The Hydrogen Atom and Harmonic Oscillator(s)

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ZGS, Mar 24, 2023

Harmonic oscillator universe?

Harmonic oscillator in physics

- Hooke's law
- QHO
- Einstein solid
- Atom-radiation interaction
- (Second) quantization of electromagnetic fields
- QFT
- ...
- Gravity?
  Can the Coulomb-Kepler problem be mapped to SHO's?

Coulomb-Kepler problem revisited

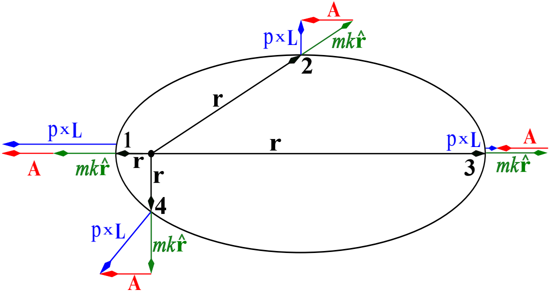
Two particles attracted to each other by central potential $V(r) = -k/r$:

$$H = \frac{\vec{p}^2}{2\mu} - \frac{k}{r}.$$

Constants of motion: H, $\vec{L} = \vec{r} \times \vec{p}$, and $\vec{A}$, the Laplace-Runge-Lenz vector:

$$\vec{A} = \vec{p} \times \vec{L} - \mu k \frac{\vec{r}}{r}.$$

Coulomb-Kepler problem revisited



$\vec{A}$ is in the plane of the orbit (so $\vec{A} \cdot \vec{L} = 0$), with $A^2 = \mu^2 k^2 + 2\mu E L^2$.

$\vec{A}$ determines the shape and orientation of the orbit

Coulomb-Kepler problem revisited

$\vec{A}$ determines the shape and orientation of the orbit:

- Shape: from

$$\vec{A} \cdot \vec{r} = \vec{r} \cdot (\vec{p} \times \vec{L}) - \mu k = (\vec{r} \times \vec{p}) \cdot \vec{L} - \mu k = L^2 - \mu k = Ar \cos\theta$$

  we get the orbit equation

$$\frac{1}{r} = \frac{\mu k}{L^2} \left(1 + \epsilon \cos\theta\right), \quad \text{eccentricity } \epsilon = \frac{A}{|\mu k|} = \sqrt{1 + \frac{2EL^2}{\mu k^2}} \geq 0$$

- Orientation: $\vec{A}$ points from source to periapsis

Aside: History of the LRL vector

Unclear origin, gets rediscovered repeatedly:

- None of Laplace, Runge, or Lenz discovered it. Laplace (1799)
- Jakob Hermann discovered $|\vec{A}|$ (1710), recognized its relation to ϵ
- Johann Bernoulli generalized to $\vec{A}$ (1710)
- Hamilton "rediscovered" $\vec{A}$ as $\vec{A}/\mu k$ (~1850)

Pauli and the LRL vector in early QM:

- Used $\vec{A}$ to derive the spectrum of hydrogen (pre-SE!)
- Derived energy shifts in the presence of $\vec{E}$ and $\vec{B}$

Further readings (so fun):

- History: [1], [2], [3], [4], [5]
- "Discoveries" and application: [6], [7], [8], [9], [10], [11]

The Hydrogen Atom

The energy levels and wavefunctions for the bound states of hydrogen are gotten by solving the Schrödinger equation:

$$\left\{\frac{\hbar^2}{2m}\nabla^2 + \frac{e^2}{r}\right\}\psi = E\psi, \qquad E < 0.$$

With

$$\lambda = \frac{8}{a} \qquad \alpha^4 = -\frac{8E}{e^2 a}, \qquad a = \frac{\hbar^2}{\mu e^2}, \tag{1}$$

the SE becomes

$$\left\{4\nabla^2 + \frac{\lambda}{r} - \alpha^4\right\}\psi = 0. \tag{2}$$

Where are the harmonic oscillators?

Following [12], introduce coordinates $\zeta_A, \zeta_B \in \mathbb{C}$ and demand

$$x + iy = 2\zeta_A\overline{\zeta_B} \qquad\qquad z = \zeta_A\overline{\zeta_A} - \zeta_B\overline{\zeta_B}.$$

With this,

$$r = \sqrt{x^2 + y^2 + z^2} = \zeta_A\overline{\zeta_A} + \zeta_B\overline{\zeta_B}.$$

Note:

- Each pair (ζ_A, ζ_B) gives a unique point (x, y, z)
- Converse is true up to arbitrary but equal arguments of ζ_A, ζ_B

Where are the harmonic oscillators?

Let $\sigma = \arg(\zeta_A \zeta_B)$. Can write ζ_A, ζ_B in spherical coordinates:

$$\zeta_A = r^{1/2} e^{i(\sigma+\varphi)/2} \cos\frac{\theta}{2} \qquad \zeta_B = r^{1/2} e^{i(\sigma-\varphi)/2} \sin\frac{\theta}{2} \tag{3}$$

$\implies$ (x, y, z) determines (ζ_A, ζ_B) up to $e^{i\sigma}$.

With this, can show that

$$r\nabla^2\psi = (\partial_A \partial_{\bar{A}} + \partial_B \partial_{\bar{B}})\psi.$$

$\implies$ Can now write SE in terms of $\zeta_A, \zeta_B, \overline{\zeta_A}, \overline{\zeta_B}$.

Where are the harmonic oscillators?

SE in terms of $\zeta_A, \zeta_B, \overline{\zeta_A}, \overline{\zeta_B}$:

$$\left\{4\partial_A\partial_{\bar{A}} + 4\partial_B\partial_{\bar{B}} + \lambda - \alpha^4(\zeta_A\overline{\zeta_A} + \zeta_B\overline{\zeta_B})\right\}\psi = 0. \tag{4}$$

Since $\psi(x, y, z)$ independent of σ,

$$\frac{\partial\psi}{\partial\sigma} = 0 \quad \Longleftrightarrow \quad (\overline{\zeta}_A\partial_{\bar{A}} - \zeta_A\partial_A)\psi = -(\overline{\zeta}_B\partial_{\bar{B}} - \zeta_B\partial_B)\psi. \tag{5}$$

Together, (4) and (5) are equivalent to SE (2).

Where are the harmonic oscillators?

Let $\zeta_A = q_1 + iq_2$ and $\zeta_B = q_3 + iq_4$, then (4) is the equation for a 4D HO

$$[\partial_1^2 + \partial_2^2 + \partial_3^3 + \partial_4^2 + \lambda - \alpha^4(q_1^2 + q_2^2 + q_3^2 + q_4^2)]\psi = 0 \tag{6}$$

with frequency ω and energy ϵ given by (1):

$$\alpha^2 \equiv \sqrt{-\frac{8E}{e^2 a}} = \frac{\mu\omega}{\hbar} \qquad \lambda \equiv \frac{8}{a} = \frac{2\mu\epsilon}{\hbar}.$$

And the condition (5) becomes

$$(q_1\partial_2 - q_2\partial_1)\psi = -(q_3\partial_4 - q_4\partial_3)\psi. \tag{7}$$

$\Longrightarrow$ really two 2D HO's with equal and opposite angular momenta!

From harmonic oscillators to hydrogen

Separating variables $\psi = \psi(q_1, q_2)\psi(q_3, q_4)$,

$$[\partial_1^2 + \partial_2^2 + \lambda_A - \alpha^4(q_1^2 + q_2^2)]\psi_A = 0,$$

with $\lambda_A = 2\mu\epsilon_A/\hbar^2$. Solution for A:

$$\psi_{An_Am_A} = C_{n_Am_A}\left(\frac{\zeta_A}{\overline{\zeta_A}}\right)^{m_A/2}\left(\alpha^2\zeta_A\overline{\zeta_A}\right)^{|m_A|/2} e^{-\frac{\alpha^2\zeta_A\overline{\zeta_A}}{2}} L_{n_A+|m_A|}^{|m_A|}\left(\alpha^2\zeta_A\overline{\zeta_A}\right)$$

$n_A = 0, 1, 2, \ldots \quad m_A = 0, \pm 1, \pm 2, \ldots$

Energy: $\epsilon_{An_Am_A} = \hbar\omega(2n_A + |m_A| + 1) = \dfrac{\hbar^2\lambda_{An_Am_A}}{2\mu}$

Angular momentum: $L_{An_Am_A} = m_A\hbar$

Similar solution for B. $\lambda_A + \lambda_B = \lambda$ and $m_A = -m_B = m$ due to (7).

From harmonic oscillators to hydrogen

Full solution

$$\psi_{n_A n_B m} = \psi_{A n_A m}\left(\zeta_A, \overline{\zeta_A}\right)\psi_{B n_B - m}\left(\zeta_B, \overline{\zeta_B}\right).$$

Can relate this back to the hydrogen atom. From

$$\lambda = \lambda_A + \lambda_B = 4\alpha^2(n_A + n_B + |m| + 1) = \frac{8}{a}$$

can get energy in terms of n_A, n_B, m:

$$E = \frac{-\alpha^4 e^2 a}{8} = -\frac{\alpha^4 e^2}{\lambda} = \frac{-e^2}{2a(n_A + n_B + |m| + 1)^2} \equiv \frac{-e^2}{2aN^2}.$$

From harmonic oscillators to hydrogen

How about the wavefunctions? Going to parabolic coordinates (ξ, η, φ):

$$x = \sqrt{\xi\eta}\cos\varphi \qquad y = \sqrt{\xi\eta}\sin\varphi \qquad z = (\xi - \eta)/2$$
$$\Longleftrightarrow \xi = 2r\cos^2(\theta/2) = 2|\zeta_A|^2 \qquad \eta = 2r\sin^2(\theta/2) = 2|\zeta_B|^2.$$

we get

$$\psi_{n_A n_B m} = K_{n_A n_B m} e^{im\varphi} (\xi\eta)^{|m|/2} e^{-\frac{\alpha^2(\xi^2+\eta^2)}{4}} L^{|m|}_{n_A+|m|}\left(\frac{\alpha^2\xi}{2}\right) L^{|m|}_{n_B+|m|}\left(\frac{\alpha^2\eta}{2}\right).$$

These are simultaneous eigenfunctions of $\mathbf{H}$, $\mathbf{L}_z$, and $\mathbf{M}_z$ where

$$\mathbf{M} = \frac{1}{2\mu}(\mathbf{p}\times\mathbf{L} - \mathbf{L}\times\mathbf{p}) - \frac{e^2}{r}\mathbf{r}.$$

is the Laplace-Runge-Lenz operator, symmetrized by Pauli, 1926.

From harmonic oscillators to hydrogen

From how (ζ_A, ζ_B) is defined:

$$\mathbf{M}_z = \frac{e^2 a}{r}\left[|\zeta_B|^2 \partial_A \partial_{\bar{A}} - |\zeta_A|^2 \partial_B \partial_{\bar{B}} - \frac{1}{a}(|\zeta_A|^2 + |\zeta_B|^2)\right].$$

CSCO is $\{\mathbf{H}, \mathbf{L}_z, \mathbf{M}_z\}$ instead of $\{\mathbf{H}, \mathbf{L}^2, \mathbf{L}_z\}$. Eigenvalue equations:

$$\begin{aligned}
\mathbf{H}\psi_{n_A n_B m} &= \frac{-e^2}{2aN^2}\psi_{n_A n_B m} \\
\mathbf{L}_z \psi_{n_A n_B m} &= m\hbar \psi_{n_A n_B m} \\
\mathbf{M}_z \psi_{n_A n_B m} &= \frac{e^2(n_B - n_A)}{N}\psi_{n_A n_B m}.
\end{aligned}$$

Aside: Quantum numbers

- $\{\mathbf{H}, \mathbf{M}_z, \mathbf{L}_z\}$ and $\{\mathbf{H}, \mathbf{L}^2, \mathbf{L}_z\}$ are CSCO, but:

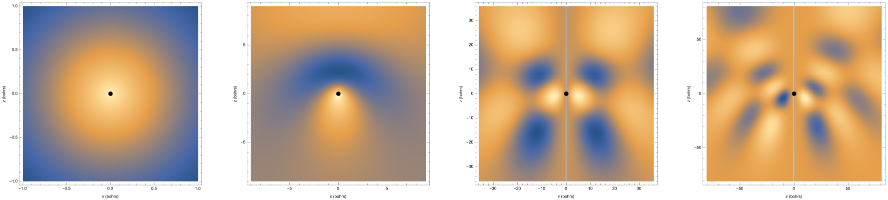
$$[\mathbf{M}_z, \mathbf{L}^2] \neq 0, \qquad [\mathbf{M}_z, \mathbf{M}^2] \neq 0, \qquad [\mathbf{M}^2, \mathbf{H}] = [\mathbf{M}^2, \mathbf{L}^2] = [\mathbf{M}^2, \mathbf{L}_z] = 0.$$

- $\{\psi_{nlm}\}$ are also eigenfunctions of $\mathbf{M}^2$. Nothing new here.
- $\{\psi_{n_A n_B m}\}$ simultaneously diagonalize CSCO $\{\mathbf{H}, \mathbf{L}_z, \mathbf{M}_z\}$.
- m is the magnetic quantum number
- $N = n_A + n_B + |m| + 1$ is the principal quantum number

Aside: Hydrogen wavefunctions in parabolic coordinates

What do eigenfunctions of $\mathbf{M}_z$ look like?

$$\psi_{n_A n_B m} = K_{n_A n_B m} e^{im\varphi} (\xi\eta)^{|m|/2} e^{-\frac{\alpha^2(\xi^2+\eta^2)}{4}} L^{|m|}_{n_A+|m|}\left(\frac{\alpha^2\xi}{2}\right) L^{|m|}_{n_B+|m|}\left(\frac{\alpha^2\eta}{2}\right).$$



$(0,0,0)$ $(2,0,0)$ $(2,1,2)$ $(4,1,3)$

Figure: $|\psi_{n_A n_B m}(x,0,z)|^2$ for different values of (n_A, n_B, m)

Shouldn't the correspondence be classical?

Following [13]

Something deeper?

Lie group theory, deeper stuff comes from Chapter 14 of Gilmore [14]

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Extra: $(x, y, z) \to (\zeta_A, \zeta_B)$

Extra: Parabolic coordinates