PHYS261 Atomic Physics and Physical Optics

Lectures Tuesday 22. October 2008
Thursday 24. October 2008

Topics:

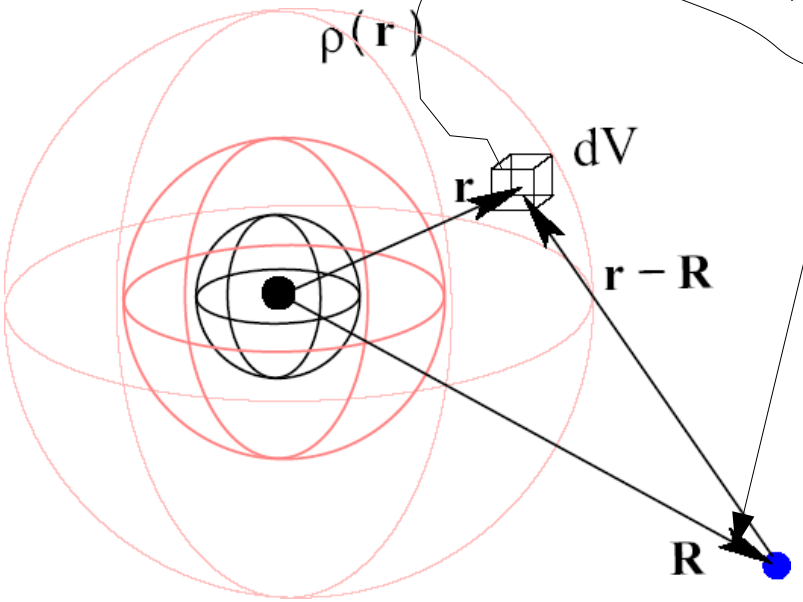
Many-electron atoms

Review of selfconsistent field
Variational formulation
Hartree-Fock equations
Configuration mixing
Density Functional Theories
Herman – Skilmann program (Fortran)

Comment: **This is a preliminary collection of 2 lectures;**

Density of electric charge picture from PHYS264
The spheres of different «weight» represent radially changing density (included in the previous slide)

$$W(\vec{r}) = \int \frac{(-e)^2 \sum_{i=1}^{N} |\psi_i(\vec{x})|^2}{|\vec{r} - \vec{x}|} \, d^3x$$



we have reviewed all the parts discussed

selfconsistent field

Variational formulation

Hartree-Fock equations

We went through the notes collection

(we shall put some clips of those pages here …)

End of lecture 21.10.2008

Many electron atoms

Self consistent field
independent particles
electrons
iteration

$\langle \phi | H | \phi \rangle$
for
Slater det.

Hartree-Fock
method
[variational
Methods

Periodic
System
Ionization
potentials

Experimental....
Spectra

Density Functional Theory
Configuration mixing

Experimental....

Spectra

Density Functional Theory

Configuration mixing

Slater Det $\longrightarrow$ products of single orbitals

Ground state of a syst. with N-electrons

Helium $\longrightarrow$ correllations important

$\psi(r_1, r_2) \neq \varphi_1(r_1)\,\varphi_2(r_2)$ [Hylleraas

$\approx \varphi_1(r_1)\,\varphi_2(r_2)\, f(|r_1 - r_2|)$

How else ? Configuration mixing in Helium

Explaining the mathematics of "Configuration Mixing"

$f(x) \longrightarrow H_0 \varphi_i(x) = E_i \varphi_i(x) \longrightarrow f(x) = \sum_i c_i \varphi_i(x)$

$g(x,y)$ – for each fixed y $\quad g(x,y) \to F_y(x)$

$F_y(x) \longrightarrow \sum_i c_i(y)\, \varphi_i(x)$

$c_i(y) \longrightarrow H_0 \psi_j(y) = \varepsilon_j \psi_j(y) \to c_i(y) = \sum_j d_j^{(i)} \psi_j(y)$

$g(x,y) \longrightarrow F_y(x) \longrightarrow \sum_j \sum_i d_j^{(i)} \psi_j(y)\, \varphi_i(x)$

This assumes that in x and y there were 2 different systems descr. by $H_0(x)$ and $H_0(y)$

In Helium $\longrightarrow$ both electrons have the same H_0
φ_i and ψ_j are same func.

$$\psi(\vec{r}_1, \vec{r}_2) = \sum_i \sum_j d_{ij}\ \varphi_i(\vec{r}_1)\, \varphi_j(\vec{r}_2)$$

$$f(x) \longrightarrow H_0 \varphi_i(x) = E_i \varphi_i(x) \longrightarrow f(x) = \sum_i c_i \varphi_i(x)$$

$g(x,y)$ – for each fixed y $\quad g(x,y) \to F_y(x)$

$$F_y(x) \longrightarrow \sum_i c_i(y)\, \varphi_i(x)$$

$$c_i(y) \to H_0 \psi_j(y) = \varepsilon_j \psi_j(y) \to c_i(y) = \sum_j d_j^{(i)} \psi_j(y)$$

$$g(x,y) \longrightarrow F_y(x) \to \sum_j \sum_i d_j^{(i)} \psi_j(y)\, \varphi_i(x)$$

This assumes that in x and y there were 2 different systems descr. by $H_0(x)$ and $H_0(y)$

In Helium → both electrons have the same H_0
φ_i and ψ_j are same func.

$$\psi(\vec{r}_1, \vec{r}_2) = \sum_i \sum_j d_{ij}\ \varphi_i(\vec{r}_1)\, \varphi_j(\vec{r}_2)$$

$$\Psi(\vec{r}_1, \vec{r}_2) = \sum_i \sum_j d_{ij}\, \varphi_i(\vec{r}_1)\, \varphi_j(\vec{r}_2)$$

i: electron 1 ; j: electron 2

[Antisymmetrize it ...]

$$= \sum_i \sum_j d_{ij} \begin{vmatrix} \varphi_i(r_1) & \varphi_j(r_1) \\ \varphi_i(r_2) & \varphi_j(r_2) \end{vmatrix}$$

one electron in i-th orbital } configuration
" " in j-th orbital }

Configuration mixing

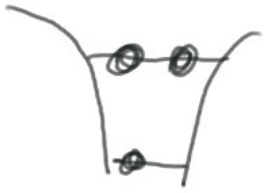
For N-particles ... just the same

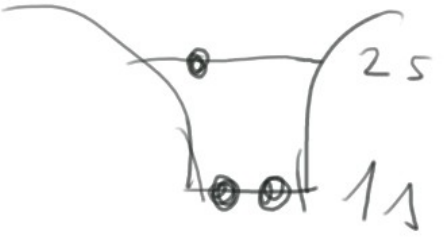
Physical interpr. probability $|d_{ij}|^2$ in configuration $\varphi_i \varphi_j$

Configuration Mixing
Physical Interpretation

φ_{1s} φ_{1s} φ_{2s}

φ_{1s} φ_{2s} φ_{2s}





$|d_{1s\,1s\,2s}|^2$

How to find the d's?

$\Rightarrow |d_{1s\,2s\,2s}|^2$

Ψ ; H ;

$|\psi\rangle = \sum' c_\alpha |\alpha\rangle$

$\langle\beta|H|\alpha\rangle$ $\quad H_{\beta\alpha}$

Diagonalization;
Finding Eigenvalues

$H|\psi\rangle = E|\psi\rangle$

$$\begin{bmatrix} & H & \end{bmatrix} \begin{bmatrix} c \end{bmatrix} = E \begin{bmatrix} c \end{bmatrix}$$

Diagonalize the Hamiltonian matrix

Diagonalization; Finding Eigenvalues Matlab or Octave (Linpack, lapack etc … DEMO: matrix eigenvalues in octave

Matrix n-configuration squared

→ n eigenvalues → n "levels"

Do they "exist"? Many do

Spectra of complex atoms → many states

DFT LDA (SCF)

Self-consistent determination of orbitals

Ionization potential

DFT Density Functional Theory

Kohn 1964 Nobel Prize Chemistry 1998

Talk for chemists and Review of Modern physics article

Visiting NIST spectra of atoms

He I and Be II

(first spectrum neutral atom – I

Second spectrum – ion – one electron missing)

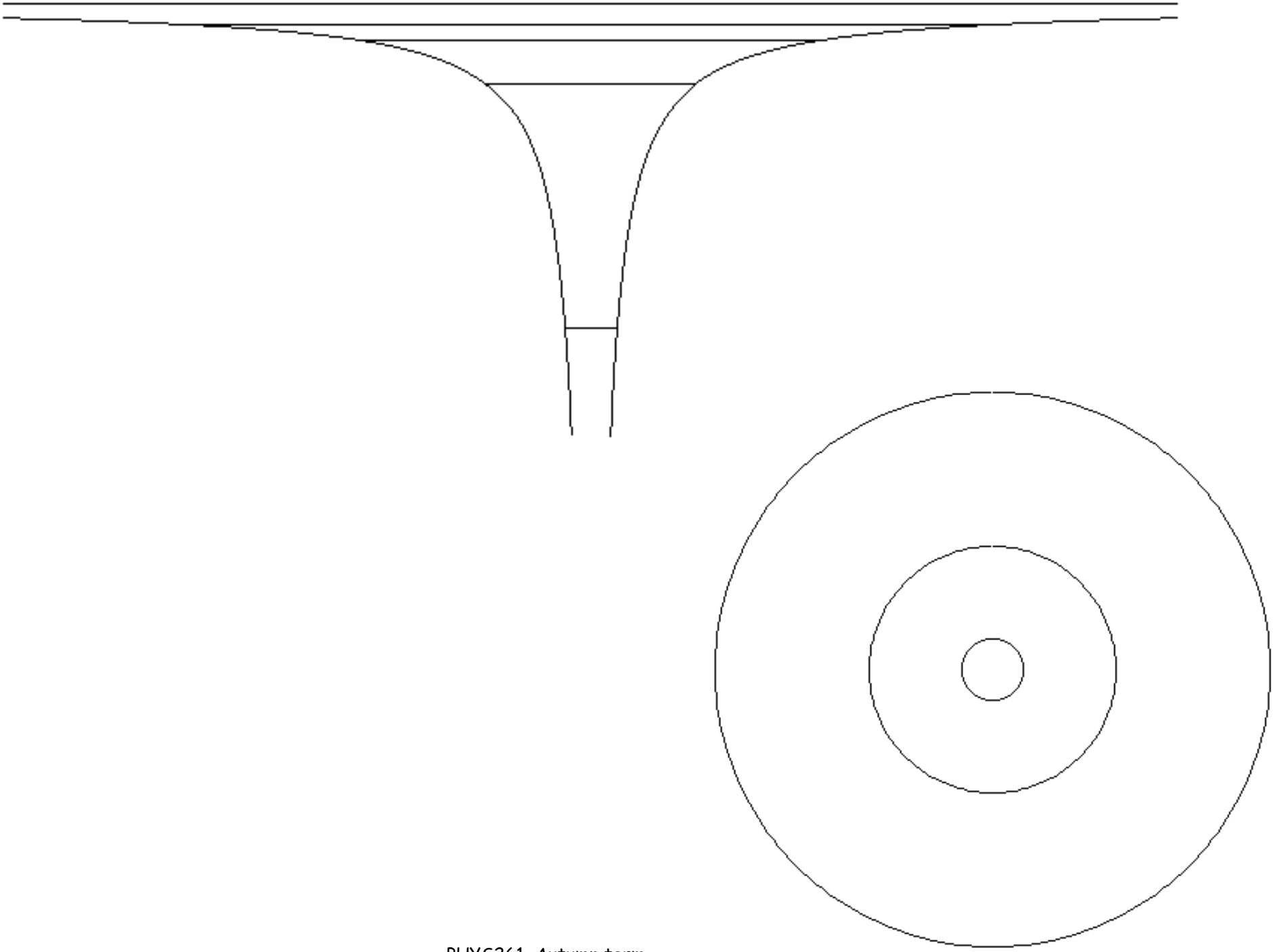
Herman – Skillman program – Hartree model

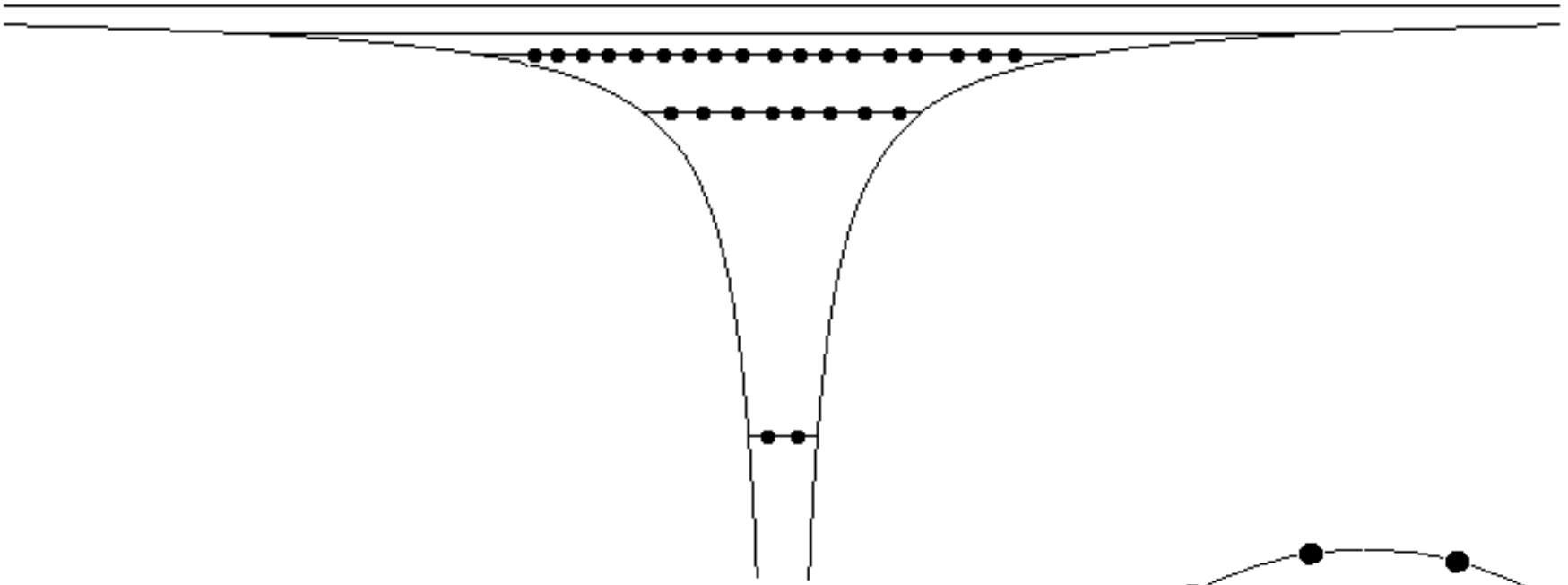
Calculation ofwavefunctions

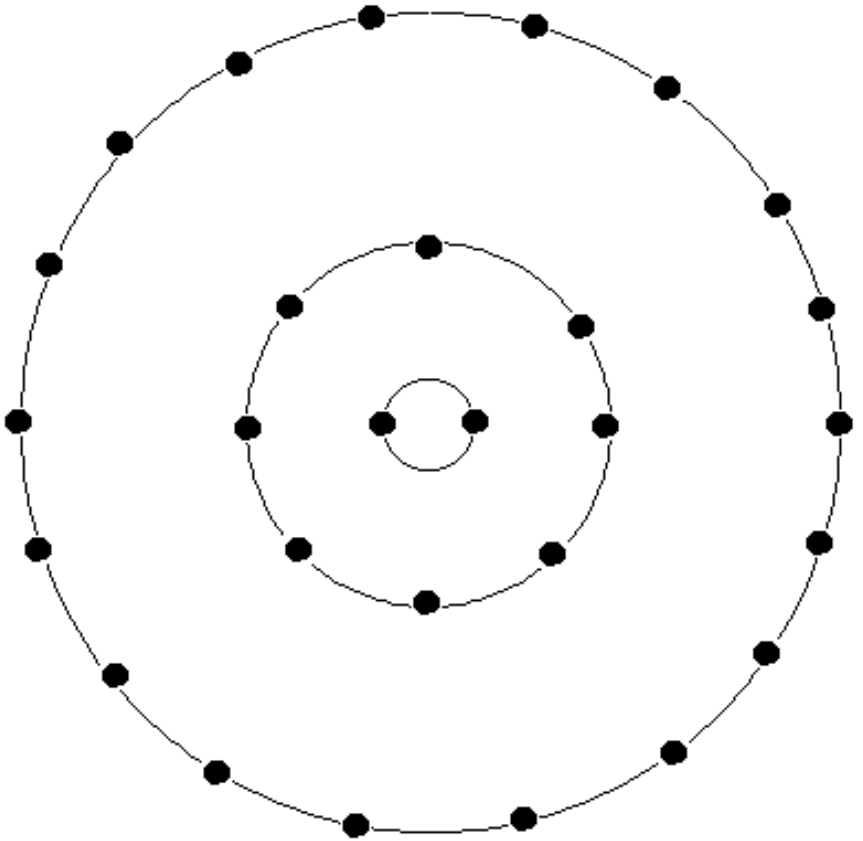
Plotting; applications

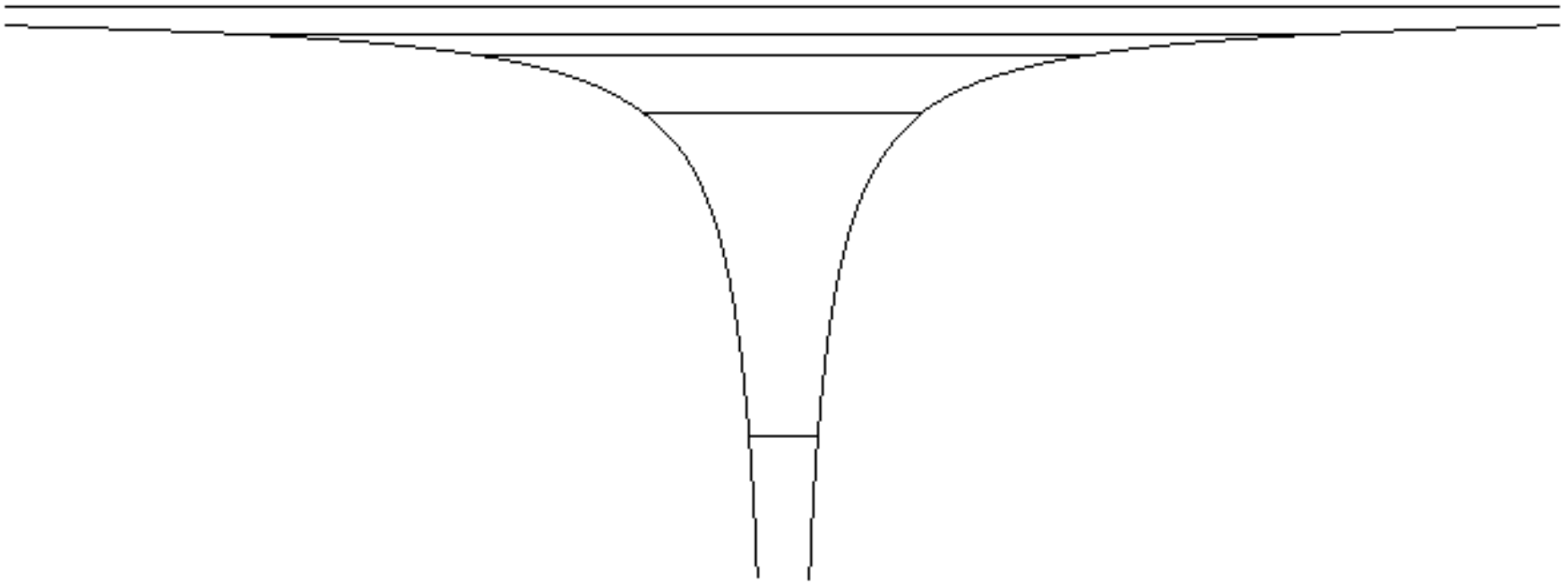
End of lecture 23.10.2008

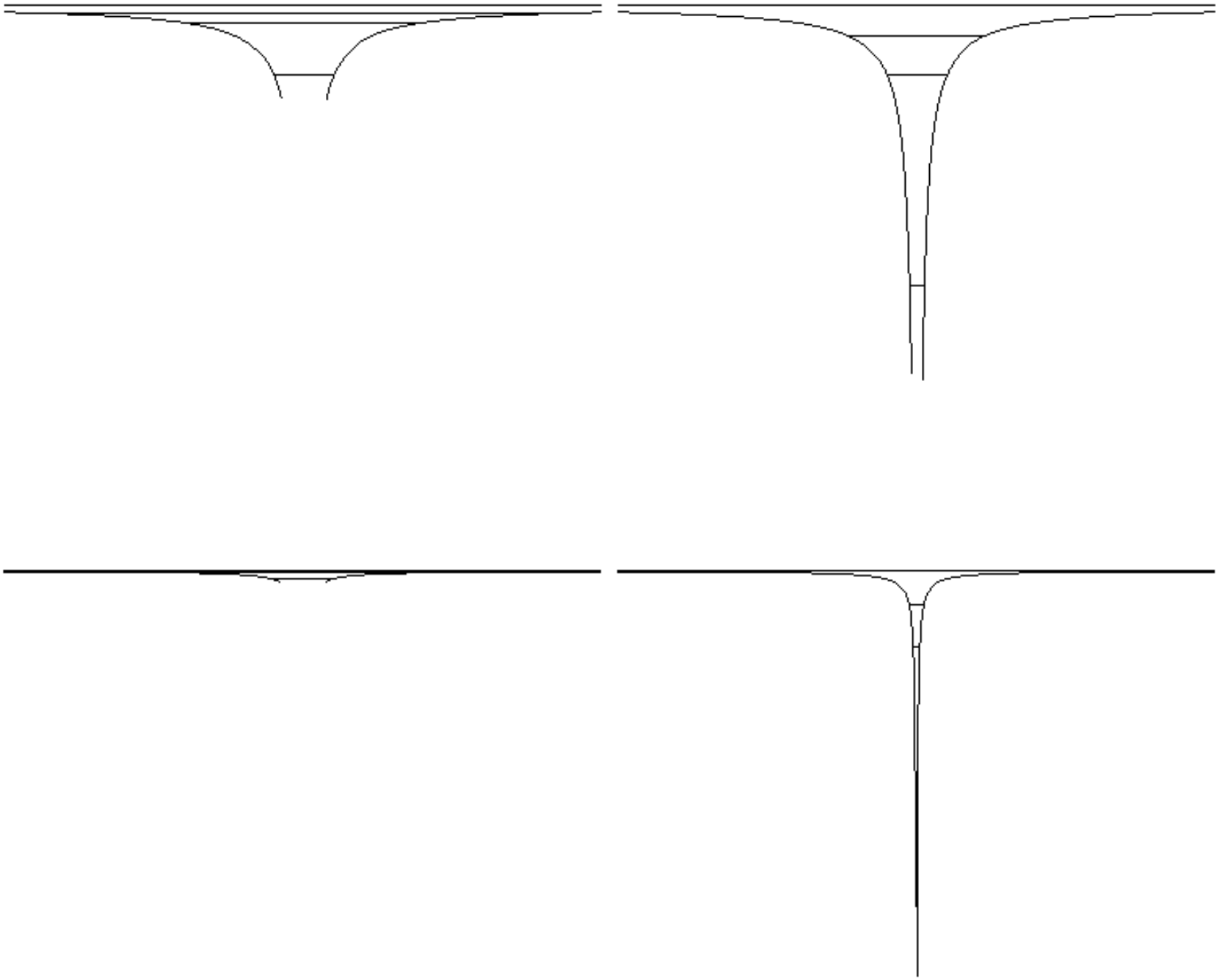
The following elements can be used for visualization of the many-electron atoms and configuration mixing

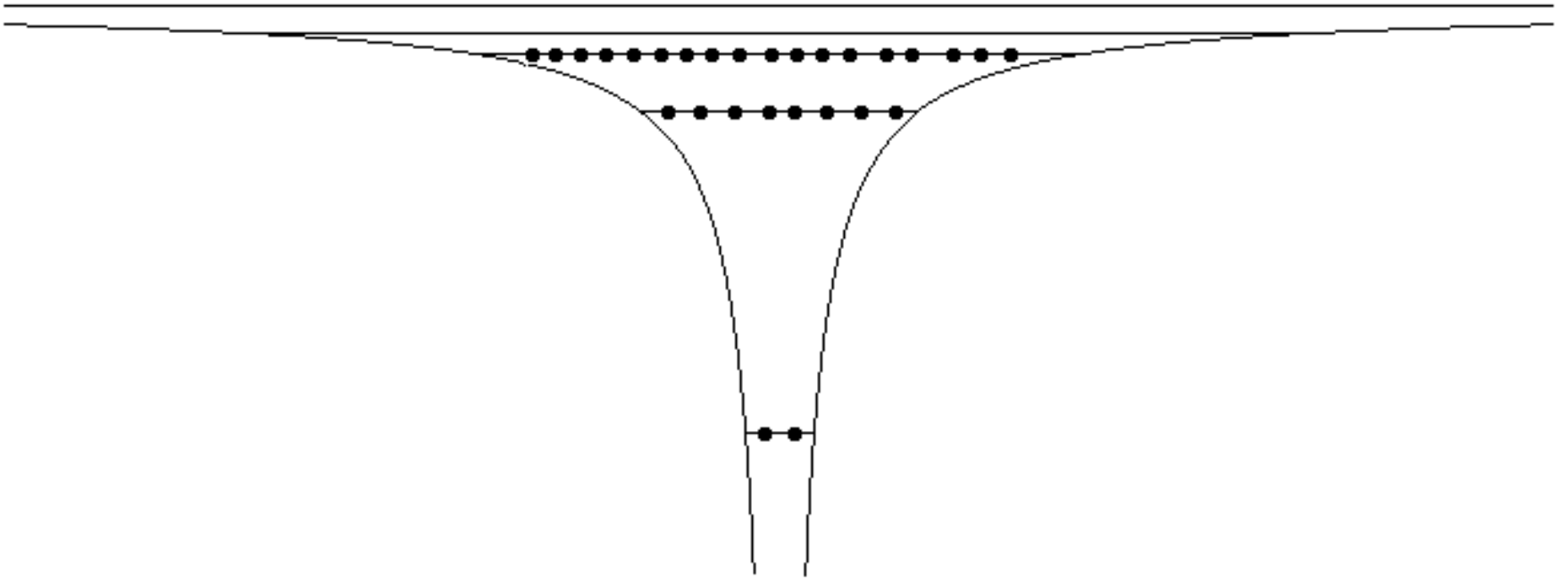


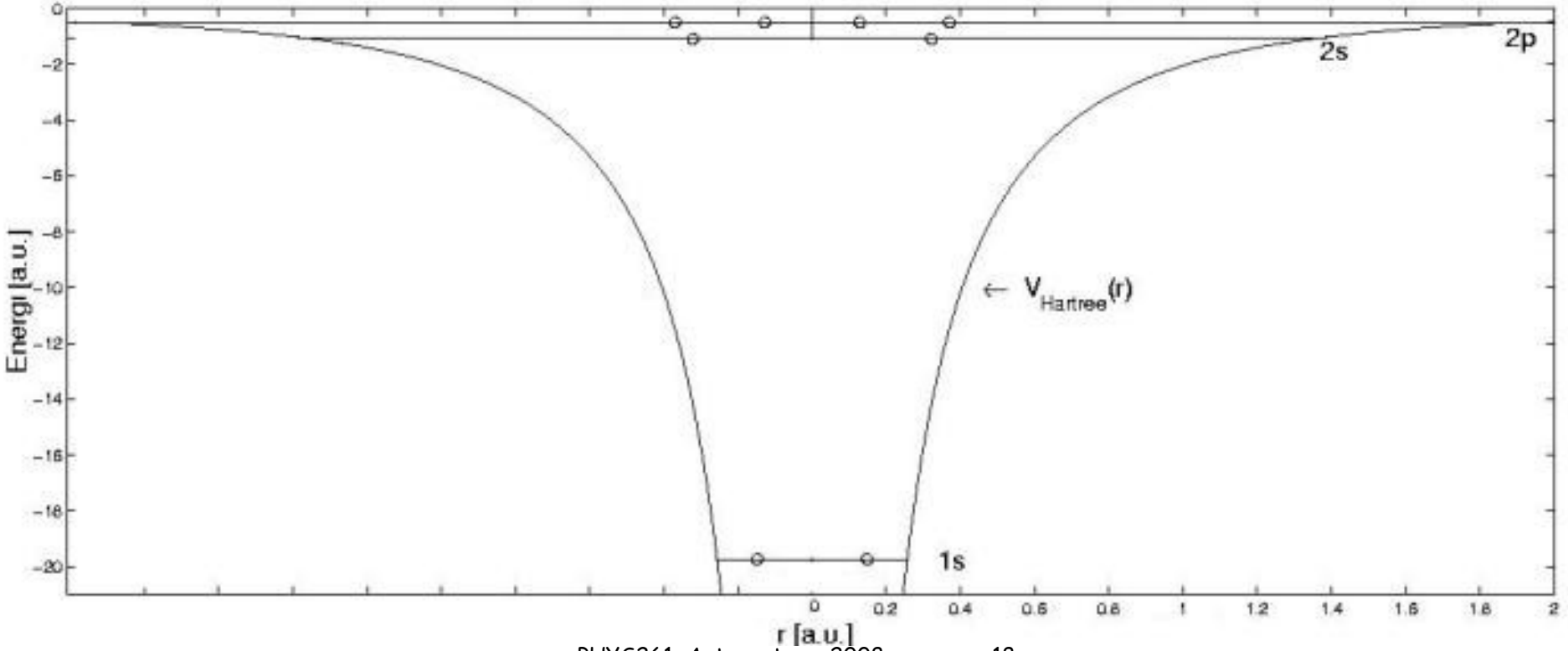











Energi [a.u.]
r [a.u.]
2s
2p
1s
← V_Hartree(r)