PHY 482 ANNOTATED BIBLIOGRAPHY

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[1] S. Maher, F. P. M. Jjunju and S. Taylor. (2015). *Colloquium*: 100 years of mass spectrometry: Perspectives and future trends. *Rev. Mod. Phys., 87(1), 113-135*, https://dx.doi.org/10.1103/RevModPhys.87.113

In this review, the authors discuss the main concepts of mass spectrometry, its historical development, and the future of the field. The introduction of this article starts with an explanation of the basic principles of MS that all methods have in common. Every method of MS seeks to analyze substances according to their mass to charge ratio, m/z, with the usage of electric and/or magentic fields. Most methods are done in vacuo, with samples entering into a vacuum system to be ionized. From their, they are passon onto low pressure regions that separate ions by their m/z ratio. After the separation, there is typically a detector that emits a signal to be processed in order to show a mass spectrum. While there are many ways to go about the separation process, these main features are the same throughout.

After introducing the concepts of MS, the historical development is detail. The impetus for MS were "canal rays," rays with positive charge of the same magnitude as the charge on Thompson's cathode rays. The difference between these canal rays and Thompson's cathode rays was that they did not have a uniform m/z like the cathode rays. This fact led Thompson to create the parabola spectrograph, the first scanning MS device. This machine consisted of a parabolic metal slit at the end of the tube containing the rays. Instead of using a photographic plate, a Faraday cup was used to collect the ions and get counts. The switch to the Faraday cup gave a more quantatative descpription of what was happening. Using magnetic fields, Thompson could select the m/z that he wanted to pass through the slit and the number of counts could be used to determine the intensity of that particular species. From this, Thompson was able to create a mass spectrum based on the intensity with which particles at different masses hit the detector.

After the pioneering work, a lot of MS involved improving upon this original design and applying it to understand phenomena. For instance, Aston using successive electric and magnetic field to collimate beams independent of their velocity and used this refined technique to find the existence of hundreds of isotopes. Dempster made a pump that took particles around a 180 degree angle at a given radius. Knowing that a particle with a constant velocity, v, in a constant magnetic field, B, with a specific m/z would move along a unique radius, r, such that:

(1) $$\frac{m}{z} = \frac{Ber}{v}$$

He was able to select what m/z would hit the detector by controlling the other parameters. This could be focused for other m/z to create a mass spectrum. Early methods of MS involved constant electric and magnetic fields and were not dynamic methods of detecting mass spectra. Time of Flight MS made use of the dynamics of the particles passing through to create a mass spectrum. This method was based on the idea that partilces with a give m/z in an electrostatic potential, U, with a constant kinetic energy would take different amounts of time to traverse the same length, l, following:

(2) $$t = \sqrt{m/z}\frac{1}{\sqrt{2Ue}}$$

Armed with this equation and data about the time it took ions to reach the detector, one could create a mass spectrum. Another dynamic method is Ion Cycltron Resonance, which relies on the a given m/z in a cycltron corresponding to a frequency, f:

(3) $$\frac{m}{z} = \frac{eB}{2\pi f}$$

Ions could be brought to resonante based on Equation (3) by scanning the magnetic field and a mass spectrum could be created. The method of Quadrupole MS makes use of an alternating and a static electric potential, V and U, to select for m/z. The set up involves for hyperbolic electrodes spaced equally apart and selects for m/z that follow a stable path through the aparatus. The motion of particles in this situation for V with an angular frequency ω are goverend by the Mathieu equations:

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

With u being the (x,y) displacement, $\xi = \omega t2$, and stability parameters a_u and q_u. The stability parameters depend on the amplitude of the alternating voltage, the size of the static potential, the mass of the partilce, and the spacing of the electrodes. Knowing the relations between these parameters allows for the selection of particles with a given m/z that is stable in a certain set up. Tandem MS involves combining multiple steps of MS for given scans. For instance, one could scan for an intial m/z in a subtance and then fragment that particle to find out about its own constituents. There are a number of ways to fragment a given particle, but the review gives details on Collision Induced Dissociation. In this case, the projectile is sent toward a target and fragments once it collides. The authers mention that photons and electron capture can also be used to dissociate projectiles.

In addition to developing new techniques for selecting m/z, other advances in MS involved new ways of ionizing substances. One such method was electron impact

ionization, which inovlved electrons from a heated source interacting with a neutral gas in order to create ions. Another method to get ions is Electrospray Ionization. In this method, a substance being studied is in liquid form and passed through a needle with an applied voltage. This creates charged droplets that evoporate into an ionized gas that will go on through the MS process. Membrane Induced MS allowed for the introduction of specific elements to the vacuum with the usage of a semipermeable membrane. Plasma desorption ionization involved bombarding a substance with fission products to achieve ionization.

After the discussion of the techniques of MS, the authors go on to discuss where createing mass spectra have useful applications. One such application is the detection of isotopic abundances in different substances. In the realm of Physics, this has many applications. Using MS techniques, it is possible to separate a certain isotope from a substance or to detect the ratio of different isotopes in a given material. Having precision measurements of mass is also helpful for understanding nuclear structure and informing models that are based highly on theory. Mass measurements will help to inform our knowledge of the binding energy of different nuclei, which can be found from its mass and knowing the mass of the particles that make it up. With better mass measurements, we can get a better understanding of nuclear structure and the forces involved. In biomedicine, being able to separate isotopes is helpful for the detection of certain drugs. For instance, ratios of $^{14}C/^{13}C$ can be tested for in urine samples to detect the presence of performance enhancing drugs. MS is also useful for the study of proteins and identifying them by the constituents that make them up. An example of this was the use of MS in testing diseased and healthy cardiac tissue in a search for a biomarker that could detect chronic heart failure early and allowing for early intervention for those who had that specific protein. MS can also be used for imaging different structures using mass spectra, spatial, and time information. Not only does this method provide an image of the substance being studied, it also gives chemical information about what makes it up, which other methods are unable to do. Regarding the future, the authors talk about the possibility of small scale mass spectrometers that can be used outside of laboratory settings for analysis of substances, such as harmful chemicals and illict drugs. Its ability to analyze the contents of tissue makes it possible to see MS in cancer treatment in the future, as well.

Overall, this article has taught me a lot about the underlying ideas of MS. Using some method to create ions, manipulating their motion with the use of electric and magnetic fields, and making use of the equations of motion to select for given quantities along the way, and accurately predicting with those equations to determine what m/z has arrived at the target at the end, it is possible to come up with a mass spectrum for the target. Depending on what someone wants to study about a given material, there are many different methods to select from to come up with a solution that pertains to the problem. From here, I am curious about reading more on its applications in nuclear physics and the reference in this article have given me some

ideas of where else to start looking for information.

[2] W. Paul. (1990). Electromagnetic Traps for Charged and Neutral Particles. *Rev. Mod. Phys.*, *62(3)*, 521-540, https://dx.doi.org/10.1103/RevModPhys.62.531

To learn more about where the Mathieu Equations come in to play in Quardupole MS, I read this paper, which included some information on its development. The main inspiration for the setup was the idea that if there was some force $F = -cr$ acting on the particles, they would be bound to the axis runningn down the center of the mass analyzer. To accomplish this, one would need a potential given by:

$$\Phi \sim \alpha x^2 + \beta y^2 + \gamma z^2 \tag{5}$$

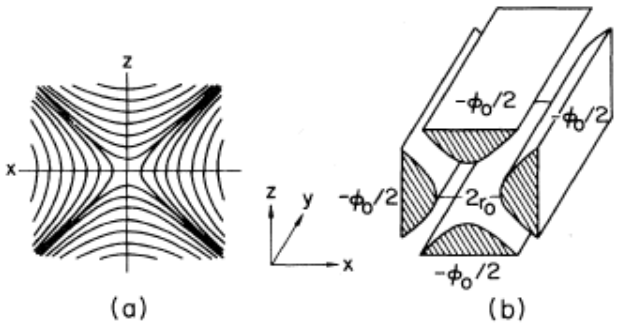

FIGURE 1. An visual representation of the Quadrupole Mass Spectrometer potential and its set up. In (a), the equipotential lines are pictured. A schematic of the set up is pictured in (b).

In the quadrupole mass analyzer set up, pictured in Figure 1 the field looks like:

$$\Phi = \frac{\Phi_0}{2r_0^2}(\alpha x^2 + \beta y^2 + \gamma z^2) \tag{6}$$

And by the fact that the Laplacian should be equal to zero, the following condition that $\alpha + \beta + \gamma = 0$ is imposed on the field. One way to achieve this is $\alpha = -\gamma = 1, \beta = 0$. This is the case found in the quadrupole mass spectrometer. Another case, applied in the ion trap, is $\alpha = \beta = 1, \beta = -2$.

First, in the quadrupole mass spectrometer, a potential of Φ_0 is applied between the two sets of electrodes, giving rise to the following potential:

$$\Phi = \frac{\Phi_0(x^2 - z^2)}{r0^2} \tag{7}$$

With fields $E_x = -\frac{\Phi_0}{r_0^2}x, E_y = 0, E_z = \frac{\Phi_0}{r_0^2}z$. From this, the x and z equations of motion for a particle entering from the y-direction into the mass analyzer can be obtained:

$$\ddot{x} + \frac{e}{mr_0^2}(U + Vcos(\omega t))x = 0$$
$$\ddot{z} - \frac{e}{mr_0^2}(U + Vcos(\omega t))z = 0$$

Where U is the value of an electrostatic potential, V is the aplitude of an rf voltage oscillating at ω, m is the mass of the particle, and e is its charge. Using the following dimensionless parameters, $a = \frac{4eU}{mr_0^2\omega^2}, q = \frac{2eV}{mr_0^2\omega^2}, and \tau = \frac{\omega t}{2}$, the equations can be rewritten as:

$$\frac{d^2x}{d\tau^2} + (a + 2qcos(2\tau))x = 0$$
$$\frac{d^2z}{d\tau^2} - (a + 2qcos(2\tau))z = 0$$

Which are in the form of the Mathieu equations. These equations allow for two solutions: stable motion and unstable motion. For stable solutions, the particle will have limited oscillations in x and z. In the unstable case, there would be exponential growth in either x, z, or both x and z that would lead to the particle hitting the electrodes. For fixed r_0, ω, U, and V, particles with the same charge to mass ratio e/m have the same stable operating point, lying on the line a/q = 2U/V = constant. According to the article, for U=0, q such that 0 ¡ q ¡ 0.92 is stable. By changing U and V together to keep a/q constant, it is possible to analysis multiple masses on the operating line and to create a mass spectrum.

The case of the ion trap follows a similar mathematical principal as the quadrupole mass analyzer, except that the z components are scaled up by 2 and the r equation behaving like x from before. The equation for the potential in this case looks like:

$$\Phi = \frac{\Phi_0(r^2 - 2z^2)}{r0^2 + 2z_0^2} \tag{8}$$

With $r_0 = 2z_0$. There are hyperbolic caps on the z-axis and hyperbolic electrode that wraps around in the x-y plane at a radius r. This set up again gives rise to stable oscillations for particles on the same operating line. The particles in the trap can be selected by oscillating the rf voltage at the same frequency as the particle with the desired mass oscillates, causing resonance. The amplitude of the selected particles will grow and they can escape through a bore hole to be detected. By bringing various masses into resonance, a mass spectrum can be found for the sample.

Another particle trap that was discussed in this article was the Penning Trap. In this case, there is no rf voltage to select for stability. This time, a magnetic field is applied in the z direction, creating a force on a charge particle that will lead to

circular motion in x and y, if the magnetic field is sufficiently strong compared to the electric field. The frequency ω will be smaller than the cycltron frenquency:

$$\omega = \omega_c - \frac{\omega_z^2}{2\omega} \tag{9}$$

With $\omega_z^2 = 2eU/mr_0^2$ being the square of the frequency of the osciallion in the z-direction.

The last trap discussed in this article was one for neutral particles. The article mentions that the potential energy of a particle in a magnetic field is given by $U = -\mu \cdot B$ and that for a non-uniform B, the force is given by $F = \nabla(\mu \cdot B)$. Neutral particles, including the neutron, can still have a magnetic moment that will align parallel or anti-parallel to the field. Particles that are aligned parallel will be focused, and those that are not will be defocused. Having a magnetic sextupole set up will lead to a B field that behaves like r^2 and will have ∇B, and therefore a force, that behaves like r, similar to the approach with electric fields. Particles that do not have a large velocity will have their spin follow the direction of the B field and allows for the trapping of the particle. The set up has the poles in a hexagon set up and there are two closed storage volumes that can be used to trap particles this way. One is a spherical trap, which involves three rings- one large one in the middle and two smaller ones on the top and the bottom- set up to create the sextupole field. The other set up is a torus, which has all six electrodes wrap around in a circle to create the closed storage volume.

In reading this article, I got a better understanding of the physics of some of the traps mentioned in the overview letter. While it does not talk about all of the traps that were mentioned, I feel like I understand the physics behind mass analyzers and ion trap mass spectrometers more than just knowing what equations govern them. Seeing how the equations of motion arose in the first place was interesting and provides a good description of the e and m principles governing these devices.

[3] B. Sun et. al. (2008). Nuclear structure studies of short-lived neutron-rich nuclei with the novel large-scale isochronous mass spectrometry at the FRS-ESR facility. *Nucl. Phys. A*, *812(1-4)*, 1-12, `https://doi.org/10.1016/j.nuclphysa.2008.08.013`

In this paper, I took a look at an article that discussed a specific application of MS in nuclear physics. The experiment I read about used Isochronous MS in order to get mass measurements for different exotic nuclides. The goal of this experiment was to get mass measurements of nuclei that were unknown but predicted by the extrapolations from different theoretical models. The exotic nuclei were made by collisions of high energy per nucleon ^{238}U with a Berryllium target. Using a time of flight detector to observe the revolutions per second of different particles and to collect their time stamps, mass measurements were made for 71 different nuclei all close to the r-process path and a spectrum was created based on the intensity of different nuclides.

In analyzing the data from this experiment, 35 of the newly measured nuclides were found within ± 120 keV, a typical precision for these kinds of measurements. There were more than 71 nuclides that were present in the process of detection, but the resolving power was not enough to identify what was causing certain peaks. The problem of resolving power in certain methods is one that I want to keep an eye out for further to understand if the effectiveness of different methods of MS are limited. Even still, this experiemnt gave the researchers a good opportunity to compare with extrapolations from different theoretical models. Various models existed at the time of the measurement that matched will with known data; however, in the region where there was no data, the theories deviated. With these measurements, the researchers were able to find out what models made better predictions in this previously unknown area. It also gave insight into where prevailing theories failed. The researchers found a consistent reason for the failure of the main theory, which was the over-binding of the nuclear mass surface in neutron rich nuclei. Based on the results of this experiment, I understand the idea of precision mass measurements of unknown nuclei being able to inform theoretical models. Currently, there is uncertainty in the models that are out there that can be resolved with good data in regions that have not been studied before. Based on the ability to use MS to get precision results in this experiment and provide a consistent explanation for where the theory fell short, I believe that this technique can be helpful down the road in understanding nuclear structure.