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Two-electron atoms

We considered several examples of atoms and molecules,

	potential
H	$-1/r$
H_2^+	$-1/r_a - 1/r_b + 1/R$

Here, we consider two-electron atom, helium, and its isoelectronic ions

	Z	
negative ion	1	H^-
neutral atom	2	He
positive ions	3	Li^+
	4	Be^{++}
	...	

(1)

with the potential

$$V = -\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}. \tag{2}$$

Firstly, let us consider a larger class of three-body Coulomb systems,

$$V(\boldsymbol{r}_0, \boldsymbol{r}_1, \boldsymbol{r}_2) = -\frac{Z_0 Z_1}{r_{01}} - \frac{Z_0 Z_2}{r_{02}} + \frac{Z_1 Z_2}{r_{12}}. \tag{3}$$

Hydrogen molecular ion H_2^+ and the two-electron isoelectronic series (1) both belong to this class,

	Z_0	Z_1	Z_2	m_0	m_1	m_2
H_2^+	-1	1	1	1	∞	∞
two-electron atom/ions	Z	-1	-1	∞	1	1

If at least one of two-particle interactions is attractive, e.g. $Z_0 Z_1 < 0$, then the potential V is not bound from below (since in this case r_{13} could be as small as possible). Therefore, V has no absolute minimum. Local minima of V do not exist, because V is a harmonic function, i.e. $\boldsymbol{\nabla}_0^2 + \boldsymbol{\nabla}_1^2 + \boldsymbol{\nabla}_2^2 = 0$ (there exist appropriate theorems).

We generalize the problem to D dimensions by endowing each vector with D components,

$$\boldsymbol{r}_\alpha \equiv \left(r_\alpha^{(1)}, r_\alpha^{(2)}, \ldots, r_\alpha^{(D)} \right), \quad \alpha = 0, 1, 2 \tag{4}$$

and considering generalized Laplacians

$$\boldsymbol{\nabla}_\alpha^2 \equiv \sum_{i=1}^{D} \frac{\partial^2}{\partial {r_\alpha^{(i)}}^2}, \quad \alpha = 0, 1, 2. \tag{5}$$

For the states with zero total angular momentum, the wave function Ψ depends only on three variables r_{01}, r_{02}, r_{12} which are internal distances,

$$\Psi(\boldsymbol{r}_0, \boldsymbol{r}_1, \boldsymbol{r}_2) = \psi(r_{01}, r_{02}, r_{12}). \tag{6}$$

As it was shown for a more general case of N particles, Schrödinger equation reads

$$[T_0 + U - E]\, P = 0. \tag{7}$$

In equation (7), P is defined as

$$P(r_{01}, r_{02}, r_{12}) = S^{\frac{D-1}{2}} \psi(r_{01}, r_{02}, r_{12}), \tag{8}$$

where

$$S(r_{01}, r_{02}, r_{12}) = \frac{1}{4} \left(2r_{01}^2 r_{02}^2 + 2r_{01}^2 r_{12}^2 + 2r_{02}^2 r_{12}^2 - r_{01}^4 - r_{02}^4 - r_{12}^4 \right)^{1/2} \tag{9}$$

is the area of a triangle formed by three particles. "Effective" potential is

$$U(r_{01}, r_{02}, r_{12}) = V(r_{01}, r_{02}, r_{12}) + \hbar^2 K^2 \frac{r_{02}^2/m_1 + r_{01}^2/m_2 + r_{12}^2/m_3}{8S^2(r_{01}, r_{02}, r_{12})}. \quad (10)$$

where K is defined as

$$K = \frac{1}{2}\sqrt{(D-1)(D-5)}, \quad (11)$$

and

$$T_0 = -\frac{\hbar^2}{2}\left[\left(\frac{1}{m_0} + \frac{1}{m_1}\right)\frac{\partial^2}{\partial r_{01}^2} + \left(\frac{1}{m_0} + \frac{1}{m_2}\right)\frac{\partial^2}{\partial r_{02}^2} + \left(\frac{1}{m_1} + \frac{1}{m_2}\right)\frac{\partial^2}{\partial r_{12}^2}\right.$$
$$+ \frac{1}{m_0}\frac{r_{01}^2 + r_{02}^2 - r_{12}^2}{r_{01}r_{02}}\frac{\partial^2}{\partial r_{01}\partial r_{02}} + \frac{1}{m_1}\frac{r_{01}^2 + r_{12}^2 - r_{02}^2}{r_{01}r_{12}}\frac{\partial^2}{\partial r_{01}\partial r_{12}}$$
$$\left. + \frac{1}{m_2}\frac{r_{02}^2 + r_{12}^2 - r_{01}^2}{r_{02}r_{12}}\frac{\partial^2}{\partial r_{02}\partial r_{12}}\right]. \quad (12)$$

Henceforth, let us consider the case of two-electron atom. We use approximation of infinitely heavy nucleus, $m_0 = \infty$, and use atomic units where $m_1 = m_2 = 1$, $\hbar = 1$, $Z_1 = Z_2 = -1$. We use notations $r_1 \equiv r_{01}$, $r_2 \equiv r_{02}$. Then,

$$T_0 = -\frac{\hbar^2}{2}\left[\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + 2\frac{\partial^2}{\partial r_{12}^2}\right.$$
$$\left. + \frac{r_1^2 + r_{12}^2 - r_2^2}{r_1 r_{12}}\frac{\partial^2}{\partial r_1 \partial r_{12}} + \frac{r_2^2 + r_{12}^2 - r_1^2}{r_2 r_{12}}\frac{\partial^2}{\partial r_2 \partial r_{12}}\right] \quad (13)$$

and

$$U = V + \frac{2K^2(r_1^2 + r_2^2)}{2r_1^2 r_2^2 + 2r_1^2 r_{12}^2 + 2r_2^2 r_{12}^2 - r_1^4 - r_2^4 - r_{12}^4}, \quad (14)$$

or alternatively,

$$U = V + \frac{K^2}{2}\left(\frac{1}{h_1^2} + \frac{1}{h_2^2}\right), \quad (15)$$

where

$$h_1 = r_1 \sin\theta_{12}, \quad h_2 = r_2 \sin\theta_{12}, \quad \cos\theta_{12} = \frac{r_1^2 + r_2^2 - r_{12}^2}{2r_1 r_2}. \quad (16)$$

The effective potential U unlike V is bounded from below, since

$$U = V + \frac{K^2}{2}\left(\frac{1}{h_1^2} + \frac{1}{h_2^2}\right) \geq V + \frac{K^2}{2}\left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)$$
$$> -\frac{Z}{r_1} + \frac{K^2}{2r_1^2} - \frac{Z}{r_2} + \frac{K^2}{2r_2^2} \geq -\frac{Z^2}{2K^2} - \frac{Z^2}{2K^2} = -\frac{Z^2}{K^2}, \quad (17)$$

with the lower bound $-\frac{Z^2}{K^2}$ equal to the energy of two hydrogen-like atoms in the limit of large D.

Often, coordinates (R_1, R_2, θ) are used instead of internal distances (r_1, r_2, r_{12}), where

$$R_1 = r_1, \quad R_2 = r_2, \quad \theta = \theta_{12}. \quad (18)$$

It has advantage of absence of mixed derivatives in the kinetic energy,

$$\overline{T}_0 = -\frac{1}{2}\left[\frac{\partial^2}{\partial R_1^2} + \frac{\partial^2}{\partial R_2^2} + \left(\frac{1}{R_1^2} + \frac{1}{R_1^2}\right)\frac{\partial^2}{\partial \theta^2}\right] \quad (19)$$

To find the limit at $D \to \infty$, we make scaling transformation

$$\begin{aligned} r_1 &= K^2 \widetilde{r}_1, \\ r_2 &= K^2 \widetilde{r}_2, \\ r_{12} &= K^2 \widetilde{r}_{12}, \end{aligned} \quad (20)$$

where for large D

$$K \sim \frac{D-3}{2} + o(1). \quad (21)$$

Then, we arrive to Schrödinger equation with an effective potential

$$\widetilde{U} = \frac{1}{2}\left(\frac{1}{\widetilde{h}_1^2} + \frac{1}{\widetilde{h}_2^2}\right) + \widetilde{V}, \quad (22)$$

where

$$\begin{aligned} \widetilde{V} &= -\frac{Z}{\widetilde{r}_1} - \frac{Z}{\widetilde{r}_2} + \frac{1}{\widetilde{r}_{12}}, \\ \widetilde{h}_1 &= \widetilde{r}_1 \sin\theta_{12}, \\ \widetilde{h}_2 &= \widetilde{r}_2 \sin\theta_{12}, \end{aligned} \quad (23)$$

in which $1/K$ plays the role of Planck's constant, and the energy is $\widetilde{E} = K^2 E$. For large K, the wave function concentrates around the minimum of $\widetilde{U}$, the energy tends to

$$\widetilde{E}_0 = \widetilde{U}\left(\widetilde{r}_1^{(0)}, \widetilde{r}_2^{(0)}, \widetilde{r}_{12}^{(0)}\right), \tag{24}$$

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

Finding the minimum in analytic form could be done in many ways. Minimization of the function (24) requires purely algebraic manipulations with polynomials. Here, we adopt a different approach which was originally used by several authors [2, 6] that is based on trigonometric equalities. Let us rewrite the effective potential as a function of variables $(\widetilde{r}_1, \widetilde{r}_2, \theta)$,

$$W(\widetilde{r}_1, \widetilde{r}_2, \theta) = U(\widetilde{r}_1, \widetilde{r}_2, \widetilde{r}_{12}) = \frac{1}{2\sin^2\theta}\left(\frac{1}{\widetilde{r}_1^2} + \frac{1}{\widetilde{r}_2^2}\right) - \frac{Z}{\widetilde{r}_1} - \frac{Z}{\widetilde{r}_2} + \frac{1}{(\widetilde{r}_1^2 + \widetilde{r}_2^2 - 2\widetilde{r}_1\widetilde{r}_2\cos\theta)^{1/2}}. \tag{25}$$

The case of symmetric minimum $(\widetilde{r}_1^{(0)} = \widetilde{r}_2^{(0)})$ was considered for the first time by Mlodinow and Papanicolaou in 1981 [4]. Finding the symmetric minimum reduces to minimization of the function of two variables,

$$w(R, \theta) \equiv W(R, R, \theta) = \frac{1}{R^2\sin^2\theta} - \frac{2Z}{R} + \frac{1}{2R\sin\frac{\theta}{2}}. \tag{26}$$

At minimum, $\frac{\partial w}{\partial \theta} = 0$, or

$$-\frac{2\cos\theta}{R^2\sin^3\theta} - \frac{\cos\frac{\theta}{2}}{4R\sin^2\frac{\theta}{2}} = 0. \tag{27}$$

It allows to express R via θ as

$$R = -8\frac{\cos\theta}{\sin^3\theta}\frac{\sin^2\frac{\theta}{2}}{\cos\frac{\theta}{2}} = -\frac{\cos\theta}{\sin\frac{\theta}{2}\cos^4\frac{\theta}{2}}, \tag{28}$$

where we used a trigonometric equality $\sin\theta = 2\sin\frac{\theta}{2}\cos\frac{\theta}{2}$. At minimum, $\frac{\partial w}{\partial R} = 0$, or

$$-\frac{2}{R^3\sin^3\theta} + \frac{2Z}{R^2} - \frac{1}{2R^2\sin\frac{\theta}{2}} = \frac{-\frac{4}{\sin^2\theta} + 4ZR - \frac{R}{\sin\frac{\theta}{2}}}{2R^3} = 0. \tag{29}$$

It means that numerator in r.h.s. of equation (29) is zero, i.e.

$$-\frac{4}{\sin^2\theta} + 4ZR - \frac{R}{\sin\frac{\theta}{2}} = 0. \tag{30}$$

Using equation (28), the sum of 1-st and 3-rd terms in equation (30) could be simplified as

$$-\frac{4}{\sin^2\theta} - \frac{R}{\sin\frac{\theta}{2}} = -\frac{1}{\sin^2\frac{\theta}{2}\cos^2\frac{\theta}{2}} + \frac{\cos\theta}{\sin^2\frac{\theta}{2}\cos^4\frac{\theta}{2}} =$$
$$\frac{1}{\sin^2\frac{\theta}{2}\cos^4\frac{\theta}{2}}\left(-\cos^2\frac{\theta}{2} + \cos\theta\right) = \frac{1}{\sin^2\frac{\theta}{2}\cos^4\frac{\theta}{2}}\left(-\frac{1+\cos\theta}{2} + \cos\theta\right) =$$
$$\frac{1}{\sin^2\frac{\theta}{2}\cos^4\frac{\theta}{2}}\left(\frac{\cos\theta - 1}{2}\right) = -\frac{1}{\cos^4\frac{\theta}{2}}, \tag{31}$$

where we subsequently used equalities $\sin\theta = 2\sin\frac{\theta}{2}\cos\frac{\theta}{2}$, $\cos^2\frac{\theta}{2} = \frac{1+\cos\theta}{2}$, and $\frac{1-\cos\theta}{2} = \sin^2\frac{\theta}{2}$. The 2-nd term in equation (30) could rewritten using equation (28) as

$$4ZR = -4Z\frac{\cos\theta}{\sin\frac{\theta}{2}\cos^4\frac{\theta}{2}}. \tag{32}$$

Combining of equations (31) and (32), we obtain the numerator, equation (30), as a sum

$$-\frac{1}{\cos^4\frac{\theta}{2}} - 4Z\frac{\cos\theta}{\sin\frac{\theta}{2}\cos^3\frac{\theta}{2}} = \frac{1}{\cos^4\frac{\theta}{2}}\left(-1 - 4Z\frac{\cos\theta}{\sin\frac{\theta}{2}}\right) = 0. \tag{33}$$

Since neither $\cos\frac{\theta}{2}$ nor $\sin\frac{\theta}{2}$ are zero, it follows that

$$\sin\frac{\theta}{2} = -4Z\cos\theta, \tag{34}$$

Rising both sides of equation (34) to square, we obtain

$$\sin^2\frac{\theta}{2} = \frac{1-\cos\theta}{2} = 16Z^2\cos^2\theta, \tag{35}$$

or

$$32Z^2\cos^2\theta + \cos\theta - 1 = 0. \tag{36}$$

Since $0 < \theta < \pi$, $\sin\frac{\theta}{2} > 0$, and from equation (28), $\cos\theta < 0$. Now, let us define a variable

$$\xi = -\cos\theta \tag{37}$$

that should be *positive*. Then, equation (36) could be rewritten as a quadratic equation for ξ,

$$32Z^2\xi^2 - \xi - 1 = 0. \tag{38}$$

Its positive root is

$$\xi = \frac{1+\sqrt{1+128Z^2}}{64Z^2}. \tag{39}$$

For helium ($Z = 2$), $\xi = -\cos\theta = 0.092$, and $\theta = 95.3°$. It is interesting to note, that the second (negative) root of equation (38) (with minus sign in front of square root in equation (39)) gives the value of $-\cos\theta$ for a hypothetical system with inter-electron repulsion replaced by attraction, e.i. $V = -Z/r_1 - Z/r_2 - 1/r_{12}$, that gives $\theta = 85.1°$ for the modified attractive helium.

After replacing in equation (28) $\sin\frac{\theta}{2}$ by $(-4Z\cos\theta)$ according to equation (34) and $\cos^4\frac{\theta}{2}$ by $\left(\frac{1+\cos\theta}{2}\right)^2$, we obtain

$$R = \frac{\cos\theta}{4Z\cos\theta\frac{1}{4}(1+\cos\theta)^2} = \frac{1}{Z(1+\cos\theta)^2} = \frac{1}{Z(1-\xi)^2}. \tag{40}$$

The distance $\widetilde{r}_{12}^{(0)}$ could be expressed via the variable ξ too,

$$\widetilde{r}_{12}^{(0)} = 2R\sin\frac{\theta}{2} = -2\frac{\cos\theta}{\cos^4\frac{\theta}{2}} = \frac{8\xi}{(1-\xi)^2}, \tag{41}$$

and finally the energy ... (need to finish).

Summarizing equations (40) and (41), we found that the location of minimum and the energy $\widetilde{E}_0$ are rational functions of the variable ξ,

$$\begin{aligned} \widetilde{r}_1^{(0)} &= \widetilde{r}_2^{(0)} = \frac{1}{Z(1-\xi)^2}, \\ \widetilde{r}_{12}^{(0)} &= \frac{8\xi}{(1-\xi)^2}, \\ \widetilde{E}_0 &= -\frac{(1-\xi)^3}{32\xi^2}. \end{aligned} \tag{42}$$

When $Z = Z_\star = \frac{\sqrt[4]{3}}{8}\left(1+\sqrt{3}\right)^2 \approx 1.228$, one of second derivatives is zero. If $Z > Z_\star$, then we have a minimum, if $Z < Z_\star$ then there is a saddle point.

Loeser (1987) [3] found a symmetric solution for the case of N electrons. It is expressed through a positive root of 4-th degree polynomial

$$8Z^2\xi^2\left[2-(N-2)\xi\right]^2 - \xi - 1 = 0. \tag{43}$$

Again, the location of minimum and the energy $\widetilde{E}_0$ are some rational functions of the variable ξ,

$$\begin{aligned} \widetilde{r}_n^{(0)} &= \frac{1}{Z[1-(N-1)\xi]^2}, \quad n = 1, \ldots, N \\ \widetilde{r}_{mn}^{(0)} &= \frac{4\xi[2+(2-N)\xi]}{[1-(N-1)\xi]^2}, \quad m \neq n, \\ \widetilde{E}_0 &= -\frac{N[1-(N-2)\xi][1-(N-1)\xi]^3}{16\xi^2[2-(N-2)\xi]^2}. \end{aligned} \tag{44}$$

In a particular case of $N = 2$, equations (43) and (44) reduce to a more simple equations (38) and (42).

In non-symmetric case, $\widetilde{r}_1^{(0)} \neq \widetilde{r}_2^{(0)}$, it is convenient to use instead of

$(\widetilde{r}_1, \widetilde{r}_2, \widetilde{r}_{12})$ another variables (x, y, z) defined as

$$\begin{aligned} x &= \frac{\widetilde{r}_1 + \widetilde{r}_2}{\widetilde{r}_{12}}, \\ y &= \frac{\widetilde{r}_1 \widetilde{r}_2}{\widetilde{r}_{12}^2}, \\ z &= \widetilde{r}_{12}. \end{aligned} \tag{45}$$

Then, the potential (22) is expressed through new variables as

$$\widetilde{U} = \frac{y - Zx}{yz} + \frac{1}{4z^2} \frac{x^2 - 2y}{x^2 - 2y + 2x^2 y - 1/2 - x^4/2}. \tag{46}$$

It was proven [1] that the variable x corresponding to the minimum is determined as one of roots of 7-th degree polynomial

$$x(1+x)^3 - 2Z(1 + 8x^2 + 3x^4) + 16Z^2 x = 0. \tag{47}$$

Variables y and z where (46) reaches its minimum are determined by formulas

$$\begin{aligned} y &= \frac{x^2(1-x^2)[(1+x^2)^2 - 8xZ]}{(1+x^2)(1-5x^4) - 8Zx(1-3x^2)}, \\ z &= \frac{xy(-1 + x^4 - 4x^2 y + 8y^2)}{(1-x^2)^2(1-x^2+4y)^2}, \end{aligned} \tag{48}$$

and finally, the distances $\widetilde{r}_1^{(0)}$, $\widetilde{r}_2^{(0)}$ and $\widetilde{r}_{12}^{(0)}$ are determined by the formulas

$$\begin{aligned} \widetilde{r}_1^{(0)} &= \frac{z}{2}\left[x \pm (x^2 - 4y)^{1/2}\right], \\ \widetilde{r}_2^{(0)} &= \frac{z}{2}\left[x \mp (x^2 - 4y)^{1/2}\right], \\ \widetilde{r}_{12}^{(0)} &= z. \end{aligned} \tag{49}$$

The minimum exists only if $1 < Z < Z_{\star\star} \approx 1.235$. $Z_{\star\star}$ could be expressed through radicals, but the expression is lengthy.

For $Z = 1$ (hydrogen anion H^-), neither symmetric nor asymmetric minima exist, and the method cannot be used without further modifications

such as "complex dimensional scaling" (expansion around a saddle point) [5] or "renormalization" [7]. For $Z = 1, 2, 3, \ldots$, only the symmetric minimum exists.

However, if we consider N-electron atoms, then for sufficiently large $N \geq 15$, an asymmetric minimum exists, and it is lower than symmetric, i.e. absolute minimum.

The degree of assymmetry could be measured through a variable

$$\eta = \frac{\widetilde{r}_1 - \widetilde{r}_2}{\widetilde{r}_1 + \widetilde{r}_2}, \quad -1 < \eta < 1, \tag{50}$$

where $\eta = 0$ corresponds to symmetric case.

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

$$u(\eta) = \min \widetilde{U}\left(\widetilde{r}_1, \widetilde{r}_2, \widetilde{r}_{12}\right), \tag{51}$$

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 $Z > Z_{\star\star}$, and two asymmetric minima at $Z < Z_\star$, see Fig. 1.

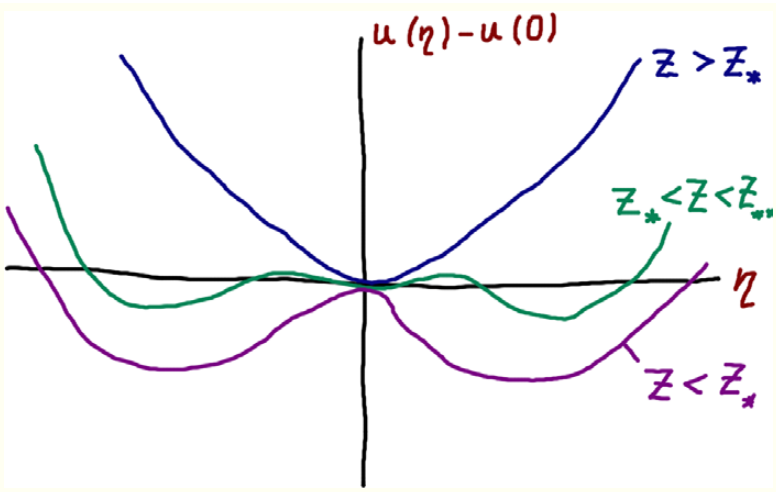

FIG. 1. Shape of the effective potential for two-electron atoms in the direction of soft antisymmetric mode.

Numerically, for $Z = 2$ (helium)

$$\begin{aligned} \widetilde{r}_{1,2}^{(0)} &= 0.607, \\ \widetilde{r}_{12}^{(0)} &= 0.897, \\ \theta_{12}^{(0)} &= 95.3^\circ, \\ \widetilde{E}_0 &= -2.738. \end{aligned} \tag{52}$$

To find large-D behavior in a rigorous fashion, we perform second scaling transformation

$$\begin{aligned} \widetilde{r}_1 &= \widetilde{r}_1^{(0)} + K^{-1/2} x_1, \\ \widetilde{r}_2 &= \widetilde{r}_2^{(0)} + K^{-1/2} x_2, \\ \widetilde{r}_{12} &= \widetilde{r}_{12}^{(0)} + K^{-1/2} x_3. \end{aligned} \tag{53}$$

Then, Schrödinger equation is rewritten as

$$\begin{aligned} \Bigg\{ -\frac{1}{2K} \left[\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + 2\frac{\partial^2}{\partial x_3^2} + \cos\theta_1^{(0)} \frac{\partial^2}{\partial x_1 \partial x_3} + \cos\theta_2^{(0)} \frac{\partial^2}{\partial x_2 \partial x_3} \right] \\ + \widetilde{U}\left(\widetilde{r}_1^{(0)}, \widetilde{r}_2^{(0)}, \widetilde{r}_{12}^{(0)}\right) + \frac{1}{2K} \sum_{i,j=1}^{3} \frac{\partial^2 \widetilde{U}}{\partial \widetilde{r}_i \widetilde{r}_j} - \widetilde{E} \Bigg\} Y(x_1, x_2, x_3) = 0, \end{aligned} \tag{54}$$

where

$$\cos\theta_1^{(0)} = \cos\theta_2^{(0)} = \frac{\widetilde{r}_2^{(0)^2} - \widetilde{r}_1^{(0)^2} + \widetilde{r}_{12}^{(0)^2}}{2\widetilde{r}_2^{(0)} \widetilde{r}_{12}^{(0)}} = \frac{\widetilde{r}_{12}^{(0)}}{2\widetilde{r}_1^{(0)}}, \tag{55}$$

second derivatives of $\widetilde{U}$ are taken at the point $\left(\widetilde{r}_1^{(0)}, \widetilde{r}_2^{(0)}, \widetilde{r}_{12}^{(0)}\right)$, and $\widetilde{r}_3 \equiv \widetilde{r}_{12}$,

$$Y(x_1, x_2, x_3) = P\left(\widetilde{r}_1^{(0)} + K^{-1/2} x_1, \widetilde{r}_2^{(0)} + K^{-1/2} x_2, \widetilde{r}_{12}^{(0)} + K^{-1/2} x_3\right), \tag{56}$$

and terms of order $o(1/K)$ are omitted.

Multiplying equation (54) by K, we obtain

$$\left[-\frac{1}{2} \sum A_{ij} \frac{\partial^2}{\partial x_i \partial x_j} + \frac{1}{2} \sum B_{ij} x_i x_j - \varepsilon \right] Y = 0, \tag{57}$$

where $\varepsilon = K(\widetilde{E} - \widetilde{E}_0)$,

$$\mathsf{A} = \begin{pmatrix} 1 & 0 & \cos\theta_1^{(0)} \\ 0 & 1 & \cos\theta_2^{(0)} \\ \cos\theta_1^{(0)} & \cos\theta_2^{(0)} & 2 \end{pmatrix}, \quad B_{ij} = \left.\frac{\partial^2 \widetilde{U}}{\partial \widetilde{r}_i \widetilde{r}_j}\right|_{\widetilde{r}_1^{(0)}, \widetilde{r}_2^{(0)}, \widetilde{r}_{12}^{(0)}}. \tag{58}$$

Using Sylvester's criterion, we could prove that the matrix a is positive definite (note that $\det\mathsf{A} = 2 - 2\cos^2\theta_1^{(0)} > 0$ since $\theta_1^{(0)} \neq 0, \pi$). We have an equation for anisotropic harmonic oscillator. Its solution reduces to diagonalization of the matrix (solution could be considered in appendix)

$$\mathsf{C} \equiv \mathsf{A}^{1/2}\mathsf{B}\mathsf{A}^{1/2}. \tag{59}$$

There exists a unitary matrix U ($\mathsf{U}^{\mathrm{T}} = \mathsf{U}^{-1}$) so that

$$\mathsf{U}^{\mathrm{T}}\mathsf{C}\mathsf{U} = \Omega^2 = \begin{pmatrix} \omega_1^2 & 0 & 0 \\ 0 & \omega_2^2 & 0 \\ 0 & 0 & \omega_3^2 \end{pmatrix}, \tag{60}$$

where U is a matrix of transformation to normal-mode coordinates,

$$\begin{pmatrix} q_1 \\ q_2 \\ q_3 \end{pmatrix} = \mathsf{U} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}, \tag{61}$$

and $\omega_1, \omega_2, \omega_3$ are frequencies of normal-mode vibrations. The equation is separable in coordinates (q_1, q_2, q_3), and

$$\varepsilon = \sum_{i=1}^{3} \left(n_i + \frac{1}{2}\right)\omega_i. \tag{62}$$

The normal mode with smallest frequency is called "antisymmetric stretch" (see Fig. 2),

$$q_3 = \frac{\sqrt{2}}{2}(x_1 - x_2), \tag{63}$$

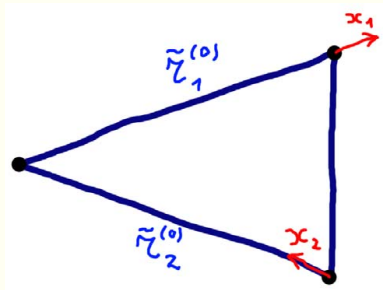

FIG. 2. Vibrations of particles along antisymmetric stretch mode.

two other modes are mixtures of "symmetric stretch" and "bend", see Fig. 3 that was copied from the paper of Herschbach [2].

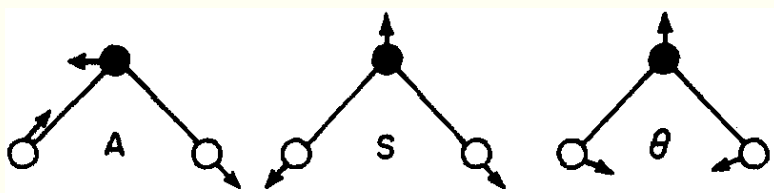

FIG. 3. Vibrations corresponding to antisymmetric stretch (A), symmetric stretch (S), and bend (θ) modes. The figure was copied from [2].

Numerically for helium

$$\begin{aligned} q_1 &= 0.811x_1 + 0.811x_2 - 1.048x_3 \qquad & \omega_1 &= 11.763 \\ q_2 &= -0.667x_1 - 0.667x_2 - 0.053x_3 \qquad & \omega_2 &= 5.426 \\ q_3 &= -0.707x_1 + 0.707x_2 \qquad & \omega_3 &= 3.549 \end{aligned} \tag{64}$$

$1/D$-expansion could be obtained as follows,

$$E = \frac{\widetilde{E}}{K^2} = \frac{\widetilde{E}_0 + \frac{1}{K}\varepsilon}{K^2} = \frac{\widetilde{E}_0}{K^2} + \frac{1}{K^3}\varepsilon. \tag{65}$$

After substitution $K = \frac{1}{2}(D-3) + o(1)$, we obtain

$$E = \frac{4\widetilde{E}_0}{D^2}\left(1 - \frac{3}{D}\right)^{-2} + \frac{8\varepsilon}{D^3} + o(D^{-3}) = \frac{4\widetilde{E}_0}{D^2} + \frac{24\widetilde{E}_0 + 8\varepsilon}{D^3} + o(D^{-3}). \tag{66}$$

Herschbach with co-authors [2] calculated third term $\sim D^{-4}$ by taking into account anharmonic corrections. They approximated correction to the

energy (a difference between E and the sum of first three terms of $1/D$-expansion) using interpolation to $\delta \equiv 1/D = 1/3$ between two limiting cases, $\delta_1 = 1$ $(D = 1)$ and $\delta_2 = 0$ $(D = \infty)$.

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