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# Alternative $D$-scaling (linked to Bohr model)

## I. TRADITIONAL VS. ALTERNATIVE $D$-SCALING FOR TWO-ELECTRON ATOMS

A wave function of $D$-dimensional generalization of two-electron atoms depends on $2D$ variables (Cartesian coordinates of two electrons). For S-states (if $L^2\Psi = 0$), the wave function depends only on three distances, $r_1$, $r_2$, $r_{12}$. Here, it is convenient to choose another variables, $(r_1, r_2, \theta)$ (both sets of variables are called internal coordinates). Then,

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi(r_1, r_2, \theta).$$

Kinetic energy then takes the form, see Eq. (1) in classroom notes [3],

$$\begin{aligned} -\frac{1}{2}\left(\boldsymbol{\nabla}_1^2 + \boldsymbol{\nabla}_2^2\right)\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) &= T_D\psi(r_1, r_2, \theta) \\ & -\frac{1}{2}\left[\frac{1}{r_1^{D-1}}\frac{\partial}{\partial r_1}r_1^{D-1}\frac{\partial}{\partial r_1} + \frac{1}{r_2^{D-1}}\frac{\partial}{\partial r_2}r_2^{D-1}\frac{\partial}{\partial r_2} + \right. \\ & \left. \left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\frac{1}{\sin^{D-2}\theta}\frac{\partial}{\partial\theta}\sin^{D-2}\theta\frac{\partial}{\partial\theta}\right]\psi(r_1, r_2, \theta). \end{aligned} \tag{1}$$

The kinetic energy rewritten in internal coordinates depends on $D$ as a parameter.

We need to solve three-dimensional Schrödinger equation

$$\left(T_3 + V - E_{\text{phys}}\right)\psi_{\text{phys}} = 0, \tag{2}$$

where

$$V = -\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \tag{3}$$

is the potential and $E_{\text{phys}}$ is the energy for physical value of $D = 3$.

### A. Summary of the traditional method of $D$-scaling

Instead of solving equation (2) at $D = 3$ that cannot be done in closed form, we consider its $D$-dimensional generalization

$$(T_D + V - E_D)\,\psi_D = 0. \tag{4}$$

Since at large $D$ the energy $\sim D^{-2}$, we approximate it as

$$E_D \approx \left(\frac{2}{D-1}\right)^2 \widetilde{E}_0. \tag{5}$$

In equation (5), we use factor of two for convenience (to make the expression in parenthesis equal to one at $D = 3$), and use $D - 1$ instead of $D$ in the denominator in order to properly take into account a second order pole at $D = 1$ of the energy as a function of $D$ [5]. The coefficient $\widetilde{E}_0$ is found by solving the equation exactly in the limit of $D \to \infty$. Finally the physical energy is approximated by

$$E_{\rm phys} \approx \widetilde{E}_0. \tag{6}$$

Finding large-$D$ limit could be done in two steps.

First, we eliminate first derivatives by considering a new function

$$P(r_1, r_2, \theta) = (r_1 r_1)^{\frac{D-1}{2}} \sin^{\frac{D-2}{2}}\theta\, \psi(r_1, r_2, \theta) \tag{7}$$

and by re-writing Schrödinger equation as (see Eq. (28) and (30) in [3])

$$\left\{ -\frac{1}{2}\left[\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\frac{\partial^2}{\partial \theta^2}\right] + \frac{1}{2}\left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\left[\frac{(D-2)(D-4)}{4\sin^2\theta} - \frac{1}{4}\right] + V - E_D \right\} P(r_1, r_2, \theta) = 0. \tag{8}$$

Notice that we use the power of $\frac{D-2}{2}$ of $\sin\theta$ in equation (7). If we would use $\frac{D-1}{2}$ instead of $\frac{D-2}{2}$ as we did when we wrote the equation in coordinates

$(r_1,\, r_2,\, r_{12})$, then there will be a remaining term with first order derivative $\frac{1}{2}\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\cot\theta\,\frac{\partial}{\partial\theta}$, see the solution of a last week homework problem [2].

Second, we perform scaling transformation of distance variables, $r_1 = K^2\widetilde{r}_1$, $r_2 = K^2\widetilde{r}_2$, where $K = \frac{1}{2}\sqrt{(D-2)(D-4)}$. Then we arrive to an equation where $1/K$ plays the role of Planck's constant, and where the potential is

$$\widetilde{U}(\widetilde{r}_1,\widetilde{r}_2,\theta) = \frac{1}{2\sin^2\theta}\left(\frac{1}{\widetilde{r}_1^2}+\frac{1}{\widetilde{r}_2^2}\right) + V(\widetilde{r}_1,\widetilde{r}_2,\theta), \tag{9}$$

In the large-$D$ limit, $E \to K^{-2}\widetilde{E}_0$, where $\widetilde{E}_0$ is the minimum of the function $\widetilde{U}$.

As we found earlier, at the minimum, the angle could be determined from the equation [4]

$$\cos\theta = -\frac{1+\sqrt{1+128Z^2}}{64Z^2}. \tag{10}$$

For helium ($Z = 2$), $\cos\theta \approx -\frac{\sqrt{2}}{8Z} \approx -0.09$, and the angle is 95.3°. The energy is expressed through $\xi \equiv -\cos\theta$ as

$$\widetilde{E}_0 = -\frac{(1-\xi)^3}{32\xi^2}, \tag{11}$$

that gives $\widetilde{E}_0 = -2.738$ for helium, which is 5.7% less than ground state helium energy ($-2.9037$).

### B. Alternative $D$-scaling for helium

The idea is to define a modified kinetic energy operator $T'_D$ by replacing $\sin^{D-2}\theta \to \sin\theta$ in the definition of $T_D$ given by equation (1),

$$T'_D = -\frac{1}{2}\left[\frac{1}{r_1^{D-1}}\frac{\partial}{\partial r_1}r_1^{D-1}\frac{\partial}{\partial r_1} + \frac{1}{r_2^{D-1}}\frac{\partial}{\partial r_2}r_2^{D-1}\frac{\partial}{\partial r_2} + \left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right]. \tag{12}$$

Here, we keep the angular part three-dimensional, but allow dependence on $D$ in the radial part. This operator no longer gives the kinetic energy of $D$-dimensional generalization of the problem. The only reason to have the dependence on $D$ in the radial part is to allow exact solution at $D \to \infty$, while giving physical (three-dimensional) kinetic energy at $D = 3$.

We are going to solve the equation

$$(T'_D + V - E'_D)\,\psi'_D = 0. \tag{13}$$

in the large $D$ limit and again approximate the energy as

$$E'_D \approx \left(\frac{2}{D-1}\right)^2 \widetilde{E}'_0. \tag{14}$$

Finally, we have

$$E_{\text{phys}} \approx \widetilde{E}'_0. \tag{15}$$

Since $T'_D$ is in some sense closer to $T_{\text{phys}}$ than $T_D$ (because it has unchanged angular part), one could expect that the approximation (15) may be more accurate than (6).

Again, we find large-$D$ limit in two steps.

First, we eliminate first derivatives by considering a new function

$$P'(r_1, r_2, \theta) = (r_1 r_1)^{\frac{D-1}{2}}\,\psi(r_1, r_2, \theta). \tag{16}$$

Notice that in contrast to equation (7), we *do not* multiply the function by $\sin^{\frac{D-2}{2}}\theta$. Then, we re-write Schrödinger equation as

$$\begin{aligned}\Bigg\{-\frac{1}{2}\left[\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right] + \frac{(D-1)(D-3)}{8}\left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)& \\ + V(r_1, r_2, \theta) - E'_D\Bigg\}P'(r_1, r_2, \theta) = 0.&\end{aligned} \tag{17}$$

Second, we perform scaling transformation of distance variables, $r_1 = K'^2\widetilde{r}_1$, $r_2 = K'^2\widetilde{r}_2$, where $K' = \frac{1}{2}\sqrt{(D-1)(D-3)}$. Then, we arrive to an equation

$$\Big\{ -\frac{1}{2K'^4}\left[\frac{\partial^2}{\partial\widetilde{r}_1^2} + \frac{\partial^2}{\partial\widetilde{r}_2^2} + \left(\frac{1}{\widetilde{r}_1^2} + \frac{1}{\widetilde{r}_2^2}\right)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right] + \frac{K'^2}{2K'^4}\left(\frac{1}{\widetilde{r}_1^2} + \frac{1}{\widetilde{r}_2^2}\right) + \frac{1}{K'^2}V(\widetilde{r}_1,\widetilde{r}_2,\theta) - \frac{1}{K'^2}\widetilde{E}'_D\Big\}\widetilde{P}'(\widetilde{r}_1,\widetilde{r}_2,\theta) = 0, \quad (18)$$

where $\widetilde{E}'_D \equiv K'^2 E'_D$. After multiplying equation (18) by $K'^2$, we obtain

$$\Big\{ -\frac{1}{2K'^2}\left[\frac{\partial^2}{\partial\widetilde{r}_1^2} + \frac{\partial^2}{\partial\widetilde{r}_2^2} + \left(\frac{1}{\widetilde{r}_1^2} + \frac{1}{\widetilde{r}_2^2}\right)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right] + \frac{1}{2}\left(\frac{1}{\widetilde{r}_1^2} + \frac{1}{\widetilde{r}_2^2}\right) + V(\widetilde{r}_1,\widetilde{r}_2,\theta) - \widetilde{E}'_D\Big\}\widetilde{P}'(\widetilde{r}_1,\widetilde{r}_2,\theta) = 0. \quad (19)$$

In the limit of $K' \to \infty$, the energy $\widetilde{E}' \to \widetilde{E}'_0$, where $\widetilde{E}'_0$ is the minimum of the function

$$\widetilde{U}'(\widetilde{r}_1,\widetilde{r}_2,\theta) = \frac{1}{2}\left(\frac{1}{\widetilde{r}_1^2} + \frac{1}{\widetilde{r}_2^2}\right) - \frac{Z}{\widetilde{r}_1} - \frac{Z}{\widetilde{r}_2} + \frac{1}{\sqrt{\widetilde{r}_1^2 + \widetilde{r}_2^2 - 2\widetilde{r}_1\widetilde{r}_2\cos\theta}}, \quad (20)$$

where we gave explicit form of $V(\widetilde{r}_1,\widetilde{r}_2,\theta)$.

Finding the minimum of the function $\widetilde{U}'(\widetilde{r}_1,\widetilde{r}_2,\theta)$ is much simpler task than finding the minimum of $\widetilde{U}(\widetilde{r}_1,\widetilde{r}_2,\theta)$ in case of traditional $D$-scaling. For given values of $\widetilde{r}_1$ and $\widetilde{r}_2$, the expression (20) reaches its minimum if the denominator of the last term is maximal, i.e. $\cos\theta = -1$, or $\theta = 180^\circ$. It considerably differs from traditional $D$-scaling, when the angle is close to $90^\circ$. The angle of $180^\circ$ allows to minimize the repulsive potential between electrons, while the angle of $90^\circ$ allows to minimize the term $\frac{1}{\sin^2\theta}$ which is absent in the alternative approach.

Assuming again that $\widetilde{r}_1 = \widetilde{r}_2 \equiv \widetilde{r}$ at the minimum, the problem reduces to finding a minimum of the function of one variable,

$$\widetilde{u}(\widetilde{r}) = \widetilde{U}'(\widetilde{r}, \widetilde{r}, \pi) = \frac{1}{\widetilde{r}^2} - \frac{2Z}{\widetilde{r}} + \frac{1}{2\widetilde{r}}. \tag{21}$$

The equation $\widetilde{u}' = 0$ give the equation for the minimum,

$$-\frac{2}{\widetilde{r}^3} + \frac{2Z - 1/2}{\widetilde{r}^2} = 0, \tag{22}$$

that has a solution

$$\widetilde{r} = \frac{1}{Z - 1/4}. \tag{23}$$

The minimum of the function is

$$\widetilde{E}_0' = \frac{1}{(Z - 1/4)^2}. \tag{24}$$

For helium ($Z = 2$), $\widetilde{E}_0' = 49/16 = -3.0625$ which is 5.5% larger than the ground state energy ($-2.9037$).

### C. Comparison of two approaches

In Table I C, results of two different approaches are compared for helium atom.

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[1] *Bohr Model of Helium*, Article in Wikipedia, on-line encyclopedia, `http://cac07science.wikispaces.com/Bohr+Model+of+Helium`.

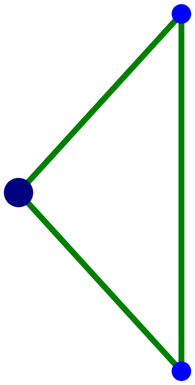
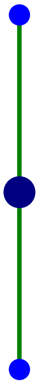
[2] *Change of variables $r_1 = R_1$, $r_2 = R_2$, $r_{12} \to \theta$ (Correct statement of the problem)*, Classroom homework notes (Math 689 Spring 2009 4/23/2009).

[3] *Schrödinger equation in coordinates* $(r_1, r_2, \theta)$ *for two-electron atoms*, Classroom notes, `http://www.dimensionality.info/notes/twoelham.pdf`.

[4] *Two-electron atoms*, Classroom notes, `http://www.dimensionality.info/notes/twoel.pdf`.

[5] D. R. Herschbach, *Dimensional interpolation for two-electron atoms*, J. Chem. Phys. **84** (1986), 838–851.

TABLE I. Comparison of two models of helium atom, based on traditional and alternative $D$-scaling. The second model is reminiscent of pre-quantum Bohr-like model of helium [1].

| | Traditional $D$-scaling | Alternative $D$-scaling |
|---|---|---|
| Configuration |  |  |
| $\widetilde{r}_1 = \widetilde{r}_2$ | 0.607 | 0.571 |
| $\widetilde{r}_{12}$ | 0.897 | 1.143 |
| $\theta$ | 95.3° | 180° |
| Energy (% error) | -2.738 (-5.7%) | -3.0625 (+5.5%) |