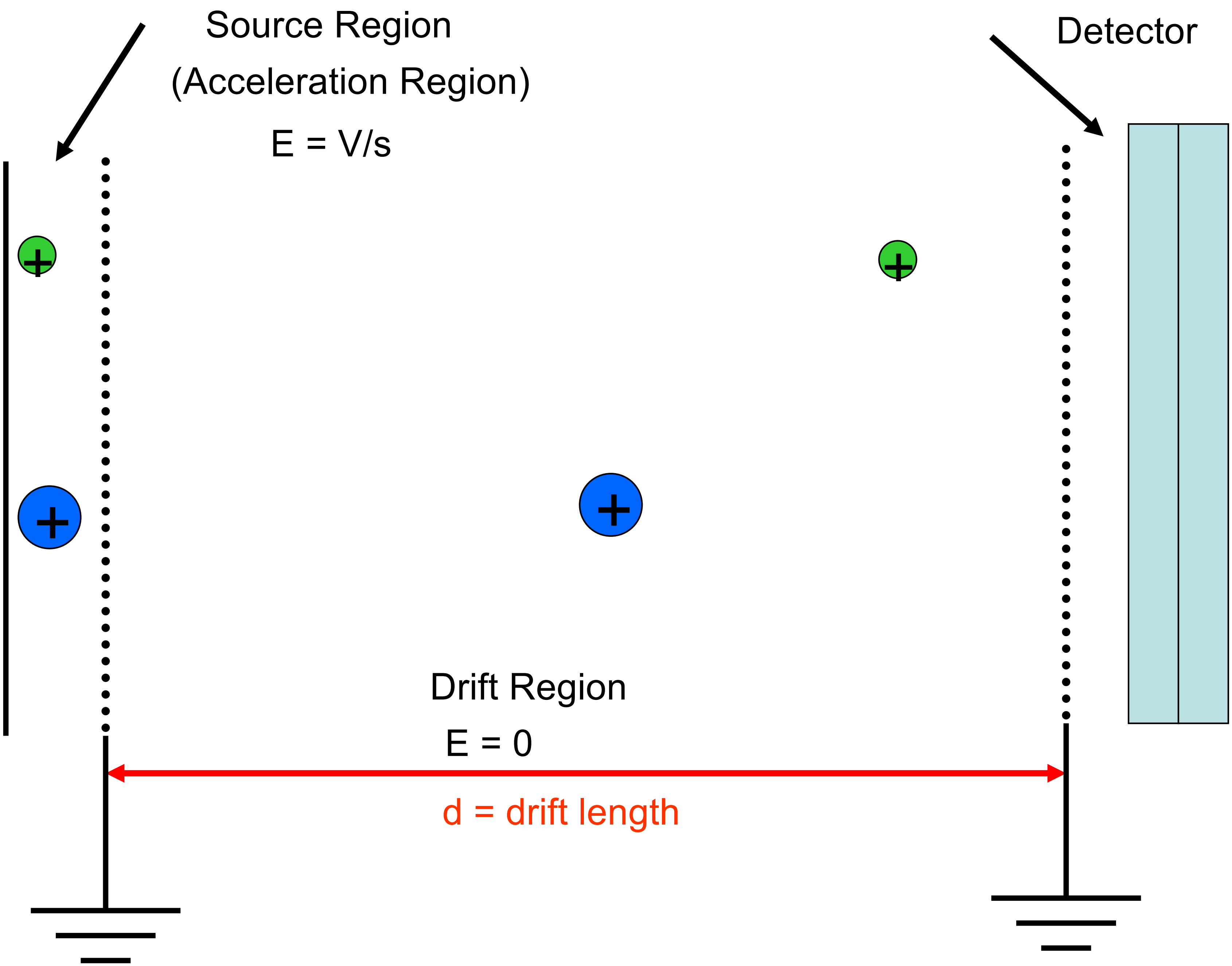
Time of Flight

Mathematical Derivations


Source Region
(Acceleration Region)
E = V/s
Detector
Drift Region
E = 0
d = drift length

Equations for Simplest TOF (CEA)

Constant Energy Acceleration

$$eV = \frac{1}{2}mv^2$$

Kinetic Energy given to the Ion in the Source Region

$$v = \left(\frac{2eV}{m}\right)^{\frac{1}{2}}$$

Solving for Velocity

$$v = \frac{d}{t}$$

Solve for Flight Time

$$t = \left(\frac{m}{2eV}\right)^{\frac{1}{2}} d$$

So, with a constant acceleration voltage and a known drift length, the drift time is proportional to the square root of the mass to charge ratio (m/e).

The prior equation is only good for ions that are formed the same distance from the backing plate, but if the ions are formed at different locations within the source region the equation must be modified.

Time in the source region (t_s) must be added to the time in the drift region (t_d).

$$t = t_s + t_d$$

Let s = the location of the ion within the source region.

$$E = \frac{V}{s}$$ So, $$V = Es$$

Now the Field (E) is constant, but the voltage (V) depends on s.

So, in the source region

$$v = \frac{dt}{ds}$$ and $$v = \left(\frac{2eEs}{m} \right)^{\frac{1}{2}}$$

Integrate,

$$\int_0^{t_s} dt = \int_0^{s} \left(\frac{m}{2eE}\right)^{\frac{1}{2}} \frac{ds}{s^{\frac{1}{2}}}$$

So, $$t_s = \left(\frac{m}{2eE}\right)^{\frac{1}{2}} 2s^{\frac{1}{2}}$$

In the drift region:

$$t_d = \left(\frac{m}{2eEs}\right)^{\frac{1}{2}} d$$

We rearrange t_s :

$$t_s = \left(\frac{m}{2eEs}\right)^{\frac{1}{2}} 2s$$

And the combined drift equation is:

$$t = t_s + t_d = \left(\frac{m}{2eEs}\right)^{\frac{1}{2}} \left[2s + d\right]$$

The drift time shows the same square root of m/e dependence.

Mass Resolution

Mass spectrometrists define resolution as: $$\frac{m}{\Delta m}$$

In TOF we start from the drift time equation:

$$m = \left(\frac{2eV}{d^2}\right)t^2$$

And the derivative is:

$$dm = \left(\frac{2eV}{d^2}\right)2tdt$$

So,

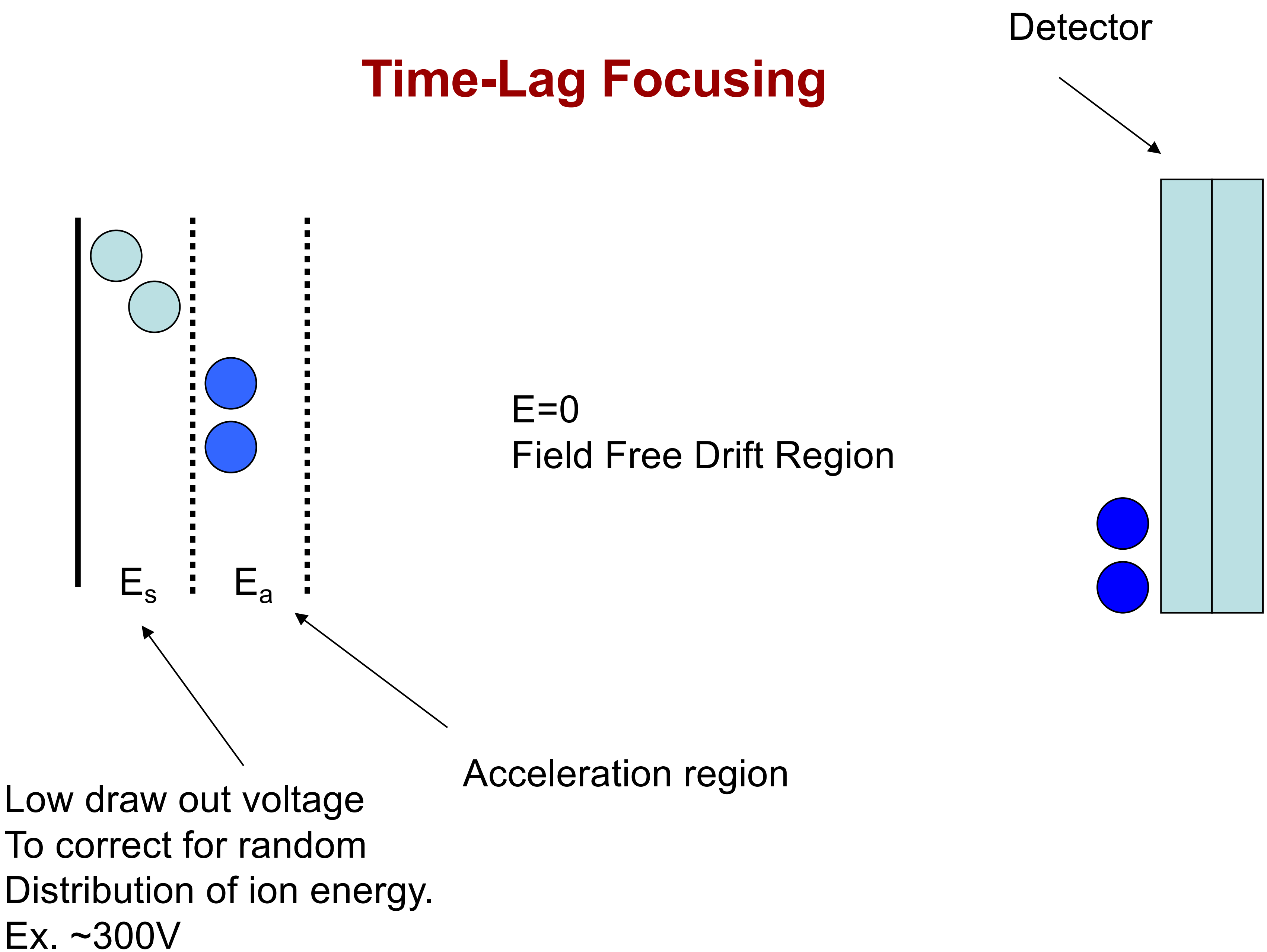
$$\frac{m}{dm} = \frac{t}{2dt}$$

So time-of-flight resolution is defined by:

$$\frac{m}{\Delta m} = \frac{t}{2\Delta t}$$

Δt is usually defined a peak width at half height.

Time-Lag Focusing



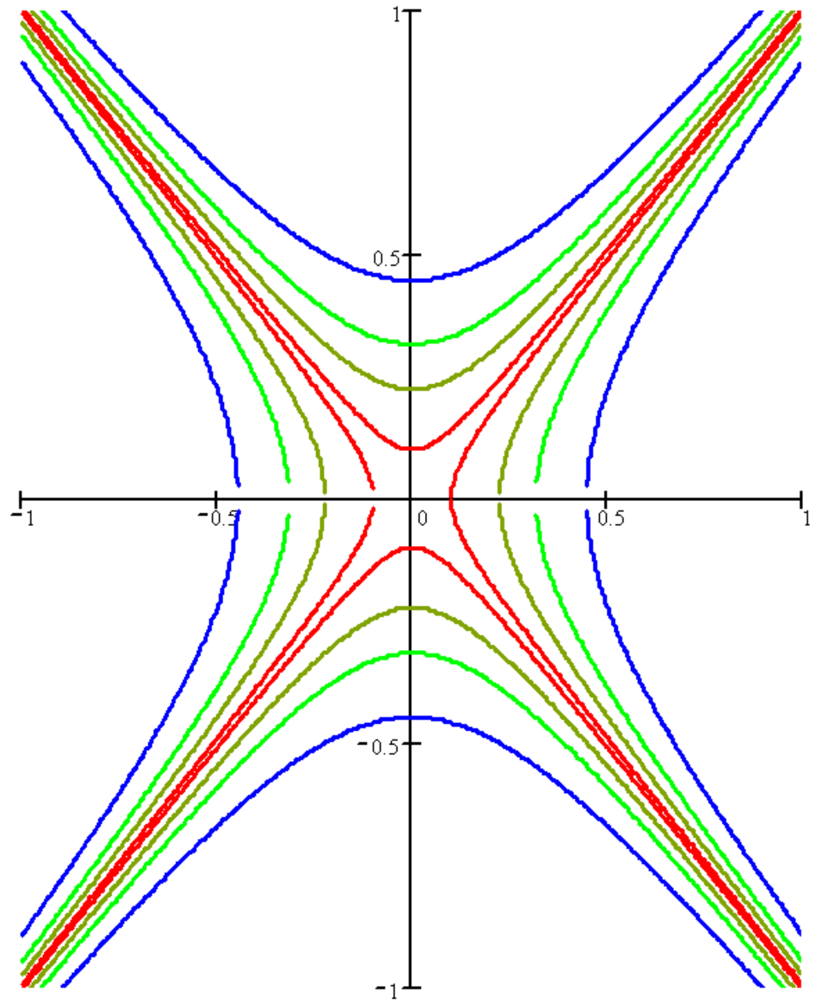
Divergance("del" operator)

$$\nabla = \left(\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \right)$$

The Leplacian ("del squared")

$$\nabla^2 = \left(\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \right) \bullet \left(\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \right)$$

$$= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$



The equipotential field plot

The Quadrupole Field (ideal, no space charge effects):

The potential at any point (x,y,z) is defined as:

$$\phi = \frac{\phi_o}{r_o^2}(\lambda x^2 + \sigma y^2 + \gamma z^2)$$

Where,

ϕ_o= the applied field

λ, σ, γ are weighing constants for their coordinate

r_o= constant for the device

The applied field is the combination of a RF and DC (U) field:

$$\phi_o = U - V\cos(\Omega t)$$

V= 0 to Peak
Ω (rad/s) = 2πf(Hz)

Conditions must be defined within the confines of the Laplace eq.:

$$\nabla^2 \phi = 0$$

Functions that satisfy the Laplace Equation are harmonic!

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = 0$$

What functions can be used? Electrostatic Potential in a Charge-Free Region, Steady-State Temperature, or Gravitational Potential without Matter.

Evaluating each of the partial derivatives:

$$\frac{\partial^2 \phi}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{\partial}{\partial x}\left(\frac{\phi_o}{r_o^2}\lambda x^2\right)\right)$$

$$\frac{\partial^2 \phi}{\partial x^2} = \frac{\phi_o}{r_o^2} 2\lambda$$

$$\frac{\partial^2 \phi}{\partial x^2} = \frac{\phi_o}{r_o^2} 2\lambda \qquad \frac{\partial^2 \phi}{\partial y^2} = \frac{\phi_o}{r_o^2} 2\sigma$$

$$\frac{\partial^2 \phi}{\partial z^2} = \frac{\phi_o}{r_o^2} 2\gamma$$

Plugging back into the Laplace eq.:

$$\nabla^2 \phi = \frac{\phi_o}{r_o^2} 2(\lambda + \sigma + \gamma) = 0$$

All quadrupole devices must conform to the below constraints:

$$\lambda + \sigma + \gamma = 0$$

Or the trivial solution:

$$\phi_o = 0$$

The Force (F) can be solved in any direction:

$$F = ma = -eE$$

$$F_x = m\frac{d^2x}{dt^2} = -e\frac{\partial\phi}{\partial x}$$

$$\frac{\partial\phi}{\partial x} = \frac{2\lambda x}{r_o^2}\left(U - V\cos(\Omega t)\right)$$

$$F_x = m\frac{d^2x}{dt^2} = \frac{-2\lambda ex}{r_o^2}\left(U - V\cos(\Omega t)\right)$$

Equations for motion can be determined from the Force eq.:

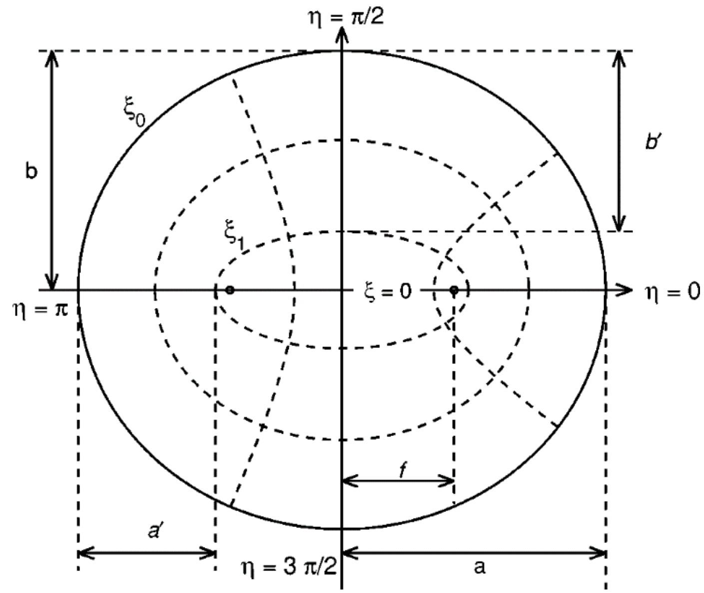
$$\frac{d^2 x}{dt^2} + \frac{-2\lambda e}{r_o^2 m}\left(U - V\cos(\Omega t)\right)x = 0$$

$$\frac{d^2 y}{dt^2} + \frac{-2\sigma e}{r_o^2 m}\left(U - V\cos(\Omega t)\right)y = 0$$

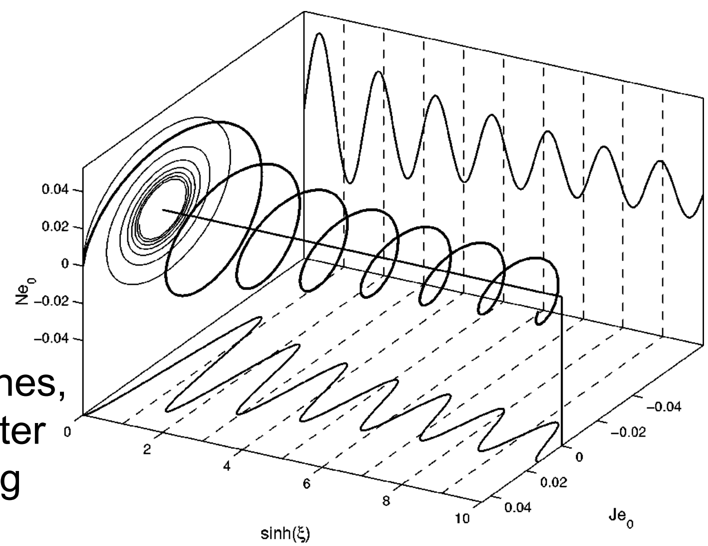
$$\frac{d^2 z}{dt^2} + \frac{-2\gamma e}{r_o^2 m}\left(U - V\cos(\Omega t)\right)z = 0$$

How do we solve this second order DE?

Mathieu's Function



$$\frac{d^2u}{d\xi^2} + (a_u - 2q_u \cos 2\xi)u = 0$$



"Mathieu equations occur in two main categories of physical problems. First, in applications involving elliptic geometries, for example in the analysis of the vibrating modes in elliptic membranes, the propagating modes in elliptic pipes, and the oscillations of water in a lake of elliptic shape. Mathieu equations arise after separating the wave equation using elliptic coordinates. Second, Mathieu equations arise in problems involving periodic motion, such as the trajectory of an electron in a periodic array of atoms, the mechanics of the quantum pendulum, and the oscillations of floating vessels."

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Mathieu's Equation (canonical form), solutions to the second order differential equations of the form:

$$\frac{d^2u}{d\xi^2} + (a_u - 2q_u \cos 2\xi)u = 0$$

Our equation of motion can fit the Mathieu form, where:

$$\xi = \frac{\Omega t}{2} \qquad \frac{d^2}{dt^2} = \frac{\Omega^2}{4}\frac{d^2}{d\xi^2}$$

$$a_x = \frac{8\lambda e U}{m r_o^2 \Omega^2} \qquad q_x = \frac{4e\lambda V}{m r_o^2 \Omega^2}$$

Similarly with y.

Quadrupole Field:

Linear Quads

$$\phi = \frac{\phi_o}{r_o^2}(\lambda x^2 + \sigma y^2 + \gamma z^2)$$

We remember the constraints from the Laplace eq.:

$$\lambda + \sigma + \gamma = 0$$

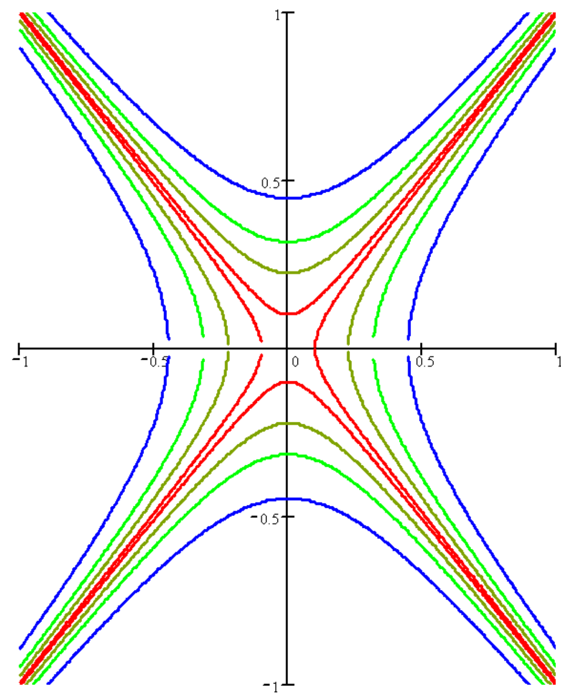
If we are only interested in quadrupole MS (x,y) then:

$$\gamma = 0$$

$$\lambda = -\sigma$$

If we set λ=1, then:

$$\phi = \frac{\phi_o}{r_o^2}(x^2 - y^2)$$

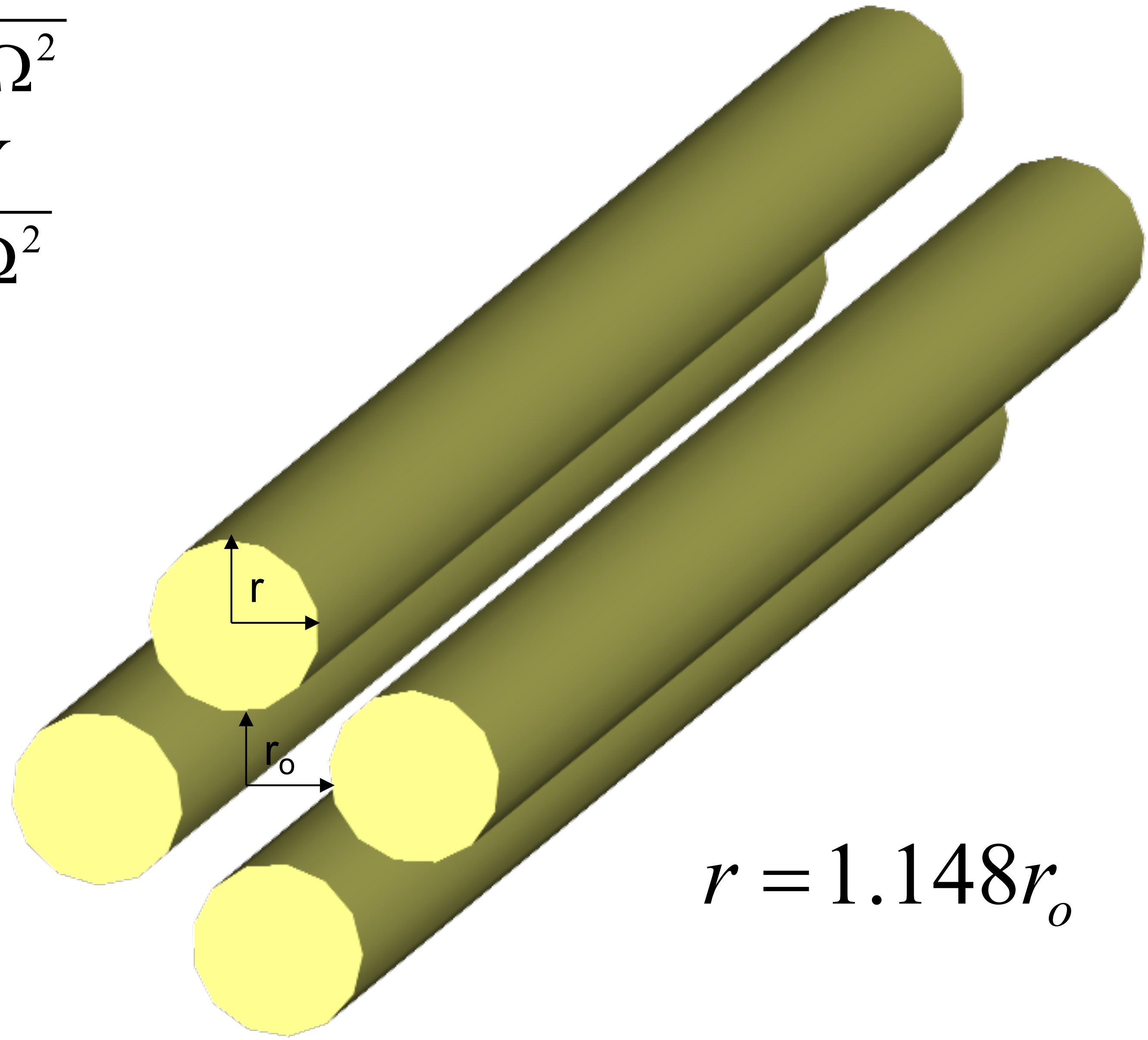


The equipotential field plot

Linear Quads

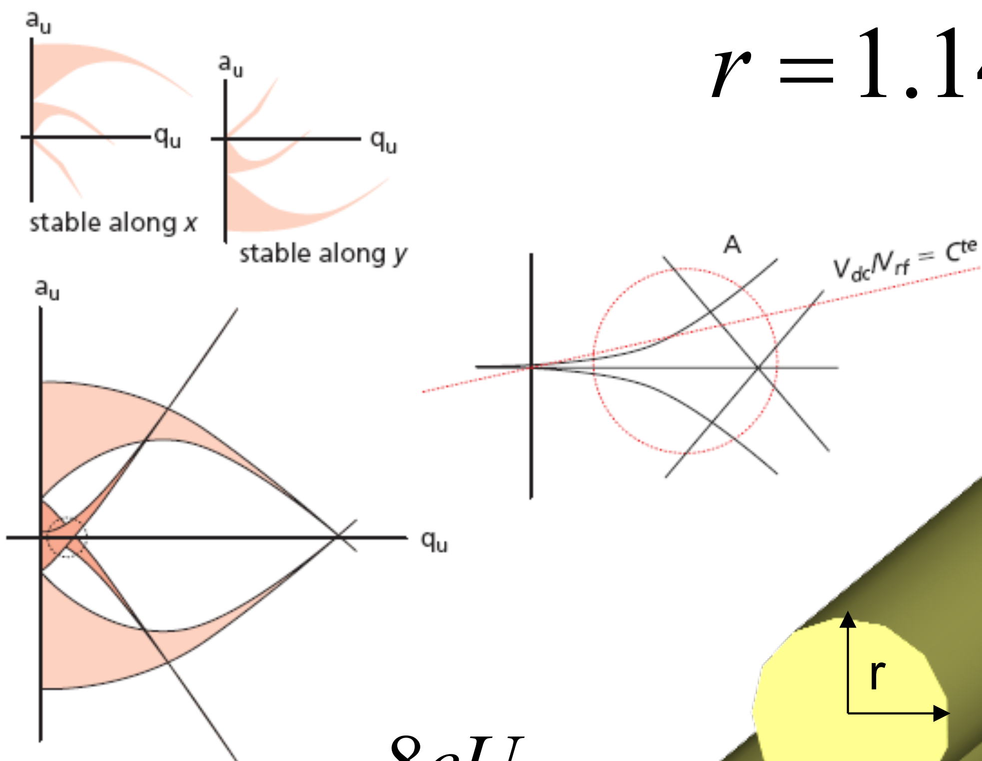
$$a_x = -a_y = \frac{8eU}{mr_o^2\Omega^2}$$

$$q_x = -q_y = \frac{4eV}{mr_o^2\Omega^2}$$

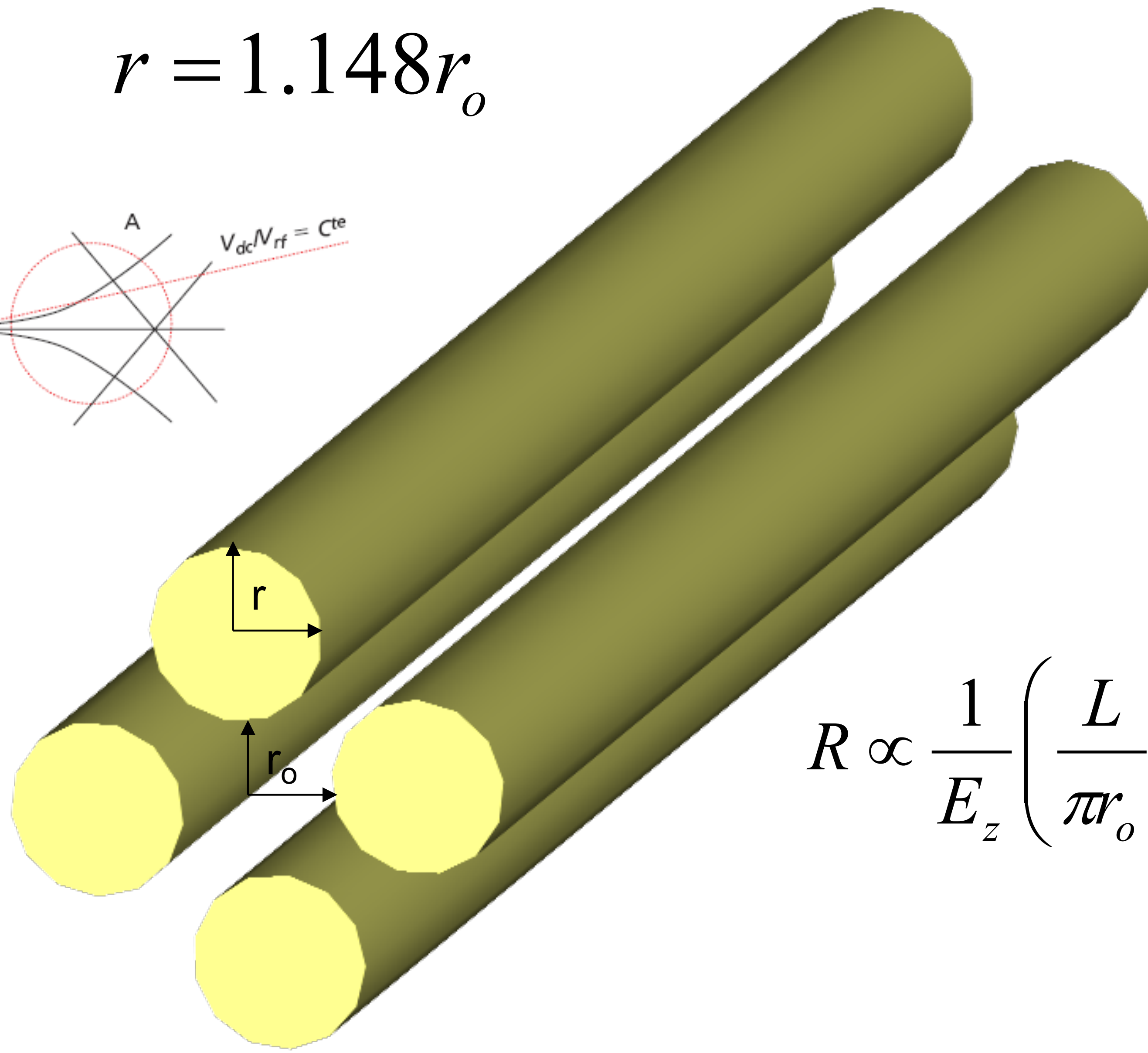


$$r = 1.148 r_o$$

Linear Quads



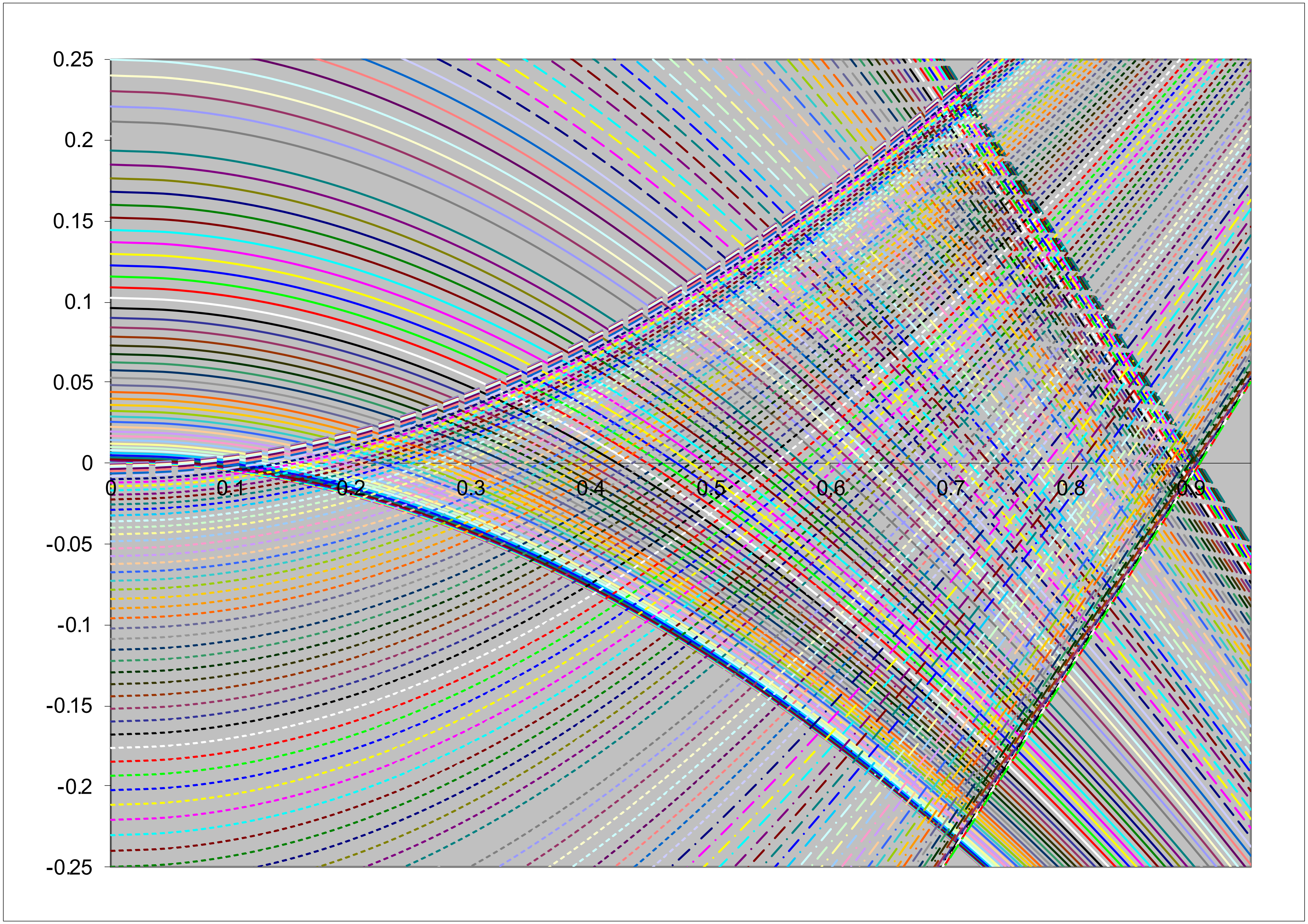
$$r = 1.148 r_o$$

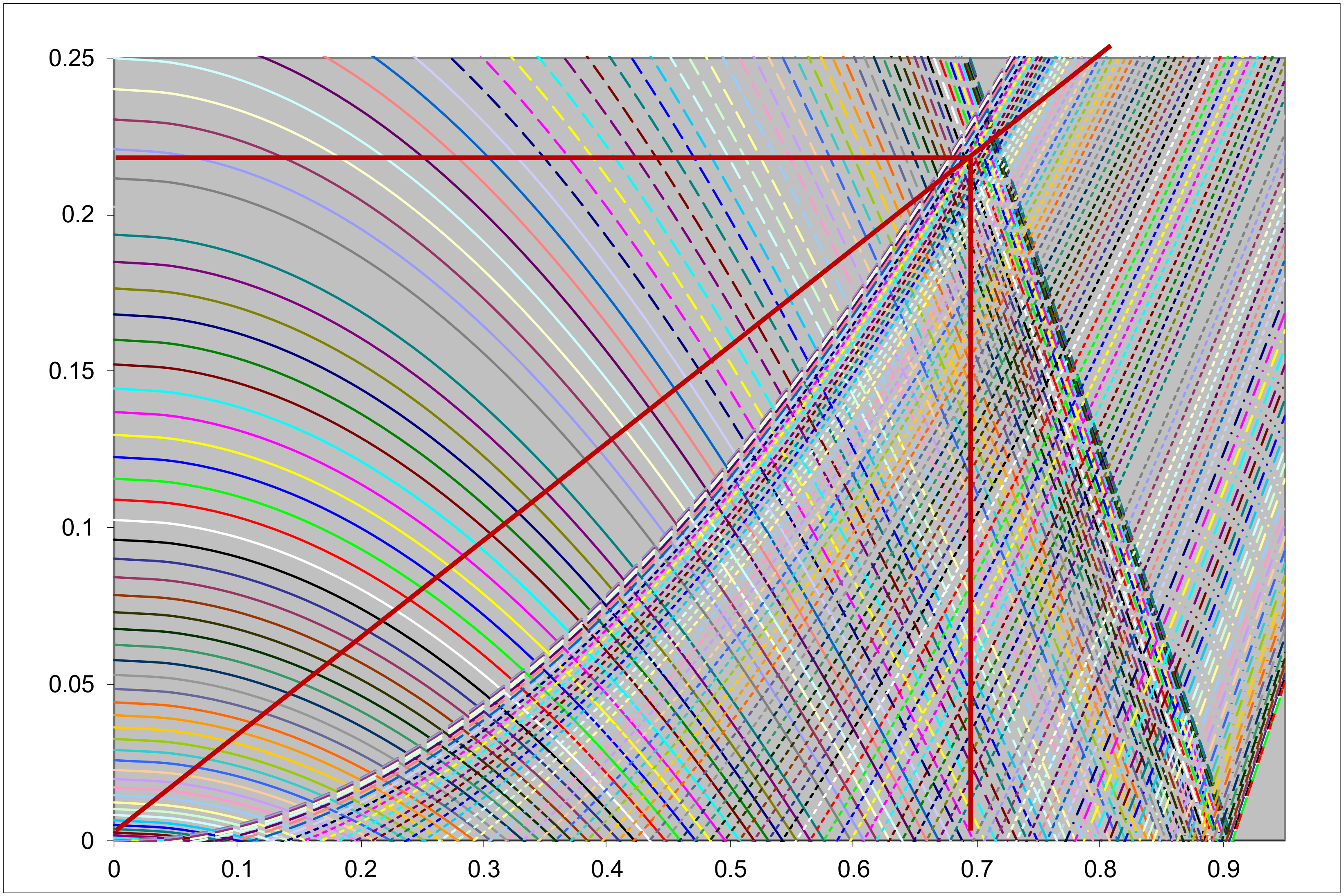


$$a_x = -a_y = \frac{8eU}{m r_o^2 \Omega^2}$$

$$q_x = -q_y = \frac{4eV}{m r_o^2 \Omega^2}$$

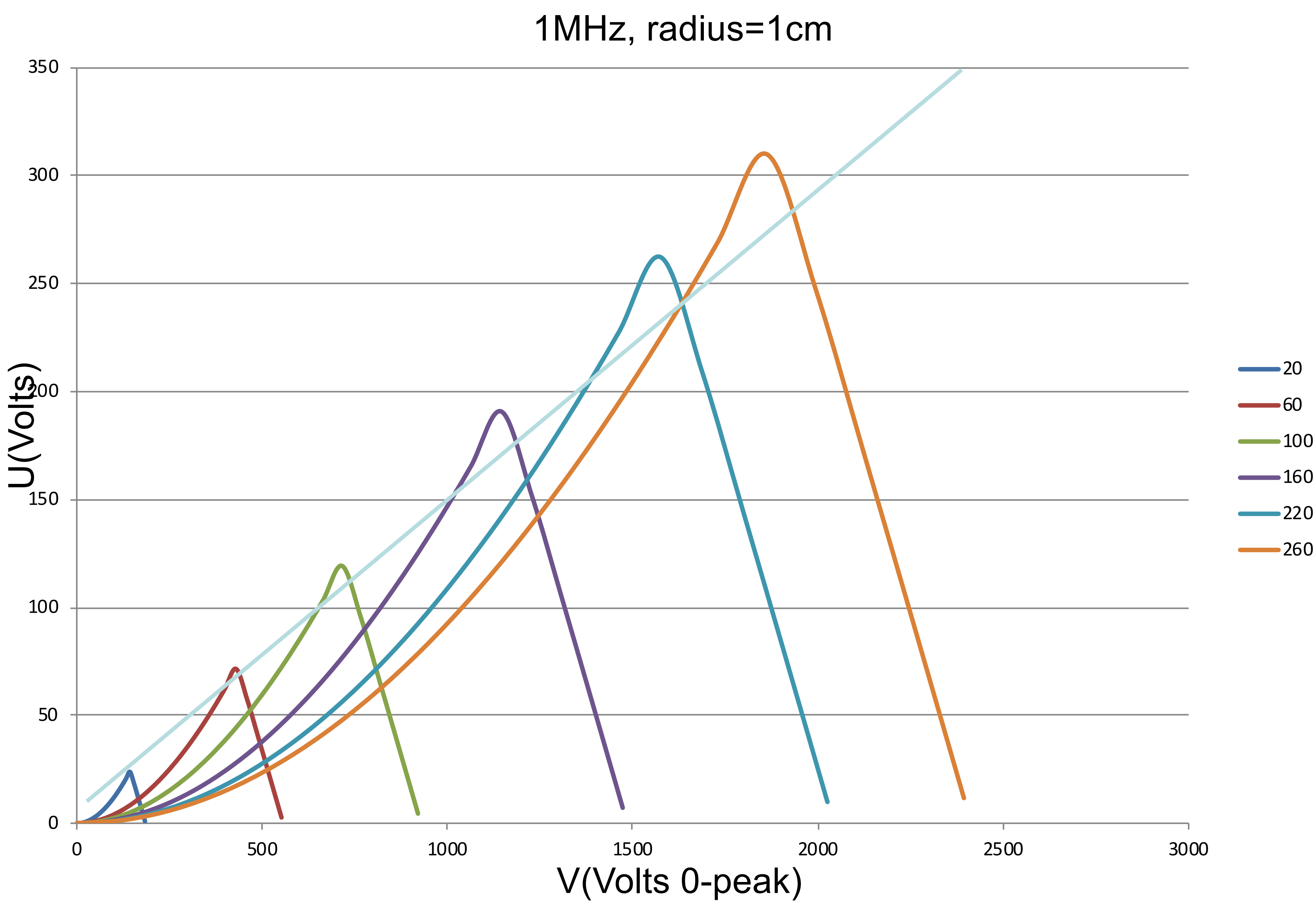
$$R \propto \frac{1}{E_z}\left(\frac{L}{\pi r_o}\right)^2$$


0.25
0.2
0.15
0.1
0.05
0
-0.05
-0.1
-0.15
-0.2
-0.25
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9



0.25
0.2
0.15
0.1
0.05
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9

r1		0.01 m		
Omega		700000 Hz		4397400
e		1.60E-19 C		
a		0.217		
q		0.695		
m/z	m	U	V	
	10	1.66058E-26	5.44E+00	3.48E+01
	15	2.49087E-26	8.15E+00	5.22E+01
	20	3.32116E-26	1.09E+01	6.96E+01
	25	4.15144E-26	1.36E+01	8.71E+01
	30	4.98173E-26	1.63E+01	1.04E+02
	35	5.81202E-26	1.90E+01	1.22E+02
	40	6.64231E-26	2.17E+01	1.39E+02
	45	7.4726E-26	2.45E+01	1.57E+02
	50	8.30289E-26	2.72E+01	1.74E+02
	55	9.13318E-26	2.99E+01	1.92E+02
	60	9.96347E-26	3.26E+01	2.09E+02
	65	1.07938E-25	3.53E+01	2.26E+02
	70	1.1624E-25	3.81E+01	2.44E+02
	75	1.24543E-25	4.08E+01	2.61E+02
	80	1.32846E-25	4.35E+01	2.79E+02
	85	1.41149E-25	4.62E+01	2.96E+02
	90	1.49452E-25	4.89E+01	3.13E+02
	95	1.57755E-25	5.16E+01	3.31E+02
	100	1.66058E-25	5.44E+01	3.48E+02
	105	1.74361E-25	5.71E+01	3.66E+02
	110	1.82664E-25	5.98E+01	3.83E+02
	115	1.90966E-25	6.25E+01	4.00E+02
	120	1.99269E-25	6.52E+01	4.18E+02
	125	2.07572E-25	6.80E+01	4.35E+02
	130	2.15875E-25	7.07E+01	4.53E+02
	135	2.24178E-25	7.34E+01	4.70E+02
	140	2.32481E-25	7.61E+01	4.88E+02


1MHz, radius=1cm
350
300
250
200
150
100
50
0
U(Volts)
0
500
1000
1500
2000
2500
3000
V(Volts 0-peak)
20
60
100
160
220
260

Quad Ion Traps

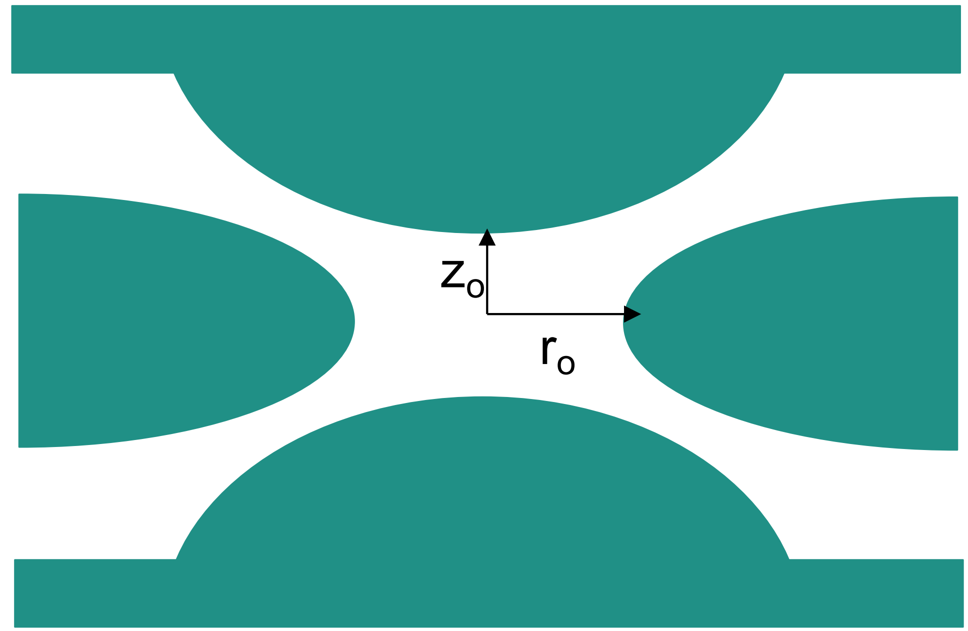
Again we choose the simplest values to satisfy the Laplace constraints. Since the x and y positions = r_o

$$\lambda + \sigma + \gamma = 0$$

$$\lambda = \sigma = 1$$

$$\gamma = -2$$

$$\phi = \frac{\phi_o}{r_o^2}(x^2 + y^2 - 2z^2)$$



Transform into cylindrical coordinates:

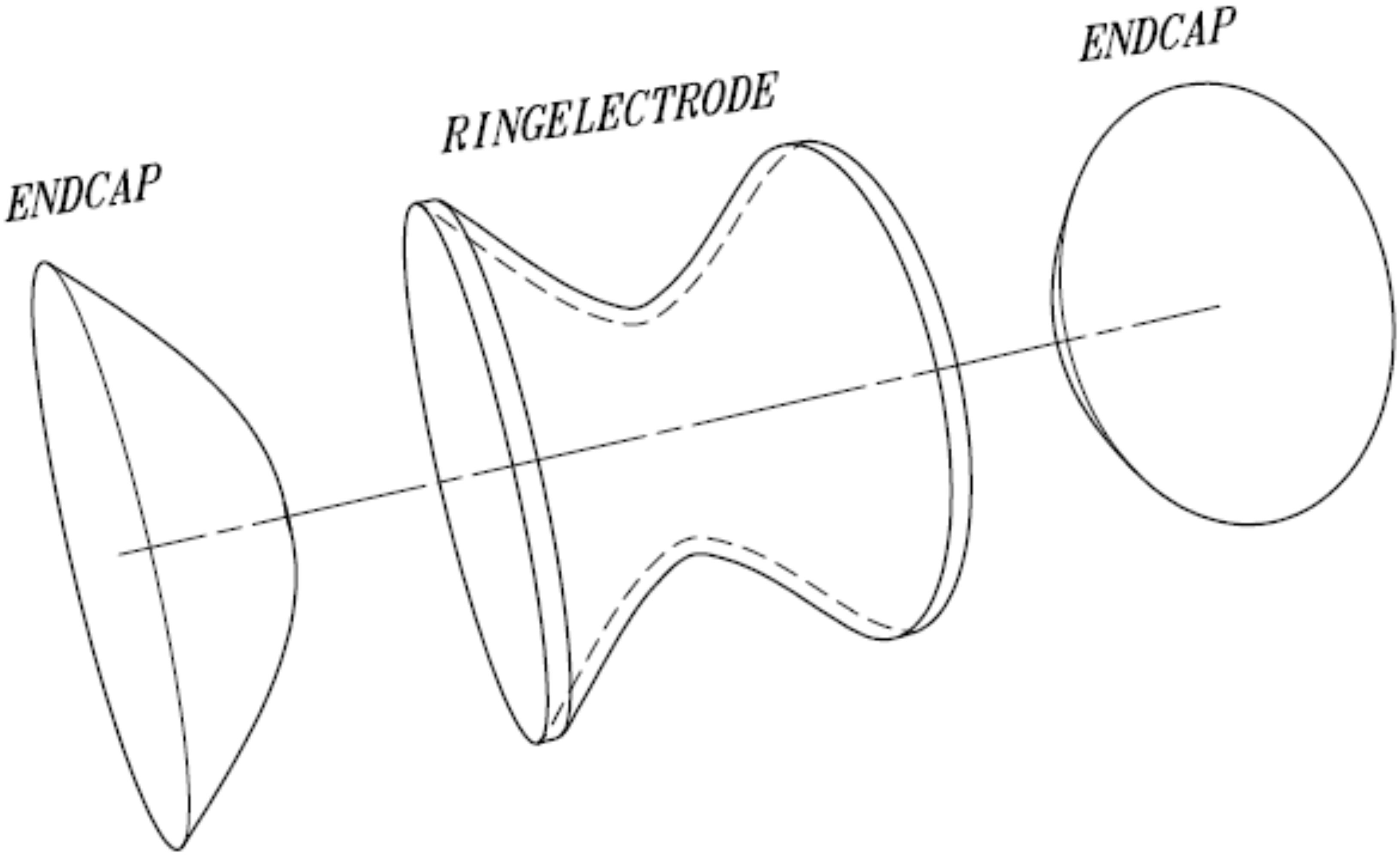
$$\phi = \frac{\phi_o}{r_o^2}(r^2 \cos^2\theta + r^2 \sin^2\theta - 2z^2) \qquad (\cos^2\theta + \sin^2\theta = 1)$$

$$\phi = \frac{\phi_o}{r_o^2}(r^2 - 2z^2)$$

Geometrical constraints:

$$r_o^{\ 2} = 2z_o^{\ 2}$$

Quad Ion Traps



Equations of motion are:

$$\frac{d^2x}{dt^2} + \frac{2e}{r_o^2 m}\left(U - V\cos(\Omega t)\right)r = 0$$

$$\frac{d^2z}{dt^2} + \frac{-4e}{r_o^2 m}\left(U - V\cos(\Omega t)\right)z = 0$$

To fit the Mathieu Equation:

$$\xi = \frac{\Omega t}{2} \qquad \frac{d^2}{dt^2} = \frac{\Omega^2}{4}\frac{d^2}{d\xi^2}$$

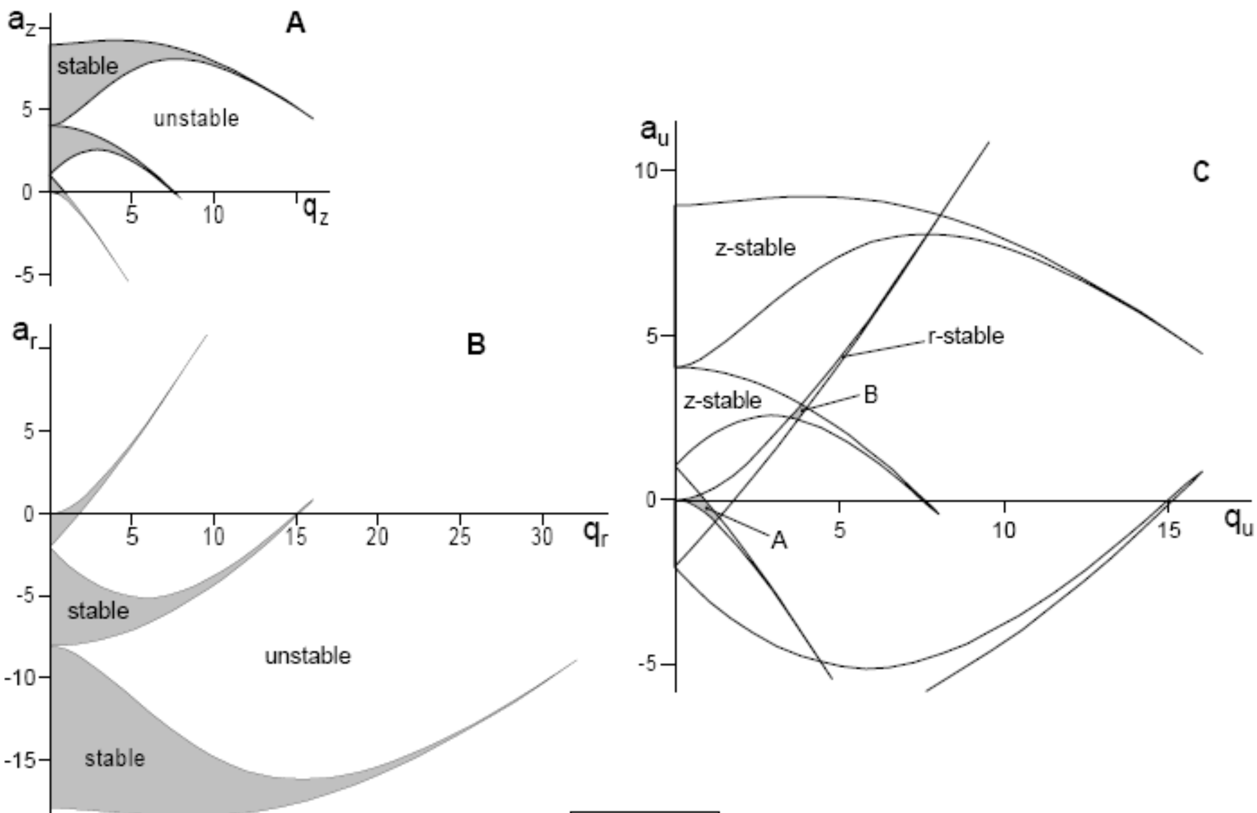
$$a_z = -2a_r = \frac{-16eU}{mr_o^2\Omega^2}$$

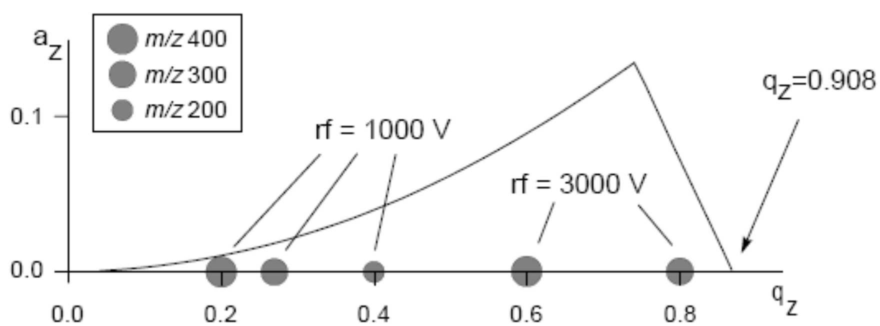
$$q_z = -2q_r = \frac{-8eV}{mr_o^2\Omega^2}$$

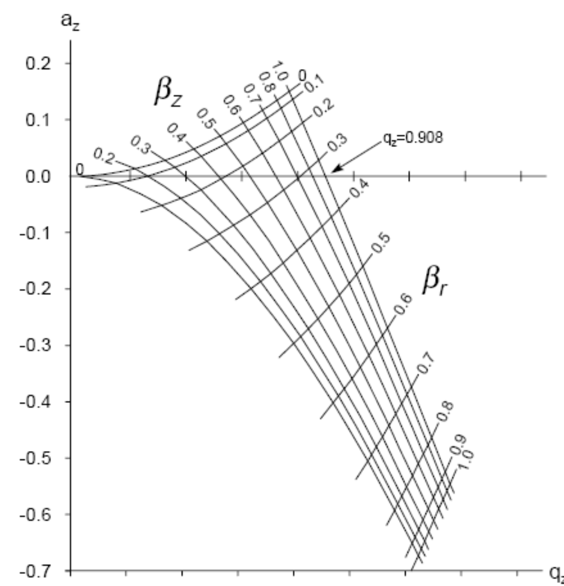
Quad Ion Traps

$$a_z = -2a_r = \frac{-16eU}{mr_o^2\Omega^2}$$

$$q_z = -2q_r = \frac{-8eV}{mr_o^2\Omega^2}$$



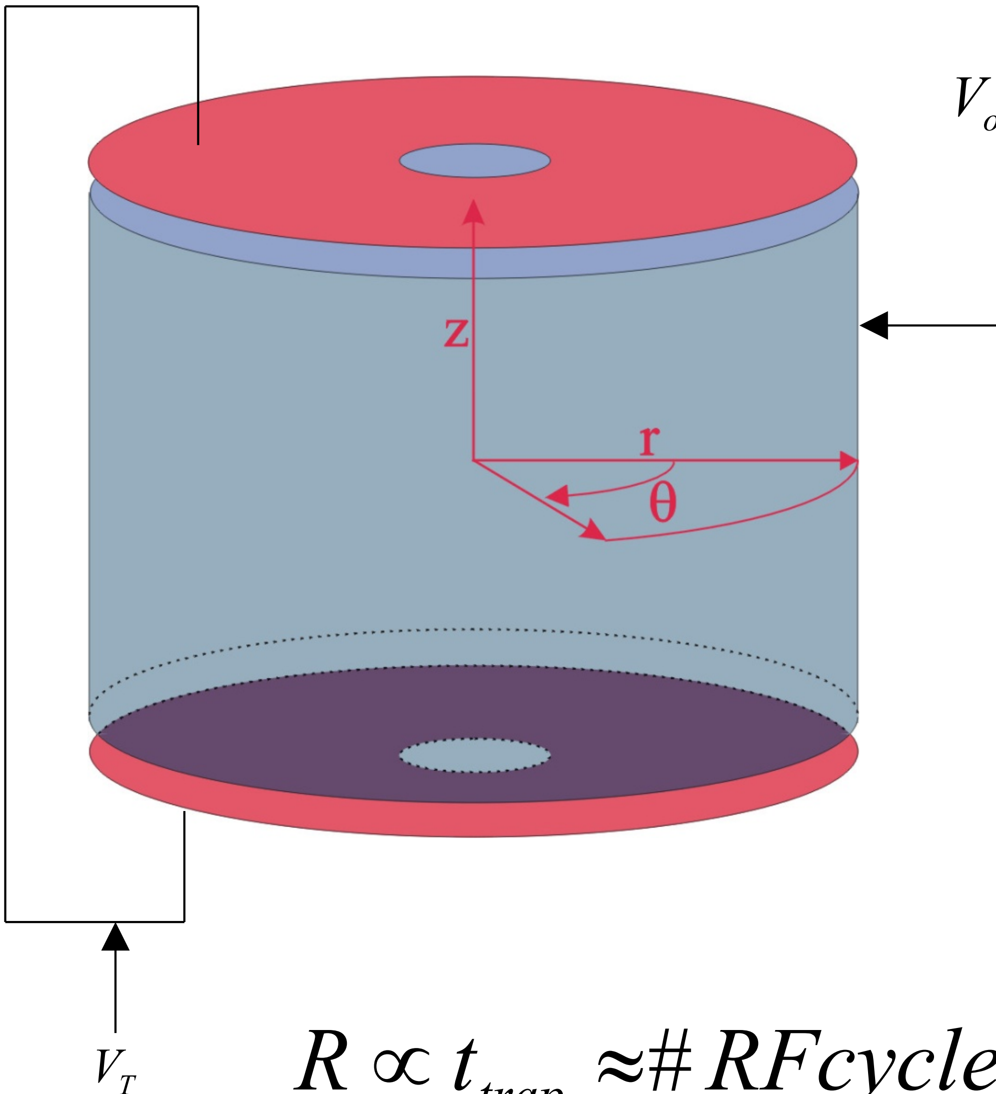




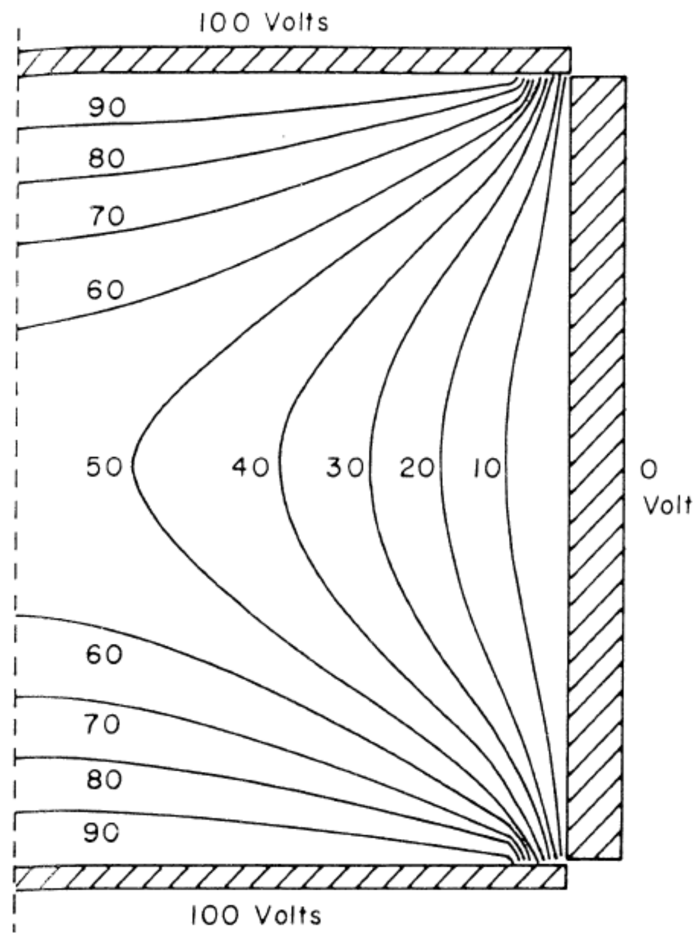
$$R \propto t_{trap} \approx \# RFcycles$$

Cylindrical Ion Traps

$$V_o = -\left(V_{dc} - V_{ac}\cos(\Omega t)\right)$$



$$R \propto t_{trap} \approx \# RF cycles$$



Ion Motion in a Static Magnetic Field:

Lorentzian Force:

$$\vec{F} = q(\vec{v} \times \vec{B}) \tag{1.1}$$

$$m\vec{a} = q(\vec{v} \times \vec{B}) \tag{1.2}$$

- The cross product states that the particles acceleration is always orthonormal to the direction of the magnetic field.
- This will be true even if B varies with position (r), but will change if B varies with time (t).

Lets take a constant magnetic field in the direction z:

$$\vec{B} = \vec{k} B_o \quad \text{Unit vector in the z-direction (k).} \tag{1.3}$$

$$m\vec{a} = q(\vec{v} \times \vec{k} B_o) = qB \begin{vmatrix} i & j & k \\ v_x & v_y & v_z \\ 0 & 0 & 1 \end{vmatrix} \tag{1.4}$$

Ion Motion in a Static Magnetic Field:

Expanding components into their unit vectors:

$$m(\vec{i}\, a_x + \vec{j}\, a_y + \vec{k}\, a_z) = qB_o(\vec{i}\, v_y + \vec{j}\, v_x + \vec{k}\, 0\ ) \qquad (1.5)$$

Equating components to produce the equations of motion:

$$\begin{aligned} ma_x &= qB_o v_y \\ ma_y &= -qB_o v_x \\ ma_z &= 0 \end{aligned} \qquad (1.6)$$

Then, convert to the differential equations and solve:

$$\begin{aligned} m\ddot{x} &= qB_o \dot{y} \\ m\ddot{y} &= -qB_o \dot{x} \\ m\ddot{z} &= 0 \end{aligned} \qquad (1.7)$$

Ion Motion in a Static Magnetic Field:

The results from solving the Diff.Eq. (1.7):

- We know that v_z=constant
- The position in the x,y plane is as follows:

$$x = a + A\cos\left(\frac{qB_o}{m}t + \theta_o\right)$$

$$y = b - A\sin\left(\frac{qB_o}{m}t + \theta_o\right) \tag{1.8}$$

- A,a,b, and θ_o are constants of integration, where;

A is the cyclotron radius (r)

a and b are initial position in x and y respectively (x_o,y_o)

θ_o is the position along the rotation

Ion Motion in a Static Magnetic Field:

If we then differentiate equations 1.8, we get the linear velocity equations with respect to time:

$$v_x = -A\frac{qB_o}{m}(\sin\omega t + \theta_o)$$

$$v_y = -A\frac{qB_o}{m}(\cos\omega t + \theta_o) \qquad (1.9)$$

$$v_z = v_{zo}$$

Now, find angular velocity (v_{xy}):

$$v_{xy} = \sqrt{v_x{}^2 + v_y{}^2} \qquad (1.10)$$

$$v_{xy} = \sqrt{(-A\frac{qB_o}{m})^2(\sin^2(\omega t) + \cos^2(\omega t))}$$

$$v_{xy} = A\frac{qB_o}{m} \qquad (1.11)$$

Cyclotron Motion:

From our initial derivation from the Lorentzian force (1.6), we derived:

$$m\vec{a} = qv_{xy}B_o \qquad (2.1)$$

Substituting angular acceleration into the above equation, we get:

$$v_{xy} = \sqrt{v_x^{\ 2} + v_y^{\ 2}}$$ Velocity in the x,y plane (1.10)

$$a_{xy} = \frac{v_{xy}^{\ 2}}{r};$$ Angular acceleration (2.3)

$$m\frac{v_{xy}^{\ 2}}{r} = qv_{xy}B_o \qquad (2.4)$$

Cyclotron Motion:

$$\omega = \frac{v_{xy}}{r} \qquad (2.5)$$

Angular velocity

Substitute angular velocity:

$$m\omega^2 r = qB_o \omega r \qquad (2.6)$$

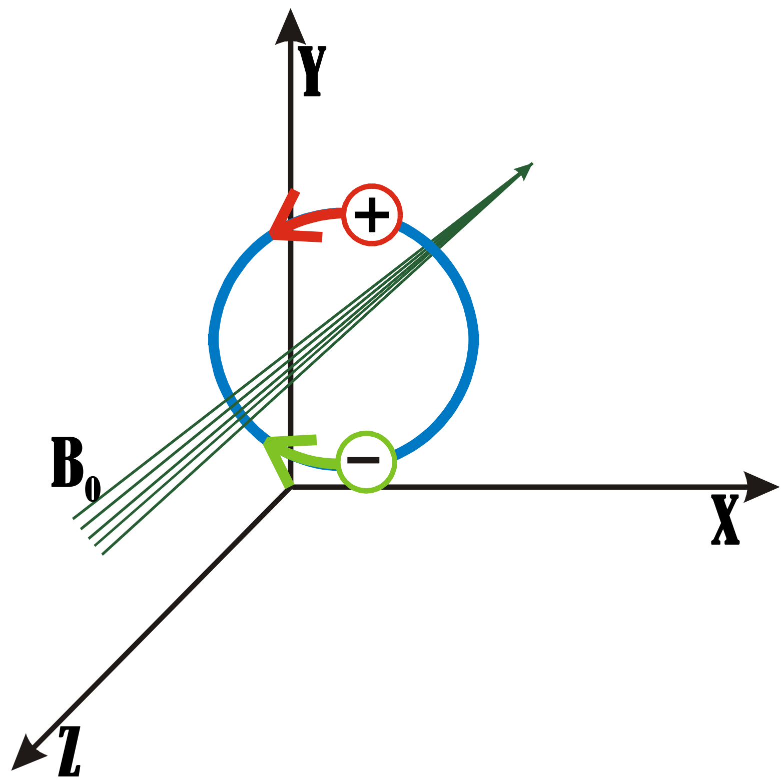
Simplify into the celebrated “ion cyclotron equation”:

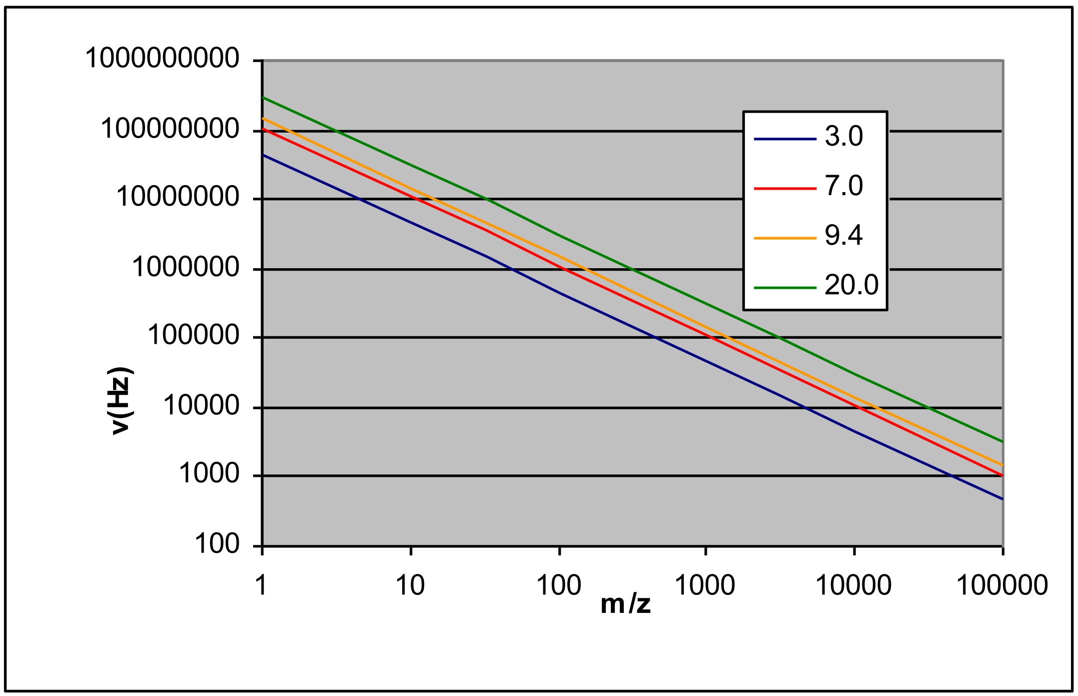
$$\omega = \frac{qB_o}{m} \qquad (2.7)$$

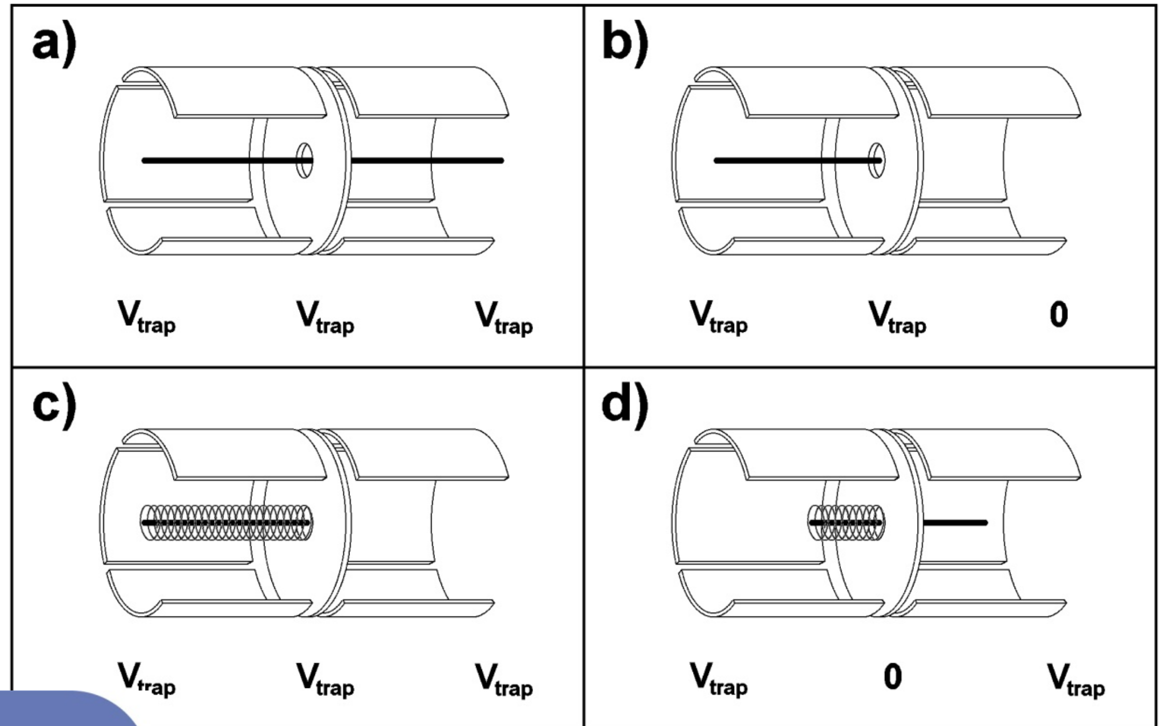
- **This equation is the heart of ICR. It tells us that the cyclotron frequency is independent of the ions initial velocity, and all ions with the same mass/charge (m/q) will have the same frequency.**

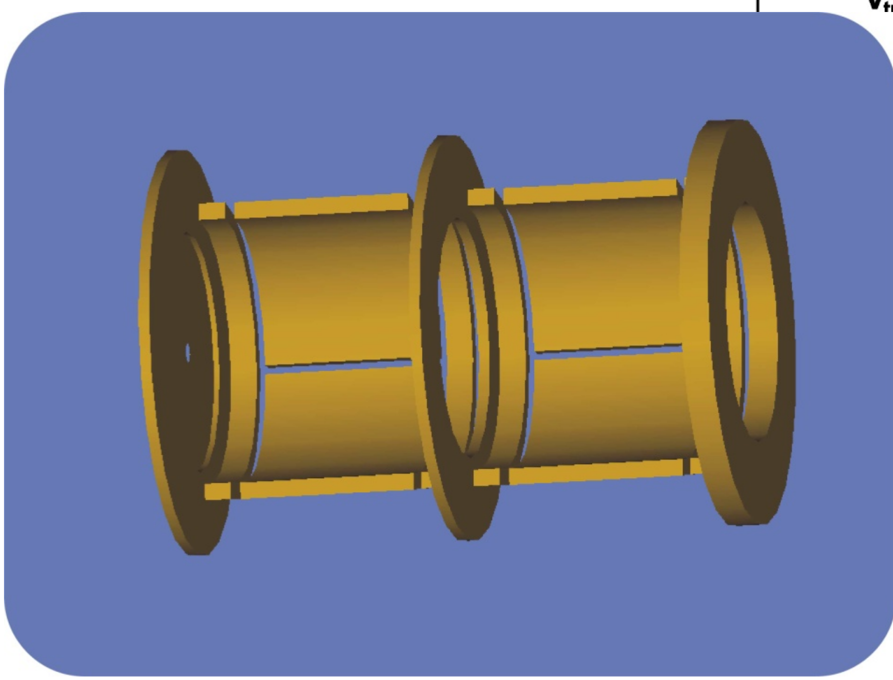
Cyclotron Motion:

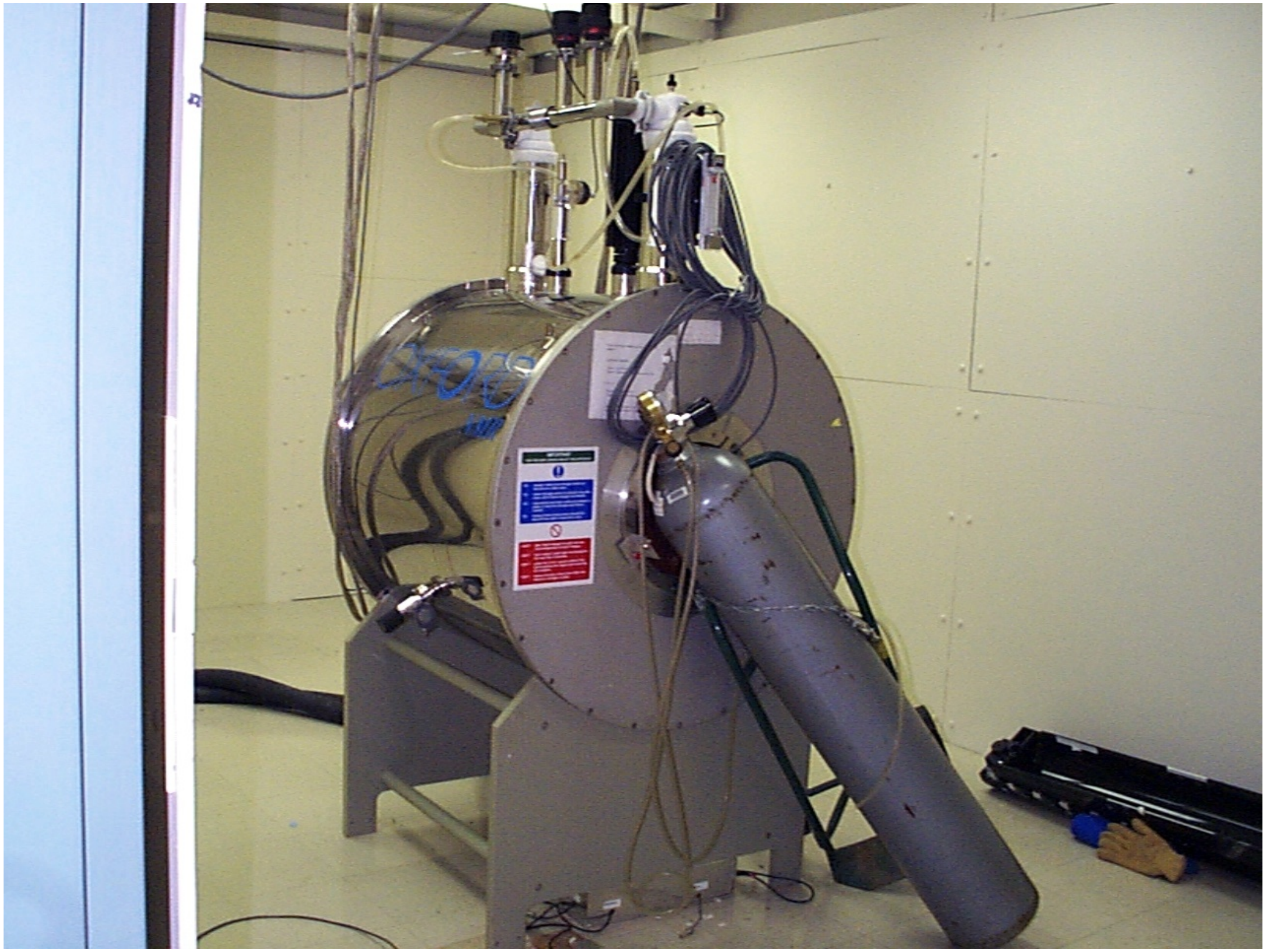
•We can see from our equations that cations will cyclotron counter-clockwise to the in-the-plane magnetic field direction, while anions will cyclotron clockwise






a)
V_{trap} V_{trap} V_{trap}
b)
V_{trap} V_{trap} 0
c)
V_{trap} V_{trap} V_{trap}
d)
V_{trap} 0 V_{trap}





Cyclotron Motion: Other Useful Equations of Cyclotron Motion:

From Eq. 2.4, we can set up the relationship between cyclotron radius and angular velocity:

$$r = \frac{mv_{xy}}{qB_o} \qquad (2.8)$$

2 useful equations can be derived from 2.8;

1. Calculated velocity of a ion with a specific radius:

$$v_{xy} = \frac{qB_o r}{m} \qquad (2.9)$$

2. Calculated translational energy of an ion with a specific radius:

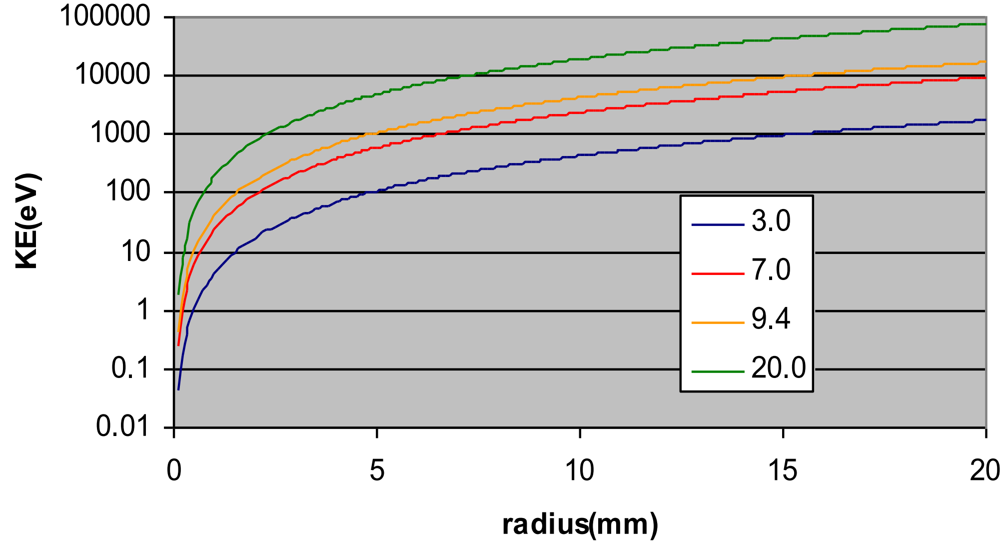
$$E = \frac{mv_{xy}^{2}}{2} \qquad E_{trans} = \frac{q^2 B_o^{2} r^2}{2m} \qquad (2.10)$$

Cyclotron Motion: Other Useful Equations of Cyclotron Motion:

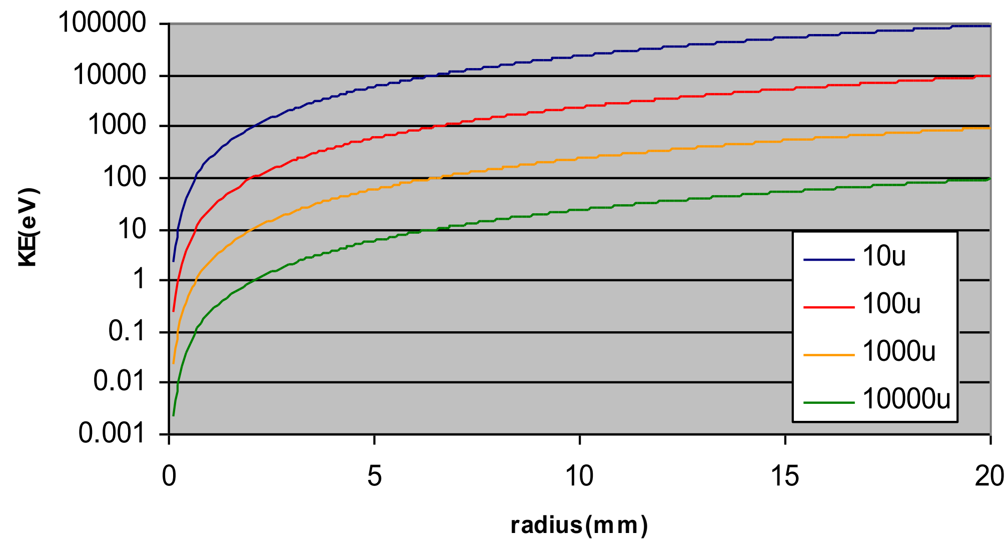
- Translational energy of the ion as a function of cyclotron radius at differing magnet fields (Eq. 2.10) with a mass of 100u.

$$E_{trans} = \frac{48.243 z^2 B_o^{\ 2} r^2}{m}$$

- From the simplified equation above, E(eV),B(T),r(mm), m(g/mol).



- Translational energy of the ion at differing masses as a function of radius in a 7.0 Tesla field.



Cyclotron Motion: Other Useful Equations of Cyclotron Motion:

One of the most useful derivations of cyclotron motion is finding the radius at specific temperatures. To do this we use the Boltzman equation and solve:

We assume: $$\frac{m < v_{xy}{}^{2} >}{2} \cong kT$$

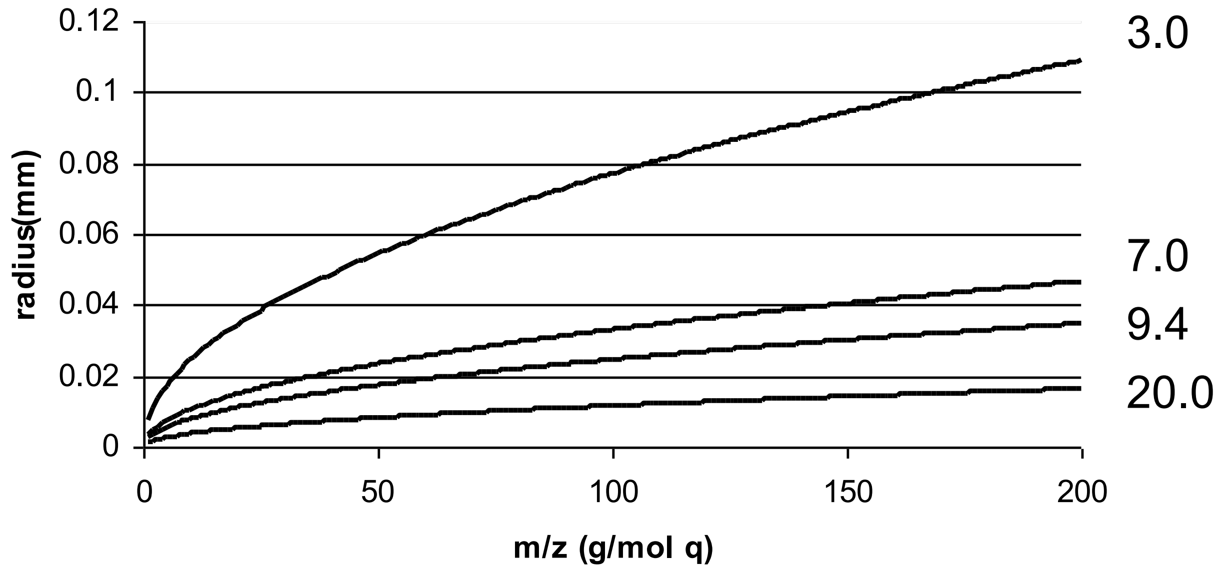
$$r = \frac{\sqrt{2mkT}}{qB_o} \qquad (2.11)$$

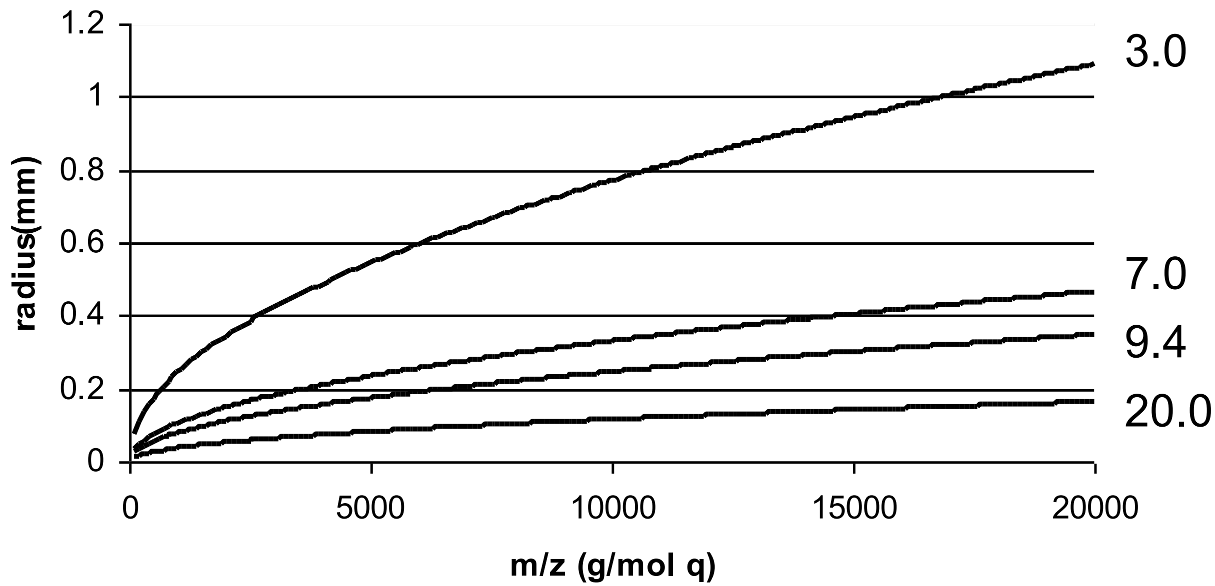
Cyclotron Motion: Other Useful Equations of Cyclotron Motion:

•Here we displayed the cyclotron radius of the conventional cryomagnets as a function of m/z at room temperature. (Eq. 2.11)

$$r = \frac{1.3365 \times 10^{-3} \sqrt{mT}}{zB_o}$$

•For the above simplified equation; r(mm), m(g/mole), B(T), T(K).





Mass Resolving Power in FT-ICR MS:

Start with the cyclotron equation:

$$\omega = \frac{qB_o}{m}$$

Take the first derivative with respect to mass (m):

$$\frac{d\omega}{dm} = -\frac{qB}{m^2}$$

Rearrange to the resolution equation:

$$\frac{m}{\Delta m} = \frac{qB}{m\Delta\omega}$$

Though from first glance the field has a direct effect on resolution, remember that ion velocity will also increase as a function of B, so collision frequency (therefore $\Delta\omega$) will increase making resolution independent of B.

Upper Mass Limit in FT-ICR MS:

Rewriting the cyclotron equation:

$$m = \frac{qBr}{v_c}$$

For thermalized ions the cyclotron velocity becomes the rms average velocity:

$$v_c(thermal) = \sqrt{\frac{2kT}{m}}$$

Substituting in we get:

$$m(thermal) = \frac{q^2 B^2 r^2}{2kT}$$

So in a 7T field with a 2cm radius cell the max mass will be 9114 kD. However there is no room to excite and magnetron and axial motion is not included into this equation.

Upper Mass Limit in FT-ICR MS:

Note: Magnetron motion and cell shapes:

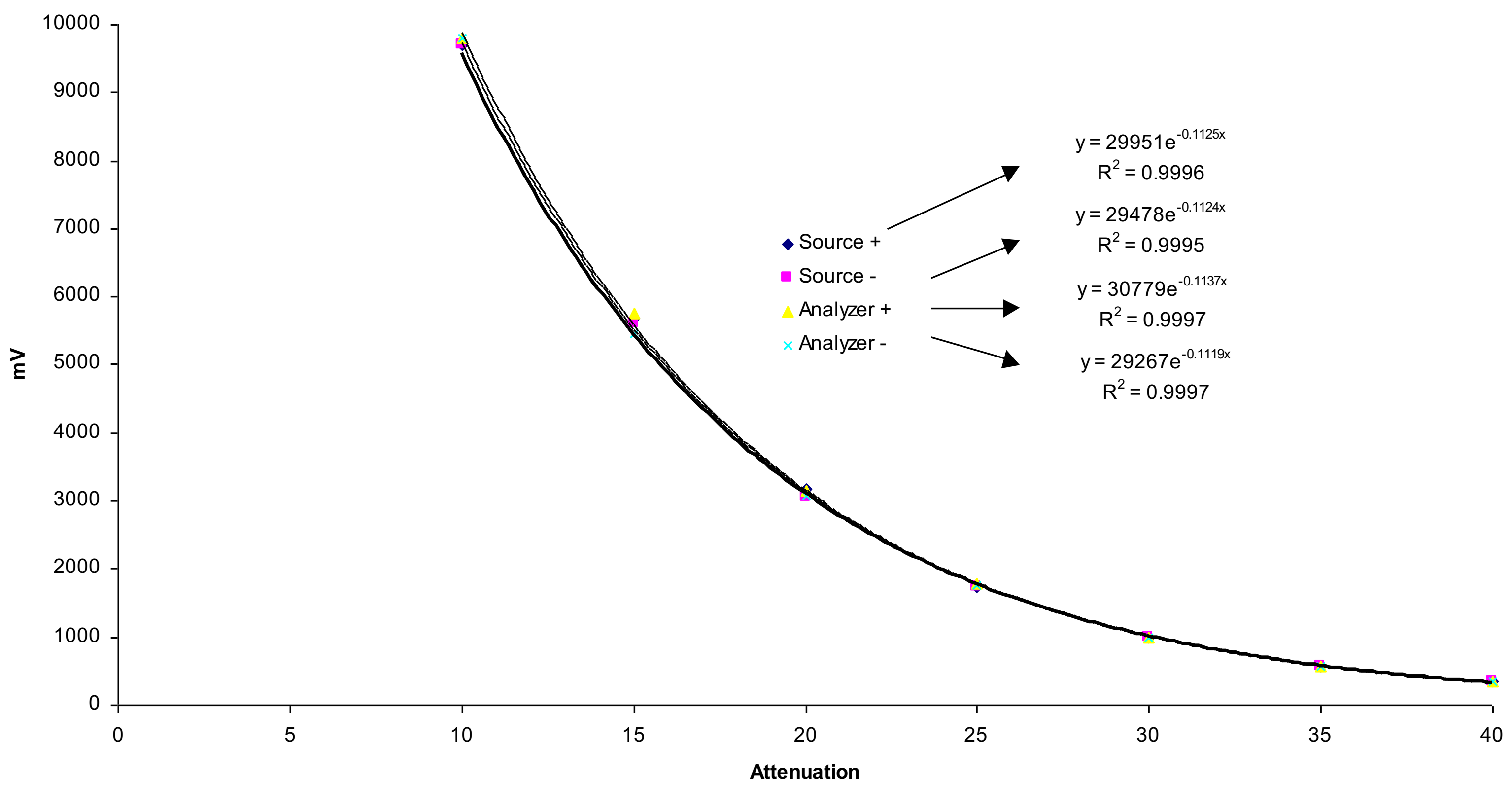
$$\frac{m}{q} = \frac{a^2 B^2}{4\alpha V_T}$$

So in a 7T field in a cylindrical trap of 2cm radius the mass limit will be about 250 kD.

FTICR Maintenance: Checking excitation peak-to-peak voltage:

Attenuation	Source +	Source -	Analyzer +	Analyzer -
40	342	341	335	345
35	583	572	570	577
30	992	983	991	999
25	1740	1730	1780	1770
20	3180	3040	3160	3070
15	5690	5620	5760	5470
10	9700	9700	9800	9800
Frequency				
663243	661157	657895	657895	658762

Peak to Peak Voltage Check as a Function of Attenuation

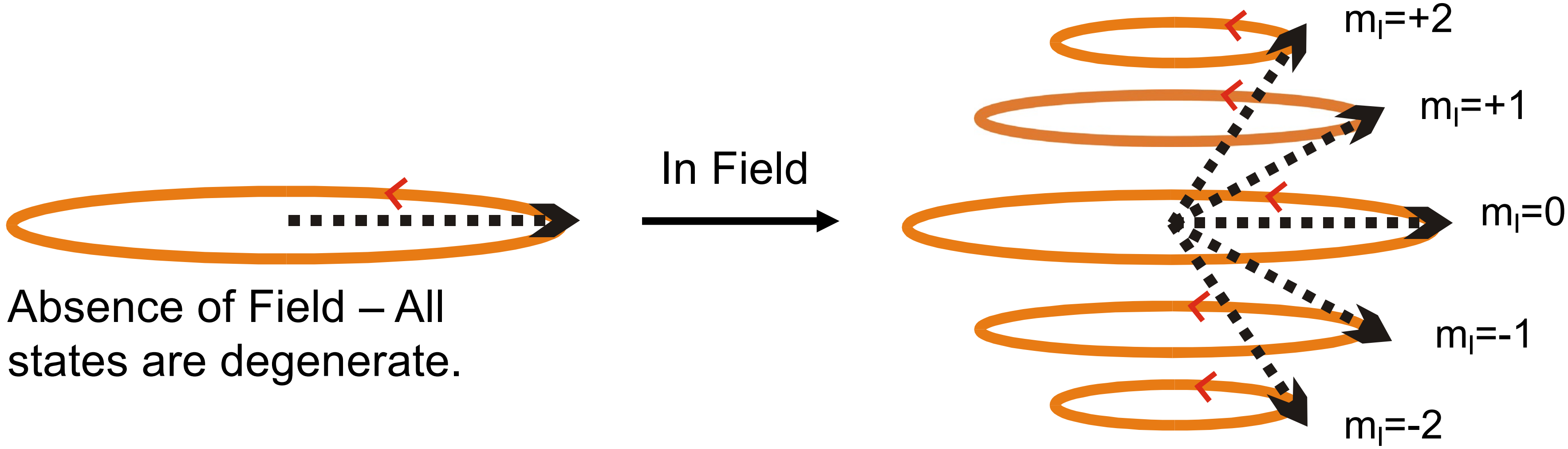


The effect of Magnetic Fields on Angular Momentum

Orbital Angular Momentum (m_l):

Orbital magnetic moment of an electron:

$$\mu_z = \gamma_e m_l \hbar = -\frac{e m_l \hbar}{2m_e} = -\mu_B m_l \qquad (5.1)$$

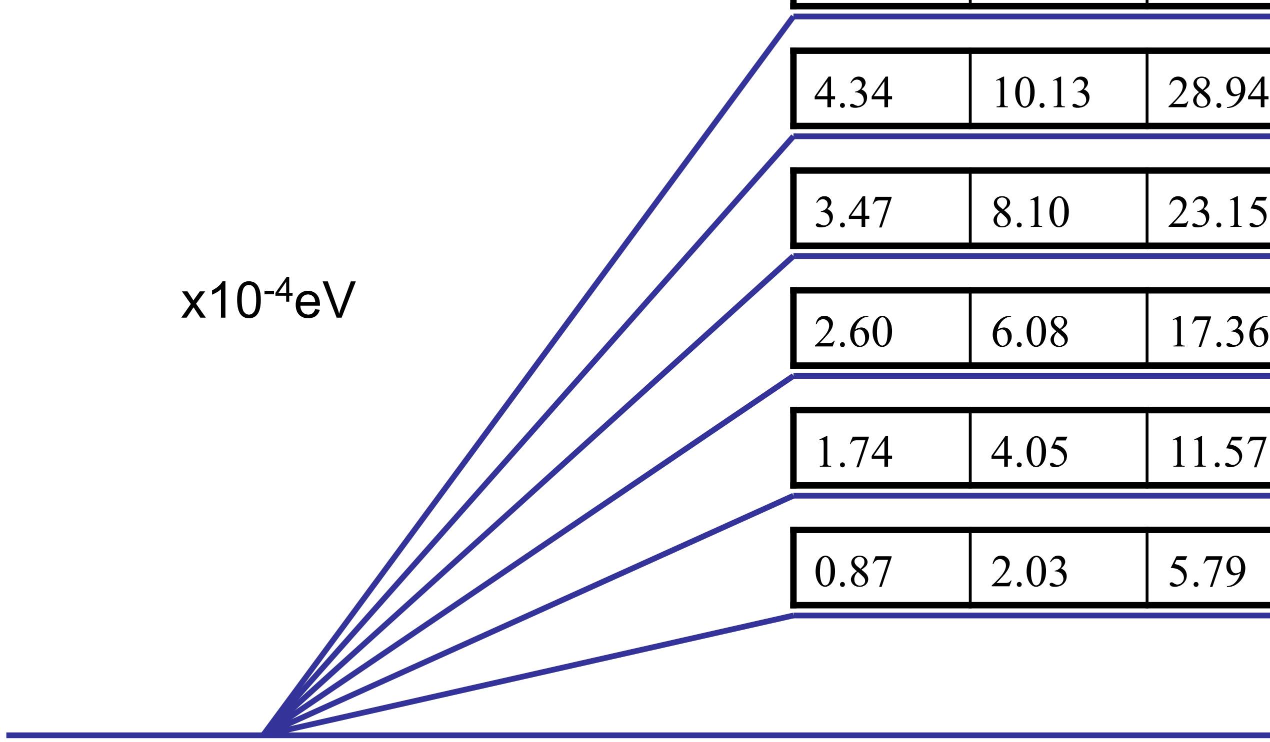


$$\mu_B = \frac{e\hbar}{2m_e} = 9.274 \times 10^{-24}\, JT^{-1} \qquad (5.2)$$

Bohr Magneton

The effect of Magnetic Fields on Angular Momentum

$$\Delta E = -\mu_z B = \mu_B m_l B \qquad (5.3)$$



$\times 10^{-4}$ eV

	3T	7T	20T
$m_l = 3$	5.21	12.16	34.73
$m_l = 5/2$	4.34	10.13	28.94
$m_l = 2$	3.47	8.10	23.15
$m_l = 3/2$	2.60	6.08	17.36
$m_l = 1$	1.74	4.05	11.57
$m_l = 1/2$	0.87	2.03	5.79
$m_l = 0$			

The effect of Magnetic Fields on Angular Momentum

Spin Angular Momentum (m_s):

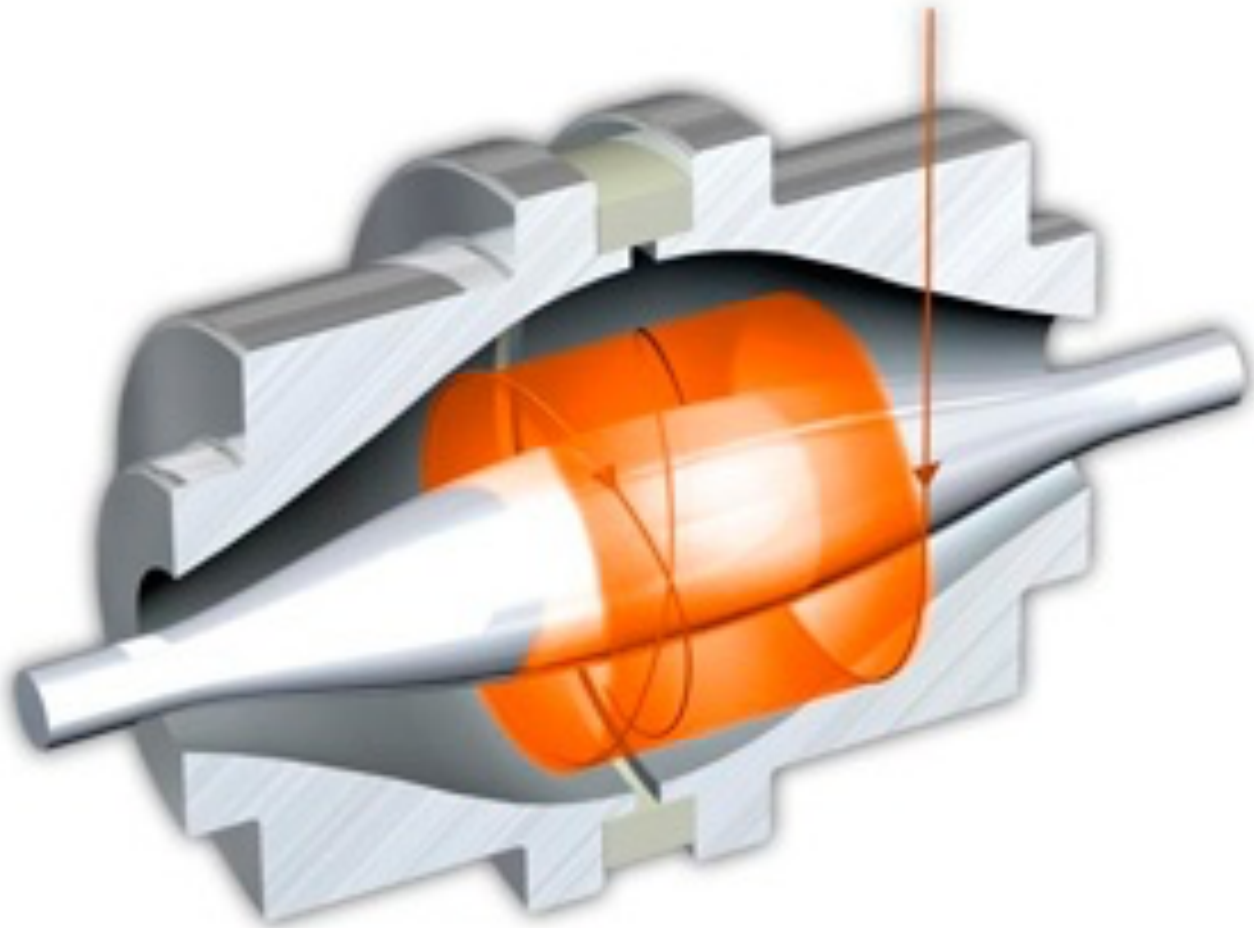
Spin magnetic moment of an electron:

$$\mu_z = g_e \gamma_e m_s \hbar = -\frac{g_e e m_s \hbar}{2m_e} = -g_e \mu_B m_s \qquad (5.4)$$

$$g_e = g - factor = 2.0023$$

$$\Delta E = -\mu_z B = g_e \mu_B m_s B \qquad (5.5)$$

- This comes out with the ΔE values being about twice Of the orbital angular momentum.



References:

Ion Motion in a Static Magnetic Field:

1. Fowles, G.R., Analytical Mechanics, 2^{nd} Ed., Holt, Rinehart, and Winston, Inc., New York, (1970), p.95-98

2. Schey, H.M., Div Grad Curl and All That, 3^{rd} Ed., W.W. Norton, New York, (1997), p.2-10,85-90.

Cyclotron Motion:

1. Marshall, A.G., Verdun, F.R., Fourier Transforms in NMR, Optical, and Mass Spectrometry, Elsevier, Amsterdam, (1990), p. 225-278.

2. Beauchamp, J.L., *Annu. Rev. Phys. Chem.*, 22, (1971), p.527-562.

3. Hanson, C.D., Kerley, E.L., Russell, D.H., *Recent Developments in Experimental Fourier Transform-Ion Cyclotron Resonance*, from Treatise on Analytical Chemistry, Pt.1, 2^{nd} Ed., 11, (1989).

4. Marshall, A.G., Guan, S., *Rap. Comm. Mass Spec.,*10, (1996), 1819-1823.

5. Marshall, A.G., *Int. J. Mass Spec.*, 200, (2000), 331-356.

References:

The effect of Magnetic Fields on Angular Momentum:

1. Atkins, P., Physical Chemistry, Ed. 5, W.H. Freeman and Company, New York, (1994), p. 456-457.