Three-electron coalescence conditions

or

"How does the wave function look like when three electrons touch?"

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Hydrogen-like ions: electron-nucleus coalescence for S states

What happen when an electron and a nucleus meet each other?

$$\hat{H}\psi = E\psi$$

$$\left(-\frac{\nabla^2}{2} + \hat{V}\right)\psi = E\psi$$

$$-\frac{1}{2}\left(\frac{d^2\psi}{dr^2} + \frac{2}{r}\frac{d\psi}{dr}\right) - \frac{Z}{r} = E\psi$$

For small r, let's approximate the wave function as

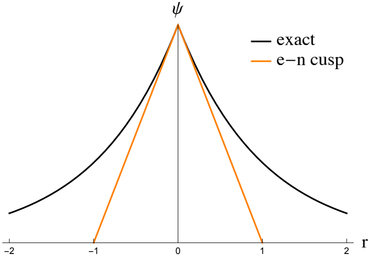
$$\psi = 1 + \alpha r + O(r^2)$$

Then,

$$\alpha = -Z \quad \Rightarrow \quad \boxed{\psi \sim 1 - Zr \text{ for small } r}$$

This is the electron-nucleus (e-Z) cusp!

Hydrogen atom ($Z = 1$):



Kato, Com Pure Appl Math 10 (1957) 151; Pack and Byers Brown, JCP 45 (1966) 556
Kurokawa et al, JCP 139 (2013) 044114; ibid 140 (2014) 214103

Helium-like ions: two-electron coalescence for S states

What happen when two electrons meet each other?

$$\nabla^2 = \frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1} + \frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial}{\partial r_2} + \frac{\partial^2}{\partial r_{12}^2} + \frac{4}{r_{12}}\frac{\partial}{\partial r_{12}}$$
$$+ \frac{r_1^2 + r_{12}^2 - r_2^2}{2 r_1 r_{12}}\frac{\partial^2}{\partial r_1 \partial r_{12}} + \frac{r_2^2 + r_{12}^2 - r_1^2}{2 r_2 r_{12}}\frac{\partial^2}{\partial r_2 \partial r_{12}}$$
$$\hat{V} = -\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

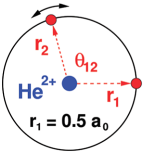
Let's assume r_{12} is tiny compared to r_1 and r_2

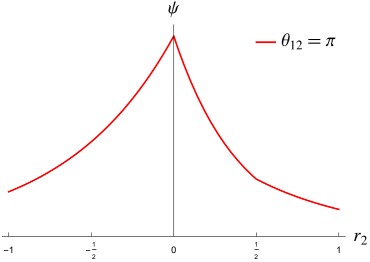
$$\psi = 1 + \beta r_{12}$$

Then,

$$\beta = \frac{1}{2} \quad \Rightarrow \quad \boxed{\psi \sim 1 + \frac{r_{12}}{2} \text{ for small } r_{12}}$$

This is the electron-electron (e-e) cusp!





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Fock expansion: three-particle coalescence for S state

What happen when two electrons meet a nucleus?

In 1935, Bartlett, Gibbons, and Dunn showed that a wave function of the form

$$\psi(r_1, r_2, r_{12}) = \sum_{lmn} c_{lmn} r_1^l r_2^m r_{12}^n$$

cannot satisfying the Schrödinger equation for He [Phys Rev 47 (1935) 679]
Assuming that r_1 and r_2 are small, Fock showed

$$\psi(R, \alpha, \theta) = \sum_{k=0}^{\infty} \sum_{p=0}^{\lfloor k/2 \rfloor} R^k (\ln R)^p \psi(\alpha, \theta) \qquad R = \sqrt{r_1^2 + r_2^2} \text{ is the hyperradius}$$

In particular,

$$\boxed{\psi = 1 - Z(r_1 + r_2) + \frac{r_{12}}{2} - Z\frac{\pi - 2}{3\pi}(r_1^2 + r_2^2 - r_{12}^2) \ln R + O(R^2)}$$

The wave function is non-analytic at the three-particle coalescence!

Fock, Izv. Akad. Nauk. SSSR, Ser. Fiz. 18 (1954) 161
Gottschalk et al, J. Phys. A 20 (1987) 2077; ibid 20 (1987) 2781

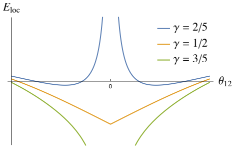
Why do we care?

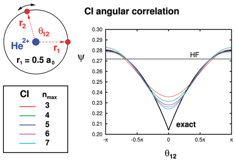
Kato cusp: two-particle coalescence $\Leftrightarrow$ divergence in E_{loc} and rate of convergence

Helium-like ions:

$$\psi_\gamma = \exp\left[-Z\left(r_1 + r_2\right) + \gamma r_{12}\right]$$

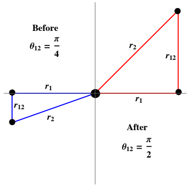
$$E_{\text{loc}}(\gamma) = \frac{\hat{H}\psi_\gamma}{\psi_\gamma}$$

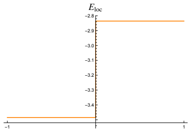




Fock expansion: three-particle coalescence $\Leftrightarrow$ finite discontinuity in E_{loc}

$$E_{\text{loc}}(1/2) = -\left(Z^2 + \frac{1}{4}\right) + \frac{Z}{2}\left(\frac{\boldsymbol{r}_1 \cdot \boldsymbol{r}_{12}}{r_1 r_{12}} + \frac{\boldsymbol{r}_2 \cdot \boldsymbol{r}_{12}}{r_2 r_{12}}\right)$$





E_{loc} is not well defined at the triple-collision limit!

Myers et al. JCP 44 (1991) 5537; Hattig et al, Chem. Rev. 112 (2012) 4; Drummond et al, PRB 70 (2004) 235119

What happen when three electrons collide?

Nathaniel Bloomfield

Peter Gill

Three electrons in a harmonic well

$$\hat{H}\Phi = E\Phi \qquad \text{where} \qquad \hat{H} = \frac{1}{2}\sum_{i=1}^{3}\left(-\nabla_i^2 + \omega^2\, r_i^2\right) + \kappa \sum_{i<j}^{3} \frac{1}{r_{ij}}$$

Few things

- External potential doesn't matter $\Rightarrow \omega^2 = 1$
- We consider S states $\Rightarrow$ we can get rid of 3 degrees of freedom

Jacobi coordinates

$$\boldsymbol{\sigma} = (\boldsymbol{r}_1 + \boldsymbol{r}_2 + \boldsymbol{r}_3)/\sqrt{3}$$
$$\boldsymbol{\rho} = (\boldsymbol{r}_1 - \boldsymbol{r}_2)/\sqrt{2}$$
$$\boldsymbol{\lambda} = (2\,\boldsymbol{r}_3 - \boldsymbol{r}_1 - \boldsymbol{r}_2)/\sqrt{6}$$

Spatial wave function

$$\Psi(\boldsymbol{\sigma}, \boldsymbol{\rho}, \boldsymbol{\lambda}) = \psi(\rho, \lambda, \boldsymbol{\rho}\cdot\boldsymbol{\lambda})\Omega(\boldsymbol{\sigma})$$
$$\Omega(\boldsymbol{\sigma}) = \pi^{-3/4}\exp(-\sigma^2/2)$$
$$E_\Omega = 3/2$$

White and Stillinger, PRA 3 (1971) 1521
Loos, Bloomfield and Gill, JCP 143 (2015) 181101

Wave function expansion at the three-electron coalescence

Schrödinger-like equation

$$\boxed{\left(\nabla^2 - 2\,\kappa\,\hat{U} + 2\,\epsilon - \hat{V}\right)\psi = 0} \qquad \epsilon = E - E_\Omega$$

Kinetic:

$$\begin{aligned}\frac{\nabla^2}{2} = {} & \frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} + \frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{2 r_{12} r_{13}}\frac{\partial^2}{\partial r_{12}\partial r_{13}} \\ & + \frac{\partial^2}{\partial r_{13}^2} + \frac{2}{r_{13}}\frac{\partial}{\partial r_{13}} + \frac{r_{12}^2 + r_{23}^2 - r_{13}^2}{2 r_{12} r_{23}}\frac{\partial^2}{\partial r_{12}\partial r_{23}} \\ & + \frac{\partial^2}{\partial r_{23}^2} + \frac{2}{r_{23}}\frac{\partial}{\partial r_{23}} + \frac{r_{13}^2 + r_{23}^2 - r_{12}^2}{2 r_{13} r_{23}}\frac{\partial^2}{\partial r_{13}\partial r_{23}}\end{aligned}$$

Interelectronic potential:

$$\hat{U} = r_{12}^{-1} + r_{13}^{-1} + r_{23}^{-1}$$

External potential:

$$\hat{V} = r_{12}^2 + r_{13}^2 + r_{23}^2$$

Fock expansion

Assuming r_{12}, r_{13} and r_{23} small,

$$\boxed{\psi = \psi^{(0)} + \kappa\,\psi^{(1)} + \kappa^2\,\psi^{(2)} + \ldots}$$

Zeroth order:

$$\nabla^2\psi^{(0)} = 0$$

First order:

$$\nabla^2\psi^{(1)} = 2\,\hat{U}\,\psi^{(0)}$$

Second order:

$$\nabla^2\psi^{(2)} = 2\,\hat{U}\,\psi^{(1)} - 2\,\epsilon\,\psi^{(0)}$$

NB: there's no contribution from the external potential up to fourth order!

Electronic states & some definitions

Doublet State: $^2S_{1/2}$

$$S = 1/2 \qquad M_S = 1/2$$

Quartet States: $^4S_{1/2}$ **and** $^4S_{3/2}$

$$S = 3/2 \qquad M_S = 1/2 \text{ or } 3/2$$

Some useful quantities

Symmetric polynomials:

$$s_1 = r_{12} + r_{13} + r_{23} \qquad s_2 = r_{12}\, r_{13} + r_{12}\, r_{23} + r_{13}\, r_{23} \qquad s_3 = r_{12}\, r_{13}\, r_{23}$$

The good old hyperradius:

$$R = \sqrt{\frac{r_{12}^2 + r_{13}^2 + r_{23}^2}{3}}$$

Heron's formula:

$$\begin{aligned} \Delta &= \sqrt{s_1 (s_1 - 2 r_{12})(s_1 - 2 r_{13})(s_1 - 2 r_{23})} \\ &= \text{ area of the triangle defined by the three interelectronic distances} \end{aligned}$$

Pauncz, *Spin Eigenfunctions* (Plenum, New York, 1979)

Doublet state ${}^2S_{1/2}$

Matsen's spin-free formalism [Matsen, JPC 68 (1968) 3282]

$$ {}^2\Phi = \frac{1}{\sqrt{3}} \left[\alpha(1)\alpha(2)\beta(3)\, {}^2\Psi(\underbrace{\boldsymbol{r}_1, \boldsymbol{r}_2}_{\alpha} | \underbrace{\boldsymbol{r}_3}_{\beta}) - \alpha(1)\beta(2)\alpha(3)\, {}^2\Psi(\boldsymbol{r}_1, \boldsymbol{r}_3 | \boldsymbol{r}_2) - \beta(1)\alpha(2)\alpha(3)\, {}^2\Psi(\boldsymbol{r}_3, \boldsymbol{r}_2 | \boldsymbol{r}_1) \right] $$

Symmetry [White and Stillinger, JCP 52 (1970) 5800; PRA 3 (1971) 1521]

$$ {}^2\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2 | \boldsymbol{r}_3) = -{}^2\Psi(\boldsymbol{r}_2, \boldsymbol{r}_1 | \boldsymbol{r}_3) \quad \Longleftrightarrow \quad \text{Pauli principle} $$

$$ {}^2\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2 | \boldsymbol{r}_3) = {}^2\Psi(\boldsymbol{r}_1, \boldsymbol{r}_3 | \boldsymbol{r}_2) + {}^2\Psi(\boldsymbol{r}_3, \boldsymbol{r}_2 | \boldsymbol{r}_1) \quad \Longleftrightarrow \quad \text{Pure doublet state} $$

Frobenius method (Fock expansion too difficult for us...)

$$ {}^2\psi^{(0)} = r_{13}^2 - r_{23}^2 $$

$$ {}^2\psi^{(1)} = \frac{s_1}{8}(r_{13} - r_{23})(3r_{13} + 3r_{23} - r_{12}) $$

$$ {}^2\psi^{(2)} = {}^2N^{(2)}(2r_{12}^2 - r_{13}^2 - r_{23}^2)\, {}^2\psi^{(0)} \ln(3R^2) + O(R^4) $$

$$ {}^2N^{(2)} = \frac{27\pi^2}{40}(11\sqrt{3} - 6\pi) \approx 1.352401 $$

Quartet state $^4S_{1/2}$

Matsen's spin-free formalism [Matsen, JPC 68 (1968) 3282]

$$^4\Phi_{1/2} = \frac{1}{\sqrt{3}}\Big[\alpha(1)\alpha(2)\beta(3)+\alpha(1)\beta(2)\alpha(3)+\beta(1)\alpha(2)\alpha(3)\Big]\ ^4\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3)$$

Symmetry [White and Stillinger, PRA 3 (1971) 1521]

$$^4\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3) = -{}^4\Psi(\boldsymbol{r}_1,\boldsymbol{r}_3,\boldsymbol{r}_2) = -{}^4\Psi(\boldsymbol{r}_2,\boldsymbol{r}_1,\boldsymbol{r}_3) = -{}^4\Psi(\boldsymbol{r}_3,\boldsymbol{r}_2,\boldsymbol{r}_1) \iff \text{Single permutation}$$

$$^4\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3) = +{}^4\Psi(\boldsymbol{r}_2,\boldsymbol{r}_3,\boldsymbol{r}_1) = +{}^4\Psi(\boldsymbol{r}_3,\boldsymbol{r}_1,\boldsymbol{r}_2) \iff \text{Double permutation}$$

Frobenius method (Fock expansion still too hard...)

$$^4\psi_{1/2}^{(0)} = (r_{12}^2-r_{13}^2)(r_{12}^2-r_{23}^2)(r_{13}^2-r_{23}^2) \qquad {}^4N_{1/2}^{(2)} = 27\pi^2\left(\frac{11\pi}{1280}-\frac{7641\sqrt{3}}{501760}\right) \approx 0.165672$$

$$^4\psi_{1/2}^{(1)} = \frac{(r_{12}-r_{13})(r_{12}-r_{23})(r_{13}-r_{23})}{192}\left(\frac{8}{5}s_2^2-\frac{312}{5}s_1s_3+\frac{272}{5}s_1^2s_2-6s_1^4\right)$$

$$^4\psi_{1/2}^{(2)} = {}^4N_{1/2}^{(2)}\,\frac{\frac{1}{7}\left(r_{12}^2r_{13}^2+r_{12}^2r_{23}^2+r_{13}^2r_{23}^2\right)-\frac{4}{7}\Delta^2}{r_{12}^2+r_{13}^2+r_{23}^2}\ {}^4\psi_{1/2}^{(0)}\ln(3R^2)+O(R^8)$$

Quartet state $^4S_{3/2}$

Interdimensional trick **[Herrick, J Math Phys 16 (1975) 281; Loos and Bressanini, JCP 142 (2015) 214112]**

$$^4\Phi_{3/2} = \alpha(1)\alpha(2)\alpha(3) D(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)\, {}^4\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)$$

where

$$D(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) = \begin{vmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix} = \boldsymbol{r}_1 \cdot (\boldsymbol{r}_2 \times \boldsymbol{r}_3)$$

and $^4\Psi$ is a bosonic (totally symmetric) solution of the Schrödinger-like equation in five dimensions!

Frobenius method

$$^4\psi_{3/2}^{(0)} = 1 \qquad {}^4N_{3/2}^{(2)} = \frac{3\pi^2}{35}\left(15\sqrt{3} - 8\pi\right) \approx 0.717397$$

$$^4\psi_{3/2}^{(1)} = \frac{1}{4}(r_{12} + r_{13} + r_{23})$$

$$^4\psi_{3/2}^{(2)} = {}^4N_{3/2}^{(2)} \frac{\frac{4}{7}\left(r_{12}^2 r_{13}^2 + r_{12}^2 r_{23}^2 + r_{13}^2 r_{23}^2\right) - \frac{11}{14}\Delta^2}{r_{12}^2 + r_{13}^2 + r_{23}^2} \ln(3R^2) + O(R^2)$$

Electronic states of He

Singlet $^1S^e(1s^2)$ [Fock, Izv. Akad. Nauk. SSSR, Ser. Fiz. 18 (1954) 161]

$$
\begin{aligned}
{}^1\psi^{(0)} &= 1 & {}^1N^{(2)} &= \frac{\pi-2}{3\pi}\\
{}^1\psi^{(1)} &= -Z(r_1+r_2)+\frac{\kappa}{2}r_{12}\\
{}^1\psi^{(2)} &= {}^1N^{(2)}(r_1^2+r_2^2-r_{12}^2)\ln(r_1^2+r_2^2)+O(R^2)
\end{aligned}
$$

Triplet $^3S^e(1s2s)$ [Pluvinage, J. Physique 43 (1982) 439]

$$
\begin{aligned}
{}^3\psi^{(0)} &= r_1^2-r_2^2 & {}^3N^{(2)} &= \frac{7\pi-20}{60\pi}\\
{}^3\psi^{(1)} &= -\frac{2}{3}Z(r_1^3-r_2^3)-Zr_1r_2(r_1-r_2)+\frac{\kappa}{4}(r_1^2-r_2^2)r_{12}\\
{}^3\psi^{(2)} &= {}^3N^{(2)}(r_1^2+r_2^2-r_{12}^2)(r_1^2-r_2^2)\ln(r_1^2+r_2^2)+O(R^4)
\end{aligned}
$$

NB: $^3P^e(2p^2)$ and $^1P^e(2p^2)$ can be obtained via $^1S^e(1s^2)$ and $^3S^e(1s2s)$ using interdimensional degeneracy [Loos and Bressanini, JCP 142 (2015) 214112]

Remarks & Future Works

Few remarks...

- All states have non-analytic terms appearing at second order
- Quartets have peculiar logarithmic terms
- Apply to 3D and 2D systems [Loos, Bloomfield & Gill, JCP 143 (2015) 181101]
- Method can be generalized to higher-order collision (Zeee in lithium for example)
- Universal, i.e. conditions are valid for any electronic systems

Lots of work to do...

- Improve convergence of variational energy ⇔ integrals are tricky!
- Incorporating these coalescence conditions in Jastrow/correlation factors is not trivial [Agboola et al, JCP 143 (2015) 084114]
- Remove discontinuity in local energy ⇔ higher order terms needed
- Imposing e-e and e-e-e coalescence conditions simultaneously ⇔ exponentation?

Myers et al. JCP 44 (1991) 5537

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