda_i \varphi_i(r)$$

nonlocal potentials $\longrightarrow$ velocity dependent

$V(r,r')$ schematically:

$$V(r,r') = V(r,r) + \underbrace{\frac{dV}{dr}}_{\left(i\hbar \frac{d}{dr}\right)\ \text{momentum}}(r-r') + \frac{d^2V}{dr^2}(r-r')^2 \ldots$$

$\psi(r') = \psi(r) + \ldots$

2004.09.30/black0017.pdf

Hartree + simulated exchange (exchange corrections)

Density functional method

[prescription for exchange is more appropriate]

The effect of selfconsistent field

n, l degeneracy is split

Hydrogen-like E_n

Atomic field $E_{n,l}$

$$\boxed{E_{2s} < E_{2p}}$$

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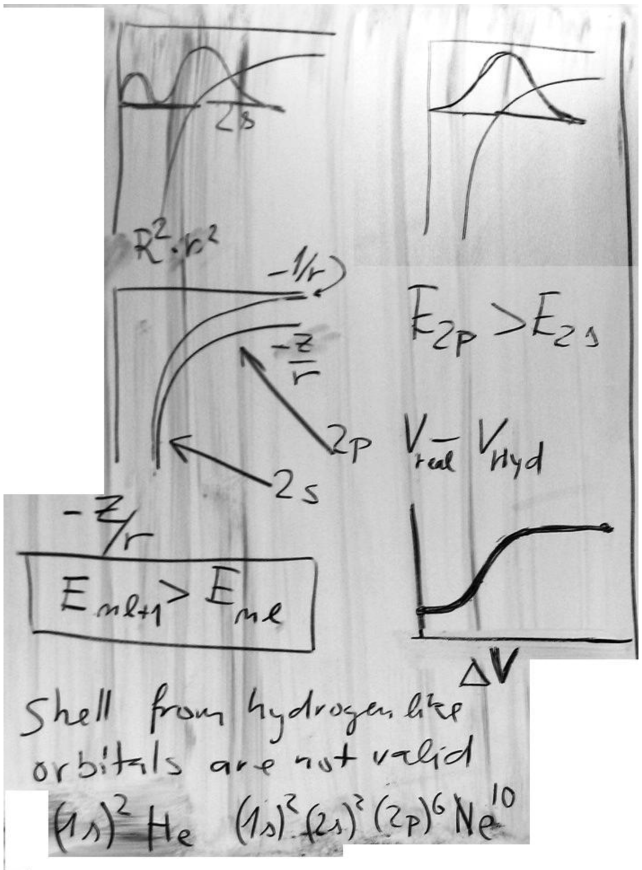

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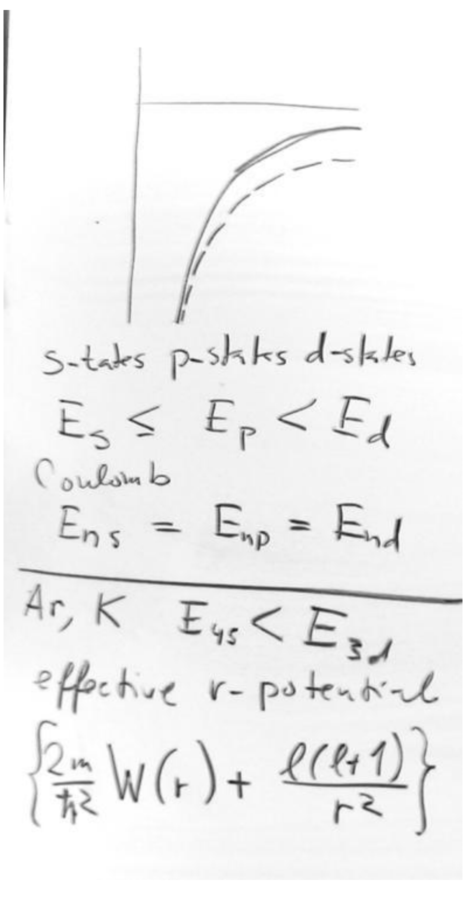

2004.10.06/img$_1$207.*pdf*

Herman-Skillman code
"Atomic Structure course"

NIST

Single-particle orbitals
- Single particle energies
Self-consisdent field

$\varepsilon_{1s} + \varepsilon_{1s} + \varepsilon_{2s} + \varepsilon_{2s} + \varepsilon_{2p} \cdots$

$$= \sum_{i=1}^{N} \varepsilon_{\text{orbital}} \stackrel{?}{=} E_{\text{atom}}$$

cannot be! The interaction
is counted twice

$$T_i + V_i + \sum_{\text{pairs}} \frac{e^2}{r_{ij}}$$

2004.10.06/$\text{img}_1$208.*pdf*

$$\sum_{\text{all } i}{}' \left(T_i + V_i + \frac{1}{2} \sum_{\text{all } j}{}' V_{ij} \right)$$

Single particle

$$\sum_{i}{}' \left[T_i + V_i + \sum_{\text{all } j}{}' V_{ij} \right]$$

$$\rightarrow \sum_{\text{all orbitals}}{}' \varepsilon_i$$

The repulsion counted twice

$$E_{GS} = \left(\sum_{\text{orbitals}}{}' \varepsilon_i \right) - E_{\text{repulsion}}$$

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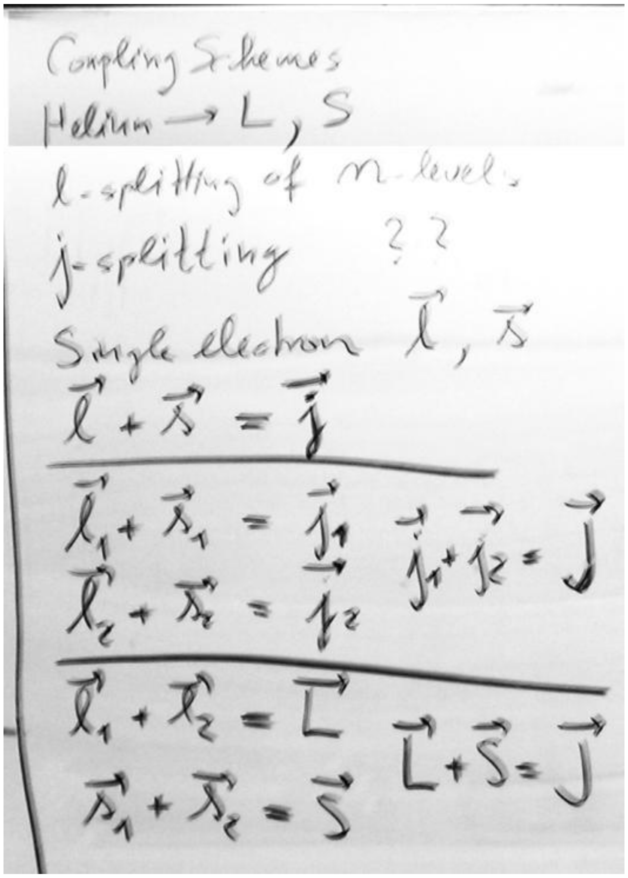

Coupling Schemes

Helium $\rightarrow L, S$

l-splitting of n-levels

j-splitting ??

Single electron $\vec{l}, \vec{s}$

$\vec{l}+\vec{s}=\vec{j}$

$\vec{l}_1+\vec{s}_1=\vec{j}_1$

$\vec{l}_2+\vec{s}_2=\vec{j}_2$ $\quad \vec{j}_1+\vec{j}_2=\vec{J}$

$\vec{l}_1+\vec{l}_2=\vec{L}$

$\vec{s}_1+\vec{s}_2=\vec{S}$ $\quad \vec{L}+\vec{S}=\vec{J}$

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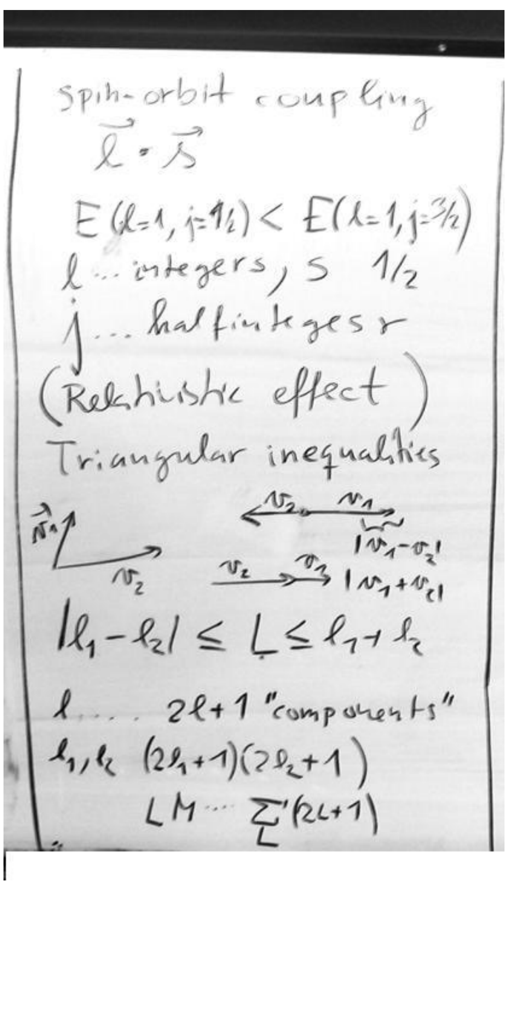

spin-orbit coupling

$\vec{l}\cdot\vec{s}$

$E(l=1, j=1/2) < E(l=1, j=3/2)$

l ... integers, s $1/2$

j ... halfintegers

(Relativistic effect)

Triangular inequalities

$|l_1-l_2| \le L \le l_1+l_2$

l .... $2l+1$ "components"

l_1, l_2 $\quad (2l_1+1)(2l_2+1)$

$LM \cdots \sum_L{}'(2L+1)$

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Spectroscopy

Spectra – collections, systems

– understanding
interpretation

Experimental / Measurement

Theoretical spectroscopy

(Exotic species U^{89+}

Li-like Uranium

Basic research

Standards → very important for applications

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Spectroscopic notation

$$^{2S+1}L_J$$

$\boxed{\text{Terms}}$ $L = \sum_i l_i$ $\vec{J} = \vec{L} + \vec{S}$

$S = \sum_i s_i$

(Selection rules, parities etc...)

Configuration → Terms

$l_1, l_2 \longrightarrow {}^{2S+1}L_J$

Exercise 1s and 2p (configuration)
How many terms can you make?
2p 3p configuration → terms?

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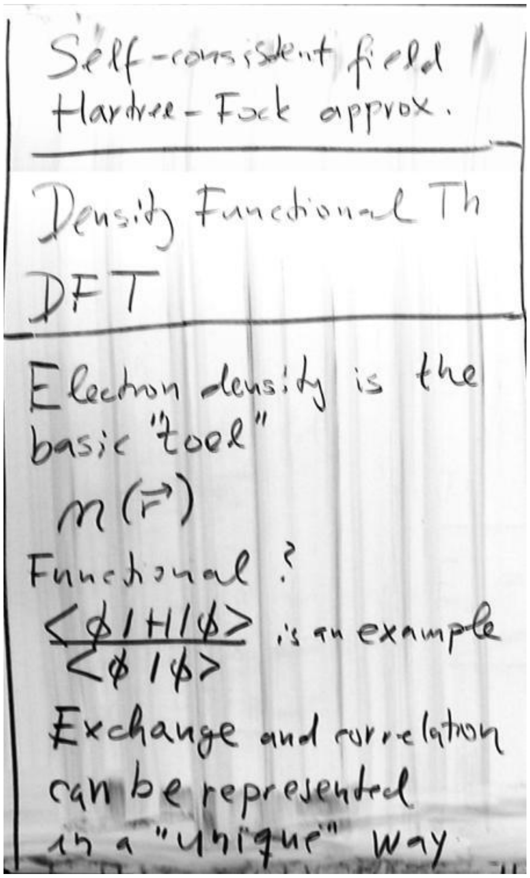

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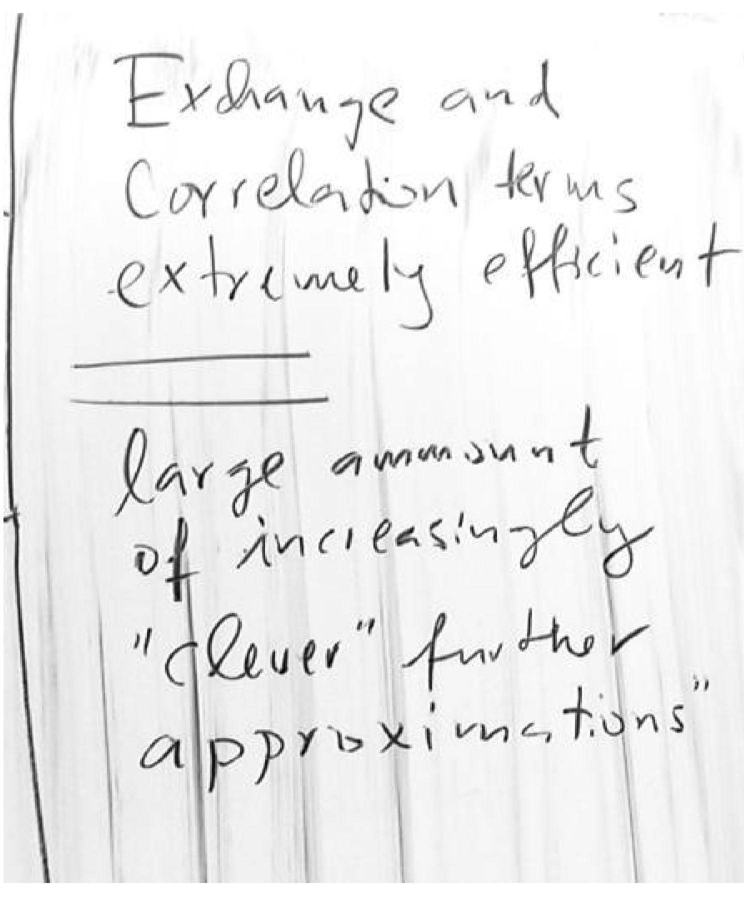

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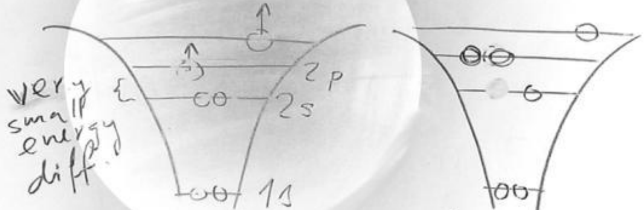
Helium G.S $1s^2$

Carbon GS $1s^2\,2s^2\,2p^2$

exc $1s^2\,2s^2\,2p\,3s$



^3P_J

perhaps it can mix

$$\Psi(x_1 \dots x_6) = \sum_{\substack{\text{all}\\ \text{possible}\\ \text{configurations}}}' \underline{\underline{c_m}}\, \Phi_m$$

m stands for various config.

2004.10.07/img$_1$229.pdf

H contains electron-electron repulsions

Single particle picture

[Slater determinants, mean field does not minimize the repulsion]

Variational principle: The lowest energy → the G.S.

$1s\,2s \rightarrow 2p\,2p \dots\dots$

$$\begin{bmatrix} \text{Matrix} \end{bmatrix} \begin{bmatrix} c_n \end{bmatrix} = E \begin{bmatrix} c_n \end{bmatrix}$$

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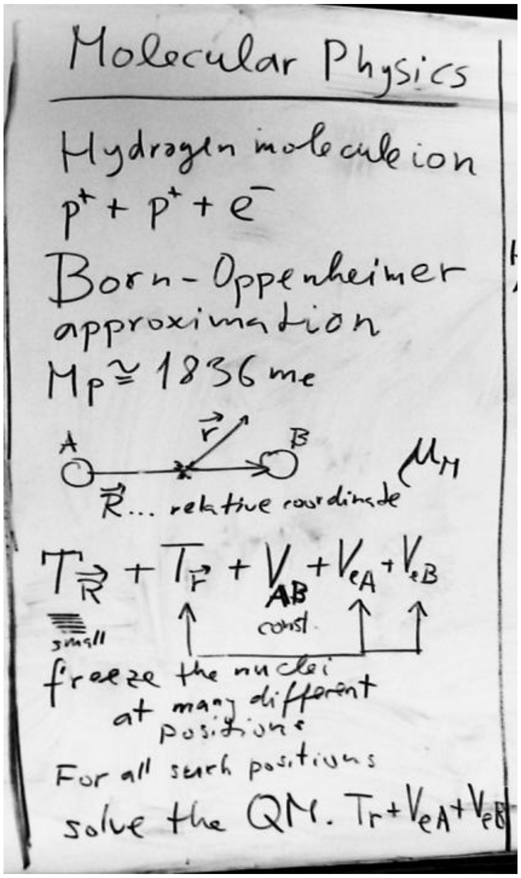

Molecular Physics

Hydrogen molecule ion

$p^+ + p^+ + e^-$

Born-Oppenheimer approximation

$M_p \cong 1836\, m_e$

A B $\vec{r}$ μ_M

$\vec{R}$... relative coordinate

$T_{\vec{R}} + T_{\vec{r}} + V_{AB} + V_{eA} + V_{eB}$

small const

freeze the nuclei at many different positions

For all such positions

solve the QM. $T_r + V_{eA} + V_{eB}$

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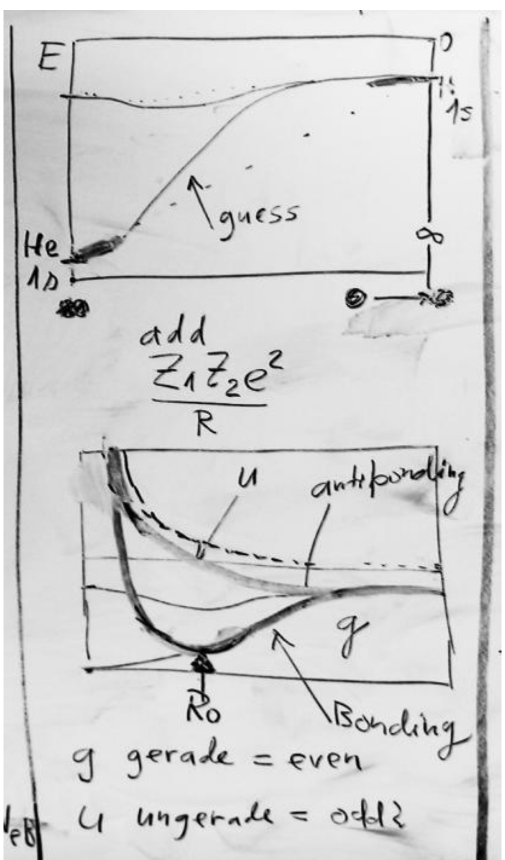

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Electron energies

Electron "spectra"

scale: 2-3 eV

Vibrational motion

$$\frac{1}{2} k \Delta R^2 \to \frac{1}{2} m\omega_e^2 \Delta R^2$$

$$\frac{1}{2} k \to \frac{1}{2} m\omega^2$$

$$m_e \omega_e^2 \approx M_N \omega_V^2$$

$$\omega_e^2 \propto 2000\, \omega_V^2$$

$$\omega_e^2 \overset{5}{\propto} 10^4\, \omega_V^2$$

$$\hbar \omega_V \approx 0.01 \hbar \omega_e$$

$$\Delta E_V \approx 0.01 \times 2\,\mathrm{eV}$$

$$k_B T_{300K} \approx \frac{1}{40}\,\mathrm{eV}$$

2004.10.07/img$_1$233.*pdf*

r ω

$$v = r\omega \qquad \frac{1}{2} m v^2 \longrightarrow \frac{1}{2} \underbrace{m r^2} \omega^2$$

$$m r^2 \to \mathcal{I} \qquad E_{rot} = \frac{1}{2} \mathcal{I} \omega^2$$

$$L = \mathcal{I}\omega \qquad E_{rot} = \frac{1}{2\mathcal{I}} L_{rot}^2$$

$$L \propto \hbar \qquad E_{rot} \propto \frac{1}{2\mathcal{I}} \hbar^2$$

$$E_{el} \propto \frac{\hbar^2}{2 m a_0^2} \qquad \mathcal{I} \propto M a_0^2$$

$$\frac{E_{el}}{E_{rot}} \propto \frac{\hbar^2}{2 m_e a_0^2} \Big/ \frac{\hbar^2}{2 M a_0^2} \approx \frac{M}{m_e}$$

$$\boxed{\frac{E_{vib}}{E_{el}} \propto \sqrt{\frac{m_e}{M}} \qquad \frac{E_{rot}}{E_{el}} \propto \frac{m_e}{M}}$$

2004.10.07/img$_1$234.*pdf*

$$\left[T_{\vec r} - \frac{Z_1 e^2}{r_1} - \frac{Z_2 e^2}{r_2}\right]\psi(r) = E\psi(r)$$

$r_1 = |\vec r + \tfrac{1}{2}\vec R|$ $\quad R$ fixed

$r_2 = |\vec r - \tfrac{1}{2}\vec R|$

$$\psi(\vec r, \vec R) = c_1\varphi_A(\vec r_1) + c_2\varphi_B(\vec r_2)$$

hydrogen like - orbitals

φ_1:

$$H(c_1\varphi_1 + c_2\varphi_2) = E(c_1\varphi_1 + c_2\varphi_2)$$

$$c_1\langle\varphi_1|H|\varphi_1\rangle + c_2\langle\varphi_1 H|\varphi_2\rangle = E(c_1\langle\varphi_1|\varphi_1\rangle + c_2\langle\varphi_1|\varphi_2\rangle)$$

and similar. **Best when** $\langle\varphi_1|\varphi_2\rangle = 0$

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E\begin{pmatrix} 1 & S_{12} \\ S_{21} & 1 \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}.$$

2004.10.07/img$_1$235.*pdf*

$H_{11}(R)\ H_{12}(R)$

$H_{21}(R)\ H_{22}(R)$

$$H_{11} \to \underline{\underline{E_1}} - \langle\varphi_1|\frac{Ze^2}{|\vec r - \vec R|}|\varphi_1\rangle$$

$$E_1 - \frac{1}{R}\cdot G(R)$$

$$H_{12} \to \langle\varphi_1 \xleftrightarrow{R} \varphi_2\rangle$$

$$\propto e^{-R}F(R)$$

$$\begin{pmatrix} E_1 & \Delta \\ \Delta & E_2 \end{pmatrix}$$

E_2

$\sqrt{(E_2-E_1)^2+\Delta^2}$

E_1

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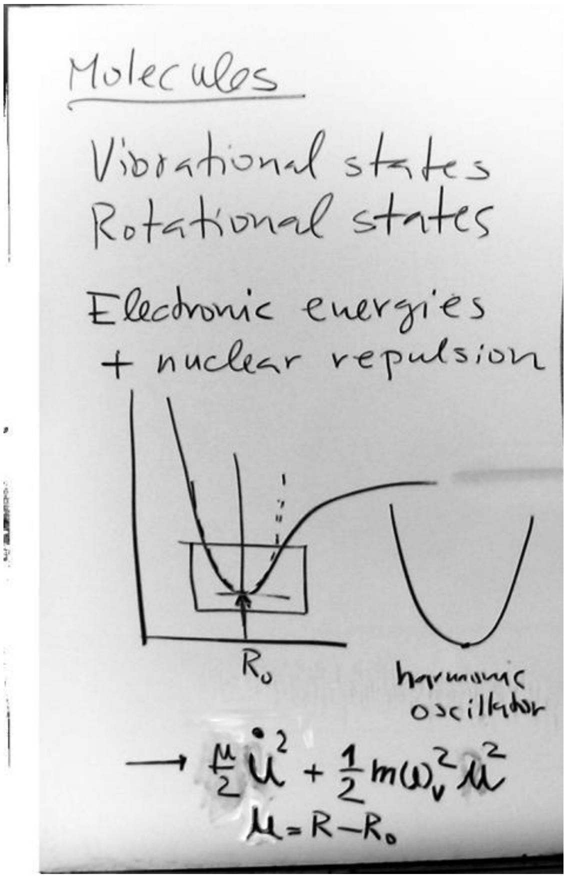

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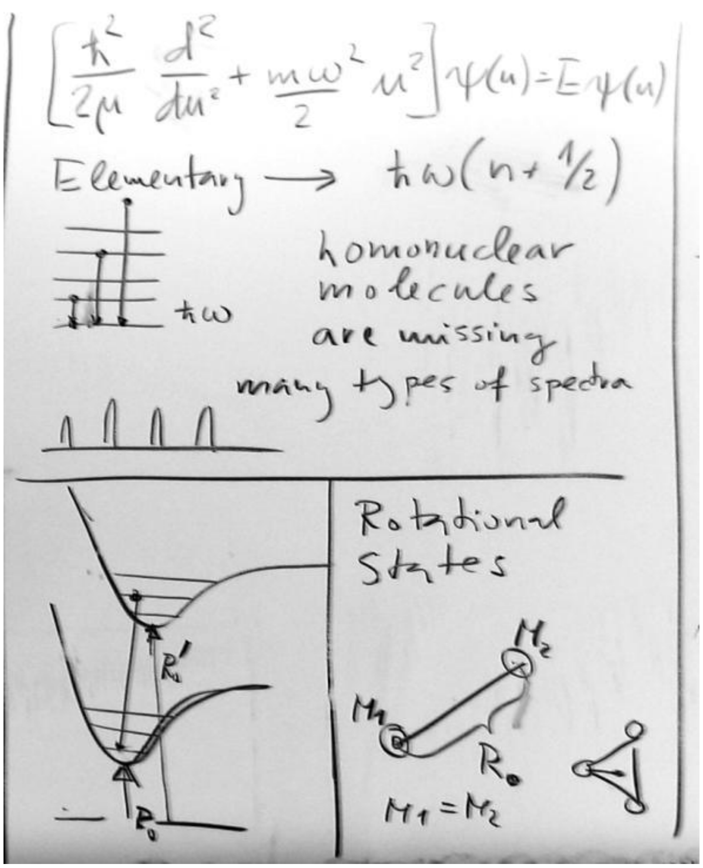

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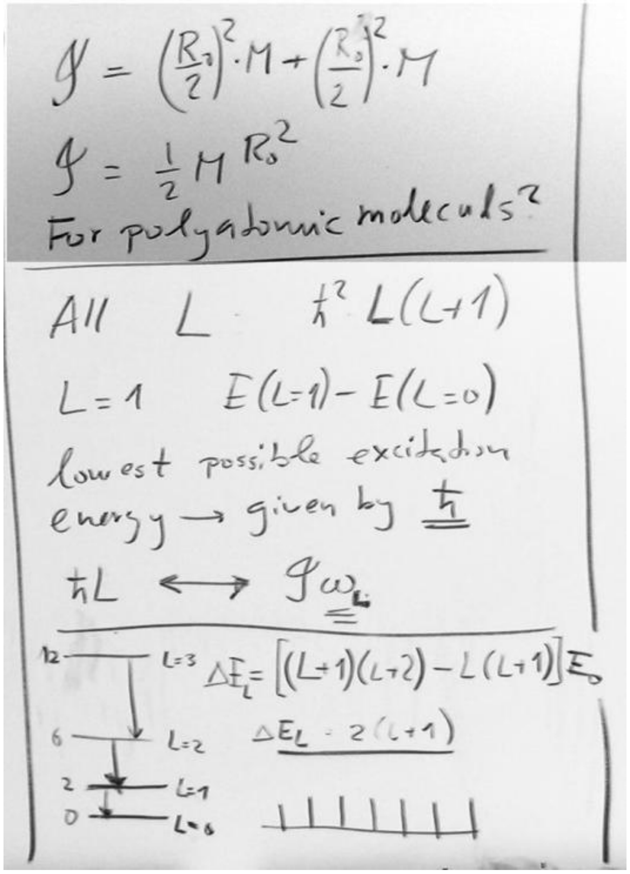

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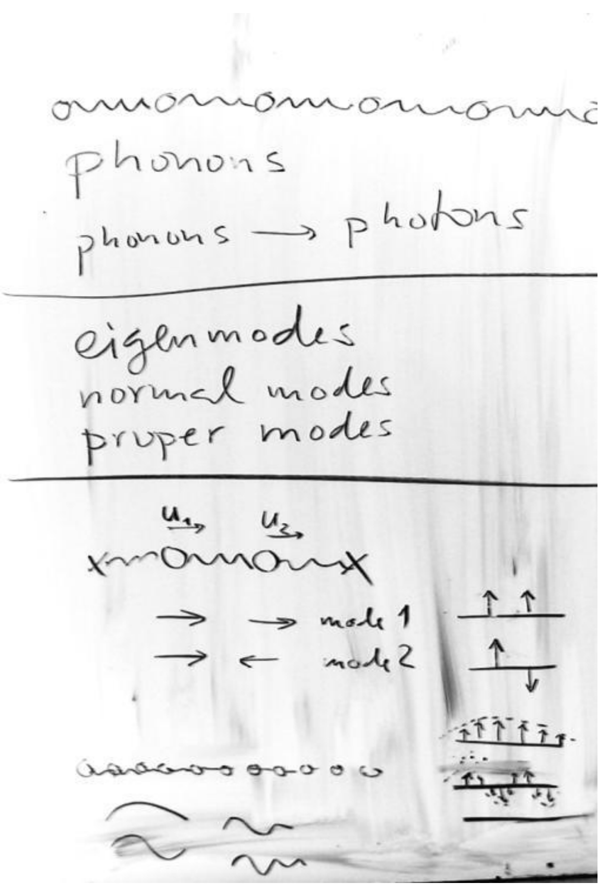

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eigenmodes
→ independent harmonic oscillations

Decomposition

System of many vibration-like degrees of freedom
→ decompose into independent eigenmodes
$\hbar\omega_k$ ... "Quanta"
→ phonons, photons and all such animals

standing waves (superpos.)
travelling waves infinite

2004.10.27/$\text{img}_1 301$.*pdf*

Electromagnetic field

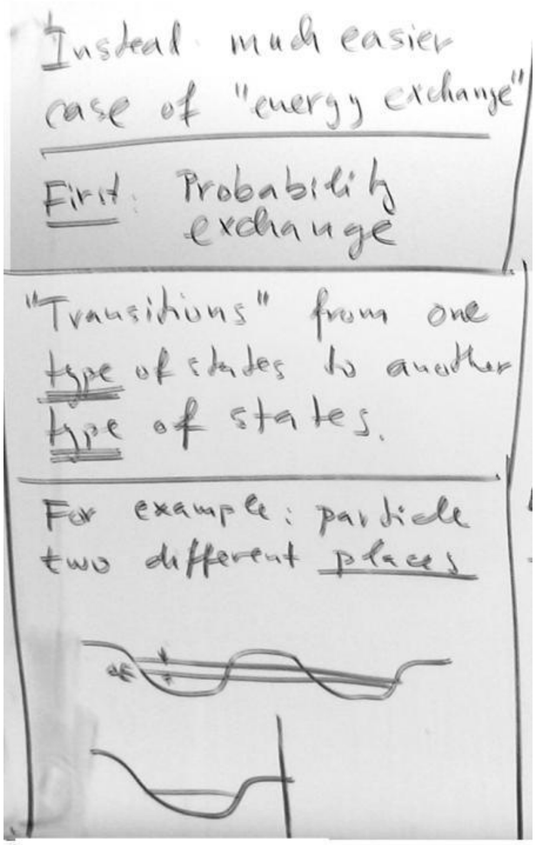
Microwave oven

Systems:

1) Electromagnetic field
   states $\hbar\omega_k \cdot n_k$
   each eigenmode
2) atoms (atom)
   E_k ... (atomic states)
3) interaction
   → atom in El.mag field

$$H_a + H_b + H_{ab}$$

2004.10.27/$\text{img}_1 302$.*pdf*



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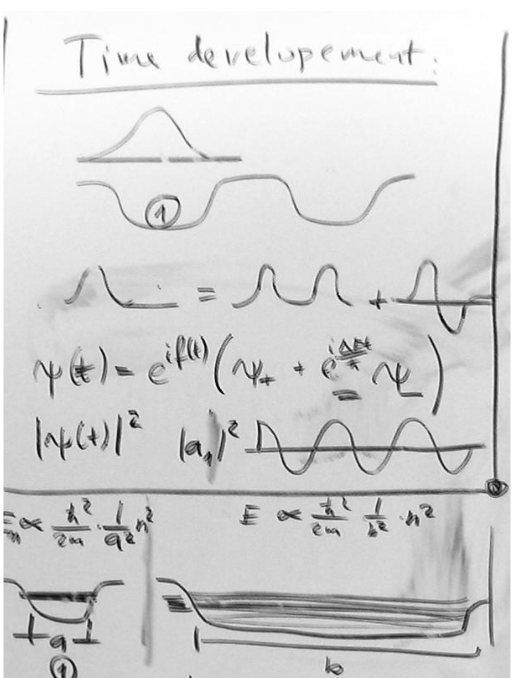

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Travelling waves v.s Standing waves

Harmonic oscillator quantization

$$\frac{1}{2}\left(P^2+Q^2\right)\hbar\omega \qquad \cancel{\left(\sqrt{m\omega\hbar}\right)}$$

$$\frac{1}{2m}p^2+\frac{1}{2}m\omega^2 q^2$$

$$\frac{1}{2}\left(P+iQ\right)\left(P-iQ\right)\hbar\omega$$ ~~if~~ P,Q numbers

$$[q,p]=i\hbar \qquad [Q,P]=i$$

$$\to \frac{1}{2}\left(P+iQ\right)\left(P-iQ\right)+\left(P-iQ\right)\left(P+iQ\right)$$

2004.10.28/img$_1$309.pdf

$$\frac{1}{2}\left(P^2+Q^2\right)=\frac{1}{2}\left(aa^+ + a^+a\right)$$

$$a=\frac{1}{\sqrt{2}}\left(P+iQ\right)$$

$$a^+=\frac{1}{\sqrt{2}}\left(P-iQ\right) \qquad [Q,P]=i$$

$$aa^+ - a^+a = 1$$

$$N=a^+a$$

$$[N,a^+]=a^+aa^+ - a^+a^+a$$

$$=a^+\underbrace{\left(aa^+ - a^+a\right)}_{1}$$

$$[N,a^+]=a^+$$

$$\frac{1}{2}\left[P^2+Q^2\right]\hbar\omega=\hbar\omega\left(N+\frac{1}{2}\right)$$

Eigenstates of H are eigenstates of N

2004.10.28/img$_1$310.pdf

$$N|E\rangle = E|E\rangle$$

$$a^+|E\rangle$$

$$N(a^+|E\rangle) = a^+N|E\rangle + a^+|E\rangle$$

$$(Na^+ - a^+N = a^+)$$

$$= E a^+|E\rangle + 1\, a^+|E\rangle$$

$\|E\rangle \longrightarrow E$	H	$E\hbar\omega$
$a^+\|E\rangle \longrightarrow E+1$	H	$(E+1)\hbar\omega$

$a|E\rangle \longrightarrow E-1$ $\therefore$ minimum must exist

$a|0\rangle \quad 0-1 \Rightarrow a|0\rangle = 0$

$$\boxed{H = \hbar\omega a^+ a + \frac{\hbar\omega}{2}}$$

2004.10.28/img$_1$311.*pdf*

Microwave oven

1) find all eigenmodes

2. ... ω_i

3 Total energy operator for microoven:

$$H = \sum_i \hbar\omega_i \left[a_i^+ a_i + \frac{1}{2}\right]$$

Casimir effect

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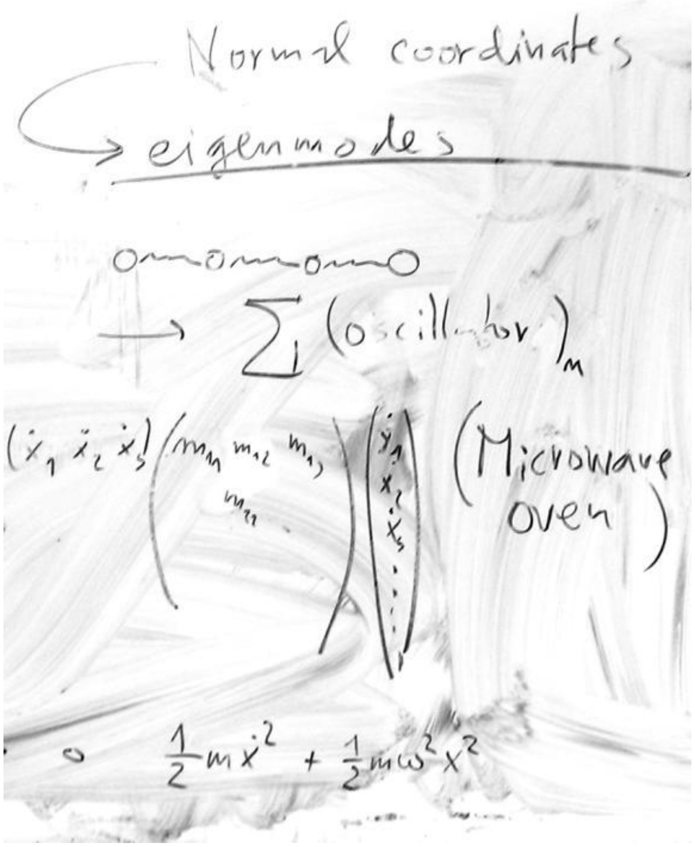
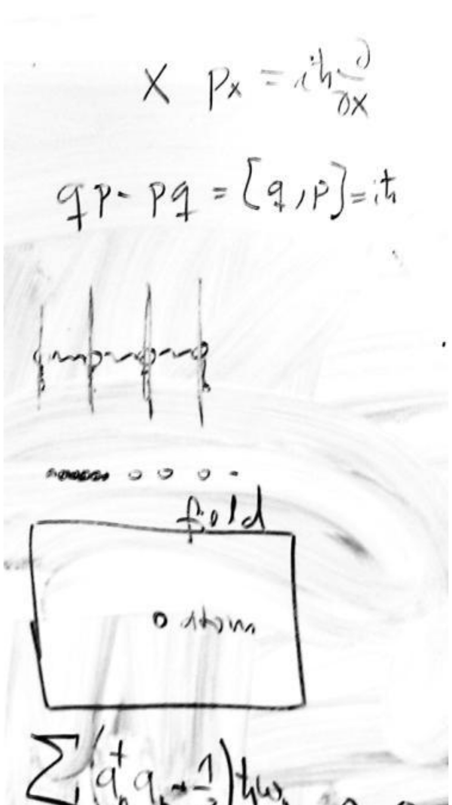
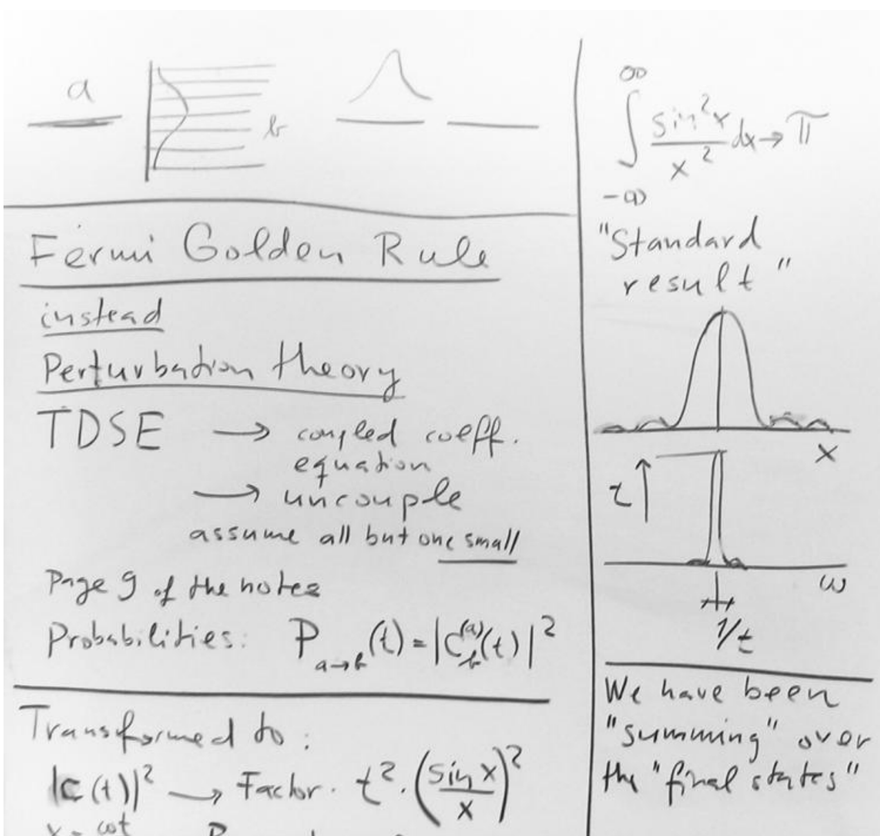


2004.11.04/1-normalmodes.pdf



2004.11.04/2-operatr-microwave.pdf

2004.11.04/3-elmag-fermi.pdf



2004.11.10/p1.pdf

Fermi Golden Rule
Stated

Probability to populate
Group of states

$P \propto$ Number $\cdot\, t$
increase linear
with time

The RATE

$$\boxed{\frac{dP}{dt} = W}$$

constant transition
rate

[$\alpha_1 \rightarrow 1$ approximation
allows this constant rate]

include decay
$\rightarrow$ leads to broadening

Damped vibration
constant rate out

$\rightarrow$ exponential decrease

$dP \quad -P\,W\,dt$

$\Longrightarrow P = P_0 \cdot e^{-Wt}$

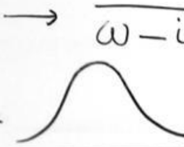
$\rightarrow$ the integrals
in the approximations

$e^{-\frac{W}{2}t}$

Now it looks like damped
vibration

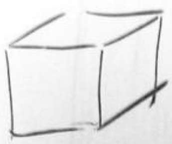
$$e^{i\omega t - \frac{W}{2}t} \longrightarrow \frac{1}{\omega - i\frac{W}{2}}$$

$$\longrightarrow \frac{\Gamma^2}{\omega^2 + \Gamma^2}$$



2004.11.10/p2.pdf

Discretization



microwave
oven
not good
enough

$\rightarrow$ travelling waves

$e^{2\pi k} = 1 \longrightarrow k_n = \frac{2\pi}{L}\, n$

$\Delta k = \frac{2\pi}{L}$ in all 3 dim

$\sum_i \sigma \dashrightarrow \int \sigma\, \rho(E)\, dE$

all
discretized

$\int \sigma\, \rho(\vec{k})\, d^3k$

$$\sum_{\text{all } k} \longrightarrow \frac{1}{\Delta k^3} \sum (\Delta k)^3$$

$$\longrightarrow \left(\frac{1}{\Delta k}\right)^3 \int d^3k$$

"constant" $\quad \rho(k) \rightarrow \left(\frac{L}{2\pi}\right)^3$

$k^2\, dk\, d\Omega_k \longrightarrow \rho(E)\, dE$

sometimes
integrate over $d\Omega_k$
sometimes
$\frac{d}{d\Omega_k}$ (differential
vs. total probab.
rates)

often: $\int d\Omega_k \rightarrow 4\pi$

Arrived at:

$$\rho(E) = \frac{V}{2\pi^2}\, k^2 \frac{dk}{dE}$$

$$\rho(E) = \frac{V}{2\pi^2} \left[k(E)\right]^2 \cdot \frac{dk(E)}{dE}$$

light: $\hbar\omega = \hbar k c$

$$\frac{dk}{dE} \rightarrow \frac{1}{\hbar c}$$

2004.11.10/p3.pdf

$\rho(E) \propto E^2$ photons

$\propto \sqrt{E}$ for massive particles

Fermi golden Rule

→ Numerical values

Line shape

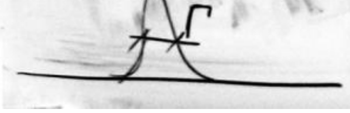
take W from Fermi

→ put in Lorenz form

$$\frac{(W/2)^2}{(\omega-\omega_0)^2 + (W/2)^2}$$

$\Gamma = \hbar W$ (possibly $\frac{1}{2}$)

line width / natural



The actual interaction

$H_i = H_a + H_b + H_{al}$

Trick: look at particle in electromagnetic field

vector potential $\mathbf{A}$

scalar potential ϕ

$$H \rightarrow \frac{\left(\vec{p} - \frac{q}{c}\vec{A}\right)^2}{2m} + q\phi$$

velocity dependent force

The procedure follows Lagrange functions

→ Hamiltonian mechanics

2004.11.10/p4.pdf

Lagrangian mechanics

$$L = T - V$$

$$\frac{\partial L}{\partial q} - \frac{d}{dt}\frac{\partial L}{\partial \dot{q}} = 0$$

$$T = \frac{1}{2} m \dot{q}^2; \quad V(q)$$

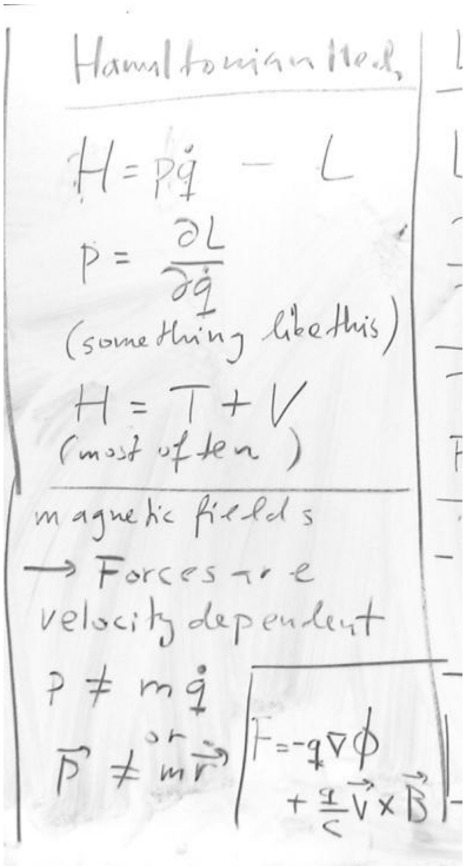
$$F(q) = -\frac{d}{dq} V(q)$$

$$-\frac{dV}{dq} \equiv \frac{\partial L}{\partial q}, \quad \frac{\partial L}{\partial \dot{q}} = m\dot{q}$$

$$-\frac{dV}{dq} - \frac{d}{dt} m\dot{q}$$

$m\ddot{q} = F$ Newtons

2004.11.11/p1.pdf



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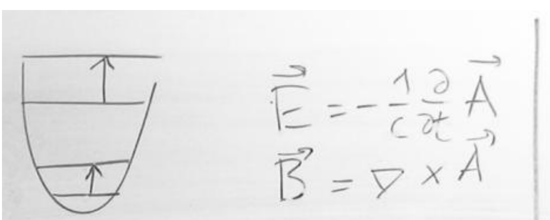


2004.11.11/p3.pdf

$\langle 1_{k\lambda} | a^+ | 0 \rangle = 1$

$\vec{A} \cdot p \rightarrow$ electronic

$\langle \varphi_{ground}(\vec{r}) | e^{i\vec{k}\cdot\vec{r}} \vec{p} | \varphi_{exc}(\vec{r}) \rangle$

Long wavelength approx

$e^{i\vec{k}\vec{r}} \longrightarrow 1$ $\quad \lambda >> a_0$

$|\langle \varphi_g | \vec{p} | \varphi_e \rangle|$

$\longrightarrow |m\omega \langle \varphi_g | \vec{r} | \varphi_e \rangle|$

$\omega = \frac{E_e - E_g}{\hbar}$

$H\vec{r} - \vec{r}H = i\frac{p}{m}$

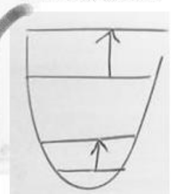
α
fine structure constant

$\alpha^3 \ldots$ $\quad \frac{e^2}{\hbar c} \approx \frac{1}{137}$

$\langle 1 | a^+ | 0 \rangle = 1$

$\langle n+1 | a^+ | n \rangle = \sqrt{n+1}$

Explains Stimulated Emission



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