I. EFFECTIVE POTENTIAL FOR TWO-ELECTRON ATOMS

After re-writing Schrödinger equation in internal coordinates r_1, r_1, r_{12}, the potential takes the form

$$\widetilde{U} = \frac{1}{2}\left(\frac{1}{\widetilde{h}_1^2} + \frac{1}{\widetilde{h}_2^2}\right) + \widetilde{V}, \tag{1}$$

where

$$\widetilde{V} = -\frac{Z}{\widetilde{r}_1} - \frac{Z}{\widetilde{r}_2} + \frac{1}{\widetilde{r}_{12}}, \quad \widetilde{h}_1 = \widetilde{r}_1 \sin\theta_{12}, \quad \widetilde{h}_2 = \widetilde{r}_2 \sin\theta_{12}. \tag{2}$$

For large D, the energy tends to

$$\widetilde{E}_0 = \widetilde{U}\left(\widetilde{r}_1^{(0)}, \widetilde{r}_2^{(0)}, \widetilde{r}_{12}^{(0)}\right), \tag{3}$$

where $\left(\widetilde{r}_1^{(0)}, \widetilde{r}_2^{(0)}, \widetilde{r}_{12}^{(0)}\right)$ is the location of the minimum.

For integer values of Z larger than one, a minimum is always symmetric, i.e. $\widetilde{r}_1 = \widetilde{r}_2$. However, in a narrow region inside the interval $(1, 2)$, the minimum could be non-symmetric. A variable

$$\eta = \frac{\widetilde{r}_1 - \widetilde{r}_2}{\widetilde{r}_1 + \widetilde{r}_2}, \quad -1 < \eta < 1, \tag{4}$$

characterize how different is the configuration from the symmetric case when $\eta = 0$.

Let us minimize $\widetilde{U}$ in respect to all variables except η,

$$u(\eta) = \min \widetilde{U}\left(\widetilde{r}_1, \widetilde{r}_2, \widetilde{r}_{12}\right), \tag{5}$$

where the minimum is taken under a constraint $\frac{\widetilde{r}_1 - \widetilde{r}_2}{\widetilde{r}_1 + \widetilde{r}_2} = \eta$.

The plot of the function $u(\eta)$ shows one symmetric minimum at $Z > Z_{\star\star}$, two asymmetric minima at $Z < Z_\star$, and co-existence of the symmetric and two flanking asymmetric minima at $Z_\star < Z < Z_{\star\star}$, see Fig. 1 - 3. See on-line animations at web address `http://www.dimensionality.info/he/veff/index.htm`.

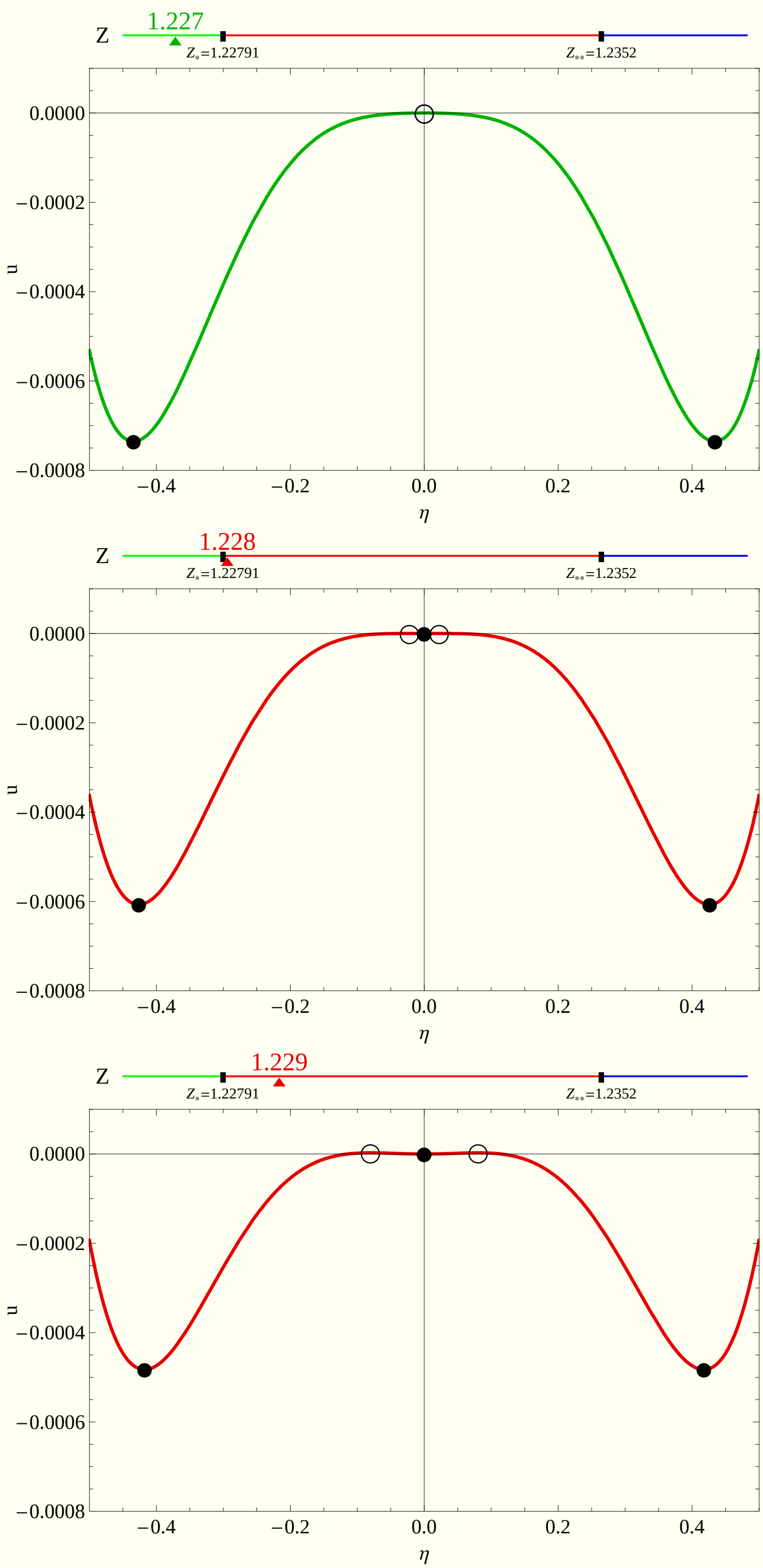

FIG. 1. Shape of the effective potential for two-electron atoms in the direction of soft antisymmetric mode. Minima are marked by filled circles, and maxima (or saddle points in all three coordinates) by empty circles. For the top plot, $Z < Z_\star$, and the minima are non-symmetric. For two lower plots, $Z > Z_\star$, and an extremely shallow symmetric (local) minimum appears.

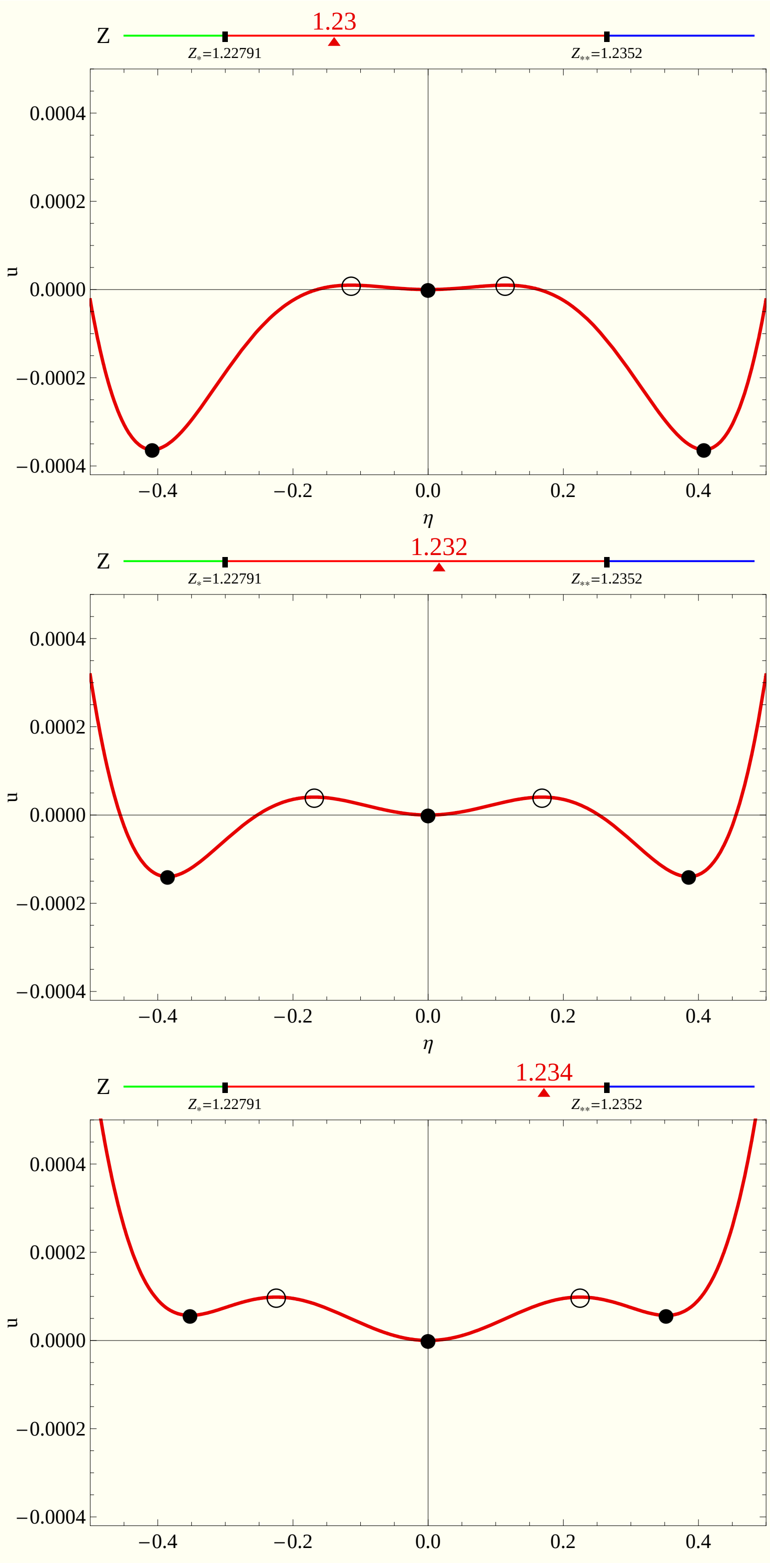

FIG. 2. Shape of the effective potential for two-electron atoms in the direction of soft antisymmetric mode. Minima are marked by filled circles, and maxima by empty circles. For all three plots, $Z_\star < Z < Z_{\star\star}$, when nonsymmetric minima co-exist with the central symmetric minimum. For sufficiently large Z (bottom plot), the symmetric minimum becomes a global minimum.

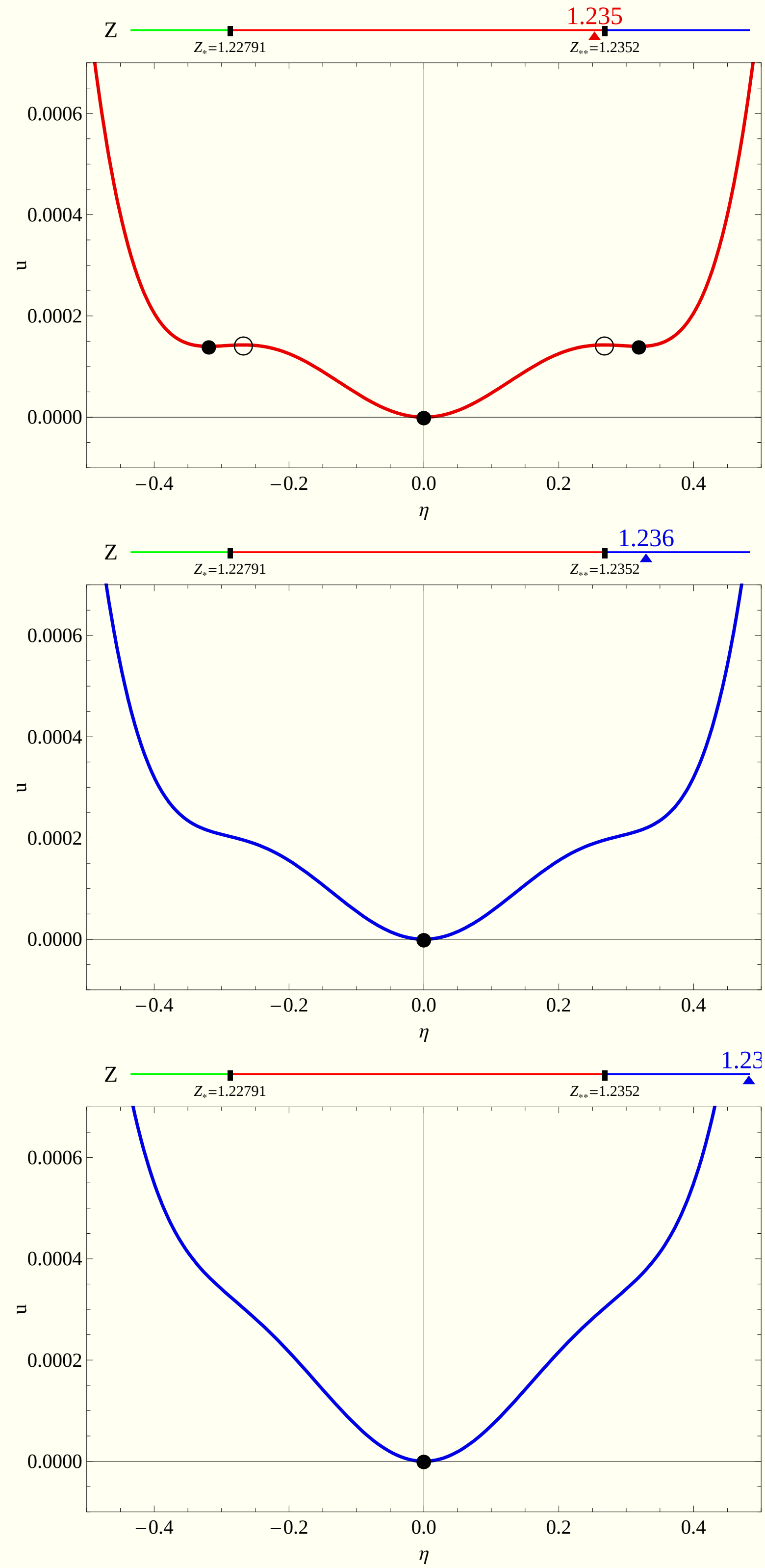

FIG. 3. Shape of the effective potential for two-electron atoms in the direction of soft antisymmetric mode. Minima are marked by filled circles, and maxima by empty circles. For the top plot, $Z_\star < Z < Z_{\star\star}$. For two lower plots, $Z > Z_{\star\star}$, when only a symmetric global minimum is present.