The Hydrogen Atom and Harmonic Oscillator(s)

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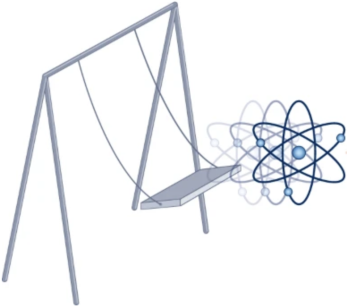
Harmonic oscillator universe?



Harmonic oscillator in physics:

- Hooke's law
- QHO
- Einstein solid
- Atom-radiation interaction
- 2nd quantization of EM fields
- QFT
- ...

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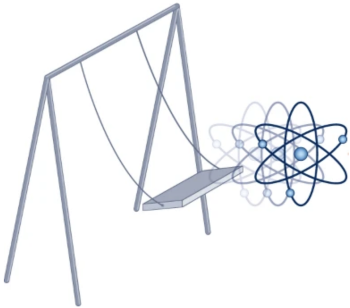

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- ...
- Gravity? Inverse-square law?

Coulomb-Kepler problem revisited

A particle in a central potential $V(r) = -k/r$:

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

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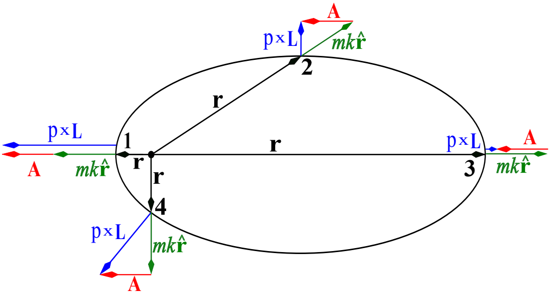
Constants of motion: H, $\vec{L} = \vec{r} \times \vec{p}$, and $\vec{A}$, the Laplace-Runge-Lenz vector:

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

Brief review:



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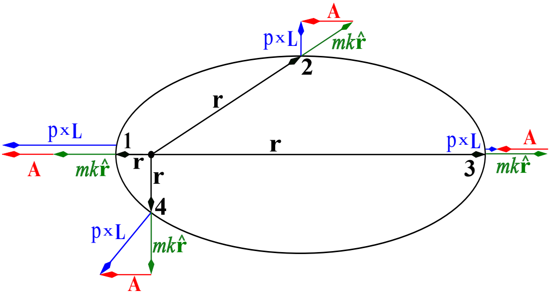

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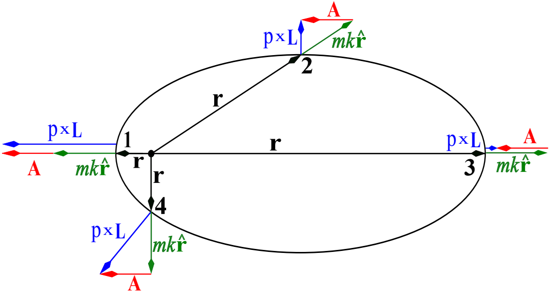

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$$\frac{1}{r} = \frac{mk}{L^2} (1 + \epsilon \cos \theta), \quad \text{eccentricity } \epsilon = \frac{A}{|mk|} = \sqrt{1 + \frac{2EL^2}{mk^2}} \geq 0$$

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

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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:

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

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With

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

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

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

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

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 $\sigma = 2\arg(\zeta_A) = 2\arg(\zeta_B)$. 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 $e^{i\sigma}$.

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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 $\zeta_A, \zeta_B, \overline{\zeta_A}, \overline{\zeta_B}$.

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

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

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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

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

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

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

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Condition (5) becomes

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

(6)+(7) : 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 $\lambda_A = 2m\epsilon_A/\hbar^2$.

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

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

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

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

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

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

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Can relate this back to the hydrogen atom.

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

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?

From harmonic oscillators to hydrogen

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

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

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we get

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

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

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

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

From harmonic oscillators to hydrogen

From how (ζ_A, ζ_B) is defined:

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

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

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

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\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}$$

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

Aside: Hydrogen wavefunctions in parabolic coordinates

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

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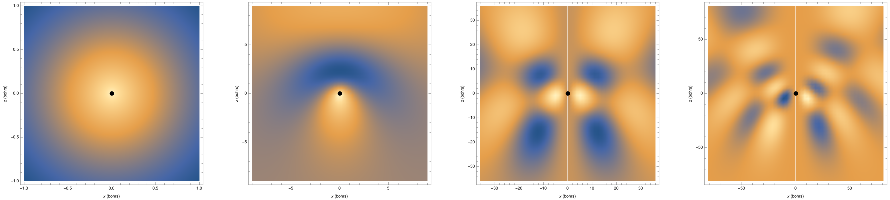

$(0,0,0)$ $(2,0,0)$ $(2,1,2)$ $(4,1,3)$

Figure: $|\psi_{n_A n_B m}(x,0,z)|^2$ for different values of (n_A, n_B, m) [13]

Shouldn't the correspondence be classical?

Following [14], use the Kustaanheimo-Stiefel transformation $S : \mathbb{R}^4 \to \mathbb{R}^3$:

$$\begin{aligned} x_1 &= 2(s_1 s_3 - s_2 s_4) \\ x_2 &= 2(s_1 s_4 + s_2 s_3) \\ x_3 &= s_1^2 + s_2^2 - s_3^2 - s_4^2 \end{aligned}$$

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Constraint on velocities: $s_2 \dot{s}_1 - s_1 \dot{s}_2 - s_4 \dot{s}_3 + s_3 \dot{s}_4 = 0$

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The equivalence: With $4|E| = m\omega^2/2$ and $\epsilon = 4k$,

$$\frac{1}{2}mv^2 - \frac{k}{r} = -|E| \quad \longrightarrow \quad \frac{1}{2}m\dot{s}^2 + \frac{1}{2}m\omega^2 s^2 = \epsilon \quad \text{(4D H.O.)}$$

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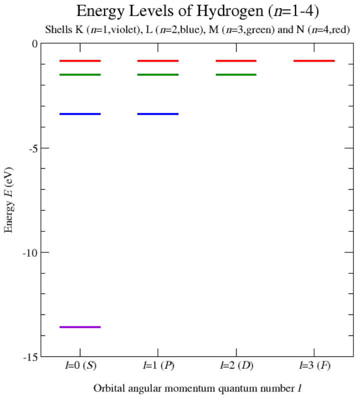
$\implies$ Two coupled 2D H.O.'s with equal angular momenta

Something deeper?

Symmetry implies degeneracy. $[\mathbf{M}, \mathbf{H}] = 0$ explains the n^2 degeneracy in H.



More info: SO(4) symmetry of H, etc. See Chapter 14 of [15].

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