PHYS261 Atomic Physics and Physical Optics

Lecture Thursday 9. October 2008

Topics:

Many-electron atoms

Comment:

After the lecture – to be continued - preliminary version;

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

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

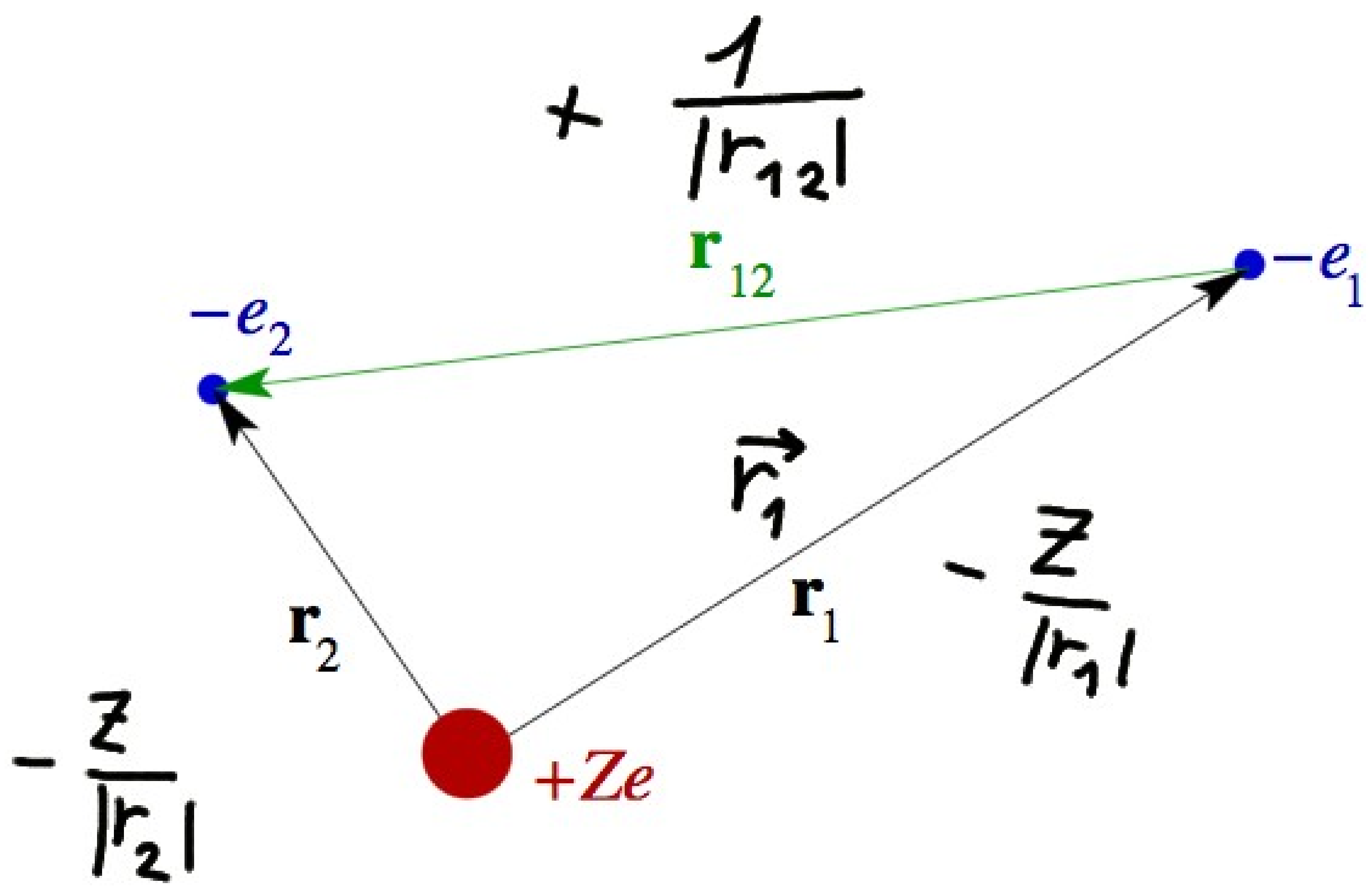
$$r_< = r_1, \quad r_> = r_2 \quad \text{for} \quad |\mathbf{r}_1| < |\mathbf{r}_2|$$
$$r_< = r_2, \quad r_> = r_1 \quad \text{for} \quad |\mathbf{r}_1| > |\mathbf{r}_2|$$

Perturbation theory result:

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

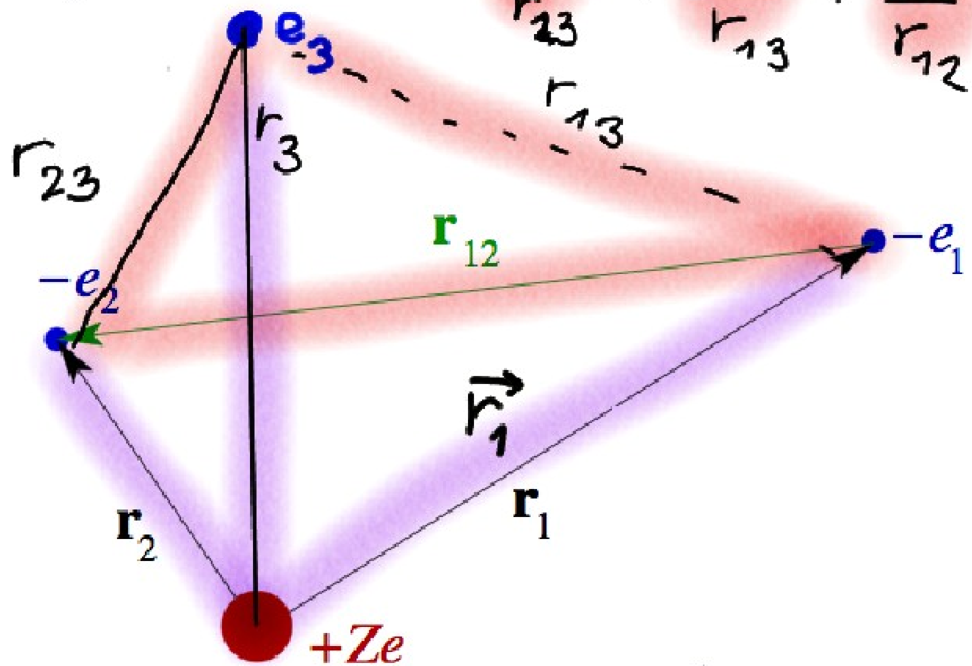
How does this work for Lithium – 3 electrons ?

The picture of the Helium Atom (coordinates)



Lithium – 3 electrons

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



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

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

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

See the Latex Document

The above in this notation

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

Slater determinant

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

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

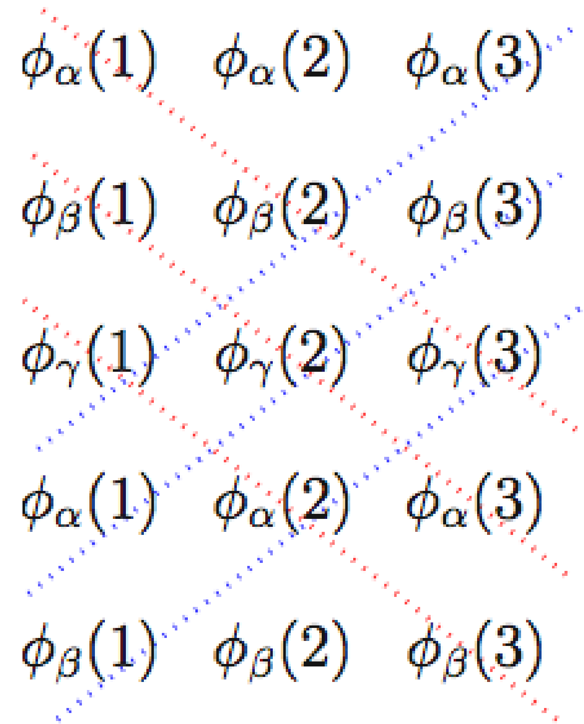
For 3 particles:

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

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



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

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

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 terms | 5 terms | 2 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. 6 terms

$\langle$ 6 terms | 9 terms | 6 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

$\langle 2 \text{ terms} | 2 \text{ terms} \rangle = 2$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\underbrace{\langle\alpha|\alpha\rangle}_{1}\underbrace{\langle\gamma|\beta\rangle}_{0}\underbrace{\langle\beta|\gamma\rangle}_{0} = 0$$

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

$\langle \alpha \; \beta \gamma \mid T_2 \mid \alpha \beta \gamma \rangle$

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

$\langle \alpha \; \beta \gamma \mid T_3 \mid \alpha \beta \gamma \rangle$

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

T_2 , T_3

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

$\langle \alpha | T_1 | \alpha \rangle \underbrace{\langle \gamma | \beta \rangle}_{0} \underbrace{\langle \beta | \gamma \rangle}_{0} = 0$

Also for 1 particle terms

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

But there are N of such terms

$\langle \alpha \beta \gamma | T_1 + T_2 + T_3 | \alpha \beta \gamma \rangle$

(6) (3) (6) $\sqrt{\frac{1}{n!}} \cdot \sqrt{\frac{1}{n!}}$

$3 \cdot 6$ non-zero

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

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

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

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

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

$(T_{\alpha\beta} = 0)$

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

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

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

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

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

$$\cdot \langle \alpha | \alpha \rangle$$

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

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

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

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

Either the same pair; or reversed pair

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

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

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

6 · 6 · 3 terms

$$\langle \alpha\beta | V_{12} | \alpha\beta \rangle - \langle \alpha\beta | V_{12} | \beta\alpha \rangle$$
$$+ \langle \beta\gamma | V_{12} | \beta\gamma \rangle - \langle \beta\gamma | V_{12} | \gamma\beta \rangle$$
$$+ \langle \alpha\gamma | V_{12} | \alpha\gamma \rangle - \langle \alpha\gamma | V_{12} | \gamma\alpha \rangle$$

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

$$\frac{1}{\sqrt{3!}}\Big\{ |a\ b_{+}\ c\rangle + |c\ a_{+}\ b\rangle + |b\ c_{+}\ a\rangle - |b\ a_{-}\ c\rangle - |c\ b_{-}\ a\rangle - |a\ c_{-}\ b\rangle \Big\}$$

$$\langle a\ b_{+}\ c|\ \frac{e^2}{r_{23}}\ |a\ b_{+}\ c\rangle \qquad \langle a|a\rangle\langle b\ c|\ \frac{e^2}{r_{23}}\ |b\ c\rangle$$

$$+\langle a\ b_{+}\ c|\ \frac{e^2}{r_{23}}\ |c\ a_{+}\ b\rangle \qquad \langle a|c\rangle\langle b\ c|\ \frac{e^2}{r_{23}}\ |a\ b\rangle$$

$$+\langle a\ b_{+}\ c|\ \frac{e^2}{r_{23}}\ |b\ c_{+}\ a\rangle \qquad \langle a|b\rangle\langle b\ c|\ \frac{e^2}{r_{23}}\ |c\ a\rangle$$

$$-\langle a\ b_{+}\ c|\ \frac{e^2}{r_{23}}\ |b\ a_{-}\ c\rangle \qquad \langle a|b\rangle\langle b\ c|\ \frac{e^2}{r_{23}}\ |a\ c\rangle$$

$$-\langle a\ b_{+}\ c|\ \frac{e^2}{r_{23}}\ |c\ b_{-}\ a\rangle - \qquad \langle a|c\rangle\langle b\ c|\ \frac{e^2}{r_{23}}\ |b\ a\rangle$$

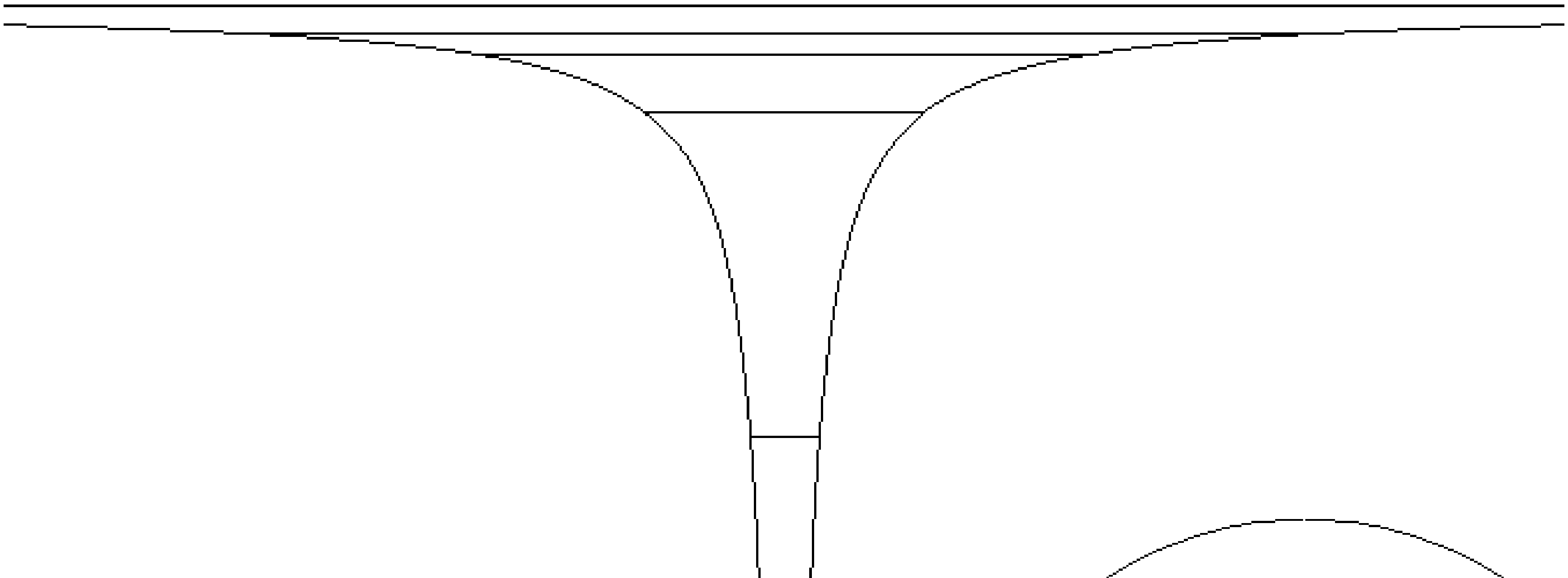
$$-\langle a\ b_{+}\ c|\ \frac{e^2}{r_{23}}\ |a\ c_{-}\ b\rangle \qquad \langle a|a\rangle\langle b\ c|\ \frac{e^2}{r_{23}}\ |c\ b\rangle$$

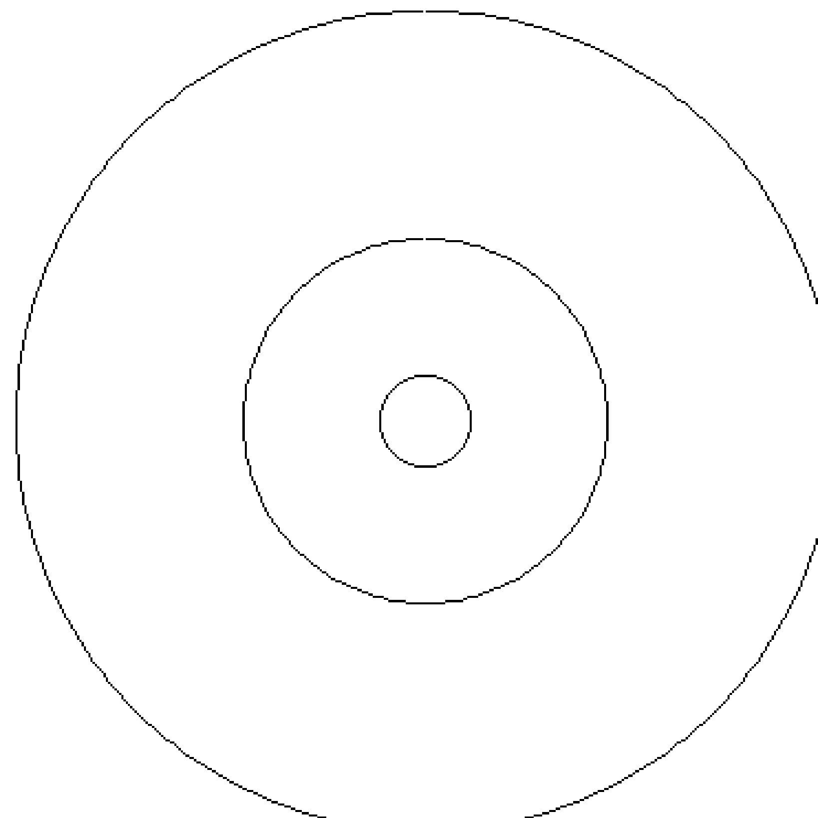
Sum of orbitals

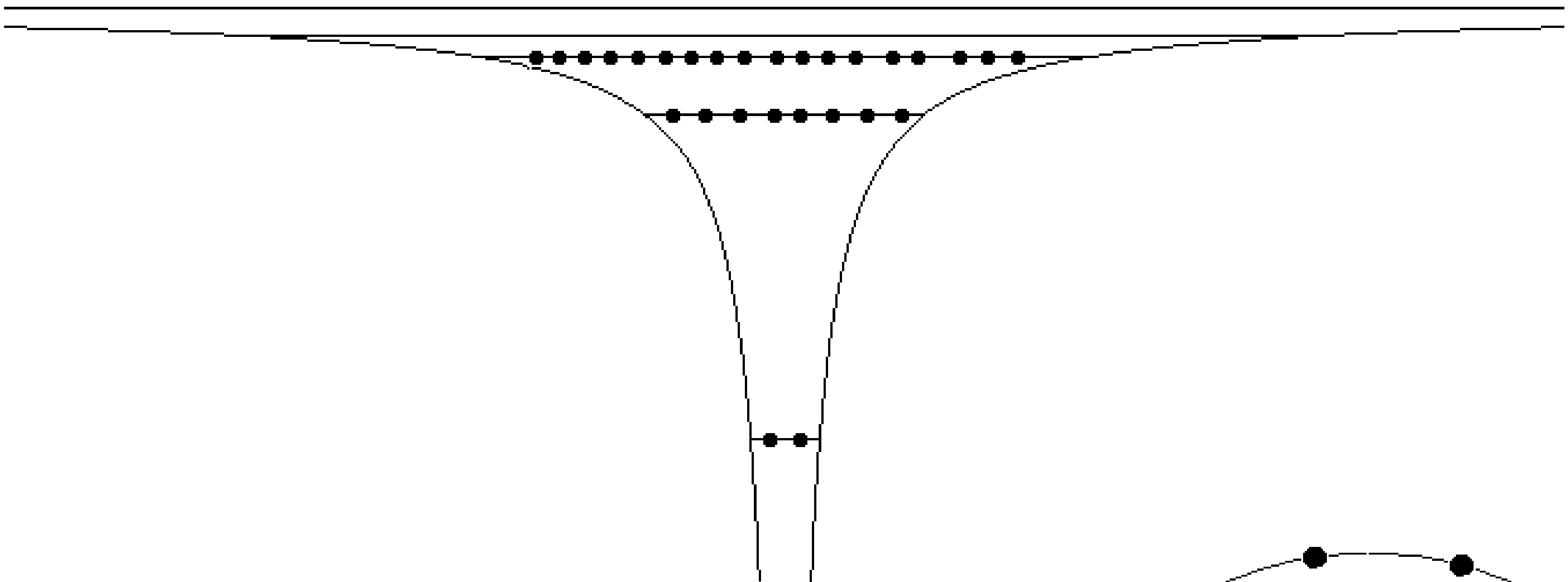
+

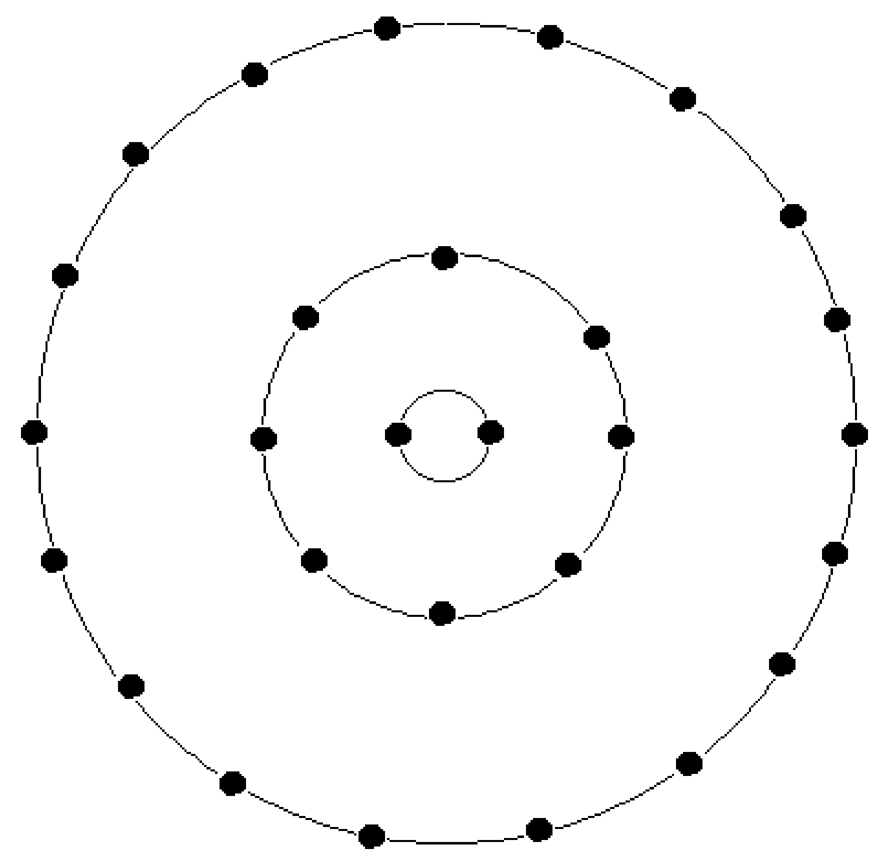
Sum over pairs of orbitals with exchange terms

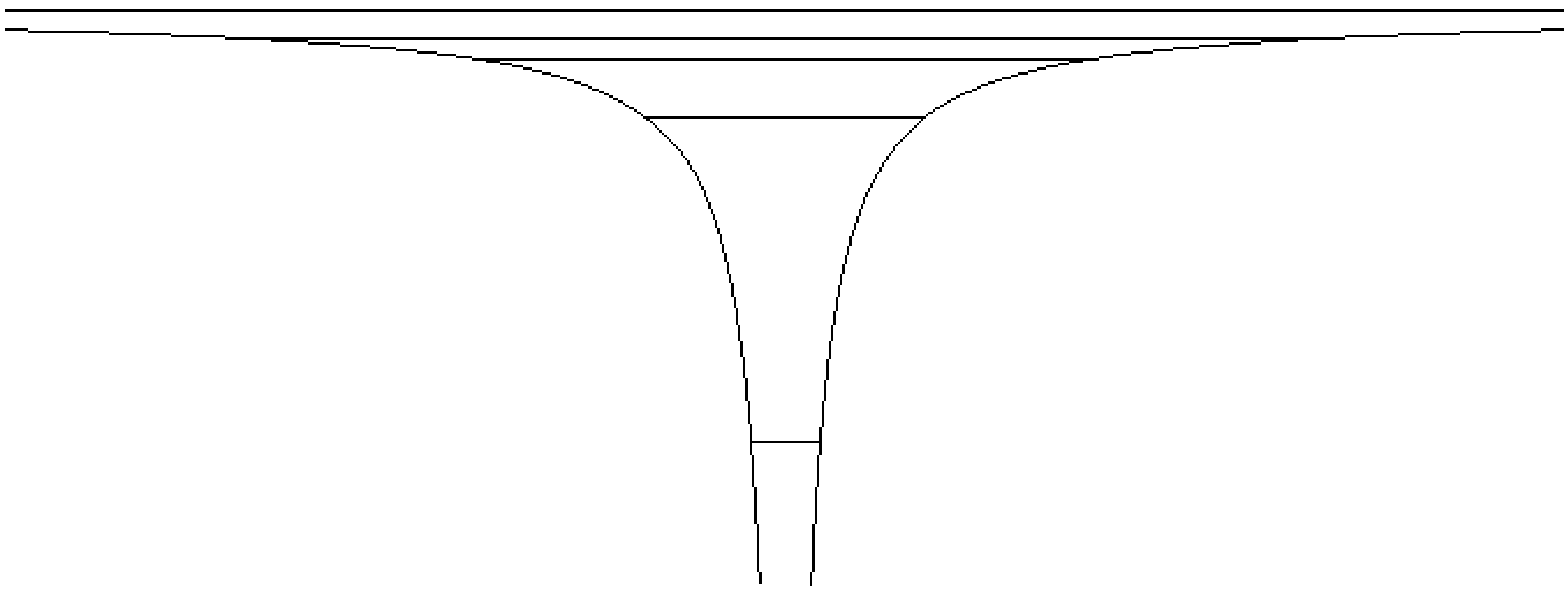
End of Lecture Thursday 9. October 2008



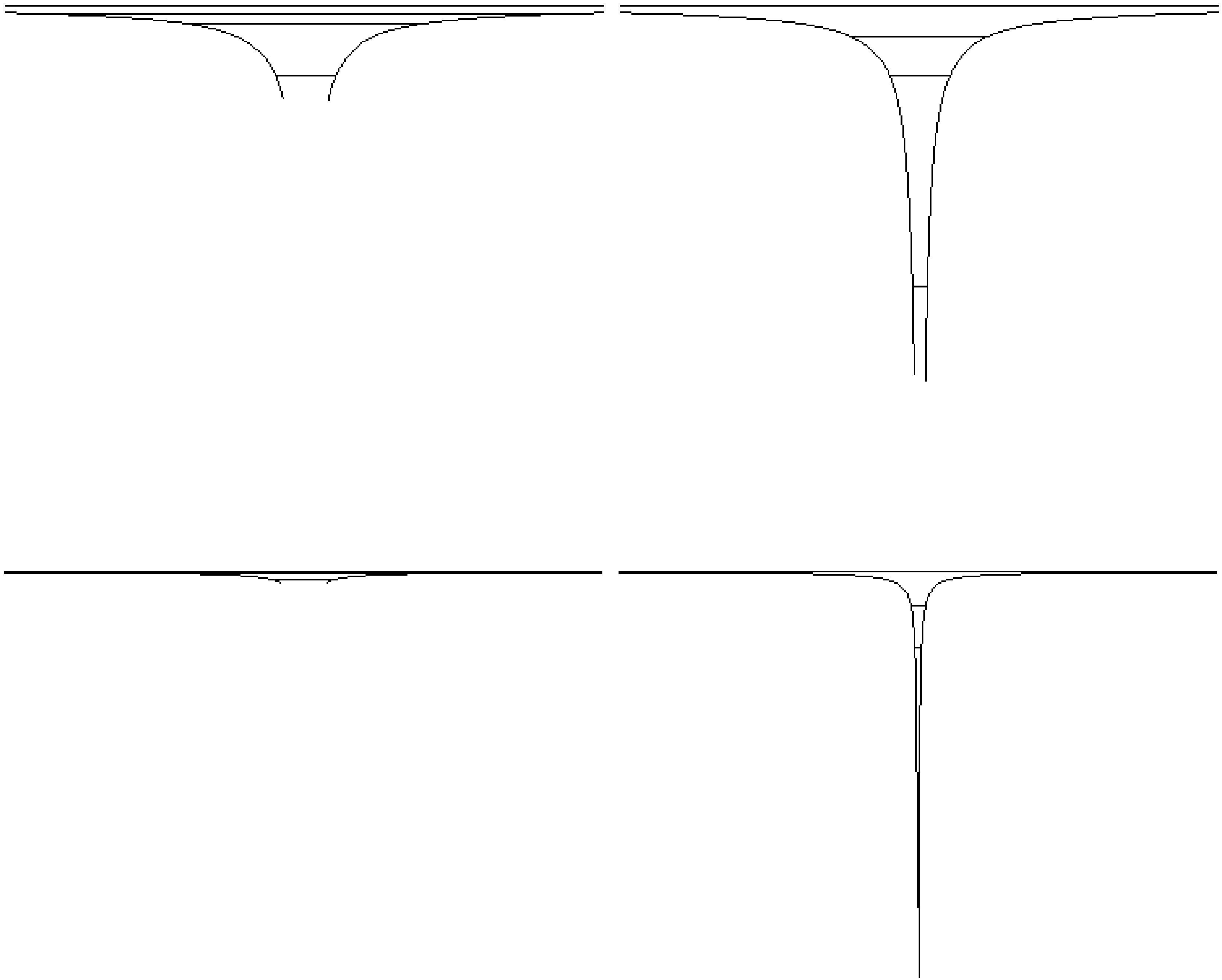


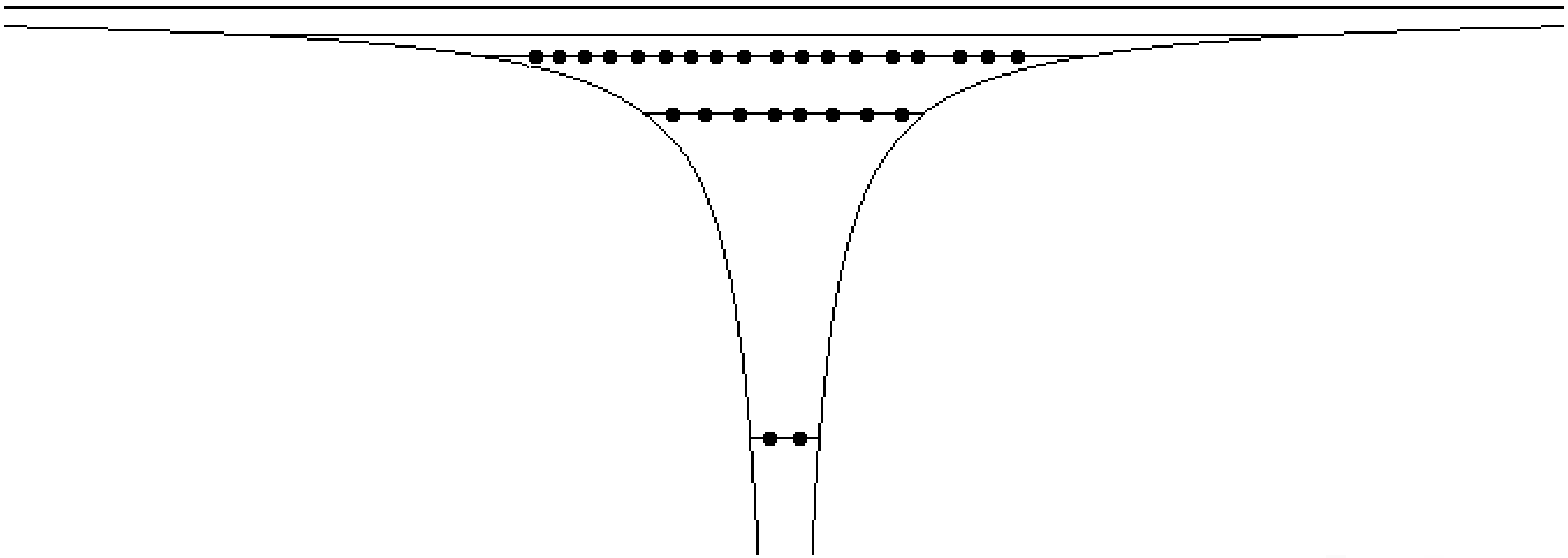


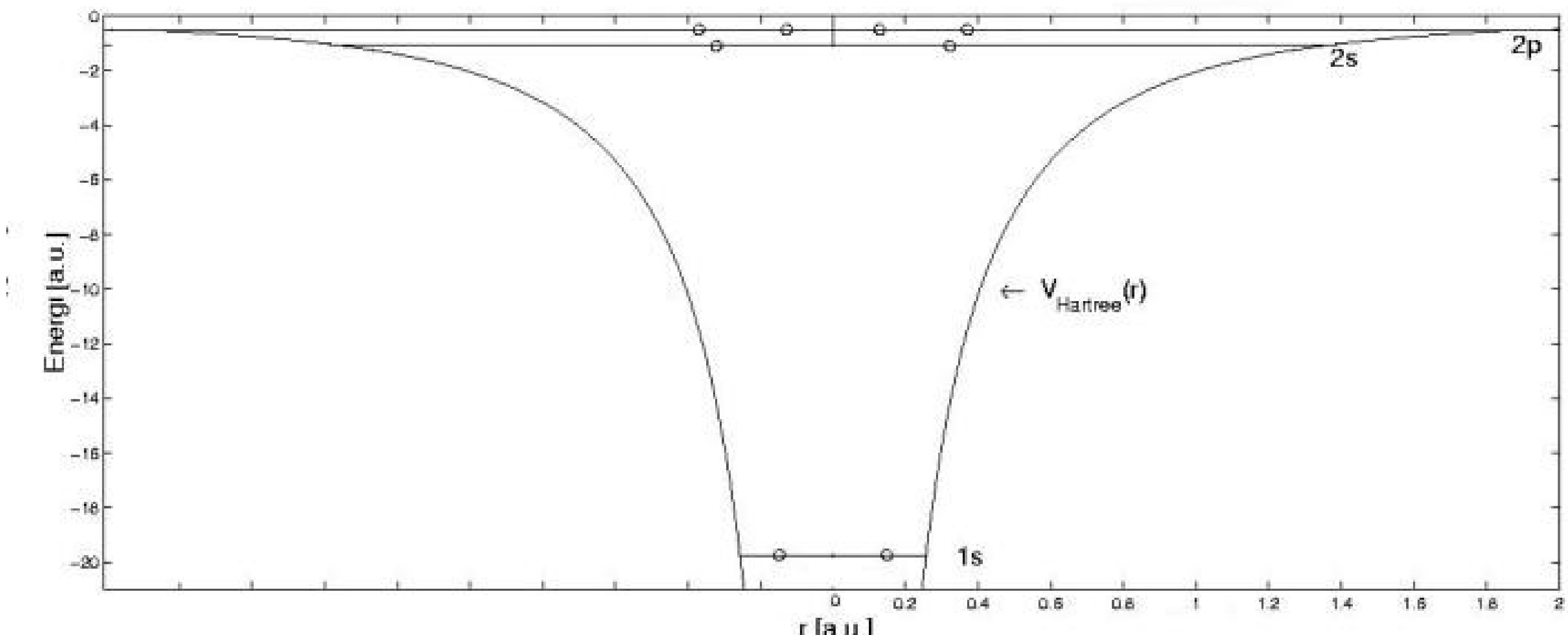




Torsdag 7. mars 2002







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