

Variational calculations of ionization energies of few-electron atoms with a variable charge

The trial wave function is constructed as a linear combination of products of single-particle functions of the form

$$Y_{l,m}(\theta, \varphi) r^l \exp(-ar) \chi_s, \quad (1)$$

where $Y_{l,m}$ is a spherical harmonics, χ_s is a spin function ($\chi_1 = \alpha$, and $\chi_2 = \beta$).

Firstly, consider a two-electron atom. For the ground state, we construct the trial function as

$$e^{-a_1 r_1 - a_2 r_2} + e^{-a_2 r_1 - a_1 r_2}. \quad (2)$$

Parameters a_1 and a_2 are found by minimization of the energy functional, e. i. an expectation value of Hamiltonian

$$-\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}. \quad (3)$$

The energy functional is a rational function of a_1 , a_2 (however, the expression is lengthy).

Results for helium ($Z = 2$), H^- ($Z = 1$), and Li^+ ($Z = 3$) are given in the following table.

Z	a_1	a_2	E_{var}	% of exact
1	1.04	0.28	-0.5133	97.3
2	2.18	1.19	-2.8757	99.0
3	3.29	2.08	-7.2467	99.6

Ionization energy $E_1(Z) = -1/(2Z^2) - E(Z)$ is shown on Fig. 1 together with results of summation of $1/Z$ -expansion. Ionization energy is zero at $Z_0 = 0.9538$ that is larger than exact critical charge $Z_c = 0.9110$. Below $Z_1 = 0.9276$, that corresponds to $E = -0.4246$, $a_1 = 1.014$, and $a_2 = 0.156$, the minimum of the energy functional disappears (turns to a complex stationary point). At $Z = Z_1$, the energy has a singularity $\sim (Z - Z_c)^{3/2}$. Derivatives of the energy shown on fig. 2 and 3 have

singularities also. Note that exponential parameters a_1 , a_2 shown on fig. 4 remain positive at $Z = Z_1$.

Similar calculations were done for a simplified trial function that does not include exchange:

$$e^{-a_1 r_1 - a_2 r_2} . \quad (1a)$$

Fig. 4.1 shows the results. We found a symmetric minimum at $a_1 = a_2 = Z - 5/16$ that gives well-known approximation $E = -(Z - 5/16)^2$. For sufficiently small Z , we found also an asymmetric minimum which turns to a global minimum at $Z < 1.08$ (however it grossly underestimates the energy). So, including exchange (trial function (1)) significantly improves an accuracy for weakly bound states (near the critical charge).

For the lowest triplet state of a two-electron atom, we construct the trial function as

$$e^{-a_1 r_1 - a_2 r_2} - e^{-a_2 r_1 - a_1 r_2} , \quad (4)$$

where parameters a_1 and a_2 are found by minimization of the corresponding energy functional.

Results for helium ($Z = 2$) and Li^+ ($Z = 3$) are given in the following table.

Z	a_1	a_2	E_{var}	% of exact
2	1.97	0.32	-2.1606	99.3
3	2.93	0.60	-5.0718	99.2

Ionization energy $E_1(Z) = -1/(2Z^2) - E(Z)$ is shown on Fig. 5 together with results of summation of $1/Z$ -expansion. Ionization energy is zero at $Z_0 = 1$. Below $Z_1 = 0.9928$, that corresponds to $E = -0.4929$, $a_1 = 1.00003$, and $a_2 = -0.0135$, the minimum of the energy functional disappears (turns to a complex stationary point). At $Z = Z_1$, the energy has a singularity $\sim (Z - Z_c)^{3/2}$. Derivatives of the energy shown on fig. 6 and 7 have singularities also. Note that one of exponential parameters a_1 , a_2 (shown on fig. 8) turns to zero at $Z = Z_0$, that means that a trial wave function (4) is non square integrable at $Z = Z_0$. Finding a critical index, i. e. establishing behavior $E_1 \sim (Z - Z_0)^\alpha$ is of particular interest. In order to find α , we plot $(Z - Z_0) \frac{dE_1 / dZ}{E_1}$ vs. Z at $Z \approx Z_0$. Fig. 9 shows that the limit of this quantity at $Z \rightarrow Z_0$ is around $\alpha = 2$.

Fig. 10 shows the ratio of variational ionization energy to exact one ($1/Z$ -expansion) for singlet and triplet states. When it is close to one, the variational method is accurate. For both states,

accuracy increases with Z , because an electron interaction weakens, and Hartree - Fock approximation is more accurate for large Z . For the triplet state, accuracy increases also when Z approaches to one. It can be explained by separation of the outer electron from the core electron that makes Hartree - Fock approximation more accurate. In this region, the second derivative tends to 1 (see fig. 7) that is $E_1 \sim (Z-1)^2 / 2$ when $Z \rightarrow 1$. It can be interpreted as the binding energy of the outer electron on the ground state in an effective Coulomb potential $-(Z-1)/r$ moving on an orbit of big radius $1/(Z-1)$.

P-states of two-electron atoms

Let us consider a doubly excited $2p^2 \ ^3P$ state that is equivalent to the ground state in five-dimensional space. We construct a trial wave function in the same spirit as

$$Y_{1,0}(\theta_1, \varphi_1)r_1 \exp(-a_1 r_1) \cdot Y_{1,1}(\theta_2, \varphi_2)r_2 \exp(-a_2 r_2) + Y_{1,0}(\theta_2, \varphi_2)r_2 \exp(-a_1 r_2) \cdot Y_{1,1}(\theta_1, \varphi_1)r_1 \exp(-a_2 r_1). \quad (\text{A})$$

However, there is an ambiguity in the choice. Along with a trial function (A), we consider another one,

$$Y_{1,0}(\theta_1, \varphi_1)r_1 \exp(-a_1 r_1) \cdot Y_{1,1}(\theta_2, \varphi_2)r_2 \exp(-a_2 r_2) + Y_{1,0}(\theta_1, \varphi_1)r_1 \exp(-a_2 r_1) \cdot Y_{1,1}(\theta_2, \varphi_2)r_2 \exp(-a_1 r_2) + (r_1 \Leftrightarrow r_2). \quad (\text{B})$$

If $a_1 = a_2$ then the functions (A) and (B) are the same. Comparison of results of minimization of the energy functional for helium ($Z = 2$) for trial functions (A) and (B) are given in the following table.

Trial function	a_1	a_2	E_{var}	% of exact
A	0.84	0.84	-0.6988	98.4
B	1.04	0.62	-0.7044	99.1

Ionization energy $E_1(Z) = -1/(8Z^2) - E(Z)$ is shown on Fig. 11. We found that the choice (B) significantly improves an accuracy. When $Z < 1.2$, obtained ionization energy increases at least two times. For the choice (A), there is a secondary minimum with $a_1 \neq a_2$ that turns to a global one when $Z < 1.12$. However, it gives a considerable under-estimation of the true ionization energy. For the choice (A), the curve does not have singularities near $Z = 1$. At $Z = 1$, it goes to zero with zero derivative, while one of exponential parameters goes to zero. For the choice (B), the curve goes to

zero near $Z = 1.02$. At the point $Z_1 = 1.0160$, that corresponds to $E = -0.1280$, $a_1 = 0.496$, and $a_2 = 0.114$, there is a singularity. It reflects existence of critical charge $Z_c = 0.9948$. In a very narrow region $1 < Z < Z_1$, there is another minimum of the energy functional for the trial function (B) that gives a positive ionization energy (it is not shown on the figure 11).

Let us consider the lowest P-states, $1s2p\ ^1P$ and $1s2p\ ^3P$. The trial function was chosen in the form

$$Y_{1,0}(\theta_1, \varphi_1) r_1 \exp(-a_1 r_1) \cdot \exp(-a_2 r_2) \pm (r_1 \leftrightarrow r_2) \quad (5)$$

Results for helium ($Z = 2$) are given in the following table.

State	a_1	a_2	E_{var}	% of exact
$1s2p\ ^1P$	2.00	0.48	-2.1224	99.93
$1s2p\ ^3P$	1.99	0.54	-2.1307	99.88

Ionization energy $E_1(Z) = -1/(2Z^2) - E(Z)$ is shown on Fig. 12 for $1s2p\ ^3P$ state. The curve touches the ionization border ($E_1 = 0$) at the point $Z_0 = 1$ that is an exact critical charge. However, there are no singularities near $Z = Z_0$. Note that another trial function similar to (B) may be constructed also, but they remain to be tested.

Ground state of three-electron atoms

A standard choice of a three-electron Hartree - Fock trial function is a Slater determinant. We construct a Slater determinant from exponential coordinate functions:

$$\begin{vmatrix} e^{-a_1 r_1} \alpha(1) & e^{-a_2 r_1} \beta(1) & e^{-a_3 r_1} \alpha(1) \\ e^{-a_1 r_2} \alpha(2) & e^{-a_2 r_2} \beta(2) & e^{-a_3 r_2} \alpha(2) \\ e^{-a_1 r_3} \alpha(3) & e^{-a_2 r_3} \beta(3) & e^{-a_3 r_3} \alpha(3) \end{vmatrix}. \quad (A)$$

Along with a trial function (A), we consider another one,

$$\begin{vmatrix} e^{-a_1 r_1} \alpha(1) & e^{-a_2 r_1} \beta(1) & e^{-a_3 r_1} \alpha(1) \\ e^{-a_1 r_2} \alpha(2) & e^{-a_2 r_2} \beta(2) & e^{-a_3 r_2} \alpha(2) \\ e^{-a_1 r_3} \alpha(3) & e^{-a_2 r_3} \beta(3) & e^{-a_3 r_3} \alpha(3) \end{vmatrix} - \begin{vmatrix} e^{-a_1 r_1} \beta(1) & e^{-a_2 r_1} \alpha(1) & e^{-a_3 r_1} \alpha(1) \\ e^{-a_1 r_2} \beta(2) & e^{-a_2 r_2} \alpha(2) & e^{-a_3 r_2} \alpha(2) \\ e^{-a_1 r_3} \beta(3) & e^{-a_2 r_3} \alpha(3) & e^{-a_3 r_3} \alpha(3) \end{vmatrix}. \quad (B)$$

Finally, we used the choice (B). The reason is consistency of three-electron energy functional with two-electron energy functional, when the third electron goes to infinity ($a_3 \rightarrow 0$) which happens when the system ionizes. The limit $a_3 \rightarrow 0$ of the energy functional corresponding to (A) is a function that is *not* symmetric in variables a_1, a_2 . So, it cannot be the same as two-electron energy functional corresponding to a trial function (2) that is symmetric in a_1, a_2 . It can be shown, that the limit $a_3 \rightarrow 0$ of the energy functional corresponding to (B) is the same as two-electron energy functional corresponding to a trial function (2).

Results for lithium ($Z = 3$), Be^+ ($Z = 4$), and B^{2+} ($Z = 5$) are given in the following table.

Z	Trial function	a_1	a_2	a_3	E_{var}	% of exact
3	A	2.67	2.67	0.34	-7.4014	99.0
3	B	3.28	2.07	0.34	-7.4266	99.3
4	B	4.34	2.97	0.62	-14.2392	99.4
5	B	5.37	3.91	0.90	-23.2955	99.4

Ionization energy is calculated as a difference between the minimum of two-electron energy functional (trial function (2)) and a minimum of three-electron energy functional (trial function (B)). Because of consistency of these functionals mentioned above, we have always zero ionization energy, as soon as the third electron ionizes ($a_3 \rightarrow 0$).

Ionization energy is shown on Fig. 12 together with numerical results of P. Serra (1998) that are much more accurate than our variational results and can be considered as „exact“. Our variational results look qualitatively the same as exact results with slightly underestimation. Variational ionization energy and its derivatives (fig. 13 - 15) are very similar to the triplet state of two-electron atoms that was discussed above. One of exponential parameters a_1, a_2, a_3 (shown on Fig. 16) turns to zero at $Z = Z_0 = 2$, that means that a trial wave function is non square integrable at $Z = Z_0$. Below $Z_1 = 1.9884$, that corresponds to $E = -2.8369$, $a_1 = 2.1702$, $a_2 = 1.1784$, and $a_3 = -0.0215$, the minimum of the energy functional disappears (turns to a complex stationary point). On Fig. 17, we plot $\alpha(Z) = (Z - Z_0) \frac{dE_1 / dZ}{E_1}$ vs. Z at $Z \approx Z_0$. The limit of this quantity at $Z \rightarrow Z_0$ is around $\alpha = 2$.

Ground state of four-electron atoms

A standard choice of a three-electron Hartree - Fock trial function is a Slater determinant. We construct a Slater determinant from exponential coordinate functions:

$$\begin{vmatrix} e^{-a_1 r_1} \alpha(1) & e^{-a_2 r_1} \beta(1) & e^{-a_3 r_1} \alpha(1) & e^{-a_4 r_1} \beta(1) \\ e^{-a_1 r_2} \alpha(2) & e^{-a_2 r_2} \beta(2) & e^{-a_3 r_2} \alpha(2) & e^{-a_4 r_2} \beta(2) \\ e^{-a_1 r_3} \alpha(3) & e^{-a_2 r_3} \beta(3) & e^{-a_3 r_3} \alpha(3) & e^{-a_4 r_3} \beta(3) \\ e^{-a_1 r_4} \alpha(4) & e^{-a_2 r_4} \beta(4) & e^{-a_3 r_4} \alpha(4) & e^{-a_4 r_4} \beta(4) \end{vmatrix}. \quad (\text{A})$$

Along with a trial function (A), we consider another one,

$$\begin{vmatrix} e^{-a_1 r_1} \alpha(1) & e^{-a_2 r_1} \beta(1) & e^{-a_3 r_1} \alpha(1) & e^{-a_4 r_1} \beta(1) \\ e^{-a_1 r_2} \alpha(2) & e^{-a_2 r_2} \beta(2) & e^{-a_3 r_2} \alpha(2) & e^{-a_4 r_2} \beta(2) \\ e^{-a_1 r_3} \alpha(3) & e^{-a_2 r_3} \beta(3) & e^{-a_3 r_3} \alpha(3) & e^{-a_4 r_3} \beta(3) \\ e^{-a_1 r_4} \alpha(4) & e^{-a_2 r_4} \beta(4) & e^{-a_3 r_4} \alpha(4) & e^{-a_4 r_4} \beta(4) \end{vmatrix} - \begin{vmatrix} e^{-a_1 r_1} \beta(1) & e^{-a_2 r_1} \alpha(1) & e^{-a_3 r_1} \alpha(1) & e^{-a_4 r_1} \beta(1) \\ e^{-a_1 r_2} \beta(2) & e^{-a_2 r_2} \alpha(2) & e^{-a_3 r_2} \alpha(2) & e^{-a_4 r_2} \beta(2) \\ e^{-a_1 r_3} \beta(3) & e^{-a_2 r_3} \alpha(3) & e^{-a_3 r_3} \alpha(3) & e^{-a_4 r_3} \beta(3) \\ e^{-a_1 r_4} \beta(4) & e^{-a_2 r_4} \alpha(4) & e^{-a_3 r_4} \alpha(4) & e^{-a_4 r_4} \beta(4) \end{vmatrix} + \begin{vmatrix} e^{-a_1 r_1} \beta(1) & e^{-a_2 r_1} \alpha(1) & e^{-a_3 r_1} \beta(1) & e^{-a_4 r_1} \alpha(1) \\ e^{-a_1 r_2} \beta(2) & e^{-a_2 r_2} \alpha(2) & e^{-a_3 r_2} \beta(2) & e^{-a_4 r_2} \alpha(2) \\ e^{-a_1 r_3} \beta(3) & e^{-a_2 r_3} \alpha(3) & e^{-a_3 r_3} \beta(3) & e^{-a_4 r_3} \alpha(3) \\ e^{-a_1 r_4} \beta(4) & e^{-a_2 r_4} \alpha(4) & e^{-a_3 r_4} \beta(4) & e^{-a_4 r_4} \alpha(4) \end{vmatrix} - \begin{vmatrix} e^{-a_1 r_1} \alpha(1) & e^{-a_2 r_1} \beta(1) & e^{-a_3 r_1} \beta(1) & e^{-a_4 r_1} \alpha(1) \\ e^{-a_1 r_2} \alpha(2) & e^{-a_2 r_2} \beta(2) & e^{-a_3 r_2} \beta(2) & e^{-a_4 r_2} \alpha(2) \\ e^{-a_1 r_3} \alpha(3) & e^{-a_2 r_3} \beta(3) & e^{-a_3 r_3} \beta(3) & e^{-a_4 r_3} \alpha(3) \\ e^{-a_1 r_4} \alpha(4) & e^{-a_2 r_4} \beta(4) & e^{-a_3 r_4} \beta(4) & e^{-a_4 r_4} \alpha(4) \end{vmatrix}. \quad (\text{B})$$

Finally, we used the choice (B). The reason is consistency of four-electron energy functional with three-electron energy functional, when the third electron goes to infinity ($a_3 \rightarrow 0$) which happens when the system ionizes, and also symmetry of the trial function (B) in respect to permutations $a_1 \leftrightarrow a_2$ and $a_3 \leftrightarrow a_4$.

Results for Li^- ($Z = 3$), Be ($Z = 4$), and B^+ ($Z = 5$) are given in the following table.

Z	Trial function	a_1	a_2	a_3	a_4	E_{var}	% of exact
3	B	3.28	2.06	0.33	0.14	-7.4317	
4	A	3.65	3.65	0.53	0.53	-14.5065	99.2
4	B	4.35	2.94	0.53+0.17i	0.53-0.17i	-14.5335	99.4
5	B	5.40	3.84	0.81+0.30i	0.81-0.30i	-24.1435	99.4

Ionization energy is calculated as a difference between the minimum of three-electron energy functional and a minimum of four-electron energy functional (trial function (B)).

Variational ionization energy and its derivatives (fig. 18 - 20) are very similar to the singlet state of two-electron atoms that was discussed above. Exponential parameters a_1, a_2, a_3, a_4 are

shown on Fig. 21. Note that parameters a_3, a_4 became complex-conjugate when $Z > 3.25$. However, the wavefunction (B) remains real because it is a symmetric function in respect to interchange $a_3 \leftrightarrow a_4$. Below $Z_1 = 2.9343$, that corresponds to $E = -7.0554$, $a_1 = 1.0944$, $a_2 = 0.6838$, $a_3 = 0.1116$ and $a_4 = 0.0246$, the minimum of the energy functional disappears (turns to a complex stationary point).

Ground state of five-electron atoms

We construct a trial function in the form

$$\begin{aligned} & \left| \begin{array}{ccccc} e^{-a_1 r_1} \alpha(1) & e^{-a_2 r_1} \beta(1) & e^{-a_3 r_1} \alpha(1) & e^{-a_4 r_1} \beta(1) & Y_{1,0}(\theta_1, \phi_1) e^{-a_5 r_1} \alpha(1) \\ e^{-a_1 r_2} \alpha(2) & e^{-a_2 r_2} \beta(2) & e^{-a_3 r_2} \alpha(2) & e^{-a_4 r_2} \beta(2) & Y_{1,0}(\theta_2, \phi_2) e^{-a_5 r_2} \alpha(2) \\ e^{-a_1 r_3} \alpha(3) & e^{-a_2 r_3} \beta(3) & e^{-a_3 r_3} \alpha(3) & e^{-a_4 r_3} \beta(3) & Y_{1,0}(\theta_3, \phi_3) e^{-a_5 r_3} \alpha(3) \\ e^{-a_1 r_4} \alpha(4) & e^{-a_2 r_4} \beta(4) & e^{-a_3 r_4} \alpha(4) & e^{-a_4 r_4} \beta(4) & Y_{1,0}(\theta_4, \phi_4) e^{-a_5 r_4} \alpha(4) \\ e^{-a_1 r_5} \alpha(5) & e^{-a_2 r_5} \beta(5) & e^{-a_3 r_5} \alpha(5) & e^{-a_4 r_5} \beta(5) & Y_{1,0}(\theta_5, \phi_5) e^{-a_5 r_5} \alpha(5) \end{array} \right| \\ & - |\beta\alpha\alpha\beta\alpha| + |\beta\alpha\beta\alpha\alpha| - |\alpha\beta\beta\alpha\alpha|, \end{aligned}$$

where $|\beta\alpha\alpha\beta\alpha|$ etc. denote determinants with some α and β interchanged.

Results for B ($Z = 5$) and C^+ ($Z = 6$) are given in the following table.

Z	a_1	a_2	a_3	a_4	a_5	E_{var}	% of exact
5	5.42	3.85	0.72+...i	0.72-...i	1.24	-24.4512	99.5
6	6.45	4.75	0.99+...i	0.99-...i	1.79	-37.1528	99.5

Ionization energy is calculated as a difference between the minimum of four-electron energy functional and a minimum of five-electron energy functional.

Variational ionization energy and its derivatives are shown on Fig. 22 - 24. Exponential parameters a_1, a_2, a_3, a_4, a_5 are shown on Fig. 25. Ionization energy is zero at $Z_0 \approx 4.1$ that is larger than exact critical charge $Z_c \leq 4$. Actually, there is a secondary minimum (not shown on Fig. 22 - 24) that becomes a global minimum at $Z < 4.1$ and goes to zero at $Z \rightarrow 4$ (cf. with similar Fig. 4.1 and 11).

Ground state of six-electron atoms

We construct a trial function in the form

$$\begin{vmatrix}
e^{-a_1 r_1} \alpha(1) & e^{-a_2 r_1} \beta(1) & e^{-a_3 r_1} \alpha(1) & e^{-a_4 r_1} \beta(1) & Y_{1,0}(\theta_1, \phi_1) e^{-a_5 r_1} \alpha(1) & Y_{1,1}(\theta_1, \phi_1) e^{-a_5 r_1} \alpha(1) \\
e^{-a_1 r_2} \alpha(2) & e^{-a_2 r_2} \beta(2) & e^{-a_3 r_2} \alpha(2) & e^{-a_4 r_2} \beta(2) & Y_{1,0}(\theta_2, \phi_2) e^{-a_5 r_2} \alpha(2) & Y_{1,1}(\theta_2, \phi_2) e^{-a_5 r_2} \alpha(2) \\
e^{-a_1 r_3} \alpha(3) & e^{-a_2 r_3} \beta(3) & e^{-a_3 r_3} \alpha(3) & e^{-a_4 r_3} \beta(3) & Y_{1,0}(\theta_3, \phi_3) e^{-a_5 r_3} \alpha(3) & Y_{1,1}(\theta_3, \phi_3) e^{-a_5 r_3} \alpha(3) \\
e^{-a_1 r_4} \alpha(4) & e^{-a_2 r_4} \beta(4) & e^{-a_3 r_4} \alpha(4) & e^{-a_4 r_4} \beta(4) & Y_{1,0}(\theta_4, \phi_4) e^{-a_5 r_4} \alpha(4) & Y_{1,1}(\theta_4, \phi_4) e^{-a_5 r_4} \alpha(4) \\
e^{-a_1 r_5} \alpha(5) & e^{-a_2 r_5} \beta(5) & e^{-a_3 r_5} \alpha(5) & e^{-a_4 r_5} \beta(5) & Y_{1,0}(\theta_5, \phi_5) e^{-a_5 r_5} \alpha(5) & Y_{1,1}(\theta_5, \phi_5) e^{-a_5 r_5} \alpha(5) \\
e^{-a_1 r_6} \alpha(6) & e^{-a_2 r_6} \beta(6) & e^{-a_3 r_6} \alpha(6) & e^{-a_4 r_6} \beta(6) & Y_{1,0}(\theta_6, \phi_6) e^{-a_5 r_6} \alpha(6) & Y_{1,1}(\theta_6, \phi_6) e^{-a_5 r_6} \alpha(6)
\end{vmatrix}$$

$$-|\beta\alpha\alpha\beta\alpha\alpha| + |\beta\alpha\beta\alpha\alpha\alpha| - |\alpha\beta\beta\alpha\alpha\alpha|,$$

where $|\beta\alpha\alpha\beta\alpha\alpha|$ etc. denote determinants with some α and β interchanged.

Results for C ($Z = 6$) and N^+ ($Z = 7$) are given in the following table.

Z	a_1	a_2	a_3	a_4	a_5	a_6	E_{var}	% of exact
6	6.47	4.76	0.90+...i	0.90-...i	1.59	1.59	-37.5493	99.6
7+...i	...-...i	99...

Ionization energy is calculated as a difference between the minimum of five-electron energy functional and a minimum of six-electron energy functional.

Variational ionization energy and its derivatives are shown on Fig. 26 - 28. Exponential parameters $a_1, a_2, a_3, a_4, a_5, a_6$ are shown on Fig. 29. Ionization energy is zero at $Z_0 \approx 5.1$ that is larger than exact critical charge $Z_c \leq 5$. Actually, there is a secondary minimum (not shown on Fig. 26 - 28) that becomes a global minimum at $Z < 5.1$ and goes to zero at $Z \rightarrow 5$ (cf. with similar Fig. 4.1, 11, and 22).