PHYS261 Atomic Physics and Physical Optics

Lectures Thursday 9. October 2008
Tuesday 14. October 2008
Thursday 16. October 2008

Topics:

Many-electron atoms

Evaluation of Slater Determinant $<\phi \mid H_{total} \mid \phi>$
Hartree method; selfconsistent field
Iteration – selfconsistency
Variational Methods for Schrödinger Equation
Variation derivation of Hartree-Fock equations

Comment: **This is a preliminary collection of 3 lectures;**
Contains extra figures at the end (atomic potentials)
Missing: The latex-based materials

The Perturbation Theory as we did for Helium

$$\left[-\frac{\hbar^2}{2m_e}\nabla_{r_1}^2 - \frac{Z\,e^2}{r_1} - \frac{\hbar^2}{2m_e}\nabla_{r_2}^2 - \frac{Z\,e^2}{r_2} + \frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}\right]\Psi\left(\mathbf{r}_1,\mathbf{r}_2\right) = E\,\Psi\left(\mathbf{r}_1,\mathbf{r}_2\right)$$

Repulsion expectation Value

Evaluation of the repulsion term using the multipole expansion

$$\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} = \sum_{LM}\frac{4\pi}{2L+1}\,\frac{r_<^L}{r_>^{L+1}}\,Y_{LM}^{\star}\left(\hat{r}_1\right)Y_{LM}\left(\hat{r}_2\right)$$

where

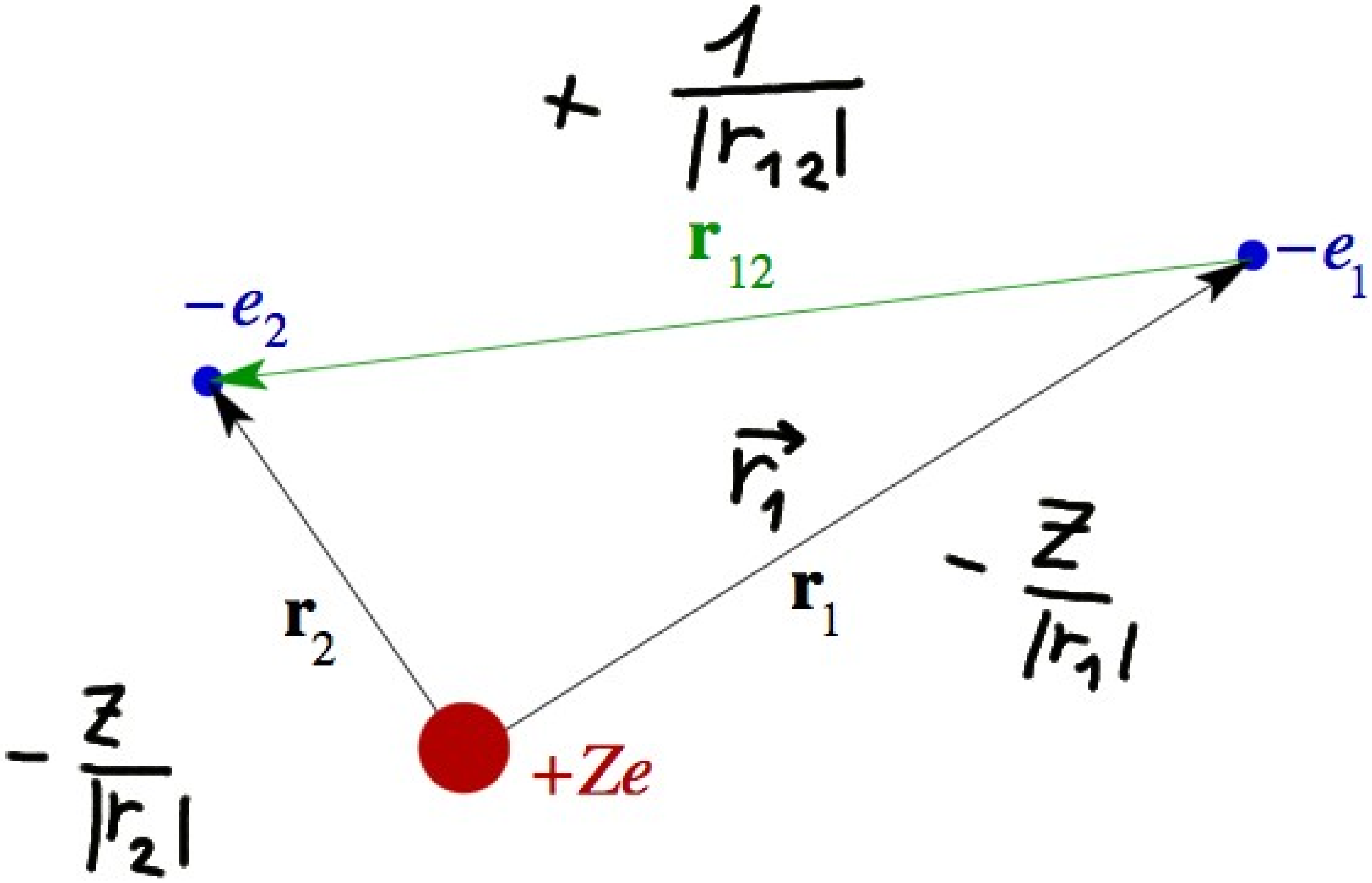
$$r_< = r_1, \quad r_> = r_2 \quad \text{for} \quad |\mathbf{r}_1| < |\mathbf{r}_2|$$
$$r_< = r_2, \quad r_> = r_1 \quad \text{for} \quad |\mathbf{r}_1| > |\mathbf{r}_2|$$

Perturbation theory result:

$$\int d^3\mathbf{r}_1\int d^3\mathbf{r}_2\;\psi_{100}^{\star}\left(\mathbf{r}_1\right)\psi_{100}^{\star}\left(\mathbf{r}_2\right)\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}\psi_{100}\left(\mathbf{r}_1\right)\psi_{100}\left(\mathbf{r}_2\right) = \frac{5}{8}\frac{Ze^2}{a_0}$$

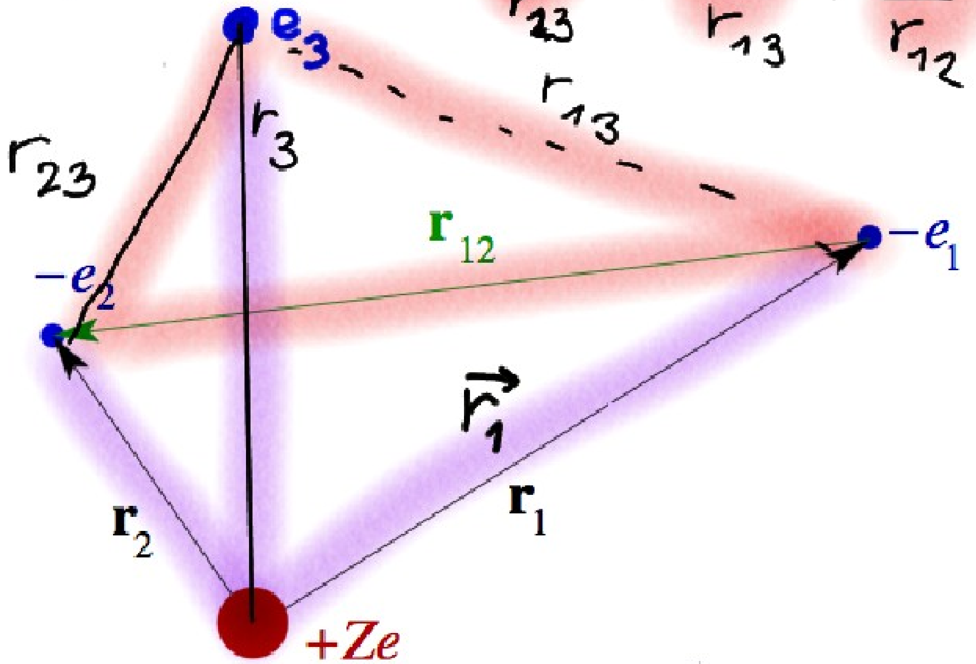
How does this work for Lithium – 3 electrons ?

The picture of the Helium Atom (coordinates)



Lithium – 3 electrons

Number of PAIRS $V = + \frac{e^2}{r_{23}} + \frac{e^2}{r_{13}} + \frac{e^2}{r_{12}}$



$$T = T_1 + T_2 + T_3 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} - \frac{Ze^2}{r_3}$$

Make a link to 2-electron energies
Make a link to The LATEX for Helium

$$\Psi(x_1, x_2, ...x_n) = \sum_{perm(\alpha,\beta,...\nu)} (-1)^{P(perm(\alpha,\beta,...\nu))} perm\left(\phi_\alpha \phi_\beta ....\phi_\nu\right)(x_1)(x_2)....(x_n)$$

where each term in the sum looks as $\phi_\beta(x_1)...\phi_\nu(x_2)...\phi_\alpha...$, summing over all permutations, and $P(perm(\alpha, \beta, ...\nu))$ is the number of swaps of the given permutation $perm(\alpha, \beta, ...\nu)$

This is very close to the definition of the determinant

$$\det(A) = \sum_{\sigma \in S_n} \left(\operatorname{sgn}(\sigma) \prod_{i=1}^{n} A_{i,\sigma(i)} \right)$$

The above in this notation

See the Latex Document

$$\Psi(x_1, x_2, ...x_n) = \sum_{\sigma \in S_n} \operatorname{sgn}(\sigma) \prod_{i=1}^{n} \phi_{\alpha_{\sigma(i)}}(x_i)$$

Slater determinant

The antisymmetric combination for n-particles can be written as a determinant in this way:

$$\begin{vmatrix} \phi_\alpha(x_1) & \phi_\alpha(x_2) & ... & \phi_\alpha(x_n) \\ \phi_\beta(x_1) & \phi_\beta(x_2) & ... & \phi_\beta(x_n) \\ ... & ... & ... & ... \\ \phi_\nu(x_1) & \phi_\nu(x_2) & ... & \phi_\nu(x_n) \end{vmatrix}$$

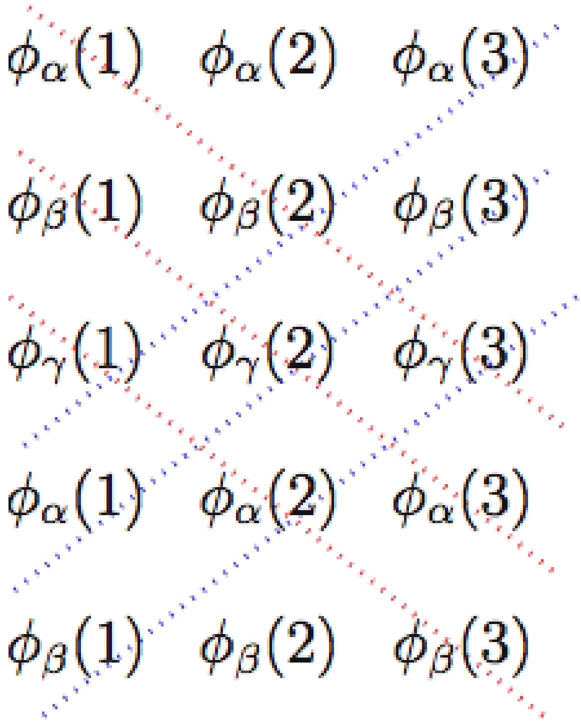
For 3 particles:

3 particle Slater determinant

$$\begin{vmatrix} \phi_\alpha(x_1) & \phi_\alpha(x_2) & \phi_\alpha(x_3) \\ \phi_\beta(x_1) & \phi_\beta(x_2) & \phi_\beta(x_3) \\ \phi_\gamma(x_1) & \phi_\gamma(x_2) & \phi_\gamma(x_3) \end{vmatrix}$$

3 × 3 determinant

$$\begin{vmatrix} \phi_\alpha(1) & \phi_\alpha(2) & \phi_\alpha(3) \\ \phi_\beta(1) & \phi_\beta(2) & \phi_\beta(3) \\ \phi_\gamma(1) & \phi_\gamma(2) & \phi_\gamma(3) \end{vmatrix} \longrightarrow$$



$$\begin{array}{ccc} \phi_\alpha(1) & \phi_\alpha(2) & \phi_\alpha(3) \\ \phi_\beta(1) & \phi_\beta(2) & \phi_\beta(3) \\ \phi_\gamma(1) & \phi_\gamma(2) & \phi_\gamma(3) \\ \phi_\alpha(1) & \phi_\alpha(2) & \phi_\alpha(3) \\ \phi_\beta(1) & \phi_\beta(2) & \phi_\beta(3) \end{array}$$

$$\phi_\alpha(1)\ \phi_\beta(2)\ \phi_\gamma(3) \ + \ \phi_\beta(1)\ \phi_\gamma(2)\ \phi_\alpha(3) \ + \ \phi_\gamma(1)\ \phi_\alpha(2)\ \phi_\beta(3)$$

$$-\ \phi_\gamma(1)\ \phi_\beta(2)\ \phi_\alpha(3) \ - \ \phi_\alpha(1)\ \phi_\gamma(2)\ \phi_\beta(3) \ - \ \phi_\beta(1)\ \phi_\alpha(2)\ \phi_\gamma(3)$$

Slater

Hartree : Selfconsistent field

Fock (Фок)

Hartree-Fock method

Fock space

(Second quantization

(in the field theory of particles, photons)

[next week ....]

next next

He: $T_1 + T_2 + V_1 + V_2 + V_{12}$

$\langle 2 \text{ terms} \mid 5 \text{ terms} \mid 2 \text{ terms} \rangle$

Li $T_1 + T_2 + T_3 + V_1 + V_2 + V_3$ $\frac{n(n-1)}{2}$ pairs

n! permutations $+ V_{12} + V_{13} + V_{23}$

$\phi(r_1, r_2, r_3)$ is Slater determin. $\underbrace{6 \text{ terms}}$

$\langle 6 \text{ terms} \mid 9 \text{ terms} \mid 6 \text{ terms} \rangle$

$T_1 + T_2 + T_3 + T_4 + V_1 + V_2 + V_3 + V_4$

$V_{12} + V_{13} + V_{14} + V_{23} + V_{24} + V_{34}$

24 terms

$\phi(r_1 r_2 r_3 r_4)$

Normalization for general antisymmetrized state of Helium

Many of these terms will be zero !

Normalization

$$\langle 2\,\text{terms} \mid 2\,\text{terms} \rangle = 2$$

$$\longrightarrow \frac{1}{\sqrt{2}}$$

$$\langle \phi_a(1)\,\phi_b(2) - \phi_b(1)\,\phi_a(2) \mid$$

$$\mid \phi_a(1)\,\phi_b(2) - \phi_b(1)\,\phi_a(2) \rangle$$

$$\overbrace{\langle \phi_a | \phi_a \rangle}^{1} \overbrace{\langle \phi_b | \phi_b \rangle}^{1} = 1 \quad (2\ \text{terms})$$

$$\int \phi_a(1)\,\phi_b(2)\;\phi_a(1)\,\phi_b(2)\,d1\,d2$$

$$\int \phi_a(1)\,\phi_a(1)\,d1 \int \phi_a(2)\,\phi_b(2)\,d2$$

$$\langle \phi_a | \phi_b \rangle \langle \phi_b | \phi_a \rangle = 0 \quad (2\ \text{terms})$$

$\phi_\beta(1)\ \phi_\alpha(2)\ \phi_\gamma(3)$

$\phi_\gamma(1)\ \phi_\beta(2)\ \phi_\alpha(3)$

$\phi_\alpha(1)\ \phi_\beta(2)\ \phi_\gamma(3)$

$\phi_\beta(1)\ \phi_\alpha(2)\ \phi_\gamma(3)$

$\phi_\beta(1)\ \phi_\alpha(2)\ \phi_\gamma(3)$

$\phi_\beta(1)\ \phi_\alpha(2)\ \phi_\gamma(3)$

For the text document:
Play with the permutations
of «orbitals» and coordinates

Download ODP
and do as homework

$$\alpha(1)\,\beta(2)\,\gamma(3) + \beta(1)\,\gamma(2)\,\alpha(3) + \gamma(1)\,\alpha(2)\,\beta(3)$$

$$- \gamma(1)\,\beta(2)\,\alpha(3) - \beta(1)\,\alpha(2)\,\gamma(3) - \alpha(1)\,\gamma(2)\,\beta(3)$$

$$|\alpha\rangle|\beta\rangle|\gamma\rangle + |\beta\rangle|\gamma\rangle|\alpha\rangle + |\gamma\rangle|\alpha\rangle|\beta\rangle$$

$$- |\gamma\beta\alpha\rangle - |\beta\rangle|\alpha\rangle|\gamma\rangle - |\alpha\rangle|\gamma\rangle|\beta\rangle$$

(also $|\alpha\beta\gamma\rangle + |\beta\gamma\alpha\rangle$ ......

$$\langle\alpha|\,\langle\beta|\,\langle\gamma| \quad |\alpha\rangle\,|\beta\rangle\,|\gamma\rangle$$

$$\langle\alpha|\alpha\rangle\,\langle\beta|\beta\rangle\langle\gamma|\gamma\rangle = 1$$

$$\langle\alpha|\,\langle\gamma|\,\langle\beta| \quad |\alpha\rangle\,|\beta\rangle\,|\gamma\rangle$$

$$\underset{1}{\langle\alpha|\alpha\rangle}\;\underset{0}{\langle\gamma|\beta\rangle}\,\underset{0}{\langle\beta|\gamma\rangle} = 0$$

Only $n!$ nonzero terms out of $(n!)^2$ total

$$\langle \alpha\ \beta\ \gamma | T_2 | \alpha\ \beta\ \gamma \rangle$$

$$\langle \alpha | \alpha \rangle \langle \beta | T_2 | \beta \rangle \langle \gamma | \gamma \rangle$$

$$\langle \alpha\ \beta\ \gamma | T_3 | \alpha\ \beta\ \gamma \rangle$$

$$\langle \alpha | \alpha \rangle \langle \beta | \beta \rangle \langle \gamma | T_3 | \gamma \rangle$$

T_2 , T_3

$$\langle \alpha | \langle \gamma | \langle \beta | T_1 | \alpha \rangle | \beta \rangle | \gamma \rangle$$

$$\langle \alpha' | T_1 | \alpha \rangle \langle \gamma \underset{0}{|} \beta \rangle \langle \beta \underset{0}{|} \gamma \rangle = 0$$

Also for 1 particle terms

Only $n!$ nonzero terms out of $(n!)^2$ total

But there are M of such terms

$\langle \alpha\beta\gamma | T_1 + T_2 + T_3 | \alpha\beta\gamma \rangle$ $\qquad \sqrt{\frac{1}{n!}} \cdot \sqrt{\frac{1}{n!}}$

$(6) \qquad (3) \qquad (6)$

$3 \cdot 6$ non-zero

$\langle \alpha | T_1 | \alpha \rangle \quad \langle \alpha | T_2 | \alpha \rangle \quad \langle \alpha | T_3 | \alpha \rangle$

$$\int \varphi_\alpha^*(r_1)\, T_{r_1}\, \varphi_\alpha(r_1)\, d^3r_1 = \int \varphi_\alpha^*(r_3)\, T_3\, \varphi_\alpha(r_3)\, d^3r_3$$

6 terms $\langle \alpha | T_1 | \alpha \rangle$ $T_{\alpha\alpha}$

6 terms $\langle \beta | T_1 | \beta \rangle$ $T_{\beta\beta}$

6 terms $\langle \gamma | T_1 | \gamma \rangle$ $T_{\gamma\gamma}$ $\quad (T_{\alpha\beta} = 0)$

$$\sqrt{\frac{1}{6}} \sqrt{\frac{1}{6}} \cdot 6 \left(T_{\alpha\alpha} + T_{\beta\beta} + T_{\gamma\gamma} \right)$$

$$\langle \alpha\beta\gamma | T_1 + V_1 + T_2 + V_2 + T_3 + V_3 | \alpha\beta\gamma \rangle$$
$$= (T+V)_{\alpha\alpha} + (T+V)_{\beta\beta} + (T+V)_{\gamma\gamma}$$

Sum over particles for 1-particle operations -> Sum over «orbitals»

$$\langle \alpha \beta \gamma | V_{23} | \alpha \beta \gamma \rangle$$

$$\int d2 \int d3 \; \varphi_\beta^*(2) \varphi_\gamma(3) \; V_{23}(2,3) \; \varphi_\beta(2) \varphi_\gamma(3)$$

$$, \langle \alpha | \alpha \rangle$$

$$\langle \alpha \beta \gamma | V_{23} | \alpha \gamma \beta \rangle = \langle \alpha | \alpha \rangle \cdot$$

$$\langle \beta \gamma | V_{23} | \gamma \beta \rangle$$

$$\langle \alpha \beta \gamma | V_{23} | \beta \alpha \gamma \rangle = 0$$

$$= \underbrace{\langle \alpha | \beta \rangle}_{\text{zero}} \underbrace{\langle \beta \gamma | V_{23} | \alpha \gamma \rangle}_{\text{nonzero}}$$

Either the same pair ; or reversed pair

$\langle 6 \text{ terms} \mid 3 \text{ pairs} \mid 6 \text{ terms} \rangle$ $\sqrt{\frac{1}{6}}\sqrt{\frac{1}{6}}$

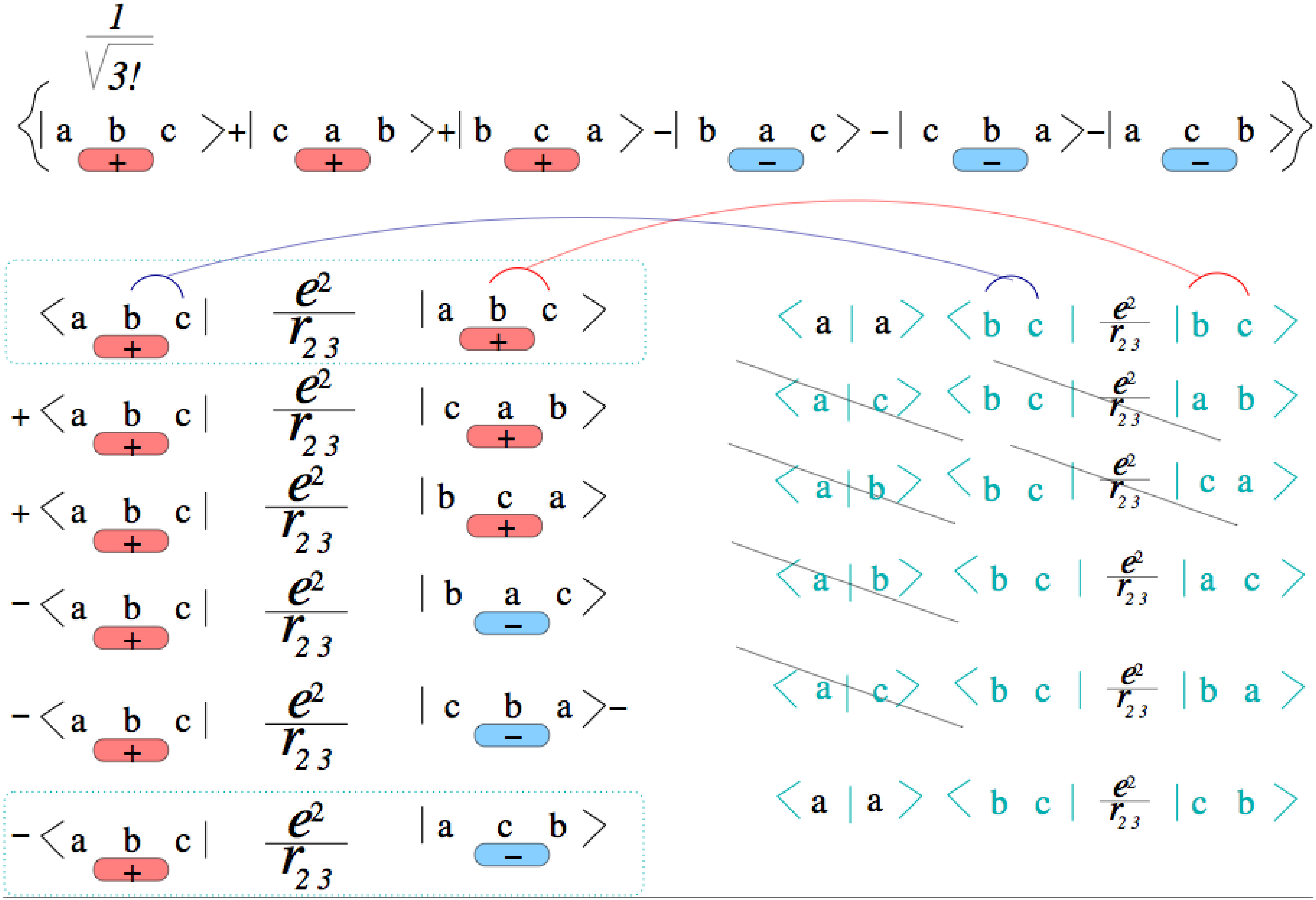
$\langle \alpha\beta \mid \text{pair} \mid \alpha\beta \rangle$

$\langle \alpha\beta \mid \text{pair} \mid \beta\alpha \rangle$

$6 \cdot 6 \cdot 3$ terms

$$\begin{aligned}
&\langle \alpha\beta \mid V_{12} \mid \alpha\beta \rangle - \langle \alpha\beta \mid V_{12} \mid \beta\alpha \rangle \\
+ &\langle \beta\gamma \mid V_{12} \mid \beta\gamma \rangle - \langle \beta\gamma \mid V_{12} \mid \gamma\beta \rangle \\
+ &\langle \alpha\gamma \mid V_{12} \mid \alpha\gamma \rangle - \langle \alpha\gamma \mid V_{12} \mid \gamma\alpha \rangle
\end{aligned}$$

Sum over pair of coordinates
becomes
Sum over pairs of
orbitals but with exchange
term



$$\frac{1}{\sqrt{3!}}\left\{ |a\ \underset{+}{b}\ c\rangle + |c\ \underset{+}{a}\ b\rangle + |b\ \underset{+}{c}\ a\rangle - |b\ \underset{-}{a}\ c\rangle - |c\ \underset{-}{b}\ a\rangle - |a\ \underset{-}{c}\ b\rangle \right\}$$

$$\langle a\ \underset{+}{b}\ c|\ \frac{e^2}{r_{2\,3}}\ |a\ \underset{+}{b}\ c\rangle \qquad \langle a|a\rangle\langle b\ c|\ \frac{e^2}{r_{2\,3}}\ |b\ c\rangle$$

$$+\langle a\ \underset{+}{b}\ c|\ \frac{e^2}{r_{2\,3}}\ |c\ \underset{+}{a}\ b\rangle \qquad \cancel{\langle a|c\rangle}\cancel{\langle b\ c|\ \frac{e^2}{r_{2\,3}}\ |a\ b\rangle}$$

$$+\langle a\ \underset{+}{b}\ c|\ \frac{e^2}{r_{2\,3}}\ |b\ \underset{+}{c}\ a\rangle \qquad \cancel{\langle a|b\rangle}\cancel{\langle b\ c|\ \frac{e^2}{r_{2\,3}}\ |c\ a\rangle}$$

$$-\langle a\ \underset{+}{b}\ c|\ \frac{e^2}{r_{2\,3}}\ |b\ \underset{-}{a}\ c\rangle \qquad \cancel{\langle a|b\rangle}\langle b\ c|\ \frac{e^2}{r_{2\,3}}\ |a\ c\rangle$$

$$-\langle a\ \underset{+}{b}\ c|\ \frac{e^2}{r_{2\,3}}\ |c\ \underset{-}{b}\ a\rangle- \qquad \cancel{\langle a|c\rangle}\langle b\ c|\ \frac{e^2}{r_{2\,3}}\ |b\ a\rangle$$

$$-\langle a\ \underset{+}{b}\ c|\ \frac{e^2}{r_{2\,3}}\ |a\ \underset{-}{c}\ b\rangle \qquad \langle a|a\rangle\langle b\ c|\ \frac{e^2}{r_{2\,3}}\ |c\ b\rangle$$

Sum of orbitals

+

Sum over pairs of orbitals with exchange terms

End of Lecture Thursday 9. October 2008

PHYS261 Atomic Physics and Physical Optics

Lecture

Tuesday 14. October 2008

Topics:

Many-electron atoms

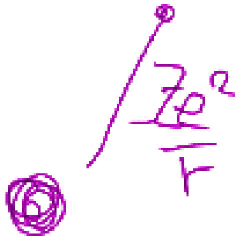
Hartree method; selfconsistent field

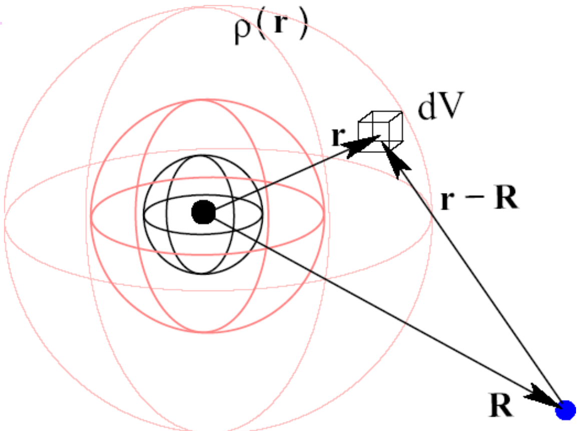
Iteration – selfconsistency

Selfconsistent field

Hartree (Hartree and Hartree)

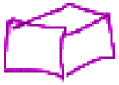
H-like





Interaction with a cloud

Density of the cloud → $\rho(\vec r_1)$

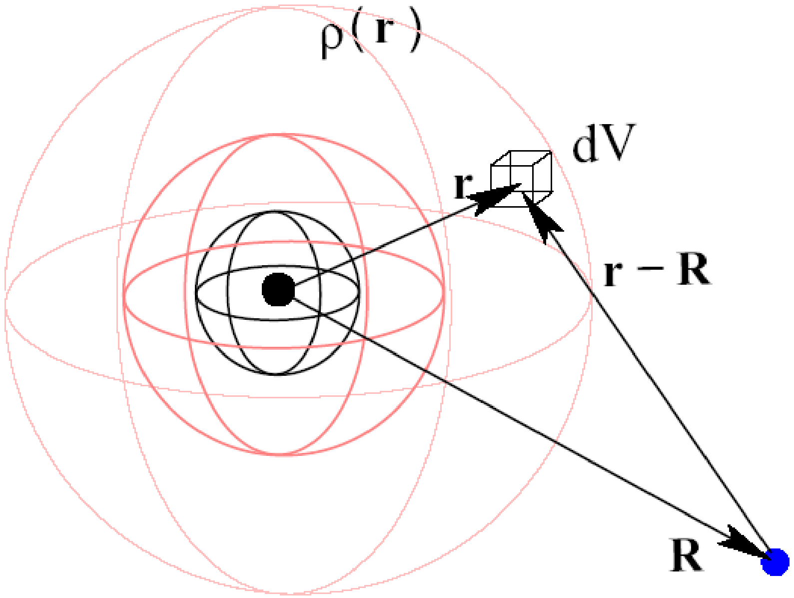
$q(\vec r_1) =$  $dV \cdot \rho(\vec r_1)$ is density at $\vec r_1$

$$\boxed{\frac{e \cdot q(\vec r_1)}{|\vec r - \vec r_1|}}$$

→ Sum over all

→ integrate over it.

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



$$\psi_0 \longrightarrow \rho^{(0)} \longrightarrow W^{(1)}$$

$$[T + V + W^{(1)}]\,\psi_{(1)} = E_{(1)}\,\psi_{(1)}$$

$$\psi_1 \longrightarrow \rho^{(1)} \longrightarrow W^{(2)}$$

$$[T + V + W^{(2)}]\,\psi^{(2)} = E^{(2)}\,\psi^{(2)}$$

$$\vdots$$

n-times

until it does not change

SELFCONSISTENT FIELD

Solid state phys ......

Quantum chemistry ...

SCF

Does it "converge"?

We allways take $\underline{m}$ lowest energy

And then there was this "theorem"

- Ground state is allways lower than any approximation . . . .

PHYS261 Atomic Physics and Physical Optics

Lecture Thursday 16. October 2008

Topics:

Many-electron atoms

Variational Methods for Schrödinger Equation
Variation derivation of Hartree-Fock equations

A more formal derivation of SCF's . . . .

Variational method . . . .

$\langle \phi | H | \phi \rangle$, made $\phi(z)$

$$\langle \phi | H | \phi \rangle \longrightarrow F(z) \longrightarrow \frac{dF(z)}{dz} = 0$$

$$\langle \phi(z) | H(z) | \phi(z) \rangle \longrightarrow \text{best } z$$

"Variational Principle" <u>Newton</u>

<u>instead</u> Lagrange, Hamilton

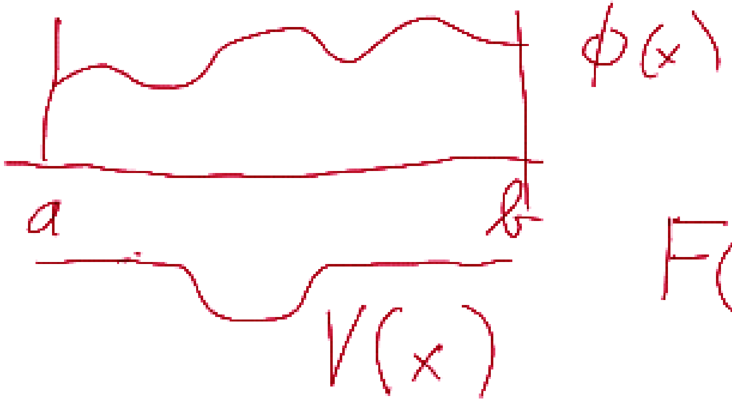
<u>Best possible function</u>

Function<u>al</u> depends on functions

$$\begin{tikzcd}
\text{Derivative} \arrow[dr] & \text{Variation} \\
\text{differential} \arrow[ur] & \text{Functional derivative} \cdots
\end{tikzcd}$$

Functional of $\phi(x)$ $\int_a^b |\phi(x)|^2 dx$

F



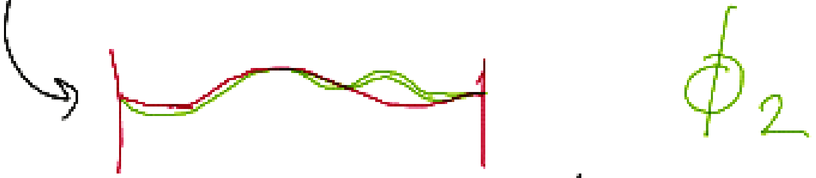
$T + V$

$$F(\phi) = \int_a^b |\phi(x)|^2 V(x)\,dx$$

if ϕ was $\phi(x)$ → we hade done it

each ϕ is a <u>point</u> in the space of functions

ϕ_1 and ϕ_2 are "close"



variation is $\phi_1(x) - \phi_2(x)$

$\delta\phi =$

$\phi + \delta\phi$

<u>analogy of differential</u>

$x + dx$

$\phi + \delta\phi$

funcional derivative $\dfrac{\delta F(\phi)}{\delta(\phi)}$

<u>limit</u> as $\delta\phi \to 0$

$x \longrightarrow d + dx$ | $\phi \longrightarrow \phi + \delta\phi$

$f(x) \longrightarrow f + df$ | $F(\phi) \longrightarrow F + \delta F$

functional)

Extremum

$df = 0$

Extremum

$\delta F = 0$

All possible "paths" $\vec{x}(t)$

The real path satisfies

$$A(t) = \int_{t_1}^{t_2} L(t')\, dt'$$

has a minimum .....

$$A(x(t)) = \int L(x(t))\, dt'$$

$\delta A = 0$ for $\delta(x)$ ....

$\longleftrightarrow$ Lagrange equations

$\longrightarrow$ The same as Newton

Lagrange : $A = \int dt \left(\frac{1}{2} m \dot{x}^2 \cancel{+} - \frac{1}{2} x^2 \right)$

$$\delta A = \int dt \left(m \dot{x}\, \delta \dot{x} - x\, \delta x \right)$$

as if x would be variable

$$A = \int dt\, \phi^5(t) \longrightarrow \delta A = \int dt\, 5 \phi^4(t)$$

$F(\phi) = \langle \phi | H | \phi \rangle \qquad \int \phi^2 + \text{something})$

$$\delta F = \langle \phi | H | \delta \phi \rangle$$

$$= \langle \underbrace{\delta \phi} | H | \phi \rangle$$

DEF

$\delta F = 0 \longrightarrow \langle \delta \phi | H | \phi \rangle = 0$

?? $H | \phi \rangle = 0$

WHAT TO DO

Minimum of a function with a constraint

find minimum of $F(x,y)$

while $\boxed{x_0\ y_0}$ $g(x,y)=0$

Given $F(x,y)$

Find i'ts minimum on a circle

$x^2+y^2=5$

$U(x,y)=F(x,y)+\lambda\, g(x,y)$

$U(x,y)$ equal $F(x,y)$ on the circle

$$\boxed{\begin{array}{cc} \frac{\partial}{\partial x}U(x,y)=0 & \frac{\partial}{\partial y}U(x,y)=0 \\ \multicolumn{2}{c}{g(x,y)=0} \end{array}}$$

$x_0\ y_0$

λ

$$F(\phi) = \langle \phi | H | \phi \rangle \qquad g(\phi) = \langle \phi | \phi \rangle - 1$$

$$\boxed{g(\phi) = 0}$$

$$U(\phi) = \langle \phi | H | \phi \rangle - \lambda \left(\langle \phi | \phi \rangle - 1 \right)$$

$$\delta U = \underbrace{\langle \delta\phi |}_{} H | \phi \rangle - \lambda \underbrace{\langle \delta\phi |}_{} \phi \rangle = 0$$

$$H | \phi \rangle = \lambda | \phi \rangle$$

Variational principle for Schrödinger equation

$\langle \Phi | H | \phi \rangle$ with Φ Slater determinants

$$\sum_{\substack{\alpha \\ \text{orbitals}}} \langle \phi_\alpha | T + V_C | \phi_\alpha \rangle$$

$$+ \sum_{\substack{\text{pairs} \\ \alpha, \beta}} \Big\{ \langle \phi_\alpha \phi_\beta | V_{12} | \phi_\alpha \phi_\beta \rangle$$

$$- \langle \phi_\alpha \phi_\beta | V_{12} | \phi_\beta \phi_\alpha \rangle \Big\}$$

with constraints

$\xcancel{\langle \phi_\alpha | \phi_\beta \rangle} = \delta_{\alpha\beta}$ $\langle \phi_\alpha | \phi_\alpha \rangle = 1$

for all α used

n-different orbitals

The Slater determinant

$$\Phi^{HF}_{a,b,\dots N}\left(r_1, r_2, \dots r_N\right) \rightarrow \left| \begin{array}{l} \psi_a(r_1)\psi_b(r_1)\dots\dots\psi_N(r_1) \\ \psi_a(r_2)\psi_b(r_2)\dots\dots\psi_N(r_2) \\ \dots\dots\dots \\ \psi_a(r_N)\psi_b(r_N)\dots\dots\psi_N(r_N) \end{array} \right|$$

Evaluate

$$\begin{aligned} \left\langle \Phi^{HF} \right| H \left| \Phi^{HF} \right\rangle &= \sum_{j=1}^{N} \langle \psi_j | \, T - \frac{Ze^2}{r} \, | \psi_j \rangle \\ &+ \sum_{(i,j) pairs} \int \langle \psi_j \psi_i | \, \frac{e^2}{|\vec{r} - \vec{r}'|} \, | \underline{\psi_j} \; \psi_i \, \rangle \\ &- \sum_{(i,j) pairs} \int \langle \psi_j \psi_i | \, \frac{e^2}{|\vec{r} - \vec{r}'|} \, | \underset{\uparrow}{\psi_i} \; \psi_j \, \rangle \end{aligned}$$

Hartree method can be derived from "variational method" if we neglect exchange terms

Hartree-Fock method

The exchange terms lead to

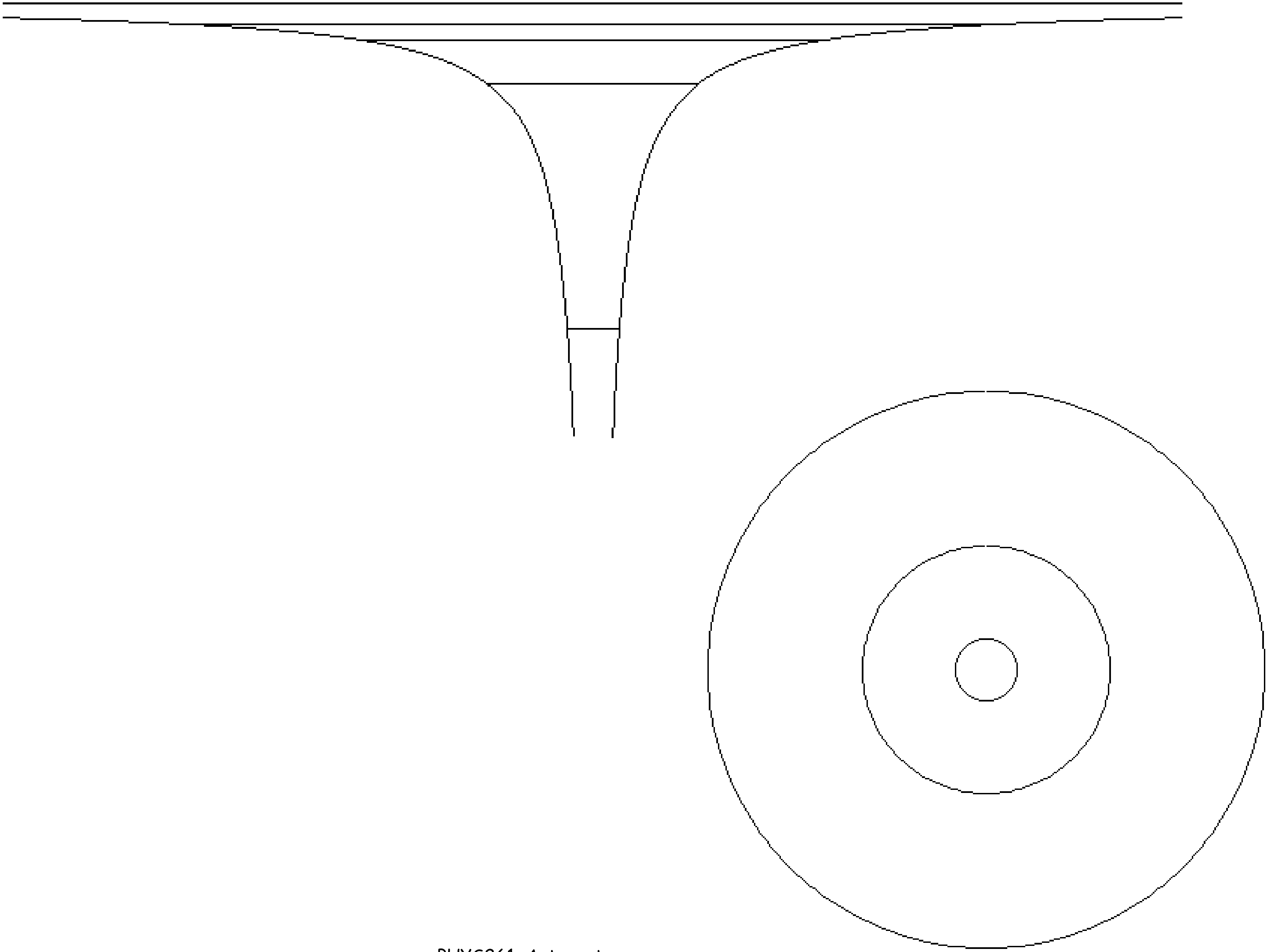
Exchange potential

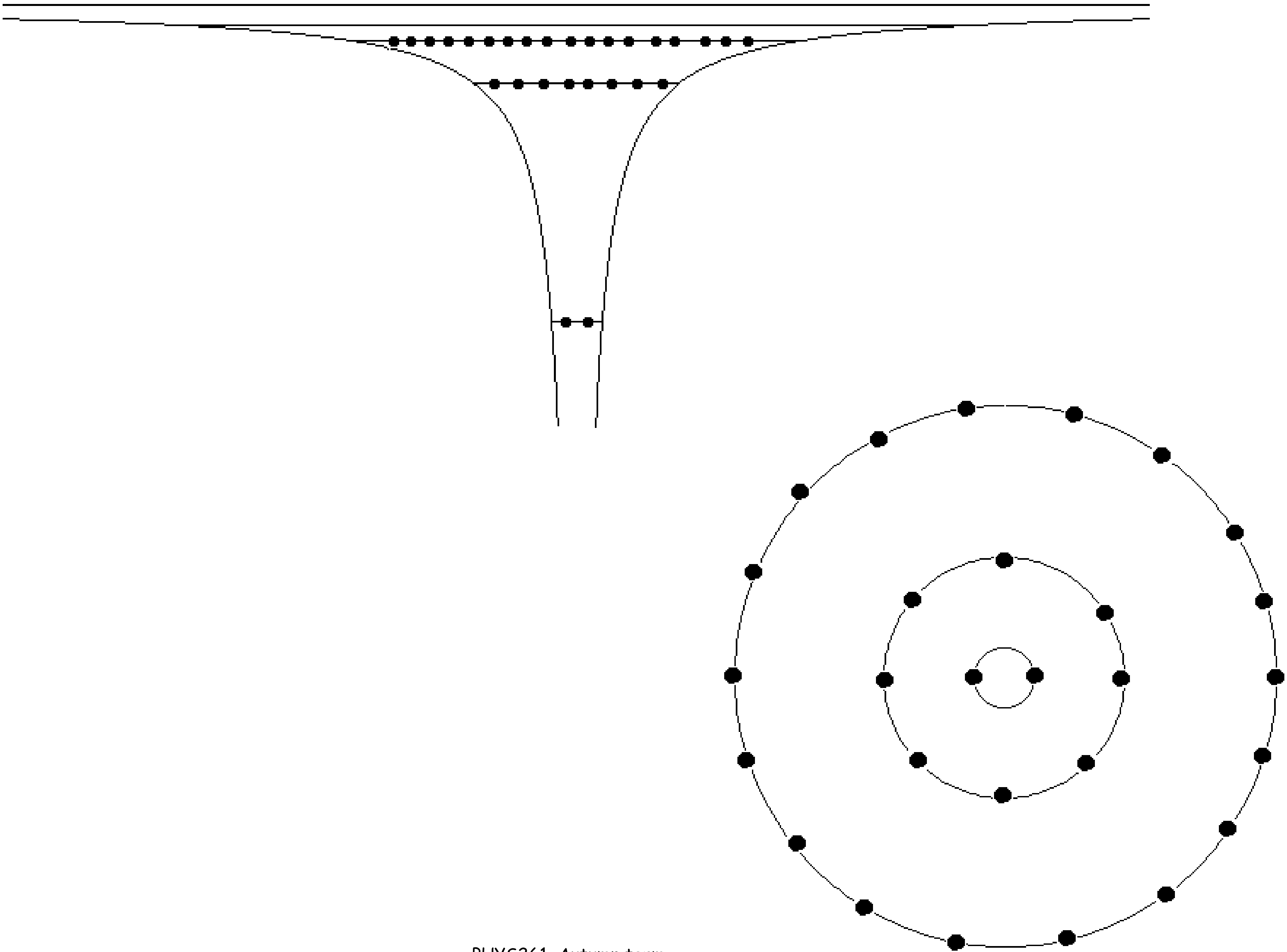
Exchange potential is nonlocal

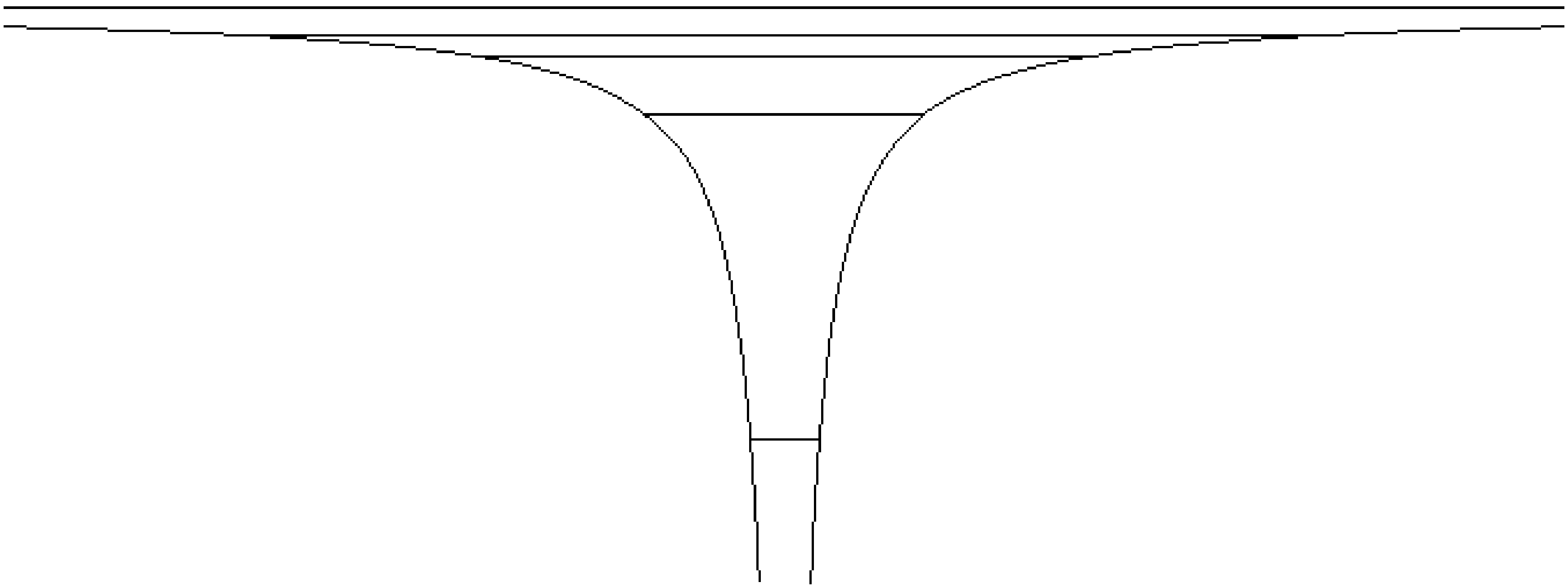
Local

$V\psi \rightarrow V(x)\psi(x)$ $\qquad W\psi \rightarrow \int V(x,x')\psi(x')$

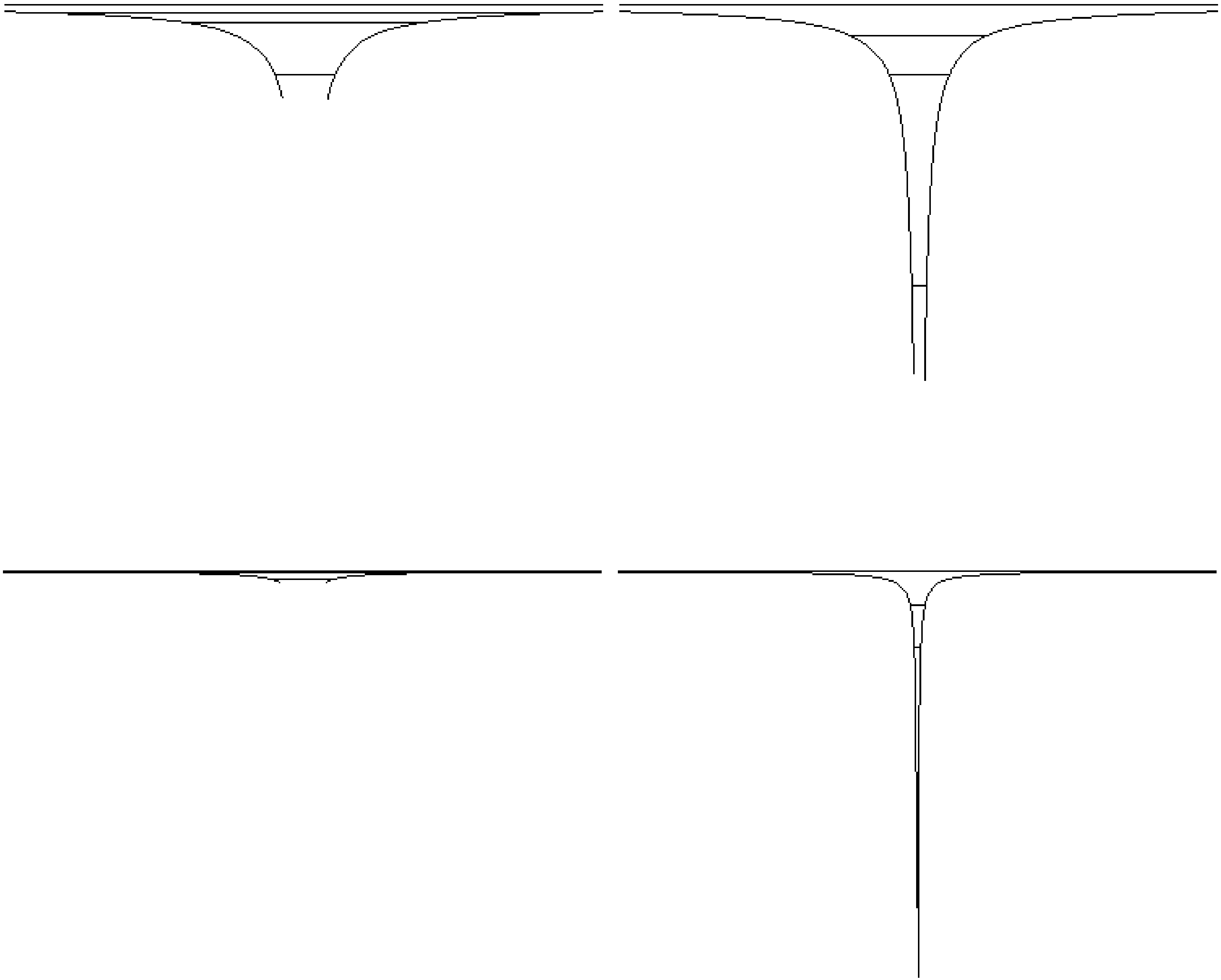
End of lecture 16.10.2008

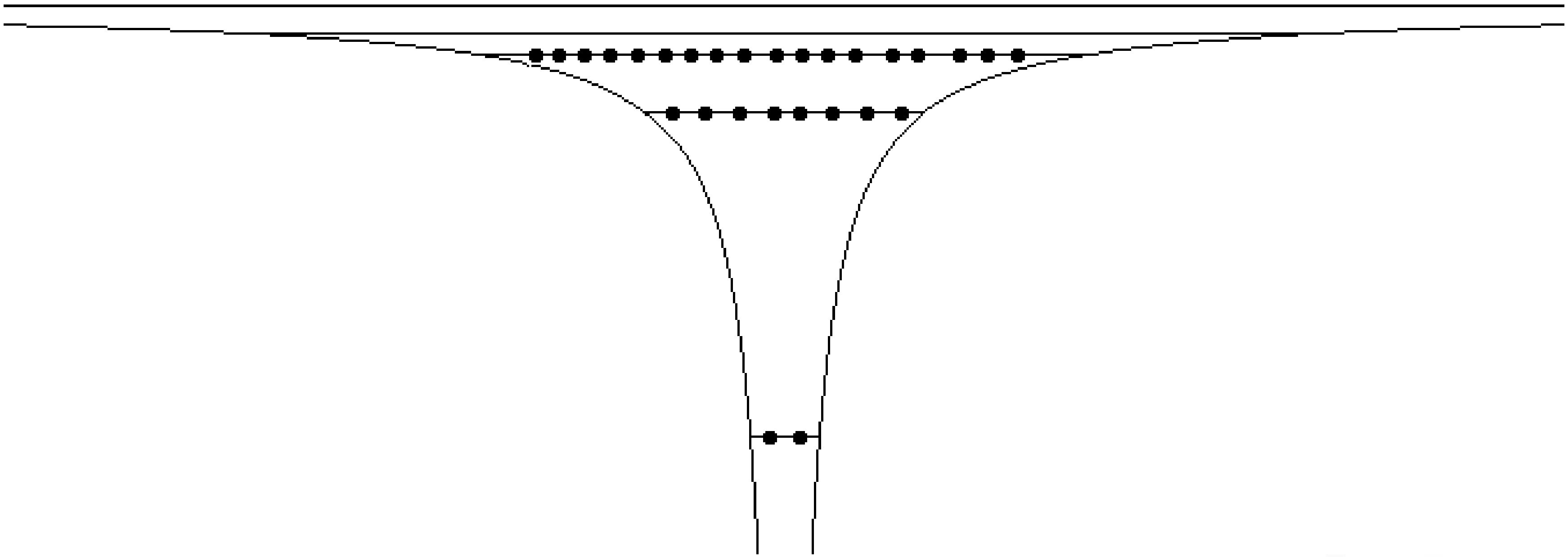


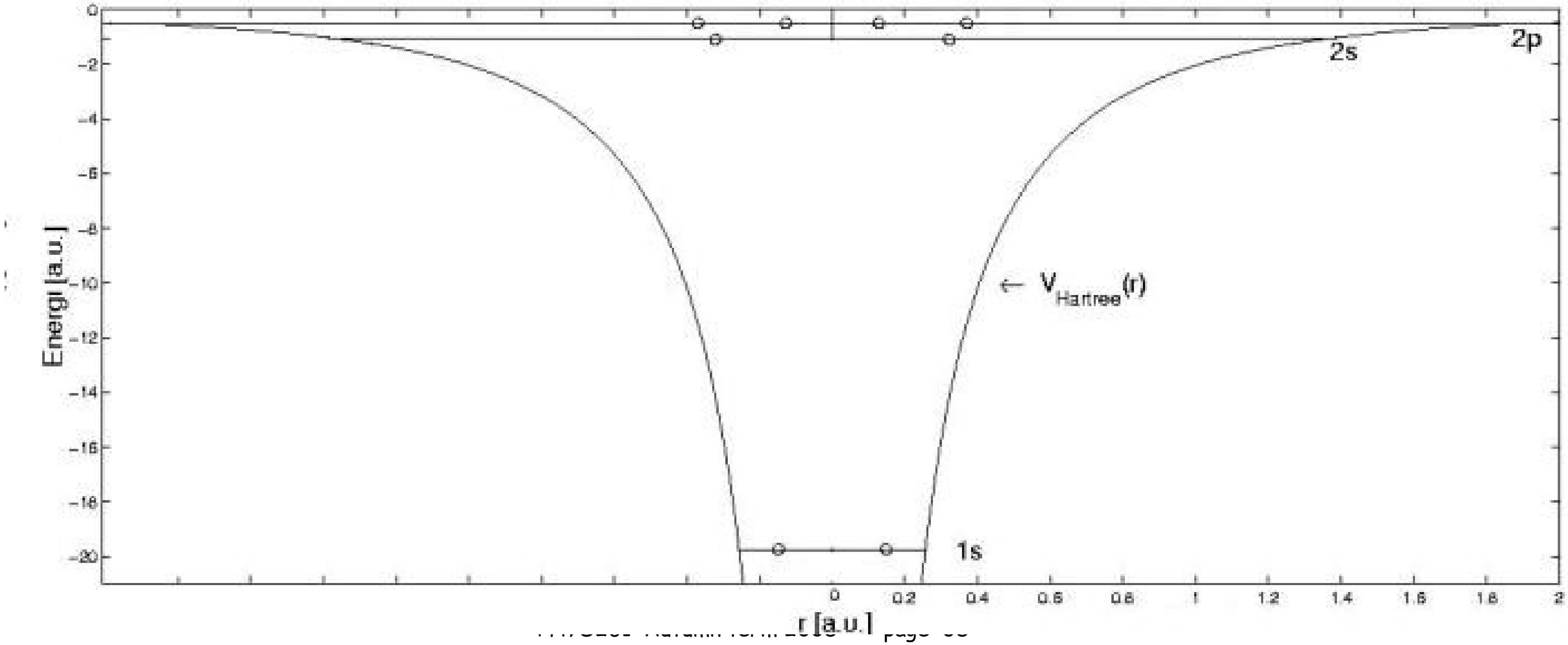




Torsdag 7. mars 2002






0
-2
-4
-6
-8
-10
-12
-14
-16
-18
-20
Energi [a.u.]
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
r [a.u.]
2s
2p
1s
← $V_{Hartree}(r)$