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Schrödinger equation in coordinates (r_1, r_2, θ) for two-electron atoms

I. LAPLACIAN IN COORDINATES (r_1, r_2, θ)

Let us prove that if a function depends only on three variables,

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

then

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

Firstly, we calculate $\boldsymbol{\nabla}_1^2\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2)$, where $\boldsymbol{\nabla}_1^2 = \sum_{i=1}^D \frac{\partial^2}{\partial r_{1i}^2}$. First derivatives are

$$\frac{\partial}{\partial r_{1i}}\psi(r_1, r_2, \theta) = \left(\frac{\partial r_1}{\partial r_{1i}}\frac{\partial}{\partial r_1} + \frac{\partial\theta}{\partial r_{1i}}\frac{\partial}{\partial\theta}\right)\psi(r_1, r_2, \theta). \quad (2)$$

Second derivatives are

$$\frac{\partial}{\partial r_{1i}^2}\psi(r_1, r_2, \theta) = \left[\left(\frac{\partial r_1}{\partial r_{1i}}\right)^2\frac{\partial^2}{\partial r_1^2} + 2\frac{\partial r_1}{\partial r_{1i}}\frac{\partial\theta}{\partial r_{1i}}\frac{\partial^2}{\partial r_1\partial\theta} + \left(\frac{\partial\theta}{\partial r_{1i}}\right)^2\frac{\partial^2}{\partial\theta^2} + \frac{\partial^2 r_1}{\partial r_{1i}^2}\frac{\partial}{\partial r_1} + \frac{\partial^2\theta}{\partial r_{1i}^2}\frac{\partial}{\partial\theta}\right]\psi(r_1, r_2, \theta). \quad (3)$$

Derivatives of r_1 are

$$\begin{aligned}\frac{\partial r_1}{\partial r_{1i}} &= \frac{r_{1i}}{r_1},\\ \frac{\partial^2 r_1}{\partial r_{1i}^2} &= \frac{1}{r_1} - \frac{r_{1i}^2}{r_1^3}.\end{aligned} \quad (4)$$

After summation over i, we obtain

$$\sum_{i=1}^{D}\left(\frac{\partial r_1}{\partial r_{1i}}\right)^2=\sum_{i=1}^{D}\frac{r_{1i}^2}{r_1^2}=1, \tag{5}$$

$$\sum_{i=1}^{D}\frac{\partial^2 r_1}{\partial r_{1i}^2}=\sum_{i=1}^{D}\left(\frac{1}{r_1}-\frac{r_{1i}^2}{r_1^3}\right)=\frac{D-1}{r_1}. \tag{6}$$

Combining equations (5) and (6), we obtain

$$\sum_{i=1}^{D}\left[\left(\frac{\partial r_1}{\partial r_{1i}}\right)^2\frac{\partial^2}{\partial r_1^2}+\frac{\partial^2 r_1}{\partial r_{1i}^2}\frac{\partial}{\partial r_1}\right]=\frac{1}{r_1^{D-1}}\frac{\partial}{\partial r_1}r_1^{D-1}\frac{\partial}{\partial r_1}, \tag{7}$$

which gives the first term in square brackets in equation (1).

In order to find $\partial\theta/\partial r_{1i}$, we use an identity

$$(\boldsymbol{r}_1,\boldsymbol{r}_2)=r_1r_2\cos\theta. \tag{8}$$

Differentiating equation (8) once, we obtain

$$r_{2i}=\frac{r_{1i}}{r_1}r_2\cos\theta-r_1r_2\sin\theta\frac{\partial\theta}{\partial r_{1i}}. \tag{9}$$

Solving equation (9) in respect to $\frac{\partial\theta}{\partial r_{1i}}$, we obtain

$$\frac{\partial\theta}{\partial r_{1i}}=\frac{r_{1i}r_2\cos\theta-r_{2i}r_1}{r_1^2r_2\sin\theta}. \tag{10}$$

Using equations (4) and (10), we calculate

$$\sum_{i=1}^{D}\frac{\partial r_1}{\partial r_{1i}}\frac{\partial\theta}{\partial r_{1i}}=\sum_{i=1}^{D}\frac{r_{1i}^2r_2\cos\theta-r_{1i}r_{2i}r_1}{r_1^2r_2\sin\theta}=\frac{r_1^2r_2\cos\theta-r_1r_2\cos\theta r_1}{r_1^2r_2\sin\theta}=0, \tag{11}$$

and

$$\sum_{i=1}^{D}\left(\frac{\partial\theta}{\partial r_{1i}}\right)^2=\sum_{i=1}^{D}\frac{r_{1i}^2r_2^2\cos^2\theta-2r_{1i}r_{2i}r_1r_2\cos\theta+r_{2i}^2r_1^2}{r_1^4r_2^2\sin^2\theta}=$$

$$\frac{r_1^2r_2^2\cos^2\theta-2r_1^2r_2^2\cos^2\theta+r_1^2r_2^2}{r_1^4r_2^2\sin^2\theta}=\frac{r_1^2r_2^2\sin^2\theta}{r_1^4r_2^2\sin^2\theta}=\frac{1}{r_1^2}. \tag{12}$$

Differentiating equation (8) twice, we obtain

$$0 = \frac{\partial^2 r_1}{\partial r_{1i}^2} r_2 \cos\theta - 2\frac{\partial r_1}{\partial r_{1i}} r_2 \sin\theta \frac{\partial \theta}{\partial r_{1i}} - r_1 r_2 \cos\theta \left(\frac{\partial \theta}{\partial r_{1i}}\right)^2 - r_1 r_2 \sin\theta \frac{\partial^2 \theta}{\partial r_{1i}^2}. \quad (13)$$

After summation over i and with use of (6), (11), and (12) we obtain

$$0 = \frac{D-1}{r_1} r_2 \cos\theta - r_1 r_2 \cos\theta \frac{1}{r_1^2} - r_1 r_2 \sin\theta \sum_{i=1}^{D} \frac{\partial^2 \theta}{\partial r_{1i}^2}, \quad (14)$$

from which we obtain

$$\sum_{i=1}^{D} \frac{\partial^2 \theta}{\partial r_{1i}^2} = \frac{D-2}{r_1^2} \frac{\cos\theta}{\sin\theta}. \quad (15)$$

Combining equations (12) and (15), we obtain

$$\sum_{i=1}^{D} \left[\left(\frac{\partial \theta}{\partial r_{1i}}\right)^2 \frac{\partial^2}{\partial \theta^2} + \frac{\partial^2 \theta}{\partial r_{1i}^2} \frac{\partial}{\partial \theta} \right] = \frac{1}{r_1^2 \sin^{D-2}\theta} \frac{\partial}{\partial \theta} \sin^{D-2}\theta \frac{\partial}{\partial \theta}, \quad (16)$$

which gives a part of the third term in square brackets in equation (1).

Using equation (3) and combining (7), (11), (16) we find

$$\boldsymbol{\nabla}_1^2 \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{r_1^{D-1}} \frac{\partial}{\partial r_1} r_1^{D-1} \frac{\partial}{\partial r_1} + \frac{1}{r_1^2 \sin^{D-2}\theta} \frac{\partial}{\partial \theta} \sin^{D-2}\theta \frac{\partial}{\partial \theta}. \quad (17)$$

Adding a similar expression for $\boldsymbol{\nabla}_2^2 \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2)$, we finally prove (1).

II. ELIMINATION OF FIRST-ORDER DERIVATIVES

Because the Laplacian could be expressed as (1), the kinetic energy operator has the form

$$T = -\frac{1}{2}(\boldsymbol{\nabla}_1^2 + \boldsymbol{\nabla}_2^2) = -\frac{1}{2}\left[\frac{1}{r_1^{D-1}} \frac{\partial}{\partial r_1} r_1^{D-1} \frac{\partial}{\partial r_1} + \frac{1}{r_2^{D-1}} \frac{\partial}{\partial r_2} r_2^{D-1} \frac{\partial}{\partial r_2} + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right) \frac{1}{\sin^{D-2}\theta} \frac{\partial}{\partial \theta} \sin^{D-2}\theta \frac{\partial}{\partial \theta} \right], \quad (18)$$

or alternatively

$$T = -\frac{1}{2}\frac{\partial^2}{\partial r_1^2} - \frac{D-1}{2}\frac{\partial}{\partial r_1} - \frac{1}{2}\frac{\partial^2}{\partial r_2^2} - \frac{D-1}{2}\frac{\partial}{\partial r_2} - \frac{1}{2}\left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\frac{\partial^2}{\partial \theta^2} - \frac{D-2}{2}\,\frac{\cos\theta}{\sin\theta}\,\frac{\partial}{\partial\theta}. \quad (19)$$

Let us define

$$\Phi(r_1, r_2, \theta) \equiv J^{1/2}(r_1, r_2, \theta)\psi(r_1, r_2, \theta), \quad (20)$$

where J is some positive function. Then, Schrödinger equation for the function ψ,

$$\left[T + V - E\right] J^{-1/2}(r_1, r_2, \theta)\Phi(r_1, r_2, \theta) = 0, \quad (21)$$

after multiplying by $J^{1/2}$ could be rewritten as an equation for the function Φ,

$$\left[\bar{T} + V - E\right] \Phi(r_1, r_2, \theta) = 0, \quad (22)$$

where

$$\bar{T} = J^{1/2}\,T\,J^{-1/2}. \quad (23)$$

Let us choose

$$J(r_1, r_2, \theta) = (r_1 r_2)^{D-1}\sin^{D-2}\theta. \quad (24)$$

Then, using equation (18), we obtain

$$\bar{T} = -\frac{1}{2}\Bigg[r_1^{-\frac{D-1}{2}}\frac{\partial}{\partial r_1}r_1^{D-1}\frac{\partial}{\partial r_1}r_1^{-\frac{D-1}{2}} + r_2^{-\frac{D-1}{2}}\frac{\partial}{\partial r_2}r_2^{D-1}\frac{\partial}{\partial r_2}r_2^{-\frac{D-1}{2}} + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\sin^{-\frac{D-2}{2}}\theta\frac{\partial}{\partial\theta}\sin^{D-2}\theta\frac{\partial}{\partial\theta}\sin^{-\frac{D-2}{2}}\theta\Bigg]. \quad (25)$$

After taking derivatives of products, it is evaluated as

$$\bar{T} = -\frac{1}{2}\left\{ \frac{\partial^2}{\partial r_1^2} - \frac{(D-1)(D-3)}{4r_1^2} + \frac{\partial^2}{\partial r_2^2} - \frac{(D-1)(D-3)}{4r_2^2} \right. \\ \left. + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\frac{\partial^2}{\partial\theta^2} + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\left[-\frac{(D-2)(D-4)}{4}\frac{\cos^2\theta}{\sin^2\theta} + \frac{D-2}{2}\right]\right\}. \tag{26}$$

This expression has no first-order derivatives. Let us rewrite it as

$$\bar{T} = \bar{T}_0 + V_{\mathrm{c}}, \tag{27}$$

where

$$\bar{T}_0 = -\frac{1}{2}\left[\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\frac{\partial^2}{\partial\theta^2}\right], \tag{28}$$

and

$$V_{\mathrm{c}} = -\frac{1}{2}\left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\left[-\frac{(D-1)(D-3)}{4} - \frac{(D-2)(D-4)}{4}\frac{\cos^2\theta}{\sin^2\theta} + \frac{D-2}{2}\right]. \tag{29}$$

The potential V_{c} could be further simplified as

$$V_{\mathrm{c}} = \frac{1}{2}\left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\left[\frac{(D-2)(D-4)}{4\sin^2\theta} - \frac{1}{4}\right]. \tag{30}$$

Finally, we have the same expression for kinetic energy as in equations (18a), (18b) of Herschbach's paper [1].

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