Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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Layout

Fourier Analysis

- Examine Fourier series, example and apply to application

Discrete Fourier Transform & Fast Fourier Transform

- Define the operation, examine why complex numbers simplify and look at a FFT method

Instrument

- Understand what mass spectrometer is, the physics involved and how ICR is different

EJS Model

Conclusion

Fourier Series & Coefficients

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$$a_0 = \frac{1}{2\pi} \int_{-\pi}^{\pi} f(x)\, dx$$

$$a_n = \frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \cos(nx)\, dx \qquad \text{for } n = 1, 2, 3, \ldots,$$

$$b_n = \frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \sin(nx)\, dx \qquad \text{for } n = 1, 2, 3, \ldots,$$

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$$a_n = \frac{1}{\pi}\int_{-\pi}^{\pi} x\cos(nx)\,dx = \left.\frac{\cos(nx)}{n^2\pi} + \frac{x\sin(nx)}{n\pi}\right]_{-\pi}^{\pi} = 0$$

$$b_n = \frac{1}{\pi}\int_{-\pi}^{\pi} x\sin(nx)\,dx = \left.\frac{\sin(nx)}{n^2\pi} - \frac{x\cos(nx)}{n\pi}\right]_{-\pi}^{\pi}$$

$$= \frac{\cos(n\pi)}{n} - \frac{\cos(-n\pi)}{n} = -\frac{2}{n}\cos(n\pi) = \frac{2}{n}(-1)^{n+1}$$

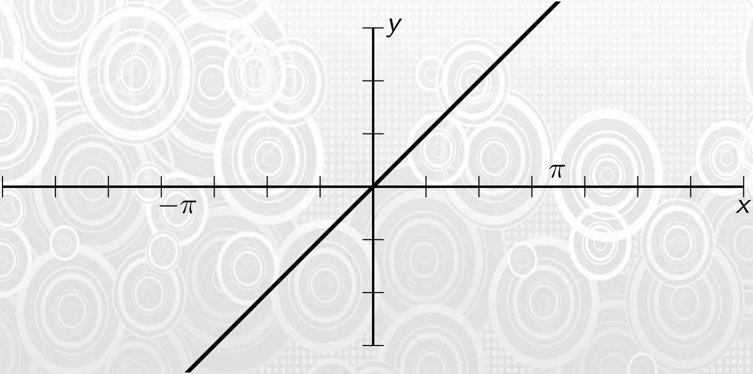
Example Cont.

Therefore the Fourier series of $f(x) = x$ on $[-\pi, \pi]$ is

$$\sum_{n=1}^{\infty} \frac{2}{n}(-1)^{n+1} \sin(nx).$$

Graph

Figure: Graph of Fourier Series for $f(x) = x$ with $f(x)$ black and the Fourier series $n = 1$, $n = 3$ and $n = 5$ in colors red, green, blue respectively.



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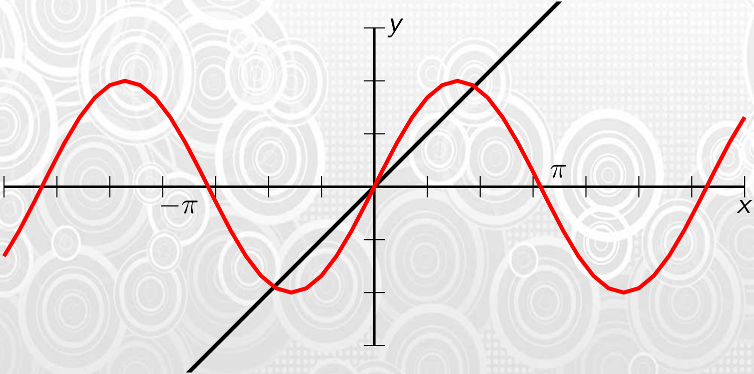

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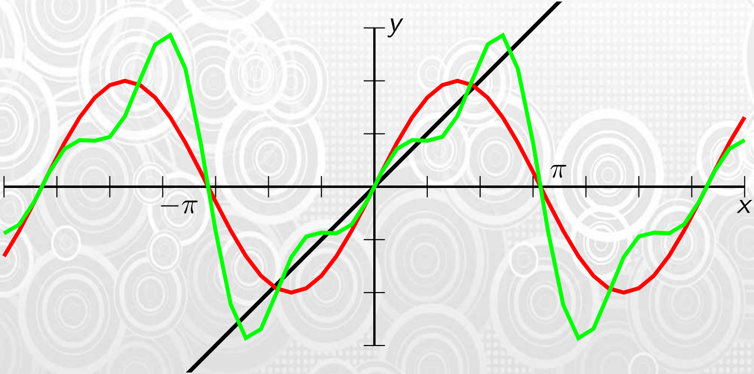

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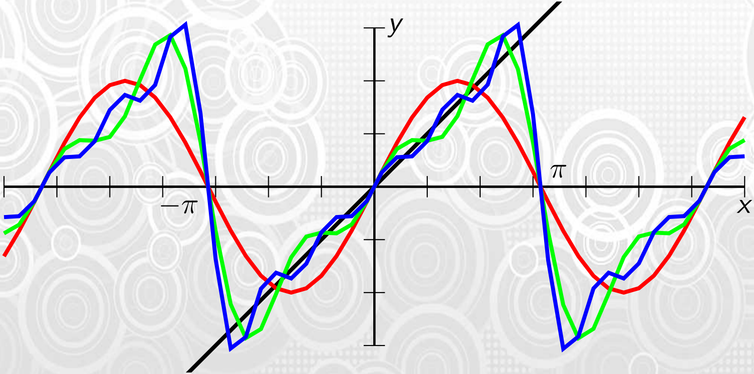

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FT-ICR Discrete time voltage signal

Discrete because...

- sampled periodically
- stored digitalized

$$f(t) \propto \sum_{i=1}^{M} N_i \; e^{\frac{-t}{\tau_i}} \; \cos(\omega_i \, t + \phi_i)$$

Discrete Fourier Transform

The DFT of a n point polynomial is $DFT_n(a) = y$ such that

$$y_k = \sum_{j=0}^{n-1} a_k (w_n^k)^j \qquad \forall\ k \in \mathbb{Z} : 0 \leq k < n$$

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Function of mathematical operation:

- Time Domain ⇔ Frequency Domain
- Point-value form ⇔ Coefficent form

Complex n^{th} root of unity

Let's look at an example:

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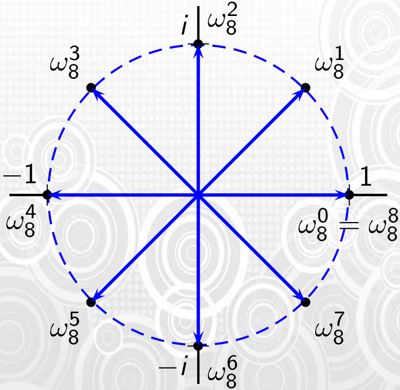
ω_n is called the

principal n^{th} root of unity



Fast Fourier Transform

- Cooley-Turkey FFT
- Divide-and-conquer
  1. Divide into two separate DFTs
  2. Repeat until left with DFT_2

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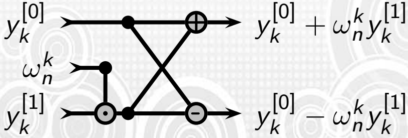

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A FFT Algorithm

$half \leftarrow n/2;\ gap \leftarrow n/2$
while $gap > 0$ **do**
  $i \leftarrow 0;\ j \leftarrow 0;\ p \leftarrow 0$
  while $i < half$ **do**
    repeat
      $new[i] \leftarrow cur[j] + omega[p] \cdot cur[j + gap]$
      $new[i + half] \leftarrow cur[j] - omega[p] \cdot cur[j + gap]$
      $i \leftarrow i + 1;\ j \leftarrow j + 1$
    until $j \bmod gap = 0$
    $j \leftarrow j + gap;\ p \leftarrow p + gap$
  end while
  swap(cur, new)
  $gap \leftarrow gap/2$
end while

Physics

Newton's 2^{nd} law of motion:

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Ion Acceleration:

$$\frac{d\vec{v}}{dt} = \frac{q}{m}[\vec{E} + (\vec{v} \times \vec{B})]$$

Mass Spectrometry

- Analytical technique for measuring mass-to-charge ratio of charged particles
- FT-ICR technique was first published in 1974 [Comisarow]

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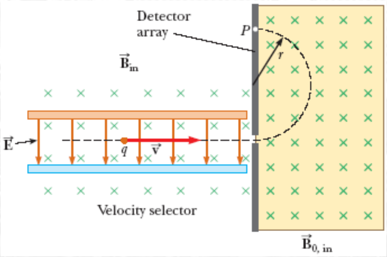


Figure: Sector mass analyzer with velocity selector

Cubic Ion Trap

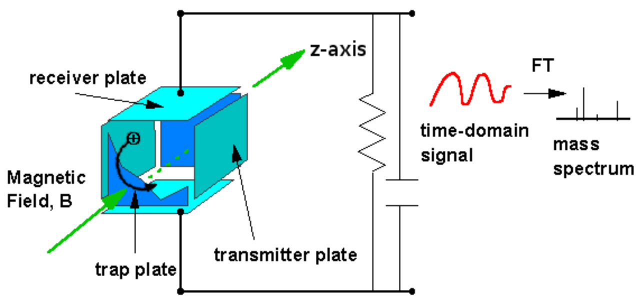
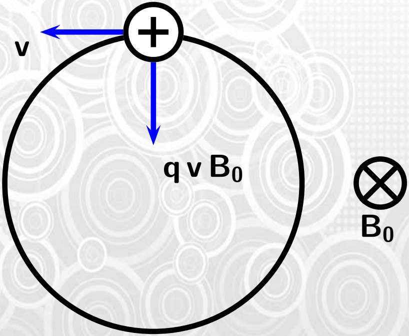


Figure: Diagram of FT-ICR Mass Spectrometer. [http://www.chem.ucsb.edu/˜devries/groupsite/labicr.htm]

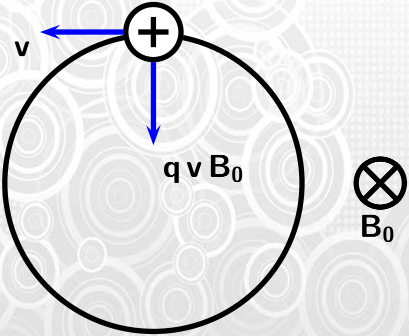
Ion Cyclotron Motion

Perspective of x-y plane



Ion Cyclotron Motion

Perspective of *x*-*y* plane



Ion cyclotron frequency

$$\boxed{\omega = \frac{q\,B_0}{m}}$$

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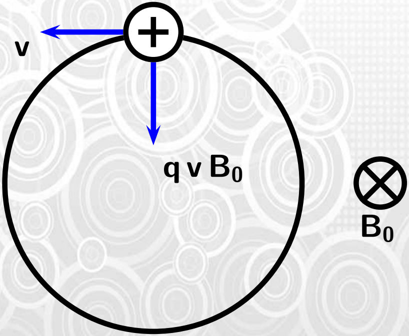


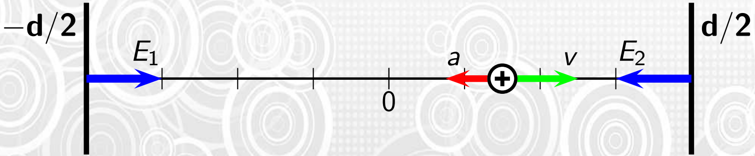
Ion cyclotron frequency

$$\boxed{\omega = \frac{q\,B_0}{m}}$$

- Unique frequency ω for every $\frac{m}{q}$
- Independent of initial velocity

Trapping oscillation

Perspective of z-axis



Electric Field in Z-direction:

$$E(z) = -k\,z \qquad \text{where} \qquad k = \frac{4V_t}{d^2}$$

Excitation & Detection

Excitation of specific ion:

$$E(t) = E_0 \cos(\omega_0\, t)\, y$$

Detected potential voltage:

$$\frac{1}{\frac{d}{2} - x} - \frac{1}{\frac{d}{2} + x}$$

Easy Java Simulations

- Free tool to generate Java Simulations
- Built-in ODE editor and solvers

$$\frac{dv_x}{dt} = \frac{q}{m}[\cancel{E_x} + (v_y B_z - \cancel{v_z B_y})]$$
$$\frac{dv_y}{dt} = \frac{q}{m}[E_y + (\cancel{v_z B_x} - v_x B_z)]$$
$$\frac{dv_z}{dt} = \frac{q}{m}[E_z + (\cancel{v_x B_y} - \cancel{v_y B_x})]$$

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Question