SUMMARY OF MASS SPECTROMETRY RESEARCH FOR PROJECT

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Mass spectrometry (MS) is a technique that was introduced by J.J. Thompson in the early 1900s that has continued to grow and develop since. Although the method was originally used to understand a particular phenomenon, its applications have grown over the years to encompass multiple scientific discplines and commercial purposes. Early work in MS involved leveraging electricity and magnetism to create more sensitive tools and to select for different qualities. It was realized that the dynamics of particles could be taken into account in order to create mass spectra, a strategy that will be discussed in detail later on in the report. [1] Mass spectra have turned out to be useful in many areas, but nuclear physics is one subfield in particular that makes use of the capabilities of MS and could benefit from further use of the technique.

Before discussing the development of MS, it is import to detail the typical process that all of the methods follow in order to create mass spectra. All of the methods analyze substances to create a spectrum of their masses through the application of principles of electromagnetism and mechanics to select for certain qualities.[1] While it is common to select for the charge to mass ratio, m/z, there are other detectors that can select for velocity, energy, and mass times energy over the charge squared.[2] Looking at trajectories of particles and using the relevant equations to determine their masses is another way to create a mass spectrum. A majority of the methods involve the ionization of particles in vacuo prior to entering into one or more selection devices, which are typically in regions of low pressure. Once the particles pass through the mass analyzer regions, they go on to the detectors and the signals measured are used to create a spectrum for the given particles.[1]

While MS has grown in its applications and techniques, it began in J.J. Thompson's quest to understand "canal rays" at the start of the 1900s. These rays were found to carry the same charge as cathode rays, but with the opposite sign; however, unlike the cathode rays, its constituents did not have a uniform m/z. This inspired Thompson to create a parabola spectrograph. This device was the first to scan for different mass to charge ratios in order to create a spectrum of the masses contained in the substance being studied. Using a Faraday cup to detect ions and get counts for how many were present, it was possible to plot the intensity of the different m/z in a sample. To scan for ions of different masses, Thompson tuned magnetic fields to select for certain m/z to pass through a slit on a metal sheet. This process of selecting certain ions and getting counts to determine their m/z gave birth to all of the concepts that make up MS.[1]

After Thompson's initial work on the subject, most of the development that followed involved buidling upon his methods in order to get better resolutions and measurements. Aston followed up Thompson's work and made measurements that confirmed the existence

of hundreds of isotopes. Dempster refined Thompson's method by using the knowledge that a particle with a given m/z at a constant velocity v in a constant magnetic field B would follow a uniqe radius r, given by:

$$\frac{m}{z} = \frac{Br}{v} \tag{1}$$

These particles were taken along a 180 degree turn at this radius to get to a detector. Selecting for B, v, and r allowed him to scan for different m/z and create a spectrum. The velocity selector made use of Wein's crossed E and B fields.[1] In the set up of crossed E and B fields, it is possible to select for a charged particle that experiences zero net force at a certain velocity in that region, while those with other velocities will hit into the walls of a slit.[2] Wein's crossed fields rely on the application of $F = q(v \times B + E)$ for a charged particle moving through this region. Balacing the direction and magnitudes of the electric and magnetic forces allows for the selection of a given velocity to make it through into Dempster's detector.

While much of the early work involved using electricity and magnetism as the main tools for selection of particles, more methods were pioneered that involved the dynamics of the particles in these regions. Wolfgang Pauld developed many different methods that leveraged the particles motion in a given field in order to create mass spectra. Two methods of his that are similar in their approach are the quadrupole mass spectrometer and the ion trap. Both of these techniques arise from the idea that a particle is confined when it is bound elastically to a central axis. In order to have this elasticity, it is necessary that a restoring force of the form $F = -cr$ acts on a particle to pull it back it as it moves away. To have a force of this form, one should have a potential that looks like:

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

Paul chose a quadrupole set up knowing that the electostatic potential behaved like $r^{m/2}$, where m was the number of poles in his mass analyzer set up. The condition that $\nabla^2\Phi = 0$ imposed another condition on the set up of the instrument. One option that satisfied this equation was $\alpha = -\gamma = 1, \beta = 0$, which is used in quadrupole MS. His set up involved two pairs of hyperbolic poles on a given axis being separated by a distance r_0 and with potentials of $\pm\Phi_0$ applied on either end, giving rise to the following equation:

$$\Phi = \frac{\Phi_0(x^2 - z^2)}{r_0^2} \tag{3}$$

And causing electrostatic fields of $E_x = -\frac{\Phi_0}{r_0^2}x, E_y = 0, E_z = \frac{\Phi_0}{r_0^2}z$. In this set up, particles enter the mass analyzer region moving along the y-axis and have the following equations of motion in x and z:

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

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:

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

Which are in the form of the Mathieu equations. These equations have two solutions, which are stable and unstable motion. Particles that satisfy the conditions for stability in the set up will have limited oscillations in x and z, which is what this set up was intended to do. If a particle does not meet the stability criteria, then it will oscillate without bound in either x, z, or both x and z and hit the walls of the set up, not making it to the detector. Because of this fact, if one understands the conditions for stability, it is possible to make a device that analyzes the different masses contained in a substance. According to Paul, particles with the same m/z lie on the stable operating line a/q = 2U/V = constant. It is detailed that, for U = 0, 0 <q <0.92 are stable and that by changing U and V together to keep their ratio constant, different masses on the operating line can be focused on an analyzed.

Another case that satisfied the condition of the Laplacian being zero is $\alpha = \beta = 1, \beta = -2$, which is used in the ion trap. This device consists of a hyperbolic cap surrounded by a hyperbolic ring in the x-y plane. While the set up is different, it follows the same principles of stability to trap charges. Partilces on the same stable operating line will oscillate at different frequencies. By picking an rf such that it causes resonance for a particle of given mass, one can make a mass spectrum. When the selected particle resonates, it is allowed to escape through a bore hole in the device and into a detector. By scanning across different frequencies, the ion trap can be used to make this spectrum.[3]

Another method of detection that makes use of the dynamics of a given particle is the Time of Flight (TOF) detector. This technique uses the knowledge that a partcile with a give m/z moves a certain distance under the influence of an electrostatic potential U in a time t such that:

$$t \propto \sqrt{m/z}\frac{1}{\sqrt{U}} \tag{4}$$

Using this relationship and analyzing the trajectories of different particles in a detector, it is possible to create a mass spectrum. Cyclotrons make for MS detectors in addition to particle accelerators, since particles of a given m/z have a given cyclotron frequency f that satisfies[1] :

$$\frac{m}{z} = \frac{B}{2\pi f} \tag{5}$$

Sun et al. provide an example of the use of TOF in combination with cyclotron MS in their measurement of the masses of exotic nuclides. In this experiemnt, exotic nulcides were created by high energy collisions of ^{238}U with a Be target. The TOF detector observed how many revolutions per second different particles in the accelerator made and used this information to determine the different m/z in the sample. This experiment demonstrated both the power and the possible limitations of the method. The researchers were able to identify 71 nuclies, with 35 of them hitting typical precison for one of these measurements; however, the fact that two different particles could have the same charge to mass ratio led to the contamination of some of the peaks of the mass spectrum. Because of this, they could only indentify the 71 nuclies mentioned in their publication, even though much more were observed to have been created. Even without all of the peaks, it was possible to compare to the theoretical predictions of unknown massses and determine how they compared to the reality. Looking at where theory failed to match up with the data, the researchers were able to account for the features of the theory that were causing it to not quite describe the data.[4]

Heading forward on this project, I want to delve more into how MS has been applied in nuclear physics and the possible applications that it still has. At this point, after reading Sun et al. and the Overiew paper, MS seems to have a big role in testing theories related to nuclear structure. I am aware that the understanding the masses of these exotic nuclides closer to the neutron and proton drip line will inform these theories and our ideas about nucleosynthesis. In order to give a more detailed idea of why precision mass measurements are important, I plan to look for an overview paper on nuclear physics about how these measurements play into understanding the theory. It would also be interesting to see if any measurements have been made since Sun et al. that would further back the idea that MS is a powerful and informative tool for this field. I have also found another paper that talks about using cyclotron MS to create mass spectra. In this article, the author talks about ways to avoid the problem of contamination due to different peaks; however, it may not be a fair comparison, since he deals with light nuclei at lower energy than Sun et al. In this method, the use of gold foil thick enough to stop the contaminant, but not the desired particle, helps to filter what is being detected. In this case, the particle being selected is ^{14}C and ^{14}N is being stopped. Both are ionized to carry the same charge and both will be brought into resonance at the same frequency, following Equation (5). This is also done at a beam energy of 62 MeV to prevent any reaction products contaminating the measurements. It is also proposed that a detector for the energy loss with respect to difference could be employed, since different particles will have different signatures in this detector. Particles of the same m/z having the same resonance frequency may not be a problem if there is a way to tell them apart.[5] Altogher, the research that I have so far provides a solid basis for understanding MS and different methods to apply it. Another interesting topic in MS that has come up is Tadem MS, which combines different methods to select for different qualities. By reading more into applications of MS in general and about how Tandem MS is employed to get better resolution, I hope to understand how it could limit error with a more detailed selection process. Dempster's use of crossed E and B fields is already and example of using two types of analyzers to improve the resolution of a measurement. It would be interesting to know of something similar exists in cyclotron MS to improve resolution.

References

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